# Chapter 4

# Study on Influence of Oil Contamination on Desalination and Power Plants

by
Kunio Kikuchi
Masaji Kanayama
Noboru Kioka
Keiichi Ohta
Masaru Sakai

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## 4.1 Properties of Spilled Oil and its Influence on Plant Performance

In order to study how spilled oil influences desalination and power plants when raw sea water is polluted by oil, it is necessary to investigate the chemical and physical properties of spilled oil and their change with the passage of time.

### 4.1.1 Changing of Spilled Oil with Passage of Time

It is believed that oil spilled into the sea change, initially by the processes of evaporation, dissolution, formation of water-in-oil and oil-in-water emulsion and by photochemical reaction.

Further, oil in sea water changes its properties through oxidation, polymerization, digestion and decomposition by bacteria, etc., and finally disappears. The natural purification process can generally be illustrated as in Figs. 4.1.1 and 4.1.2

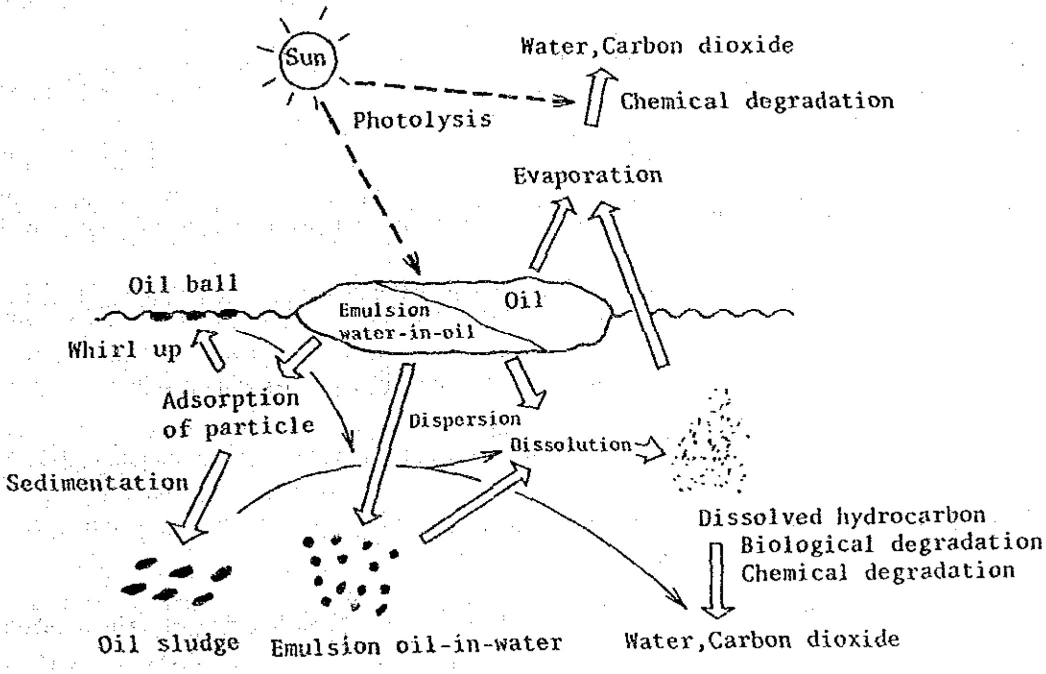


Fig. 4.1.1: Natural Changes in Spilled Oil

In the initial stages of an oil spill in the sea, low molecular weight components evaporate faster than they are dissolved in the sea water, and dissipate into the air. Components of oil with a boiling point of less than 270 °C are believed to evaporate within about 24 hours under normal, natural conditions i.e. temperature; approx. 20 °C, wind velocity; average 4 to 5 m/s, wave height; 30 to 50 cm. Gasoline, kerosene, and about 50% of the contents of gas oil fall into the above category.

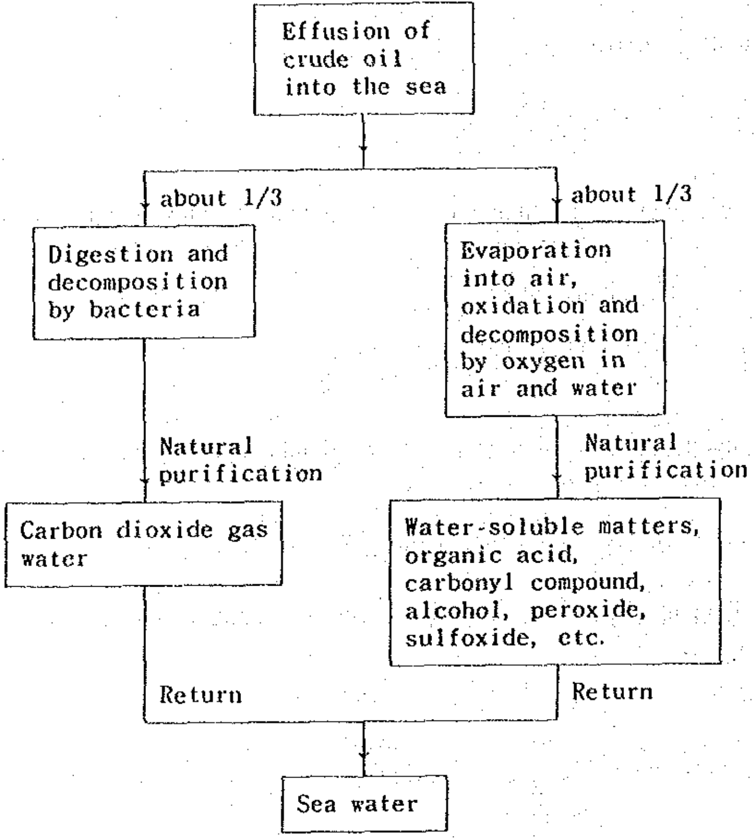


Fig. 4.1.2: Decomposition and Purification Process of Spilled Oil

In cases where crude oil is spilled, a laboratory scale experiment indicates that 1) 10% to 40% will evaporate, 1% to 3% will dissolve, and the balance will remain in emulsion. However, under real sea conditions, there are many unknown factors which affect these estimates.

As the remaining heavy oil (after the evaporation of its light distillate components) will be agitated by waves, a considerable amount of water will mix with the oil. This causes a chemical change due to an acceleration of oxidation and polymerization.

On the other hand, fine particles of oil are digested and decomposed by bacteria in the sea to form carbon dioxide and water, which later disappears into the sea water. There is some evidence that a part of the oil adheres to particles (sand etc.) which are stirred up from the seabed near the shore and is deposited later on the seabed.

The components undigested by bacteria are oxidized and decomposed by oxygen in the air or sea water, and change into water-soluble substances (accelerated by the photochemical decomposition effect of sunlight), and then dissipate into the sea water.

It has been confirmed by experiments that the speed of natural decomposition increases as the particle size of the oil is reduced, as water and air temperatures rise (normally, if the temperature drops to less than 12 °C, the rate of reduction decreases rapidly), as wave height increases, and as the paraffin component increases.

Generally, the most remarkable change in the property of the oil, which occurs during the first 48 hours after the crude oil is spilled into the sea, is the increase in viscosity of the oil due to the evaporation of the light components. A part of the spilled oil forms an emulsion and disperses into the sea water.

Normally, oil particles with a diameter of about 100 $\mu$m form a primary emulsion which is generally unstable and is easily separated by gravity when the emulsion is settled. If the emulsion is subjected to a stronger energy then a secondary emulsion with a particle size of 20 $\mu$m or less is formed, which remains stable for one week to one month and is hard to separate. 2)

If a surface active agent is present, the interfacial tension between the oil and water decreases and forms minute oil particles with an increased emulsion stability.

The formation of oil balls is believed to take a longer period, say five months or more according to a trial calculation. 3) The so-called oil balls have various forms such as jelly, grease or solid, with variations in their hardness and sizes, Jellied oil balls contain much water but they are chemically almost the same as the original oil.

### 4.1.2 Changes in Physical and Chemical Properties of Spilled Oil

#### (a) Water Content

The most obvious change in the physical property of crude oil spilled into sea water is an increase in its water content. That is, oil embraces sea water particles to form a high viscosity water-in-oil emulsion (W/O). An increase in specific gravity, viscosity, and pour point is observable as the water content increases. Fig. 4.1.3 shows the time-series changes in the water content of the crude oil floating on the ocean surface.

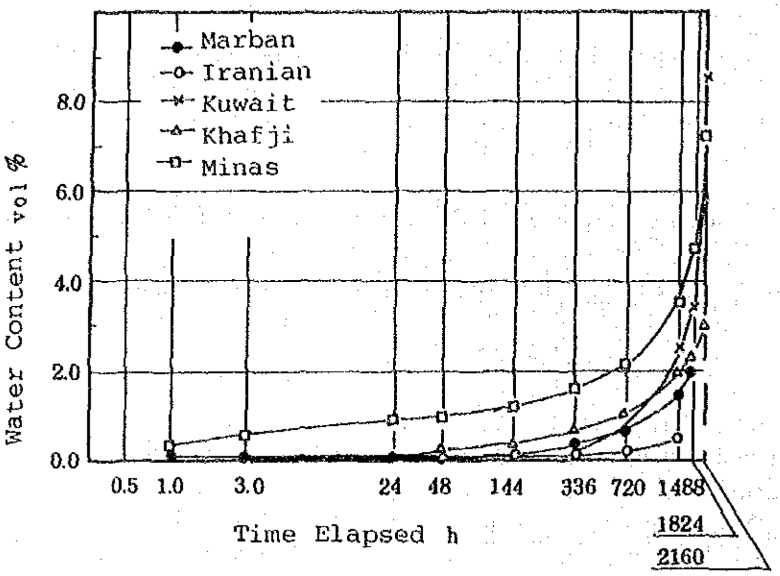


Fig. 4.1.3: Changes in Water Content of Crude Oil in Sea Water

(b) Specific Gravity

Due to the increase in the water content of spilled oil and the evaporation of its volatile components, the specific gravity of the floating oil increases as time elapses. When sands, dusts, suspended particles, organisms, etc., adhere to the oil, its specific gravity becomes greater than sea water (about 1.02 to 1.03) causing it to sink to the seabed. Fig. 4.1.4. shows the test results of changes in the specific gravity of crude oil with the passage of time.

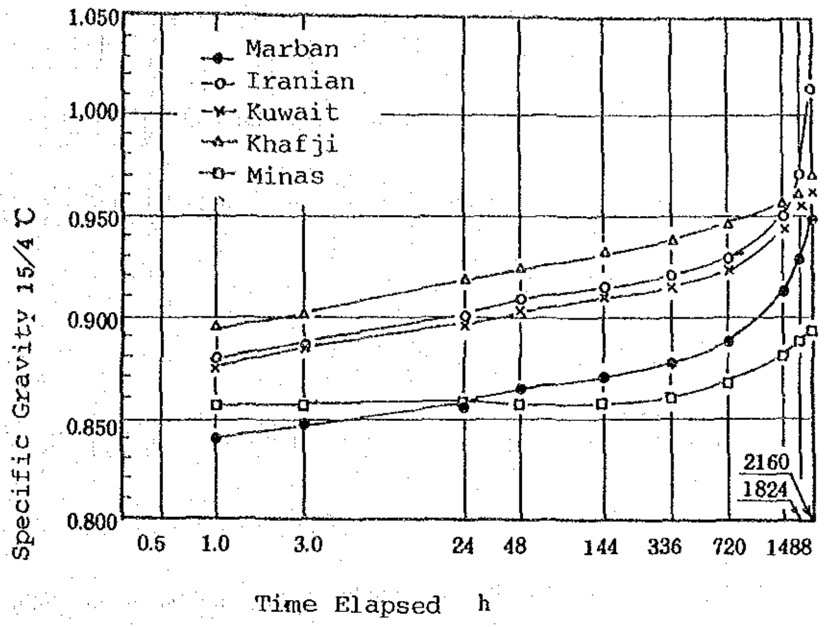


Fig. 4.1.4: Changes in Specific Gravity of Crude Oil with Passage of Time

(c) Viscosity

The viscosity of spilled oil increases as its water content increases. Fig. 4.1.5 shows the test results of changes in the viscosity of crude oil with the passage of time.

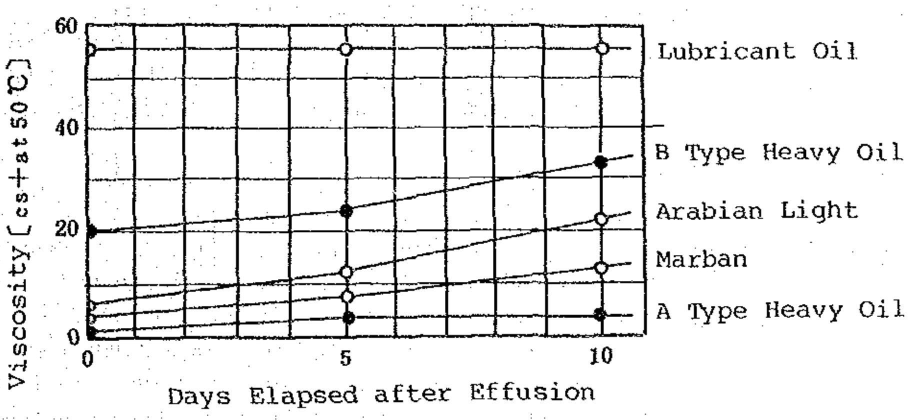


Fig. 4.1.5: Changes in Viscosity of Crude Oil with Passage of Time

(d) Pour Point

It can be said that the lower the pour point of the oil, the more easily it is dispersed in sea water, and the higher the pour point, the greater the tendency for the oil to form oil balls. According to measurements made on actual oil balls collected from the sea, the pour point rises when its asphaltene/wax content is high. There is a clear correlation between pour point and asphaltene/wax content. Fig. 4.1.6 shows the test results of changes in the pour point of crude oil with the passage of time.

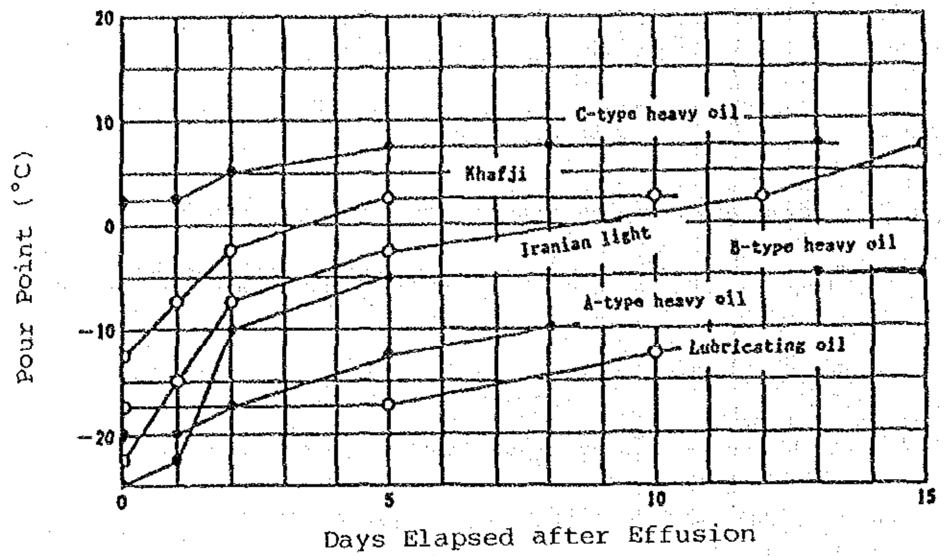


Fig. 4.1.6: Changes in Pour Points of Crude Oil in Sea Water with Passage of Time

(e) Evaporation

The first and greatest change observed when oil spills into the sea is the evaporation of its volatile component, and thus it changes in the constituents of the spilled oil remarkably. The loss of the volatile component of the oil proceeds rapidly. Generally the oil spilled in the sea is spread thinly over the sea surface and is exposed to various weather conditions such as wind, waves, sunshine, heat, etc. Therefore, the rate of loss at sea should be considerably greater than that measured in the laboratory experiments.

In one experiment in which several kinds of oil with an initial film thickness of 1.6 mm were kept as they were, naptha disappeared by evaporation in about 20 minutes, gasoline in about 8.5 hours, and kerosene, crude oil and gas oil were reduced to about 12%, 60% and 70% respectively of their initial volumes. 7) According to the experimental test results concerning the evaporation of crude oil, hydrocarbons with carbon numbers of 15 to 17 or less were almost completely reduced or dissipated, but hydrocarbons of higher carbon numbers underwent little change.

(f) Dissolution

According to experimental results concerning the dissolution rates of crude oil and gas oil in sea water, it was reported that crude oil dissolved in the sea water (50 °C synthetic sea water) at a rate of 40 to 100 mg/l, and gas oil dissolved in the sea water (20 °C natural sea water) at a rate of 20 to 250 mg/l. 3)8)

Further, as a result of examining the maximum concentration of dissolved oil in a closed vessel, it was found that about 1,700 mg/l of benzene, about 100 mg/l of gasoline, about 10 to 15 mg/l of crude oil and about 1 mg/l of kerosene and gas oil are dissolved. The dissolved components were almost all light components.

Also, the amount of light aromatic components existing in the water layer is more than that of the oil film layer, in the case of gasoline, naptha and crude oil. When ultraviolet ray irradiation was applied, the concentration of the dissolved components increased except in the case of naptha. A particularly remarkable increase was observed in the case of kerosene and gas oil. At that time, the presence of a component having an absorption peak in the vicinity of wave number 3,025 $cm^{-1}$ was observed and presumed to have been caused by soluble oxides. 7)

According to a test result, almost no change was observed in the concentration of crude oil in the synthetic sea water with the passage of time. However in natural sea water, the oil concentration decreases through disintegration by bacteria. Fig. 4.1.7 shows the changes in concentration of crude oil in synthetic sea water with the passage of time.

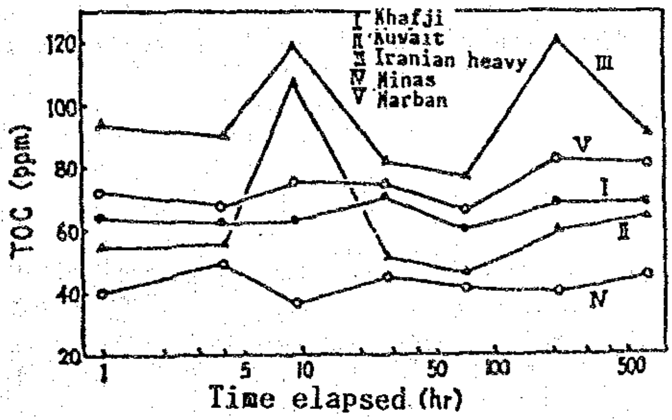


Fig. 4.1.7: Changes in Oil Concentration in Synthetic Sea Water with Passage of Time (TOC value of organic components in water)

Generally the solubility of the of oil into water depends upon the kind of hydrocarbon as follows: 2)

* Solubility increases as the molecular weight decreases.

Volatility and solubility show a similar tendency, and light hydrocarbons can dissolve and evaporate easily.

* Solubility increases as the un-saturation degree increases.

Table 4.1.1 shows an example of this tendency.

* Hydrocarbons with a larger polarity and smaller molecular weight dissolve more easily.

Table 4.1.1: Solubility of Hydrocarbons (mg/l)

| Straight chain hydrocarbon C6 | Straight chain hydrocarbon C6 | Cyclic hydrocarbon C6 |
|---|---|---|
| n-octane<br>0.66 | n-hexane<br>9.5 | cyclohexane<br>55 |
| octene-1<br>2.7 | hexene-1<br>50 | cyclohexene<br>213 |
| | | benzene<br>1650 |

(g) Increase in Resin Content

Fig. 4.1.8 shows changes in the resin content of the spilled oil with the passage of time. The resin content increases as time passes, and soft asphaltene resin in oil suspension increases. Further, it is said that by measuring the resin component, the time passed since spillage can be inversely estimated. This estimation of time in the case of heavy oil is fairly accurate. 6)

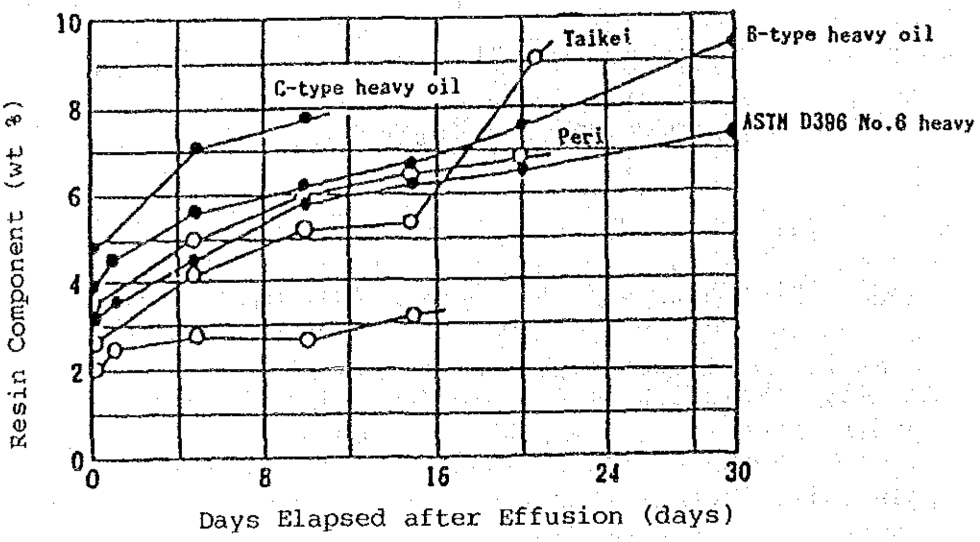


Fig. 4.1.8: Changes in Resin Component of Oil with Passage of Time

(h) Residual Carbon

The existing ratio of residual carbon in every type of oil except lubricating oil indicates a large increase in correlation with the time elapsed after the spillage. 6)

### (i) Total Acid Value

Due to the processes of oxidation, hydrolysis, etc., formation of polar radicals such as carboxyl could be assumed. Sano 9) examined changes of polar radicals by the I.R. absorption method for an index of oxidation and hydrolysis. 4) It was observed that the amount of polar radicals in sea water was very small and could not detect the change.

Accordingly they concluded that considerable formation and decomposition of polar radicals does not occur. As acid radicals can be analyzed by measuring the total acid value, even though of extremely small quantity, changes in it can be measured with the passage of time.

A rapid increase in the total acid value can be observed after 1,000 hours have elapsed. This is considered to be due to the commencement of chemical changes caused by oxidation, hydrolysis etc. 9)

### 4.1.3 Conclusion

The following conclusion of the survey is based on technical literature available.

The oil spilled into sea changes and disperses in a complicated manner owing to evaporation into the atmosphere, dissolution into sea water, the formation of oil emulsion consisting of fine oil particles, the formation of oil balls, etc. These phenomena vary considerably, and their concentration and properties depend upon the condition of the oil leak.

The changes with the passage of time also depend upon the kinds and components of the crude oil and product oils. Consequently, when studies are conducted concerning the influence on the power and desalination plant and on countermeasures against oil contamination, it is necessary to conduct studies covering the various conditions of the pollution, as the type of pollution varies with regards to the type of oil spill, time elapsed since spillage and distance from the oil spill point.

By the use of oil fence and by adopting a deep sea water intake system the intake of floating oil into the plant can be avoided. Furthermore, most of the oil balls coming to the intake can be caught by screens. However, dissolved oil components and oil emulsion are likely to be drawn into the plant.

Judging from various literature, the oil concentration coming in the intake in the case of a large oil spill is considered to be 1,000 mg/l or less. Therefore, it should be sufficient if this concentration range is taken into account and covered in the study of the influence of oil contamination on the plants and the countermeasures available.

## 4.2 Influence on Efficiency of Sea Water Desalination Plant

When a sea water desalination plant is operated using sea water polluted by oil, there is concern that an increase of heat transfer resistance caused by adhesion of oil to the heat transfer surface of the evaporator, a functional disorder due to pollution of the facilities and equipment, may occur causing a decline in performance of the desalination plant and difficulties in its operation. The influence of oil polluted sea water on the efficiency of all equipment in the sea water desalination plant will be studied herein.

### 4.2.1 Effect on Pumps

The oil polluted sea water enters the desalination plant through the intake screens and intake pumps. Here, large solids are separated and removed by the intake screens, while the oil dissolved in sea water or in particle form of diameter 200 $\mu m$ passes through the oil fence and the screens and enters the intake pumps, where it is further atomized without adhering to the pumps. The same process occurs with pumps other than the intake pumps; no influence on the performance of the pumps is observed. 10)

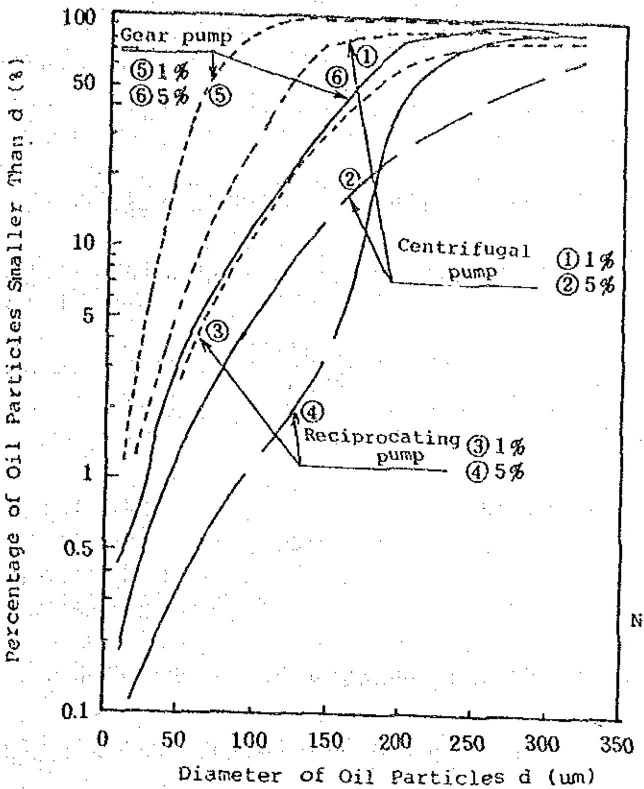
Table 4.2.1 shows the specifications of the the commercial pumps used in the oil atomization tests. 7)

According to the test results shown in Fig. 4.2.1 the lower the oil concentration, the more the oil is atomized by each pump, and when comparing oil of the same concentration, atomization tends to be better achieved by the gear pump, then the centrifugal pump and the reciprocating pump, in this succession.

Fig. 4.2.2 shows the particle distribution of oils in freshwater and sea water according to the kinds of oil when a centrifugal pump is used. The figure clearly indicates that a tendency exists for atomization to be best achieved in the order of gas oil, kerosene and B-type heavy oil. Further, for each oil the atomization rate is higher in freshwater than in sea water.

Table 4.2.1: Specifications of Pumps Used in Atomization Tests

| Item<br>Pump | Type | Operating Condition | | |
|---|---|---|---|---|
| | | No. of rotations | Discharge pressure $kg/cm^2$ | Flow rate $m^3/hr$ |
| Centrifugal | Single suction single stage (closed impeller) | 1500 rpm | 0.7 - 0.9 | 1.0 |
| Reciprocating | Horizontal Duplex Cylinder | 92 1.0 stroke/min | | 3.0 |
| Gear | External gear | 950 rpm | 1.0 | 4.0 |



Note: Percentage indicates Concentration of Gas Oil in Sea Water

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Fig. 4.2.1: Types of Oil and Water Feed Pumps and Particle Distribution

- ① Gas oil and fresh water
- ② Kerosen and fresh water
- ③ Gas oil and sea water
- ④ Kerosen and sea water
- ⑤ B type heavy oil and fresh water
- ⑥ B type heavy oil and sea water

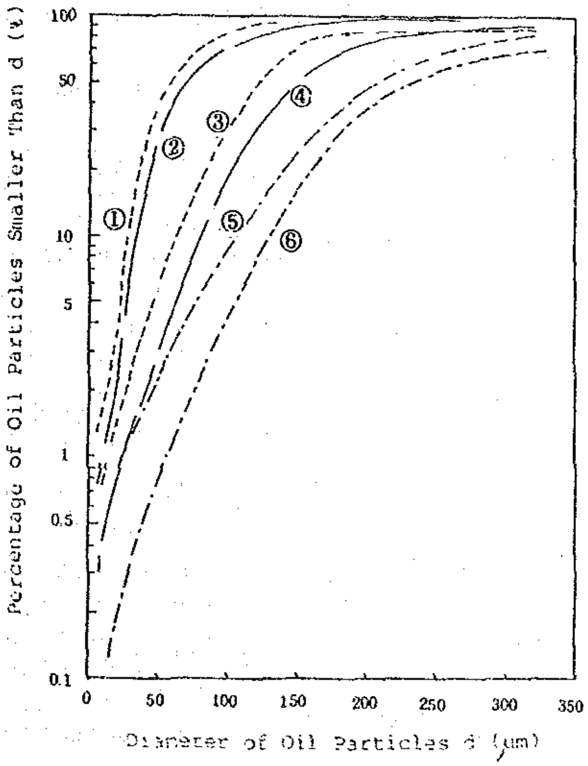

Fig. 4.2.2: Particle Distribution in Combined Oil and Water (Oil Concentration 1%)

### 4.2.2 Influence on Heat Transfer Tubes

A decline in the performance of the heat exchanger is generally caused by fouling on the surface of the heat transfer tubes, which increases heat transfer resistance. Causing of fouling include scaling, precipitation of corrosive substances, sedimentation of polluting substances in the sea water, such as sand, silt and other organic sludges etc.

As a countermeasure to this contamination, a designer first estimates the fouling factor and then provides for a margin in the heat transfer area. Therefore, the heat exchanger shows more than the design begins until the fouling factor reaches the design value. Once the design value is reached and the performance starts to fall below the guaranteed level, the contaminant must be removed at this time.

If oil adheres to the equipment due to the use of oil polluted sea water, the intervals between the cleanings of the equipment should be shortened. The basic procedure for removing contamination is acid cleaning. In the Middle East it is usual to resort also to an additional method of mechanical cleaning using sponge balls (which can be performed on-line) in order to reduce the frequency of complicated acid cleaning.

#### (1) Oil Adhesion to Heat Transfer Tubes caused by Oil Contaminated Sea Water

Toyama, et al. 11) conducted experiments concerning oil adhesion to the tube surface and the separation of adhered oil films using glass beads, in order to obtain information about the fouling process of the tube surface by oil particles in the sea water, and about the process of mechanical removing of the contamination.

According to the above experiments, even though considerable irregularity was observed in the adhesion rate of oil particles in the initial stage of fouling, it was observed that adhered oil particles increased as the time passed and reached an equilibrium after repeated coalescence and separation. Fig. 4.2.3 illustrates the recorded results of the adhesion of oil particles to the wall surface, indicating from the top each stage of initial adhesion, growth, coalescence and coalescence-separation.

Fig. 4.2.4 shows the variations in the amount of oil adhesion which takes place with the passage of time, in an acrylic resin test tube, which confirms that the adhesion quantity of oil particles is greatly affected by flow velocity and properties of sea water the test tubes.

The rate of fouling depends upon many factors such as properties of the oil, its concentration, the shearing force of the fluid, properties of the tubing material etc. In relation to the experiments concerning the removal of fouling, it was found that the separation rate of the paraffin film which adhered earlier, presented a linear relation with time, and that the separation rate was almost proportional to the inflow rate of glass beads and to the two point fifth power of the particle velocity.

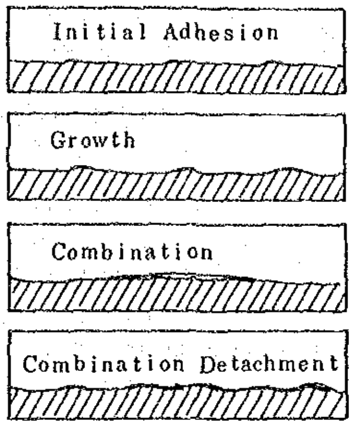

Fig. 4.2.3: Process of Adhering of Oil Drops (Model)

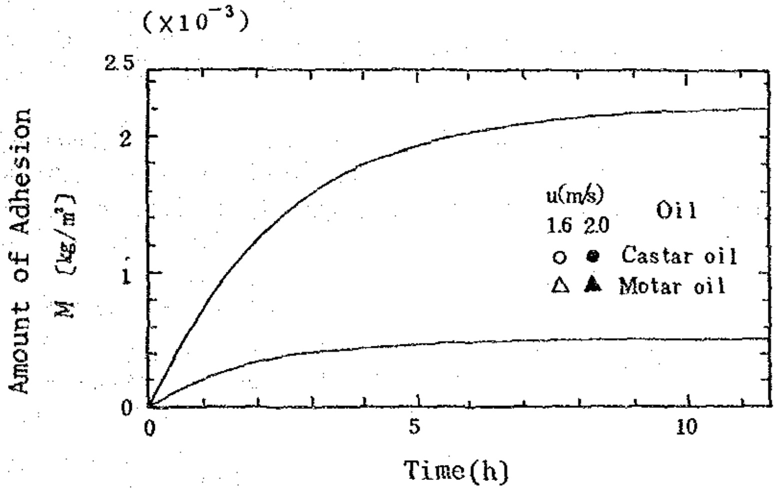

Fig. 4.2.4: Changes in Oil Adhesion Quantity with Passage of Time (Acrylic Resin Test Tube)

In the experiment, castor oil, motor oil and A-type heavy oil (ASTM D 396 No.5 light) were used as a 1% (vol) concentration in sea water. However, an example is reported in which nearly no adhesion was observed in stainless steel tube.

Takami et. al 12) observed an adhesion phenomenon on the inner surface of acrylic resin pipe using B-type heavy oil (concentration of the oil; 500 to 1,000 mg/l, average diameter of oil particles: less than 100 $\mu$m).
As a result, it was reported that the two processes, i.e. the adhesion of core-forming oil particles and their growth, were both observed.

Furthermore, when the adhered particles grew to a considerable extent, separation and flow of the adhered oil along the internal surface of the pipe were ocurred by the shearing force of the main stream (average flow velocity 0.8 to 1.9 m/s). The total amount of fouling increased gradually and eventually reached to saturation point.

As described above, although the test conditions were not fully consistent with the actual conditions of oil contamination in the sea water desalination plant, it should be taken into consideration that oil generally adheres to the heat transfer tubes, the extent of which varies depending upon the material of the tube, the properties of the oil, concentration of oil, flow velocity etc.

### (2) Overall Heat Transfer Coefficient and Fouling Factor

Corrosion products, scales and other substances adhering to the heat transfer surface increase heat transfer resistance and decrease the overall heat transfer coefficient of the heat transfer tubes. The relationship between the overall heat transfer coefficient (U) and fouling factors $R_i$ and $R_o$ , which are an index of fouling, is expressed in Equation (4.2).

In Equation (4.2), when the oil is mixed with sea water, the main factors which affect the heat transfer are $h_i$ and $R_i$. When the oil is shifted to the condensation chamber and condenses on the outer surface of the heat transfer tube, $h_o$ and $R_o$ will change.

Therefore, each of these factors will be studied.

$$1/U = 1/(h_i\ r_i) + \ln\ (r_o/r_i)/\lambda_T + 1/h_o\ r_o + R_i/r_i + R_o/r_o \qquad (4.2)$$

Where,

$U$: Overall heat transfer coefficient (per unit length) (kcal/m h °C)
$h_i$: Inner wall laminar heat transfer coefficient (kcal/m² h °C)
$h_o$: Outer wall condensation heat transfer coefficient (m)
$\gamma_i$: Inside radius of tube (m)
$\lambda_T$ : Heat conductivity of tube (kcal/m h °C)
$R_i$: Fouling factor inside tube (m² h °C/(kcal)
$R_o$: Fouling factor outside tube (m² h °C/(kcal)
h : Hour

(a) The inner wall heat transfer coefficient $h_i$ is expressed by Equation (4.3). Here, when sea water flows inside the tube, the factors of (a) bulk brine viscosity and (b) adhesion of contaminating oil to the heat transfer surface, will affect heat transfer.

$$h_i = 0.027\ R_e^{0.3} P_r^{1/3} (\mu_b/\mu_w)^{0.14} k/2\gamma_i \qquad (4.3)$$

Where,

Re: Reynolds number ($=2\gamma_1 G/\mu_b$) (-)
Pr: Prandtl number ($C_p\mu\ g/k$) (-)
$\mu_b$: Bulk brine viscosity (kg/m h)
$\mu_w$: Brine viscosity on tube wall (kg/m h)
k: Heat conductivity of fluid (kcal/m h °C)
G: Mass velocity of brine (kg/m² h)
Cp: Specific heat under constant pressure (kcal/kg °C)
g: Gravity acceleration (m/h²)

At first, in relation to (a), Equation (4.3) shows that $h_i$ is proportional to $1/\mu_b^{0.467}$. Therefore, according to this equation, when the viscosity increases by 0.5%, $h_i$ decreases by 0.3%. When oil contamination is calculated to be less than 0.1%, the variations in the viscosity of the oil contaminated sea water is considered to be less than 0.5%, (since there is no literature concerning the viscosity of oil contaminated sea water, the value is assumed from the viscosity of ordinary slurry. 15)

Accordingly, the influence on $h_i$ is very small, a decrease of 0.3% at the most.

Further, in relation to (b), when contaminating oil adheres to the heat transfer surface, the extent of the decrease in the U value may be calculated using Equation (4.2). When the U value is calculated on the assumption that sea water flows at the inner wall heat transfer coefficient $h_i$ of 3,000 kcal/m² h °C in a tube made of copper alloy with a nominal diameter of 25A, to which oil (heat conductivity 0.123 kcal/m² h °C) is uniformly adhered in a circumferential direction with a thickness of 2μm (refer Fig. 4.2.4), the U value decreases only by 0.5% of its original value without oil adhesion.

The above stated condition is hardly considered in actual cases, and it would be more probable to expect the adhesion of the oil to the uneven surface of the alkaline scale already formed on the tube. However, no evidence has been found so far in connection with this.

(b) The outer wall condensation heat transfer coefficient $h_0$ is shown in Equation (4.4) when the volume of non-condensation gas is large.

$$h_0 = 0.33\ Pr^{0.33}\ Re0^{0.6} \qquad (4.4)$$

From Equation (4.4), the influence of the viscosity can be said to be the same as $h_i$ because ho is proportional to $1/\mu_b^{0.27}$.

However, as will be described in 4.4.3 (2) <Example 3>, there is a information that when oil and water vapor condense to form an emulsion, the oil behaves differently. Therefore, it will be necessary to confirm the above phenomena in this respect.

Furthermore, Hazelton and Baker developed Equation (4.5) for the condensation of a two-component vapor such as water and benzene, toluene or chlorobenzene etc. 13) It is evident from this equation that when the ratio of oil to condensing water is very low, the influence on the outer wall condensation heat transfer coefficient h 0 is also low.
In the case of a horizontal tube:

$$h_o = 257\{[wt\% \quad h_o = 257\{[(wt\%)_o \lambda_o + (wt\%)_w \lambda_w]/(wt\%)_o D\}^{1/4} \qquad (4.5$$

λo: Condensation latent heat of organic matters
λw: Condensation latent heat of vapor
D: Inside diameter of tube

(c) Values of inner wall fouling factors $R_1$, which are adopted as the standard values corresponding to the different kinds of fluid, are shown in Tables 4.2.2 through 4.2.4. 14) 15)

When sea water and fuel oil are compared, the fouling factor of fuel oil is ten times greater than that of sea water, and in the case of gasoline and kerosene 2 times and in the case of gas oil fouling factor is 4 to 6 times greater than that of sea water. These values, however, are applicable to a 100% oil, and the fouling factor in the case of a 0.1% oil in sea water may be regarded as almost the same as that of sea water.

As described above, the influence of oil contamination on $h_1$, $h_0$, and $R_1$, is extremely small. Its total effect on the overall heat transfer coefficient U is also small as can be seen from Equation (4.2).

In the design of a sea water desalination plant for the Middle East it is recommended to employ the values indicated in Table 4.2.8 for the fouling factors in order to maintain highly reliable and satisfactory performance. 16)

The fouling factors prescribed in the specifications for the subject plant in UAN have the same or greater values as those indicated in Table 4.2.8 and a sufficient allowance has been provided for the heat transfer area. Therefore, if fouling of the heat transfer area takes place to some extent due to oil contamination, it will not directly affect the performance of the plant.

Also, as a ball cleaning system is provided in the heat recovery section and the brine heater, the allowance should be further expanded.

Table 4.2.2: Fouling Factors Used by TEMA 15) (Water)

Unit: $m^2$ h °C/kcal

| Conditions | | |
|---|---|---|
| Temperature of heating fluid (°C) | up to 115 | |
| Temperature of water (°C) | 52 or less | |
| Velocity of water (m/s) | 1 or less | Above 1 |
| Fluids | | |
| Sea water | 0.0001 | 0.0001 |
| Top water, Well water, Boiler feed water, Cooling water | 0.0002 | 0.0002 |
| Distilled water | 0.0001 | 0.0001 |
| Hard water (15 grains/gas or more) | 0.0006 | 0.0006 |
| River water (average) | 0.0006 | 0.0006 |

Remark: 1 grain = 0.0648 g

Table 4.2.3: Fouling Factors Used by TEMA 15) (Various Fluids)

Unit: $m^2$ h °C/kcal

| Oil | | Gas/Vapor | | Liquid | |
|---|---|---|---|---|---|
| Fuel Oil | 0.001 | Organic Matter Vapor | 0.0001 | Organic Matters Rrigerant Liquid | 0.0002 |
| Machine Oil | 0.0002 | Water Vapor (without Oil Bearing) | 0.0001 | | |
| Transformer Oil | | Alcohol Vapor | | Brine (for Cooling) | |
| Clean Lubricating Oil | | Water Vapor (with Oil Bearing) | 0.0002 | | |
| Quenching Oil | 0.0008 | Refrigerant Vapor | 0.0002 | | |
| Vegetable Oil | 0.0006 | Air | 0.0004 | | |

Table 4.2.4: Fouling Factors Used by TEMA 15) (Various Oil Products)

$m^2$ h °C/kcal

| | |
|---|---|
| Gasoline | 0.0002 |
| Naptha | 0.0002 |
| Kerosene | 0.0002 |
| Gas Oil | 0.0004 - 0.0006 |
| Heavy Oil | 0.001 |

Table 4.2.5 Fouling Factors in Seawater Desalination Plants

| Sections | Fouling Factors $m^2$ h °C/kcal |
|---|---|
| Brine Heater | 0.0003 |
| Heat Recovery Section | 0.00017 |
| Heat Rejection Section | 0.0002 |

### 4.2.3 Control and Instrumentation

As the control and instrumentation systems are indispensable for maintenance and operation, the function of the sensors which monitor the conditions of plant operation, such as the flow rate, temperature, pressure, etc., must not be interfered with by oil contamination.

These control and instrumentation systems are divided into two categories depending upon the importance of their operation and control. One is the control of process conditions, and if any abnormality occurs in their function then operation itself becomes impossible. The following control systems belong to this category:

(a) Brine temperature control system
(b) Flow rate control system
(c) Level control system

The other category is the control and monitoring required for maintaining the stable performance of the plants, although if any abnormality occurs then operation can be continued for a short period without the support of these systems. The following control and instrumentation systems belong to this category.

(d) Conductivity measurement system
(e) Chemical injection control system

a) Anti-scalant injection control system
b) pH control system

(f) Dissolved oxygen measurement system
(g) Temperature and pressure gauges installed in various sections of the plant.

Now, in the subject plants, all control systems other than the (e)-b) pH control system and the dissolved oxygen measurement system are installed as indicated in Fig. 2.1.2 and Fig. 2.1.6. Of those control and measurement systems, the (e)-a) anti-scalant injection control system has no connection with oil contamination since it does not come into contact with sea water.

In cases where oil adheres to the (d) conductivity measurement system and the (g) temperature and pressure gauges, they can be taken out during operation for a short time and cleaned by organic solvents. Therefore, the effects on the (a) maximum brine temperature control system, the (b) flow rate control system and the (c) liquid level control system will be studied here.

(1) Maximum Brine Temperature Control System

The control system for the maximum brine temperature in the subject plant is of a type in which the brine temperature at the outlet of the brine heater is controlled by adjusting the vapor volume at the inlet of the brine heater. The temperature is monitored by a thermocouple which is covered by a protector tube made of stainless steel. Accordingly even if oil is mixed with the brine, there is almost no influence on heat conductivity, and unless the protector tube is corroded or the thermocouple is damaged, the system should never be affected detrimentally.

(2) Flow Rate Control System

Orifice type flow meters are used for the measurement of the flow rates of the sea water used for cooling the heat rejection section, circulating brine, make-up sea water and product water in the subject plant.

This is a system which converts the differential pressure occurring before and behind the orifice, into a flow rate, and even if oil is mixed with the fluid to be measured, the indication of the flow rate is never affected.

### (3) Level Control System

Another important control system related to oil contamination is the liquid level control system located in the flash chamber of the final stage. This system controls the brine flow rate in the final stage by adjusting the opening rate of the blowline outlet valve which branches off from the brine circulation pump. The monitoring signal for the liquid level is the vertical displacement of the float; the effect of oil contamination in the displacement of the liquid level is negligible.

### 4.2.4 Influence on Degasifier (Deaerator)

Since the subject plants employ a chemical injection method for the prevention of scaling, no decarbonator is installed, which places the deaerator *1 as the subject in the study of the degasifier.

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Note: *1 Shape of the deaerator is not a tower shape but a similar shape as a evaporator.

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Also, of the two types of the subject plants, West No. 1 - 6 units adopt a combined deaeration system of the make-up water spray method and the steam stripping method which uses steam generated from the 14th stage. On the other hand, East No. 1 - 3 units employ only the make-up waters spray deaeration method.

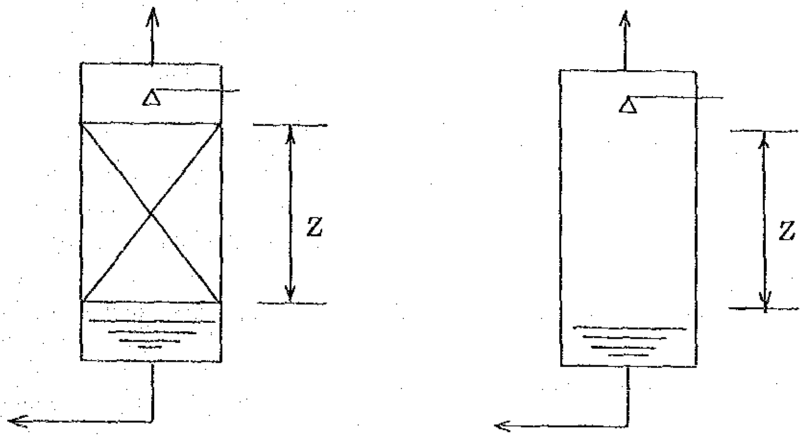
While the performance of deaeration is subject to many factors such as internal structure, venting rate, etc., each deaeration system is most influenced by the height of the tower which is determined by Equation (4.6) in cases where the quantity of process water per unit cross section of the tower is constant.

$$Z = (NTU) \times (HTU) \tag{4.6}$$

Where,

Z: Effective height of tower (m)
(in the case of a spray tower, the height of spray stratum)
(NTU): Number of transfer unit (-)
(HTU): Capacity coefficient (-)

Diagram of Spray Tower



In Equation (4.6), while NTU is readily determined by the difference in concentration before and after processing, but there are different ways to calculate HTU depending on the internal structure of the tower, the method of processing, etc. Further, the design engineers possess practical know-how and often employ different equations. Since Equation (4.7) 17) has already been ascertained as applicable to the spray tower, the influence of oil contaminated sea water inflow will be studied by making use of this equation in this paper.

$$HTU/d = 0.021 (d_N/Z)^{-0.67} (R_o) (W_e)^{-0.67} \times (G_a)^{-0.20} (S_c)^{0.5} \qquad (4.7)$$

Where,

$\mu_L$: Viscosity of liquid (kg/m h)
$\rho_L$: Density of liquid (kg/m³)
$D_L$: Diffusion coefficient (m²/h)
$d_N$: Diameter of spray nozzle (m)
$R_e$: Reynolds number (= $d_N U_N \rho_L / \mu_l$ ) (-)
$G_a$: Galilei number (= $d_N^3 g \rho_L^2 / \mu_L^2$ ) (-)
$W_e$: Weber number (= $d_N U_N^2 \rho_L / \sigma$ ) (-)
$S_c$: Schmidt number (= $\mu_L / \rho_L D_L$ ) (-)
$U_N$: Flow velocity at nozzle (m/s)
g: Gravity acceleration (m/s²)
$\sigma$: Surface tension (kg/s²)
z: Effective height of tower (m)

When the deaerator employed in the subject plant is regarded as the spray tower system and attention is directed to Equation (4.7), the factor most influenced by the oil contaminated sea water is assumed to be the viscosity of liquid $\mu_L$. When the terms of viscosity are extracted in Equation (4.7), HTU is proportional to $1/\mu_L^{0.1}$.

For example, if an increase in viscosity is at a level of only 10%, HTU decreases by 1%, which means that the performance of the spray tower is slightly more favorable.

Other than in the above situation, a study of oil adhesion on the nozzle, as another influential factor on HTU, will be necessary. That is, when heavy oil flows into a nozzle with a hole diameter of several millimeters, the oil adheres to the nozzle and causes a change in the shape of the spray. In this place, only the hole diameter and flow speed are changed.

HTU becomes proportional to $d_N^{0.06}$ $U_N^{-0.34}$ , and is affected by the changes in Equation (4.7). Even in the case where the hole diameter becomes smaller, the flow velocity, $U_N$ , increases in proportion to the square of the hole diameter, $d_N$ , so long as an allowance remains in the pump capacity. Consequently, in total, HTU is proportional $d_N^{0.74}$ For example, if the hole diameter is reduced 10%, HTU decreases by 8%, giving a favorable tendency to the effective height of the tower as in the case of an increase in viscosity.

Nevertheless, in reality, as most of the heavy oil is removed at the strainer, screens and elsewhere before it reaches the nozzle, the influences of the hole diameter and the flow velocity need not be taken into consideration. A change in the shape of the spray caused by a chemical reaction between the nozzle material and the oil would, rather, have a greater effect.

### 4.2.5 Influence on Brine Heater

The brine heater generates a driving force to enable the brine to evaporate in the evaporation chamber and, in the case of the subject plant, to raise the temperature about 80 °C to 90 °C. When oil is included under such conditions, gasification and transmutation of the oil does not occur at those temperatures, but the viscosity will be somewhat reduced due to a rise in the temperature, resulting in better fluidity. Therefore, it is difficult to believe that the oil mixture would cause a deterioration in the heat transfer efficiency.

### 4.2.6 Influence on Vacuum System

The vacuum system mentioned is a system which (a) vents incondensable gas from the evaporation chamber and (b) deaerated gas and water vapor from the deaeration tower, (c) releases the exhaust gas to the atmosphere, and (d) transfers the condensed water (drain) outside the system. The equipment comprises of a steam ejector which reduces the pressure in the system and extracts incondensable gas, and a vent condenser or an ejector condenser which cools and condenses the exhaust gas.

From the deaerator, incondensable gas such as oxygen, nitrogen, large quantities of water vapor, and components of oil with low boiling points are vented.

On the other hand, since volatile oil other than those removed at the deaeration tower is condensed along with water vapor after evaporation, the gasses vented outside the system are mainly composed of uncondensed water vapor, oil vapor and carbon dioxide gas produced by the decomposition of $HCO_3^-$ on contained in sea water.

Now if these gases flow into the system, there is the possibility that the gases will not be entirely condensed but discharged into the atmosphere. This will depend on the cooling capacity of the vent condenser or the ejector condenser.

Also, the drain produced here contains oil components with low boiling points. Since the subject plant is of a type which returns the produced drain to the condensation chamber, the drain is mixed with the product water and is partially recirculated into the vacuum system. Therefore, it should be necessary to make arrangements to discharge the drain outside the system or to remove oil from the drain transferred to the condensation chamber.

Further, as the vent gas has a foul odor and contains trihalomethane mentioned in 4.5, there is the possibility that it will cause air pollution.

### 4.2.7 Influence on Evaporation Chamber

The components of volatile oil other than those removed at the deaerator are flash-evaporated in the evaporation chamber and condensed onto the external surfaces of the heat transfer tubes, after passing through the demister along with the water vapor. The condensed water and oil forms a binary liquid phase or an emulsion state, partially forming a mono-liquid phase in which oil is dissolved into water.

A problem with the evaporation chamber is that the oil separated into the binary liquid phase adheres to and contaminates the product water trays or the side walls in the condensation chamber.

### 4.2.8 Conclusion

As mentioned above, influences on the performance of equipment and systems when oil contaminated sea water is used as raw sea water in the desalination plant, have been discussed. In relation to the influence on heat transfer, which is the most fundamental technology, if the concentration of the contaminating oil is as small as 0.1% or less, the influence on the properties of the sea water (viscosity, specific heat, etc.), is so small that the oil mixed in sea water is not considered as capable of directly affecting the heat transfer efficiency.

If there is any influence on efficiency, it will probably be a reduction in the heat transfer efficiency caused by fouling, but such influence arises very slowly. The amount of oil adhesion in the heat transfer tubes differs markedly depending upon the surface condition of the heat transfer tubes when the oil is mixed in. However, in actual practice, the influence will not be so great as to cause changes in operational conditions, over a short period of time (one week to 10 days). There may be some influence to cause the timing of acid cleaning to be advanced.

However, in order to make a more precise evaluation, it is necessary to learn more about the properties of the emulsion, such as adhesion of emulsion to metals, etc.

The problems which directly affect the performance of hardware are the deformation of the spray nozzle in the deaerator, caused by the adhesion of oil, and the accompanying decline in the performance of the deaerator. If the nozzle is made of metal, almost no problem may arise, but if it is made of an organic material, the above problem is likely to occur. Therefore full attention must be paid when the nozzles are replaced.

The greatest problem is the deterioration in quality of the product water, which is one of the important topics under investigation. The quantitative aspects relating to the deterioration in water quality will be described in detail in 4.4.

## 4.3 Influence on Performance of Power Station

The power station WEST No.1 to 6 units, the subject of this study, is of a conventional type, using sea water as the cooling medium of the surface condenser and of various other kinds of coolers. When the power station is operated using oil polluted sea water there is the possibility that there will be a reduction in the cooling efficiency of various cooling equipment, caused by the increase in contamination and following increase in the heat transfer resistance which occurs on the cooling surfaces due to oil particle adhesion and the dissolved oil in sea water.

As clarified in detail in 4.1.2, considerable changes in the physical and chemical properties of the spilt oil can be observed by the time it arrives at the intake point of the power station, and it is difficult to estimate the exact nature of the changes which would occur. Therefore,

some presumptions are forced to make about the influence of oil in a wide range of areas.

Where sea water is contaminated with oil, the floating oil is almost completely removed by the oil pollution protection devices and the intake structure equipment, but oil dissolved in sea water, or undissolved but in the form of emulsion, would be able to pass through such devices and equipment and reach the power station equipment.

Accordingly, presuming that the influence on the cooling efficiency on the systems arise from a combination of the two phases 40), the influence of dissolved oil on heat transfer and the influence of a reduction in the cooling area due to the adhesion of minute oil particles, undissolved but in emulsion (fouling), will be clarified in 4.3.3 (1) to (3) and 4.3.3 (1) to (2) respectively.

Among all the equipment subject to oil pollution, the most essential equipment in the power station is the surface condenser where the steam exhausting from the steam turbine is condensed at a saturation pressure (below atmospheric pressure, that is, a vacuum), corresponding to the condensate temperature attainable by sea water cooling.

The potential for a reduction in the condenser cooling efficiency influences the steam turbine exhaust pressure and thus the performance of the power station.

The relationship between condenser pressure and turbine heat rate for a typical turbine generator is shown in Fig. 4.3.1. The power station performance, thermal efficiency of the power station being the product of the turbine efficiency (turbine heat rate) and boiler efficiency, is decreased by the increase of the condenser pressure.

Fig. 4.3.2, which shows the relationship between condenser pressure and condenser tube cleanliness, makes it clear that the decrease in the condenser vacuum (increase in condenser pressure), due to a decrease in the condenser tube cooling efficiency, decreases the thermal efficiency of the power station.

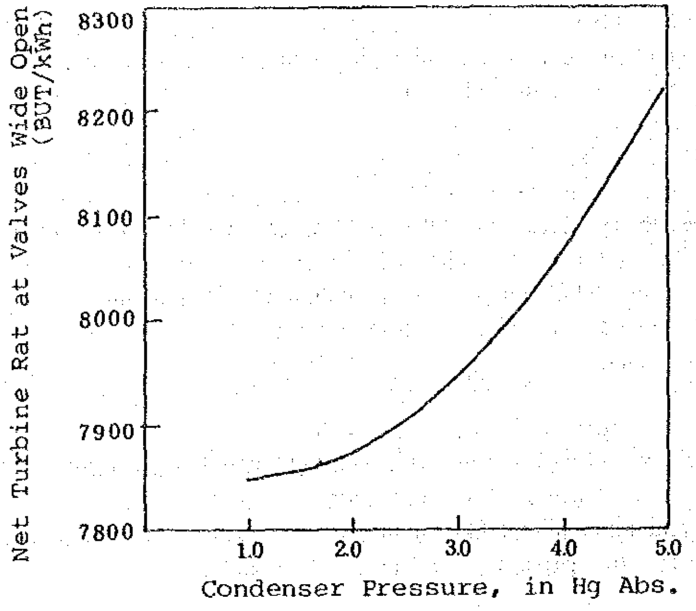


Fig. 4.3.1: Net Turbine Heat Rate versus Condenser Pressure for Typically Large Turbine Generator 41)

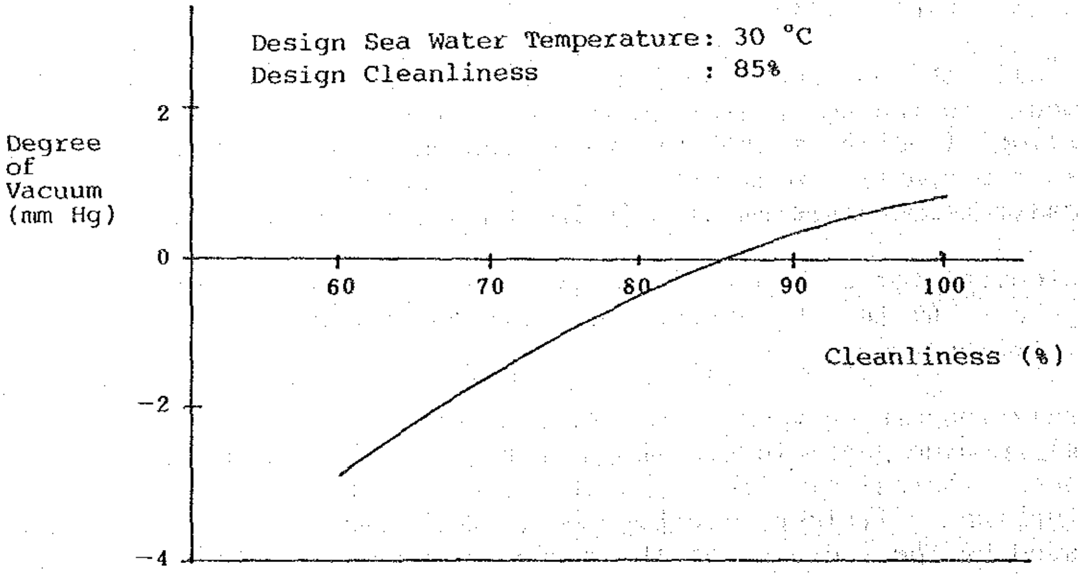


Fig. 4.3.2: Degree of Vacuum versus Tube Cleanliness for Typical Condenser 42)

As specific turbine generator/condenser relationship curves for the subject station under consideration were not available, both figures mentioned above are for a typical value. In Fig. 4.3.2, with an increase in cleanliness of approx. 1%, the condenser vacuum decreases approx. 0.1 mmHg (the condenser pressure increase, approx. 0.1 mmHg).

While in Fig. 4.3.1, with the condenser pressure increase of approx. 1mmHg, the turbine generator heat rate rises (worsens) approx. 0.05% at the vacuum design point, 3.5 in Hg abs. (0.115 bar abs). This means that with a decrease in condenser tube cleanliness of approx. 1%, the decreased rate of thermal efficiency of the station is about 0.005%.

The cleanliness decrease equals the overall heat transfer coefficient decrease, or the decrease of the cooling efficiency.

### 4.3.1 Influence on Pumps

The power station has vertical water pumps only, in the sea water cooling system, which are subject to oil pollution, common to the adjacent distillers. The influence on pump performance is described in 4.2.1.

### 4.3.2 Influence on Instrumentation

Only the pressure gauges and thermometers are in the sea water cooling system of the power station, and are subject to oil pollution. The influence on their performance is described in 4.2.3. The sea water cooling system diagram is shown in Fig. 2.1.13.

### 4.3.3 Influence on Heat Transfer at Condenseer Tubes

#### (1) Influence on Overall Heat Transfer Coefficient of Surface Condenser

#### 1) Approach to Study on Influence

Overall heat transfer coefficient K is generally calculated as follows:

$$K = \frac{Q}{A\ (LMTD)} \quad (\mathrm{kcal/m^2\ h\ ^\circ C}) \qquad (4.8)$$

Where,

Q : Total heat to be cooled in the condensers
A : Cooling area on the sea water side of condensers
(LMTD) : Logarithmic mean temperature difference

In parallel, the overall heat transfer coefficient K is generally expressed also as follows;

$$K = \frac{\alpha_w \cdot \alpha_s}{\alpha_w + \alpha_s} \times F\,(\mathrm{kcal/m^2 ^\circ C}) \qquad (4.9)$$

Where,

$\alpha_w$: Heat transfer coefficient on the sea water side (of turbulent heat transfer inside tubes) of condensers
$\alpha_s$: Heat transfer coefficient on steam side (of condensing heat transfer outside tubes) of condensers
F: Cleanliness factor of condenser tubes

Oil polluted sea water passing through the condenser cooling tubes does not affect $\alpha_s$ because of its position on the steam side. The influence of dissolved oil is expressed by the decrease in $\alpha_w$, as clarified in the above equation (4.9). Also, the influence of the condenser cooling area reduction caused by the adhesion of minute oil particles, undissolved but in emulsion, means a decrease in A, in the above equation (4.8), or a decrease in F in the equation (4.9).

The approach to the study of the influence is, accordingly, to estimate the decrease of $\alpha_w$ and A separately, and to clarify the influence on the surface condenser overall heat transfer, through the equation (4.9).

### 2) Influence of Oil Particle Adhesion on Heat Transfer

Within the inflowing oil-in-water emulsion, minute oil particles which adhere to the cooling surface eventually impede its heat transfer function.

According to experimental test results on oil adhesion 12), the oil adhesion rate of approx. $55\text{x}10^{-4}$ cc could be saturated after more than 6 hours of inflowing oil-in-water emulsion with an oil concentration of 500 to 1,000 ppm, at water temperature of 15 to 16 °C, using B heavy oil of specific weight 0.92, viscosity 140 cSt (20 °C), in acrylic resin pipe of 20 mm O.D. and 1.0 m length. The test water velocity inside the pipe was 1.5 to 1.9 m/s, which is almost equal to the actual sea water velocity inside the condenser cooling tubes.

Using the test results, it can be estimated that the oil particle adhesion area inside the pipe would be less than approx. 0.6% of the total area, on the assumption that the mean size of the oil particles is 20 micron, in the emulsion flow.

Although tests on steel tubes and/or sea water which were conducted under conditions similar to those of the specific surface condenser of the station have not been found, the tests estimate that a decrease in the cooling area, or decrease of heat transfer due to oil particle adhesion, would be less than 1 to 2% for the surface condenser, which can actually be neglected.

### 3) Influence of Dissolved Oil on Heat Transfer

Let us estimate herein how K is decreased by the decrease of $\alpha_w$, keeping $\alpha_s$ and F constant in the equation (4.9).

The heat transfer coefficient on the sea water side $\alpha_w$ can be expressed as follows 38), because Reynolds number Re is calculated as $3 \times 10^4$, which means complete turbulent flow inside the cooling tubes.

$$\alpha_w = N_u \times \lambda_w/di = 0.023 \times Re^{0.8} \times Pr^{0.4} \times \lambda_w/di \ (kcal/m^2\ h\ °C) \tag{4.10}$$

The heat transfer coefficient on the steam side $\alpha_s$ can be expressed as follows 38). Outside the cooling tubes, the heat is transferred through laminar flow film formed by condensation.

$$\alpha_s = 1.51 \cdot (4G/g \cdot \eta_s)^{-1/3} \cdot (g \cdot \eta_s^2/\gamma\lambda_s^3\alpha_s^2)^{-1/3} (kcal/m^2h°C) \tag{4.11}$$

Where,

$N_U$: Nusselt number
$R_e$ : Reynolds number = $W_i \cdot d_i/W_w$
$P_r$ : Prandtl number = $W_w/a_w$
$W_i$ : Cooling sea water velocity inside the tubes
= 1.9 (m/s) = $6.48 \times 10^3$ (m/h)
$d_i$ : Inside diameter of the tubes = 0.020 (m)
$V_w$: Kinematic viscosity of cooling sea water
= $g \cdot \eta_w/\alpha_w$ ($m^2$/h)
$a_w$: Thermal diffusivity of cooling sea water
= $\lambda_w/C_{pw} \cdot \alpha_w$ ($m^2$/h)
$\eta_w$: Condensate flow rate per tube length, 1m (kg/h $m^2$)
$\eta_s$: Viscosity of cooling sea water (kg h/$m^2$)
$\gamma$ : Viscosity of condensate (kg h/ $m^2$ )
A: Evaporation heat (kcal/kg)
$\lambda_w$: Thermal conductivity of cooling sea water (kcal/h m °C)
$\lambda_s$: Thermal conductivity of condensate (kcal/h m °C)
$\alpha_w$: Specific weight of cooling water (kg/$m^3$)
$\alpha_s$: Specific weight of condensate (kg/$m^3$)
Cpw: Specific heat at constant pressure of cooling sea water (kcal/kg °C)

$\alpha_w$ can be expressed as follows, changing the equation (4.10).

$$\begin{aligned}\alpha_w &= 0.023 \times R_e^{0.8} \times P_r^{0.4} \times \lambda_w/d_i \\ &= 0.023\ (wi\ di\ \alpha w/g\eta w)0.8 \cdot (g \cdot Cpw \cdot \eta_w/\lambda_w)^{0.4} (\lambda_w/di) \\ &= 0.0338 \cdot \lambda_w^{0.6} \cdot \alpha_w^{0.8} C_{pw}^{0.4} \eta_w^{-0.4}\end{aligned} \tag{4.12}$$

When t(%) is a concentration ratio of dissolved oil in sea water,

$\lambda_w = 0.583\ (1 - 0.782 \times 10^{-2} \times t)$ (kcal/h m °C)
$\alpha_w = 1020\ (1 - 0.118 \times 10^{-2} \times t)$ (kg/$m^3$)
$\eta_w = 2.28 \times 10^{-8}\ (1 + 1.220 \times 10^{-2} \times t)^3$ (kg h/$m^2$)
$Cpw = 0.956\ (1 - 0.530 \times 10^{-2} \times t)$ (kcal/kg °C)

Then, the following equation can be obtained from the equation (4.12).

$$\alpha_w = 6.99 \times 10^3 \times f(t) \qquad (4.13)$$

$$f(t) = (1 - 0.782 \times 10^{-2} \times t)^{0.67} \times (1 - 0.118 \times 10^{-2} \times t)^{0.8} \times (1 - 0.530 \times 10^{-2} \times t)^{0.4} \times (1 + 1.220 \times 10^{-2} \times t)^{-1.2}$$

The following numbers are adopted in the above equation on the assumption that sea water temperature is approx. 30 °C.

| Items | Sea Water | Crude oil |
|---|---|---|
| $\lambda$ (kcal/h m °C) | 0.583 | 0.127 |
| $\alpha$ (kg/m³) | 1020 | 900 |
| $\eta$ (kcal/kg °C) | 0.956 | 0.448 |
| E (kg s/m²) | $0.82 \times 10^{-4}$ | $9.00 \times 10^{-4}$ |

The result of the calculation of $K^1/K$ is shown in Fig. 4.3.3, where $K_1$ is an overall heat transfer coefficient of the condenser tubes under the concentration ratio, t, of dissolved oil, and K is the same coefficient without oil pollution.

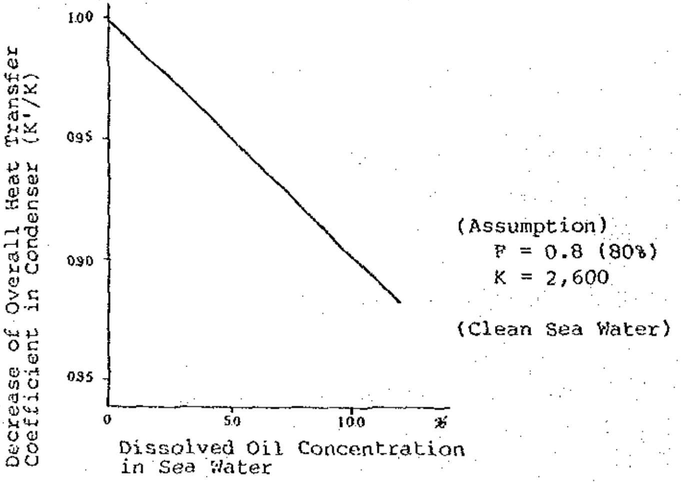
$K^1/K$ is expressed as follows from the equation (4.9).

$$K^1/K = f(t) \times (\alpha_w \times \alpha_s) / (f(t) \times \alpha_w \times \alpha_s)$$
$$= f(t) \times F \times \alpha_w / (F \times f(t) \times \alpha_w - f(t) \times K + K)$$

If t = 0.1, f(t) can be calculated as 0.998 and then $K^1/K = 0.999$.

This number means:

Even under a concentration of 1% of dissolved oil in sea water, the decrease of the overall heat transfer coefficient would be estimated at only approx. 1% for the surface condenser, without oil adhesion inside the cooling tubes.



K': K under oil-polluted sea water

Fig. 4.3.3: Decrease of Overall Heat Transfer Coefficient versus Dissolved Oil Concentration in Sea Water (without Oil Adhesion)

Fig. 4.3.4 shows the solubility of hydrocarbons and petroleum fractions in water at total steam pressure under laboratory conditions. 39) By this curve, it can be seen that the oil concentration ratio in complete dissolution would be 0.002 to 0.05 mol % in water under 100 to 200 °F.

However, as explained in Chapter 2, oil properties would be changed widely by the following phenomena, and the actual decrease of the overall heat transfer coefficient, theoretically calculated as 0.1% in the above, would probably either be magnified further with the secular increase of oil solubility, or be lessened further if the oil is in the pre-dissipation state, as dissolved oil properties become closer to those of sea water.

* Water content in oil increases with the time elapsed and the specific weight as well as the viscosity increase with the water content increase (refer to Figs. 4.1.3 and 4.1.5).

* Specific weight of oil increases with the time elapsed through the evaporation of the volatile components (refer to Fig. 4.1.4).

* Approx. 50% of the gasoline, kerosene and gas oil components are evaporated within 24 hours of the oil spilled. The heavier weight components remain in the spill oil (refer to 4.1.1).

* Spilled oil finally dissipates itself in sea water (Fig. 4.1.2).

Taking the above into consideration, it can be estimated that the overall heat transfer coefficient would actually be decreased to less than approx. 1%, since there are two opposite tendencies to increase and derease.

### (2) Influence on Overall Heat Transfer Coefficient of Various Different Kinds of Coolers

The overall heat transfer coefficient K is also expressed in Equations (4.8) and (4.9), for the coolers.

In comparison with surface condensers , the sea water flow in service water coolers and turbine oil coolers, both of the shell and tube type, is quite complicated due to the turbulent flow occurring outside the tubes, partly parallel to the tubes lengthwise, partly perpendicular to them, partly diagonally, as well as partly bypassing through the leakage between shell walls and baffle plates. The estimation of the heat transfer coefficient under such conditions would be complicated.

It can at least be presumed that oil particle adhesion (outside the tubes) can hardly take place in the service water coolers and turbine oil coolers, while it would be at the same level as the surface condensers in the generator air coolers, because sea water flows inside the tubes.

The influence on the overall heat transfer coefficient of the various different kinds of coolers would consequently be at the same level as that of the surface condensers or less. As a slight decrease in the cooling efficiency neither affects the operation nor performance of the power station, numerical estimation is omitted herein.

(Note) Cleanliness means reducing the rate of the overall heat transfer coefficient of the condenser tubes from a 100% clean condition, as defined by the Heat Exchanger Institute, USA, to some lower value. General practice is to use an 85% cleanliness factor. Fig. 4. 3. 3 Decrease of Overall Heat Transfer Coefficient Versus Dissolved Oil Concentration in Sea Water (without oil adhesion)

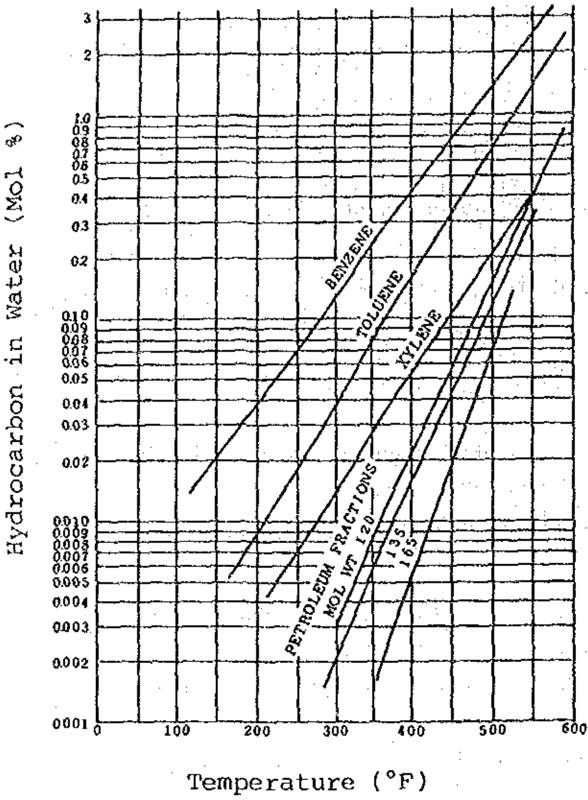


Fig. 4. 3. 4: Solubilities of Hydrocarbons and Petroleum Fractions in Water at Total System Pressure 39)

### 4.3.4 Conclusion

(1) The influence of oil polluted sea water in the thermal power station consists of the decrease in the heat transfer coefficient at the cooling tubes caused by dissolved oil, and the decrease in cooling surface (fouling) caused by the adhesion of minute oil particles, undissolved oil but in an emulsion, in the flow.

(2) The volume of oil dissolved in the sea water is greater in some cases, and lesser in others, than theoretical or tested values, because of the considerable secular changes in the physical and chemical properties of the spilled oil which occur by the time it reaches the power station equipment. Taking the solubility of oil as equal to 1,000 ppm or less in sea water, the decrease of the overall heat transfer coefficient of the surface condensers would be less than 1 to 2%.

(3) On the other hand, the decrease in heat transfer caused by the adhesion of oil particles at the cooling surface, though there are still many unknown factors, would be less than 1% at most, where the estimated oil concentration is less than 1,000 ppm in sea water.

(4) Among the equipment in the power station, the surface condensers are subjected to oil contaminatnion and the decrease of the thermal efficiency of the station due to a decrease in the cooling efficiency of the surface condensers can be estimated less than 0.02%.

Other equipment in the power station subject to oil contamination are the service water coolers, turbine air coolers and generator air coolers, in which a slight decrease of efficiency would not affect the operation and thermal efficiency of the station, under the above mentioned oil concentration in the sea water.

## 4.4 Influence on Quality of Product Water

Inasmuch as there is a complete difference in behavior of oil components in the sea water desalination process between the case where oil and water are simply mixed each other (two-liquid phase) and the case where oil is dissolved in water (single liquid phase), it is necessary to consider the behavior separately.

### 4.4.1 Behavior of Volatile Components During Sea Water Desalination Process

According to the report [18] concerning the behavior of oil components during the sea water desalination process, the vapor pressure of a water and oil mix vapor shows a similar value to that of the independent water and oil vapors.

When these two liquid phases are evaporated, the weight ratio of water to oil in the gaseous phase may be expressed by the following equation:

$$W_o/W_W = M_o \cdot P_o / M_w \cdot P_w \tag{4.9}$$

Where, $W_o$ and $W_w$ are the weight of the oil and water in the gaseous phase, and $P_o$ and $P_w$ are the vapor pressure, and $M_o$ and $M_w$ are their molecular weights. From this equation, if the molecular weight and the vapor pressure are known, the composition of distillates at various temperatures can be calculated.

When oil contaminated raw sea water is drawn into the desalination plant which employs the evaporation process, the oil component is evaporated in the evaporation chamber by a kind of steam distillation pursuant to Equation (4.9), along with almost all of the light component, high vapor pressure distillated from the brine.

For example, if 300 m³ of sea water contaminated with 100 mg/l of gas oil is drawn in as raw sea water and the plant is operated at the product water recovery rate of 0.42 (the ratio of product water to raw sea water), the oil components which are drawn over to mix with the 126 m³ of product water reaches a maximum of 238 mg/l, that is, the oil is concentrated up to the amount of the reciprocal number times the recovery rate.

### 4.4.2 Study of Numerical Simulation

(1) Simulation model

Nakazawa, et al. [19] have designed a computer simulation program using a mathematical model in order to study the behavior of hydrocarbons in the evaporator under operating conditions where raw sea water is contaminated is contaminated with oil. The model uses the 3000 m³/d MSF test plant as a model plant.

In this study, some improvements were made to the actual conditions of the subject plant. Simulated calculations of the evaporation rate of oil at each stage of the evaporator process, using various oil concentrations, were conducted. The operating conditions of Umm Al Nar West Nos. 1 to 6 units are used for this study, such as: maximum brine temperature - 42 °C, product water - 750 t/h, make-up sea water - 2,475 t/h, number of stages - 18. The flow of the simulated calculation is shown in Fig. 4.4.1.

Firstly, the following constants and given conditions were inputted in order to conduct the calculation: The hydrocarbon composition as a component of crude oil; each factor contained in Antoine's formula to obtain the vapor pressure of hydrocarbon and water; the normal probability to calculate the retention time of brine in the evaporation chamber; and, equipment data ( number of stages, temperature at each stage, quantity of make-up sea water, and quantity of product water at each stage).

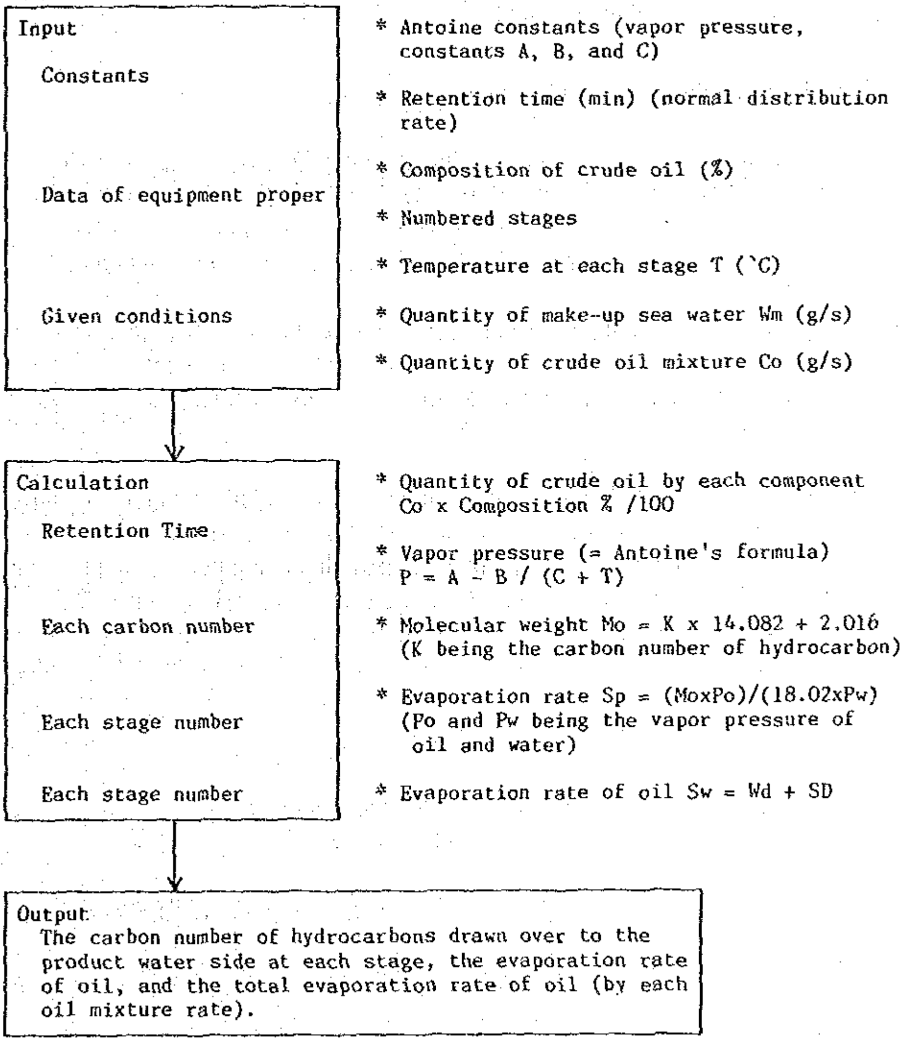


Fig. 4.4.1: Flow of Simulated Calculation for Behavior of Oil Components in MSF Evaporator

The retention time of the oil was calculated by assuming that the evaporation rates of hydrocarbons are proportional to the retention time of the brine in each evaporation chamber. As part of this calculation, the retention time of the brine at each evaporation chamber was assumed to be relative to the normal distribution of each portion of the brine in an average retention time.

Then the crude oil mixture rate relative to the actual case to be calculated was input.

When the two kinds of parameters mentioned above were input, the retention time of oil in each evaporation chamber, the evaporation rate of each component of the crude oil at each stage, and the transfer rate of oil to the next stage were calculated then in accordance with the program.

The items to be printed are (a) carbon number of hydrocarbon evaporated at each stage, (b) rate of evaporation and (c) the total evaporation rate of the mixture oil.

(2) Results of Simulated Calculation

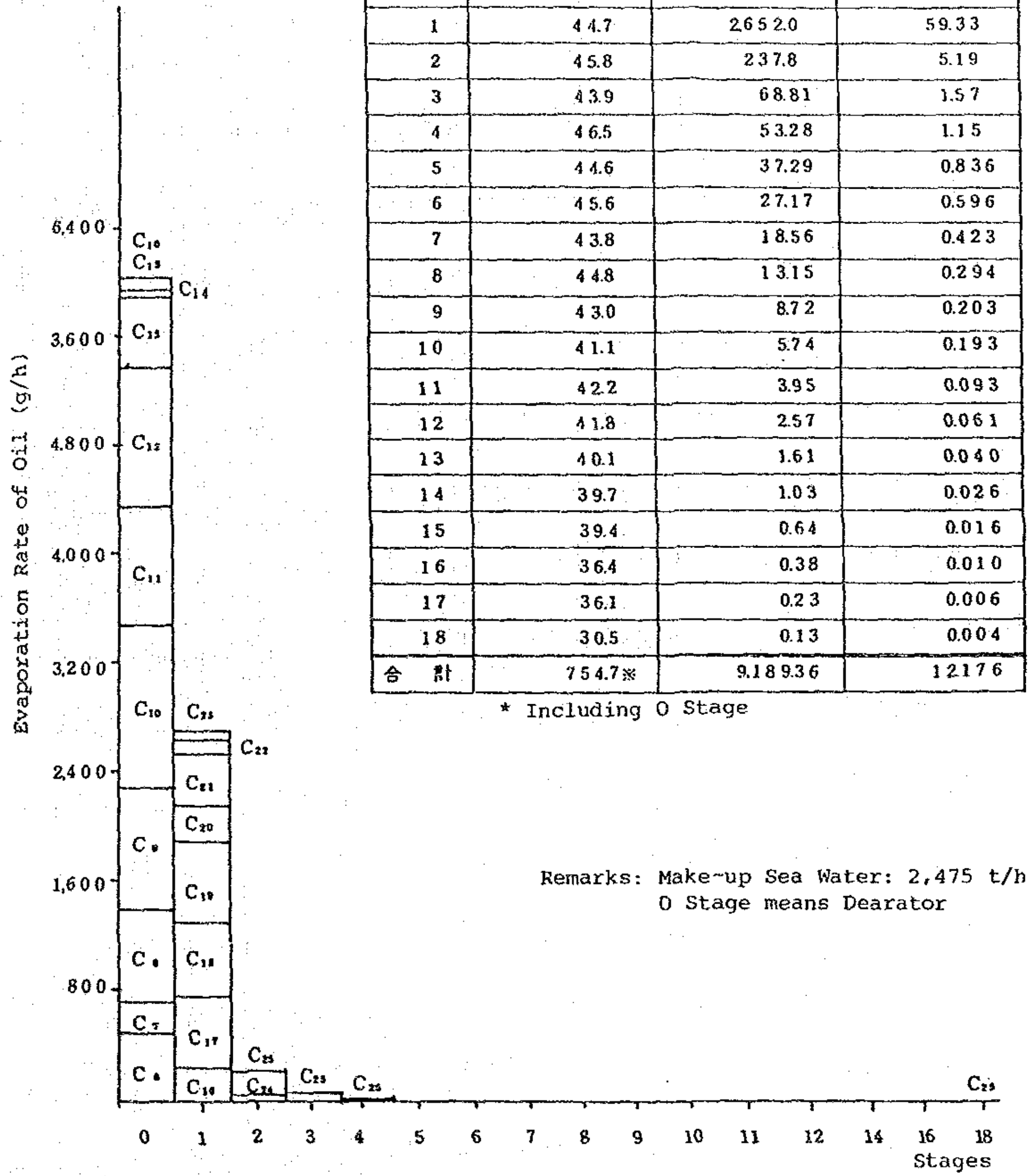
Examples of one such calculation, the behavior of crude oil mixed with sea water at the rates of 1,000, 100, and 10 mg/l are shown in Fig. 4.4.2 (1) through Fig. 4.4.2. (4). Since actual crude oil contains a great many kinds of organisms, the simulation was simplified as follows:

Hydrocarbons with a carbon number up to 10 were regarded as gasoline components, carbon numbers 11 to 14 as kerosene components, carbon numbers 15 to 20 as gas oil components and carbon numbers 21 and above as heavy oil components.

For the purposes of simplification, only straight-chain compounds with carbon numbers of 6 to 30 were considered to be present at the rate indicated in Fig. 4.4.3. Further, it was considered that in the evaporation chamber, distillation starts with the component with the lowest boiling point and continues successively through to the the component with the highest boiling point.

| Stage | Evaporation Water (t/h) | Evaporation Oil (g/h) | Concentration (mg/l) |
|---|---|---|---|
| 0 | 4.7 | 6,056.3 | 1,288.5 |
| 1 | 44.7 | 2,652.0 | 59.33 |
| 2 | 45.8 | 237.8 | 5.19 |
| 3 | 43.9 | 68.81 | 1.57 |
| 4 | 46.5 | 53.28 | 1.15 |
| 5 | 44.6 | 37.29 | 0.836 |
| 6 | 45.6 | 27.17 | 0.596 |
| 7 | 43.8 | 18.56 | 0.423 |
| 8 | 44.8 | 13.15 | 0.294 |
| 9 | 43.0 | 8.72 | 0.203 |
| 10 | 41.1 | 5.74 | 0.193 |
| 11 | 42.2 | 3.95 | 0.093 |
| 12 | 41.8 | 2.57 | 0.061 |
| 13 | 40.1 | 1.61 | 0.040 |
| 14 | 39.7 | 1.03 | 0.026 |
| 15 | 39.4 | 0.64 | 0.016 |
| 16 | 36.4 | 0.38 | 0.010 |
| 17 | 36.1 | 0.23 | 0.006 |
| 18 | 30.5 | 0.13 | 0.004 |
| 合 計 | 754.7※ | 9,189.36 | 1,217.6 |

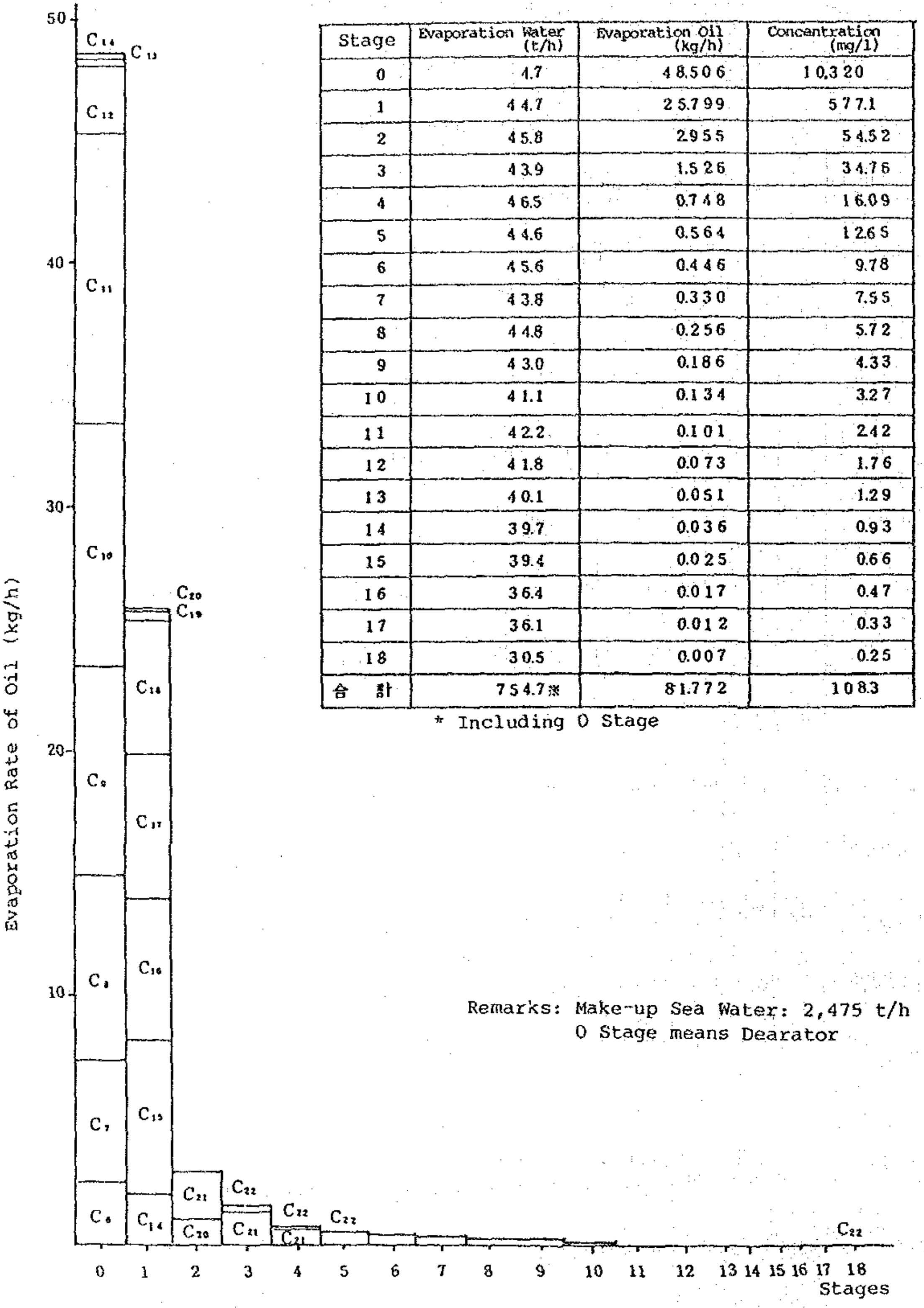
* Including 0 Stage



Remarks: Make-up Sea Water: 2,475 t/h
0 Stage means Dearator

Fig. 4.4.2 (1): Evaporation Rate of Oil at Each Evaporation Stage of Oil-Contaminated Sea Water

Case of 10 mg/l Oil Content in Sea Water (Oil Content 0.02475 t/h)



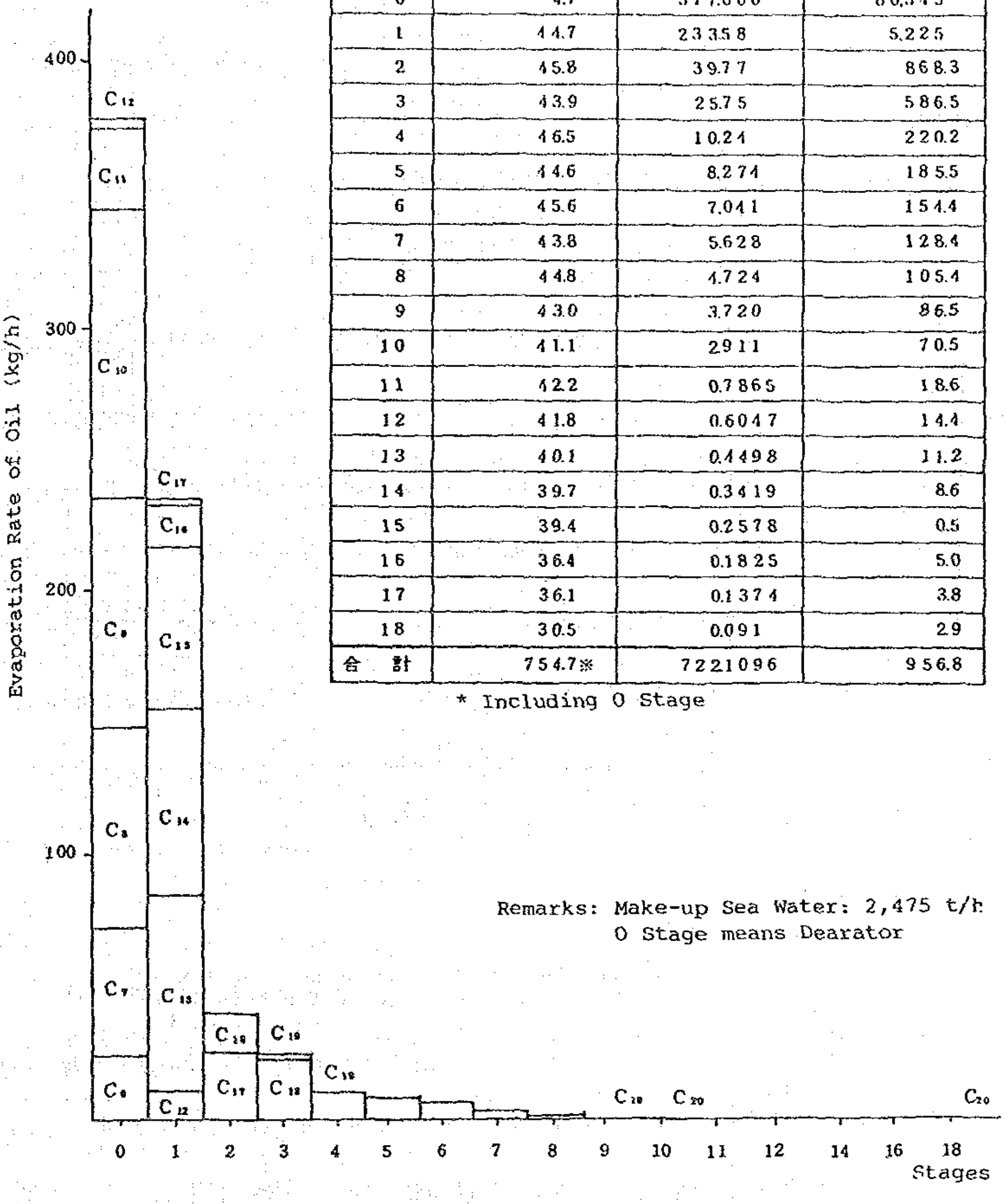
| Stage | Evaporation Water (t/h) | Evaporation Oil (kg/h) | Concentration (mg/l) |
|---|---|---|---|
| 0 | 4.7 | 48.506 | 10,320 |
| 1 | 44.7 | 25.799 | 577.1 |
| 2 | 45.8 | 2.955 | 54.52 |
| 3 | 43.9 | 1.526 | 34.76 |
| 4 | 46.5 | 0.748 | 16.09 |
| 5 | 44.6 | 0.564 | 12.65 |
| 6 | 45.6 | 0.446 | 9.78 |
| 7 | 43.8 | 0.330 | 7.55 |
| 8 | 44.8 | 0.256 | 5.72 |
| 9 | 43.0 | 0.186 | 4.33 |
| 10 | 41.1 | 0.134 | 3.27 |
| 11 | 42.2 | 0.101 | 2.42 |
| 12 | 41.8 | 0.073 | 1.76 |
| 13 | 40.1 | 0.051 | 1.29 |
| 14 | 39.7 | 0.036 | 0.93 |
| 15 | 39.4 | 0.025 | 0.66 |
| 16 | 36.4 | 0.017 | 0.47 |
| 17 | 36.1 | 0.012 | 0.33 |
| 18 | 30.5 | 0.007 | 0.25 |
| 合 計 | 754.7※ | 81.772 | 1083 |

* Including 0 Stage

Remarks: Make-up Sea Water: 2,475 t/h
0 Stage means Dearator

Fig. 4. 4. 2 (2) : Evaporation Rate of Oil at Each Evaporation Stage of Oil-Contaminated Sea Water

Case of 100 mg/l Oil Content in Sea Water (Oil Content 0. 2475 t/h)



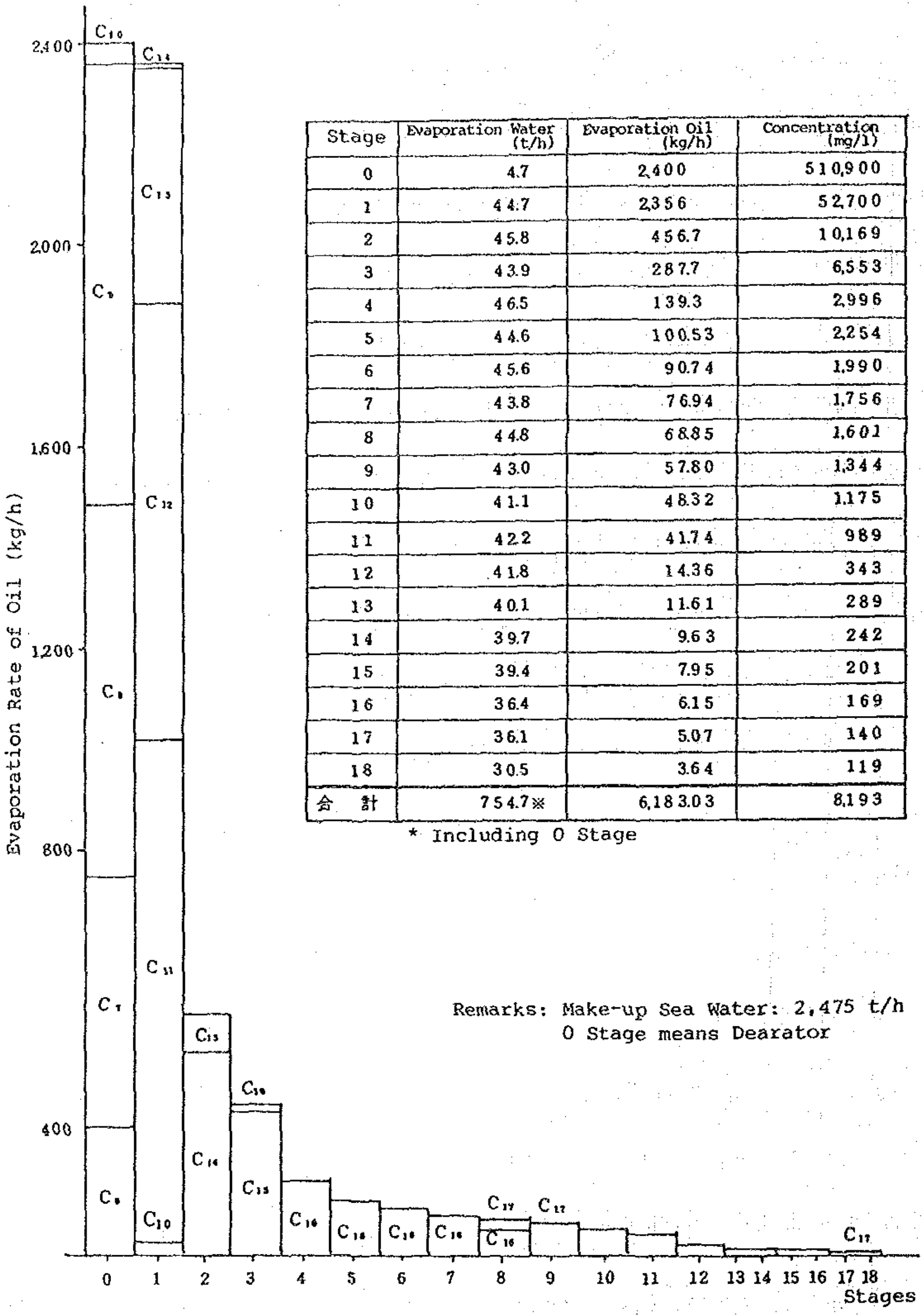
| Stage | Evaporation Water (t/h) | Evaporation Oil (kg/h) | Concentration (mg/l) |
|---|---|---|---|
| 0 | 4.7 | 377.000 | 80,345 |
| 1 | 44.7 | 233.58 | 5,225 |
| 2 | 45.8 | 39.77 | 868.3 |
| 3 | 43.9 | 25.75 | 586.5 |
| 4 | 46.5 | 10.24 | 220.2 |
| 5 | 44.6 | 8.274 | 185.5 |
| 6 | 45.6 | 7.041 | 154.4 |
| 7 | 43.8 | 5.628 | 128.4 |
| 8 | 44.8 | 4.724 | 105.4 |
| 9 | 43.0 | 3.720 | 86.5 |
| 10 | 41.1 | 2.911 | 70.5 |
| 11 | 42.2 | 0.7865 | 18.6 |
| 12 | 41.8 | 0.6047 | 14.4 |
| 13 | 40.1 | 0.4498 | 11.2 |
| 14 | 39.7 | 0.3419 | 8.6 |
| 15 | 39.4 | 0.2578 | 0.5 |
| 16 | 36.4 | 0.1825 | 5.0 |
| 17 | 36.1 | 0.1374 | 3.8 |
| 18 | 30.5 | 0.091 | 2.9 |
| 合 計 | 754.7※ | 7221096 | 956.8 |

* Including 0 Stage

Remarks: Make-up Sea Water: 2,475 t/h
0 Stage means Dearator

Fig. 4.4.2 (3): Evaporation Rate of Oil at Each Evaporation Stage of Oil-Contaminated Sea Water

Case of 1,000 mg/l Oil Content in Sea Water (Oil Content 2.475 t/h)



| Stage | Evaporation Water (t/h) | Evaporation Oil (kg/h) | Concentration (mg/l) |
|---|---|---|---|
| 0 | 4.7 | 2,400 | 510,900 |
| 1 | 44.7 | 2,356 | 52,700 |
| 2 | 45.8 | 456.7 | 10,169 |
| 3 | 43.9 | 287.7 | 6,553 |
| 4 | 46.5 | 139.3 | 2,996 |
| 5 | 44.6 | 100.53 | 2,254 |
| 6 | 45.6 | 90.74 | 1,990 |
| 7 | 43.8 | 76.94 | 1,756 |
| 8 | 44.8 | 68.85 | 1,601 |
| 9 | 43.0 | 57.80 | 1,344 |
| 10 | 41.1 | 48.32 | 1,175 |
| 11 | 42.2 | 41.74 | 989 |
| 12 | 41.8 | 14.36 | 343 |
| 13 | 40.1 | 11.61 | 289 |
| 14 | 39.7 | 9.63 | 242 |
| 15 | 39.4 | 7.95 | 201 |
| 16 | 36.4 | 6.15 | 169 |
| 17 | 36.1 | 5.07 | 140 |
| 18 | 30.5 | 3.64 | 119 |
| 合 計 | 754.7※ | 6,183.03 | 8,193 |

* Including 0 Stage

Remarks: Make-up Sea Water: 2,475 t/h
0 Stage means Dearator

Fig. 4.4.2 (4): Evaporation Rate of Oil at Each Evaporation Stage of Oil-Contaminated Sea Water

Case of 10,000 mg/l Oil Content in Sea Water (Oil Content 24.75 t/h)

According to the results of the simulated calculation, it is clear that the *low boiling point components of crude oil evaporate very easily* and so move readily to the freshwater side. If a deaerator is installed in the plant , most of the oil components will evaporate in the deaerator when the raw sea water is contaminated by *only a small* amount of crude oil (an oil concentration of about 10 mg/l). (refer to Fig. 4. 4. 2 (1))

Even if the sea water is contaminated by oil with a concentration of 1, 000 mg/l, the gasoline components will evaporate in the deaerator and both the kerosene and gas oil components will mostly evaporate between the first and the fourth high temperature stages. Since the vapor pressure of oil components with comparatively higher carbon numbers ($C_{20}$ or higher) rapidly declines as the temperature drops, only a small amount moves to the freshwater side at the medium temperature stage. (refer to Fig. 4. 4. 3)

On the other hand, even if the sea water is contaminated by a large quantity of crude oil (with a concentration of 10, 000 mg/l), most of the kerosene and gas oil *components evaporate at the high temperature stages* and only a small amount the components with a high boiling point, such as gas oil, gradually move into the product water side at the medium and low temperature stages. Herein before it was considered that all evaporated oil moved into the product water.

Further study will be conducted concerning the behavior of evaporated oil components at the condenser of the evaporation chamber.

With regard to the relation between the vapor pressure and the temperature of each kind of hydrocarbon, the vapor pressure of hydrocarbons with $C_6$ *or less is higher than that of water, as shown* in Fig. 4. 4. 4, but the vapor pressure of hydrocarbons with $C_8$ or more is lower than that of water. Therefore, hydrocarbons with $C_6$ or less are not condensed but are

vented from the evaporation chamber as vent gas, and hydrocarbons with $C_8$ or more are condensed along with water vapor.

When the condensation of evaporated oil components is studied, it is found that since the latent heat of hydrocarbon condensation is much smaller than that of water ( for example, the latent heat of octane condensation is 70 kcal/kg or 1/7. 7 of the 539 kcal/kg of water), an amount of hydrocarbons several times that of water can be condensed by the same cooling rate. Accordingly, all of the evaporated hydrocarbons with $C_8$ or more, move into the product water.

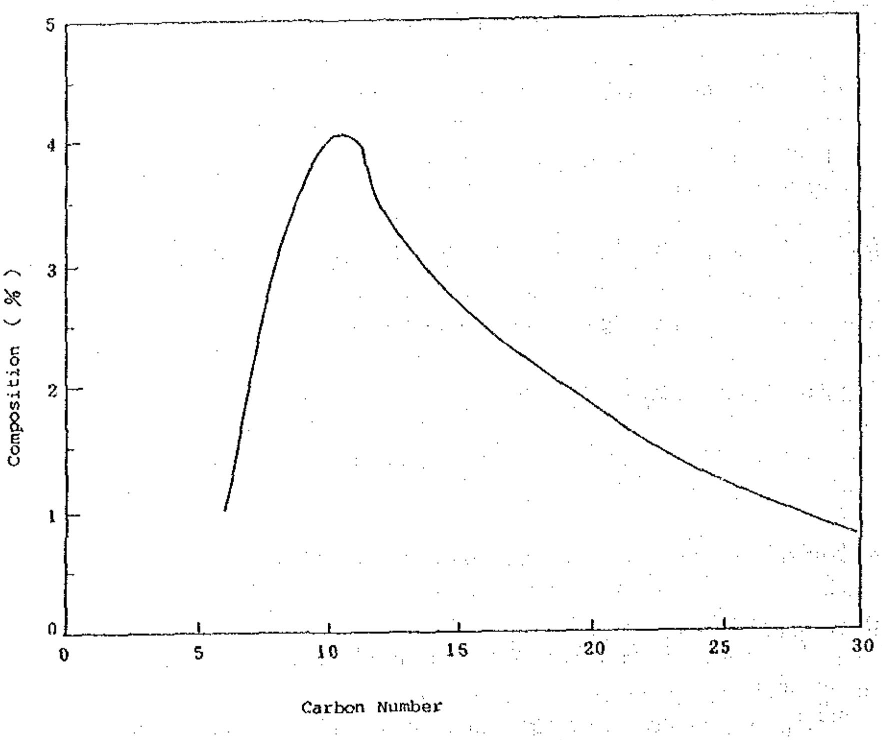


Fig. 4.4.3: Composition Model of Crude Oil used in Simulation

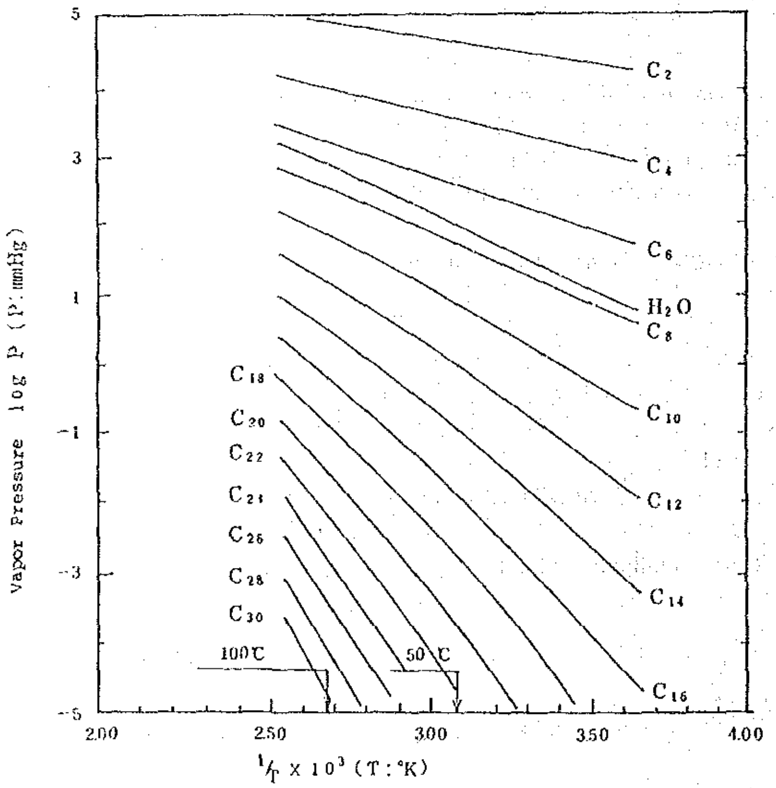


Fig. 4.4.4: Arrhenius Plot of Water and Hydrocarbon Vapor Pressure

### 4.4.3 Behavior of Dissolved Oil in Desalination Process

#### (1) Evaporation of Dissolved Oil

The solubility of gas into water and saline water due to diffusion generally follows Henry's law, if it is a dilute solution. While there are many ways to express Henry's law, one is indicated here by Equation 4.10 as an example.

$$C = HP \tag{4.10}$$

Where,

C: Concentration of solution (mol/$m^3$)
H: Henry's constant (mol/kg atm)
P: Partial pressure (atm)

Dissolution and evaporation of volatile oil can be assumed to follow this law. Table 4.4.1 indicates Henry's constants of volatile oil components to water and saline water, and Fig. 4.4.5 indicates the relation between the partial pressure and the concentration of the solution.

Table 4.4.1: Henry's Constants of Volatile Oil Components

(Unit: mol/kg atm)

| Matters | Ionic strength | Henry's constants H | | Remarks |
|---|---|---|---|---|
| | | 25℃ | 40 ℃ | |
| Benzene | 0 | 0.1728 | 0.0922 | |
| | 1 | 0.1031 | | |
| | 2 | 0.0736 | | |
| Toluene | 0 | 0.1674 | 0.0795 | |
| | 1 | 0.1034 | | |
| | 2 | 0.0592 | | |
| Ethyl benzene | 0 | 0.2083 * | | * 35 ℃ |
| Heptane | | $1.69 \times 10^{-3}$ | $2.24 \times 10^{-4}$ | |
| Octane | | $1.85 \times 10^{-4}$ | | |

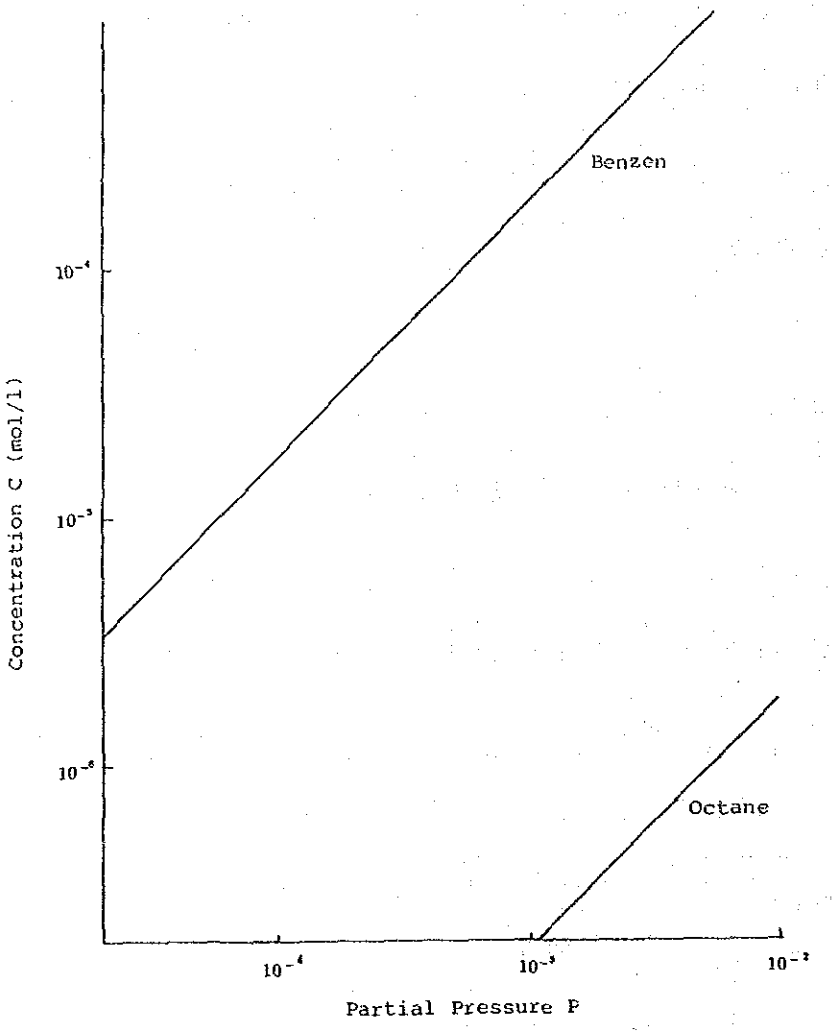
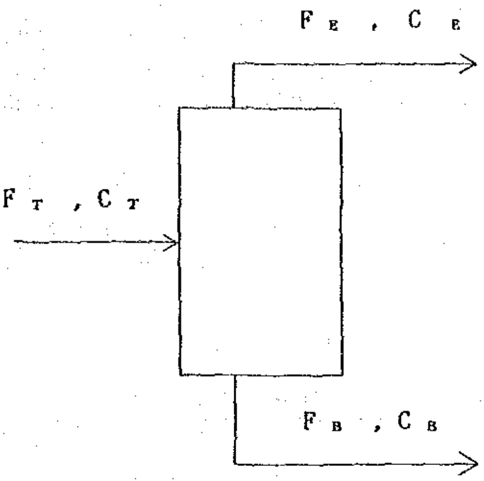


Fig. 4.4.5: Relation between Concentration C of Volatile Oil Components and Partial Pressure P

### (2) Material Balance of Dissolved Oil in MSF Plant

The following describes a method to retain the quality of the product water when sea water containing soluble oil components is used as raw water. Here, benzene and toluene which are typical soluble components in crude oil, will be taken up as the soluble oil components which are influencing the quality of the product water, and a study will be made on the volumetric relation of these components when they are transferred to the freshwater side and dissolved into the product water.

Regarding the actual movement of materials, the desalination plant is roughly divided into the stages of deaerator, flash evaporator, and condenser. In order to make clear the material balance and equilibrium relation of the gas, saline water, and water in each of the above stages, the following model is now studied.



If each part in the above figure is substituted by the deaerator, evaporator, and condenser, Equations 4.11 and 4.12 can be effected.

$$Ft = Fb + Fe \tag{4.11}$$
$$Ft\ Ct = Fb\ Cb + Fe\ Ce \tag{4.12}$$

Where,

F: Flow rate (kg/h)
C: Concentration (mol/kg)

Suffix t: Supplied water
b: Treated water
e: Evaporated gas

Here, the evacuation rate will be defined as $R = Fe/Ft$ and the non-equilibrium condition will be defined as $Ne = Cb*/Cb$ (<1).

Also, the distribution coefficient will be expressed by:

$$Ce* /Cb* = m$$

Where,

C*: Concentration in equilibrium

Further, assuming $Ce = Ce*$, then from Equation 4.12:

$$Ct = m\ Ne\ CB + (1 + R)\ CB \tag{4.13}$$

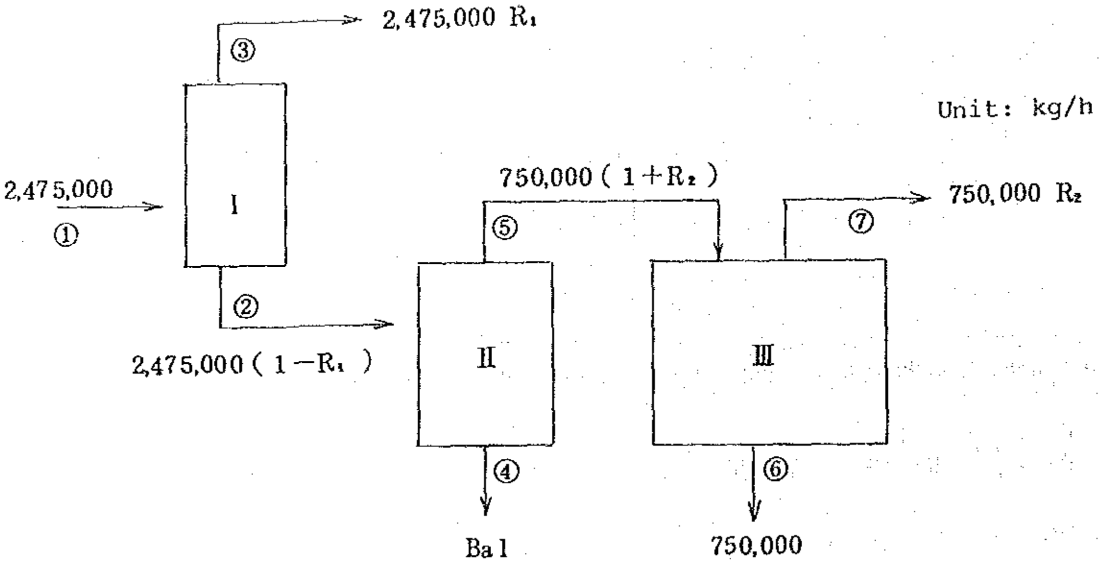
Therefore,

$$Cb = Ct/(R\ m\ Ne + 1 - R) \tag{4.14}$$

$$Ce = m\ Ne\ Ct/(R\ m\ Ne + 1 - R) \tag{4.15}$$

Here, m: Ce/Cb = 55.5/H PH20, and Ne is about 0.5 from actual data results.

On the other hand, as an example, the material balance of the subject plant, West No. 1 to No. 6 (quantity of product water 750 ton/h), can be expressed by the Fig. 4.4.6.



I: Deaerator, II: Evaporator, III: Condenser, Bal: Balance

Fig. 4.4.6: Typical Example of Material Balance in Subject Plant

Also, if the inlet concentration, concentration of treated water, and concentration of evaporated gas at each of stages I, II and III is substituted by $C_T$, $C_B$ and $C_E$ respectively, the Equations 4.14 and 4.15 can be applied as they are. In this case, evacuation rates $R_1$ and $R_2$ are complementary conditions which will inevitably be determined in the planning and design of the plant.

Now, assuming that the concentration of treated water obtained from calculation of Stage I is the inlet concentration at Stage II, the concentration of water vapor at Stage II is the inlet concentration at Stage III, and the treated water at Stage III is product water, the concentration of water vapor at Stage III is the inlet concentration of vent condenser, the concentration under the following conditions will be calculated.

<Temperature>

Benzene-water system: 35 °C, 50 °C, 60 °C , 70 °C, 80 °C

Benzene-sea water system: 35 °C, 50 °C

Toluene-water system: 35 °C

Here, 35 °C corresponds to the temperature of the deaerator.

<Evacuation rate>

$R_1 = R_2 = 10^{-3}$

<Concentration of chloride ion>

Sea water: 0.732 mol/l (26,000 mg/l)

Brine: 1.051 mol/l (concentration ratio 1.436)

The result of the calculation is shown in Table 4.4.2. As is clear from Table 4.4.2, about 90% of aromatic hydrocarbons such as benzene, toluene, etc., are transferred to vent gas and blow brine, and the rest is dissolved in the product water. For example, if the concentration of benzene in sea water at the inlet is 10 mg/l, 0.12 mg/l is transferred into the product water, and the concentration of benzene in the vent gas will be as much as about 5,000 mg/l.

The difference between the sea water system and the water system is such that first, the solubility by salting-out effect is different, and solubility into sea water decreases.

The effect of temperature is not great, and almost no difference was observed compared with the effect at normal temperatures. This is because the solubility itself decreases but the vapor pressure of water increases (P), making the effect on the distribution coefficient smaller.

Then, most of the n-octane which is a kind of volatile fatty hydrocarbon is volatilized in the deaerator as indicated in Table 4.4.2, and the final amount of concentration transferred to the product water is as small as 0.001 mg/l. Thus according to this result, the amount of transfer of volatile fatty hydrocarbon to the product water is so small that it can be neglected.

On the other hand, aromatic hydrocarbons such as ethyl benzene (boiling point; 136.2 °C) and xylene (boiling points; ortho- 000.4 °C, meta- 139.2 °C and para- 138.4 °C) are similar to benzene in boiling and para- 138.4 °C) are similar to benzene in boiling point, vapor pressure and structure, and are thought to show similar behavior to benzene. These compounds are constituents of gasoline and are considered to be most influential in the pollution of sea water because of their solubility into water and their volatility.

In other words, it is not necessary to consider the effect of fatty hydrocarbons on the product water but it is necessary to pay attention to aromatic hydrocarbons such as benzene. Since the WHO standard specifies the allowable concentration of benzene in drinking water to be as small as 10 $\mu$g/l, the utmost emphasis must be placed on countermeasures against benzene.

Table 4.4.2: Calculation Result of Evaporation and Dissolution Behaviors of Volatile Oil Components

| Phase | Temp. (°C) Oil Conc. | Deaerator Inlet (mg/l) | Deaerator Outlet (mg/l) | Evaporation Water (mg/l) | Product Water (mg/l) | Removal Ratio (%) |
|---|---|---|---|---|---|---|
| Benzene/Water | 35 | 1 | 0.19 | 0.63 | 0.12 | 88 |
| | 35 | 10 | 1.9 | 6.3 | 1.2 | 88 |
| | 50 | 10 | 1.9 | 6.3 | 1.2 | 88 |
| | 60 | 10 | 1.9 | 6.3 | 1.2 | 88 |
| | 70 | 10 | 1.9 | 6.3 | 1.3 | 87 |
| | 80 | 10 | 1.9 | 6.2 | 1.3 | 87 |
| Benzene/Sea Water | 35 | 10 | 1.4 | 4.5 | 0.87 | 91.3 |
| | 50 | 10 | 1.4 | 4.5 | 0.93 | 90.7 |
| Toluene/Water | 35 | 10 | 1.8 | 6.4 | 1.1 | 89 |
| n-Octane/Water | 35 | 10 | 0.005 | 0.018 | | 9.9 |
| Etylbenzen | 35 | 10 | 2.94 | 9.67 | 2.84 | 71.6 |

Remark: $\text{Removal Ratio} = \dfrac{\text{Deaeration Inlet} - \text{Product Water}}{\text{Deaeration Inlet}} \times 100$

Evacuation rate: $R_1 = 10^{-3}$, $R_2 = 10^{-3}$

If the transfer rate of benzene at each stage of the subject plant is calculated pursuant to the above system, Equation 4.16 expresses, as is clearly shown in Table 4.4.2, the effect of the temperature being neglected.

$$C = C_0 C_R^{n} \tag{4.16}$$

Where,

C: Concentration of product water at outlet of n-stage (mg/l)
(n = 0 means concentration at inlet at first stage)
$C_0$: Concentration of brine at inlet of the first stage (mg/l)
$C_R$: Remaining rate (mg/l) ($C_R$ = 0.1 in benzene-sea water system)
n: Number of stages

As stated above, a trial calculation related to transfer of oil components to product water in the MSF plant was made on two cases, ie., (a) the case where oil and water (sea water) are present as a two-liquid phase, and (b) the case where oil dissolves into water (sea water) and is present as a single liquid phase.

However, as stated in 4.4.1, the transfer is not governed by either of the above cases but the oil and water are present in a single liquid phase until each oil component reaches saturation and then becomes a two-liquid phase only after the mixing of each component has started.

Therefore, there is no problem to employ case (a) until the component reaches about 100 mg/l.

However, when the oil reaches saturated solubility and the oil component with compositions different from crude oil starts to be separated as two-liquid phase, evaporation also starts based on case (a). Now, it is difficult to determine unconditionally by which system the transfer of oil components should be regulated, because the dispersion speed of each component in the oil, the evaporation speed of the oil components, and the dissolution speed of each oil component into water are delicately entangled. Since no literature related to this matter has been found, it will be a subject for further study.

### 4.4.4 Examples of Problems Encountered when Plant is Contaminated by Oil

Although there have been only a few instances in the past where raw sea water, used in the sea water desalination plants employing the evaporation process, has been contaminated by oil and where oil components have moved into the product water, deteriorating its quality, the following three examples of raw sea water are referred to as a reference.

#### (1) Takashima Desalination Plant (Japan)

This multi-effect desalination plant employs a system in which solar heat is collected by heat collectors and used as an energy source for the plant operation. As indicated in Fig. 4.4.5, this plant is of a type in which evaporation takes place outside the horizontal tubes, and where evaporation chambers are stacked vertically in two rows.

The vapor produced outside the tubes flows into heat transfer tubes contained in the evaporation chamber, where the vapor is condensed into water. The condensation stage is inverse to that of a MSF evaporation plant. No deaerator is installed.

When this plant started operation in 1981, at first the raw sea water had an oily smell. As the raw sea water was taken from wells sunk near the shore, it is thought that, for some reason, oil which had accumulated in layers of sand contaminated the sea water intake. It is also thought that perhaps it was a result of an oil spill accident which occurred at a nearby refinery several years before. The real cause, however, remains unknown. According to recorded data, the following is indicated:

Oil in sea water: 0.5 - 0.6 mg/l (Extraction of carbon tetrachloride from standard B-type heavy oil - measured by infrared ray absorption method.)

Oil in fresh water: 1.2 mg/l (Ditto)

The movement of oil components into the product water corresponds with the result of the simulated calculation mentioned herein before.

Since the water was undrinkable due to its oily smell, an activated carbon filter was installed in the product water line to remove the oil and the product water was able to be used as potable water. So far, an oil contamination accident has never occurred.

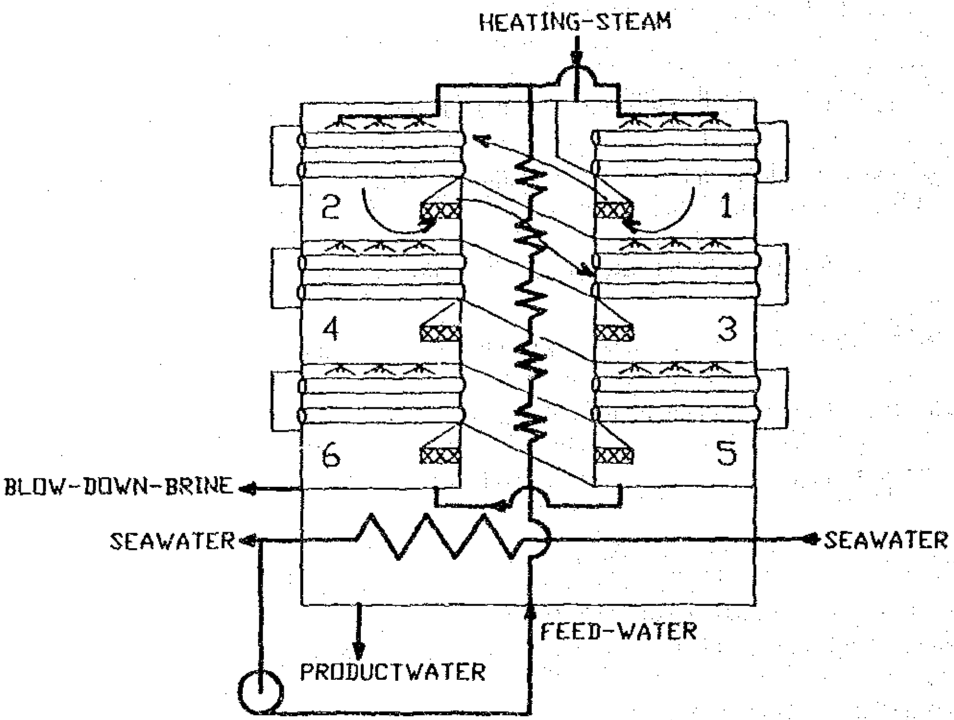


Fig. 4.4.7: Conceptual Representation of Vertically Arranged Horizontal Tube Type Multi-Effect Sea Water Desalination Plant

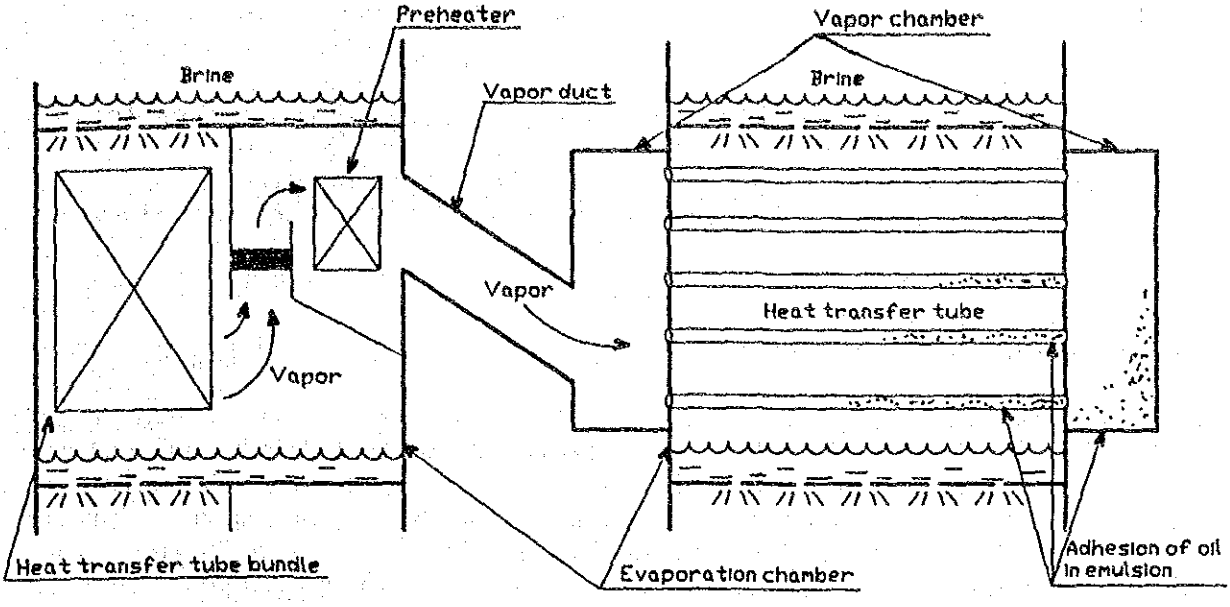


Fig. 4.4.8: State of Oil Adhesion in Plant

### (2) Singapore Desalination Plant

An oil contamination accident occurred at the multi-effect sea water desalination plant (same as example (1)), in February, 1986, of which the product water is used for the boilers and other plant equipment.

The oil contamination of the plant was discovered as oil was found in the ion exchanger resin. However, the cause of the oil contamination, the source of contamination, and the rate of the contamination are unknown. Inspection of the inside of the evaporation chamber revealed that oil in emulsion had adhered to the condensation part of the heat transfer tube and to the inside of the vapor chamber. The adhered oil was easily removed by water jet cleaning (refer to Fig. 4.4.6).

The points to be noted in this example are that the oil which was evaporated and transferred to the heat transfer tubes adhered in emulsion state and that the adhesion occurred only in the heat transfer tubes, there being no trace of oil adhesion in the pumps or pipings.

### (3) Umm Al Nar Power and Sea Water Desalination Plant (Abu Dhabi)

On February 22, 1988, gas oil (fuel oil) leaked from a tanker near the No.3 sea water intake while oil was being loaded into the tanker from an electrolysis shop near the plant. The spilled oil entered the nearest (No. 3) intake and completely covered the surface of the sea water with a film of oil about 2 mm thick. Other intakes (Nos. 1 and 2) were not affected by the spilled oil.

In order to keep the extent of the oil pollution to a minimum, the sea water intake rate was reduced and the spilled oil was removed from the intake.

According to the results of an analysis of the concentration of the oil contamination in the raw sea water throughout the whole plant, it was discovered that only the Umm Al Nar East Desalination Plant No. 4 plant was contaminated by oil. The results of the analysis were as follows:

| | |
|---|---|
| Raw sea water: | 0.4 mg/l |
| Ejector condenser drain: | 1.2 mg/l |
| Product water: | None |

No oily smell nor taste was found in the product water. There was an oily smell in the gas vented from the ejector condenser, but no oil was detected in the ejector condenser drain after 10 hours. Despite this accident, there was no change in the performance of the plant (productivity, G.O.R., etc.), and so far no oil has been detected in the periodical analysis of the oil components in the sea water intakes since the accident.

### 4.4.5 Critical Oil Concentration and Product Water Quality

Table 4.4.3 [20)] is an extract from the potable water quality standards of the World Health Organization (WHO), which is employed as a norm for potable water quality standards in various countries around the world. The items relating to oil pollution might include reference to benzene, under the title "organic matters" and reference to taste and smell under the title "matters related to the palate". The standard critical value of benzene is defined as being 10 $\mu$g/l. Taste and smell are defined at a level so as not to "present an unpleasant taste and smell to the majority of consumers".

The solubility in water of oil products like gasoline, kerosene and gas oil is considerably higher than the concentration stipulated in the water quality standard.

For example, while the solubility of benzene is 1,740 mg/l, the recommended critical potable water quality established in New York State in 1982 is as small as 0.2 $\mu$g/l. Both benzene and toluene are contained in the list of major organic contaminants produced by the U.S. Environment Protection Agency (EPA), and even only a small leak can easily contaminate a large quantity of water, as their allowable concentration in potable water is so small. For example, if 2% benzene is contained in gasoline and if the value of the water quality standard is defined to be 0.2 $\mu$g/l, 1 liter of gasoline will contaminate about 100,000 m$^3$ of water. 21)

## Table 4. 4. 3: WHO Guideline for Potable Water Quality (Extract)

### Table 4. 4. 3: Continued

| Category | Unit | Contamination Agent | Criteria |
|---|---|---|---|
| Bacteriological Property | Count/100 ml | Facal coliform | 0 |
| | | Facal coliform group | 0 |
| Inorganic Matter (Influence on Health) | mg/l | Arsenic | 0.05 |
| | | Cadmium | 0.005 |
| | | Chromium | 0.5 |
| | | Cyanide | 0.1 |
| | | Fluorine | 1.5 |
| | | Lead | 0.05 |
| | | Mercury | 0.001 |
| | | Nitric acid base nitrogen | 10 |
| | | Selenium | 0.01 |
| Organic Matter (Influence on Health) | μg/l | Benzene | 10 |
| | | Carbon tetra-chloride | 3 (T) |
| | | 1. 2-Dichloroethane | 10 |
| | | 1. 1-Dichloroethylene | 0.3 |
| | | Tetrachloroethylene | 10 (T) |
| | | Trichloroethylene | 30 (T) |
| | | Pentachlorolphenol | 10 |
| | | 2. 4. 6-Trichlorophenol | 10 |
| | | Chlordane | 0.3 |
| | | Benz-a-pyrene | 0.01 |
| | | Chloroform | 30 |
| | | Aldrin/Dieldrin | 0.03 |
| | | 2. 4. D | 100 |
| | | DDT | 1 |
| | | Heptachlor, Heptachlor epoxide | 0.1 |
| | | Hexachlorobenzene | 0.01 |
| | | Lindane | 3 |
| | | Methoxychlor | 30 |
| Radioactivity | Bq/l | Total a ray | 0.1 |
| | | Total b ray | 1.0 |
| Substance related to Palate | mg/l | Alminum | 0.2 |
| | | Chloride ion | 250 |
| | | Copper | 1.0 |
| | | Hardness | 500 |
| | | Iron | 0.3 |
| | | Manganese | 0.1 |
| | | Sodium | 200 |
| | | Sulfate ion | 400 |
| | | Total evaporated residue | 1.000 |
| | | Zinc | 5.0 |
| | Degree (-) | Chromaticity | 15 |
| | | Taste, smell | Presenting no unpleasant quality to the majority of consumers |
| | | Turbidity | 5 |
| | | pH | 6.5 ~ 8.5 |

Remark: (T) is a temporary value due to insufficient carcinogenic data.

Table 4.4.4: Solubilities of Various Hydrocarbons

| Compound | Non-Noxious Compounds in $H_2O$ [1] (mg/l) | Aqueous Solution in Contact with Gasoline [2] (mg/l) |
|---|---|---|
| benzene | 1740 | 65 |
| toluene | 554 | 34 |
| 2-butene | 430 | 2.4 |
| 2-pentene | 203 | 1.4 0.88 2.4 3) |
| ethylbenzene | 131 | 4.8 |
| o-xylene | 167 | 5.4 |
| p-xylene | 157 | 13.8 |
| m-xylene | 134 | 8.9 |
| 1.2.4 trimethybenzene | 61.4 | 2.7 |
| 2-menhylbutane | 51.9 | 1.1 |
| pentane | 39.5 | 3.7 |

Literature:

1) Values from Price, L.C. (1976), McAuliffe, (1966) and Landolt-Boernstein (1962) tabulated in Brookman and co-workers

2) From Brookman and co-workers

3) Isomers of 2-pentene

Generally, in comparison with the solubility of a pure substance in water, the solubility of the substance mixed with other substances is reduced. Table 4.4.3 shows equilibrium concentrations of various hydrocarbons in lead-free gasoline in water. In comparison with the solubility of a pure hydrocarbon, the solubility of substances in the presence of gasoline is smaller, but those values are much greater than the water quality standard level.

According to an experiment [22] concerning the relationship between oil concentration and smell, it was found that the concentration of oil components detectable by an ordinary person as an oily smell is 0.005 mg/l in the case of gasoline, and as high as 0.2 to 25 mg/l in the case of heavy oil and crude oil.

In the case of gas oil, the concentration in water which is detectable by smell is 0.22 mg/l but when it drops to 0.086 mg/l, no smell is detectable. It was also found that the limit of oil concentration where an oily smell is detectable on fish kept in water containing oil is about 0.1 to 0.001 mg/l.

### 4.4.6 Conclusion

As described above, simulation studies were conducted concerning the extent of contamination of the raw sea water by oil and its penetration into the product water in the desalination plant. However, this simulation was based on the assumption that oil does not dissolve in sea water and vice versa; they only exist as a mixture of two separate liquid phases. The simulation results were evaluated on the basis of actual examples and compared with the quality standard of drinking water specified by the WHO. As a result, the following points have been ascertained:

(a) The distillation of oil from sea water containing oil depends much upon its oil content. For example, when the oil concentration of the sea water is about 10 mg/l, 40% of the oil in the process is distilled, of which 60% and 40% are distilled in the deaerator and in the evaporation chamber respectively.

When the oil concentration of sea water is about 10,000 mg/l, 27% of the oil in the process is distilled, of which 20% and 75% is distilled in the deaerator and in the evaporation chamber respectively. As described above, as the oil concentration in the sea water goes up, the oil distillation rate from the evaporator increases, rather than that of the deaerator.

(b) The oil distilled in the deaerator is transferred to the vent condenser and the oil distilled in the evaporation chamber is transferred to the product water. In there processes hydrocarbons of C6 or less which have a higher vapor pressure than water are not condensed but discharged into the air passing through the ejector condenser.

(c) On the other hand, hydrocarbons of C8 or more are condensed with the water and mixed into the condenser drain and the product water.

(d) Under the conditions of oil contamination in the simultation, the oil content of the product water far exceeds the quality standards for water specified by the WHO. Low concentration gasoline components are distilled in the deaerator and therefore the contamination of the product water can be prevented provided that the vent condenser drain water is not collected as product water. However, kerosene and gas oil components are easily mixed into the product water during distillation in the evaporation chamber, and make the product water unfit for drinking due to the unacceptable taste and odor.

(e) The results, as mentioned above, are reliant upon the premise that oil and water remain as two separate liquid phases. However, as a small amount of oil actually may dissolve in the sea water (making a single liquid phase), it might be necessary to reconsider the evaporation of the oil from that kind of raw sea water, and its resolution into the product water.

## 4.5 Influence of Chlorination

In the desalination plants and the power plants, chlorine is added to the sea water intake in order to protect the intake apparatus and installations from adhesion and growth of marine organisms. It is said that when sea water is chlorinated, chlorine reacts on certain or some organic substances to form trihalomethane (THM). If the sea water is polluted by oil, the formation of THM is thought to be increased. Therefore, further investigation on the possibility of this phenomenon is necessary.

Moreover, it is surmised that THM moves to the fresh water side during the distillation process and that THM is also formed from oil components present in the product water, while the water is undergoing chlorination. The influence of such chlorination of oil contaminated sea water is studied as follows.

### 4.5.1 Chlorination and Organo-Halogenic Compounds

Since 1974, when the possible carcinogenic properties of organo-halogenic compounds were first identified by Harris, the safety of these compounds in potable water has been under review by authorities such as the U.S. Environment Protection Agency (EPA) round the world.

When water is disinfected by chlorine, some kinds of organic substances (precursors)* , react with the chlorine, thereby forming organic halides such as trihalomethane (THM), etc. All of the forming organic halides have been identified. THM is now under investigation as a principal noxious substance in water.

---

* "Precursors" may be defined as humic matter which exists naturally as a coloration components, and similar organic substances. There are two types of humic matter. One is land-based substances which are formed by the decomposition and condensation of plant components in the soil, and the other is water-based substances which are formed from organic substances and other aquatic life components flowed into water. The main components of humic matter are humic acid and fulvic acid, which are a chemical group consisting of compounds with molecular weights ranging from thousands to tens of thousands. Precursors are widely existed in surface water and underground water.

---

THM is a general term for the compounds shown below. Chloroform ($CHCl_3$) is a major component of THM which exists in potable water, and bromodichloromethane ($CHBrCl_2$), dibromodichloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) follow. The properties of these compounds are shown in Table 4.5.1.

$CHCl_3$ : Trichloromethane
$CHBrCl_2$ : Bromodichloromethane
$CHBr_2Cl$ : Dibromochloromethane
$CHBr_3$ : Tribromomethane (Bromoform)
$CHCl_2I$ : Dichloroiodomethane
$CHBrClI$ : Bromochloroiodomethane
$CHClI_2$ : Chlorodiiodomethane
$CHBr_2I$ : Dibromoiodomethane
$CHBrI_2$ : Bromodiiodomethane
$CHI_3$ : Triiodomethane (Iodoform)

In U. S. A, THM concentration in potable water has been limited to amounts of 100 μg/l or less (1979). Further, in Japan, the same level has been applied since 1981. WHO has established guideline level for chloroform at 30 μg/l.

Table 4. 5. 1: Properties of THM

| | Trichloromethane (Chloroform) | Bromodichloro-methane | Dibromochloro-methane | Tribromomethane (Bromoform) |
|---|---|---|---|---|
| Molecular Formula | $CHCl_3$ | $CHBrCl_2$ | $CHBr_2Cl$ | $CHBr_3$ |
| Specific Gravity | $d_{20}^{20}$ 1.484 $^{1)}$ | $d_4^{15}$ 2.005 | | $d_{51}^{15}$ 2.902 $^{1')}$ |
| | $d_4^{20}$ 1.4890 $^{2,\ 3)}$ | 1.52 $^{a)}$ | | $d_4^{20}$ 2.8912 $^{4')}$ |
| | | | | $d_{25}^{25}$ 2.847 $^{2')}$ |
| b.p. (°C) | 61 - 61, 61.2 $^{2)}$ | 90.1, 113.8 $^{a)}$ | 120.7 $^{a)}$ | 149 - 150, 149.5 $^{4')}$ |
| | | | | 148.1 $^{2')}$ |
| m.p. (°C) | -63.5, -63.5 $^{2)}$ | -57.1 | | +7.5 $^{1)}$, 7.7, 4.8 $^{2)}$ |
| Refraction Index | $n_0^{20}$ 1.4476, 1.4467 $^{3)}$ | $n_0^{15}$ 1.5012 | | $n_0^{15}$ 1.6005$^{1)}$<br>1.5890,<br>1.6005 (15 °C) $^{2')}$ |
| Evaporation Heat | 59.0 cal/g (b.p.) $^{2,\ 3)}$ | | | 2.76 cal/mal $^{3)}$ |
| Specific Heat | 0.234 cal/g (20 °C) $^{2,\ 3)}$ | | | 0.124 cal/g deg $^{2')}$<br>(18.50 °C) |
| Solubility | 1 ml/200 mi water (25°C) | | | Soluble in 800 parts of water<br>Water: 0.319 g<br>0.318 wt% (30 °C) |
| | Solubility 0 °C 1.062<br>in water 10 °C 0.895<br>(g/100 g 20 °C 0.822<br>water) 30 °C 0.776 | | | |

Table 4.5.1: Continued (2/2)

| | Trichloromethane (Chloroform) | Bromodichloro-methane | Dibromochloro-methane | Tribromomethane (Bromoform) |
|---|---|---|---|---|
| Toxicity | Strong Narcosism<br>Liver Trouble | | | Liver trouble<br>$LD_{50}$ (Hare skin 5')<br>Allowable Concentration<br>0.5 ppm<br>5 $mg/m^3$ 5') |
| Vapor Pressure | -60 °C 0.81 mmHg 4)<br>-50 2.06<br>-40 4.7<br>-30 10.0<br>-20 19.6<br>-10 34.75<br>0 61.0<br>+10 100.5<br>20 159.5<br>25 199.1<br>30 246.0<br>35 301.0<br>40 366.4<br>45 439.0<br>50 526.0<br>55 625.0<br>60 739.6<br>60.9 760.0<br>70 1,019<br>80 1,403 | | | 25 °C 9.4 m 6')<br>22 °C 5 mmHg 2')<br>48 °C 20 mmHg " |
| Literature 13) | 1) Merk Index<br>2) N.A. Lange Handbook of Chemistry 10 Ed ('61)<br>3) Encyclopedia of Chemical Technology<br>4) International Critical Table vol. III ('28) | a) Sever System Assn Journal 17 No. 188 (2) ('80) | | 1') Merk Index<br>2') Mellan Source Book of Ind. Solvent vol. 2 ('57)<br>3') Chemical Safety Date SD-35 ('68)<br>4') Encyclopedia of Chem. Technology<br>5') M.I. Sox Dangerous Properties of Ind. Materials p. 490<br>6') International Critical Table vol. III ('28) |

### 4.5.2 Formation of Organic Halogen Compounds by Chlorination of Sea Water

In the power and desalination plants, chlorination is provided to prevent increases in flow resistance and reduction of thermal conductivity caused by the growth and build up of organisms and slime in the intake sea water.

However, organic halogen compounds are formed by the reaction between chlorine and organic substances (like humic matter) existing in the sea water. While organic chloride is generally formed during the chlorination of potable water, organic bromide is also generally formed during the chlorination of sea water due to the fact that 68 mg/l of bromide ion (3.5% salinity matter and 19.5% Cl) is contained in the sea water, whereas bromine has a smaller oxidation potential than chlorine.

#### (1) Case Study of THM Formation

The following describes the results of the case studies of THM formation caused by the chlorination of sea water.

1) Kumai, et al.[23] conducted studies of THM contained in cooling sea water at the power station. The result of their measurements of the chlorine injection rate at the cooling water inlet, and bromoform concentration at the water outlet is indicated in Fig. 4.5.1, which shows that there is a correlation between the concentration of bromoform formed and the chlorine injection rate.

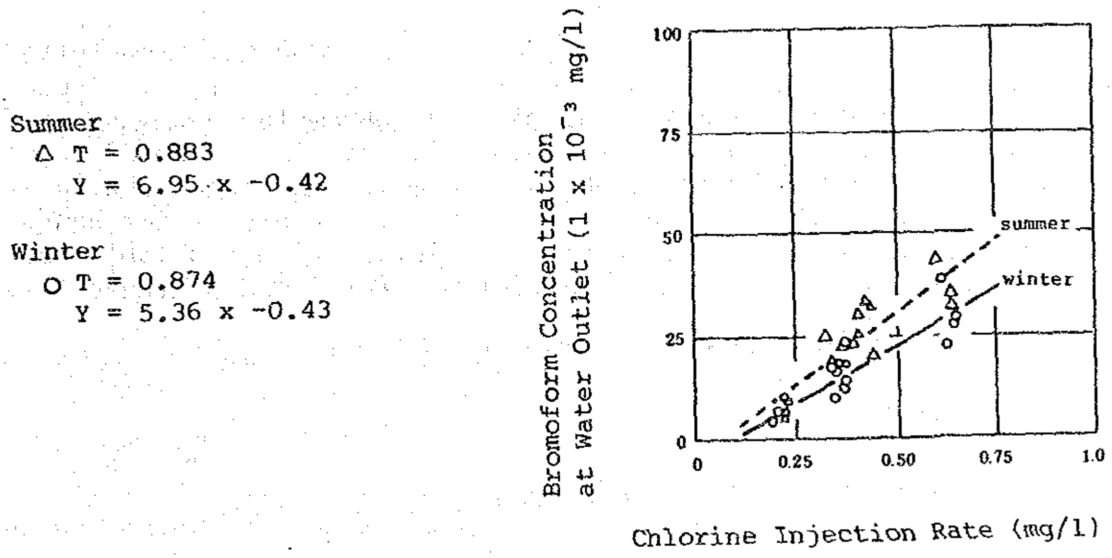


Fig. 4.5.1: Relation Between Chlorine Injection Rate and Concentration of Bromoform Formed

It was discovered that the THM formation rate (concentration at water outlet) depends on the chlorine injection rate at the cooling water inlet, and on the temperature of the water, and that the following equation can be effected.

$Y = 0.3XT$

Where,

Y: Bromoform concentration at outlet (μg/l)
X: Chlorine injection rate at cooling water inlet (mg/l)
T: Temperature of water at cooling water inlet (°C)

Further, a study of the distribution of bromoform concentration was conducted after the water was discharged. At a spot 100m downstream from the water outlet, a background value of $0.2 \times 10^{-3}$ mg/l was registered due to diffusion and dilution in sea water and evaporation into the atmosphere.

2) Ali, et al. 24) examined the distribution of THM in the sea water discharged from three desalination/power plants in Kuwait and confirmed that 95% of the THM was bromoform, and that most of the remaining THM was dibromochloromethane. They also confirmed that 95% of the THM near the water outlet reached a level of 90 μg/l, and that thereafter the concentration was reduced to 1 μg/l or less by the advection or mixed diffusion at the location several kilometers away from the water outlet.

3) N.M.Fayad et al. 25) have prepared a report concerning by-products from chlorination of the sea water in Arabian Gulf. Where the TOC content in the sea water was 10 mg/l, the bromide ion concentration was 120 mg/l and, the total oxygen demand was 0.12 mg/l, and the major component of the volatile compound formed by chlorine injection was mainly bromoform with some dibromochloromethane.

Fig. 4.5.2 and Fig. 4.5.3 show a change in concentration with the passage of time, and residual chlorine effects. Organic compounds other than THM were identified using a gas chromatograph mass spectrometer (GC/MS). The compounds 2-bromocyclohexanol, 1-bromo2-chlorocyclohexane and 1.2-dibromocyclohexane were found. These substances are unstable and changed into other compounds in twenty or so hours. At present however, there is only a little information available relating to accumulation in organisms, transfer, toxicity and degradability of these substances.

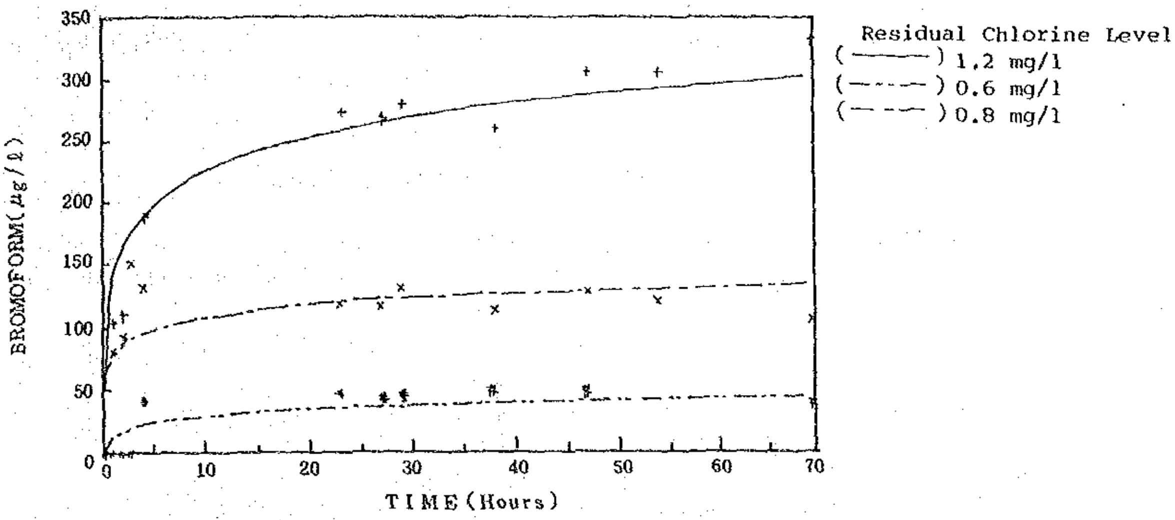


Fig. 4. 5. 2: Concentration of Bromoform Formed by Chlorination of Sea Water

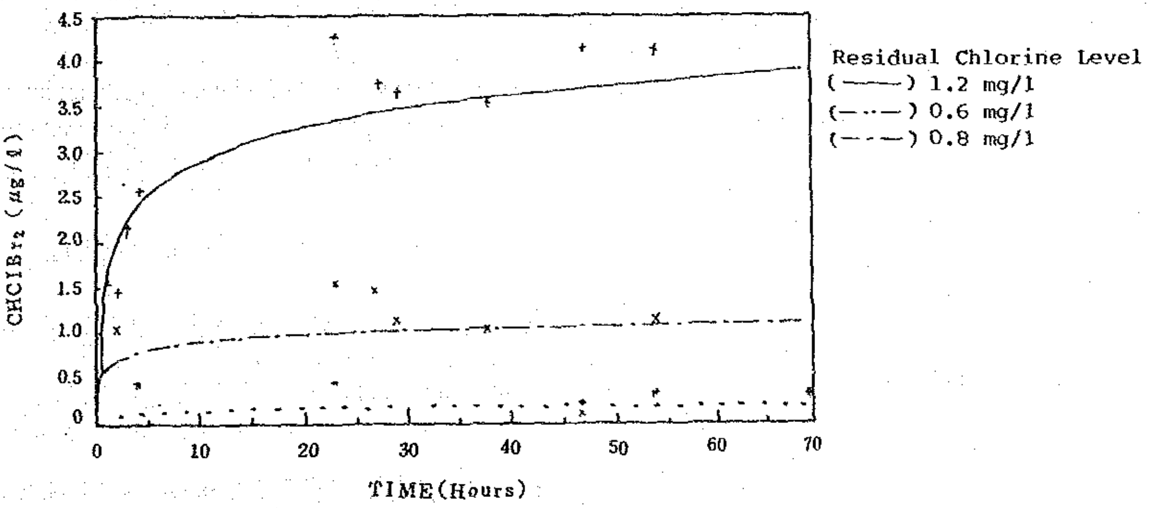


Fig. 4. 5. 3: Concentration of Dibromochloromethane Formed by Chlorination of Sea Water

4) Fayad et al. 25) made further measurements on THM concentration in the drinking water in the eastern area of Saudi Arabia. In that area a mixture of the product water from the reverse osmosis desalination plant, and underground water is used as drinking water.

The measurement results indicate that the total THM concentration in the drinking water in Damman City is an average 14 μg/l, of which bromoform is present in quantities as large as 10 μg/l. This suggests that bromoform formed by the chlorination of sea water permeates to the product water, passing through the reverse osmosis membrane.

### (2) Factors Affecting THM Formation

Many researches have been conducted concerning formation of THM by chlorination. Some of the principal studies are presented below.

1) According to the results of tests carried out by Aizawa et al. 26), the THM yield can be expressed by the following equation:

$$(\mathrm{THM})=0.33(\mathrm{C})^{1.10}(\mathrm{Cl_2})^{0.27}(\mathrm{pH})^{1.59}(\mathrm{t})^{0.22}$$

Where,

THM: THM yield (μg/l)
C: Concentration of humic acid (mg/l)
$\mathrm{Cl_2}$: Chlorine injection rate (mg/l)
pH: pH
t: Reaction time with chlorine (h)

The THM yield is greatly influenced by the concentrations of humic acid and reaction pH. Further, if chlorination is conducted in the presence of bromide ion, $\mathrm{CHCl_3}$ (chloroform) decreases and $\mathrm{CHCl_2Br}$, $\mathrm{CHClBr_2}$, $\mathrm{CHBr_3}$ are formed as the level of bromide ions increases. As well, of this amount, the brominated trihalomethane yield also increases. The relation between the brominated THM yield and the $\mathrm{Br^-}$ concentration of each reaction pH can be expressed in the following equation:

$$(\mathrm{THM_{Br}})=\mathrm{K}(\mathrm{Br^-})^{0.86}$$

Where,

$\mathrm{THM_{Br}}$: (μM)
$\mathrm{Br^-}$ : (μM)
K: Constants; 0.05 at pH 4, 0.13 at pH 7, and 0.22 at pH 10

In other words, since the quantity of brominated THM is expressed nearly as the first order reaction of co-existing $\mathrm{Br^-}$, its formation mechanism should be such that $\mathrm{Br^-}$ is oxidized to form hypobromous acid or hypobromite ions by the following reaction with chlorine, and the oxide reacts with the humic acid in the same manner as the reaction of the chlorine, and forms THM.

$$\mathrm{HClO}+\mathrm{Br^-}\longleftrightarrow\mathrm{HBrO}+\mathrm{Cl^-},\quad \mathrm{ClO^-}+\mathrm{Br^-}\longleftrightarrow\mathrm{BrO^-}+\mathrm{Cl^-}$$

2) Urano et al. 27) have studied humic acid (C) as a base substrate, and proposed the following equation, where the unit of concentration is expressed by mg/l, and the unit of time (t) is by hour:

$$[\mathrm{THM}]=0.83\times10^{-3}(\mathrm{pH}-2.8)\quad[\mathrm{C}][\mathrm{Cl^2}]^{0.25}\,\mathrm{t}^{0.35}$$

Residual chlorine is needed but the concentration of chlorine does not greatly affect the reaction rate and therefore the main force in the reaction of THM formation from humic acid is said to be the $SE_1$ reaction.*

---

* $SE_1$ reaction (Electrophilic Substitution Reaction):

When an organism is highly reactive and is able to react without depending on the properties or concentration of chlorine, the reaction rate is determined only by the concentration of the organism. This is abbreviated to a first-order reaction as "SE 1 reaction".

$$d\,[R-Cl]/dt=k[R-X]$$

When the chlorine and the organism supplemented each other, with the resulting increase in reaction energy, concentrations of both of them affect the reaction rate. This is abbreviated to a second-order reaction as "SE 2 reaction".

$$d[R-Cl]/dt=k[R-X][Cl]$$

Where,

R-Cl: Organic chloride
R-X : Organism

---

3) Wada 28) has confirmed through experiment that the THM yield is given by the following equation, where the concentration of organic substance is$[TOC]_0$,total chlorine injection rate $[Cl]_t$' , time t and rate constant k .

$$[THM]=k[TOC]_T^M t^h$$

If humic acid is urged as reagent, the values m = 0. 20 and n = 0. 36 are given. Accordingly, the following equation can be established.

$$[THM]=k[TOC]_o[Cl_2]_T^{0.20}t^{0.36}$$

Furthermore, it was reported that during the experiment, when examining the relation between temperature and the THM yield, the latter increased about seven times when the temperature rose from 10 to 50 °C.

4) According to Kumai's investigation 23) relating to chlorine injection at the cooling water inlet in the power plant, and the bromoform concentration at the water outlet, despite the rise in water temperature by 6 °C - 8 °C while the cooling water passed through the condenser, no increase in THM yield was observed.

This was due to a low concentration of residual chlorine (0.2 mg/l or less) at the cooling water inlet, and 0.01 to 0.02 at the water outlet. It can be inferred that the effective concentration of chlorine is the most influential factor in the formation reaction. Putting in order the factors affecting THM formation, according to Urano's equation the functional degree of relation between THM formation and the precursor concentration is linear. If the precursor increases 'a' times then the rate and absolute amount of chloride formation also increases 'a' times.

In relation to the chlorine concentration, almost no chloride will be formed without the presence of free chlorine. If the concentration of free residual chlorine increases, the formation of chloride will also, but according to the reaction equation, it will not have as much in- If the residual chlorine concentration is increased 10 times, both the yield amount and the rate will not even increase twice as much. Therefore, control of chlorine addition will not have as much effect as was expected. The reaction formula suggests that the effects of the pH and time factors on the formation of trihalomethane are greater than the effect of chlorine concentration.

### 4.5.3: Formation of THM by Chlorination of Oil Polluted Sea Water

One of the important objects of this study is to find out how much effect will the small amount of oil have, such as the dissolved oil and the oil in emulsion which remains in the sea water after the removal of the oil from the oil spill, or discharged from a nearby refinery, when it is drawn in the intake and chlorinated. However, little investigation has been conducted concerning whether THM will be formed when sea water containing oil is chlorinated. Accordingly, the following investigation on this problem was conducted, based on the research of chloroform formation by the reaction of organic compounds with chlorine.

#### (1) Reaction of Various Kinds of Organic Chemical Substances with Chlorine

Aizawa et al. [29] have examined the reaction of chlorine with aliphatic and aromatic compounds (57 kinds) having as substituents such groups as alkyl side chain, carboxyl, oxo, hydroxyl, etc., which were considered to be the main constituents of humic matter or the precursors for THM formation (Tables 4.5.2 to 4.5.4). They were classified into three groups according to their reactivities (Table 4.5.5).

In the first group, 40% of the consumed chlorine becomes TOCl (Total Organic Chloride), 50% of which becomes organic halogen substances other than chloroform. Finally, in the third group, the ring opening reaction of the benzene ring occurs. It was shown that organic substances in natural water indicate their values as being in the intermediate of the second and the third group.

### Table 4.5.2: TOCl, Chloroform Yield and Consumed Chlorine of Aliphatic Compounds

Conditions of chlorination: TOC: 7.2 mg/l, pH: 7.0 and Free chlorine dose: 0.4 mM, 24 hr, 20 °C

| No | Compound | TOCl<br>Compound (%) | $CHCl_3$-Cl<br>Compound (%) | $CHCl_3$-Cl<br>TOCl (%) | C-Cl<br>Compound (M/M) | TOCl<br>C-Cl (%) | $CHCl_3$-Cl<br>C-Cl (%) |
|---|---|---|---|---|---|---|---|
| 1 | Acetone | 5.48 | 1.21 | 22.1 | 0.10 | 54.8 | 12.1 |
| 2 | Metyl Ethyl Ketone | 1.88 | 1.61 | 85.6 | 0.07 | 28.2 | 24.2 |
| 3 | Metyl Butyl Ketone | 3.34 | 1.68 | 50.3 | 0.20 | 16.7 | 8.4 |
| 4 | Acetylacetone | 221.8 | 189.9 | 85.7 | 4.75 | 46.7 | 40.0 |
| 5 | Acetonylacetone | 16.2 | 11.3 | 69.5 | 0.40 | 40.6 | 28.2 |
| 6 | Diacetyl | 21.0 | 0.77 | 3.66 | 1.47 | 14.3 | 0.52 |
| 7 | Ethyl Acetoacetate | 89.3 | 0.43 | 0.48 | 2.30 | 38.8 | 0.19 |
| 8 | Acetaldehyde | 4.74 | 0.01 | 0.27 | 0.60 | 7.9 | 0.02 |
| 9 | n-Butyladehyde | 8.61 | 0.15 | 1.74 | 0.33 | 26.1 | 0.45 |
| 10 | Glyceraldehyde | 0.83 | 0.02 | 2.41 | 0.35 | 2.37 | 0.06 |
| 11 | Pyruvic Aldehyde | 4.16 | 0.15 | 3.61 | 1.50 | 2.77 | 1.85 |
| 12 | Butyric Acid | 1.48 | 0.03 | 1.82 | 0.07 | 22.2 | 0.40 |
| 13 | Capric Acid | 3.56 | 0.12 | 3.37 | 0.05 | 71.2 | 2.40 |
| 14 | Pyruvic Acid | 28.8 | 0.51 | 1.76 | 1.40 | 20.5 | 0.36 |
| 15 | Levulinic Acid | 3.48 | 0.93 | 26.6 | 0.10 | 34.8 | 9.25 |
| 16 | Citric Acid | 12.0 | 11.1 | 92.1 | 0.60 | 20.1 | 18.4 |
| 17 | Acetonedicarboxylic Acid | 238.6 | 120.4 | 50.5 | 6.17 | 38.7 | 19.5 |
| 18 | Oxalacetic Acid | 34.4 | 0.60 | 1.74 | 2.40 | 14.3 | 0.25 |
| 19 | Urea | 1.22 | 0.01 | 1.07 | 3.83 | 0.32 | 0.003 |

### Table 4.5.3: TOCl, Chloroform Yield and Consumed Chlorine of Benzene, Benzene Monosubstituted Compounds and Phenols

Conditions of chlorination: TOC 7.2 mg/l and free chlorine dose 0.4 mM, 24 hr, 20 °C)

| No | Compound | TOCl<br>Compound (%) | $CHCl_3$-Cl<br>Compound (%) | $CHCl_3$-Cl<br>TOCl (%) | C-Cl<br>Compound (M/M) | TOCl<br>C-Cl (%) | $CHCl_3$-Cl<br>C-Cl (%) |
|---|---|---|---|---|---|---|---|
| 20 | Benzen | 1.52 | 0.04 | 2.63 | 0.10 | 15.2 | 0.40 |
| 21 | Toluene | 2.30 | 0.05 | 2.17 | 0.12 | 19.2 | 0.42 |
| 22 | Benzenesulfonic Acid | 0.93 | 0.04 | 4.30 | 0.10 | 9.30 | 0.40 |
| 23 | Phenol | 94.8 | 8.47 | 8.94 | 10.4 | 9.11 | 0.81 |
| 24 | Aniline | 38.8 | 19.3 | 49.7 | 7.50 | 5.17 | 2.57 |
| 25 | Benzaldehyde | 2.31 | 0.05 | 2.16 | 0.12 | 19.3 | 0.42 |
| 26 | Benzyl Alcohol | 3.08 | 0.05 | 1.62 | 0.10 | 30.8 | 0.5 |
| 27 | Benzoic Acid | 1.61 | 0.05 | 3.11 | 0.12 | 13.4 | 0.42 |
| 28 | Nitrobenzene | 1.66 | 0.04 | 2.41 | 0.10 | 16.6 | 0.40 |
| 29 | Acetophenone | 9.64 | 8.21 | 85.2 | 0.53 | 18.2 | 15.5 |
| 30 | 1,4-Phenolsulfonic Acid | 78.3 | 5.43 | 6.94 | 9.80 | 7.99 | 0.55 |
| 31 | 1,2-Dihydroxybenzene | 10.6 | 0.33 | 3.12 | 5.00 | 2.12 | 0.07 |
| 32 | 1,3-Dihydroxybenzene | 179.3 | 155.5 | 86.7 | 8.80 | 20.4 | 17.7 |
| 33 | 1,4-Dihydroxybenzene | 8.39 | 1.58 | 18.8 | 3.80 | 2.21 | 0.42 |
| 34 | 1,2,3-Trihydroxybenzene | 11.9 | 1.08 | 9.11 | 7.90 | 1.50 | 0.41 |
| 35 | 1,2,4-Trihydroxybenzene | 200.9 | 22.3 | 11.1 | 5.30 | 37.9 | 4.21 |
| 36 | 1,3,5-Trihydroxybenzene | 543.8 | 210.3 | 38.7 | 11.0 | 49.4 | 19.1 |

Table 4.5.4: TOCl, Chloroform Yield and Consumed Chlorine of Benzoic Acid Monosubstituted Compounds, Aminoacetophenone, Hydroxyacetophenone, Aminopheno and Amino Acids

Conditions of chlorination: TOC 7.2 mg/l and
free chlorine dose 0.4 mM, 24hr, 20 °C

| No. | Compound | TOCl / Compound (%) | $CHCl_3$-Cl / Compound (%) | $CHCl_3$-Cl / TOCl (%) | C-Cl / Compound (M/M) | TOCl / C-Cl (%) | $CHCl_3$-Cl / C-Cl (%) |
|---|---|---|---|---|---|---|---|
| 37 | 1,2-Oxybenzoic Acid | 132.9 | 0.64 | 0.48 | 2.80 | 47.5 | 0.23 |
| 38 | 1,3-Oxybenzoic Acid | 91.2 | 17.9 | 19.6 | 11.0 | 8.31 | 1.63 |
| 39 | 1,4-Oxybenzoic Acid | 144.2 | 8.51 | 5.90 | 11.3 | 12.7 | 0.75 |
| 40 | 1,2-Aminobenzoic Acid | 42.7 | 16.3 | 38.3 | 6.53 | 6.53 | 2.50 |
| 41 | 1,3-Aminobenzoic Acid | 39.1 | 16.6 | 42.4 | 7.93 | 4.93 | 2.09 |
| 42 | 1,4-Aminobenzoic Acid | 54.7 | 19.6 | 35.8 | 8.17 | 6.70 | 2.40 |
| 43 | 1,3-Acetylbenzoic Acid | 10.3 | 7.60 | 74.0 | 1.80 | 57.1 | 4.20 |
| 44 | 1,4-Acetylbenzoic Acid | 11.4 | 6.60 | 57.8 | 0.30 | 38.1 | 22.0 |
| 45 | 1,2-Methoxybenzoic Acid | 16.8 | 0.35 | 2.09 | 1.87 | 8.96 | 0.19 |
| 46 | 1,4-Methoxybenzoic Acid | 7.76 | 0.92 | 11.9 | 0.80 | 9.70 | 1.15 |
| 47 | 1,2-Aminoacetophenone | 196.9 | 80.3 | 40.8 | 11.2 | 17.6 | 7.17 |
| 48 | 1,3-Aminoacetophenone | 181.1 | 93.8 | 51.8 | 11.2 | 16.2 | 8.38 |
| 49 | 1,4-Aminoacetophenone | 106.8 | 55.3 | 51.8 | 10.3 | 10.4 | 5.37 |
| 50 | 1,2-Oxyacetophenone | 159.9 | 18.1 | 11.3 | 10.7 | 15.0 | 1.70 |
| 51 | 1,3-Oxyacetophenone | 234.3 | 94.5 | 40.3 | 11.7 | 20.0 | 8.06 |
| 52 | 1,4-Oxyacetophenone | 184.2 | 54.6 | 29.7 | 10.4 | 17.7 | 5.25 |
| 53 | 1,2-Aminophenol | 59.4 | 9.90 | 16.7 | 7.0 | 8.49 | 1.41 |
| 54 | 1,3-Aminophenol | 150.8 | 31.2 | 20.7 | 9.10 | 16.6 | 3.42 |
| 55 | 1,4-Aminophenol | 5.45 | 0.12 | 2.19 | 7.0 | 0.02 | 0.78 |
| 56 | L-Tryptophan | 175.7 | 29.4 | 16.8 | 14.7 | 12.0 | 2.01 |
| 57 | L-Tyrosine | 17.9 | 2.21 | 12.4 | 7.76 | 2.30 | 0.28 |

(Notes) Tables 4.5.2 to 4.5.4

| | |
|---|---|
| TOCl/Compound | = TOCl formation rate: mole ratio of TOCl formed by reaction of 1 mole of a substance with chlorine indicated by percentage |
| $CHCl_3$ /Compound | = Chloroform formation rate: mole ratio of chlorine in chloroform formed by reaction of 1 mole of a substances with chlorine indicated by percentage |
| $CHCl_3$ /TOCl | = Existence ratio of CHC13-Cl within TOCl |
| C-Cl | = Rate of chlorine consumed by 1 mole of a compound |
| $CHCl_3$ /C-Cl | = Existence ratio of TOCl to consumed amount of chlorine |
| TOCl/C-Cl | = Existence ratio of TOCl to consumed amount of chlorine |

Source: Aizawa, Hasegawa, Adachi and Magara: Yield characteristics of total chlorides of organic compound (TOCl), Bulletin of Japan Society on Water Pollution Research, Vol.7 No.2, P.36-45 (1984).

Nagawa et al. 30) subjected organic compounds such as aldehyde, carboxylic acid, ester, alcohol, ether, phenol, amine, etc., to chlorination and estimated the amounts of chloroform and TOCl formed, and examined the effects of the change with the passage of time, and the pH.

They further classified the compounds into two groups, one which forms a large TOCl in the neutral condition but does not form chloroform (aliphatic aldehyde, amine, etc.), and the other which is in a neutral condition and easily forms chloroform (compounds with the β-2-ketone structure, phenol, etc.) (Table 4.5.6). It was stated that protein forms the same levels of chloroform and TOCl as humic acid (Table 4.5.7).

Table 4.5.5: Classification According to Reactibility
of Organic Compounsa on Chlorine

| First Group | Second Group | Third Group |
|---|---|---|
| 1 Acetone | 6 Diacetyl | 11 Urea |
| 2 Methyl Ethyl Ketone | 8 Acetoaldehyde | 23 Phenol |
| 3 Methyl Butyl Ketone | 9 n-Butyl Aldehyde | 24 Aniline |
| 4 Acetyl Acetone | 10 Glyceraldehyde | 30 1.4-Phenosulfonic Acid |
| 5 Acetonyl Acetate | 11 Pyruric Aldehyde | 31 1.2-Dihydroxy Benzene |
| 7 Ethyl Aceto Acetate | 12 Butyric Acid | 33 1.2-Dihydroxy Benzene |
| 13 Caprylic Acid | 14 Pyruric Acid | 34 1.2.3-Trihydroxy Benzene |
| 15 Levulinic Acid | 18 Oxalacetic Acid | 38 1.3-Oxybenzoic Acid |
| 16 Citric Acid | 20 Benzene | 38 1.4-Oxybenzoic Acid |
| 17 Acetonedicarboxylic Acid | 21 Toluene | 40 1.2-Amenobenzoic Acid |
| 29 Acetophenone | 22 Benzene Sulfonic Acid | 41 1.3-Amenobenzoic Acid |
| 32 1.3-Dihydroxy Benzene | 25 Benz Aldehyde | 42 1.4-Amenobenzoic Acid |
| 35 1.2.4-Trihydroxy Benzene | 26 Benzyl Alcohol | 47 1.2-Aminoacetophenone |
| 36 1.3.5-Trihydroxy Benzene | 27 Benzoic Acid | 48 1.3-Aminoacetophenone |
| 37 1.2-Oxybenzoic Acid | 45 1.2-Methoxy Benzoic Acid | 49 1.4-Aminoacetophenone |
| 43 1.3-Acetylbenzoic Acid | 46 1.4-Methoxy Benzoic Acid | 50 1.2-Oxyacetophenone |
| 44 1.4-Acetylbenzioc Acid | | 51 1.3-Oxyacetophenone |
| | | 52 1.4-Oxyacetophenone |
| | | 53 1.2-Amino Phenol |
| | | 54 1.3-Amino Phenol |
| | | 55 1.4-Amino Phenol |
| | | 56 L-Tryptophan |
| | | 57 Tyrosine |

## Table 4.5.6: TOCl, POCl and Chloroform Formed in Reaction of Various Organic Compounds with Chlorine

| | TOCl ($\mu g/l$) | POCl ($\mu g/l$) | Chloroform ($\mu g/l$) |
|---|---|---|---|
| Aldehydes | | | |
| Acetaldehyde | 6000 | 11 | 9 |
| Propionaldehyde | 660 | 50 | <5 |
| Butyraldehyde | 830 | 17 | <5 |
| Isobutyraldehyde | 160 | 13 | <5 |
| Valeraldehyde | 460 | <5 | <5 |
| Hexanal | 720 | 120 | <5 |
| Ketones | | | |
| Acetone | 690 | 360 | 270 |
| Ethyl methyl ketone | 120 | 120 | 120 |
| Acetophenone | 640 | 380 | 410 |
| 2,4-Pentanedione | 7400 | 6100 | 2000 |
| 3,5-Heptanedione | 5400 | 2800 | 2500 |
| 2,5-Hexanedione | 1100 | 600 | 480 |
| Carboxylic acid | | | |
| Pyruvic acid | 480 | 83 | 73 |
| Phenols | | | |
| Phenol | 5400 | 52 | 32 |
| 2,6-Dimethylphenol | 1800 | 470 | 360 |
| *o*-Chlorophenol | 3500 | 46 | 51 |
| 3,5-Dichlorophenol | 6900 | 680 | 640 |
| 2,4,6-Trichlorophenol | −1800 | 130 | 140 |
| Catechol | 160 | 20 | 22 |
| Resorcinol | 3700 | 3000 | 2100 |
| 2-Methylresorcinol | 1400 | 90 | 90 |
| 4-Methylresorcinol | 4900 | 3000 | 1600 |
| Hydroquinone | 590 | 110 | 120 |
| Pyrogallol | 1400 | 12 | <5 |
| Phloroglucinol | 2800 | 510 | 450 |
| 1-Naphthol | 500 | 12 | <5 |
| 1,3-Naphthalenediol | 3500 | 2700 | 2200 |
| Amines | | | |
| Triethylamine | 470 | 8 | <5 |
| Aniline | 1100 | 160 | 16 |
| *N*-Methylaniline | 1700 | 410 | 65 |
| *N*, *N*-Dimethylaniline | 1300 | 460 | 80 |
| 2,6-Dimethylaniline | 700 | 280 | 260 |
| 1-Naphthylamine | 850 | 12 | 12 |
| *o*-Phenylenediamine | 410 | <5 | <5 |
| *m*-Phenylenediamine | 1300 | <5 | <5 |

Organic compounds: 10 mg/*l*, Chlorine: 20 mg/*l*, pH: 7, Reaction time: 24 h

Remarks: TOCl = Total organic chlorine
POCl = Volatile organic chlorine

Table 4.5.7: Formation of TOCl, POCl and Chloroform at the Reaction of Proteins with Chlorine in Dilute Aqueous Solution

| | TOCl (μg/ℓ) | POCl (μg/ℓ) | Chloroform (μg/ℓ) |
|---|---|---|---|
| α-Casein | 360 | 80 | 90 |
| Hemoglobin | 510 | 140 | 160 |
| Rioonuclease | 470 | 82 | 77 |
| β-Lactoglobulin | 380 | 77 | 81 |
| Lysozyme | 840 | 150 | 170 |
| α-Chymocrypsinogen-A | 600 | 120 | 130 |
| Humic acid | 770 | | 220 |

Protein:10mg/ℓ、 Chlorine:20mg/ℓ
pH:7、 Reaction time:24h

### (2) Reaction of Components in Crude Oil with Chlorine

Since most kinds of chemical substances which tend to form THM have mostly been identified from the study concerning the reaction of organic chemical substances with chlorine (as mentioned in the preceding paragraph), these substances were compared with chemical components in crude oil, and studies were conducted concerning the possibility of THM forming when sea water containing crude oil is chlorinated.

The assumed components of spilled oil are referred to in Fig. 2.4.2. When the substances used in the THM tests were compared to the substances also present in crude oil components, it was found that the benzene and toluene of crude oil components have a smaller reactivity with chlorine.

According to Aizawa et al. about 15% to 19% of them are turned into organic chloride, of which 2% to 2.6% is chloroform, and most of them become organic chlorides other than THM. In other words, the amount of THM formed from the reaction with chlorine is very small.

Also, while there is no data concerning the napthenic acid contained in napthene based crude oil, it can be presumed that napthenic acid forms some THM, when one considers that caprylic acid and butylic acid, which are carboxylic acids (the same as napthenic acid), form THM, though the formation rate is small.

Due to a lack of data it is not certain, but it is expected that some of the components react with chlorine and form organic chloride, of which some do not form THM at all, but some do form a very small amount.

Further investigation and examination may be necessary to clear up this matter.

### (3) Reaction of Weathered Crude Oil with Chlorine

Crude oil effused into sea water is subject to weathering, oxidation or other forms of decomposition by the actions of bacteria. According to Hansen (1975), the infrared absorption peak of organic matters in the water beneath an oil film of 1700 $cm^{-1}$ by CO grup greatly increases compared with the absorption peak of 1460 $cm^{-1}$ of $CH_2$. It is believed that the absorption by -CO gruop in the oil film increases with a curve of the second-order. 31)

As a conclusion, it is said that the photochemical decomposition of oil at a water temperature of about 25 °C was 0.07%/$\delta$

Hansen established the following formula in 1975:

Hydrocarbon $C_XH_Y + O_2 \rightarrow C_{X-1}H_{Y-2}COOH$

The contents of the decomposition products of petroleum hydrocarbons were studied by Ehrhardt, et al. (1984) and Thominette et al. (1984), and the process of decomposition to form acetone-rich ketone (mainly acetone), phenol and cresol was verified. 32)

As stated above, crude oil effused into sea water is subjected to weathering, oxidation and decomposition into carboxylic acid, acetone, phenol and cresol, and forms a functional group in hydrocarbon. With acetone, 55% of the consumed chlorine participates in the formation of organic chlorides, about 22% of which is turned into chloroform.

With phenol, about 9% of the consumed chlorine is turned into organic chloride, and about 9% into chloroform. The chloroform formation rate is 8.5%.

Therefore, it is thought that oxidized and decomposed crude oil forms a significant amount of chloroform.

### (4) Reaction of Sea Water Containing Dissolved Oil with Chlorine

According to the laboratory experiments conducted by Ali [23], the main products formed by chlorination of sea water or sea water in which water soluble fractions (WSF) from Kuwait crude oil are added, are bromoform ($CHBr_3$), dibromochloromethane and a very small amount of bromodichloromethane. As shown in Fig. 4.5.4, the amount of bromoform is increased by the addition of WSF.

Consequently, it is considered that if crude oil is effused into the sea water and sea water containing dissolved oil is chlorinated as raw sea water for desalination, THM formation is increased due to the presence of crude oil components.

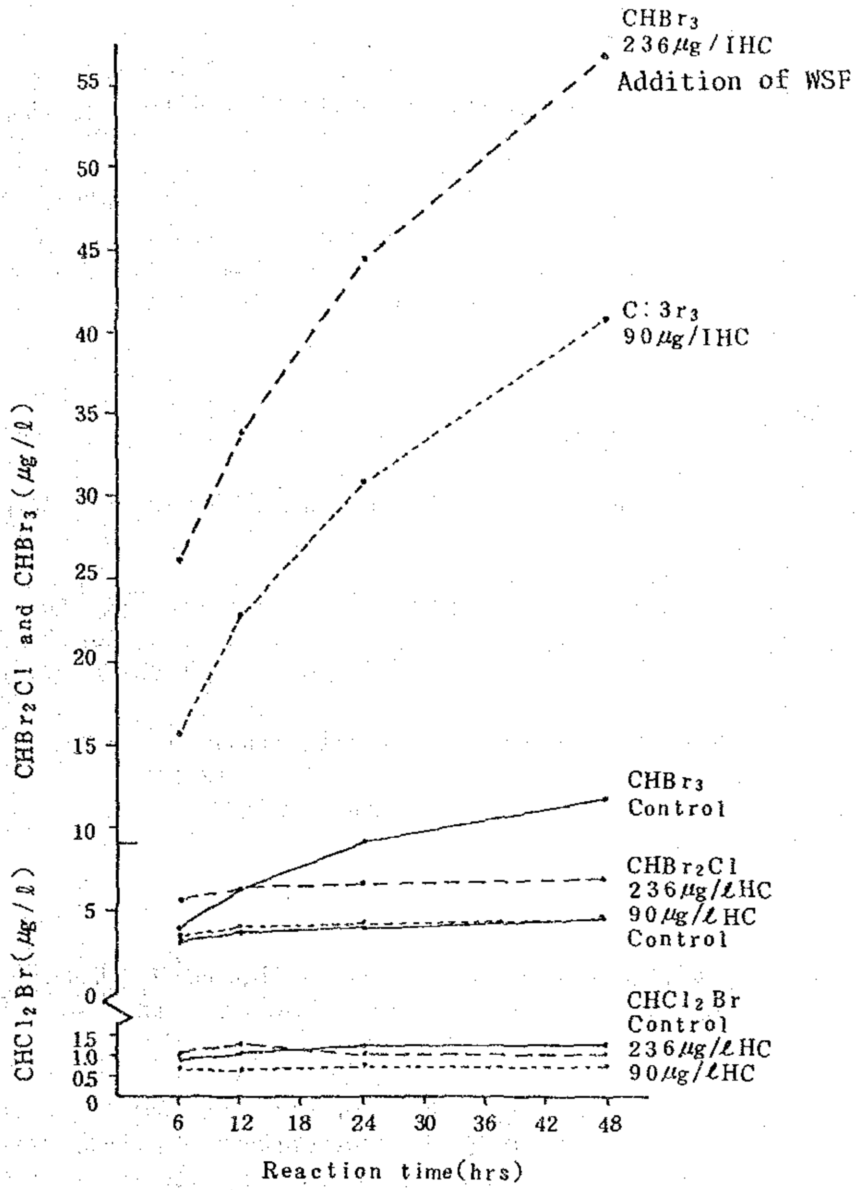


Fig. 4.5.4: Sea Water Chlorination in the Presence of Water Soluble Fractions from Kuwait Crude Oil

In consideration of the above, hydrocarbons (which are the main component of all crude oil) have a small reactivity, but other components with a reactivity or oxidation product are turned into organic chlorides by chlorination, and a part of which further reacts until THM is formed, while main part of the rest remains as organic chlorides.

Since the formation of THM varies considerably depending upon the reaction time with the chlorine, the extent of formation of THM from the raw sea water supplied to the actual desalination plant will be clearly ascertainable after chlorination tests conducted on the oil contaminated sea water sampled at the plant, and under the same conditions of chlorine injection and reaction time as those of the plant.

### 4.5.4 Possibility of Intermix of THM in Product Water

Here, a study will be made about to what extend THM and its precursory matters in sea water are transferred to product water and if formation of THM is possible by chlorination of oil-polluted components in product water.

#### (1) Formation of THM in Sea Water Desalination Plant

The conditions of sea water in the subject plant are:

| | |
|---|---|
| Temperature: | 35 to 100 °C |
| Retention time; | about 3 min |
| Residual chlorine: | 0.1 mg/l. |

Now, a study will be made on relation between the above plant conditions and the formation of THM.

When humic acid is used as substrate, the reaction formula for the formation of THM can be expressed as follows as stated in 4.5.2 (2) 2).

Unit of concentration: mg/l
Unit of time: h

$$[THM] = k\ (pH - 2.8)\ (\text{humic acid})\ [\text{chlorine}]^m t^n$$

$k = 0.83 \times 10\text{-}3$
$m = 0.25$
$n = 0.35$

The above coefficients are used in case of humic acid, and if the precursor matter and the temperature are changed, the coefficients will naturally be changed.

However, according to Urano 54), the quantity of THM from at 50 °C became 7 times as much as that at 10 °C in the specified time, but changes in coefficients m and n due to the changes in temperature can be neglected. When considering reactivity of chlorine, it appears that THM is formed after the react on has started simultaneously with injection of chlorine. Since there is no data showing actual measurement of a few minute reaction, there may be a short time induction period, though this is uncertain.

Although the experimental data describes reaction at 20 °C, if the temperature rises to 35 °C to 90 °C, the reaction speed becomes extremely fast. As clearly described in the experimental result concerning removal of THM by boiling (Fig. 6.2.2), THM starts to increase with the rise in temperature, and rapidly increases when the temperature goes up close to 100 °C. Therefore, the curve in Fig. 4.5.2 would considerably go upward and the quantity of THM formation would rapidly increase, which naturally suggests that trihalo-methane will be formed even if the retention time in the plant is only for 3 minutes.

It will be advantageous if an inhibitor which can delay such reaction of THM formation is found, but such substance has not been found up to now. However, the above mentioned reaction formula for THM formation indicates that the formation speed is reduced with decline of pH.

Fig. 4.5.5 indicates that when pH is reduced from 9 to 7, THM is also reduced by about 50%. The figure shows that quantity of molar formation (mole number of THM formation/100 mole of consumed chlorine) is a function of pH and the formation of THM is greatly promoted by elevation of pH.

It can be said from the above that reduction of THM is made possible first by the chlorination at reduced pH and then by elevating pH after the residual chlorine has disappeared. Morris and Brown reported, however, that if pH was elevated, THM would be formed even after disappeared residual chlorine. It may be because an intermediate product which was combined with chlorine at low pH forms THM by hydrolysis at elevated pH.

Accordingly, an experiment was conducted to confirm this (Table 4.5.8), which shows that the effective way is to reduce pH while in contact with chlorine. The removal of residual chlorine by ammonia forms more THM than the removal by thiosulfuric acid. In other words, reduction in THM can be effected by conducting chlorination at reduced pH and then restoring to original pH after the residual chlorine has been removed.

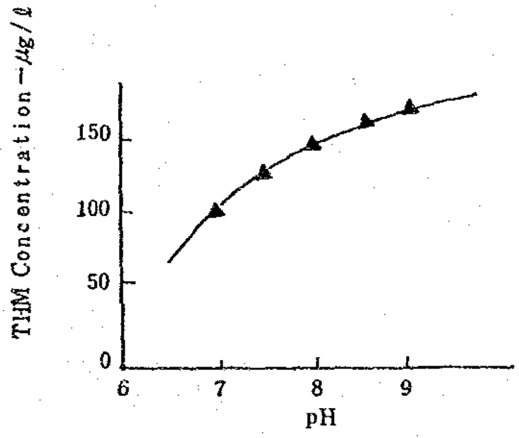


Fig. 4.5.5: Effect of pH on THM Formation

Table 4.5.8: Effect of Reduction in pH on THM Formation

| Procedure | THM- μg/l |
|---|---|
| pH 9.0; 5 mg/l; 1 h; quench | 18.0 |
| pH 6.0; 5 mg/l; 1 h; quench | 6.94 |
| pH 6.0; 5 mg/l; 1 h; pH 9.0;1 h; quench | 10.1 |
| pH 6.0; 5 mg/l; 1 h; $NH_3$; pH 9.0 | 10.7 |

Note: All samples stored 24 h at final pH before analysis

(2) Transfer of THM to Product Water

Solubility of THM into water is great and its Henry's constant is considerably greater than that of components in dissolved oil such as benzene, toluene, etc., as indicated below:

| THM | H (mol/kg atm 25 °C) |
|---|---|
| Chloroform | 0.2937 |
| Bromodichloromethane | 0.4699 |
| Dibromochloromethane | 1.2755 |
| Bromoform | 1.860 |

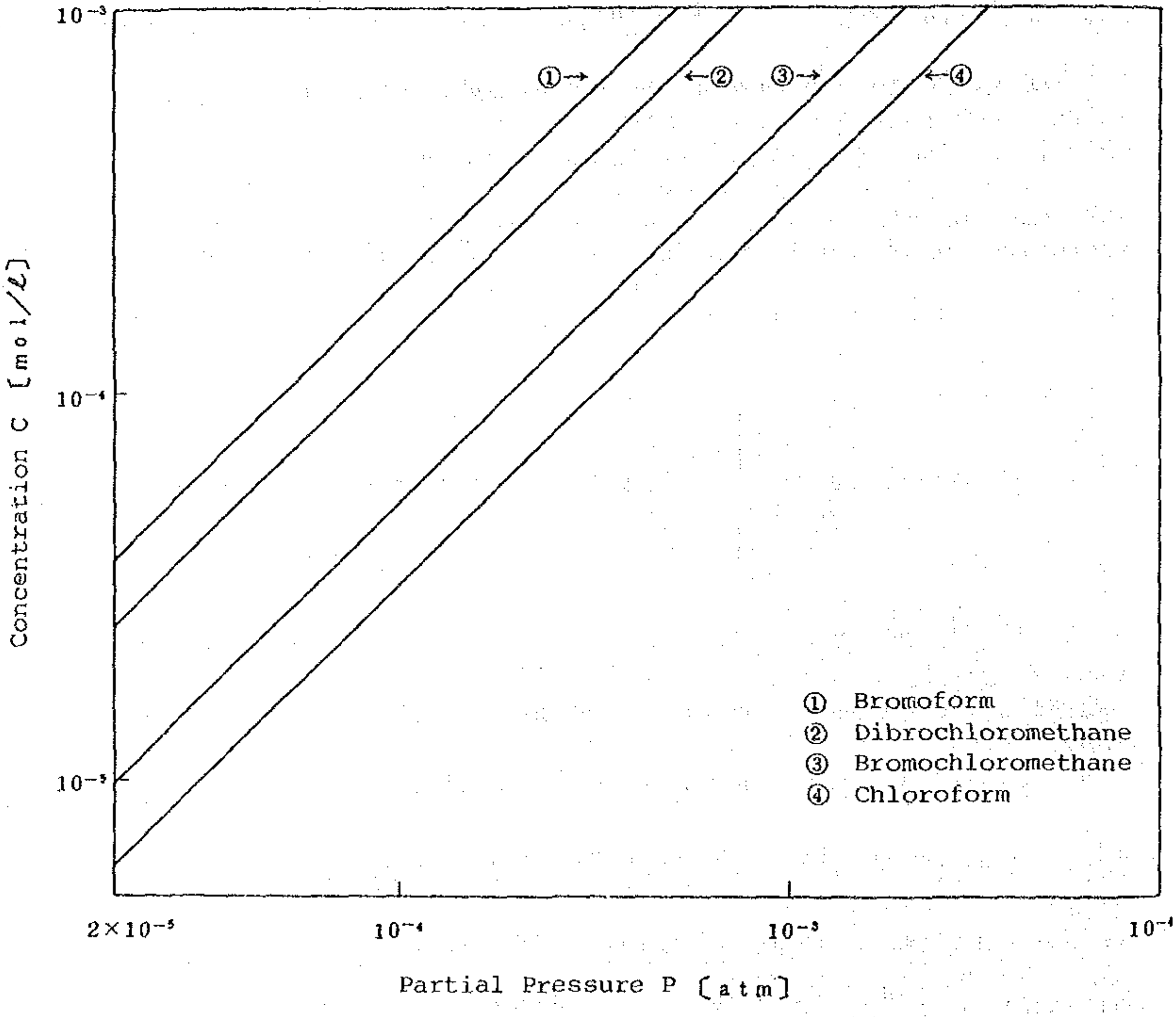


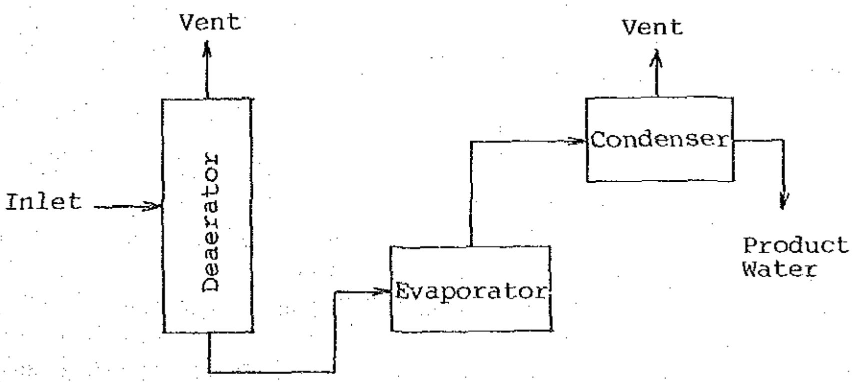
Fig. 4.5.6: Relations between THM Concentration and Partial Pressure

This relation is indicated in Fig. 4.5.6. Assuming that 100 $\mu g/l$ each of chloroform and bromoform is contained in sea water, the material balance is MSF plant calculated by Equation in 4.4.3 (2) becomes as indicated in Table 4.5.9.

Table 4.5.9: Material Balance of THM in MSF Plant

| Phase | Temp. (°C) | Deaerator Inlet (mg/L) | Deaerator Outlet (mg/L) | Evaporation Water (mg/L) | Product Water (mg/L) | Removing Ratio (%) |
|---|---|---|---|---|---|---|
| Chloroform/Water | 35 | 100 ug/l | 37 ug/l | 121 ug/l | 45 ug/l | 55 |
| Bromoform/Water | 35 | 100 ug/l | 79 ug/l | 257 ug/l | 202 ug/l | - |

Remarks: Removing Ratio $= \dfrac{\text{Deaeration Inlet} - \text{Product Water}}{\text{Deaeration Inlet}} \times 100$



This indicates that reduction rate of THM in the de-aerattor is 40 to 80% and THM cannot be completely reduced. Also, it shows that 45 $\mu g/l$ in case of chloroform and 202 $\mu g/l$ in case of bromoform is intermixed in product water, indicating that it is rather a concentration in case of bromoform.

(3) Transfer of THM Precursor Matters to Product Water

It is said that precursor matters such as humic acid, fulvo acid, etc. are generally contained in TOC at the rate of 10 mg/l. The pre-cursor matters from a high molecular compound having several thousands to seve*ral ten thousands molecular weight with almost no volatility and will not* be transferred to product water. Therefore, it is necessary to consider that precursor matters in sea water will be transferred into product water and will form THM by reaction with chlorine.

However, there is a fear that ana Exide product in crude oil becomes a precursor matter of THM as mentioned in 4.5.3. As components of the oxide product in crude oil, there are carbonxylic acid, acetone, phenol and cresol and so on. Solubility of these components into water is generally large. They are not easily diffused in the deaerator but dissolved into water through the evaporation and condensation stages.
For example, Henry's constant of acetone is 17.73 mol/l.atm (25 °C). When calculating material balance in MSF plant using this value pursuant to the equation in 4.4.3 (2) for the case where 10 mg/l acetone is mixed into sea water, the result will be as indicated in Table 4.5.10. The concentration of acetone in treated water in the deaerator is 9.6 mg/l, while its concentration in product water is 28.7 mg/l, which shows that acetone is concentrated in product water.

Table 4.5.10: Material Balance of Acetone in MSF Plant

| Phase | Temp. (°C) | Deaerator Inlet ($\mu g/l$) | Deaerator Outlet ($\mu g/l$) | Evaporation Water ($\mu g/l$) | Product Water ($\mu g/l$) |
|---|---|---|---|---|---|
| Acetone/Water | 35 | 10 | 9.6 | 30 | 28.7 |

(4) Formation of THM by Chlorination of Product Water

When product water is injected with chlorine for the after treatment, it appears that THM is formed if oxide product of crude oil is contained in product water, as described in 4.5.3. The reactivity between oxide product and chlorine varies depending on the kind of organic compounds, and it is known that many matters form chloroform.

Taking acetone as an example, when using the data as indicated in Table 4.5.6, related to the experiment of reaction by chlorine addition to 10 mg/l water solution of acetone (reaction condition; chlorine injection 20 mg/l, pH 7, reaction time 24 h), the concentration of chloroform becomes 270 ug/l by chlorination of 10 mg/l product water.

In view of these informations, if post-treatment of product water by chlorine is conducted under the condition of oil contamination of sea water, the possibility of THM formation is great.

However, since there are no enough data available to predict detail of its formation at present, it should be the subject for future study.

## 4.6 Corrosion of Plant Materials

### 4.6.1 Corrosion Mechanism by Oil Contaminated Sea Water

Although it is inconceivable that metallic materials will be corroded by hydrocarbons in the crude oil itself, if water, sulfide or chloride is present in the crude oil, the metallic materials may be corroded by water alone, or by water in sulfide or chloride solution. The corrosion occurs when the water or water solution comes into contact with the surface of the materials, or when a local cell is formed between the contact points of the oil and of the water/water solution.

The corrosion mechanism is described as follows by way of an example where corrosion pitting occurs due to oil drops adhering to the surface of carbon steel. 34)

(a) Anode Reactions

$$Fe \rightarrow Fe^{2+} + 2e \tag{4.14}$$

$$Fe^{2+} + 2OH \rightarrow Fe(OH)_2 \tag{4.15}$$

If carbon dioxide or hydrogen sulfide is present;

$$Fe(OH)_2 + CO_2 \rightarrow FeCO_3 + H_2O \tag{4.16}$$

$$FeCO_3 + H_2S \rightarrow FeS + CO_2 + H_2O \tag{4.17}$$

$$Fe(OH)_2 + H_2S \rightarrow FeS + 2H_2O \tag{4.18}$$

Further, if oxygen is present;

$$6FeS + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 6H_2S \tag{4.19}$$

$$4Fe_3O_4 + O_2 + 18H_2O \rightarrow 6Fe_2O_3 + 3H_2O) \tag{4.20}$$

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2 \tag{4.21}$$

$$SO_2 + 2H_2S \rightarrow 2H_2O + 3S \tag{4.22}$$

(b) Cathode reaction

$$2H^{+} + 2e \rightarrow H_2 \tag{4.23}$$

If oxygen is present;

$$H_2 + 1/2O_2 \rightarrow H_2O \tag{4.24}$$

As mentioned above, the pit turns black when $Fe_3O_4$ is formed, the color of the pit changes to red, and sometimes an elemental sulfur precipitates.

Fig. 4.6.1 shows a typical corrosion mechanism in an oxidizing cycle where not only hydrogen sulfide but also oxygen is present. Fig. 4.6.2 shows a typical representation of the corrosion mechanism in a reducing cycle where only hydrogen sulfide and carbon dioxide, without oxygen, are present.

Further, Table 4.6.1 shows the sulfur content in the crude oil produced in the Middle East.

### 4.6.2 Example of Corrosion by Oil Contaminated Sea Water

At the present time, there exist no reports concerning investigation or research in relation to the corrosion of desalination plants by oil contaminated sea water. In this paper therefore, corrosion by an oil/sea water mixture will be described, taking as an example the corrosion of oil tanker cargo oil tanks which are fill with ballast sea water, forming a corrosive atmosphere.

However, before proceeding to the main issue, two cases of corrosion damage caused by the crude oil itself will be introduced.

One is the corrosion test conducted by Sato et al. 35) over a period of two years on copper, copper alloy, nickel copper alloy and stainless steel, all of which can be used as materials in the hydraulic pressure control pipes laid in the crude oil tank.

The material and chemical composition of metals used in the test are shown in Table 4.6.2, setting position of test pieces in Fig. 4.6.3 and the results of the corrosion tests conducted during the two year exposure time in Table 4.6.3.

From these experiments the following can be observed.

(a) Stronger corrosion of each of the test pieces was observed, and more scale was attached to the test pieces in the gaseous phase crude oil tank (behind the deck) than in the crude oil (bottom of the tank). The weight reduction by corrosion in the gaseous phase was about three times as much as that of the crude oil, and the scale deposits were about five times greater.

(b) Copper, copper alloy and nickel copper alloy were subjected to corrosion of the general corrosion type, and albrac (aluminum brass), AP1 bronze and AP2 bronze were accompanied by intergranular corrosion. On the other hand, corrosion of AISI 18-8 stainless steel was caused by pitting.

(c) The depth of corrosion on the test piece in the gaseous phase which had a strong corrosive action was; 0.35 to 0.41 mm on albrac, AP1 bronze, and AP2 bronze, 0.47 to 0.61 mm on 10% cupronickel, 30% cupronickel and nickel copper alloy, and 1.06 to 1.09 mm on copper and 18-8 stainless steel after two years.

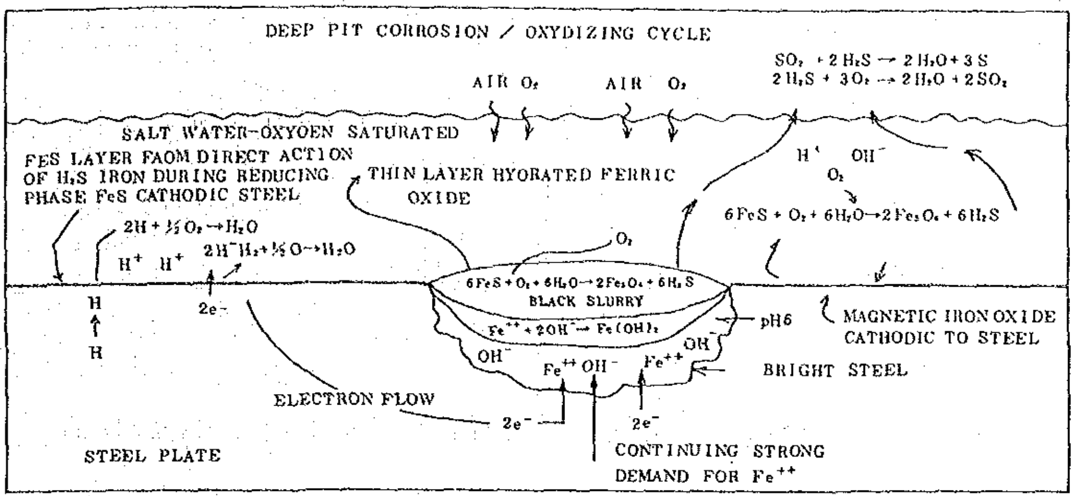


Fig. 4.6.1: Pitting Mechanism (Oxidizing Cycle)

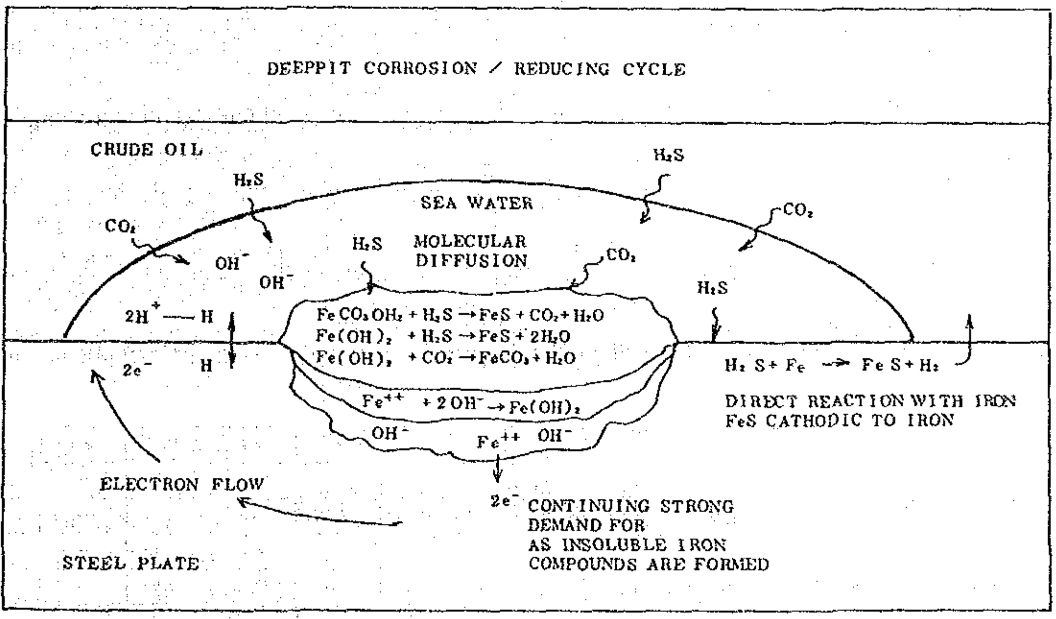


Fig. 4.6.2: Pitting Mechanism (Reducing Cycle)

Table 4.6.1: Sulfur Content in Middle East Crude Oil

| Crude Source | Hydrogen Sulfide (mg/l) | Total Sulfur (%) | Mercaptans (mg/l) |
|---|---|---|---|
| Iran (Four samples) | Up to 20 | 1.3 - 20 | 160 - 240 |
| Kuwait (Two samples) | Up to 8 | 2.6 - 3.7 | 170 - 210 |
| Libya | Negligible | 0.18 | Not Reported |
| Libya - Fes Sider | 300 | 0.32 | Not Reported |
| Saudia Arabia (Two samples) | Not Reported | 1.7 - 2.9 | 13 - 180 |
| Arabian Gulf (Qatar) | Up to 40 | 0.14 - 1.25 | Up to 4 |
| Abu Dhabi (Adleg) | Less than 20 | Less than 20 | Not Reported |
| Iraq (Basra) | Negative | 1.95 | Not Reported |
| Dubavy | Negligible | 1.43 | Present but not analyzed |

Table 4.6.2: Chemical Compositions of Test Pieces

(wt.%)

| Material | Cu | P | Fe | Pb | Zn | Al | Si | As | Ni | Mn | Sn | Cr | C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Deoxidized Copper | 99.95 | 0.018 | <0.01 | <0.01 | — | — | — | — | — | — | — | — | — |
| Albrac (Aluminium Brass) | 78.15 | — | 0.01 | <0.01 | R | 2.02 | 0.25 | 0.05 | — | — | — | — | — |
| 90-10 Cupronickel | R | — | 1.45 | <0.01 | — | — | — | — | 9.95 | 0.70 | — | — | — |
| 70-30 Cupronickel | R | — | 0.60 | <0.01 | — | — | — | — | 30.50 | 0.65 | — | — | — |
| Nickel Copper Alloy | 31.5 | — | 1.20 | <0.01 | — | — | 0.11 | — | R | 0.95 | — | — | 0.10 |
| AP-1 Bronze | R | — | <0.01 | <0.01 | — | 1.1 | 0.1 | — | — | — | 6.1 | — | — |
| AP-1 Bronze | R | — | <0.01 | <0.01 | — | 1.1 | 0.1 | — | — | — | 8.0 | — | — |
| 18-8 Stainless Steel | — | — | R | — | — | — | — | — | 8.90 | — | — | 18.70 | 0.04 |

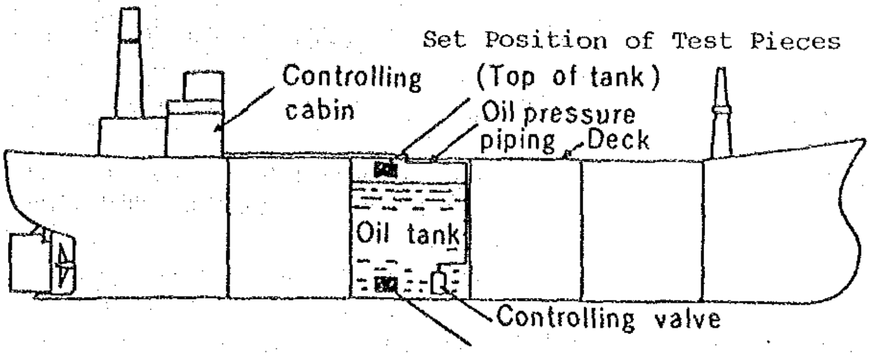


Fig. 4.6.3: Setting Positions of Test Pieces in Cargo Oil Tank

Table 4.6.3: Result of the 2-Year Corrosion Test in Cargo Oil Tank

| Position of specimens | Material | Quantity of scale | | | Weight of corrosion loss | | | Maximum depth of corrosion pits | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Range (mg/cm²) | Median (mg/cm²) | Ratio of A/B | Range (mg/cm²) | Median (mg/cm²) | Ratio of A/B | Range (mm) | Median (mm) | Ratio of A/B | (mm)* |
| Gas phase (Top of tank) (A) | Deoxidized Copper | 101.6, 195.9 | 148.8 | 4.8 | 200.0, 217.2 | 208.6 | 3.2 | 1.08, 1.09 | 1.09 | 2.4 | 1.08 |
| | Albrac | 90.7, 95.2 | 93.4 | 1.0 | 121.1, 160.7 | 140.9 | 1.1 | 0.41, 0.40 | 0.41 | 1.2 | 0.37 |
| | 90-10 Cupronickel | 136.9, 171.0 | 154.0 | 2.6 | 189.1, 201.0 | 195.1 | 1.5 | 0.61, 0.60 | 0.61 | 1.2 | 0.64 |
| | 70-30 Cupronickel | 70.4~161.6 | 116.1 | 2.1 | 177.6~218.1 | 195.2 | 1.6 | 0.39~0.64 | 0.47 | 1.5 | 0.51 |
| | Nickel Copper Alloy | 61.4, 135.5 | 98.5 | 2.7 | 83.4, 116.3 | 99.8 | 1.0 | 0.55, 0.41 | 0.48 | 1.7 | 0.58 |
| | AP-1 Bronze | 153.1, 189.6 | 171.4 | 2.1 | 173.9, 199.5 | 186.7 | 1.7 | 0.36, 0.33 | 0.35 | 1.3 | — |
| | AP-2 Bronze | 92.1~193.7 | 139.7 | 2.0 | 162.8~209.6 | 184.8 | 1.7 | 0.30~0.50 | 0.41 | 1.6 | — |
| | 18-8 Stainless Steel | 145.5, 157.3 | 151.4 | 1.9 | 66.6, 68.5 | 67.6 | 1.4 | 1.02, 1.09 | 1.06 | 1.4 | 0.81 |
| Liquid zone (Bottom of tank) (B) | Deoxidized Copper | 26.1, 36.3 | 31.2 | — | 60.0, 60.4 | 60.2 | — | 0.39, 0.50 | 0.45 | — | — |
| | Albrac | 78.9, 120.4 | 99.6 | — | 111.8, 157.4 | 134.6 | — | 0.33, 0.35 | 0.35 | — | — |
| | 90-10 Cupronickel | 57.3, 60.5 | 58·9 | — | 125.3, 135.9 | 130.6 | — | 0.47, 0.51 | 0.49 | — | — |
| | 70-30 Cupronickel | 41.5~64.1 | 54.9 | — | 120.7~128.1 | 125.1 | — | 0.26~0.28 | 0.31 | — | — |
| | Nickel Copper Alloy | 29.4, 43.2 | 36.3 | — | 95.2, 96.3 | 95.8 | — | 0.28 | 0·28 | — | — |
| | AP-1 Bronze | 77.6, 87.7 | 82.6 | — | 107.2, 111.0 | 109.1 | — | 0.24, 0.27 | 0.26 | — | — |
| | AP-2 Bronze | 60.8~75.7 | 69.2 | — | 103.0~117.6 | 107.5 | — | 0.24~0.29 | 0.25 | — | — |
| | 18-8 Stainless Steel | 76.5, 84.6 | 80.5 | — | 48.3, 49.3 | 48.8 | — | 0.53, 0.94 | 0.74 | — | — |

* Referential data of analogous test by Gilbert,4) original data on maximum depth of attack were converted into similar unit to our test data, mm/2year.

(d) Corrosion of copper, copper alloy and nickel copper alloy is considered to have been caused mainly by sulfide contained in the crude oil, because a great amount of sulfur (S) and sulfide ($Cu_2S$) were detected on the scale.

Corrosion of the 18-8 stainless steel is considered to have been caused mainly by chloride contained in the crude oil and the sea water, judging from the type of pitting corrosion.

(e) Stress corrosion cracking occurred on albrac and 18-8 stainless steel to which stress was applied. Cracks occurred on both albrac test pieces in the gaseous phase and in the crude oil phase, but those on 18-8 stainless steel test pieces only occurred in the crude oil.

(f) The action of hydrogen sulfide and oxygen can be considered as a main cause for the stress corrosion cracking in albrac, and the action of chloride for that in 18-8 stainless steel.

(g) It was discovered that corrosion was affected to a great extent by the condition of contact between the corrosive fluid and the test piece. In other words, an increase in the fluidity appears to considerably accelerate the corrosion process.

(h) Since no corrosion was observed on titanium used in the base employed to set the test pieces, titanium is acknowledged to have outstanding corrosion resistance in an atmosphere of that kind.

Furthermore, Sato 36) has reported on the results of corrosion tests conducted on different metallic materials used in heat exchangers in the hydrogen desulfurization facilities in the oil refinery.

The kind and chemical composition of metallic materials used in the test are indicated in Table 4. 6. 4, test conditions in Table 4. 6. 5, and the results obtained from this test in Table 4. 6. 6.

Table 4. 6. 4: Chemical Composition of Test Pieces (wt%)

| No | Metals and Alloys (JIS or ASTM Marks) | Cu | P | Al | Si | As | Fe | Pb | Mu | Ni | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Deoxidized Copper | 99.94 | 0.01 | – | – | – | – | – | – | – | – |
| 2 | Aluminium Brass (Albrac BsTF-2) | 78.34 | – | 2.02 | 0.22 | 0.06 | 0.02 | Tr | – | – | R |
| 3 | 70-30 Cupronickel(CNTF-3) | 67.65 | – | – | – | – | 0.71 | Tr | 0.52 | 30.09 | 0.71 |
| 4 | Aluminium Bronze | 91.90 | – | 6.82 | – | – | – | – | – | – | – |
|  |  | Al | Cu | Fe | Si | Mg | Mn | Zn | Cr |  |  |
| 5 | Aluminium Alloy (5052) | R | 0.01 | 0.23 | 0.06 | 2.49 | Tr | 0.03 | 0.25 |  |  |
|  |  | Ti | N | O | C | H | Fe | Si |  |  |  |
| 6 | Titanium (ST-40) | R | 0.01 | 0.04 | 0.01 | 0.01 | 0.04 | 0.02 |  |  |  |
|  |  | Fe | C | Si | Mn | P | S | Cr | Ni |  |  |
| 7 | Low Carbon Steel | R | 0.06 | 0.04 | 0.29 | 0.014 | 0.012 | – | – |  |  |
| 8 | 18 Cr Stainless Steel (Type 430) | R | 0.03 | – | – | – | – | 18.09 | – |  |  |
| 9 | 18-8 Stainless Steel (Type 304) | R | 0.04 | – | – | – | – | 18.09 | 7.96 |  |  |

## Table 4. 6. 5: Conditions of Field Test in Heat Exchanger of Unifiner Plant

| Heat exchanger | Fluid | Temp. ℃ | Pressure, $kg/cm^2$ | Duration of test, hr |
|---|---|---|---|---|
| A Combined feed heat exchanger | Kerosene or naphtha as charging oil containing combined sulfur | 190~230 | 45 | 6,480 |
| B Product condenser | Desulphurized oil + excess hydrogen + reactant sulfur ($H_2S$) | 170 | 45 | 6,480 |
| C Overhead condenser | Gasoline + $H_2$ + $H_2S$ | 100~145 | 12 | 19,000 |

## Table 4. 6. 6: Results of Corrosion Test

| No | Specimens | Heat Exchanger | Corrosion rate | | Degree of loss in tensile tests, % | | Depth of pits(X10μ) |
|---|---|---|---|---|---|---|---|
| | | | $mg/cm^2$ | mm / yr | tensile strength | elongation | |
| 1 | Deoxidized Copper | A • | – | – | – | – | |
| | | B • | – | – | – | – | |
| | | C • | – | – | – | – | |
| 2 | Alnminium Brass (Albrac BsTF-2) | A | 25.1 | 0.04 | 39 | 42 | – |
| | | B | 61.7 | 0.11 | 53 | 50 | – |
| | | C | 74.0 | 0.04 | 54 | 45 | – |
| 3 | 70-30 Cupronickel(CNTF-3) | A | 52.0 | 0.08 | 23 | 42 | – |
| | | B • | – | – | – | – | – |
| | | C • | – | – | – | – | – |
| 4 | Aluminium Bronze | A • | – | – | – | – | – |
| | | B • | – | – | – | – | – |
| | | C • | – | – | – | – | – |
| 5 | Aluminjum Alloy(5052) | A | 0.3 | 0.00 | 10 | 86 | 30 |
| | | B | 38.1 | 0.19 | –••• | –••• | 30 |
| | | C | 9.3 | 0.02 | 43 | 85 | 34 |
| 6 | Titanium(ST-40) | A | 0 | 0 | 0 | 0 | – |
| | | B | 4.2 | 0.01 | 0 | 34 | – |
| | | C | 0 | 0 | 0 | 0 | |
| 7 | Low Carbon Steel | A | 101.3 | 0.17 | –••• | –••• | – |
| | | B | 60.7 | 0.10 | 6 | 46 | – |
| | | C | 43.3 | 0.03 | 46 | 19 | – |
| 8 | 18 Cr Stainless Steel (Type 430) | A | 4.4 | 0.01 | 7 | 30 | 35 |
| | | B | 2.5 | 0.01 | 6 | 0 | 16 |
| | | C | 5.6 | 0.00 | 5 | 54 | 30 |
| 9 | 18-8 Stainless Steel (Type 304) | A | 1.4 | 0.00 | 17 | 0 | 18 |
| | | B | 51.2 | 0.09 | 18 | 9 | 20 |
| | | C | 1.8 | 0.00 | 7 | 21 | 37 |

• Specimen was corroded away.

•• Type of the corrosion classified by the model of corrosion by JPI : ).

••• Specimen unable to do the tensile test due to severe corrosion.

From the above the following may be observed:

(a) Corrosion by sulfide is especially noticeable on copper alloys. Among them, the brass group of copper alloy has a considerably high corrosion resistance.

(b) Titanium has a very good corrosion resistance but absorbs hydrogen under certain conditions, becoming brittle.

(c) Aluminum and stainless steel produce pitting. The corrosion factor is considered to be the action of chloride.

An example of tests conducted using sea water and oil will now be discussed:

Sakae et al. 37) conducted tests over a 430 day period in an actual ship, setting spool test specimens made of various structure materials in a tanker's oil tank. 75 kinds of test pieces are listed in Table 4.6.7, setting positions of the test pieces and conditions in the tank (test environment) in Table 4.6.8 and properties of cargo crude oil in Table 4.6.9.

Further, the rate of corrosion of metallic materials over 430 days and the survey results of the test pieces, except those with special surface-treated materials (molten metal spray coating, molten metal coating and electrolytic coating ) were obtained:

(a) The corrosion rates of mild steel, cast steel, cast iron and low alloy steels was 0.06 to 0.14 mm. There was not much difference in corrosion resistance.

(b) Corrosion rates of martensite stainless steels were about one fifth those of mild steel, and those of ferrite stainless steels were about one tenth of the same, both showing a whole surface corrosion accompanied by pitting. Austenite stainless steels showed a small amount of corrosion, a good result.

But some stainless steel of different kinds formed considerable pitting corrosion, i.e., AISI 347 stainless steel which should be resistant to intergranular corrosion showed a little resistance to pitting. From these results, it is presumed that the stress corrosion action due to pitting formation rather than intergranular corrosion becomes a factor in producing a corrosive atmosphere for stainless steels in cargo oil tanks.

(c) Copper, copper alloy and nickel alloys were covered by solid black copper sulfide and niakel sulfide films. The largest corrosive factors were found to be corrosion by sulfide. The same is the case with monel metal, and its corrosion resistance cannot be relied upon in the environment created by Middle East crude oil.

Table 4. 6. 7: Test Specimens

| Metallic Materials | | | | |
|---|---|---|---|---|
| Iron Steel | | Non- ferrous | | Copper and Copper Alloy Pipe |
| | Inco Spool Specimens | | Inco Spool Specimens | |
| Mild Steel<br>Cast Iron<br>Cast Steel<br>High Tensile Steel<br>Ni-Cr-Steel<br>Ni-Cr-Mo-Steel<br>13 Cr Steel<br>18-8 Steel<br>19-12-Mo Steel | Mild Steel<br>Cast Iron<br>Ductile Cast Iron<br>AISI 430 SS<br>AISI 410 SS<br>AISI 309 SS<br>AISI 347 SS<br>AISI 316 SS<br>AISI 304 SS | Steel Plate<br>6/4 Yellow Brass Plate<br>7/3 Yellow Brass Plate<br>Aluminium Plate<br>NP5/6 Aluminium Alloy Plate<br>Lead Plate<br>Titanium Plate<br>Cu-Steel-Clad Plate | Copper<br>Admiralty Brass<br>Yellow Brass Plate<br>Red Brass<br>Lead<br>Aluminium 25<br>Monel<br>Zinc | Copper Pipe<br>Albrac<br>Alumibrass<br>Cupronickel Pipe 70/30 for Chemical Machineries<br>Cupronickel Pipe 80/20<br>Cupronickel Pipe 90/10<br>Cupronickel Pipe 70/30 for Condenser |
| 9 kinds | 9 kinds | 8 kinds | 8 kinds | 7 kinds |

| Corrosion-resistant Coatings, Plastics, ets. | | |
|---|---|---|
| Painted Sheet | Plating & Metallikon ( 0.1 mm in Thickness ) | Electrocoating |
| Phenol Resin Rust Ban, USA<br>Phenol Resin A, Japan<br>Phenol Resin B, Japan<br>Phenol Resin C, Japan<br>Vinyl Resin A, Japan<br>Vinyl Resin B, Japan<br>Epoxy Resin A, Japan<br>Epoxy Resin B, Japan<br>Epoxy Resin C, Japan<br>Vinyliden Chloride Resin(saran)<br>Zinc-rich Paint(Organic)<br>Polyurethane Resin Paint<br>Unsaturated Polyester Resin Paint<br>Coal Tar Enamel | Zinc Hot Dipping<br>Lead Hot Dipping<br>Zn Metallikon<br>Al Metallikon<br>Pb Metallikon<br>Cu Metallikon<br>Brass Metallikon<br>13 Cr Metallikon<br>18-8 Metallikon | External Power Source Method<br>Amalgamated Al Anode<br>Mg Anode |
| | 9 kinds | 3 kinds |
| | Synthetic Rubber | Plastics |
| | Neoprene<br>HAIKA<br>GR-S | Phenol Resin Laminated Sheet<br>Phenol Melamine Resin Sheet<br>Acryle Resin Sheet<br>Hard Vinyl Chloride Resin Sheet<br>Polyester Resin Sheet |
| 14 kinds | 3 kinds | 5 kinds |
| | | Total 75 kinds<br>Total Number of Specimens<br>Sheet : 51 x 4 = 204<br>Pipe : 7 x 4 = 28<br>Inco : 17 x 2 = 34<br>Blank Test Mild Steel : 20<br>Total 286 pieces |

(NOTE 1) Size of Spool Test Specimens: Sheet : 150 x 80 x 1.6~3 mm
Pipe : 150 x 16φ~21φ
Inco : 57φ x 1~5 mm

(Note 2) 3 coats for Painting sheet, 5 coats for vinyl, saran,
3 mm in thickness for coal tar enamel

Table 4.6.8: Layout of Test Tank and Tank Conditions

| Tank | No. 3 Center | No. 5 Center | No. 6 Wing |
|---|---|---|---|
| Kind of Tank | Crude Oil,<br>Ballast Sea Water<br>Amine System Inhibitor | Crude Oil Ballast Sea Water | Crude Oil |
| Corrosion Proof | RESCOAL W 711 | Mg anode | |
| Treatment | Projection<br>3 | 6 | 3 |
| Number of Specimen | 86 sheets | 144 sheets | 56 sheets |
| Ballasting Days | 50 days | 63 days | 5 days |
| Amount of Cargo Oil | Gas Oil | Gasoline | |
| | 20,800 t + 2,000 t | 20,065 t + 1,140 t | 7,700 - 10,000 t |

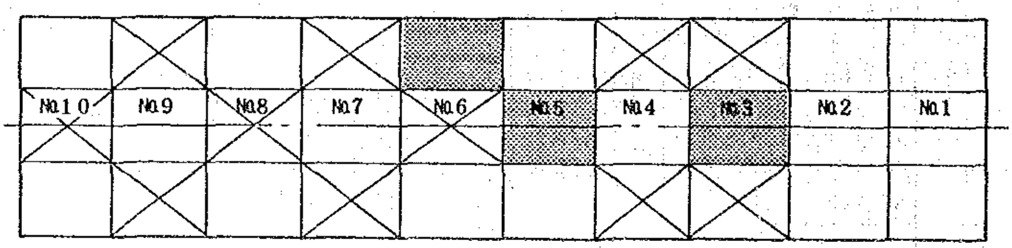


Table 4.6.9: Properties of Cargo Crude Oil

| Source<br>Item | Arabia | Syria | Iran | Qatar | Kuwait | Wafra |
|---|---|---|---|---|---|---|
| Specific Gravity °API | 34.7 | 36.9 | 33.8 | 40.0 | 31.6 | 24.2 |
| Flash Point (°F) | - | 50 | 80 | 88 | - | - |
| Pour Point (°F) | - | 55 | -10 | <0 | - | -20 |
| Viscosity 100 (°F), SSU | 44 | 33.8 | 44.9 | 36 | 53.8 | 167 |
| Moisture, Deposit (%) | 0.2 | tr | - | tr | - | - |
| Sulfur (%) | 1.56 | 0.08 | 1.46 | 1.91 | 2.49 | 3.09 |
| Evaporation Residue (%) | 3.8 | 2.6 | 45 | 6.5 | - | - |
| Wax (%) | 1.1 | - | - | 1.1 | - | - |

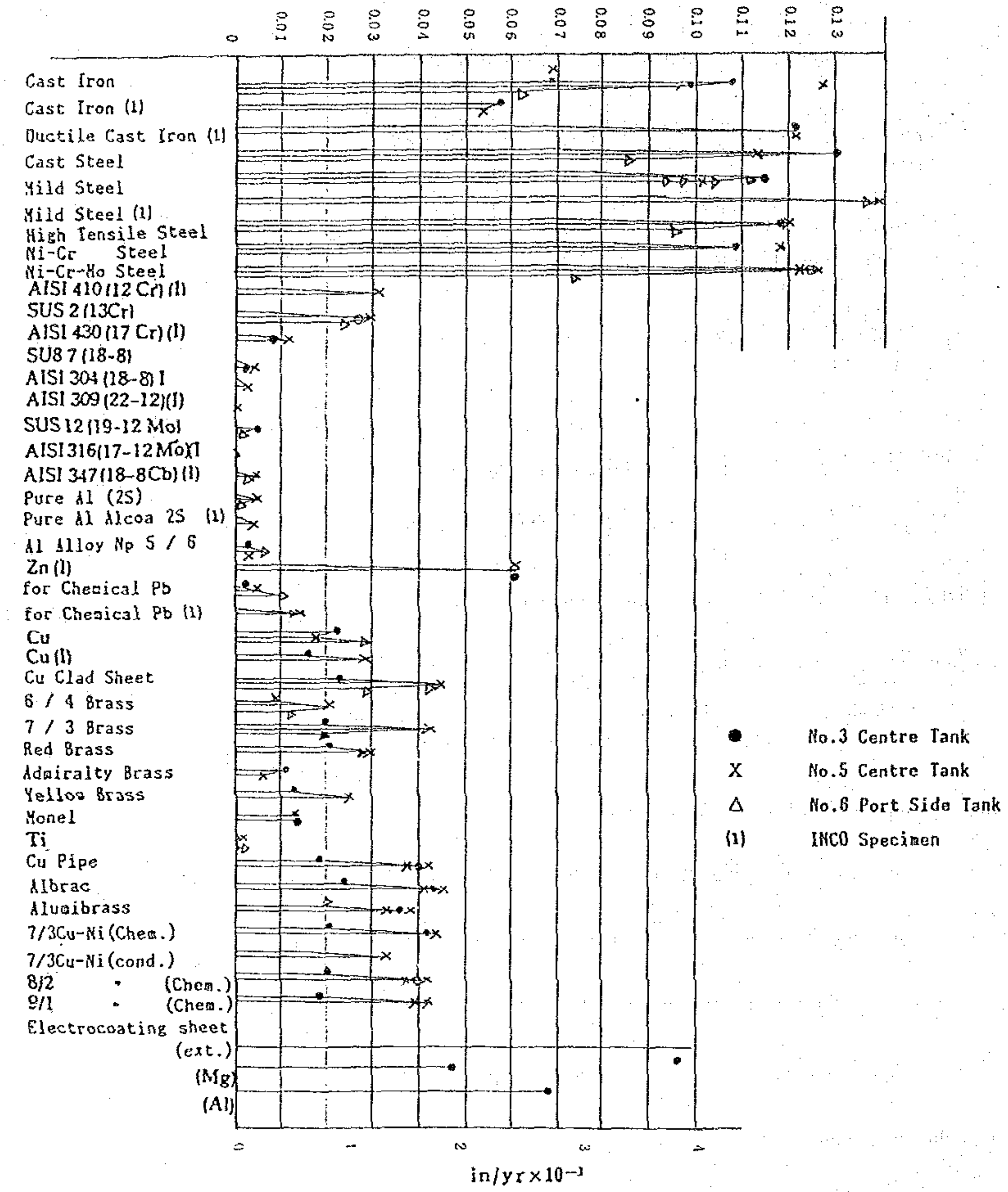


Fig. 4.6.4: Corrosion Rate of Test Specimen (Exposure Period 430 Days)

Table 4.6.10: Overall Results of Paint Tests (After 430 Days)

| Group of Paints | Name of Tank | No.3 C.O.T. | | | | | No.5 C.O.T. | | | | | No.5 W.O.T. | | | | | Gross Result |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Surveyed Items<br>Name of Paints | Bulge | Crack | Peeling | Colour Change | Result | Bulge | Crack | Peeling | Colour Change | Result | Bulge | Crack | Peeling | Colour Change | Result | |
| Phenol | Rust Ban ( U.S.A. ) | Trace | | Trace | | ○ | Slightly Large | | Some | | △ | | | Large | | × | △ |
| | Domestic Product ( A ) | | | Trace | | ○ | Slightly Large | Trace | Some | | △ | | | Large | | × | △ |
| | Same as above ( B ) | Large | | Large | | × | Slightly Large | | Trace | Trace | △ | Trace | | Some | | △ | △ |
| | Same as above ( C ) | | | Some | | △ | | | Large | | × | | | Large | | × | × |
| Epoxy | Domestic Product ( A ) | Slightly Large | | | Some | △ | Large | | | Large | × | Large | | | Large | × | × |
| | Same as above ( B ) | | | Some | Some | ○ | Some | | Trace | Some | ○ | Some | | | Some | ○ | ○ |
| | Same as above ( C ) | Slightly Large | | | Large | △ | Some | | | Large | | Large | | | Large | × | △ |
| Vinyl | Domestic Product ( A ) | Some | | | | ○ | Some | | Trace | | ○ | Some | | Trace | | ○ | ○ |
| | Same as above ( B ) | | | | | ◎ | Trace | | Trace | | ◎ | Trace | | | | ◎ | ◎ |
| | Saran | | | | | ◎ | | | | | ◎ | | | | | ◎ | ◎ |
| | Zinc Rich Paint | Large | | Large | | × | Large | | Large | | × | Large | | Some | | × | × |
| | Polyurethane | | | | | ◎ | Trace | | | | ◎ | Trace | | | | ◎ | ◎ |
| | Polyester | Some | | | Trace | ○ | Slightly Large | | Some | Large | × | Slightly Large | | Some | Some | | △ |
| | Coal Tar Enamel | | Large | | | × | Large | | Large | | × | | Large | Some | | × | × |

( NOTE ) Judgement ◎ Excellent
○ Good
△ Fairly Good
× No good

C.O.T. : Center oil tanker
W.O.T. : Wing oil tanker

(d) Among non-ferrous metals, titanium is the best; aluminum has a corrosion resistance to the same extent as that of austenite stainless steels, but has a tendency to produce slight pitting corrosion (the place of corrosion was limited to that part in contact with the spacer).

(e) Among synthetic resins, melamine plastics were not acceptable although all others were acceptable. Among synthetic rubbers, a swelling of GR-S was conspicuous, and neoprene showed bad oil resistance while the HAIKA group was the best.

(f) Among paint films, polyurethane resin paint and saran were superior, followed by vinyl, which showed good results.

On the other hand, phenol resins and epoxy resins which have generally been used as oil-proof paints were not good and proved to be unacceptable in severe conditions like the cargo oil tank. Zinc rich paint also displayed many changes in the properties of the paint film under conditions of alternate loadings of oil and sea water. Coal tar enamel also displayed a slight lack of oil resistance.

Table 4.6.11 shows the results, in which test pieces were set inside the cargo oil tank, as carried out by Sakae et al. The corrosion rate was measured and readjusted according to service conditions in the oil tank.

The Japan Committee of Trial Design of High Economy Tankers, No. 3 Subcommittee (HET-S3) determined the standard rate of corrosion of a tanker as indicated in Table 4.6.12 (based on Table 4.6.11). The rate of corrosion of these parts are two to three times as fast as that of other parts. The cause may be considered to be as follows:

(a) The crude oil includes impurities such as inorganic sulfide and organic sulfide like thiophene, mercaptan, etc., and also includes brine in the oil fields, causing local corrosion.

(b) Operating practices such as the loading of sea water ballast during the voyage from Japan, and crude oil on the return voyage, leads to large scale corrosion during the ballast loading. In the case of heavy petroleum or heavy oil, when the tank is emptied an oil film remains on the steel surfaces, which prevents corrosion, but in the case of gasoline and other light oils loading, they dissolve the remaining oil film on the steel bulkheads, leaving a clean surface exposed to the atmosphere after the gasoline adhering to the bulkhead surfaces has evaporated. This causes very rapid corrosion when sea water ballast is loaded.

The cleaning method called Butterworth, which uses warm sea water, accelerates corrosion due to an action similar to that above. A clean cargo of gasoline or light oil generally causes far greater corrosion than a dirty cargo of heavy oil.

Table 4.6.11: Rates of Corrosion of Cargo Oil Tank
(Readjusted by Service Conditions)

| Service Conditions of Tank | Corrosion Rate (mm/yr) |
|---|---|
| In Clean Ballast Water | 1.0 |
| In Dirty Ballast Water | 0.3 |
| After Ballast is Emptied | 0.3 |
| After Crude Oil is Emptied | 0.3 |
| While Crude Oil is Loaded | ~ 0 |

*1. In the case that a clean cargo tank (gasoline, light oil, etc.) is loaded with ballast sea water.
*2. In the case that a dirty cargo tank (heavy oil, etc.) is loaded with ballast sea water.

Table 4.6.12: Standard Corrosion Rates of Tanker (HET-S3)

| Kind of Tanks | Standard Corrosion Rate (mm/yr) |
|---|---|
| Exclusive Cargo Oil Tank | 0.14 |
| Dirty Ballast Tank | 0.18 |
| Clean Ballast Tank | 0.31 |
| Exclusive Ballast Tank | 0.71 |

(c) Tanks which have not carried ballast sea water are exposed to the direct rays of the sun during the day when they are empty, causing their temperature to rise to 70 °C or higher. This causes the internal water vapor to reach a saturate point which condenses on the cold bottom plates or the cool metal surfaces during the night. This produces pitting by galvanic action since the condensed water is concentrated saltwater containing strong electrolytes, and consequently pitting corrosion often occurs on the bottom plates, heating coils, horizontal reinforcements, etc.

Table 4.6.13 indicates an analytical example of this condensation which showed strong acidity with a 0.2% sulfur component (pH 1.5) in addition to a strong electrolyte content.

Table 4.6.13: Chemical Analysis of Condensate Water in Tank (%)

| Fe | Cu | Mg | S |
|---|---|---|---|
| 0.03343 | 0.04018 | 0.08175 | 0.074 |
| $H_2SO_4$ | Na | Cl | NaCl |
| 0.227 | 1.2135 | 1.8714 | 3.0847 |

### 4.6.3 Application to Subject Plant

(1) Corrosive Damage

The following is a summary of 4.6.1 and 4.6.2:

1) Pitting corrosion occurs on copper alloy and carbon steel due to hydrogen sulfide contained in crude oil.

2) While titanium shows very good corrosion resistance, stainless steel is thought to cause stress corrosion cracking due to the action of chloride.

3) Of all non-metals, epoxy, phenol, coal tar and synthetic rubber groups show heavy deterioration.

4) Heavy petroleum and heavy oil have retarding effect against general corrosion due to the oil films they form.

5) When a free interface is formed by oil, corrosion in the gaseous phase is greater than in the liquid phase.

The main structural materials of the subject plant are as shown in Table 4.6.14, and the materials coming into contact with oil leaked among them are copper alloy, organic coating materials and stainless steel.

Here, the stainless steels are omitted from the object of this study because the stress corrosion of stainless steel is a common problem of plants using sea water, without particular reference to oil pollution. When studying the effects on other materials based on the above results, firstly, copper alloy is considered to be damaged by corrosion due to the presence of hydrogen sulfide.

However since this occurs in cases where the materials are in contact with oil for many hours, this result may not always be applicable to the present case, that is, in such cases where the materials come into contact with sea water containing oil components of 1,000 mg/l or less, only for a limited time. If oil components are present in the sea water in high concentrations and the contact is made for a long time, it is possible that corrosion damage will occur.

Also, epoxy group coating materials (Hempadur) which are used as coating in the evaporation chamber in the 18,000 m³ plant, may cause deterioration in quality under the same atmospheric conditions.

In any case, the technical information so far obtained will make it possible to estimate likely plant corrosion, but will be insufficient to produce an adequate evaluation by itself alone. It will be necessary to conduct systematic investigation and research hereafter.

(2) Other Damage (Erosion, etc.)

When a mixing of oil is considered, it is necessary to study erosion besides electrochemical corrosion damage shown in (1). In this case, a study of cavitation erosion is not necessary, but erosion caused mainly by wear by sands mixed with oil or fine tar balls which have not been removed by the screens, will become the subject of further studies.

However, fine sands should not be the cause of erosion in the plant since they can be removed by the strainer installed in the intake pump, but there may be some influences such as an increase in the frequency of strainer cleaning due to clogging.

Table 4.6.14: Structural Plant Materials

| Plant Capacity | 18,000 m$^3$/d | 22,500 m$^3$/d |
|---|---|---|
| Manufacturer | IHI | SIDEM |
| Main Shell Material | CS | E.24 |
| Protective Coating | Hempadur F 492 | ANKIOL |
| Special Protective Lining | Stages 1-2:CuNi. Clad | Deaerator:SS316L |
| High Temp Water Boxes | CS + 90/10 clad | Cu.Al A20 |
| Low Temp Water Boxes | CS + 90/10 clad | Cu.Al A20 |
| Rejection Section Water Boxes | CS + 90/10 clad | Cu.Al A20 |
| Tubes | | |
| Heat Input Section | 70/30 | 70/30 |
| Heat Recovery Stages - High Temp | 70/30 | 70/30 |
| - Low Temp | Al Brass | Al Brass 22 A 12 |
| Heat Rejection Stages | 70/30 | 70/30 |
| Ejector Condenser | Ti | Ti |
| Tube Sheets | RNB | CuNi 70/30 |
| Tube Support Plants | CS | CS |
| Demister | SS | SS |
| Pipework - Sea Water Supply | Bonna | Bonna |
| Pipework - Sea Water Feed | SS 316L | Coated DCI |
| Brine Recycle - High Temp | CS + 10/10 clad | CS + ANKIOL |
| - Low Temp | CS + Epoxy | + Ankiol |
| Diatillate | SS - 304 | SS - 316L |
| Vents | SS - 304 | SS - 304 |
| Sea Water Supply Headers | Bonna | Bonna |
| Main Vessel Support Structure | Steel | Steel |

Remarks:
CS: Carbon Steel
SS: Stainless Steel
RNB: Rolled Naval Brass
CDI + C: Ductile Cast Cement Lined
70/30: CuNi 66/30/2/2
90/10: CuNi

## 4.7 References of Chapter 4

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