2. APPENDIX for M4 (Analysis of Oil Dispersed in Raw Seawater at the Heat Rejection Section of MSF Plant)

APPENDIX M4 – 1

APPENDIX M4-1

4.2 Influence on Quality of Product Water

In as much 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.

4.2.1 Behavior of Volatile Components During Sea Water Desalination Process (Two-Liquid Phase)

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:

$$W_o/W_w = (M_o \cdot P_o)/(M_w \cdot P_w) \qquad (4.2.1)$$

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 (4.2.1), along with almost all of the light component, high vapor pressure distilled from the brine.

4.2.2. Study of Numerical Simulation (Two-Liquid Phase)

4.2.2.1 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 with oil.

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 flow of the simulated calculation is shown in Fig. 4.2.1.

First, 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 (Fig. 4.2.2) 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).

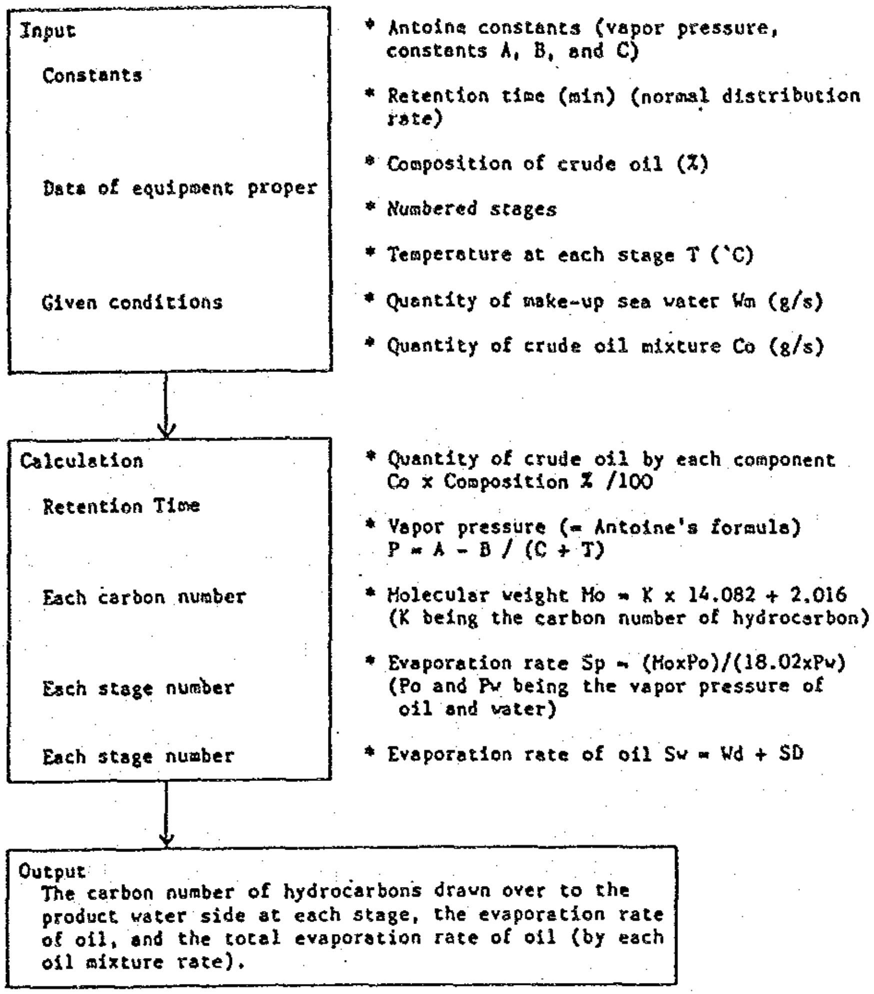


Fig. 4.2.1: Flow of Simulated Calculation for Behavior of Oil Components in MSF Evaporator

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 was inputted.

When the two kinds of parameters mentioned above were inputted, 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.

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 up to carbon number 5 were evaporated, having been previously introduced into the plant and compounds with carbon numbers from 6 to 30 were considered to be present at the rate indicated in Fig. 4.2.3. 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 component with the highest boiling point. This curved line fits the oil components of both Kuwait and Kafuji.

Input conditions for simulation on Al Jubail Phase I and II plants (AJ-I and AJ-II) are shown in Table 4.2.1.

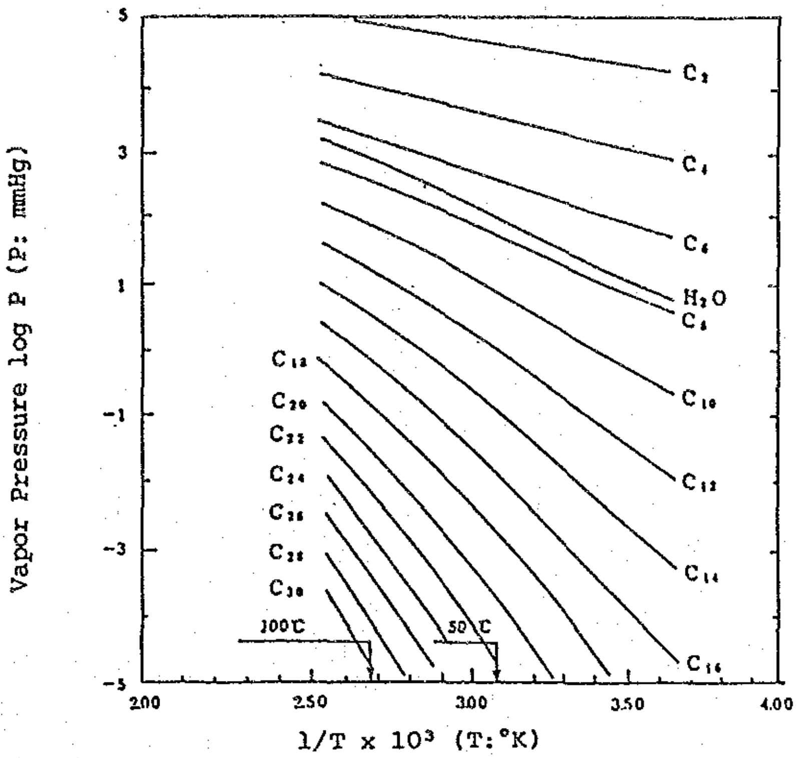


Fig. 4.2.2: Arrhenius Plot of Water and Hydrocarbon Vapor Pressure

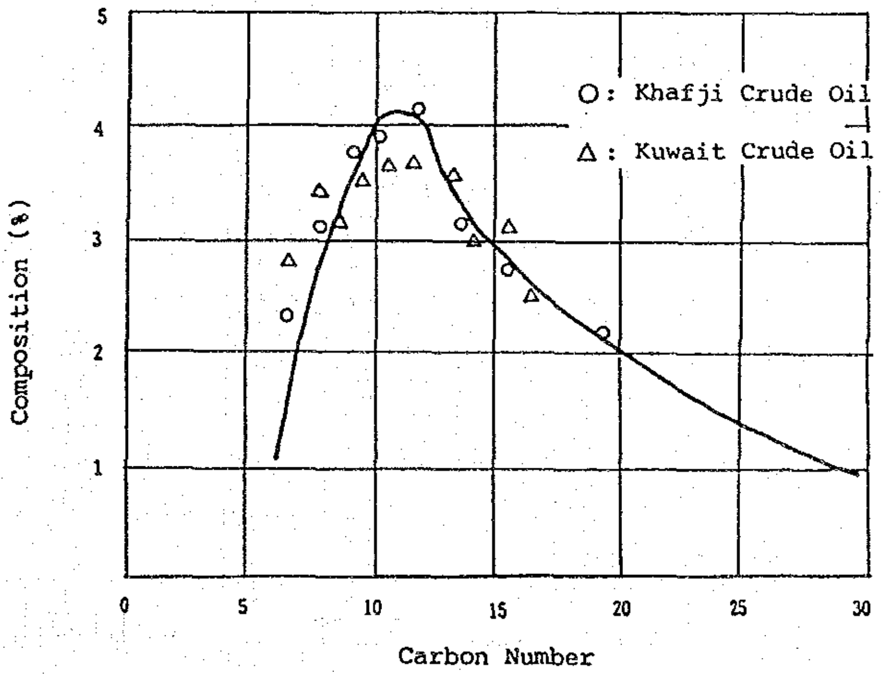


Fig. 4.2.3: Composition Model of Crude Oil used in Simulation

Table 4.2.1: Heat/Mass Balance of MSF Plants in Al Jubail

<table>
<tr><td colspan="2">PLANT NAME</td><td colspan="5">A J − I</td><td colspan="9">A J − II.</td><td rowspan="2">NOTE</td></tr>
<tr><td colspan="2">CONSTRACTOR</td><td colspan="5">SK/MHI</td><td colspan="3">SK−MHI</td><td colspan="4">IHI</td><td colspan="2">HZ</td></tr>
<tr><td colspan="2">1. OPERATING CONDITION
1.1 Capacity kg/h
t/d
kg/s</td><td colspan="5">948,800.0
22,771.2
263.5</td><td colspan="9">979,000.0
23,500.0
272.0</td><td></td></tr>
<tr><td colspan="2">1.2 Performance Ratio</td><td colspan="5">8 lb/1000BTU</td><td colspan="9">0.00344 KG/KJ</td><td></td></tr>
<tr><td colspan="2">1.3 Concentration Ratio</td><td colspan="5">1.44</td><td colspan="9">1.305</td><td></td></tr>
<tr><td colspan="2">1.4 Sea Water Temp. ℃</td><td colspan="5">35.0</td><td colspan="9">35.0</td><td></td></tr>
<tr><td colspan="2">1.5 Blow Down Temp. ℃</td><td colspan="5">41.0</td><td colspan="9">43.3</td><td></td></tr>
<tr><td colspan="2">1.6 Brine Max. Temp. ℃</td><td colspan="5">90.56</td><td colspan="9">90.6</td><td></td></tr>
<tr><td colspan="2">1.7 TDS in Sea Water ppm</td><td colspan="5">45,000.0</td><td colspan="9">46,500.0</td><td></td></tr>
<tr><td colspan="2">1.8 TDS in Rec. brain ppm</td><td colspan="5">64,800.0</td><td colspan="9">65,000.0</td><td></td></tr>
<tr><td colspan="2">2. INPUT CONDITION
2.1 Feed Sea Water kg/h
kg/s (l/s)</td><td colspan="5">2,631,000.0
730.8(711.6)</td><td colspan="9">2,908,000.0
807(785.8 at D=1.027kg/l in 40 ‰.30 ℃)</td><td></td></tr>
<tr><td colspan="2">2.2 Product Water kg/h
kg/s</td><td colspan="5">948,800.0
263.5</td><td colspan="9">979,000.0
272.0</td><td></td></tr>
<tr><td colspan="2">2.3 Oil Concent. mg/l</td><td>0.1</td><td colspan="2">1.0</td><td>10</td><td colspan="2">50</td><td>100</td><td>0.10</td><td>1.0</td><td colspan="2">10.0</td><td>50</td><td colspan="2">100</td><td></td></tr>
<tr><td colspan="2">2.4 Oil Content g/s</td><td>0.07</td><td colspan="2">0.71</td><td>7.12</td><td colspan="2">36.5</td><td>71.2</td><td>0.08</td><td>0.79</td><td colspan="2">7.85</td><td>39.25</td><td colspan="2">78.58</td><td></td></tr>
<tr><td rowspan="25">3. Temp., Evaporation Rate in Deaeration Part & Each Stage</td><td>Eva. Part</td><td colspan="2">Temp. (℃)</td><td colspan="3">Eva. Rate (t/h)</td><td colspan="2">Temp. (℃)</td><td>Eva. Rate (t/h)</td><td colspan="2">Temp. (℃)</td><td colspan="2">Eva. Rate (t/h)</td><td>Temp. (℃)</td><td>Eva. Rate (t/h)</td><td></td></tr>
<tr><td>Dea. P</td><td colspan="2">41.0</td><td colspan="3">1.28 a)</td><td colspan="2">43.3</td><td>4.0 b)</td><td colspan="2">43.3</td><td colspan="2">4.0 b)</td><td>43.74</td><td>3.0 b)</td><td></td></tr>
<tr><td>1st'g</td><td colspan="2">90.56</td><td colspan="3">50.0</td><td colspan="2">90.6</td><td>52.0</td><td colspan="2">90.6</td><td colspan="2">59.84</td><td>90.60</td><td>48.36</td><td></td></tr>
<tr><td>2</td><td colspan="2">88.1</td><td colspan="3">49.5</td><td colspan="2">88.3</td><td>51.4</td><td colspan="2">87.9</td><td colspan="2">59.84</td><td>85.08</td><td>48.96</td><td></td></tr>
<tr><td>3</td><td colspan="2">85.7</td><td colspan="3">48.8</td><td colspan="2">85.9</td><td>50.8</td><td colspan="2">85.3</td><td colspan="2">59.84</td><td>82.74</td><td>48.78</td><td></td></tr>
<tr><td>4</td><td colspan="2">83.3</td><td colspan="3">48.4</td><td colspan="2">83.6</td><td>50.1</td><td colspan="2">82.7</td><td colspan="2">59.84</td><td>80.49</td><td>48.66</td><td></td></tr>
<tr><td>5</td><td colspan="2">80.9</td><td colspan="3">47.7</td><td colspan="2">81.3</td><td>49.4</td><td colspan="2">80.2</td><td colspan="2">54.40</td><td>78.26</td><td>48.30</td><td></td></tr>
<tr><td>6</td><td colspan="2">78.5</td><td colspan="3">47.1</td><td colspan="2">79.0</td><td>48.8</td><td colspan="2">77.6</td><td colspan="2">57.12</td><td>76.01</td><td>47.88</td><td></td></tr>
<tr><td>7</td><td colspan="2">76.1</td><td colspan="3">46.6</td><td colspan="2">76.7</td><td>48.1</td><td colspan="2">75.1</td><td colspan="2">54.40</td><td>73.77</td><td>47.58</td><td></td></tr>
<tr><td>8</td><td colspan="2">73.8</td><td colspan="3">45.9</td><td colspan="2">74.5</td><td>47.4</td><td colspan="2">72.6</td><td colspan="2">51.68</td><td>71.53</td><td>47.16</td><td></td></tr>
<tr><td>9</td><td colspan="2">71.4</td><td colspan="3">45.3</td><td colspan="2">72.2</td><td>46.7</td><td colspan="2">70.1</td><td colspan="2">54.40</td><td>69.29</td><td>46.74</td><td></td></tr>
<tr><td>10</td><td colspan="2">69.1</td><td colspan="3">44.7</td><td colspan="2">70.0</td><td>46.0</td><td colspan="2">67.6</td><td colspan="2">48.96</td><td>67.06</td><td>46.32</td><td></td></tr>
<tr><td>11</td><td colspan="2">66.8</td><td colspan="3">44.1</td><td colspan="2">67.8</td><td>45.2</td><td colspan="2">65.2</td><td colspan="2">51.68</td><td>64.83</td><td>45.90</td><td></td></tr>
<tr><td>12</td><td colspan="2">64.5</td><td colspan="3">43.4</td><td colspan="2">65.6</td><td>44.6</td><td colspan="2">62.8</td><td colspan="2">48.96</td><td>62.60</td><td>44.46</td><td></td></tr>
<tr><td>13</td><td colspan="2">62.2</td><td colspan="3">43.1</td><td colspan="2">63.4</td><td>43.9</td><td colspan="2">60.4</td><td colspan="2">46.24</td><td>60.38</td><td>45.00</td><td></td></tr>
<tr><td>14</td><td colspan="2">59.9</td><td colspan="3">42.4</td><td colspan="2">61.3</td><td>43.6</td><td colspan="2">58.0</td><td colspan="2">43.52</td><td>58.17</td><td>44.52</td><td></td></tr>
<tr><td>15</td><td colspan="2">57.6</td><td colspan="3">41.5</td><td colspan="2">59.1</td><td>42.7</td><td colspan="2">55.6</td><td colspan="2">43.52</td><td>56.00</td><td>44.10</td><td></td></tr>
<tr><td>16</td><td colspan="2">55.4</td><td colspan="3">40.8</td><td colspan="2">57.0</td><td>41.8</td><td colspan="2">53.3</td><td colspan="2">46.24</td><td>53.76</td><td>43.56</td><td></td></tr>
<tr><td>17</td><td colspan="2">53.2</td><td colspan="3">40.0</td><td colspan="2">54.9</td><td>40.8</td><td colspan="2">51.0</td><td colspan="2">43.52</td><td>51.57</td><td>43.08</td><td></td></tr>
<tr><td>18</td><td colspan="2">51.0</td><td colspan="3">39.1</td><td colspan="2">52.9</td><td>39.8</td><td colspan="2">48.7</td><td colspan="2">46.24</td><td>49.39</td><td>39.66</td><td></td></tr>
<tr><td>19</td><td colspan="2">48.8</td><td colspan="3">38.3</td><td colspan="2">50.9</td><td>38.8</td><td colspan="2">46.3</td><td colspan="2">48.96</td><td>47.22</td><td>36.60</td><td></td></tr>
<tr><td>20</td><td colspan="2">46.7</td><td colspan="3">34.6</td><td colspan="2">48.9</td><td>31.0</td><td colspan="2">43.3(OL)</td><td colspan="2">----</td><td>45.19</td><td>27.42</td><td></td></tr>
<tr><td>21</td><td colspan="2">44.8</td><td colspan="3">34.9</td><td colspan="2">47.3</td><td>35.8</td><td colspan="2">----</td><td colspan="2">----</td><td>43.74</td><td>39.60</td><td></td></tr>
<tr><td>22</td><td colspan="2">42.9</td><td colspan="3">32.6</td><td colspan="2">45.5</td><td>40.3</td><td colspan="2">----</td><td colspan="2">----</td><td>41.59</td><td>46.80</td><td>OL:</td></tr>
<tr><td>TOTAL</td><td colspan="2">41.0(OL)</td><td colspan="3">950.1</td><td colspan="2">43.3(OL)</td><td>983.0</td><td colspan="2">----</td><td colspan="2">983.20</td><td>38.7(OL)</td><td>982.44</td><td>Outlet</td></tr>
</table>

NOTE・a) :Final Stage Deaeration. b):Vaccum Deaeration
・SK :Sasakura Engineering Co., Ltd
・MHI :Mitsubishi Heavy Industries. Ltd
・IHI :Isikawajima-Harima Heavy Industries Co., Ltd
・HZ :Hitachi Zohsen Co., Ltd

4.2.2.2 Results of Simulated Calculation (Two-Liquid Phase)

The behavior, of crude oil when mixed with sea water at the rates of 100, 10, 1, 0.1 mg/l and the amount of product water transported to by each plant are shown in Figs. 4.2.4(1) to (10) and Tables 4.2.2(1) to (10) with the results for the AJ-I and AJ-II plants constructed by Sasakura Engineering Co., Ltd. and Mitsubishi Heavy Industries, Ltd., Ishikawajima-Harima Heavy Industries Co., Ltd. and Hitachi Zosen Corporation.

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 product water. If a deaerator is installed like in the AJ-II 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 0.1 mg/l). (refer to Fig. 4.2.4(6))

Even if the sea water is contaminated by oil with a concentration of 100 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 fresh water side at the medium temperature stage. (refer to Fig. 4.2.4(10))

While AJ-I employs the final stage deaeration system condensation of steam, with evaporation of the deaeration part takes place in the same part of the final condensation stage and therefore separation is impossible. Inevitably, the product water contains high concentrations of oil (Figs. 4.2.4(1) to (5)).

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. 4.2.2, 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.

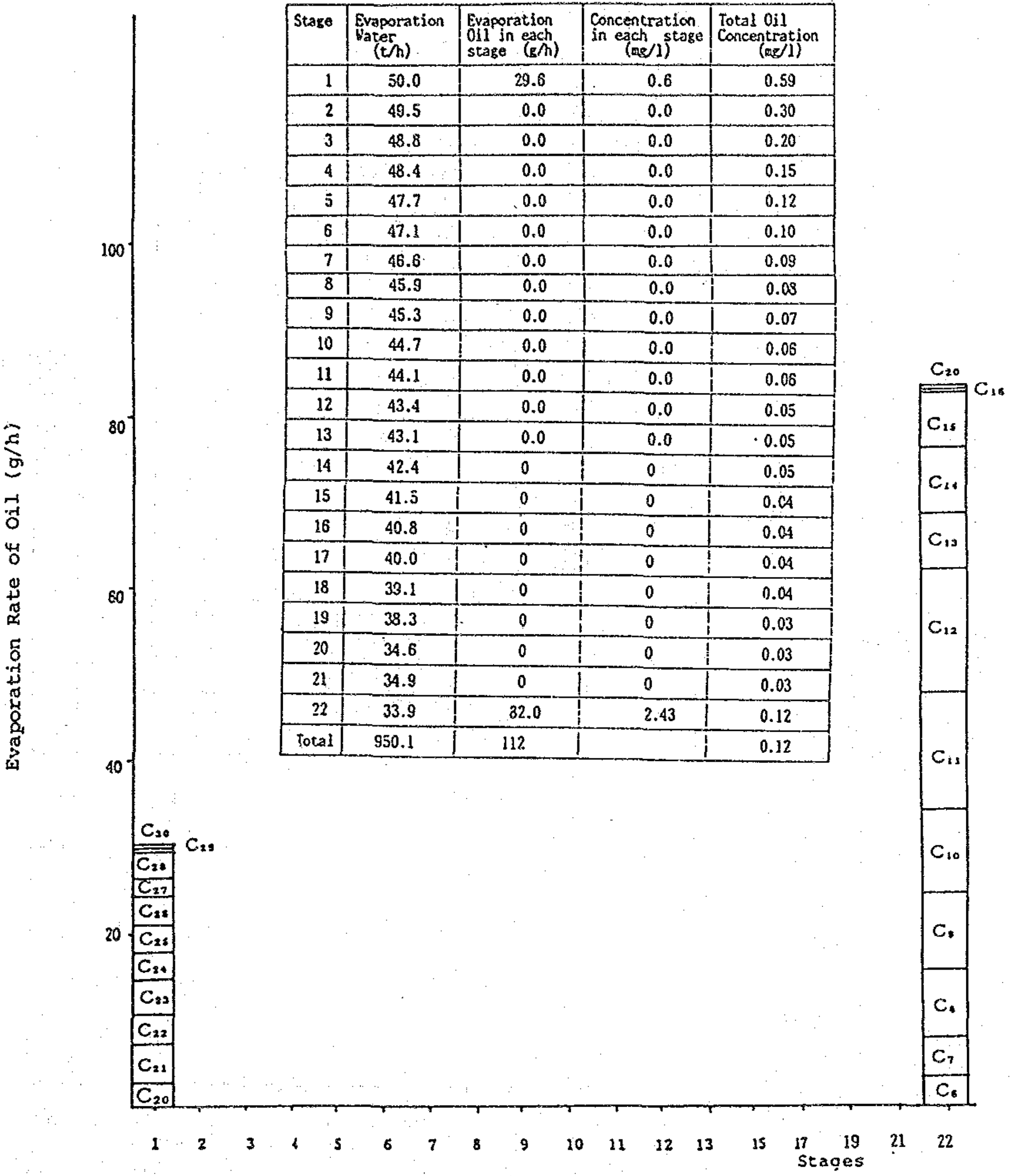
When the condensation of evaporated oil components is studied, it is found that since the latent heat of hydrocarbon condensation is much smaller than that of water (for example, the latent heat of octane condensation is 70 kcal/kg or 1/7.7 of the 539 kcal/kg of water), an amount of hydrocarbons several 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.

Contractor: SK/MHI

Plant Name: AJ－I

Feed Water: 2,631,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
1	50.0	29.6	0.6	0.59
2	49.5	0.0	0.0	0.30
3	48.8	0.0	0.0	0.20
4	48.4	0.0	0.0	0.15
5	47.7	0.0	0.0	0.12
6	47.1	0.0	0.0	0.10
7	46.6	0.0	0.0	0.09
8	45.9	0.0	0.0	0.08
9	45.3	0.0	0.0	0.07
10	44.7	0.0	0.0	0.06
11	44.1	0.0	0.0	0.06
12	43.4	0.0	0.0	0.05
13	43.1	0.0	0.0	0.05
14	42.4	0	0	0.05
15	41.5	0	0	0.04
16	40.8	0	0	0.04
17	40.0	0	0	0.04
18	39.1	0	0	0.04
19	38.3	0	0	0.03
20	34.6	0	0	0.03
21	34.9	0	0	0.03
22	33.9	82.0	2.43	0.12
Total	950.1	112		0.12



Case of 0.1 mg/l Oil Concentration in Sea Water

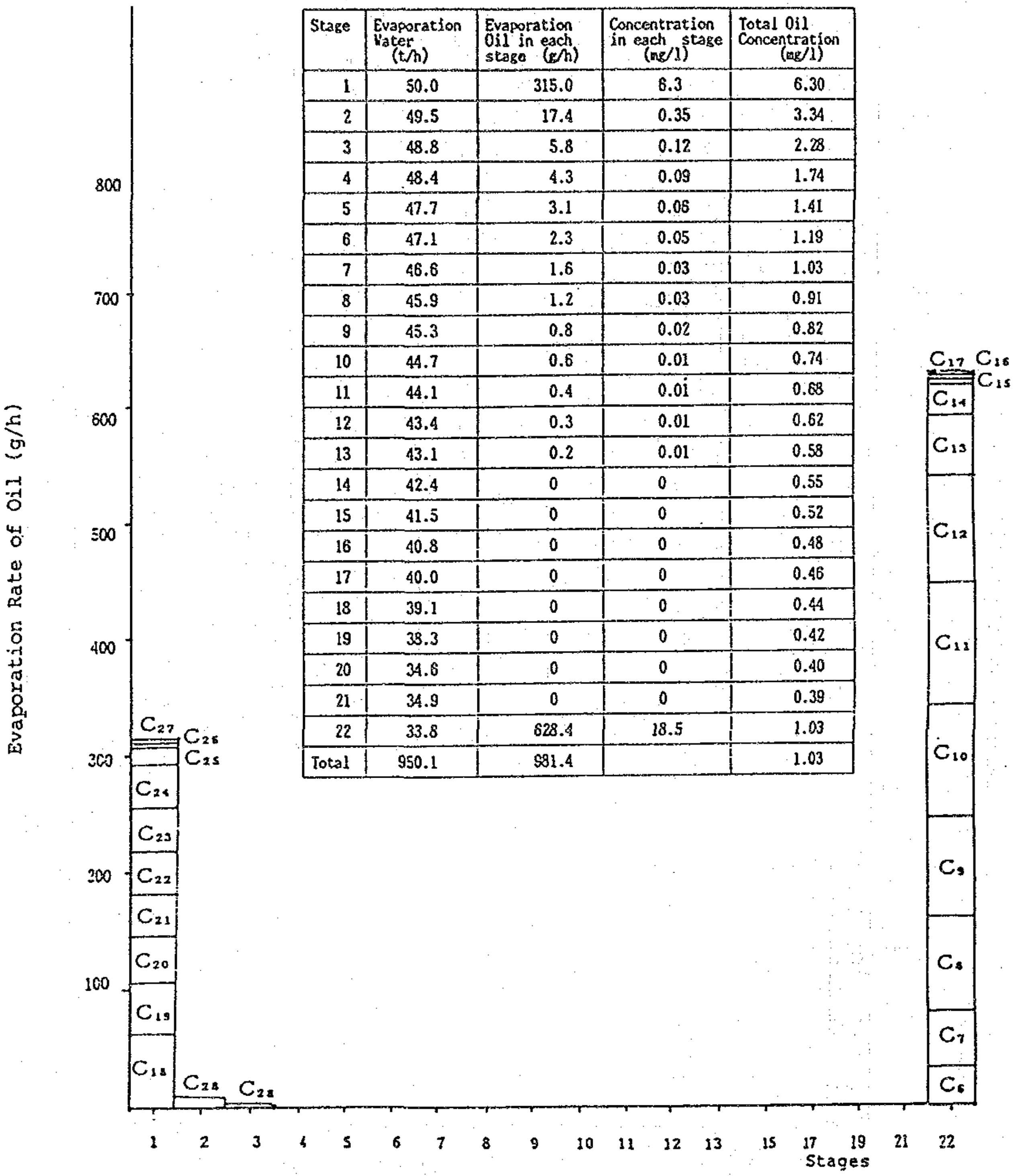
Fig. 4.2.4 (1): Evaporation Rate of Oil at Each Evaporation Stage

Contractor: SK／MHI

Plant Name: AJ－I

Feed Water: 2,631,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
1	50.0	315.0	6.3	6.30
2	49.5	17.4	0.35	3.34
3	48.8	5.8	0.12	2.28
4	48.4	4.3	0.09	1.74
5	47.7	3.1	0.06	1.41
6	47.1	2.3	0.05	1.19
7	46.6	1.6	0.03	1.03
8	45.9	1.2	0.03	0.91
9	45.3	0.8	0.02	0.82
10	44.7	0.6	0.01	0.74
11	44.1	0.4	0.01	0.68
12	43.4	0.3	0.01	0.62
13	43.1	0.2	0.01	0.58
14	42.4	0	0	0.55
15	41.5	0	0	0.52
16	40.8	0	0	0.48
17	40.0	0	0	0.46
18	39.1	0	0	0.44
19	38.3	0	0	0.42
20	34.6	0	0	0.40
21	34.9	0	0	0.39
22	33.8	628.4	18.5	1.03
Total	950.1	981.4		1.03



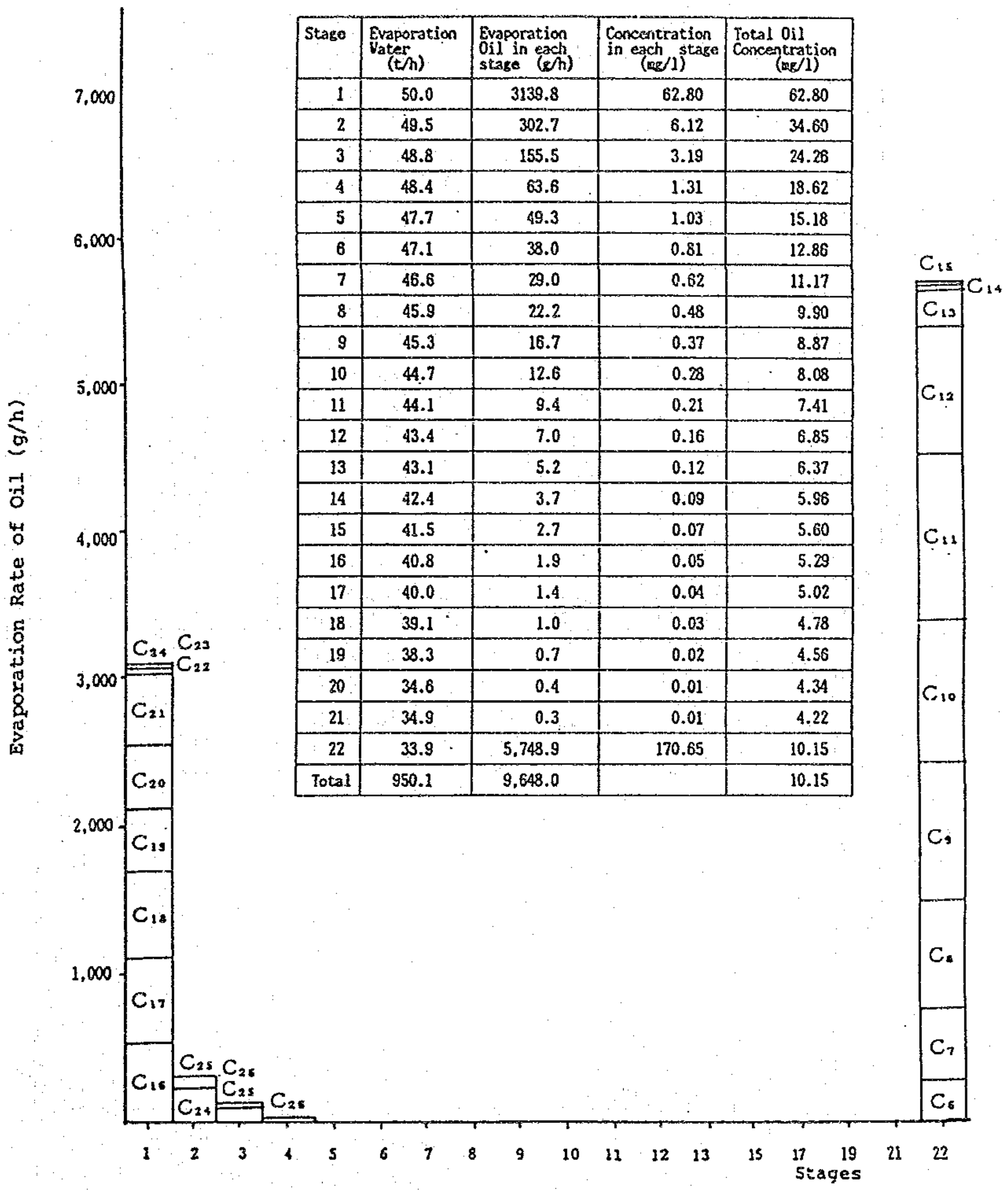
Case of 1.0 mg/l Oil Concentration in Sea Water

Fig. 4.2.4 (2): Evaporation Rate of Oil at Each Evaporation Stage

Contractor: SK/MHI

Plant Name: AJ-I

Feed Water: 2,631,000 kg/h



Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
1	50.0	3139.8	62.80	62.80
2	49.5	302.7	6.12	34.60
3	48.8	155.5	3.19	24.26
4	48.4	63.6	1.31	18.62
5	47.7	49.3	1.03	15.18
6	47.1	38.0	0.81	12.86
7	46.6	29.0	0.62	11.17
8	45.9	22.2	0.48	9.90
9	45.3	16.7	0.37	8.87
10	44.7	12.6	0.28	8.08
11	44.1	9.4	0.21	7.41
12	43.4	7.0	0.16	6.85
13	43.1	5.2	0.12	6.37
14	42.4	3.7	0.09	5.96
15	41.5	2.7	0.07	5.60
16	40.8	1.9	0.05	5.29
17	40.0	1.4	0.04	5.02
18	39.1	1.0	0.03	4.78
19	38.3	0.7	0.02	4.56
20	34.6	0.4	0.01	4.34
21	34.9	0.3	0.01	4.22
22	33.9	5,748.9	170.65	10.15
Total	950.1	9,648.0		10.15

Case of 10 mg/l Oil Concentration in Sea Water

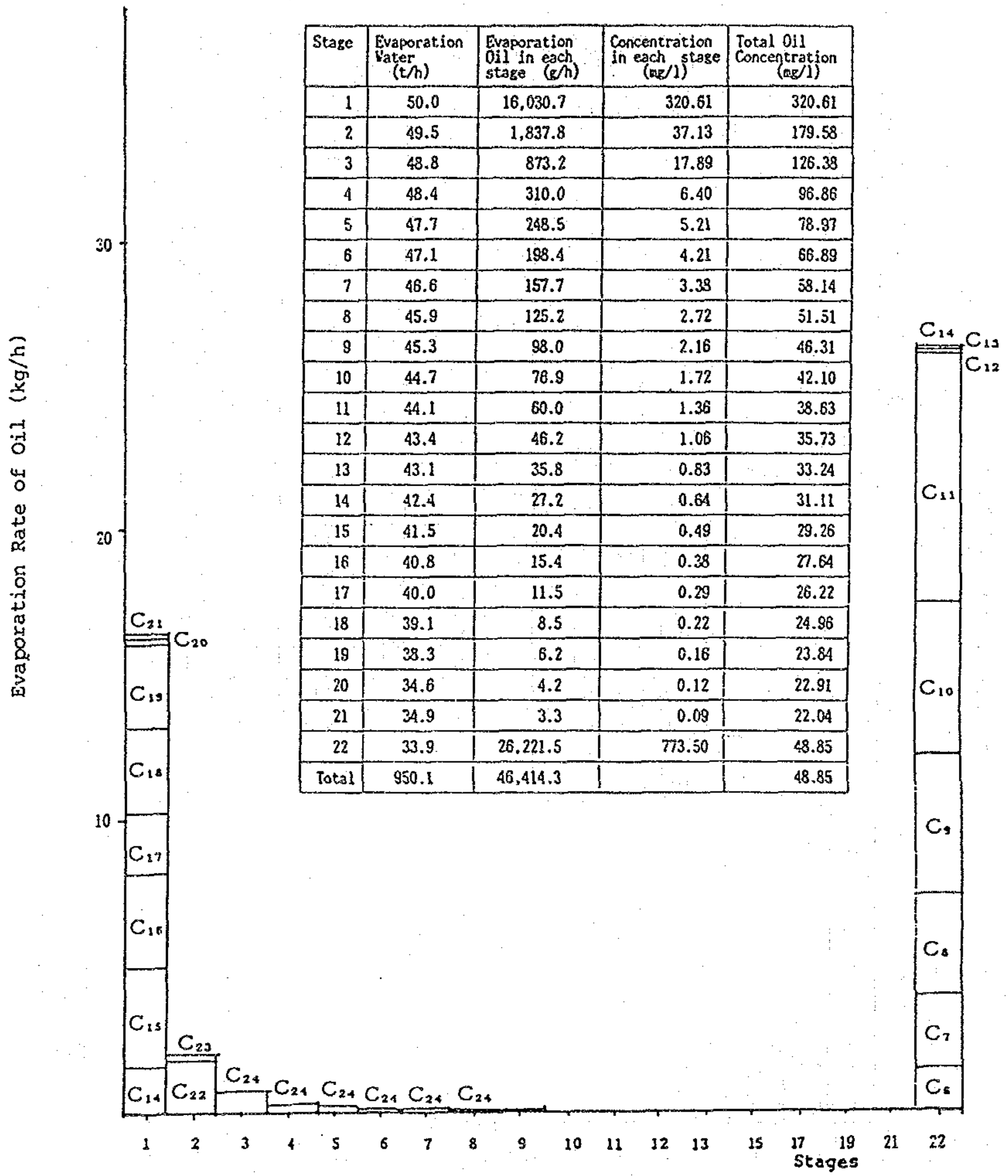
Fig. 4.2.4 (3): Evaporation Rate of Oil at Each Evaporation Stage

Contractor: SK/MHI

Plant Name: AJ-I

Feed Water: 2,631,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
1	50.0	16,030.7	320.61	320.61
2	49.5	1,837.8	37.13	179.58
3	48.8	873.2	17.89	126.38
4	48.4	310.0	6.40	96.86
5	47.7	248.5	5.21	78.97
6	47.1	198.4	4.21	66.89
7	46.6	157.7	3.38	58.14
8	45.9	125.2	2.72	51.51
9	45.3	98.0	2.16	46.31
10	44.7	76.9	1.72	42.10
11	44.1	60.0	1.36	38.63
12	43.4	46.2	1.06	35.73
13	43.1	35.8	0.83	33.24
14	42.4	27.2	0.64	31.11
15	41.5	20.4	0.49	29.26
16	40.8	15.4	0.38	27.64
17	40.0	11.5	0.29	26.22
18	39.1	8.5	0.22	24.96
19	38.3	6.2	0.16	23.84
20	34.6	4.2	0.12	22.91
21	34.9	3.3	0.09	22.04
22	33.9	26,221.5	773.50	48.85
Total	950.1	46,414.3		48.85



Case of 50 mg/l Oil Concentration in Sea Water

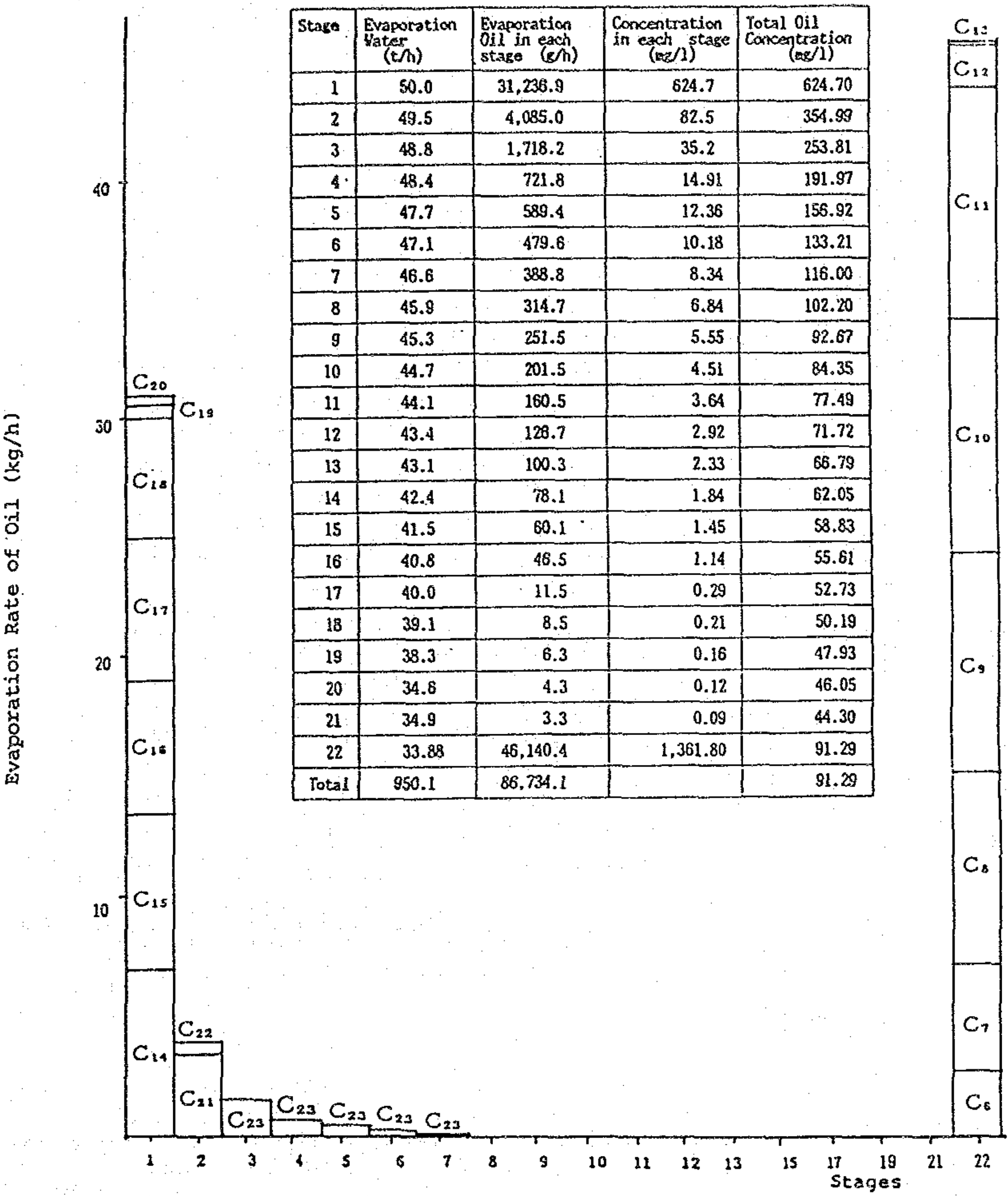
Fig. 4.2.4 (4): Evaporation Rate of Oil at Each Evaporation Stage

Contractor: SK/MHI

Plant Name: AJ－I

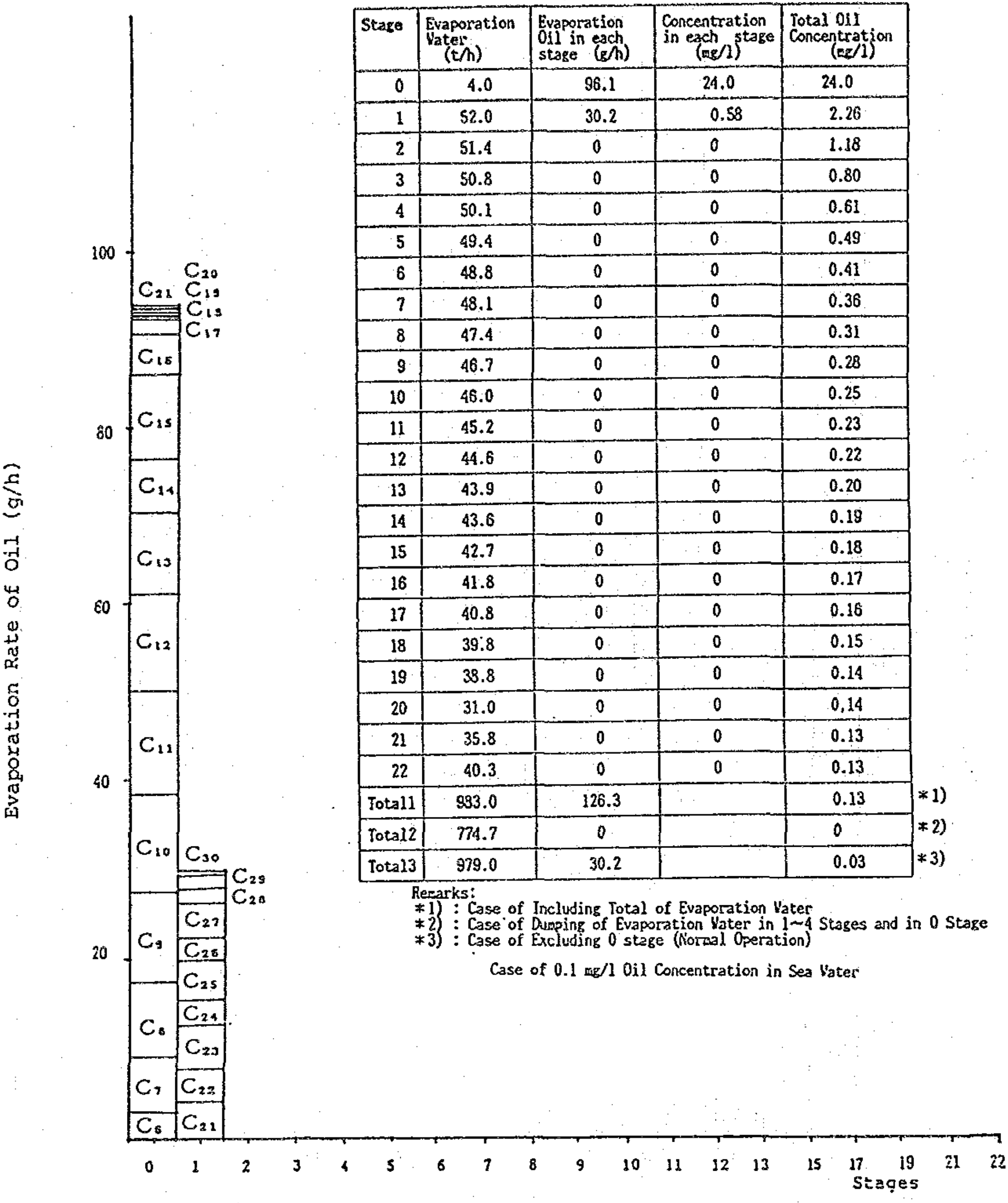
Feed Water: 2,631,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
1	50.0	31,236.9	624.7	624.70
2	49.5	4,085.0	82.5	354.99
3	48.8	1,718.2	35.2	253.81
4	48.4	721.8	14.91	191.97
5	47.7	589.4	12.36	156.92
6	47.1	479.6	10.18	133.21
7	46.6	388.8	8.34	116.00
8	45.9	314.7	6.84	102.20
9	45.3	251.5	5.55	92.67
10	44.7	201.5	4.51	84.35
11	44.1	160.5	3.64	77.49
12	43.4	128.7	2.92	71.72
13	43.1	100.3	2.33	66.79
14	42.4	78.1	1.84	62.05
15	41.5	60.1	1.45	58.83
16	40.8	46.5	1.14	55.61
17	40.0	11.5	0.29	52.73
18	39.1	8.5	0.21	50.19
19	38.3	6.3	0.16	47.93
20	34.6	4.3	0.12	46.05
21	34.9	3.3	0.09	44.30
22	33.88	46,140.4	1,361.80	91.29
Total	950.1	86,734.1		91.29



Case of 100 mg/l Oil Concentration in Sea Water

Fig. 4.2.4 (5): Evaporation Rate of Oil at Each Evaporation Stage



Contractor: SK-MHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)	
0	4.0	96.1	24.0	24.0	
1	52.0	30.2	0.58	2.26	
2	51.4	0	0	1.18	
3	50.8	0	0	0.80	
4	50.1	0	0	0.61	
5	49.4	0	0	0.49	
6	48.8	0	0	0.41	
7	48.1	0	0	0.36	
8	47.4	0	0	0.31	
9	46.7	0	0	0.28	
10	46.0	0	0	0.25	
11	45.2	0	0	0.23	
12	44.6	0	0	0.22	
13	43.9	0	0	0.20	
14	43.6	0	0	0.19	
15	42.7	0	0	0.18	
16	41.8	0	0	0.17	
17	40.8	0	0	0.16	
18	39.8	0	0	0.15	
19	38.8	0	0	0.14	
20	31.0	0	0	0,14	
21	35.8	0	0	0.13	
22	40.3	0	0	0.13	
Total1	983.0	126.3		0.13	*1)
Total2	774.7	0		0	*2)
Total3	979.0	30.2		0.03	*3)

Remarks:
*1) : Case of Including Total of Evaporation Water
*2) : Case of Dumping of Evaporation Water in 1~4 Stages and in 0 Stage
*3) : Case of Excluding 0 stage (Normal Operation)

Case of 0.1 mg/l Oil Concentration in Sea Water

Case of 0.1 mg/l Oil Concentration in Sea Water

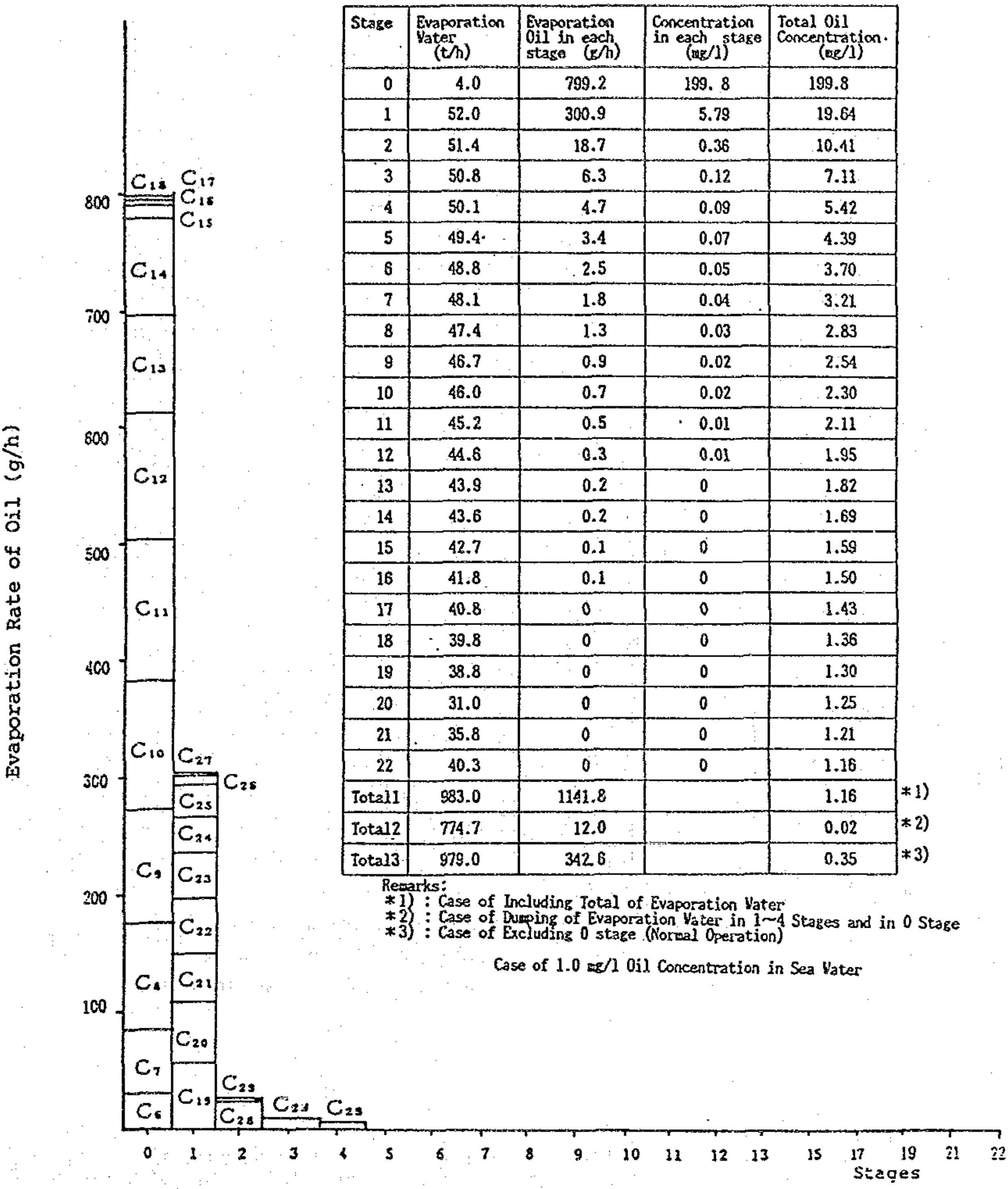
Fig. 4.2.4 (6): Evaporation Rate of Oil at Each Evaporation Stage

Contractor: SK-MHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)	
0	4.0	799.2	199. 8	199.8	
1	52.0	300.9	5.79	19.64	
2	51.4	18.7	0.36	10.41	
3	50.8	6.3	0.12	7.11	
4	50.1	4.7	0.09	5.42	
5	49.4	3.4	0.07	4.39	
6	48.8	2.5	0.05	3.70	
7	48.1	1.8	0.04	3.21	
8	47.4	1.3	0.03	2.83	
9	46.7	0.9	0.02	2.54	
10	46.0	0.7	0.02	2.30	
11	45.2	0.5	0.01	2.11	
12	44.6	0.3	0.01	1.95	
13	43.9	0.2	0	1.82	
14	43.6	0.2	0	1.69	
15	42.7	0.1	0	1.59	
16	41.8	0.1	0	1.50	
17	40.8	0	0	1.43	
18	39.8	0	0	1.36	
19	38.8	0	0	1.30	
20	31.0	0	0	1.25	
21	35.8	0	0	1.21	
22	40.3	0	0	1.16	
Total1	983.0	1141.8		1.16	*1)
Total2	774.7	12.0		0.02	*2)
Total3	979.0	342.6		0.35	*3)

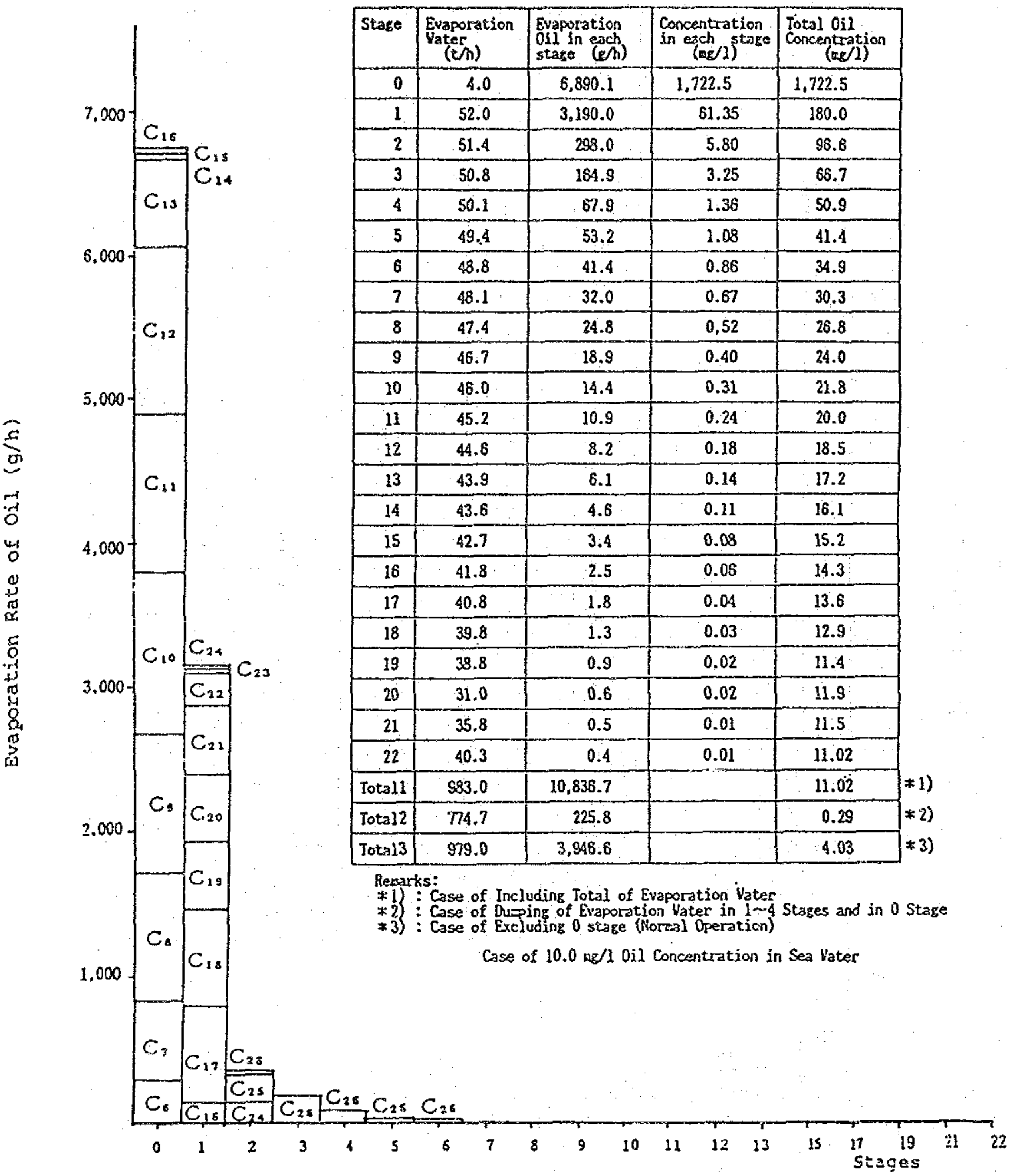
Remarks:
*1) : Case of Including Total of Evaporation Water
*2) : Case of Dumping of Evaporation Water in 1~4 Stages and in 0 Stage
*3) : Case of Excluding 0 stage (Normal Operation)

Case of 1.0 mg/l Oil Concentration in Sea Water



Case of 1.0 mg/l Oil Concentration in Sea Water

Fig. 4.2.4 (7): Evaporation Rate of Oil at Each Evaporation Stage



Contractor: SK-MHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)	
0	4.0	6,890.1	1,722.5	1,722.5	
1	52.0	3,190.0	61.35	180.0	
2	51.4	298.0	5.80	96.6	
3	50.8	164.9	3.25	66.7	
4	50.1	67.9	1.36	50.9	
5	49.4	53.2	1.08	41.4	
6	48.8	41.4	0.86	34.9	
7	48.1	32.0	0.67	30.3	
8	47.4	24.8	0,52	26.8	
9	46.7	18.9	0.40	24.0	
10	46.0	14.4	0.31	21.8	
11	45.2	10.9	0.24	20.0	
12	44.6	8.2	0.18	18.5	
13	43.9	6.1	0.14	17.2	
14	43.6	4.6	0.11	16.1	
15	42.7	3.4	0.08	15.2	
16	41.8	2.5	0.06	14.3	
17	40.8	1.8	0.04	13.6	
18	39.8	1.3	0.03	12.9	
19	38.8	0.9	0.02	11.4	
20	31.0	0.6	0.02	11.9	
21	35.8	0.5	0.01	11.5	
22	40.3	0.4	0.01	11.02	
Total1	983.0	10,836.7		11.02	*1)
Total2	774.7	225.8		0.29	*2)
Total3	979.0	3,946.6		4.03	*3)

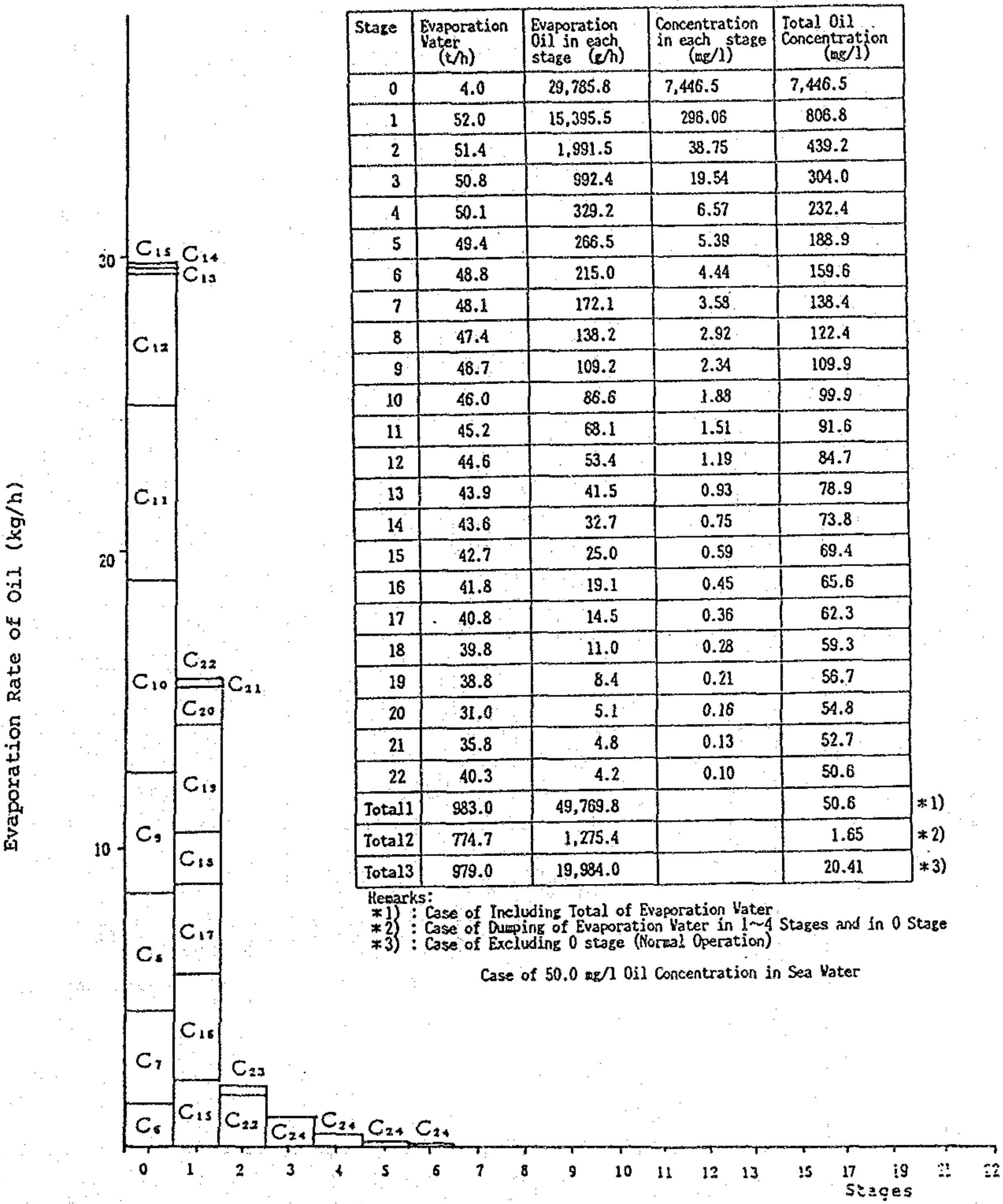
Remarks:
*1) : Case of Including Total of Evaporation Water
*2) : Case of Dumping of Evaporation Water in 1~4 Stages and in 0 Stage
*3) : Case of Excluding 0 stage (Normal Operation)

Case of 10.0 mg/l Oil Concentration in Sea Water

Case of 10 mg/l Oil Concentration in Sea Water

Fig. 4.2.4 (8): Evaporation Rate of Oil at Each Evaporation Stage

Contractor: SK-MHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h



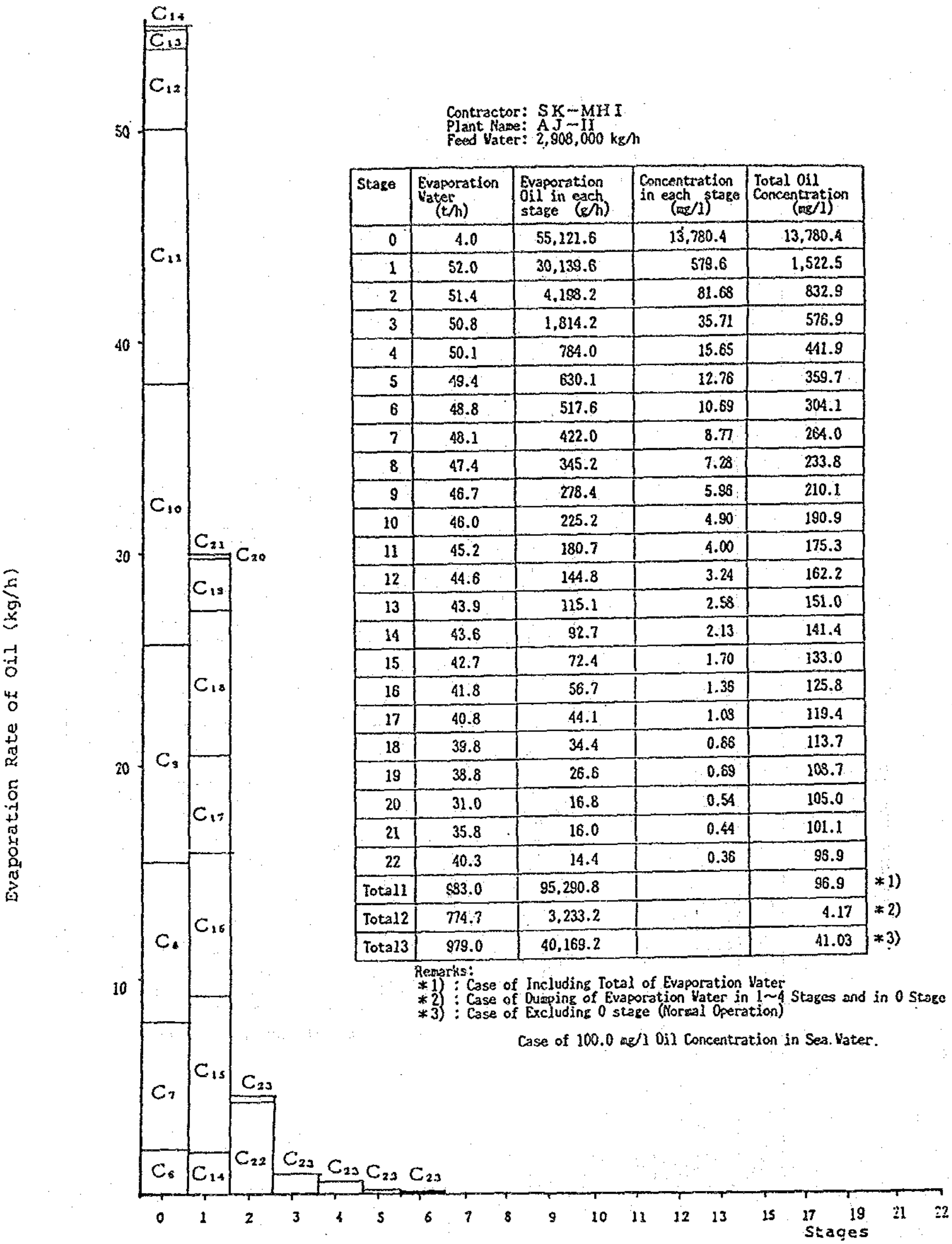
Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)	
0	4.0	29,785.8	7,446.5	7,446.5	
1	52.0	15,395.5	296.06	806.8	
2	51.4	1,991.5	38.75	439.2	
3	50.8	992.4	19.54	304.0	
4	50.1	329.2	6.57	232.4	
5	49.4	266.5	5.39	188.9	
6	48.8	215.0	4.44	159.6	
7	48.1	172.1	3.58	138.4	
8	47.4	138.2	2.92	122.4	
9	46.7	109.2	2.34	109.9	
10	46.0	86.6	1.88	99.9	
11	45.2	68.1	1.51	91.6	
12	44.6	53.4	1.19	84.7	
13	43.9	41.5	0.93	78.9	
14	43.6	32.7	0.75	73.8	
15	42.7	25.0	0.59	69.4	
16	41.8	19.1	0.45	65.6	
17	40.8	14.5	0.36	62.3	
18	39.8	11.0	0.28	59.3	
19	38.8	8.4	0.21	56.7	
20	31.0	5.1	0.16	54.8	
21	35.8	4.8	0.13	52.7	
22	40.3	4.2	0.10	50.6	
Total1	983.0	49,769.8		50.6	*1)
Total2	774.7	1,275.4		1.65	*2)
Total3	979.0	19,984.0		20.41	*3)

Remarks:
*1) : Case of Including Total of Evaporation Water
*2) : Case of Dumping of Evaporation Water in 1~4 Stages and in 0 Stage
*3) : Case of Excluding 0 stage (Normal Operation)

Case of 50.0 mg/l Oil Concentration in Sea Water

Case of 50 mg/l Oil Concentration in Sea Water

Fig. 4.2.4 (9): Evaporation Rate of Oil at Each Evaporation Stage



Contractor: SK-MHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)	
0	4.0	55,121.6	13,780.4	13,780.4	
1	52.0	30,139.6	579.6	1,522.5	
2	51.4	4,198.2	81.68	832.9	
3	50.8	1,814.2	35.71	576.9	
4	50.1	784.0	15.65	441.9	
5	49.4	630.1	12.76	359.7	
6	48.8	517.6	10.69	304.1	
7	48.1	422.0	8.77	264.0	
8	47.4	345.2	7.28	233.8	
9	46.7	278.4	5.96	210.1	
10	46.0	225.2	4.90	190.9	
11	45.2	180.7	4.00	175.3	
12	44.6	144.8	3.24	162.2	
13	43.9	115.1	2.58	151.0	
14	43.6	92.7	2.13	141.4	
15	42.7	72.4	1.70	133.0	
16	41.8	56.7	1.36	125.8	
17	40.8	44.1	1.08	119.4	
18	39.8	34.4	0.86	113.7	
19	38.8	26.6	0.69	108.7	
20	31.0	16.8	0.54	105.0	
21	35.8	16.0	0.44	101.1	
22	40.3	14.4	0.36	96.9	
Total1	983.0	95,290.8		96.9	*1)
Total2	774.7	3,233.2		4.17	*2)
Total3	979.0	40,169.2		41.03	*3)

Remarks:
*1) : Case of Including Total of Evaporation Water
*2) : Case of Dumping of Evaporation Water in 1~4 Stages and in 0 Stage
*3) : Case of Excluding 0 stage (Normal Operation)

Case of 100.0 mg/l Oil Concentration in Sea Water.

Case of 100 mg/l Oil Concentration in Sea Water

Fig. 4.2.4 (10): Evaporation Rate of Oil at Each Evaporation Stage

Table 4.2.2 (1): Evaporation Rate of Oil at Each Evaporation Stage
Case of 0.1 mg/l Oil Concentration in Sea Water
Contractor: IHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
0	4.0	96.1	24.03	24.03
1	59.84	30.7	0.51	1.99
2	59.84	0	0	1.03
3	59.84	0	0	0.69
4	59.84	0	0	0.52
5	54.40	0	0	0.43
6	57.12	0	0	0.36
7	54.40	0	0	0.31
8	51.68	0	0	0.28
9	54.40	0	0	0.25
10	48.96	0	0	0.22
11	51.68	0	0	0.21
12	48.96	0	0	0.19
13	46.24	0	0	0.18
14	43.52	0	0	0.17
15	43.52	0	0	0.16
16	46.24	0	0	0.15
17	43.52	0	0	0.14
18	46.24	0	0	0.13
19	48.96	0	0	0.12
Total1	983.2	126.8		0.12
Total2	739.8	0		0
Total3	979.2	30.7		0.03

Table 4.2.2 (2): Evaporation Rate of Oil at Each Evaporation Stage
Case of 1.0 mg/l Oil Concentration in Sea Water
Contractor: IHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
0	4.0	799.2	199.8	199.8
1	59.84	301.8	5.04	17.25
2	59.84	21.4	0.36	9.08
3	59.84	6.9	0.12	6.15
4	59.84	5.0	0.08	4.66
5	54.40	3.3	0.06	3.82
6	57.12	2.5	0.04	3.21
7	54.40	1.7	0.03	2.78
8	51.68	1.1	0.02	2.48
9	54.40	0.3	0.01	2.22
10	48.96	0.2	0	2.03
11	51.68	0.1	0	1.86
12	48.96	0.1	0	1.72
13	46.24	0.1	0	1.61
14	43.52	0	0	1.51
15	43.52	0	0	1.43
16	46.24	0	0	1.35
17	43.52	0	0	1.29
18	46.24	0	0	1.22
19	48.96	0	0	1.16
Total1	983.2	1,143.7		1.16
Total2	739.8	9.6		0.01
Total3	979.2	344.5		0.35

Table 4.2.2 (3): Evaporation Rate of Oil at Each Evaporation Stage
Case of 10.0 mg/l Oil Concentration in Sea Water
Contractor: IHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
0	4.0	6,890.1	1,722.5	1,722.5
1	59.84	3,196.3	53.4	158.0
2	59.84	296.4	4.95	83.95
3	59.84	137.6	2.30	57.32
4	59.84	74.1	1.24	43.53
5	54,40	52.3	0.96	35.75
6	57.12	41.8	0.73	30.12
7	54.40	30.4	0.56	26.20
8	51.68	21.8	0.42	23.30
9	54.40	17.3	0.32	20.87
10	48.96	11.5	0.23	19.08
11	51.68	9.1	0.18	17.50
12	48.96	2.9	0.06	16.21
13	46.24	1.5	0.03	15.16
14	43.52	1.1	0.03	14.29
15	43.52	0.7	0.02	13.51
16	46.24	0.5	0.01	12.77
17	43.52	0.3	0.01	12.15
18	46.24	0.2	0.01	11.54
19	48.96	0.2	0.01	10.96
Total1	983.2	10,786.3		10.96
Total2	739.8	191.8		0.26
Total3	979.2	3,896.2		3.97

Table 4.2.2 (4): Evaporation Rate of Oil at Each Evaporation Stage
Case of 50.0 mg/l Oil Concentration in Sea Water
Contractor: IHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
0	4.0	29,785.8	7,446.5	7,446.5
1	59.84	16,572.8	276.9	726.2
2	59.84	1,768.7	29.56	389.1
3	59.84	1,038.9	17.36	267.9
4	59.84	364.2	6.09	203.5
5	54.40	266.5	4.90	167.2
6	57.12	221.8	3.88	140.9
7	54.40	167.8	3.08	122.6
8	51.68	125.6	2.43	109.1
9	54.40	103.5	1.90	97.83
10	48.96	72.3	1.48	89.47
11	51.68	59.3	1.15	82.06
12	48.96	43.4	0.89	76.08
13	46.24	31.4	0.68	71.18
14	43.52	22.4	0.51	67.10
15	43.52	16.8	0.39	63.47
16	46.24	13.5	0.29	60.01
17	43.52	9.5	0.22	57.08
18	46.24	7.5	0.16	54.26
19	48.96	5.7	0.12	51.51
Total1	983.2	50,697.5		51.51
Total2	739.8	1,167.1		1.58
Total3	979.2	20,911.7		21.36

Table 4.2.2 (5): Evaporation Rate of Oil at Each Evaporation Stage
Case of 100.0 mg/l Oil Concentration in Sea Water
Contractor: IHI
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Total Oil Concentration (mg/l)
0	4.0	55,121.6	13,780.4	13,780.4
1	59.84	32,776.4	547.7	1,376.8
2	59.84	3,735.8	62.43	740.9
3	59.84	2,049.7	34.25	510.5
4	59.84	872.6	14.58	388.5
5	54.40	635.6	11.68	319.7
6	57.12	540.1	9.46	269.8
7	54.40	417.0	7.67	234.9
8	51.68	319.1	6.17	209.3
9	54.40	268.8	4.94	187.7
10	48.96	192.1	3.92	171.8
11	51.68	161.5	3.13	157.6
12	48.96	121.0	2.47	146.2
13	46.24	89.7	1.94	136.8
14	43.52	65.7	1.51	129.0
15	43.52	50.8	1.17	122.0
16	46.24	41.8	0.90	115.4
17	43.52	30.2	0.69	109.8
18	46.24	24.5	0.52	104.4
19	48.96	19.3	0.39	99.1
Total1	983.2	97,533.4		99.1
Total2	739.8	2,977.3		4.0
Total3	979.2	42,411.8		43.31

Table 4.2.2 (6): Evaporation Rate of Oil at Each Evaporation Stage
Case of 0.1 mg/l Oil Concentration in Sea Water
Contractor: HZ
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Oil Concentration (mg/l)
0	3.00	95.4	31.80	31.80
1	48.36	29.8	0.62	2.44
2	48.96	0	0	1.25
3	48.78	0	0	0.84
4	48.66	0	0	0.63
5	48.30	0	0	0.51
6	47.88	0	0	0.43
7	47.58	0	0	0.37
8	47.16	0	0	0.32
9	46.74	0	0	0.29
10	46.32	0	0	0.26
11	45.90	0	0	0.24
12	44.46	0	0	0.22
13	45.00	0	0	0.20
14	44.52	0	0	0.19
15	44.10	0	0	0.18
16	43.56	0	0	0.17
17	43.08	0	0	0.16
18	39.66	0	0	0.15
19	36.60	0	0	0.14
20	27.42	0	0	0.14
21	39.60	0	0	0.13
22	46.80	0	0	0.13
Total1	982.44	125.2		0.13
Total2	784.68	0		0
Total3	979.44	29.8		0.03

Table 4.2.2 (7): Evaporation Rate of Oil at Each Evaporation Stage
Case of 1.0 mg/l Oil Concentration in Sea Water
Contractor: HZ
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Oil Concentration (mg/l)
0	3.00	795.3	265.1	265.1
1	48.36	299.4	6.19	21.31
2	48.96	17.2	0.35	11.08
3	48.78	9.8	0.20	7.52
4	48.66	5.3	0.11	5.70
5	48.30	2.3	0.04	4.59
6	47.88	1.7	0.03	3.85
7	47.58	1.2	0.03	3.32
8	47.16	0.9	0.02	2.92
9	46.74	0.6	0.01	2.60
10	46.32	0.4	0.01	2.35
11	45.90	0.3	0.0	2.15
12	44.46	0.2	0.0	1.98
13	45.00	0.2	0.0	1.84
14	44.52	0.1	0.0	1.72
15	44.10	0.1	0.0	1.61
16	43.56	0.0	0.0	1.51
17	43.08	0.0	0.0	1.43
18	39.66	0.0	0.0	1.36
19	36.60	0.0	0.0	1.31
20	27.42	0.0	0.0	1.27
21	39.60	0.0	0.0	1.21
22	46.80	0.0	0.0	1.16
Total1	979.44	1,136.0		1.16
Total2	784.68	7.9		0.01
Total3	979.44	340.7		0.35

Table 4.2.2 (8): Evaporation Rate of Oil at Each Evaporation Stage
Case of 10.0 mg/l Oil Concentration in Sea Water
Contractor: HZ
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Oil Concentration (mg/l)
0	3.00	6724.1	2,241.4	2,241.4
1	48.38	3361.0	69.5	196.4
2	48.96	246.3	5.03	103.0
3	48.78	118.5	2.43	70.09
4	48.66	95.4	1.96	53.32
5	48.30	46.4	0.96	43.05
6	47.88	29.6	0.62	36.13
7	47.58	23.0	0.48	31.17
8	47.16	17.7	0.38	27.43
9	46.74	13.5	0.29	24.52
10	46.32	10.2	0.22	22.18
11	45.90	7.7	0.17	20.27
12	44.46	5.6	0.16	18.70
13	45.00	4.2	0.09	17.34
14	44.52	3.1	0.07	16.18
15	44.10	2.3	0.05	15.17
16	43.56	1.6	0.04	14.29
17	43.08	1.7	0.03	13.52
18	39.66	0.8	0.02	12.87
19	36.60	0.5	0.01	12.33
20	27.42	0.3	0.01	11.96
21	39.60	0.3	0.01	11.45
22	46.80	0.2	0.01	10.90
Total1	982.44	10,713.5		10.90
Total2	784.68	168.2		0.21
Total3	979.44	3,989.4		4.07

Table 4.2.2 (9): Evaporation Rate of Oil at Each Evaporation Stage

Case of 50.0 mg/l Oil Concentration in Sea Water
Contractor: HZ
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Oil Concentration (mg/l)
0	3.00	28720.9	9,573.6	9,573.6
1	48.36	16117.9	333.3	873.0
2	48.96	1569.9	32.10	462.6
3	48.78	696.6	14.30	315.9
4	48.66	581.9	11.95	241.1
5	48.30	457.7	9.47	195.7
6	47.88	160.7	3.36	164.3
7	47.58	129.4	2.72	141.8
8	47.16	103.3	2.19	124.9
9	46.74	82.0	1.75	111.7
10	46.32	64.7	1.39	101.1
11	45.90	50.7	1.10	92.37
12	44.46	38.6	0.87	85.25
13	45.00	30.5	0.68	79.08
14	44.52	23.4	0.52	73.80
15	44.10	18.0	0.41	69.21
16	43.56	13.5	0.31	65.21
17	43.08	10.1	0.23	61.68
18	39.66	7.0	0.18	58.74
19	36.60	4.8	0.13	56.28
20	27.42	2.7	0.10	54.56
21	39.60	3.2	0.08	52.25
22	46.80	2.8	0.06	49.76
Total1	982.44	48,886.2		49.76
Total2	784.68	1,203.1		1.53
Total3	979.44	20,165.3		20.50

Table 4.2.2 (10): Evaporation Rate of Oil at Each Evaporation Stage

Case of 100.0 mg/l Oil Concentration in Sea Water
Contractor: HZ
Plant Name: AJ-II
Feed Water: 2,908,000 kg/h

Stage	Evaporation Water (t/h)	Evaporation Oil in each stage (g/h)	Concentration in each stage (mg/l)	Oil Concentration (mg/l)
0	3.00	54,243.9	18,081.3	18,081.3
1	48.36	32,223.8	666.3	1,683.6
2	48.96	3,566.4	72.84	897.5
3	48.78	1,393.9	28.56	613.2
4	48.66	1,180.4	24.25	468.3
5	48.30	984.5	20.37	380.4
6	47.88	396.5	8.28	319.8
7	47.58	325.4	6.84	276.2
8	47.16	264.9	5.62	243.3
9	46.74	214.5	4.59	217.7
10	46.32	172.8	3.73	197.1
11	45.90	138.4	3.02	180.2
12	44.46	107.7	2.42	166.4
13	45.00	87.0	1.94	154.4
14	44.52	68.4	1.54	144.1
15	44.10	53.7	1.22	135.2
16	43.56	41.4	0.95	127.4
17	43.08	32.0	0.74	120.5
18	39.66	22.8	0.57	114.8
19	36.60	16.2	0.44	109.9
20	27.42	9.4	0.34	106.6
21	39.60	11.3	0.29	102.1
22	46.80	10.1	0.22	97.27
Total1	982.44	95,565.5		97.27
Total2	784.68	2,957.1		3.77
Total3	979.44	41,341.6		42.21

4.2.3 Behavior of Dissolved Oil in Desalination Process (Single-Liquid Phase)

Crude oil can be regarded as a mixture of chemical compounds mainly comprised of hydrocarbons. Amongst these organic compounds, sea water contains high concentrations of benzene and toluene as shown in Fig. 4.2.3. and these help to preserve gas pressure and equilibrium. They are namely in the monoliquid phase.

The concentrations of benzene and toluene, in Kuwait crude oil, which includes both of these, are 800 mg/l and 3,300 mg/l respectively.

If it is assumed that 1 kg of sea water contains 100 mg/l of crude oil, then the concentrations of Benzene and Toluene are:

80 µg (= 800 mg x 0.1 g/kg x 10^3 kg/g = 0.08 mg)
330 µg (=3,300 mg x 0.1 g/kg x 10^3 kg/g = 0.33 mg).

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 (4.2.3) as an example.

$$C = HP \tag{4.2.3}$$

Where,

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

Dissolution and evaporation of volatile oil such as benzene and Toluene can be assumed to follow this law. Table 4.2.3 indicates Henry's constants of volatile oil components to water and saline water, and Fig. 4.2.5 indicates the relations between the partial pressure and the concentration of the solution.

Table 4.2.3: Henry's Constants of Volatile Oil Components

(Unit: mol/kg atm)

Matters	Ionic Strength	Henry's Constants H		Remarks
		25 °C	40 °C	
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 *		* at 35 °C
Heptane		1.69×10^{-3}	2.24×10^{-4}	
Octane		1.85×10^{-4}		

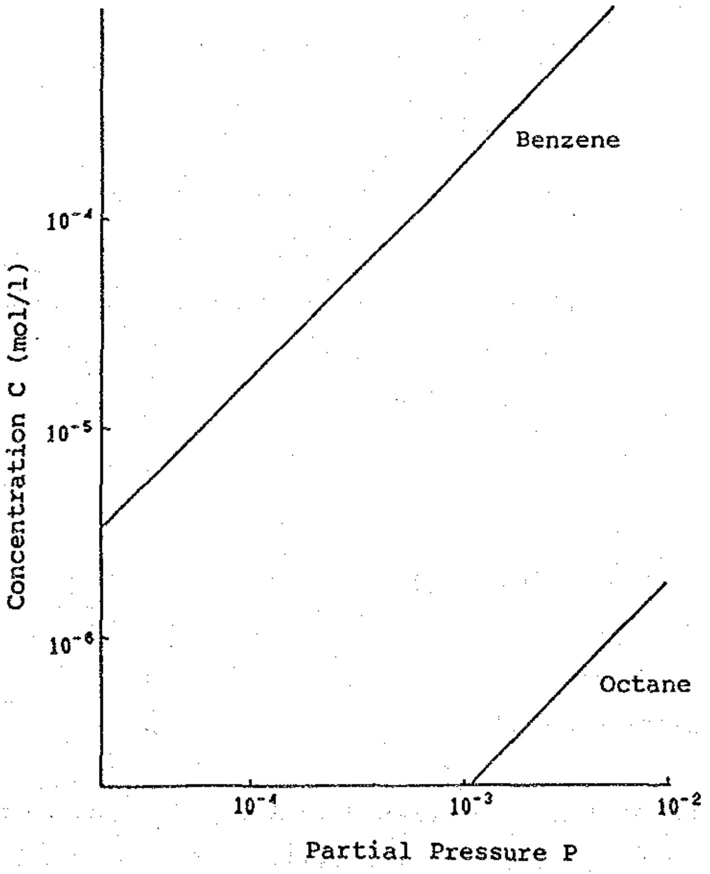
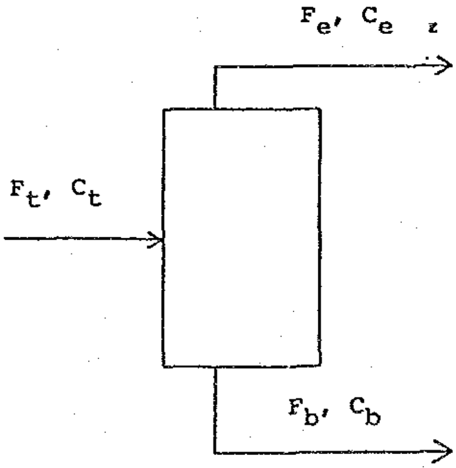


Fig. 4.2.5: Relations between Concentration C of Volatile Oil Components and Partial Pressure P

4.2.4 Study of Numerical Simulation (Single-Liquid Phase)

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 fresh water side and dissolved into the product water.



If each part in the above figure is substituted by the deaerator, evaporator, and condenser, Equations (4.2.3) and (4.2.4) can be effected.

$$F_t = F_b + F_e \tag{4.2.3}$$

$$F_t C_t = F_b C_b + F_e C_e \tag{4.2.4}$$

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 $R = F_e/F_t$ and the non-equilibrium condition will be defined as $Ne = C_b^*/C_b$ (<1).

Also, the distribution coefficient will be expressed by:

$C_e^*/C_b^* = m$

Where,

C^*: Concentration in equilibrium

Further, assuming $C_e = C_e^*$, then from Equation (4.2.4):

$$C_t = R\ m\ Ne\ C_b + (1 - R)\ C_b \qquad (4.2.5)$$

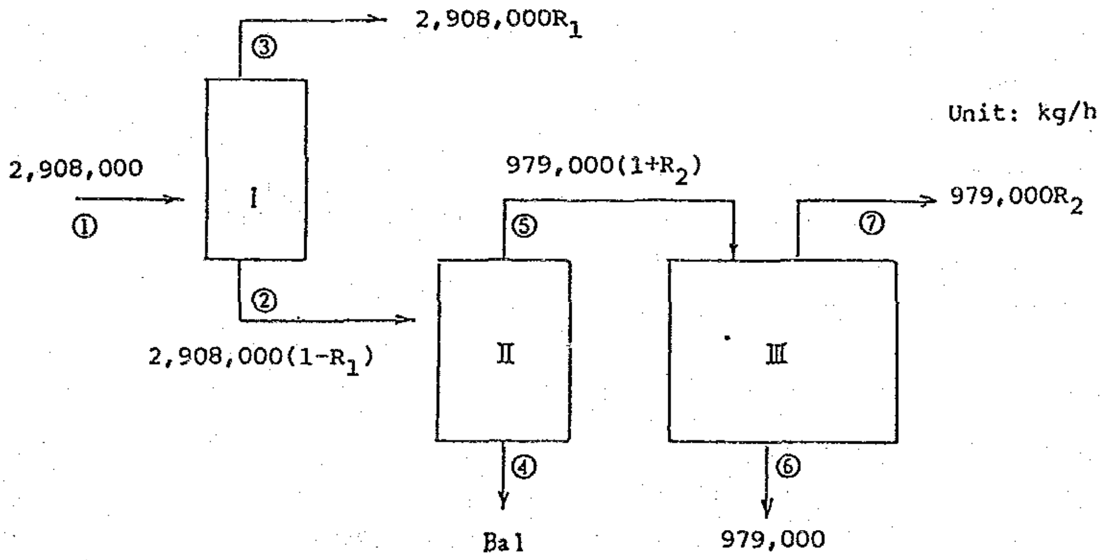
Therefore,

$$C_b = C_t/[R\ m\ Ne + (1 - R)] \qquad (4.2.6)$$

$$C_e = m\ Ne\ Ct/(R\ m\ Ne + 1 - R) \qquad (4.2.7)$$

Here, $m = C_e/C_b = 55.5/(H \cdot P_{WATER})$, and Ne is about 0.5 from actual data results.

On the other hand, as an example, the material balance of the model plants, AJ-II (quantity of product water 979 t/h), can be expressed by the Fig. 4.2.6.



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

Fig. 4.2.6: Typical Example of Material Balance in Model Plants

Also, if the inlet concentration, concentration of treated water, and concentration of evaporated gas at each of 1st, 2nd and 3rd stages 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 the 1st stage is the inlet concentration at the 2nd stage, the concentration of water vapor at the 2nd stage is the inlet concentration at the 3rd stage, and the treated water at the 3rd stage is product water, the concentration of water vapor at the 3rd stage is the inlet concentration of vent condenser, the concentration under the following conditions will be calculated.

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.

<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

<Evacuation rate>

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

<Concentration of chloride ion>

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

Brine: 1.021 mol/l (concentration ratio 1.395)

Soluble Oil Concentrations: Benzene 80 μg/l, Toluene 330 μg/l

The result of the calculation is shown in Table 4.2.4. As is clear from Table 4.2.4, 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. If the concentration of benzene in sea water at the inlet is 80 μg/l, 9.6 μg/l is transferred into the product water.

There are differences of benzene concentration in sea water system and water system, because salting-out effect is different and benzene solubility decreases in sea water system.

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 aliphatic hydrocarbon is volatilized in the deaerator as indicated in Table 4.2.4 and the final amount of concentration transferred to the product water can be ignored. Thus according to this result, the amount of transfer of volatile aliphatic 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- 144.4 °C, meta- 139.2 °C 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.

From the above, it is not necessary to consider the influence of aliphatic hydrocarbons on the product water. However, the WHO standards aromatic hydrocarbons such as benzene specifies the allowable concentration of benzene in drinking water to be as small as 10 μg/l, the utmost emphasis must be placed on countermeasures against benzene.

In this case, the concentration of benzene at the entrance of the pipe is 80 ppb and the water product concentration falls within the approved concentration of roughly 9.6 μg/l.

Consequently due consideration must be given to the removal of these aromatic hydrocarbons such as benzene from the product water.

Table 4.2.4: Distribution of Hydrocarbon Included in Oil-Polluted Sea Water for Each Part of MSF Plants (AJ-I, II)

System	Temp (°C)	Dea.Inlet (mg/l)	Dea.Outlet (mg/l)	Eva.Water (mg/l)	Pro.Water (mg/l)	Removal Rate(%)
Benzene/ Water	35	1.00	0.19	0.63	0.12	88
	35	0.08	0.0152	0.0504	0.0096	88
	50	0.08	0.0152	0.0504	0.0096	88
	60	0.08	0.0152	0.0504	0.0096	88
	70	0.08	0.0152	0.0504	0.0104	87
	80	0.08	0.0152	0.0496	0.0104	87
Benzene/ Sea Water	35	0.08	0.0112	0.036	0.0069	91.3
	50	0.08	0.0112	0.036	0.0074	90.7
Toluene/W.	35	0.33	0.059	0.211	0.0363	89
n-Octane/W	35	0.08*	$4*10^{-5}$	$1.44*10^{-4}$	$8.00*10^{-8}$	99.9
Ethylbenzene/Water	35	0.08*	0.0253	0.0773	0.0227	71.6

Note: Evacuation Rate=10^{-3}; * : Assumed Value

4.2.5 Estimation of Oil Components Found in Product Water

There are two numerical methods for calculating the oil components content transferred from the desalination plant sea water to product water in Sections 4.2.1. to 4.2.3. of which the simulations are shown below.

A: The case whereby oil and sea water do not dissolve but simply form a two-phase liquid mixture of hydrocarbon compounds.

B: The case whereby the hydrocarbons, which are mainly composed of aromatic compounds found in crude oil dissolve in sea water.

The results of the concentration of oil components found in the subject plant product water have been estimated and are shown in the following table.

1) The transfer amount of oil components to the product water in the above case A is shown in Table 4.2.5.

Table 4.2.5: Transfer Amount of Oil to Product Water

Plant Name	Concentration of Oil Components	mg/l	0.1	1.0	10.0	50.0	100.0
AJ-I	For Normal Operation	mg/l	0.12	1.09	10.15	48.85	91.29
	For Dumping the Product Water in Stages 1-4	mg/l	0.11	0.85	7.94	36.32	65.00
AJ-II	For Normal Operation	mg/l	0.03	0.35	4.03	20.41	41.03
	For Dumping the Product Water in Stages 1-4	mg/l	0.00	0.02	0.29	1.65	4.17

(Note:) At the AJ-II plant, the deaerator vents drain is dumped to the outside.

From the above results, even if the amount transferred to the product water, for the 100 mg/l crude oil mixed at the plant, is restricted to 5 mg/l, at the AJ-II plant. This can be achieved by dumping the waste of the product water of the 1st to 4th stages to the outside together with the deaerator vent drain. However, at the AJ-I plant, that employs the final stage system, it is not very effective to dump the wastes of the product water.

2) The quality of the product water with oil components in the single liquid phase, in for example the case of crude oil mixed in 100 mg/l is about 10 ppb for benzene and 330 μg/l for toluene, and in the case of benzene these limits are approved by the WHO.

However, it is thought to fall within these limits due to the fact that it is similar to the example of 1) where the high temperature stage of the product water is dumped to the outside, but as far as this process is concerned there is need for further investigation.

3) The result of 1) is case that aliphatic compounds with carbon numbers greater than C_6 do not dissolve with water and exist in the two-liquid phase. However, in fact, sea water is partially soluble, and it is expected that this will be of great value.

4.2.6 Formation of Trihalomethane (THM) by Chlorination of Oil Contaminated Sea Water

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.

4.2.6.1 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) around the world.

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

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* "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 ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) follow.

$CHCl_3$: 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.

4.2.6.2 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) 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:

$$(THM) = 0.33\ (C)^{1.10}\ (Cl_2)^{0.27}\ (pH)^{1.59}\ (t)^{0.22} \qquad (4.2.8)$$

Where,

THM:	THM yield	(μg/l)
C:	Concentration of humic acid	(mg/l)
Cl2:	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, $CHCl_3$ (chloroform) decreases and $CHCl_2Br$, $CHClBr_2$, $CHBr_3$ 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 Br^- concentration of each reaction pH can be expressed in the following Equation:

$$(THM_{Br}) = K\ (Br^-)^{0.86} \qquad (4.2.9)$$

Where,

THM_{Br} : (μ mol)

Br^- : (μ mol)

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 Br^-, its formation mechanism should be such that 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.

$$HClO + Br^- \leftrightarrow HBrO + Cl^-, \quad ClO^- + Br^- \leftrightarrow BrO^- + Cl^-$$

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:

$$[THM] = 0.83 \times 10^{-3} (pH - 2.8) [C] [Cl^2]^{0.25} t^{0.35} \qquad (4.2.10)$$

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

---

(2) Reaction of Sea Water Containing Dissolved Oil with Chlorine

According to the laboratory experiments conducted by Ali [24)], 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 ($CHBr_3$), 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.

4.2.7 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.

4.2.7.1 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 4.2.6.2(1).

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

$$[THM] = k\,(pH - 2.8)\,(\text{humic acid})\,[\text{chlorine}]^{m}\,t^{n} \qquad (4.2.10)$$

$k = 0.83 \times 10^{-3}$

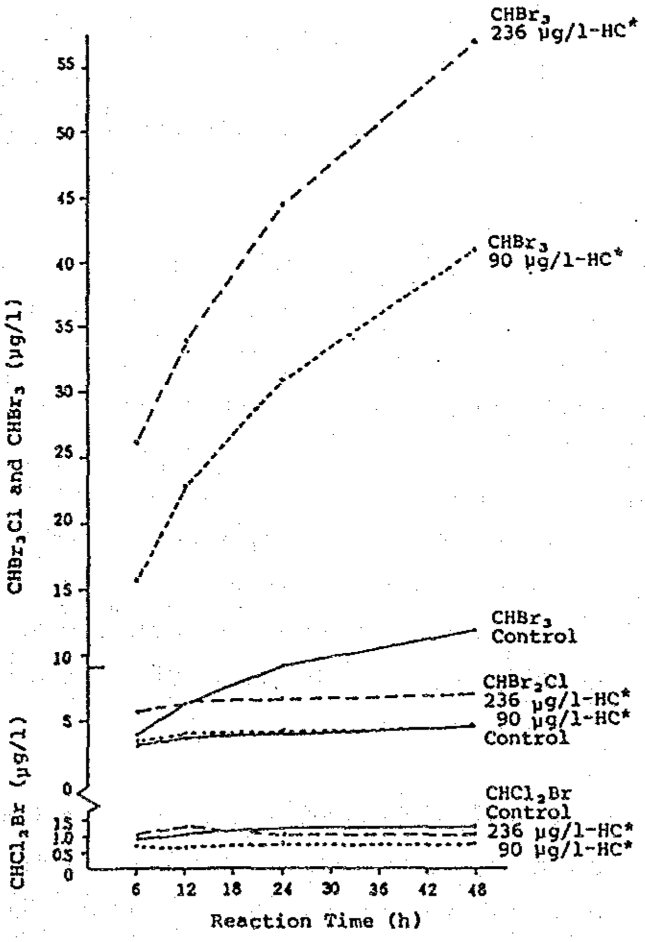
$m = 0.25$

$n = 0.35$

dibromochloromethane and a very small amount of bromodichloromethane. As shown in Fig. 4.2.7, 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.

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.



Note: * Dosing concentration of water soluble fractions (WSF)

Fig. 4.2.7: Sea Water Chlorination in Presence of Water Soluble Fractions from Kuwait Crude Oil

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 [43], the quantity of THM from at 50 °C became seven 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 reaction 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 rate becomes extremely fast and the production of THM (shown in Fig. 4.2.8) is believed to remain within the plant for up to three-minutes.

Fig. 4.2.9 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 4.2.6), 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.

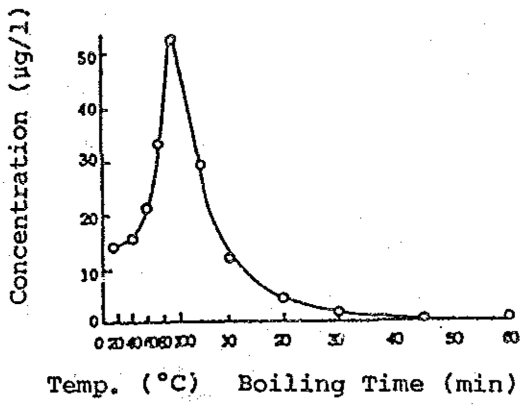


Fig. 4.2.8:
Chloroform Concentration by Boiling

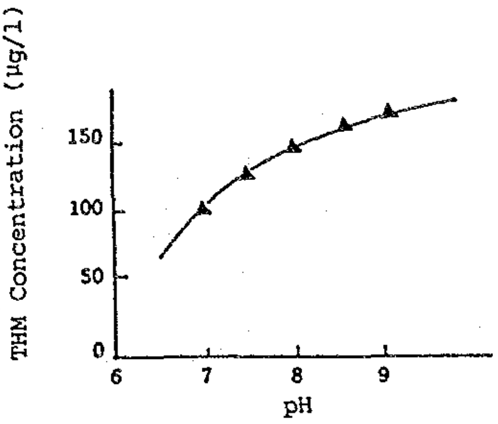


Fig. 4.2.9:
Effect of pH on THM Formation

Table 4.2.6: Effect of Reduction in pH on THM Formation

Procedure	THM (μg/l)
pH9.0; 5 mg/l; 1 h; quench	18.0
pH6.0; 5 mg/l; 1 h; quench	6.94
pH6.0; 5 mg/l; 1 h; pH 9.0;1 h; quench	10.1
pH6.0; 5 mg/l; 1 h; NH_3; pH 9.0	10.7

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

4.2.7.2 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 at 25 °C)
Chloroform	0.2937
Bromodichloromethane	0.4699
Dibromochloromethane	1.2755
Bromoform	1.860

Relations between THM concentration and partial pressure is shown in Fig. 4.2.10.

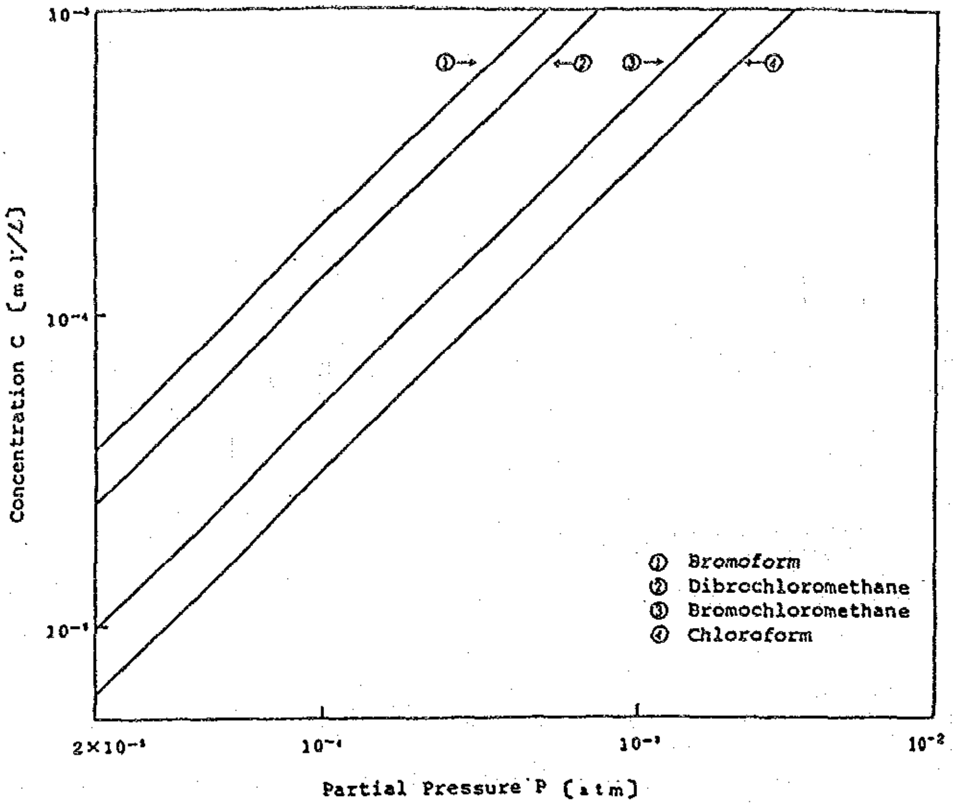


Fig. 4.2.10: Relations between THM Concentration and Partial Pressure

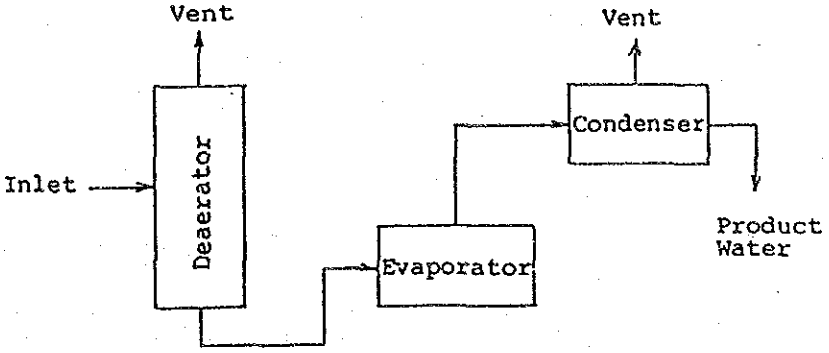
Fig. 4.2.7 illustrates the concentration of THM found in the oil-contaminated sea water that has been chlorinated, and Fig. 4.2.9 shows relations between the concentration of THM and pH value of sea water. Figs. 4.2.7 and 4.2.9 also show that the concentration of THM is estimated more than 50 µg/l in the oil contaminated sea water and it possibly reach to 100 µg/l in particular condition.

In the case that each 100 µg/l of chloroform or bromoform are contained in sea water, material balance of these kind of THM in MSF plant calculated by Equation (4.2.3) becomes as indicted in Table 4.2.7.

Table 4.2.7: Material Balance of THM in MSF Plant

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

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



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

4.2.7.3 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 precursor matters from a high molecular compound having several thousands to several 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 any oxide product in crude oil becomes a precursor matter of THM. 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 (4.2.3) for the case where 10 mg/l acetone is mixed into sea water, the result will be as indicated in Table 4.2.8. 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 4.2.8: Material Balance of Acetone in MSF Plant

Phase	Temp. (°C)	Deaerator Inlet (mg/l)	Deaerator Outlet (mg/l)	Evaporation Water (mg/l)	Product Water (mg/l)
Acetone/Water	35	10	9.6	30	28.7

4.2.8 Conclusion

Influence on the quality of product water, due to oil contaminated sea water in the desalination plants, is discussed. The results are as follows.

(1). The amount of transfer of oil components to the product water in the case whereby oil and sea water do not dissolve in water is shown in the table below.

Plant Name	Concentration of Oil Components	mg/l	0.1	1.0	10.0	50.0	100.0
AJ-I	For Normal Operation	mg/l	0.12	1.09	10.15	48.85	91.29
	For Dumping the Product Water in Stages 1-4	mg/l	0.11	0.85	7.94	36.32	65.00
AJ-II	For Normal Operation	mg/l	0.03	0.35	4.03	20.41	41.03
	For Dumping the Product Water in Stages 1-4	mg/l	0.00	0.02	0.29	1.65	4.17

(Note:) At the AJ-II plant, the deaerator vents drain is dumped to the outside.

(2) At the Al Jubail Phase I, which employs a final stage deaeration system, dumping the waste from product water in Stages 1-4 is not effective.

(3) When crude oil of 100 mg/l is mixed in with the sea water, benzene transferred to product water by MSF is estimated to be approximately 10 μg/l, a level approved by WHO as a drinking water quality limit. Also, toluene is estimated to be approximately 36 μg/l.

(4) When THM is found in the oil mixture, it is estimated that 100 μg/l each of chloroform and bromoform is contained in chlorinated sea water. The reduction rate of THM in the deaerator is 20 to 60 % and cannot be completely removed. Also, 45 μg/l of chloroform and 202 μg/l of bromoform are intermixed in product water.

APPENDIX M4—2

APPENDIX M4-2

ABSTRACT OF LITERATURE SURVEYED

1. Noriaki Nakazawa,Takeshi Sato,Kenzaburo Obata,Teiji Okubo,Toshikatu Hakuta, 'Behavior of Oily Pollutants in Sea Water Distillation Process',Bulletin of the Society of Sea Water Sience,Japan,vol.39,no.1,p.32(1985)

Fundamental reseaches were conducted in order to obtain basic data which were necessitated to investigate quantitatively the possibilities of oil contamination of the product water of distillation type sea water desalination plant when oil entered into the feed water for the plant.

A simple distillation apparatus used for experiments was composed of a distillation flask(1 L),a condenser and a sampling cell;these were made of glass. Electrical heatings(mantle heater or ribbon heater) were used for boiling.

Samples used for tests were mixtures of 700ml water and 10ml oil. When sea water was used as water,seven kinds of oil such as crude oil, grade A heavy oil,grade B heavy oil,grade C heavy oil,light oil,kerosene and p-xylene were used as oil respectively. When distilled water was used as water ,seven kinds of hydrocarbons such as p-xylene,n-hexane,cycro-hexane,n-octane, toluene and benzene were used as oil component respectively.

Experiments were carried out under an atmospheric pressure,and continued untill all oil components were distilled out or distillation temperature exceeded 100℃. Volume of distillates collected in sampling cell were determined with the eye.

Results were as follows.

No difference was observed between the results for sea water and distilled water when p-xylene was used as oil component.

A calculation method was described to determine the weight ratio of water and oil component in distillate by the equiliblium calculation for simple steam distillation of a single oil component.

Experiment results were well agreed with the calculated values for the case of toluene,cycro-hexane,benzene,n-octane and n-xylene as oil component. For the case of kerosene,light oil,A-heavy oil,B-heavy oil,C-heavy oil and crude oil,only distillation curve data for simple distillation were shown.

Lastly,a calculation method of the distillate compositions for the case of multi-components steam distillation was gigen on the assumption of an adeal solution.

2. Sigeki Toyama,Hidetosi Mori,Shuzo Yamada,Yoshinori Matuda,"Deposition and Removing Mechanisms of Oil Droplets Contained in Liquid Flow at Solid Surfaces",Bulletin of the Society of Sea Water Sience,Japan,vol.38,no.3,p.148 (1984)

Deposition of droplets at solid surfaces and removal of the deposited film by attrition of glass beads were studies to provide countermeasure toward fouling.

The droplets began to discretely deposit and gradually grow untill the equilibrium state was made by repeating coaguration and separation,while the rate of deposition was considerably unstable in the initial stage.

The equilibrium amount of deposition was evidently dependent on the velocity of flow and the material of the surface.

In the experiment of removing foul,attrition rates of initially coated paraffin were measured by charging glass beads.The rate was linearly proportional to beads concentration and proportional in 2.5 power to the velocity of beads.

3. Lt.David J.Kruth,Edward Overton,John Murphy,"Protecting an Island's Drinking Water and Desalination Plant",Proceedings of the 1987 Oil Spill Conference, American Petroleum Institute,Washington,D.C.,p.49

On February 6,1986,the barge St.Thomas struck a submerged pilling in Crown Bay,St.Thomas,U.S.Virgin Islands.It is estimated that up to 70,000 gallons of an intermediate oil were spilled from both this initial incident and a secondary spill which occurred the following day in Charlotte Amalie Harbor. The spilled oil threatened the iland's primary source of drinking water :the desalination plant. St.Thomas' only alternative source of fresh water is rain water collected in cistern. Due to it's limitted supply,potable drinking water is a precious commodity in the Caribbean Islands,and protection of the desalination plant became a crucial part of the spill response.

When officials in charge of the desalination plant believed that oil had entered the plant's intakes,they shut down the desalination plant. Residents were warned by local officials not to drink the water to avoid serious health effects. The island's hospital feared their water supply had become contaminated and began using emergency bottled water. The Commissioner of Public Works reported that the island had less than four days of water remaining in storage.

This paper discusses how the contaminated drinking water problem was resolved. Details are provided about the sampling methods and chemical analysis used in determining the water quality. Possible effects of oil on the two most common types of desalination plants are adressed. Monitoring and protection techniques for oil spill are suggested for these desalination plants. Finally,check list is provided for oil spills which threaten desalination plants.

4. J.A.Nichols,H.D.Parker,"Effects of Oil Pollution on Industrial Water Intakes" ,Proceedings of the 1989 Oil Spill Conference,p.473(1989)

Oil spills in coastral waters sometimes give rise to concerns that oil may become entrained in the sea water intakes of power stations,desalination units and other industrial plants. This paper reviews the findings of an investigation,undertaken by the International Tanker Owners Pollution Federation and Sir M.MacDonald & Partners,on the effects of oil pollution on water-cooled electricity-generation stations and desalination plants using multistage flash distillation and reverse osmosis. The various components that could be contaminated by oil are described and,using case studies wherever possible,the effects on equipment,heat transfer surfaces,and potable

water are discussed.
Then considered are various methods of minimizing the impact of oil and financial implications of oil contamination for the difference types of industrial plant.

Useful informations contained are as follows.

Sponge ball tube cleaning methods were effectively used in order to remove oil from fouled condenser tubes at several power stations when their cooling water were contaminated with heavy oil. But,combinated use of a solvent or frequent replacement of the oiled balls were necessitated.

As to the considerations on the effects of oil pollution of the feed water on the product quality of an MSF evaporator,calculation results for the transfer rates of hydrocarbons from the feed water to the distillate were given (concentrations of hydrocarbons in distillate of an MSF distillation plant with 1mg/L feed concentration were ploted as a function of boiling points). But any calculation method or calculation base was not shown.

Finally,comparison of costs of the effects of an oil spill with costs of preventable measures for a power station ,multistage flash distillation unit and reverse osmosis desalination plant was presented.

5. C.Plass,R.Koppmann,J.Rudolph,"Measurements of dissolved nonmethane hydrocarbons in sea water",Fresenius' Journal of Analytical Chemistry,vol.329, no.10,p.746(1991)

An automated stripping technique for the measurement of dissolved hydrocarbons in sea water is presented together with some results obtained during a ship cruise from Europe to Brazil.

The sea water concentrations of NMHC were determined in a three step process :degassing,preconcentration,and gas chromatographic analysis. In a stripping chamber the dissolved gases were purged from sea water with helium.
The stripped hydrocarbons were cryogenically concentrated,and after thermal desorption they were injected into the gas chromatograph. The light fraction

(C_2-C_4)was separated on a packed column and heavy fraction(C_5-C_{10}) on a capillary column. All valves were microprocessor controlled in order to achieve an automated process.

For the C_2-C_4 hydrocarbons the stripping efficiencies exceeded 90% except for acetylene(80%),the lower limit of detection was 1 to 4.5 pmol hydrocarbon per liter of sea water(0.045ppt for ethane, 0.104ppt for butane ,and etc.) and the accuracy of the method was better than 25%,depending on the individual hydrocarbons.

Typical oceanic concentrations were in the 10 and 100 pmol/l range. Alkenes were generally more abundant than the corresponding alkanes and within the homologous series the concentrations decreased with increasing number of carbon atoms.

6. Va Lawford,M.Morgan,P.Vessey,Jeg Wheaton,"An optical system for detection and measurement of hydrocarbon in the ocean",Proceedings of SPIE International Society of Optical Engineering,vol.1269 Environment and Pollution Measurement Sensors and Systems,p.158(1990)

Ultraviolet fluorescence spectroscopy is now widely used in surveys and monitoring studies for the determination of hydrocarbon concentrations in seawater. This paper describes a high sensitivity in-situ ultraviolet fluorimeter,discusses calibration methods and illustrates some applications.

The major use of the UVF is the detection of oil and similar hydrocarbons. It is difficult to produce standard solution of these materials for calibration. In the sea several different oils are usually present. So all calibrations were made using carbazole,a stable substance in solution,which has a very similar fluorescence fingerprint to oil. Good qualitative calibration is obtained by the use of carbazole.

7. C.D.McAuliffe,"Evaporation and Solution of C_2 to C_{10} Hydrocarbons from Crude Oils on the Sea Surface",Proceedings of a Symposium ,Fate and Effects of

Petroleum Hydrocarbons in Marine Ecosystems and Organisms 1976, D.A.Wofe, ed., National Oceanic and Atmospheric Administration, and Environmental Protection Agency, Seattle, p.363

Evaporation and solution of C_2 to C_{10} hydrocarbons were measured from four oceanic spills of two crude oils(24° and 39° API gravities).

Loss rate for these light hydrocarbons were in accordance with their vapor pressures. The trimethylbenzenes (C_9), the slowest of these to weather, were gone from the oil in 4 to 8 hrs.

C_2 to C_{10} hydrocarbons were found in the water under the oil slicks only during the first 30 min, in concentrations of 2 to 60 μg/l. Their relative concentrations indicated that they were residual hydrocarbons in dispersed oil droplets in the water column, and not in solution at the time of collection.

Oil discharged on a water surface is a nonequilibrium condition with respect to evaporation and solution. Hydrocarbons (alkanes, cycloalkanes, and aromatics) should dissolve from an oil slick in amounts related to their mole fraction in oil, and inversely proportional to their molecular weights. This was not observed, indicating that dissolved hydrocarbons quickly evaporated from the nearsurface waters.

The rates of loss of benzene and cyclohexane from the oils were the same. These hydrocarbons have similar vapor presures, but very different solubilities in water. This also suggests that loss by solution is minor, compared with evaporation.

These studies indicate that solution of hydrocarbons into the water column from crude oil slicks, followed by evaporation, resulted in immeasurably low concentrations (<1μg/l) of dissolved C_2 to C_{10} hydrocarbons 15 min after each spill.

8. Kevin D.Dix, "Gas Chromatographic Determination of Water in Organic Compounds and of Organic Compounds in Water after Steam Distillations", DOE Report IS-T--1477, Jan.1990

The first section is a gas chromatographic method for indirect determination of water in organic compounds using a flame ionization detector. A reaction of 2,2-dimethoxypropane with water is utilized and the amount of the product, acetone, is determined. The solid acid catalyst, Nafion, is used to give a reaction time of under 5 minutes.

The second section describes a sample preparation method for organic compounds in water. Simple steam distillation is shown to be useful for a large variety of compounds with vastly different functionalities and boiling points. Once the distillation is completed, a portion of the condensate is injected into a GC for separation and quantitative information. Many different boiling modifiers were examined with varying degrees of success.

The third and final section uses the distillation apparatus from section two, but also incorporates solid phase extraction (SPE) at the condensate collection step. A simple Teflon interface is described that allows for the determination of samples in the ppb range. The extracting resin is washed clean of analytes with an organic solvent and a portion of this wash is introduced into a gas chromatograph.

Details of the examinations described in the second section are as follows.

The aim of this section's work was to develop a method for the isolation of organic compounds from water-base dirty samples that contain large amounts of non-volatile components using distillation that was fast (under 25 minutes), effective for polar compounds like phenol, and achieved an appreciable concentration factor.

A 100ml distillation flask, a water cooled condenser and a 5ml volumetric flasks or 15ml graduated gravimetric tube were used for distillation experiments.

Test procedures were as follows.

Approximately 50ml of the purified water was added to the 100ml round bottom boiling flask. To this either 50 or 100μl of the appropriate test mixture was added via a disposable micro-pipet to make a 1ppm solution. This solution was

boiled and the distillate collected in either a 5ml volumetric flask or a 15ml gravimetric tube. The collection vessel was cooled in a water ice bath while it was being filled with distillate. In some cases,acetone was added to the vessel before boiling. The vessel containing the acetone was then cooled in an ice bath. After the distillation,a known volume of internal standard was added to the collection vessel and the vessel mixed. Immediately following,a portion of this solution was chromatographed. The peak areas of the components were compared to those of the internal standard and a ratio was calculated.
A reference solution was made up in a similar fashion using the same type of collection vessel and the same amount of test mixture that went through the distillation. Again,the internal standard was added and a ratio of the peak areas was computed for each component.The recovery percentages were obtained by comparison of the ratio of the two solutions.

The survey mixture of ten organic compounds with functional groups (boiling point:136°C～222°C) was added to 50ml of water and the solution was boiled. The results show good recoveries (>90%) for several of the compounds but low recoveries of the alkylbenzenes and halogenated benzenes. There are two reasons why the recoveries are low for these two types of compounds. First,the compounds may not be boiled out of the boiling flask. Second,the compounds are not being condensed.

In order to investigate the reason for low recoveries,tests of helium gas purging through the distillation,adding a large amount of a salt to the aqueous sample and adding a small amount of various organic solvents were carried out.

As the results of above mentioned tests,it appeared that all compounds in the survey mixture were being distilled but some were not being effectivery condensed. Therefore,the tapered adapter was placed on the end of the condenser. The adapter tip was placed into 1ml of cold acetone in the receiver. This forces any non-condensed material to be bubbled through the acetone and be trapped. Acetone is miscible with water and does not interfere with gas chromatographic separation of the sample compounds.Most compounds were recovered near 100% with this simple modification.

All experiments above were carried out with amoderate amount of heat applied from a heating mantle to the boiling flask. The boiling time required to collect 5ml of distillate is 20-22 minutes. This time can be reduced by applying more heat to the flask,adding boiling chips with a large surface area,and insurating the top of the boiling flask. The distillate was collected in cold acetone. Excellent recoveries are obtained and the time to collect 5ml of distillate becomes only 12 minutes.