Sea water 100 1/hr   Fuel oil A 1.7 ml/ min (100 ml/hr)

(P–2, sea water Tank)   (P–3, Oil Pump)

Mixed inside P–2

Ultrasonic homogenization treatment   Sea water 2 m³/hr

(100 1/hr)   (P–1,   Pump)

(UH–1, Ultrasonic Homogenizer)

Mixed inside TK–3 (Preparation Tank)

Removal of floating oil components TK–4

(Flotation Tank)

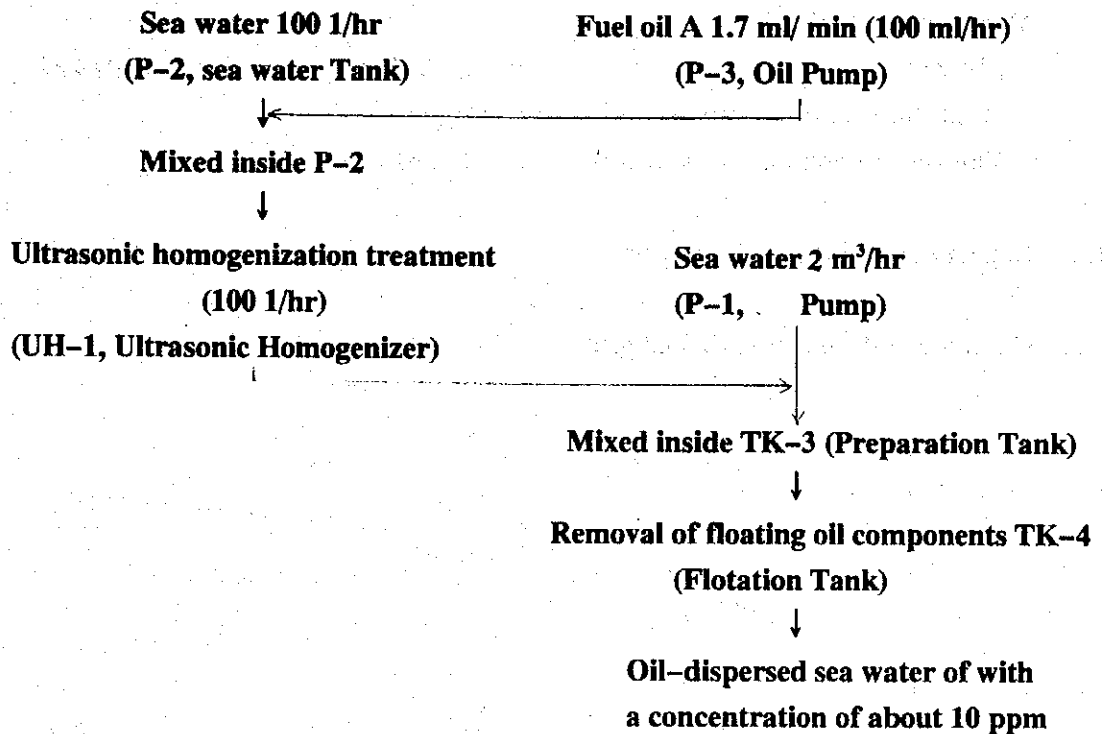Oil–dispersed sea water of with

a concentration of about 10 ppm

Fig. 12   Oil–dispersed Sea Water Preparation Method based on Oil–added
Sea Water Preparation Apparatus

(2) Investigation of oil content removal performance of various filter media

- Oil–dispersed sea water of about 5 – 10 ppm, prepared using the above method, is passed through filter columns filled with a sand, anthracite and activated carbon medium, after adding a flocculant.

- Samples are taken at the outlet of each column over time, and the oil content measured.

<u>Experimental conditions</u>

Column size	:	ϕ 10 cm, L 100 cm
Filter media	:	Sand (0.6 mm), Anthracite (1.0 mm)
		Polymer (Chemceptor CM121, 1.0 mm)
Filter height	:	50 cm
Filter media combination	:	Anthracite + Sand + Activated carbon
Feed rate	:	80 l/hr (LV 10 m/hr, SV 20/hr)
Flocculant	:	Ferric chloride
Flocculant concentration	:	10 ppm (as $FeCl_3$)

Measuring conditions

Slit width	:	Excitation 10 nm, fluorescent 10 nm
Excitation radiation wavelength	:	310 nm
Fluorescent emission wavelength	:	343 nm

(3) **Experiment results and analysis**
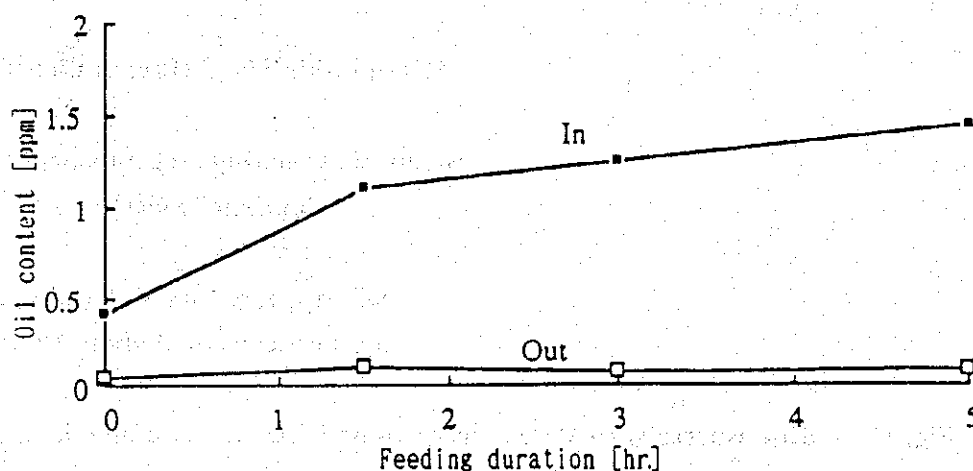
1) **Change in oil concentration (Fig. 13)**

Fig. 13   Oil Content Removal by Activated Carbon
(Note: Not corrected for the background concentration
for sea water (approx. 100 ppb))

When the filtrate having undergone flocculation and filtration via anthracite and sand media was further passed through an activated carbon column, the concentration of fluorescent material in the sample taken at the outlet of the activated carbon column was approximately 100 ppb as fuel oil A equivalent, which is about the same level as its background concentration for sea water.   Although it is not immediately possible to determine if the detected fluorescent material consisted of oil components, the experiment confirmed that activated carbon adsorption is capable of very high level oil content removal.

2) **Microscopic observation of the sample**
No oil droplets were identified during the microscopic observation of the sample (Fig. 14), and this seems to suggest that there are also very few dispersed oil components.
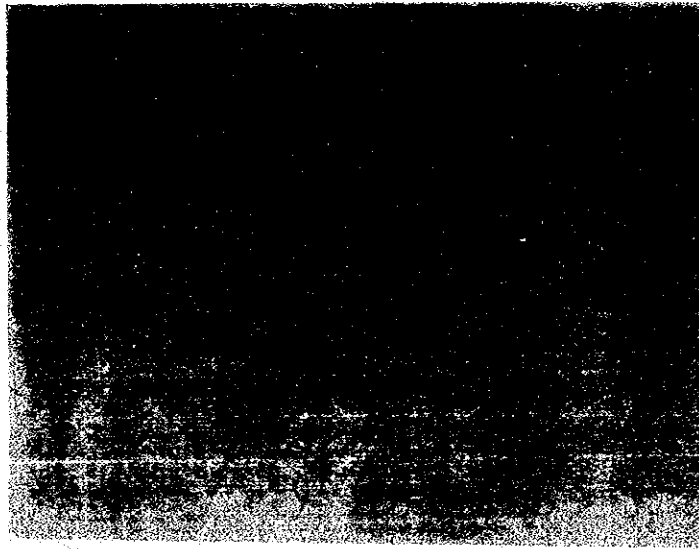
Fig. 14   Sample from the Activated Carbon Column Outlet (*100)

3.   Summary

(1)   The direct filtration method is capable of removing most of the oil components (dispersed components), but is not effective for those components which are considered to be soluble, when used with an ordinary filter medium such as anthracite or sand.   If a polymer filter medium is used, however, such components can also be removed.

(2)   The filter media combination for the pretreatment system will be determined taking the following into account:
* A guard column is needed to protect the RO membrane from being blocked by flocs in the event of the breakthrough of the filter medium.
* Direct filtration is capable of removing at least the dispersed oil components irrespective of the filter medium used.   If this is sufficient for the RO membrane, no further high level treatment is necessary.
* In cases where soluble oil components adversely affect the RO membrane, the use of polymer or activated carbon may be considered.
* The actual filter configuration will be determined, considering such factors as the water quality required by the RO membrane, regeneration performance and oil content removal capacity of various filter media, and associated costs.

4. Reference

Knap, A., "A Direct Comparaison of UV Fluorescence and GC/MS Data of Lipophilic Open–Ocean Seawater Extracts", Marine Chemistry, 26, 179–188, 1989

8.2.4 Regeneration Experiment for Oil Adsorption Tower

(8.2.4)

Contents

List of Figures

1. OBJECTIVE

The present study aims at evaluating the efficiency of oil adsorption tower consisting of two sand media filters in removing the oil by coagulation – filtration method from the artificially oil contaminated seawater. The study also includes establishment of the operating conditions for the removal of oil from oil–contaminated seawater using the coagulation – filtration method and also to achieve suitable regeneration method for the filter media.

2. EXPERIMENTAL METHOD

(1) Equipment

Artificial oil–contaminated seawater preparation unit as described in section 8.2.3. In this experiment, instead of the three small experimental column, four large adsorption tower were used in series. Each of the towers has 400mm diameter and 1500mm height. The first tower was kept empty and second one was filled with coarse sand (particle size 0.7 – 1.3 mm) and fine sand (particle size 0.6 – 0.8mm) at height of 1000mm (at 1:1 ratio). The third tower was filled up to 1000mm using fine sand (particle size 0.6 – 0.8mm) and last one was kept empty.

(2) Analytical Method

Oil content in the feed and filtrates were analyzed using Shimadzu FR–1501 spectrofluorophotometer as described in section 8.1.2.A.

(3) Experimental Procedure

Artificially–oil–contaminated seawater (about 10 pmm of oil) was passed through the four adsorption tower arranged in series after dosing coagulant $FeCl_3$(10 ppm) at a flow rate of 1.25 m^3/hr. Samples were collected from feed and the filtrates from the two sand filters for oil content analysis using spectrofluorphotometer. These analysis were conducted every 8 hours initially and prior to backwash was conducted using raw seawater at a flow rate of 6m^3/hr for 5 minutes followed by air scouring for 10 minutes followed by raw seawater wash for another 10 minutes.

3. RESULTS AND DISCUSSION

(1) Results

The results of oil content analysis using spectrofluorophotometer in the feed and filtrates from two sand filters for a period of about 390 hours are shown in Figure 1. Backwash of the filters were conducted when the differential pressure reaches $0.9 kgf/cm^2$. Backwash of the first filter was conducted at an average of every 26 hours.

(2) Discussion

It is evident from the Figure 1 that about 10 ppm of oil in the feed is reduced to about 1 ppm in the filtrates. This indicates the efficiency of oil adsorption tower in removing most of the oil from oil-contaminated seawater. This was the case with the small experimental columns (see section 8.2.3). It was also found that efficiency was unaffected even after a number of back-washings. This confirms that the present method of back washing procedure is sufficient for the sand filter regeneration.

4. CONCLUSION

Present study reveals that oil adsorption tower consisting of sand media filters are capable of removing most of the oil from the coagulated oil-contaminated seawater. Also the back washing procedure followed in this experiment is sufficient for the regeneration of sand filter media.

The present study reveals that oil adsorption tower consisting of sand media filters are capable of removing most of the oil from oil-contaminated seawater after its coagulation. Also the back washing procedure followed in this experiment is sufficient for the regeneration of sand filter media with backwash flow of $6 m^3/hr$(LV= 48 m/hr) for 5 minutes.
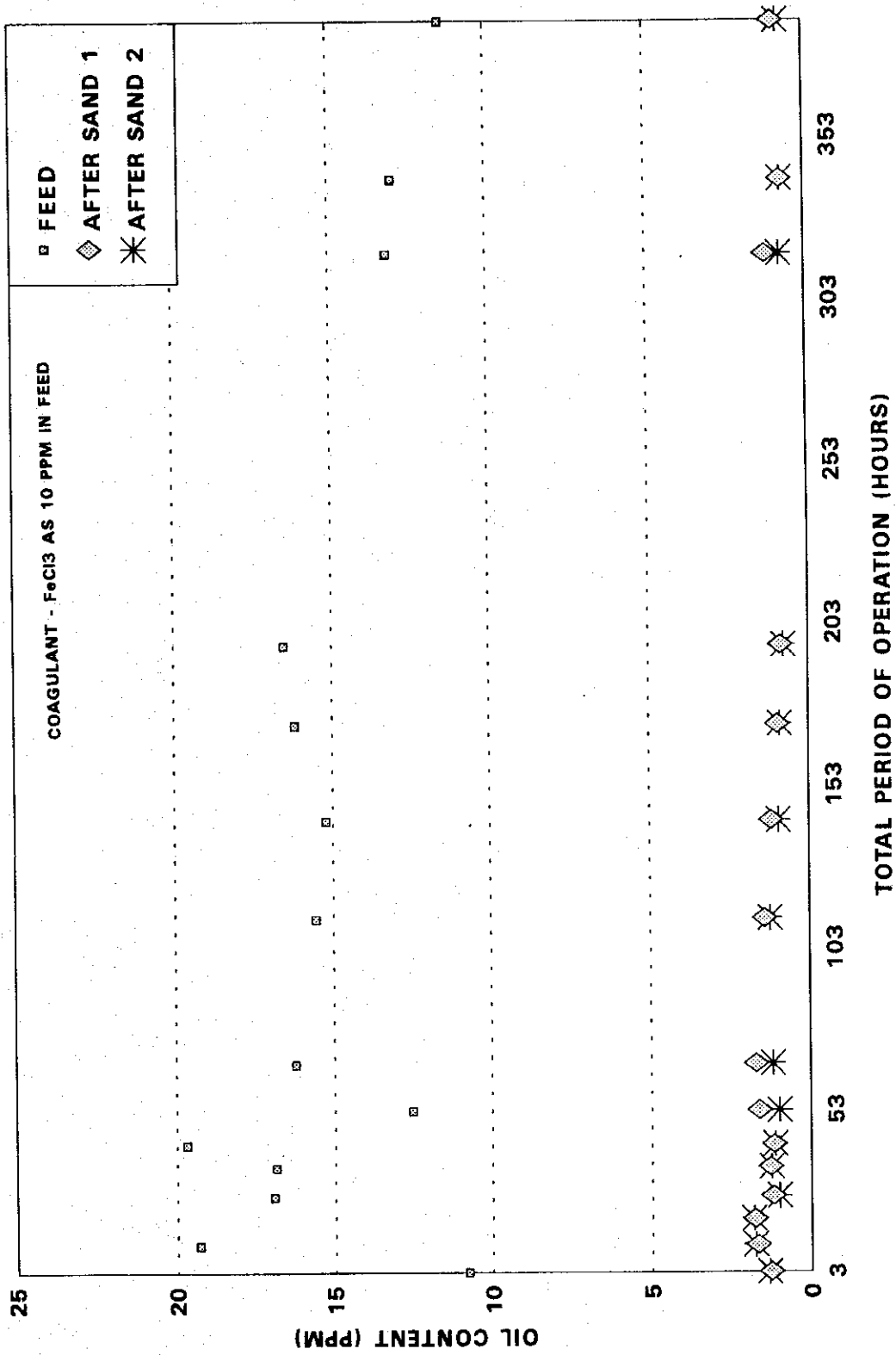
Fig. 1 Oil Removal by Coagulation – Filtration Method Using Adsorption Tower

8.3 Oil Tolerance Test with a Flat Membrane Tester

8.3.1　First Step Flat Membrane Test

8.3.1.A. Oil Tolerance Test with Flat Membrane after Immersing in Artificial Oil Contaminated Seawater

Contents

(8.3.1.A)

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List of Figures

1. Objectives of the Study

It is postulated that the performance of seawater RO (SWRO) membrane may deteriorate when feed seawater to plant is contaminated with oil/THM . The presence of such contaminants may lead to plant shutdown. The effect of those contaminants on plant performance , however, is not fully understood, and tends to be dependent on type of membrane and its tolerance to oil contamination, type of oil and its concentration, it's feed and the degree of pretreatment followed in removal of oil/THM from the feed. The main objective of this work is to establish the experimental procedure for determining the effect of oil/THM and their concentration on various commercial SWRO membranes.

2. Experimental Methods

2.1 Experimental Equipments

(1) Mini Module Tester-2

He performance of various membranes was evaluated using membrane tester RUW-5 made by Nitto Denko Corporation, Japan. The four test cells used in this test were: Nitto RO/UF test cell C 70–F made of stainless steel (SUS 316) and polyacetal resin having O–ring of size p–65 (Byton).

(2) Ultra sonic homogenizer –– Model. V 2519C –– Cho–Onpa Kogyo

(3) Front scatter method turbid–meter #Model CORONA UT–11

2.2 Materials

Pretreated seawater having SDI<3, pH =6.6 and conductivity = 60,800 μs/cm was used as the feed throughout the experiment. Chemical analysis of raw seawater is given in Table 1. Fuel oil type A with a carbon distribution range between C8 and C34 (in the Japanese Industrial Standard Corresponds to No.4 in ASTM) was used to contaminate the un-chlorinated seawater (Table 2, Fig. 1, Fig. 2, Fig.3). Four different types of commercially available flat sheet membranes were used: Toray 80S, Toray 80M, NITTO NTR 70 SWC and fluid system, TFCL–HP.

Table 1   Composition of Seawater

Temperature			26.5
pH			8.1
Conductivity		us/cm	62,800
Dissolved Oxygen	(O_2)	mg/l	6.6
Total Dissolved Solids	(TDS)	mg/l	43,800
Total Alkalinity	$(CaCO_3)$	mg/l	144
Carbon Dioxide	(CO_2)		2
Total Hardness	$(CaCO_3)$	mg/l	8,010
Calcium	(Ca^{++})	mg/l	508
Magnesium	(Mg^{++})	mg/l	1,618
Sodium	(Na^{+})	mg/l	13,440
Potassium	(K^{+})	mg/l	483
Strontium	(Sr^{++})	mg/l	17
Bicarbonate	(HCO_3^{-})	mg/l	176
Chlorine	(Cl^{-})	mg/l	24,090
Sulphate	(SO_4^{--})	mg/l	3,384
Bromide	(Br^{-})	mg/l	83
Fluoride	(F^{-})	mg/l	1

Table 2 Carbon Number and Boiling Points of Saturated Paraffin

| Numbers of Carbons	Composition %	Summation %	Boiling Point Degree C	Solubility mg/l
8	0.22	0.22	125.7	0.66
9	1.90	2.12	150.5	
10	3.48	5.60	174.0	
11	4.28	9.88	196.7	
12	4.88	14.76	216.3	
13	5.88	20.64	235.4	
14	8.19	28.83	253.7	
15	10.69	39.52	270.6	
16	10.66	50.18	287.1	
17	9.06	59.24	301.8	
18	8.42	67.66	316.1	
19	7.68	75.34	329.7	
20	6.14	81.48	343.2	
21	5.07	86.55	356.5	
22	4.07	90.62	368.6	
23	3.05	93.67	380.2	
24	2.42	96.09	391.3	
25	1.59	97.68	401.9	
26	1.09	98.77	412.2	
27	0.65	99.42	442.2	
28	0.31	99.73	431.6	
29	0.18	99.91	440.8	
30	0.08	99.99	449.7	
31	0.02	100.01	458.3	
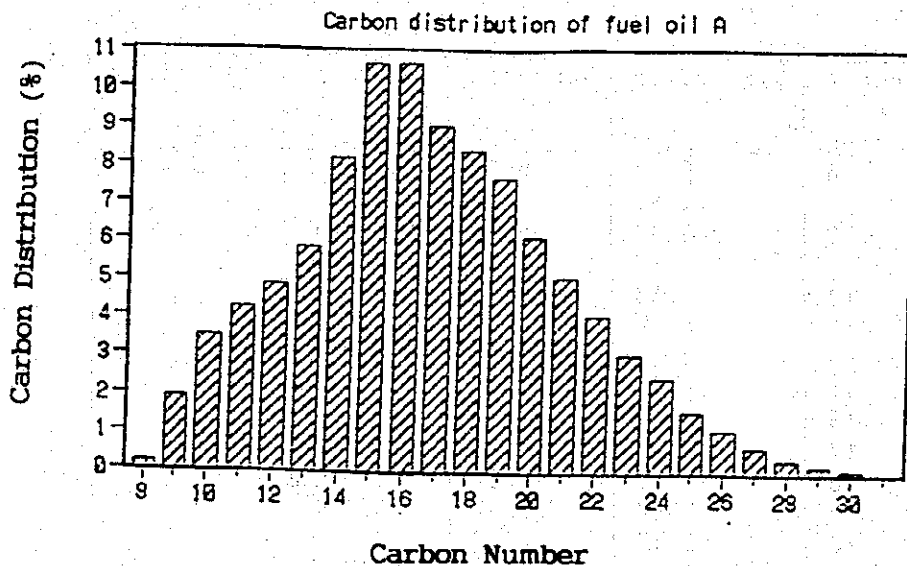
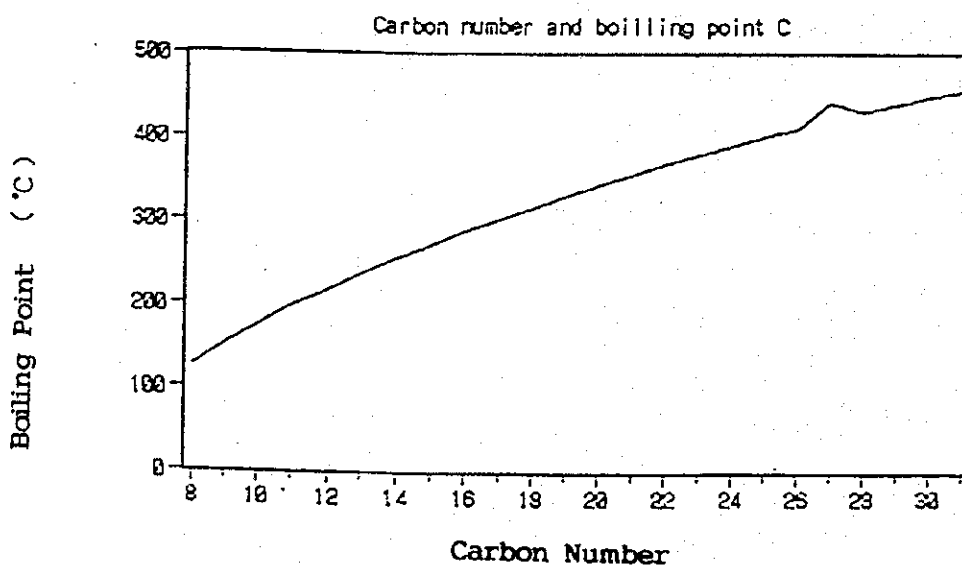Fig. 1   Carbon Distribution of the Fuel Oil "A"

Fig. 2   Carbon Number and Boiling Points of Saturated Paraffin

GC分析条件
Instrument   :Shimazu GC-14APF
Column   :Fused silica capillaaary column CBP-1
             50m x 0.20mm i.d. 0.25μm film thickness
Temperature   :Column 35°C(1.5min.)→310°C/min.
             Injection 280°C   Detector 310°C
Carrier gas   :Inlet press. 2.0 Kg/cm²
Split   :1/50
Detector   :FID Range 10²
             :Air 0.5Kg/cm² 400ml/min.
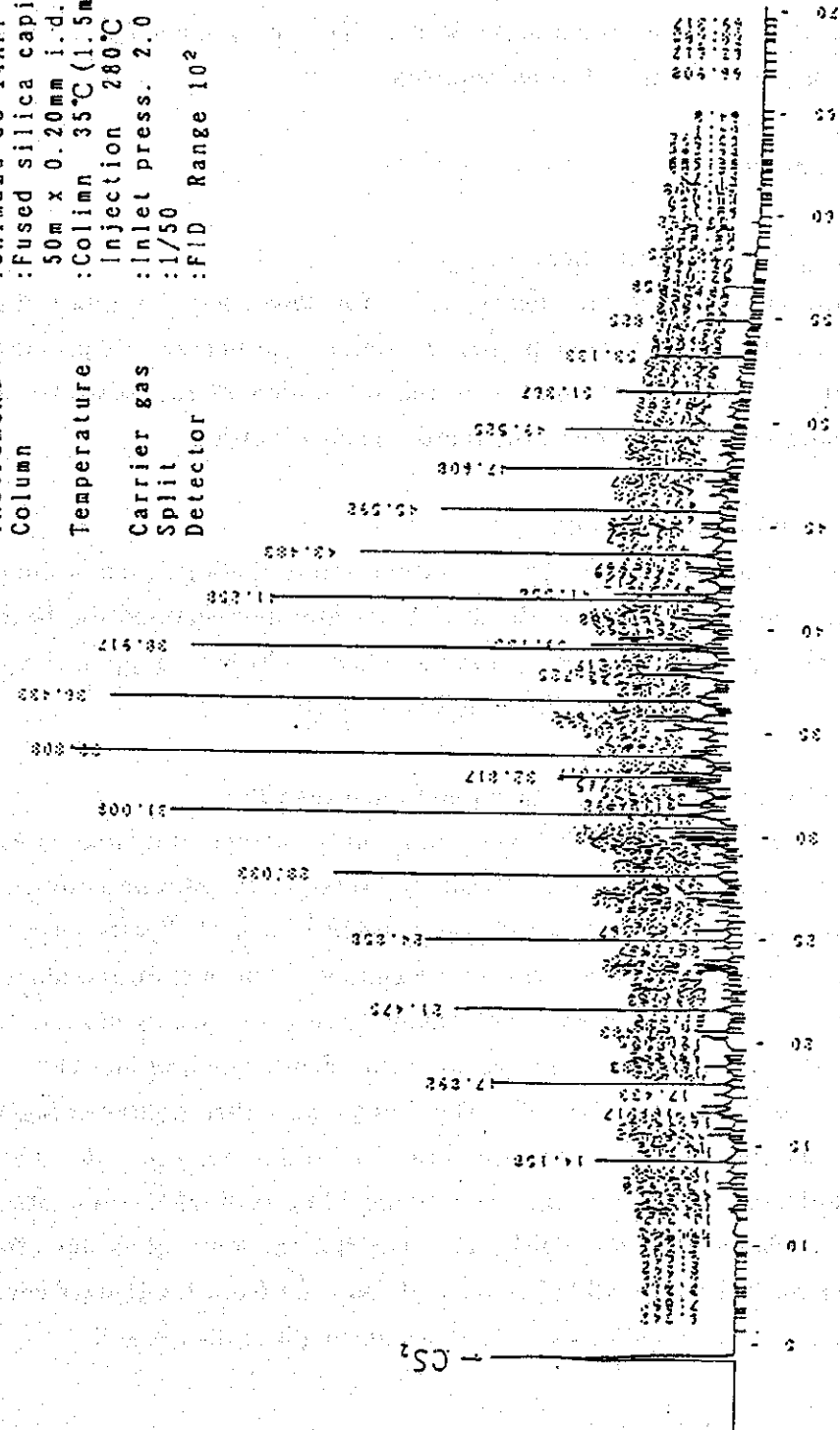   :H2   0.5Kg/cm² 40ml/min.

Fig. 3 Chromatogram of Fuel Oil "A"

2.3 Analytical method

Concentration determination of oil in seawater was done using Turbidity meter. In this experiment, the Turbidity meter was standardized as described in 2.4.(1) by taking raw seawater as blank. After the immersion of RO membranes in oil contaminated seawater, the concentration of oil was determined periodically. This was done to check the stability of oil concentration and to add more oil when required.

2.4 Experimental methods

(1) **Preparation of Contaminated Seawater**
The preparation of oil contaminated seawater was done using the standard solution of Fuel oil type A in distilled water prepared as described below. Required amount of this standard oil solution was added to known amount of raw seawater and mixed property using a stirrer to achieve the required concentration.

[Preparation of oil standard solution]
Approximately 1 gm of Fuel oil type A was injected to the inlet tube of the ultra sonic homogenizer containing 1 liter of distilled water and homogenized for 10 minutes, so as to get 1000 ppm oil in water. Three standard solutions (1 ppm, 5 ppm and 10 ppm) were prepared both in distilled and in seawater.

(2) **Immersion of RO membranes in oil contaminated seawater**
For the immersion of the flat sheet membranes in the oil contaminated seawater, three different methods were employed. In the first method, membrane samples, 75 mm in diameter were cut evenly and placed over a rubber sheet of slightly larger diameter, keeping the active side of the membrane exposed. The membrane along with the rubber sheet was then kept over a PVC flange having an opening of 65 mm diameter at the center. An O-ring was placed over the membrane and another PVC flange was placed over it carefully (Fig. 4). The flanges were then tightened together using nuts and bolts, thus only the active site of the membrane was exposed. These flanges were then immersed in a plastic tank containing 40 liters of oil contaminated seawater which was mechanically stirred (Fig. 2). The flanges were taken out after a fixed period, then washed with distilled water and removed from the flanges carefully. It was further rinsed with distilled water before placing it in the test cell.

Tightening the flanges along with membranes and o-ring could damage the membrane area in contact with the o-ring. To avoid this, another approach was used in which membranes and o-rings of larger diameters were used. The test of procedure was the same as described above. The membranes were cut carefully to the required size of 75 mm diameter after removing it from the flange.

The third method tried was to carefully cut membranes directly for the immersion without using PVC flange or rubber sheet. Here both the sides of the membranes were exposed to the oil contaminated seawater, 5 liters of which was kept in a plastic container and stirred using magnetic stirrer. After fixed period, membranes were carefully removed and washed with distilled water.

(3) Performance test of the immersed membrane with Mini-Module Tester(2)

The membranes to be tested were placed over the permeate passage material (permeate spacer cloth) on the bottom portion of the test cell C-70-F. An o-ring was placed over the membrane and the cell was tightened properly after placing the top portion of the cell. The four test cells containing 4 different types of membranes were then connected serially on the membrane tester RUW-5. The performance test was carried out using pretreated seawater feed at feed flow rate of 7 liter/min., pressure of 57 kgf/cm^2 and temperature 25$°$C. The permeate from each cell was collected separately over 30 minutes after 1 hr of operation. The volume and conductivity of the permeates were measured.

3. Results and Discussion

3.1 Results

The turbidity of oil in distilled and in seawater with time are listed in Table 3 and Table 4 and in Fig. 4 to Fig. 8. Oil distribution data in distilled water in given in Fig. 6 and the micro graphs in Fig 12 and Fig.4. The performances of the four different types of membranes were evaluated as freshly cut samples, immersion in pure seawater for 24 hours and immersion in oil contaminated (1 ppm and 10 ppm oil) seawater for 10 and 24 hours. The flux (m^3/m^{2}d) and salt rejection (percentage %) of each membrane were calculated from their respective volume and conductivity of the permeate collected in 30 minutes. These values are listed in the Table 5 and Fig.14 for the four membrane systems at different oil concentration.
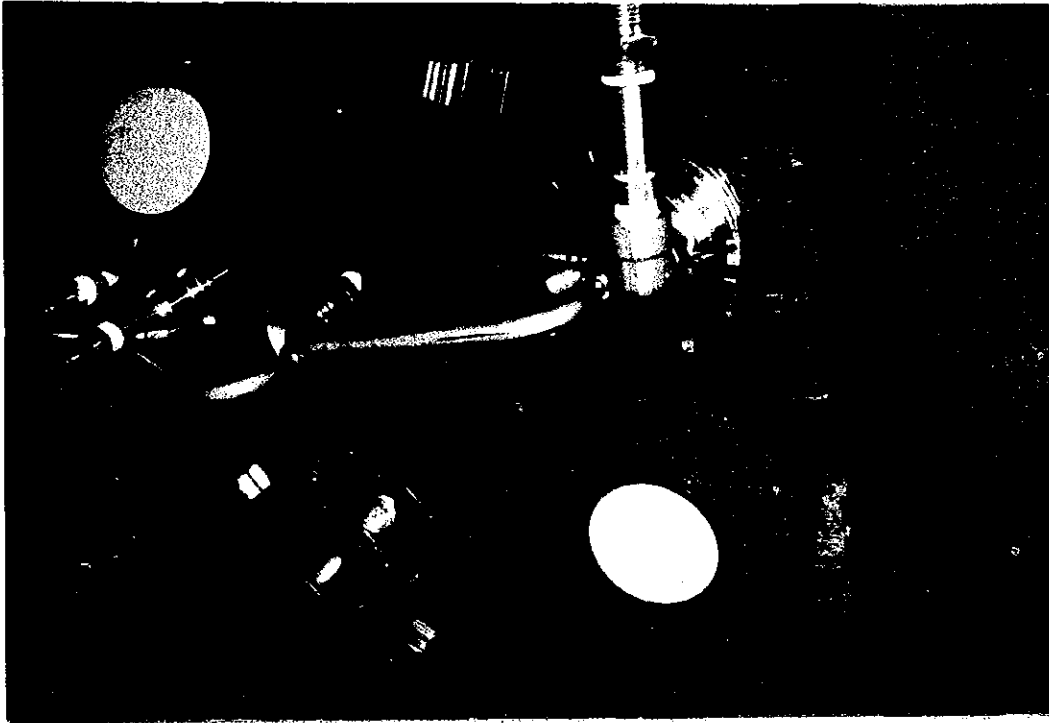
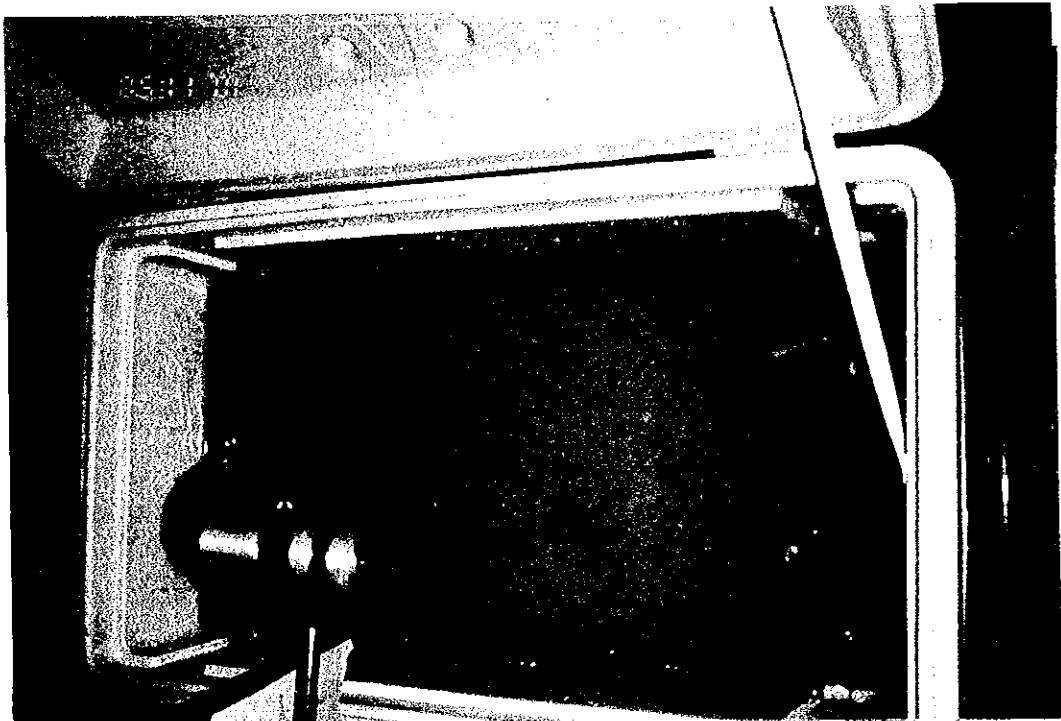Fig. 4　Flat Sheet Membrane and Flanges to Expose Active Sides
of the Membrane

Fig. 5　Oil Emulsion Seawater Tank with a Stirrer Immersing the Flat
Sheet Membranes

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Table 3 Turbidity Changes of Oil Emulsion in Distilled Water

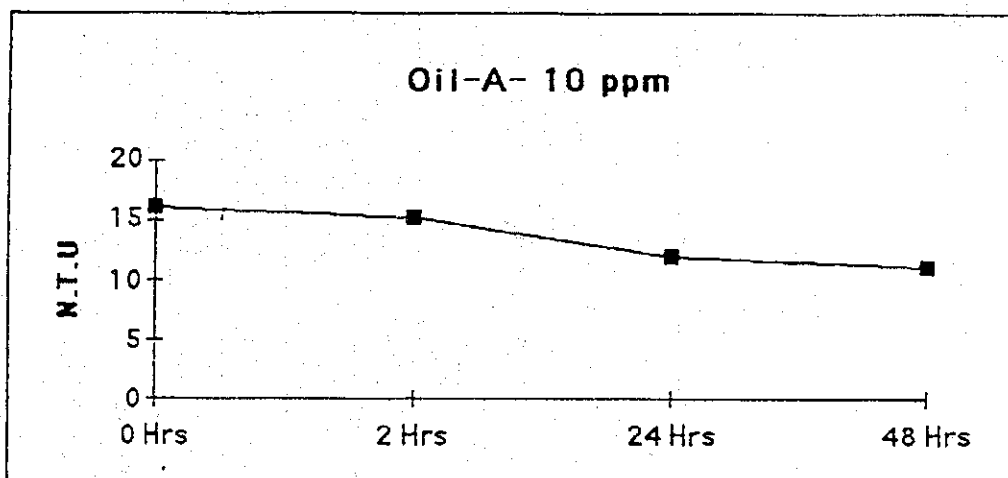| Sample/Time	0 Hrs	2 Hrs	24 Hrs	48 Hrs
DIS–Water	0	0	0	0
Oil (A) 1ppm	0.68	0.7	0.4	0.4
Oil (A) 5ppm	4.62	4	4	9
Oil (A) 10 ppm	16	15.2	12	11

Fig. 6 Turbidity Change of Oil Emulsion in Distilled Water

Table 4 Turbidity Changes of Oil Emulsion in Seawater

Sample/Time	0 Hrs	5 Hrs	24 Hrs
SW	0	0	0
Oil (A) 1ppm	0.55	0.1	0.2
Oil (A) 5ppm	3.4	2.7	2.2
Oil (A) 10 ppm	14.4	15	14

Table 5 Flux(m³/m²/d) and Salt Rejection(%) of the Membranes

| | | Fresh | | Blank | | | | 1 ppm oil | | | 10 ppm oil | | |
| | | | | S.F. | | L.F. | W.F. | 10 hrs | 24 hrs | | 10 hrs | 24 hrs | |
		Trial 1	Trial 2	Trial 1	Trial 2			W.F.	L.F.	W.F.	S.F.	S.F.	L.F.
Toray 80S	Flux	0.72	1.14	0.90	0.99	1.16	1.43	1.16	1.37	1.29	1.00	1.00	1.04
	S.R.	99.6	98.4	98.3	97.5	99.1	96.3	97.1	97.2	97.5	98.3	98.6	98.3
Toray 80M	Flux	0.60	0.80	0.77	0.69	0.95	1.04	0.90	1.00	0.87	0.66	0.74	0.73
	S.R.	99.7	98.2	97.4	95.7	75.2	89.6	96.9	97.5	97.6	98.0	96.9	97.0
Nitto NTR 70SWC	Flux	0.68	0.41	0.50	0.50	0.61	0.53	0.50	0.66	0.50	0.54	0.69	0.57
	S.R.	98.8	97.6	97.4	97.4	98.5	97.2	97.7	97.2	97.4	98.1	95.8	98.1
Fluid System TFCL-IIP	Flux	1.25	1.31	1.23	1.23	1.28	1.40	1.40	1.40	(-)	1.24	1.31	1.10
	S.R.	99.1	98.3	98.9	99.0	99.0	97.0	97.7	98.9	(-)	99.1	91.3	98.8

S.R.= Salt Rejection (%), S.F. = Small Flange
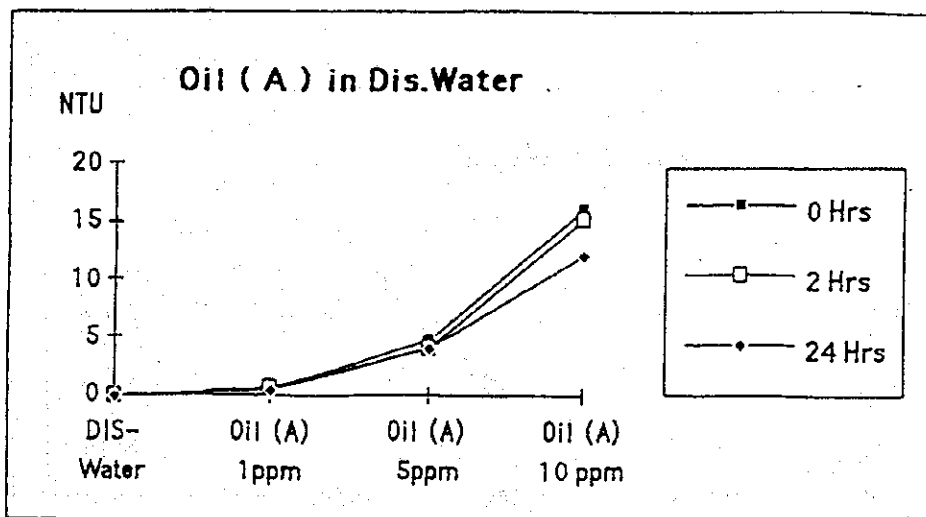
L.F.= Large Flange W.F. = Without Flange

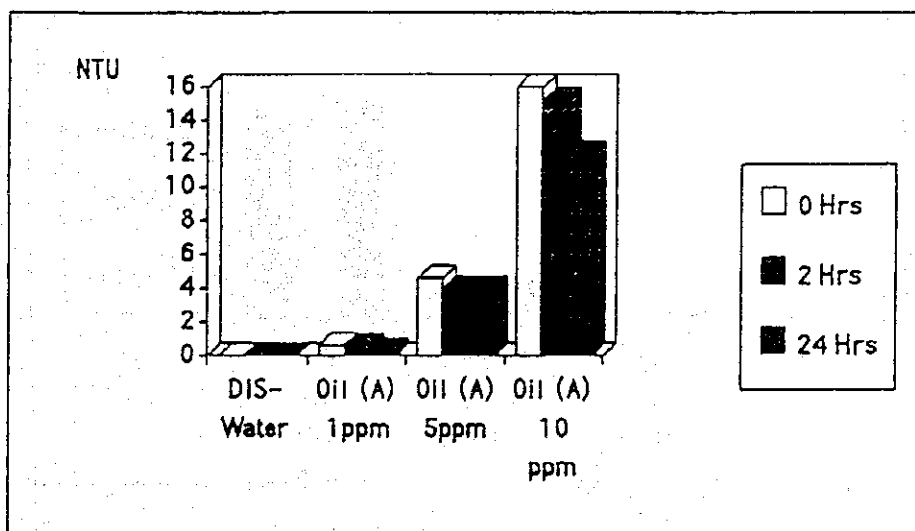Fig. 7 Turbidity Change of Oil Emulsion in Distilled Water

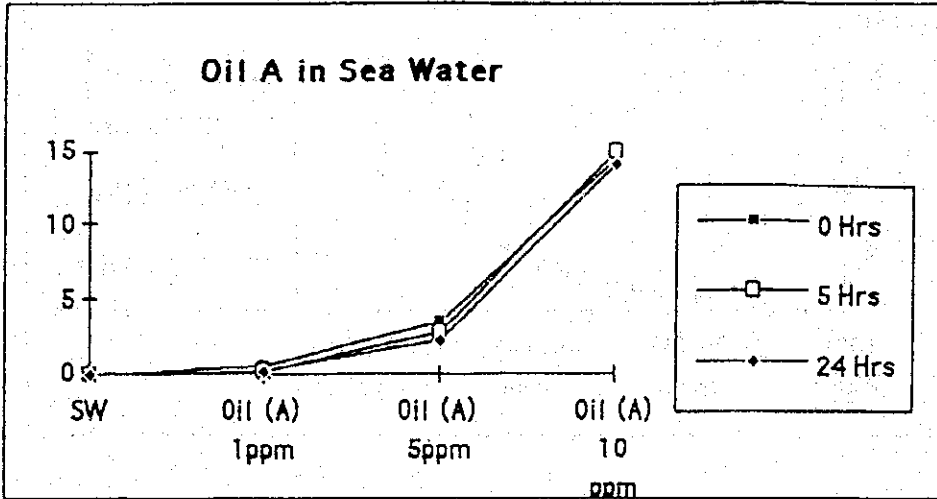Fig. 8 Turbidity Change of Oil Emulsion in Distilled Water

Oil A in Sea Water
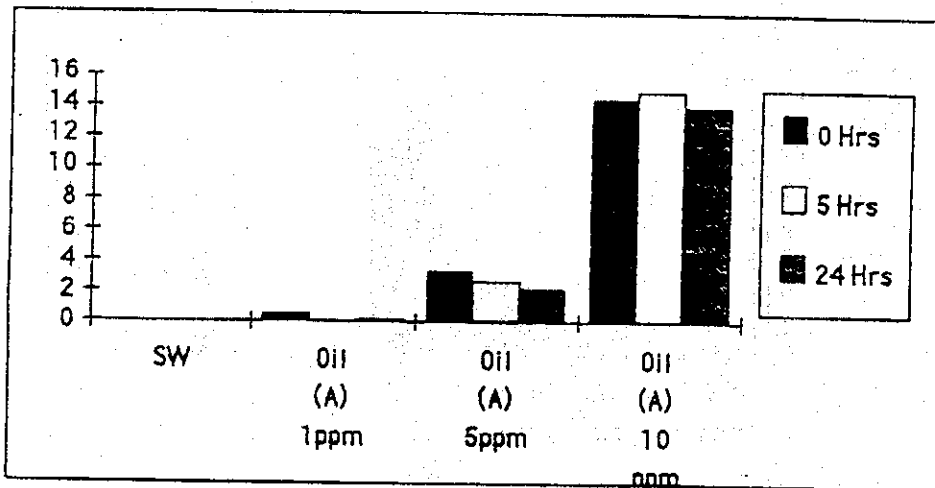

Fig. 9   Turbidity Change of Oil Emulsion in Seawater

Fig.10   Turbidity Change of Oil Emulsion in Seawater

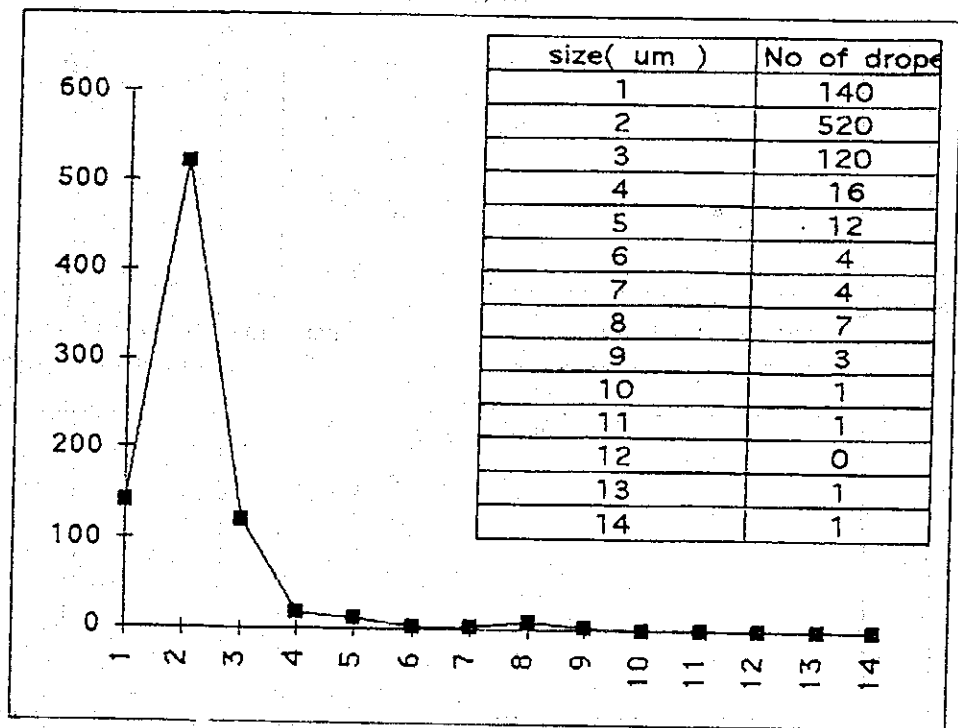| size(um)	No of drope
1	140
2	520
3	120
4	16
5	12
6	4
7	4
8	7
9	3
10	1
11	1
12	0
13	1
14	1

Fig.11 Particle Size Distribution of Oil Emulsion in Distilled Water

Fig.12
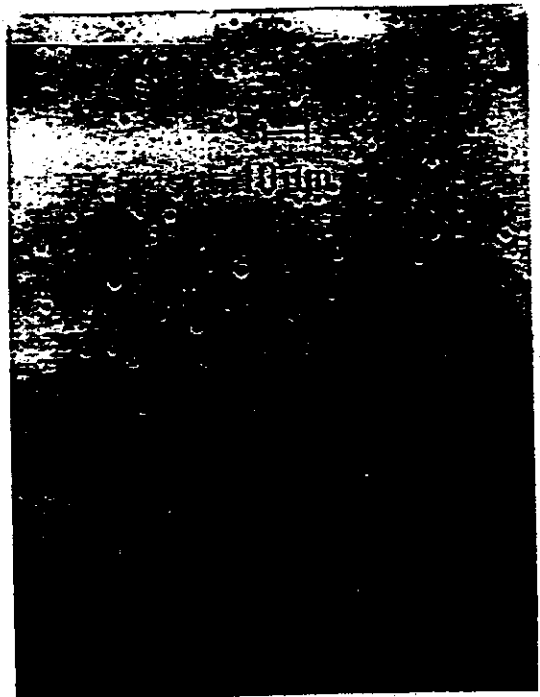
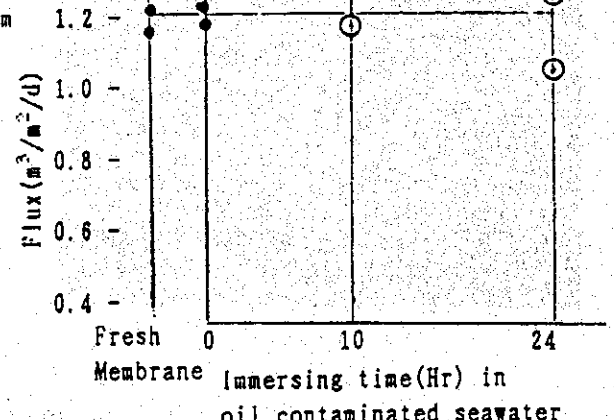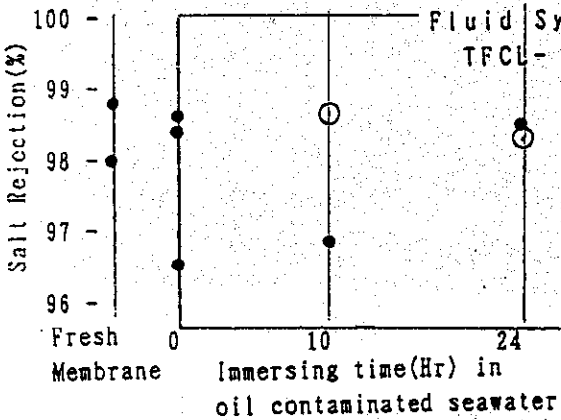Fig.13

Oil Particles in Oil Emulsion in Distilled Water
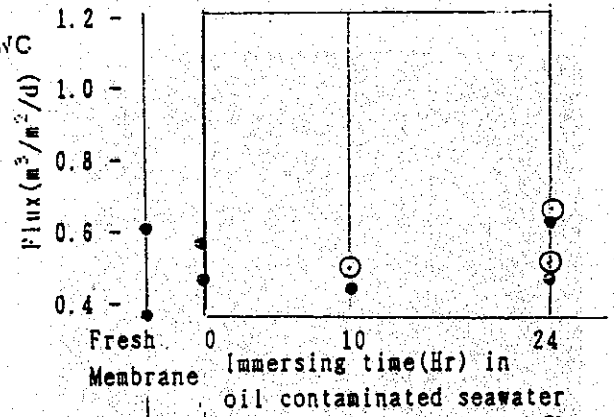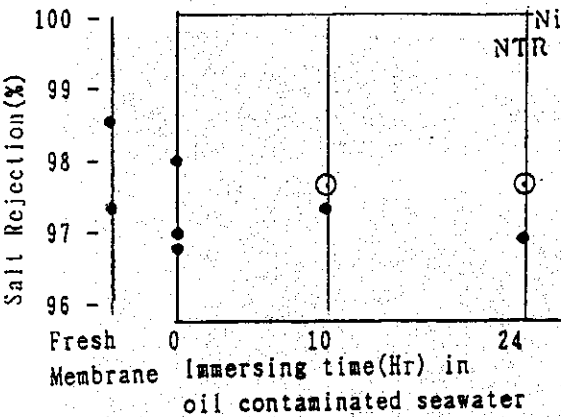
Fig.14

Fig.15

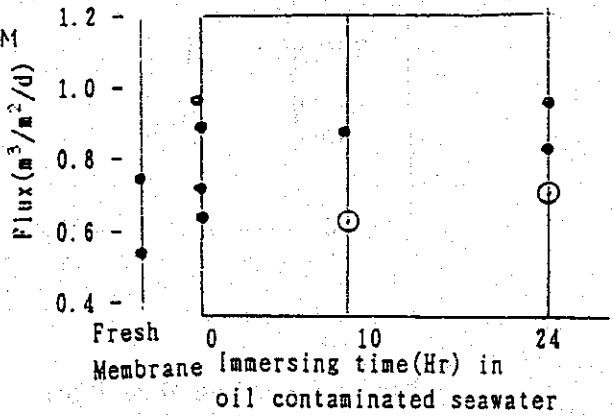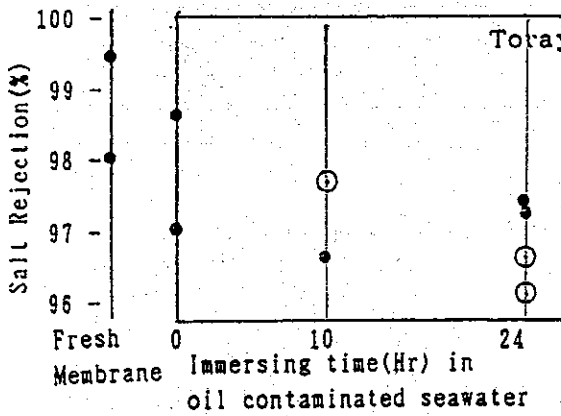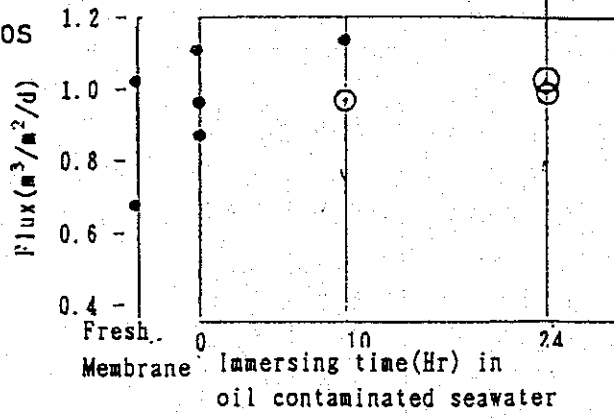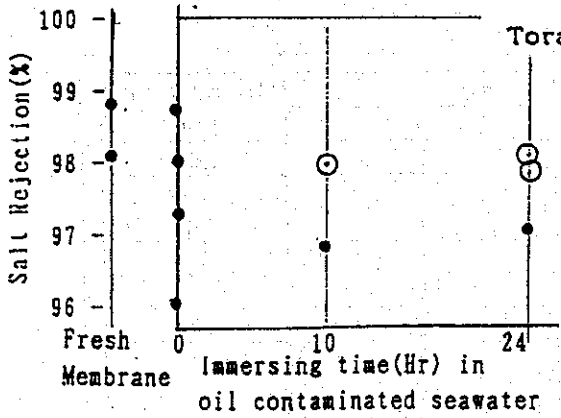**Effect of Oil Contamination on Rejection and Salt Rejection of Membranes**

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3.2   Discussion

The results of turbidity measurements show that the turbidity slightly decreases with time. This was observed both for oil in distilled water and in seawater. This could be due to the evaporation of the oil.

It is quite clear from the results given in Table 1 and Fig. 14 that for a given membrane there is no significant difference in membrane flux or salt rejection, regardless of the procedure used in contaminating the membrane.   Also, the exposure of membranes to the oil contaminated seawater containing 1 ppm and 10 ppm oil, does not reveal any performance deterioration as the flux and salt rejection are found to be within the experimental error. These finding were found to be true for all membranes.   The small variation observed could be attributed to experimental artistic.   From the results, however, it is not possible to derive a conclusive conclusion on the effect of the exposure of membranes to oil contaminated seawater on their performance.   The experiments have to be modified by using oil contaminated seawater as a continuous feed to the membrane.

4.   Conclusion

The present study involves the performance evaluation (flux and salt rejection) of four different types of membranes and the effect of their exposure to oil contaminated seawater on their performance.   The results did not give any conclusive evidence of the effect of oil as the values obtained were not significantly different.   To detect the effect of oil on membranes, oil contaminated seawater need to be fed to the membrane continuously.

5.   Summary

The results of our experimental studies of the oil tolerance of RO membranes show that we now need to use continuous water flow experimental methods to obtain results from stabilized performance tests.

On this occasion we aimed at accelerated tests by trying immersing RO flat membranes in oil–bearing seawater but, although we could see that there was a drop in the performance of RO membranes that has been immersed for 24 hours in seawater containing 10 ppm of oil, there were wide variations.

A possible reason for this is that the absolute quantity of oil that comes in contact per unit area of membrane is so small that there is little permeation to the interior of the membrane element.

Consequently, we conclude that we must pre-treat seawater with different levels of oil fouling and conduct membrane permeation tests by passing the water through the module continuously.

8.3.1.B. Oil Tolerance Test of Flat Membrance by Continuous Recirculation System

Contents

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1. Objectives

In the previous research activity, oil tolerance test was performed by measuring performance of flat sheet membrane before and after immersing them into the oil contaminated seawater. Fuel oil tyoe A of Japanese standard was used to prepare an artificial oil contaminated seawater. Both TOC meter and Turbidity meter were used to analyze oil in the contaminated seawater. However, the results show that the data obtained was not sufficient. It was recommended that another experimental method with continuous water flow is needed to know the effect of oil in seawater membrane performance. Analytical methods used in this experiments such as TOC and turbidity meter did not give accurate oil concentration. A higher sensitivity analytical method is required to obtain more accurate oil concentration data, especially for the analysis of low oil concentration in seawater.

The objectives of this experiment are as follows:

A. To analyze the effect of oil contaminated seawater on the performance of various membranes and investigate experimental method by using artificially oil contaminated seawater as continuous feed water to Mini–Module tester(2)

B. To determine the type of oil to prepare artificial oil contaminated seawater

C. To analyze oil contaminated seawater using newly installed low concentration oil measuring instrument, i.e. Fluorophotometric meter and confirm that it is useful to perform practical anlysis in experimental work.

2. Experimental Methods

2.1 Preparation of artificial oil contaminated seawater

(1) Preparation of oil standard solution
Approximately 0.1 ml of Diesel oil No.2 was injected into the inlet tube of the ultra sonic homogenizer containing 1 liter of distilled water and homogenized for 10 minutes, so as to get 100 ppm oil in water emulsion.

(2) Preparation of contaminated seawater
Oil contaminated seawater was prepared adding known amount of oil standard

solution in the feed tank of the Mini-Module tester(2) to achieve the required oil concentration and mixing well by recirculating using high pressure pump of Mini-Module tester to prevent segregation of the oil emulsion.

2.2 Experimental equipment and materials

(1) Mini-Module tester(2)

Flat sheet membrane tester RUW-5 made by NITTO DENKO Corporation, Japan. The test cells used in the test were NITTO RO/UF test cells.

(2) Analytical method for oil in seawater

Fluorophotometric oil content measurement meter
- Spectrofluorophotometer
- Fluorometric measurement cell
- Beaker (100 ml)
- Measuring flask (50ml)
- Isooctane (Fluorometric analysis grade)

(3) Oil used in this experiment

In the previous research term Fuel oil type A of Japanese Industrial Standard was used as the oil to prepare artificial oil contaminated seawater, However this kind of oil could not be obtained in Saudi Arabia. After some investigation and analysis of Fuel oil type A and oils available in Saudi Arabia, it was found that carbon distributions of Diesel oil No.2-D of ASTM and Fuel oil type A of Japanese standard which was used in the previous research is approximately same. Consequently, Diesel oil No.2-D is selected as a suitable oil for the preparation of artificial oil contaminated seawater to perform RO-2 experiment.

(4) Analysis of Diesel oil No.2-D

Carbon distribution of Diesel oil No.2-D and Japanese standard Fuel oil type A was analyzed using GC-mass analyzer. This method depends on taking summation of all peak areas of carbon molecules and impurities molecules, and dividing each large peaks(carbon molecules) by this summation to obtain concentration fraction and converted as percentage. The cumulative summation of concentration does not add to one hundred percent. Therefore, the relative concentration of each carbon in the Diesel oil No.2-D and Japanese standard oil type A was calculated by the following

2

equation:

Conc. of any carbon =[Peak are of carbon/Σ of all peaks] x 100

$\qquad$ x [100/(Σ (peak area of carbon/Σ of all

$\qquad$ peaks) x 100)]

The result shows carbon concentration of C10 to C18 fraction in Diesel oil No.2–D is slightly higher than that Fuel oil type A.

C18 – C26 concentration in Fuel oil type A is slightly higher than that in Diesel oil No.2–D.

The results of analysis of Diesel oil No.2–D and Fuel oil type A by GC–mass are shown in Table 1, Fig. 1 and Fig. 2

The general properties of this two oils are almost similar as shown in Table 2.

Table 1   Carbon Distribution of Diesel Oil No.2-D and Japanese Standard Fuel Oil "A"

| No. of Carbons	Concentration %		Boiling Point (C)
	Fuel " A "	Light Diesel # 2	
C10	0.44	2.46	174
C11	0.63	4.18	196.7
C12	1.42	5.13	216.3
C13	3.09	6.46	235.4
C14	5.27	7.67	253.7
C15	7.22	9.2	270.6
C16	8.4	9.76	287.1
C17	8.34	11.01	301.8
C18	10.1	11.18	316.1
C19	10.91	10.9	329.7
C20	10.88	8.9	343.2
C21	9.88	6.84	356.5
C22	8.49	4.42	368.6
C23	6.07	1.9	380.2
C24	4.38	-	391.3
C25	1.34	-	401.9
C26	3.13	-	412.2

*Concenration was estimated from GC-mass peak area
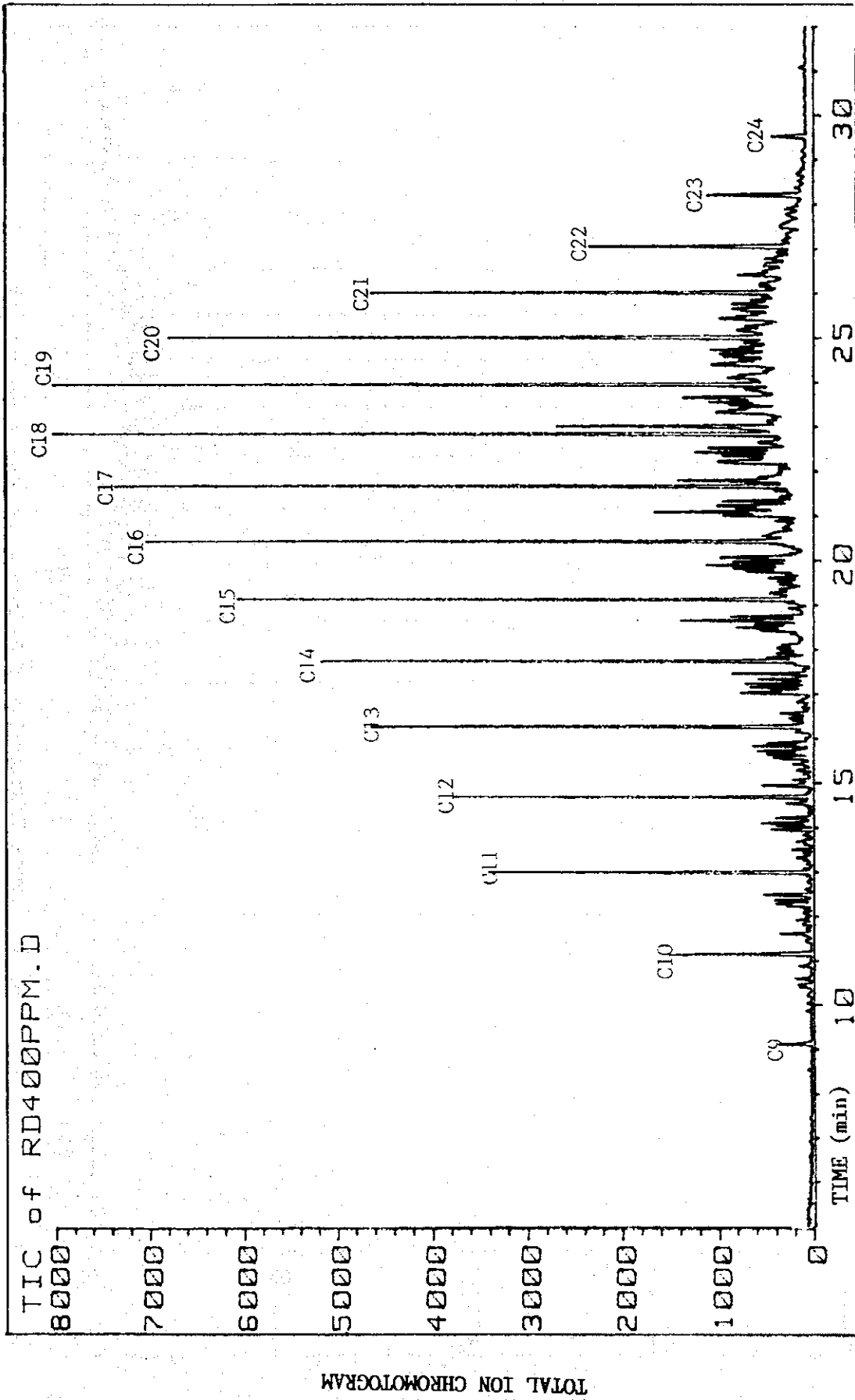
Fig. 1 Carbon Distribution of Diesel Oil No.2-D
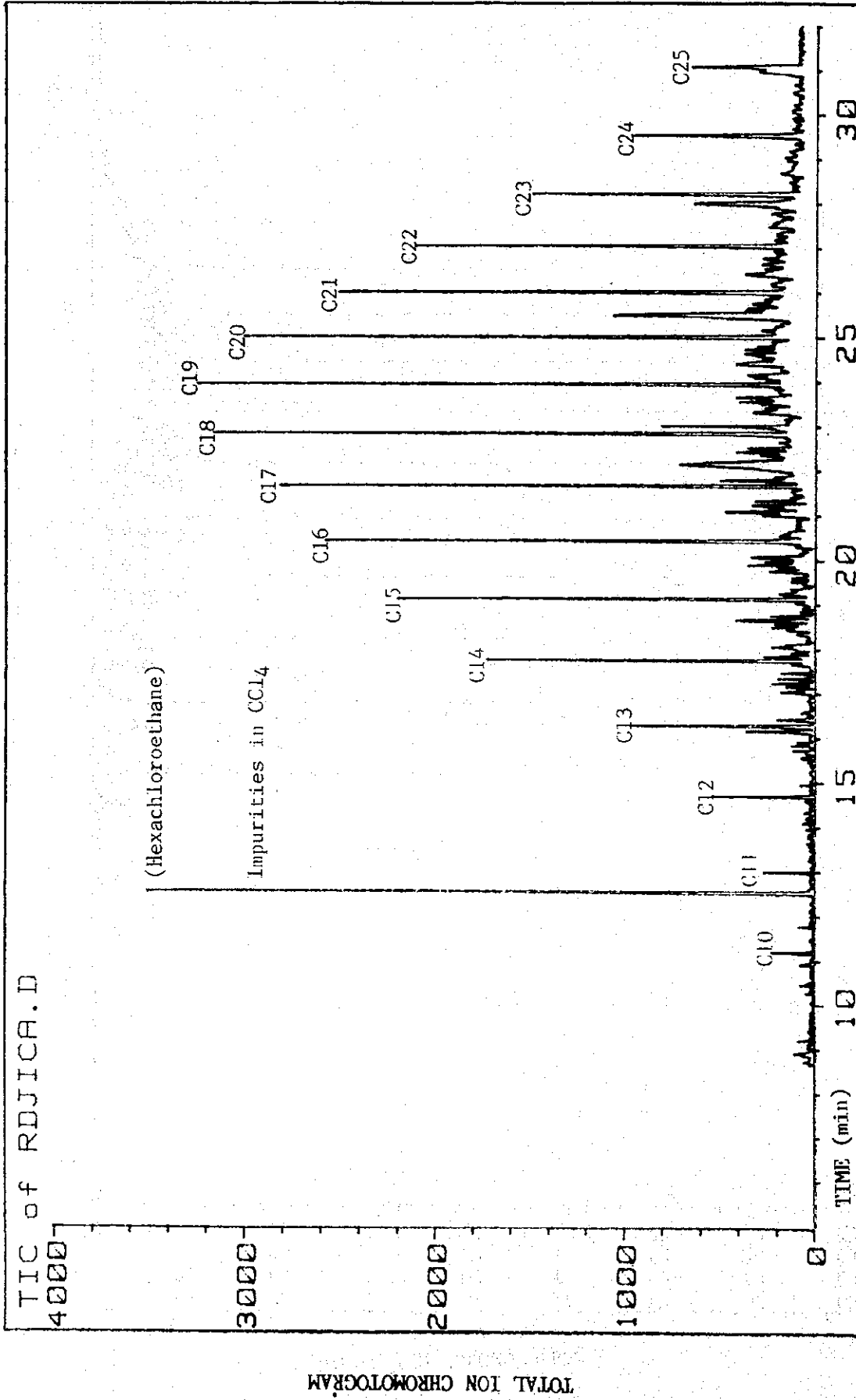
Fig. 2   Crbon Distribution of Japanese Standard Fuel Oil "A"

Table 2   General Properties of Diesel oil No.2–D and
            Fuel oil type A

	Diesel Oil No.2–D	Fuel Oil Type A
Flash Point,Degree C	52	64 – 107
Distillation Temp.,Degree C	282 – 338	
Kinematic viscosity	1.9 – 4.1	1.7 – 4.3
	at 40 C	at 50 C

ASTM Standard for Diesel oil No.2 is shown in Attached Material–1 (ASTM D 975–89a Standard Specification for Diesel Fuel Oils)

2.3   Experimental

(1)   Stability of oil contaminated seawater
      Oil concentration change of the recirculating oil contaminated seawater was measured as shown in Fig. 3.

(2)   Continuous recirculation operation of flat sheet membrane tester using artificial oil contaminated seawater.

3.   Results and Discussion

3.1   Experimental Results

Initial concentration of oil contaminated seawater prepared using ultra sonic homogenizer is not stable and changes from initial 3.2 ppm to 0.8 ppm during 24 hours as shown in Fig. 1.

3.2   Discussion

The cause of oil concentration decrease could be either collapsing of emulsified oil particles or evaporation of low boiling point hydrocarbons.   Oil concentration analysis of the feed water filtrate using 0.2 micron Micro–Filter will be able to determine the cause of oil concentration decrease.

Stability test of oil in sea water

Time (Hrs)	Oil Conc. (ppm)
0	3.2
4	1.7
24	0.8
28	0.7
48	0.65

Note : all samples taken from deep of the tank after mixing
* every sample done tow times and avearege is taken
   Temp=20-25 °C
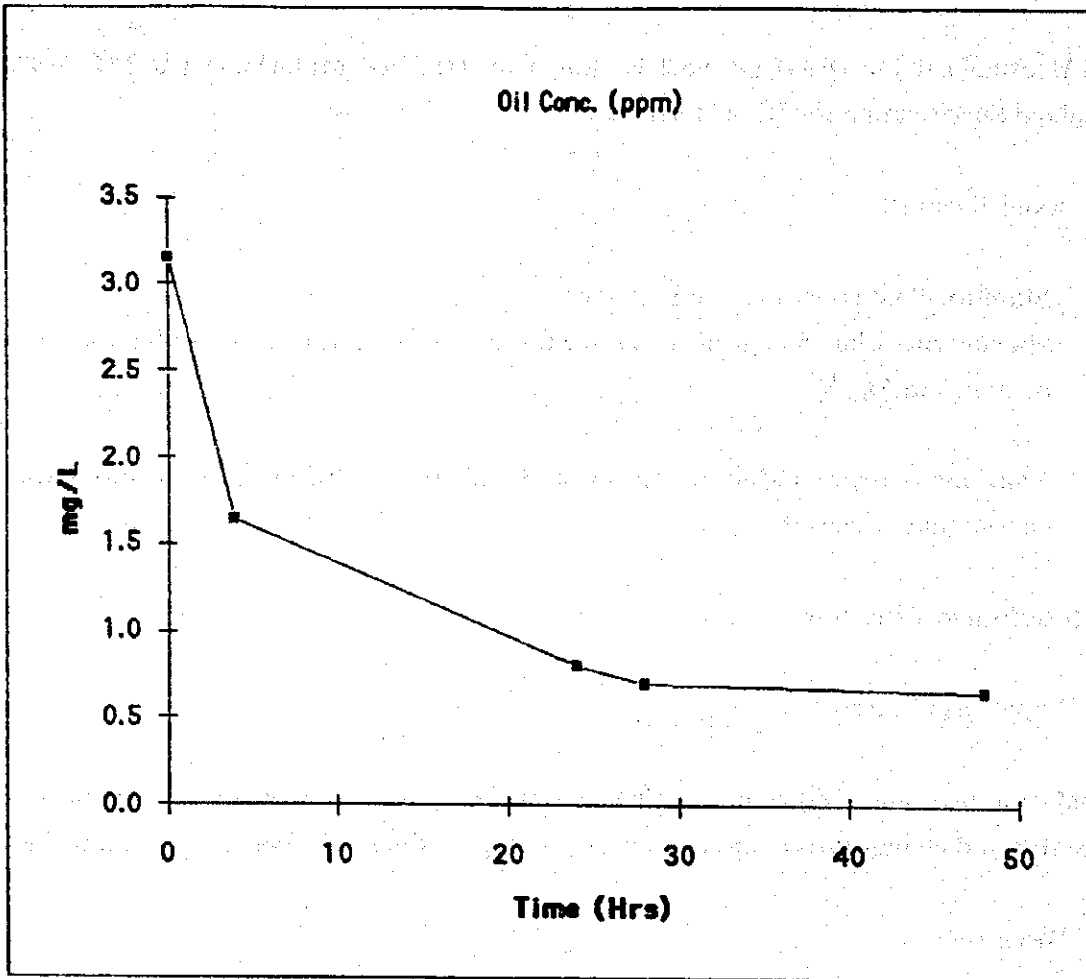
Oil Conc. (ppm)

Fig. 3   Oil Concentration Change of the Recirculating
           Artificial Oil Contaminated Seawater

(8.3.1.B)

However, this continuous recirculation oil torelance test can be applied as a simple oil torelance testing method to be performed as a preparatory experiment of the perfect continuous operation.

4. Conclusion

(1) Continuous feed recirculation to that sheet membranes can be utilized as a preparation step for the more accurate continuous operation of RO mini modules fed oil contaminated feed.

(2) Diesel oil No.2-D is a suitable oil for the preparation of artificial oil contaminated seawater s feed to RO-2 membranes.

(3) Oil torelance test can be performed by recirculating oil contaminated seawater to Mini-Module tester

5. Recommendation

Filtrate of feed water filtered by 0.2 micron Micro Filter shall be analyzed during recirculation continuous oil torelance test.

8.3.2　Experiment with Combined Pretreatment Equipment and RO Membrane

(8.3.2)

Contents

(8.3.2)

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1. OBJECTIVE

The present study aims at evaluating the effect of soluble oil present in the pretreated oil–contaminated seawater on various flat sheet RO membranes. In this experiment performance (flux and salt rejection) of three different types of flat sheet membranes obtained from different manufacturers were monitored for a period of time with the pretreated seawater feed supplied from the oil removal unit.

2. EXPERIMENTAL METHOD

(1) Equipment
Mini module tester (2) – Flat sheet membrane tester RUW–5 made by NITTO DENKO Corporation, Japan was used to evaluate the performance (flux and salt rejection) of three different types of flat sheet membranes. The test cells used in the tester were NITTO RO/UF test cell.

(2) Materials
The flat sheet membranes used in this experiment are Toray 80M, Toray 80S and Nitto NTR 70SWC.

(3) Experimental Procedure
The performance (flux and salt rejection) of the flat sheet membranes were determined using pretreated oil–contained seawater feed. The feed flow rate was 7 liter/min. and at pressure of 56 Kg/cm^2. The oil content in the feed was about 0.85 ppm as determined using spectrofluorophotometer.

3. RESULTS AND DISCUSSION

(1) Results
The results of performance evaluation (permeate flow and conductivity) of three different membranes for a period of 220 hours are shown in Figure 1. Permeate flow for Toray 80M and 80S with temperature corrections are shown in Figure 2.

(2) Discussion
It can be observed from the Figure 1 that the permeate conductivity of the all the three membranes were unaffected during the entire operation period. However, the

Figure 1 shows that permeate flow slightly decreases with time for all the three different membranes. This decrease can be attributed to the decrease in feed temperature with time. This has been confirmed by applying temperature corrections to permeate flow of Toray 80M and Toray 80S membranes (see Figure 2). From these results it can be concluded that the presence of slight amount of the dissolved oil in the feed did not affect the performance of all the three flat sheet membranes.

4. CONCLUSION

The present study reveals that all the three different types of flat sheet membranes viz, Toray 80M, Toray 80S and Nitto NTR 70DSWC are unaffected by the presence of trace amount of oil in the oil contaminated seawater feed which is supplied to the membranes by the oil removal pretreatment unit.

(OPERATION CONDITIONS: PRESSURE=56 kg/cm2, BRINE FLOW 7 L/M, OIL CONTENT = .850 PPM)
(MEMBRANES: TORAY 80S, TORAY 80M & NITTO DENKO NTR 70 SWC)

FLOW AT OPERATING TEMPERETURE

T 80 M PERMEATE FLOW AT 25 °C

FLOW AT OPERATING TEMPERETURE

T 80 S PERMEATE FLOW AT 25°C

-□-T80s —┼—T80M ▼T80S-25°C ✫T80M-25°C

PERMEATE FLOW CC/30 MIN

DURATION TIME HOURS

Fig. 1 Oil Tolerance Test for Flat SWRO Membrane vs Time

PERMEATE FLOW CC/30 MIN

DURATION TIME HOURS

DURATION TIME HOURS
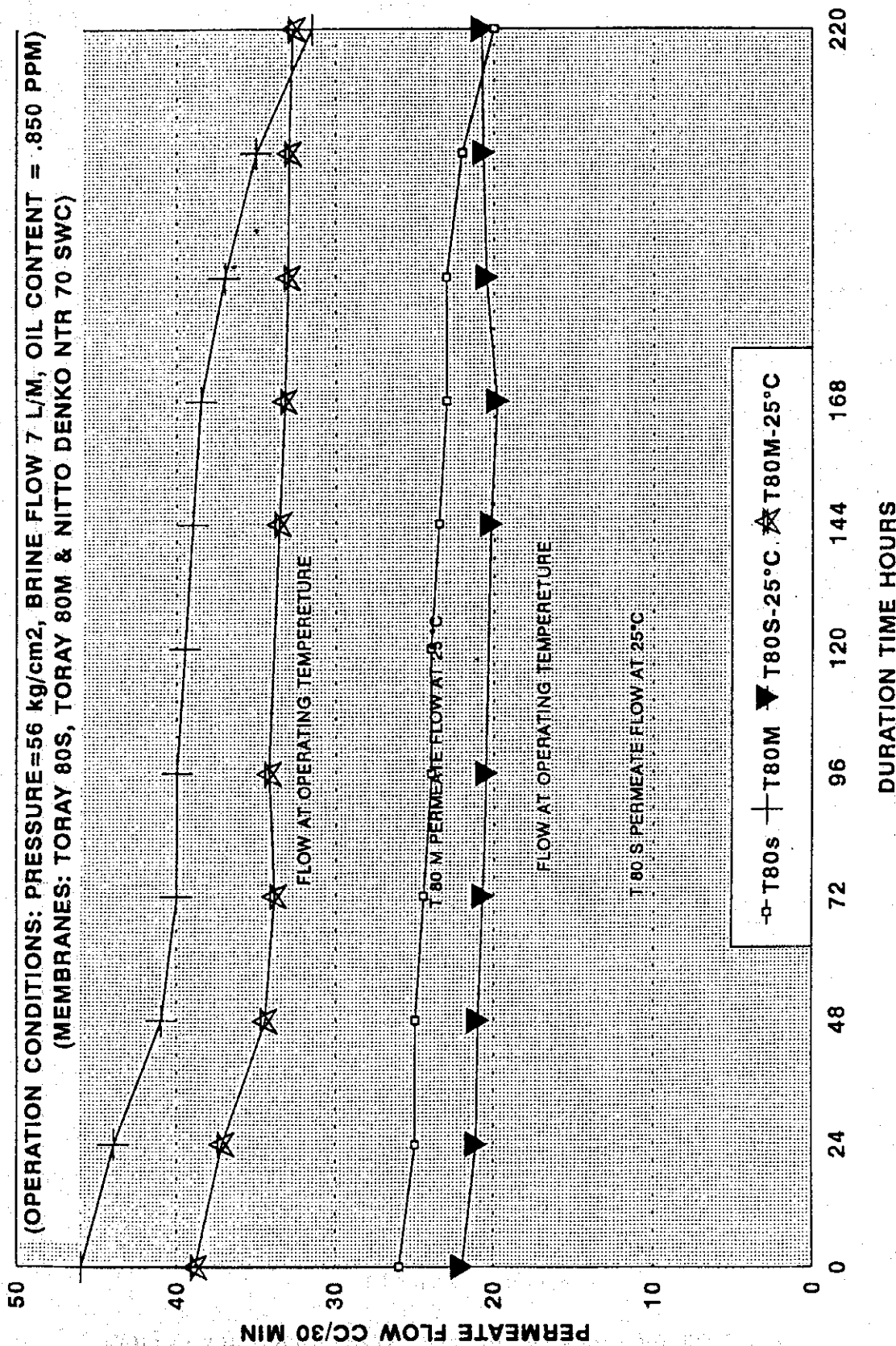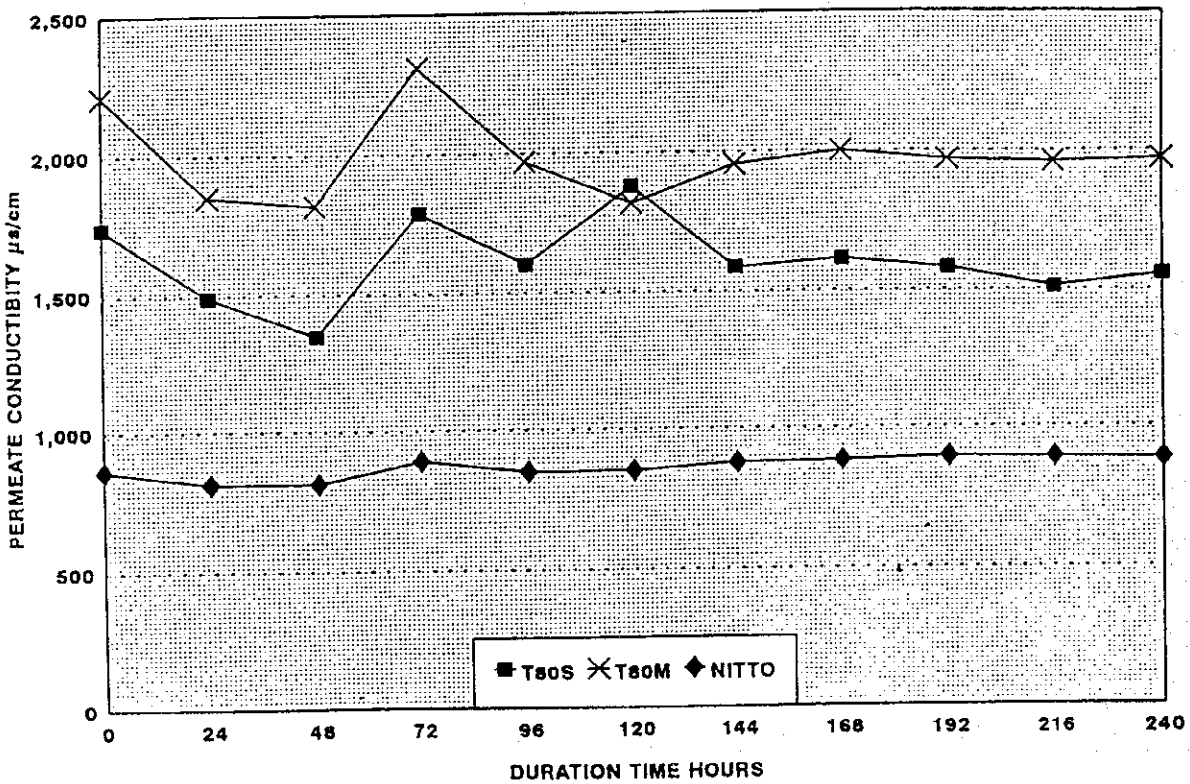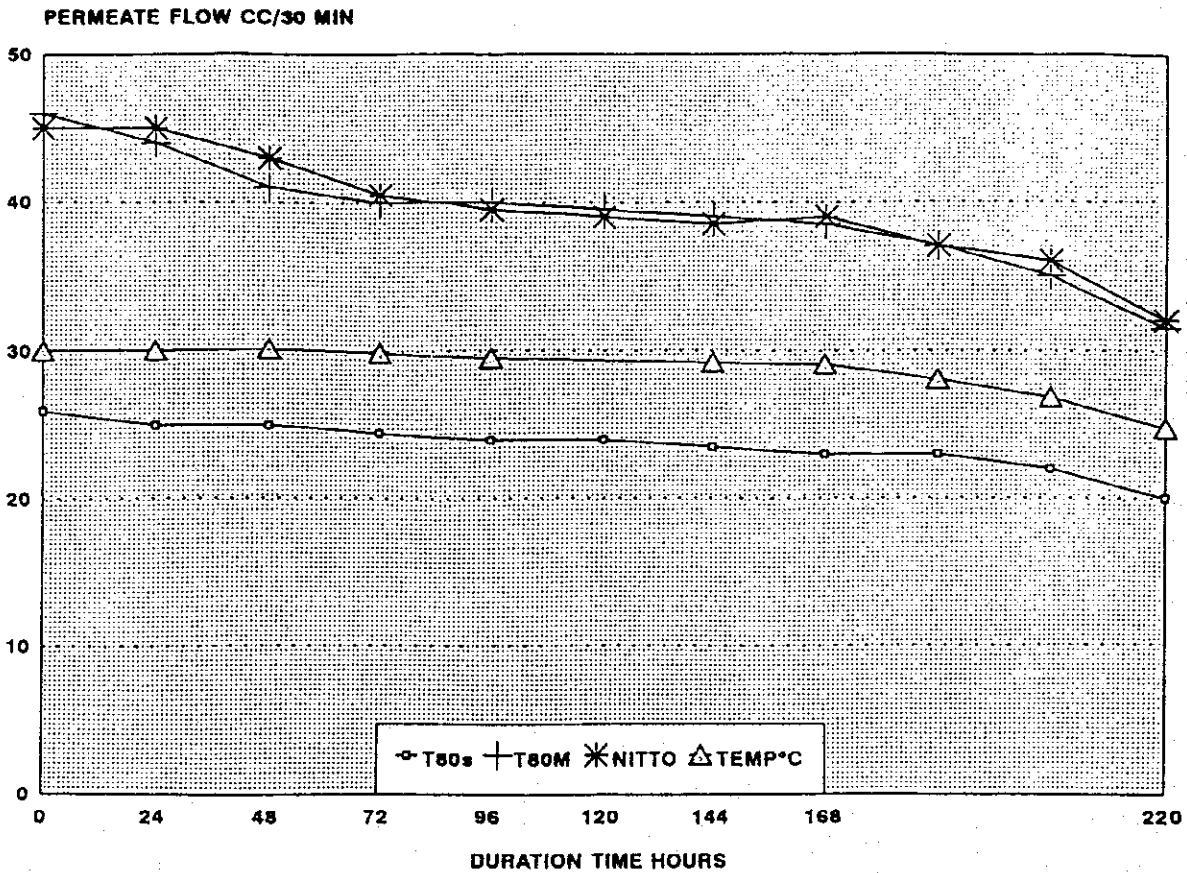
Fig. 2 Oil Tolerance Test for Flat SWRO Membrane vs Time

8.4   Experiment with RO Mini-Module (2)

(8.4)

Contents

(8.4)

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1. OBJECTIVE

The present study aims at evaluating the effect of the oil in the pretreated oil-contaminated seawater on 2.5" x 40" SWRO membrane module. In this experiment performance (flux and salt rejection) of this membrane was monitored for a period of time using the pretreated seawater obtained from oil removal unit.

2. EXPERIMENTAL METHOD

(1) Equipment

Minimodule tester (2) -RUW-5 made by NITTO DENKO Corporation, Japan was used to evaluate the performance (flux and salt rejection) of the 2.5"x40" SWRO membrane module.

(2) Materials

The 2.5"x40" SWRO membrane module used in this experiment was Nitto NTR 70 SWC.

(3) Experimental Procedure

The performance (flux and salt rejection) of the 2.5"x40" SWRO membrane module was determined using pretreated oil-contaminated seawater feed. The feed flow rate was 7 liter/min. and at pressure of 56Kg/cm^2. The pH was maintained at 6.8. The oil content in the feed, brine and permeate was also determined using spectroflurophotometer. GC-MS was also used to analyze oil content in the feed, brine and permeate in the beginning and at the end of the experiments.

3. RESULTS AND DISCUSSION

(1) Results

The results of performance (permeate flow and conductivity) evaluation and the oil content analysis using spectrofluorometer for a period of 528 hours operation are shown in Table (1). Figure (1) shows permeate flow, conductivity and bundle pressure drop with time and Figure (2) shows oil content as determined by spectrofluorometer in feed, brine and reject of the mini module. Figure 3 shows the GC-MS spectrum of oil in feed, brine and reject in the beginning of the experiment.

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(2) **Discussion**

It can be observed from the Figure 1 that the permeate conductivity of the membrane was almost unaffected throughout the experiment. However, permeate flow and bundle pressure drop were found to be affected with time. Differential pressure was found to increase and flow was found to decrease with time. One of the reason for the increase in differential pressure could be high SDI of about 5.8 of the seawater feed obtained from the oil removal unit. During the course of experiment efforts were taken to reduce the SDI value by reducing the dosing of FeCl3 from 10 ppm to 2ppm and feed flow rate in the pretreatment from 1.25 m³/hr to 1 m³/hr without affecting the oil removal efficiency. However, these changes did not improve the SDI value due to the fact that the present pretreatment system was inadequate to prevent ferric from escaping through the media filters. From these results it is difficult to find the actual cause of performance decline of this membrane. This can be either due the presence of oil in the feed or due to the high SDI value. Further study with low SDI feed is to be conducted to establish the actual cause.

The oil concentration in the feed and brine were found to be almost same, whereas in permeate it was almost zero in the beginning and there was slight increase in concentration later on. These measurements were made using spectrofluorometer (see Figure 2). However, GC–MS spectra for the feed, brine and permeate were quite identical in the beginning and also at the end of the experiment (see Figure 3). Since GC–MS is more reliable, it can be said that the soluble oil present in the feed were completely rejected by the membrane.

4. **CONCLUSION**

The performance evaluation of a 2.5"mini–module using pretreated oil contaminated seawater reveals that membrane performance is affected. Since pretreated seawater used in this experiment had high SDI value, it is difficult to conclude from this study that which factor (high SDI value or presence of oil) is responsible for the performance deterioration. Further investigation with low SDI pretreated feed is necessary to establish the actual cause. From the GS–MS analysis, it can be concluded that the membrane rejects almost all the dissolved oil in the feed.
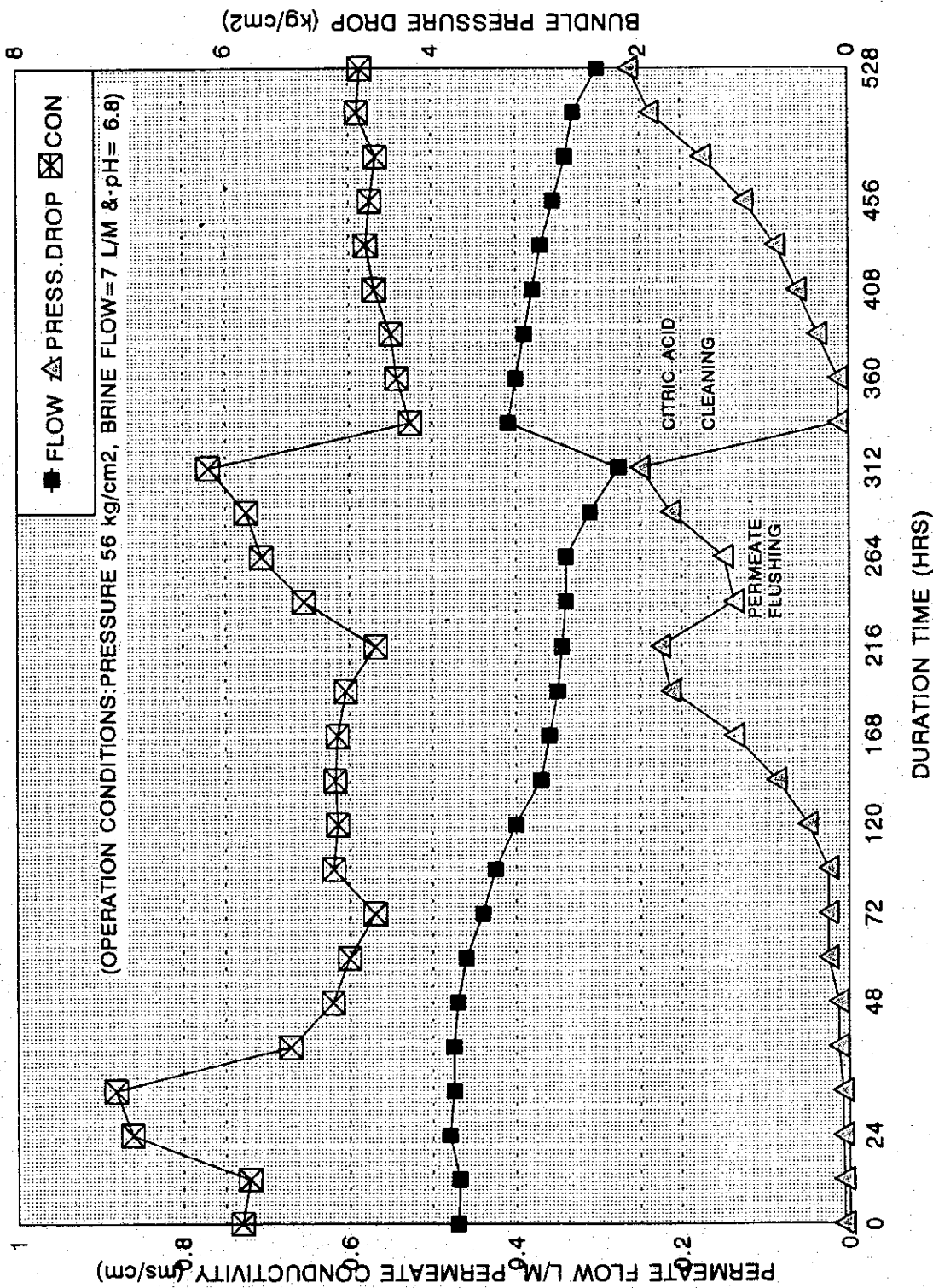
(8.4)

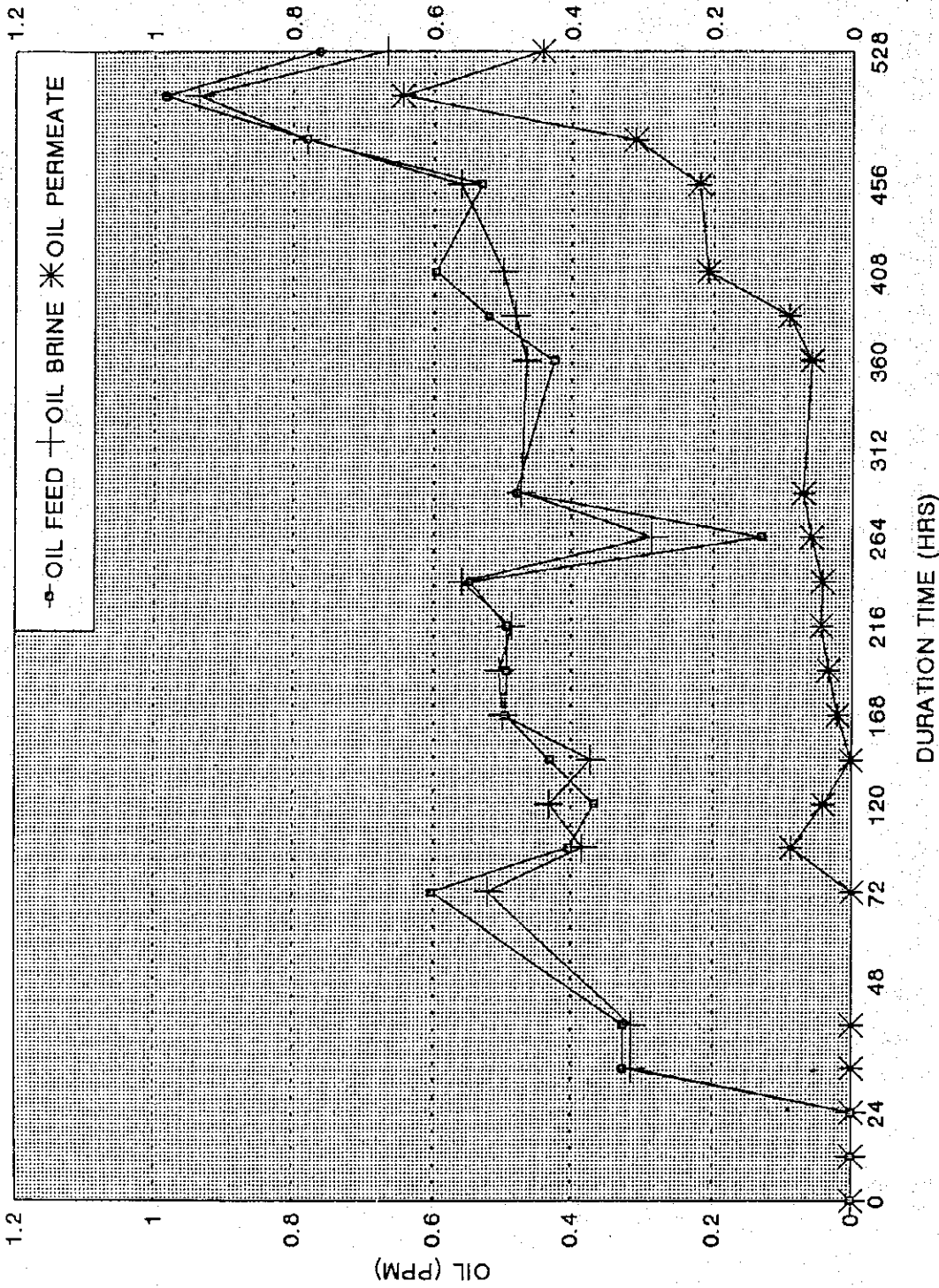Fig. 1 - Oil Turbidity Tolerance of Nitto NTR 70 SWC SWRO Membrane

3

DF8SUM

Fig.10

Fig. 2 Oil Turbidity Tolerance of Nitto NTR 70 SWC SWRO
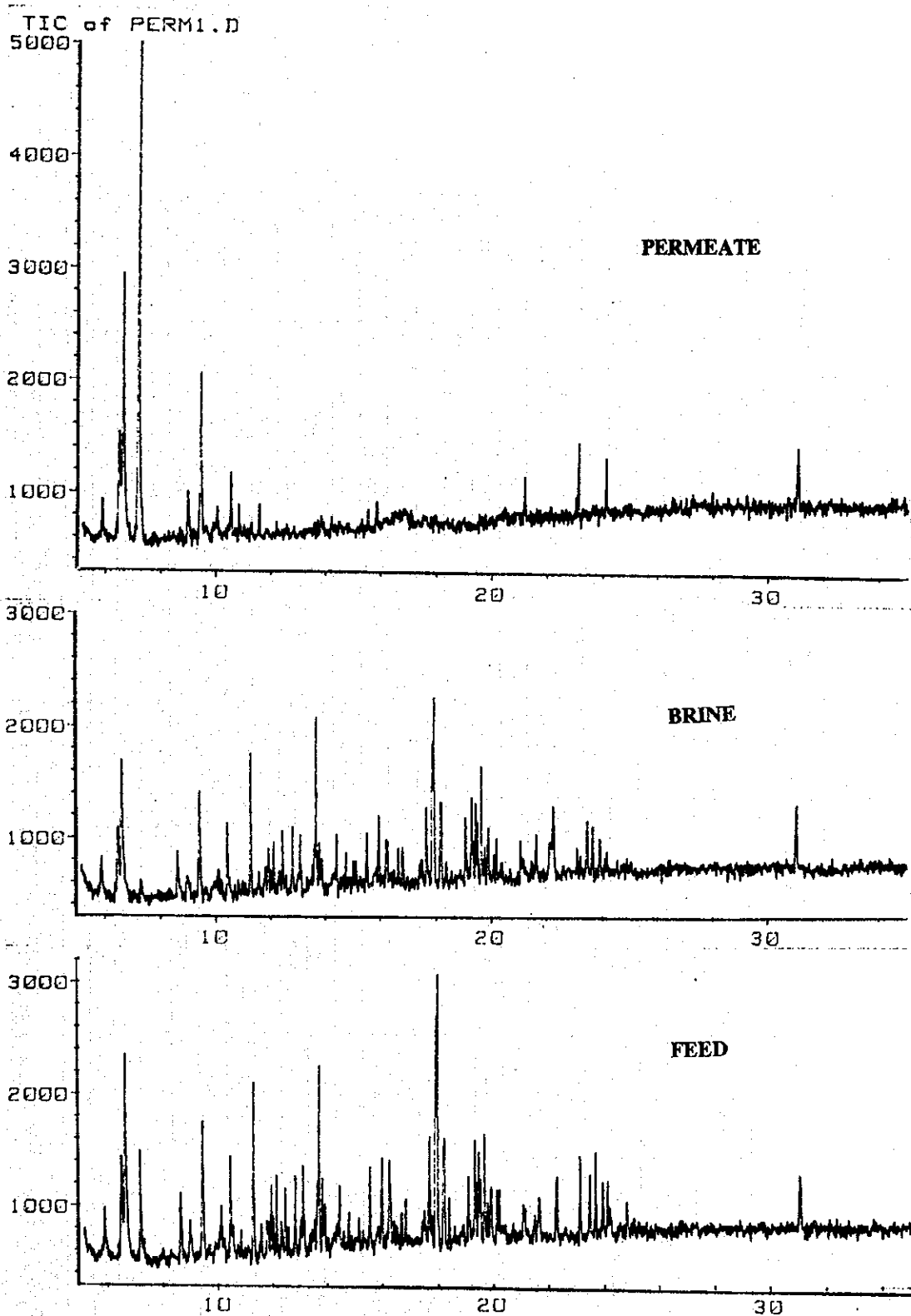Membrane Oil Content in Feed, Brine and Permeate(PPM)

Fig. 3 GC-MS spectra of oil in the Feed, brine and permeate

Table 1 Oil Turbidity Tolerance of Nitto NTR 70SWC Membrane

TIME (HRS.)	FEED	BRINE	PERMEATE	PERMEATE FLOW	PERMEATE CON.μs/CM	FEED TEMP.°C	PRESS.DROP kg/cm2	FEED CON. μs/cm	SDI	FeCl3 PPM	FLOW IN. m3/hr
0	0	0	0	0.47	730	25	0.05	60250		10	1.25
	0	0	0	0.468	721	24.7	0.06			10	1.25
24	0	0	0	0.46	662	26	0.06	60200		10	1.25
	0.32675	0.3130	0	0.475	662	25.9	0.06	60250		10	1.25
	0.32675	0.3130	0	0.475	673	25.0	0.1	60250		10	1.25
48				0.47	621	26	0.1	60300		10	1.25
				0.46	601	25.9	0.2	60200		10	1.25
72	0.600	0.52	0	0.44	570	27	0.2	61200		10	1.25
96	0.404	0.305	0.006	0.425	620	27.2	0.2	61600		10	1.25
120	0.360	0.432	0.041	0.4	615	27.3	0.4	61600		10	1.25
144	0.431	0.373	0.002	0.37	610	26.3	0.7	61500		10	1.25
160	0.495	0.499	0.02	0.36	615	26.2	1.1	61200		10	1.25
192	0.493	0.503	0.030	0.35	605	26.7	1.7	61200		0	1.25
216	0.493	0.405	0.0405	0.345	569	27.1	1.0	61000		8	1.25
240	0.547	0.559	0.0426	0.34	658	27.3	1.1	61100		8	-
264	0.131	0.266	0.050	0.34	707	27.1	1.2	61900		8	-
288	0.479	0.472	0.07	0.31	725	27.3	1.7	61000	5.02	8	-
312				0.275	770	26.9	2	61700	6.12	6	-
336				0.409	527	24.7	0.1	61400	5.95	6	-
360	0.425	0.465	0.050	0.4	543	24.7	0.1	61400	6.04	3	-
	0.52	0.401	0.091	0.39	550	25.5	0.3	61000	5.91	3	-
	0.597	0.499	0.207	0.30	570	25.9	0.5	61100	5.06	3	-
				0.37	500	25.7	0.7	61100		3	-
156	0.50	0.56	0.22	0.355	575	25	1	61000	5.69	3	-
180	0.70	0.70	0.31	0.34	560	24.4	1.4	61100	6.1	2	-
504	0.905	0.936	0.643	0.33	590	23.0	1.9		5.93	2	-
520	0.762	0.666	0.142	0.3	506	21.0	2.1	61100	5.4	2	-

OIL CONTENT IN PPM

(OPERATION CONDITIONS: PRESSURE=56 KG/CM2,BRINE FLOW=7 L/M pH=6.8)

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