



WEATHERING OF OIL SPILLS IN ICY SEAWATER AND CHARACTERISTICS OF CRUDE OIL WHICH TRAPPED INTO ICE FLOE

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ABSTRACT

The experiment on weathering of crude oil in low temperature and on characteristics of crude oil which spilled under an ice sheet were carried out. From these experimental results, evaporation rate, density and viscosity increase, and the characteristics of crude oil which trapped into an ice sheet were discussed.

1. INTRODUCTION

Exploration projects for crude oil and natural gas are currently in progress on the continental shelf in the Sea of Okhotsk off the northeast coast of Sakhalin. These exploration projects, known as Sakhalin I and II projects, are expected to yield crude oil in 2001 and 1999, respectively (Fig. 1). (Kuang and Wang, 1995)

Many oil spills have occurred since offshore oil drilling projects began. There have also been many oil spills from tankers in recent years. The main causes of these oil spills have been fires due to explosions or operational errors, damage to underwater pipelines, tanker accidents, and damage to oil rigs. In recent years, most oil spills have been due to tanker accidents.

The strong Sakhalin Current off the eastern coast of Sakhalin flows south along the Okhotsk coastline of Hokkaido to Shiretoko Peninsula, and part of the current flows through Kunashiri and Nemuro straits into the Pacific Ocean (Fig. 2). Depending on the wind direction, the surface current sometimes flows through Soya Strait into the Japan Sea. In winter, the Sea of Okhotsk along the northeastern coastline of Hokkaido is covered with drift ice that flows south from Sakhalin. Most of the drift ice is trapped at Shiretoko Peninsula but some flows south through Kunashiri and Nemuro straits into the Pacific Ocean.

Oil exploration in the Sea of Okhotsk incurs a very high risk of spillage accidents due to the severe environmental conditions in that region. If a major oil spill was to occur off the eastern coast of Sakhalin, there is a high probability that the oil flow would extend to the coast of Hokkaido (Ohtsuka et al, 1998).

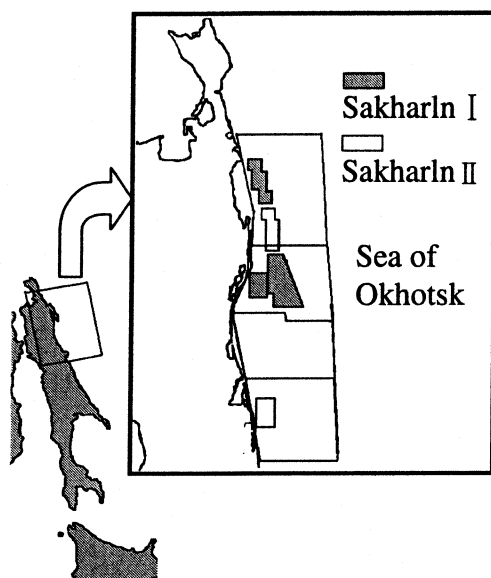


Figure 1. Oil exploration projects currently underway off the coast of Sakhalin

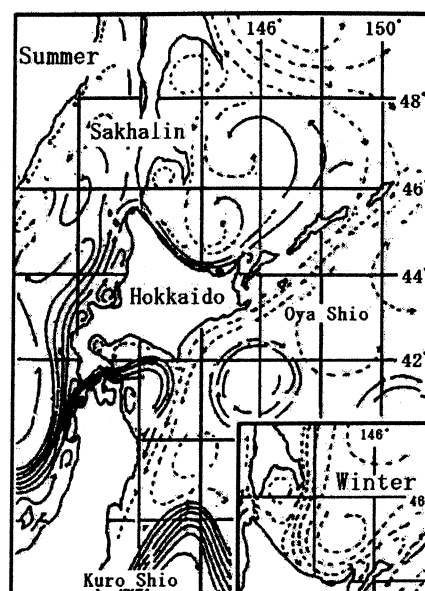


Figure 2. Currents in the Sea of Okhotsk

2. BACKGROUND AND OUTLINE OF RESERCH

2.1 Characteristics of an oil spill in sea covered by ice

In the event of an oil spill at sea, the oil first floats on the surface of the water due to the smaller density of oil, and the volatile components of the oil rapidly evaporate. The oil then undergoes a gradual process of hydration and emulsification due to the disturbance at the oil-water interface caused by the action of waves. The viscosity and specific gravity of the oil increase, and the oil is eventually transformed into a tarry asphalt or a tarry emulsion(mousse). If an oil spill were to occur in the Sea of Okhotsk in winter, the oil would either remain on or be trapped under the ice, or it may be trapped inside the ice. If the oil was trapped under the ice, the usual processes caused by weathering would not occur; there would be little evaporation of volatile matter since the oil would not be exposed to the atmosphere, and the processes of hydration and emulsification would be delayed because of the low temperature and the attenuation of waves due to the ice cover.

2.2 Weathering processes of crude oil under low temperature conditions

In the case of an oil spill at sea, the light-weight volatile components of oil first begin to evaporate, and the rate of evaporation increases as the oil spill spreads and a larger area becomes exposed to the atmosphere. Experiments were carried out to determine the weathering processes that an oil spill undergoes at very low temperatures in sea covered by ice.

3. EVAPORATION EXPERIMENTS

3.1 Method

Iranian light oil, which is similar in quality to crude oil obtained from the Sea of Okhotsk, was used in the experiments. Containers measuring 320mm × 280mm were each filled with 700ml of crude oil, and the amount of evaporation, viscosity, density and oil temperature were measured at determined time intervals. The mean thickness of the oil layer was 0.78cm. Experiments were carried out under low temperature and normal temperature conditions. For the low temperature experiment, the containers were kept in a low temperature room at about -2°C, while for the normal temperature experiment, the containers were kept outside and were sheltered from the wind.

3.2 Results

Figure 3 shows the changes in oil temperature over time in both the low and normal temperature experiments. The mean oil temperatures in the low and normal temperature experiments were 0.6°C and 20.6°C, respectively. The temporal changes in evaporation rate, calculated from the amounts of evaporation, are shown in Figure 4.

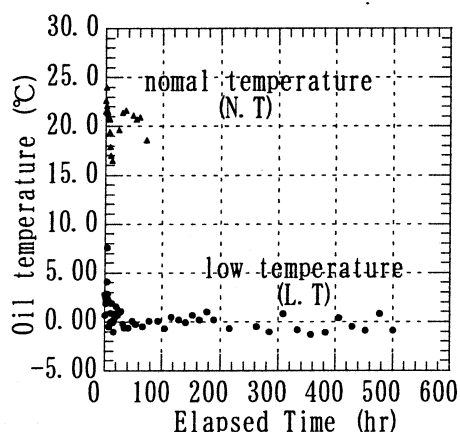


Figure 3. Changes in oil temperature

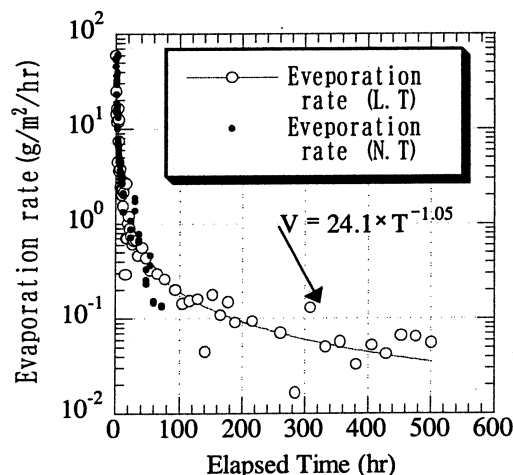


Figure 4. Temporal changes in evaporation rate

The evaporation rate peaked shortly after the start of the experiment and subsequently decreased rapidly, becoming constant at about 0.04g/m²/hr after 300hr. The evaporation rates were almost the same in both experiments. And the following relationship between the evaporation rate and elapsed time was obtained.

$$V = 24.1 \times T^{-1.05} \quad (1)$$

V ; evaporation rate (g/m²/hr), T ; elapsed time(hr)

Figure 5 shows the temporal changes in the percentage of evaporation. The evaporation percentage increased dramatically for the first 50hr after the start of evaporation, and then the

rate of increase gradually decreased. In the low temperature experiment, the evaporation percentage increased linearly from 300hr after the start of evaporation, and it is expected that evaporation would proceed slowly even after 600 hr. It is assumed that the light-weight volatile components in crude oil that have particularly strong volatility completely evaporate within 200~300hr after the start of evaporation. The percentage of evaporation at this stage is about 9.5%. It was therefore assumed that the percentage of highly volatile components in the crude oil used in the present experiments is about 9.5% and that the components that evaporate after this initial period are the remaining components that have relatively low volatility. The results of the present experiments also showed that about 80% of the volatile components had evaporated within the first 50 hr. The semi-logarithmic graph in Figure 6 shows that the evaporation percentage can be determined according to the elapsed time. The following relationship between evaporation percentage and elapsed time was obtained from the results of the present experiments:

$$Y = 3.0 + 3.0 \log T, \quad (2)$$

where Y is the evaporation percentage of crude oil (%) and T is the elapsed time (hours).

The results of the experiments clarified that 1) the evaporation of Iranian crude oil proceeds at almost the same rate under low and normal temperature conditions, 2) almost 80% of the evaporation is completed within 50 hours after exposure to the atmosphere, and 3) evaporation of the highly volatile components is completed within about 300 hours.

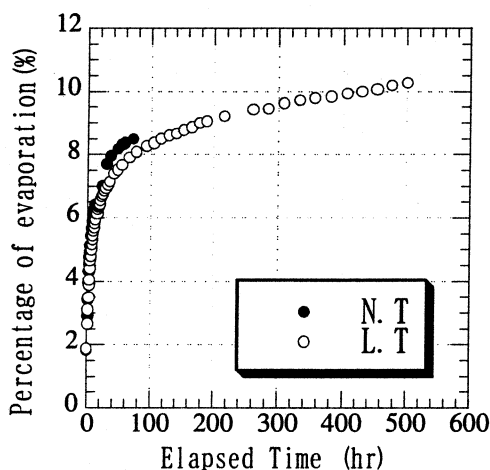


Figure 5. Temporal changes in the percentage of evaporation

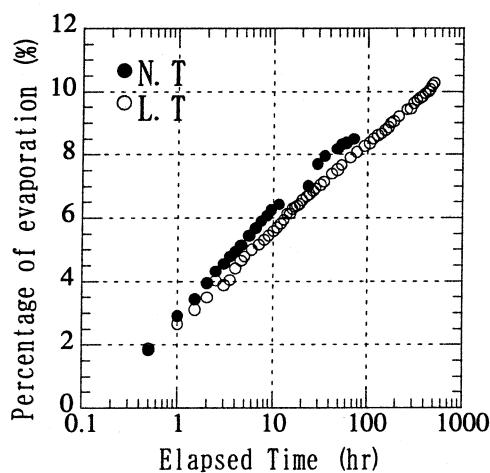


Figure 6. Temporal changes in the percentage of evaporation (semi-log graph)

3.3 Changes in viscosity and density

As shown in Figure 7, the viscosity of oil in the low temperature experiment increased at an almost constant rate for the first 300hr, then suddenly doubled, and finally reached an almost constant value of about 22dPa·s. The viscosity increased rapidly for the first 10 hr in the normal temperature experiment. However, the rate of increase then declined, and the

experiment was terminated after 70 hrs, at which time the viscosity was only $0.7 \text{ dPa} \cdot \text{s}$. Since the viscosity of oil in the normal temperature experiment was still increasing when the experiment was terminated, a comparison of the final viscosities of oil in the low and normal temperature experiments can not be made. However, the fact that the viscosity of oil in the low temperature experiment was about 10-fold greater than that in the normal temperature experiment at 70 hrs indicates that viscosity of oil is greatly influenced by temperature. Assuming that emulsification does not occur in the Sea of Okhotsk during winter, when the sea temperature is around -2°C , the viscosity of crude oil flowing in the sea can be assumed to be in the range of $0.3 \sim 22 \text{ dPa} \cdot \text{s}$ from the time of the spill until the time of completion of evaporation. If the oil is trapped under the ice, there would be little increase in the viscosity of the oil due the lack of evaporation, and the oil could be recovered in a state of relatively low viscosity. Figure 8 shows the relationship between viscosity and evaporation percentage of the oil.

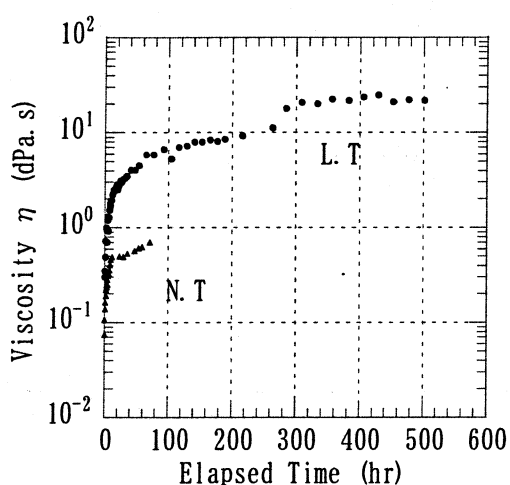


Figure 7. Temporal changes in viscosity

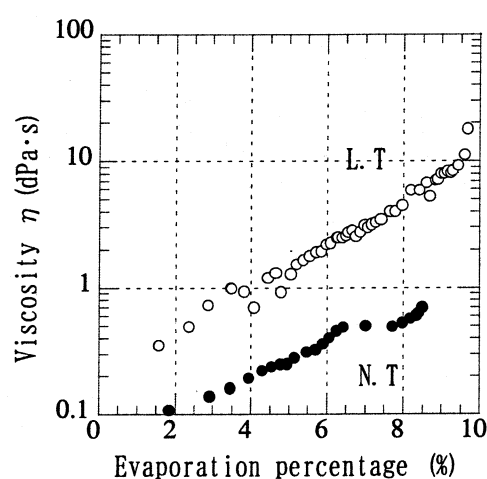


Figure 8. Relationship between viscosity and evaporation percentage

Figure 9 shows the temporal changes in density of the oil. In the normal temperature experiment, the density of the oil increased rapidly for the first 10hr and then continued to increase gradually at about the same rate as that in the low temperature experiment. The specific gravity of the oil in the low temperature experiment increased rapidly for the first 50hr and then continued to increase gradually for the next 250hr, reaching a constant value of approximately 0.926. The specific gravity of the oil in the low temperature experiment was always greater than that in the normal temperature experiment. These temporal changes in density were very similar to those in viscosity and evaporation percentage. The results of the low temperature experiment also showed that under conditions of a low oil temperature (around 0°C) and no hydration or emulsification, the density of Iranian crude oil at 500hr after exposure to the atmosphere remains less than that of sea water, and the oil will therefore continue to flow on the surface of the water. The relationship between density and evaporation percentage is shown in Figure 10.

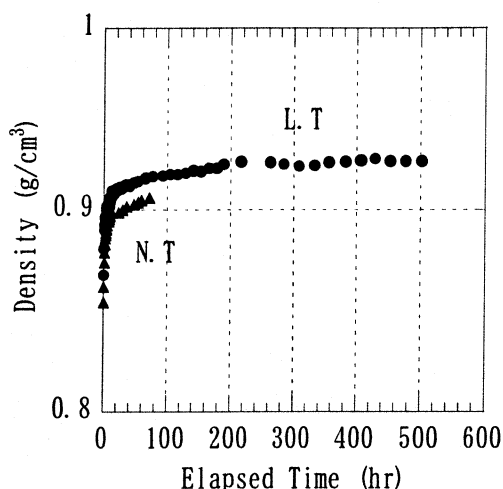


Figure 9. Temporal changes in density

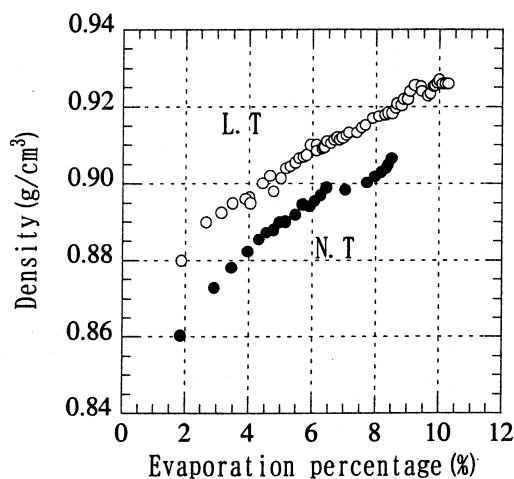


Figure 10. Relationship between density and evaporation percentage

4. PERMEATION EXPERIMENTS

4.1 Method

Some of the crude oil trapped in an ice sheet may seep into brine and air pockets in the ice. Experiments were therefore carried out to determine the amount of infiltration of oil in ice. Two water tanks were used in the experiments. Tank A (80cm in height \times 80cm in width \times 90cm in depth) was a plywood tank with a smaller transparent plastic tank placed inside. Fifty-mm-thick styrofoam was placed between the inner wall of the plywood tank and the plastic tank. A window was made in one part of the tank to enable observation of the inside (Fig. 11). When the water was subjected to freezing, the outer walls of the plastic tank were covered with 100-mm-thick insulating material to suppress heat transfer to and from the sides and bottom of the plastic tank. Tank B (32cm in height \times 71cm in width \times 28cm in depth) was made from plastic, and the tank was covered with insulating material during the experiment to suppress heat transfer.

Experiments were conducted using five different concentrations of salt in the water (cases 1~5). In case 1, tank A was used and the concentration of salt in the water was 33‰. The room temperature for the experiment was first set to -10°C and later raised to -5°C . For cases 2~4, tank B was used. The concentrations of salt in the water were 25‰, 30‰ and 34‰ for cases 2, 3 and 4, respectively. The experiments for cases 2~4 were conducted at a room temperature of -5°C . In cases 1~4, when the thickness of the ice layer reached 7~10cm, crude oil was injected under the ice layer using the device shown in Figure 12. The amount of oil injected was 180ml in cases 2~4 (The amount in case 1 could not be measured.), and an oil layer of about 8mm in thickness was formed. The water surface was made free so as to avoid pressure being exerted on the water under the ice sheet.

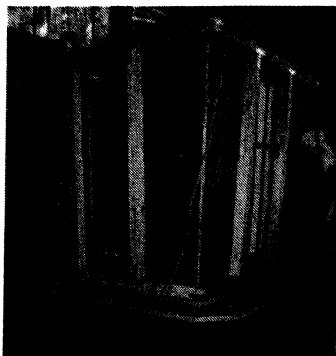


Figure 11. Picture of Tank A

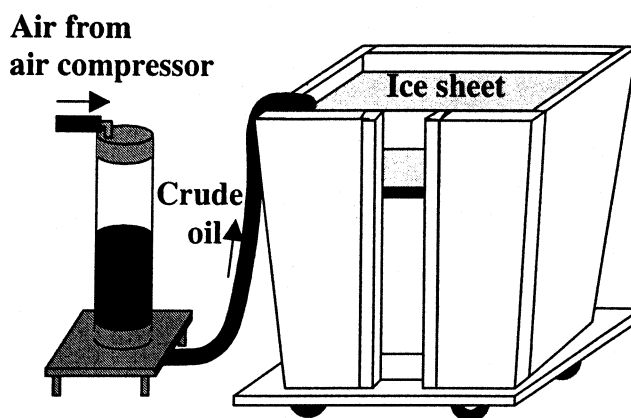


Figure 12. Experimental device

In cases 2~4, due to the small amount of oil injected into the tank, all of the oil trapped under the ice layer infiltrated the ice. In case 5, a larger volume of oil was used. Tank A was used, and the concentration of salt in the water was 33%. When the thickness of the ice layer had reached 15cm, the ice was removed from the tank, and the bottom surface of the ice layer was shaved flat. The ice was then placed back into the tank and the salt concentration was readjusted to 33%. The amount of oil injected in case 5 was about 2,000 cm³. The viscosity and density of the oil before injection were 1.73dPa·s and 0.8725 g/cm³ (at -5°C), respectively. The ice was again left to grow, and the ice layer was removed from the tank again when its thickness had reached 30cm.

The temperature of the room in which the present experiments were conducted generally had to be kept at -25°C due to consideration for other experiments that were being conducted in the same room. The temperature of the room was raised to -5°C when the oil was injected and was kept at -10°C for some time to allow the ice to form slowly. After a sufficiently thick layer of ice had formed, the room temperature was again lowered to -25°C. Due to the low temperature at which these experiments were conducted, the bottom surface of the ice layer consisted of crystals of nonuniform size.

4.2 Results

After the block of ice had reached a sufficient thickness, it was removed from the tank (Fig. 13).

Table 1 shows the mean salt concentration in each of the ice blocks. After removal from the tank, each block of ice was cut horizontally into 4 layers in cases 1~4 and into 5 layers in case 5. After allowing each of these layers of ice to melt, the crude oil and salt water were separated using a separatory rod, and the specific gravity of the salt water was measured. From these measurements, the percentages of crude oil were then calculated (Fig. 14).

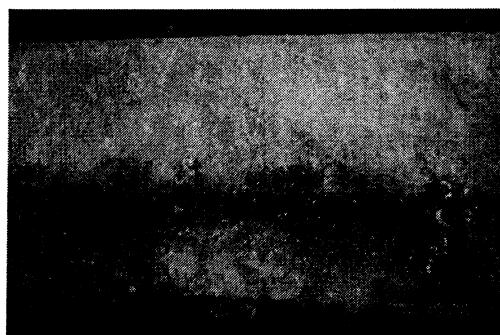


Figure 13 Cross-section view of a block of ice removed from tank

Table1. Salt concentrations in the water

	Salinity of water (‰)	Salinity of Ice (‰)
CASE1	33	6.40
CASE2	25	8.05
CASE3	30	10.33
CASE4	34	8.71

CASE5	Salinity of water (‰)	Salinity of Ice (‰)
1 st layer (5cm)	33	2.1
2 nd layer (5cm)	33	2.9
3 rd layer (5cm)	33	3.0
4 th layer (5cm)	33	2.7
5 th layer (6cm)	33	4.1

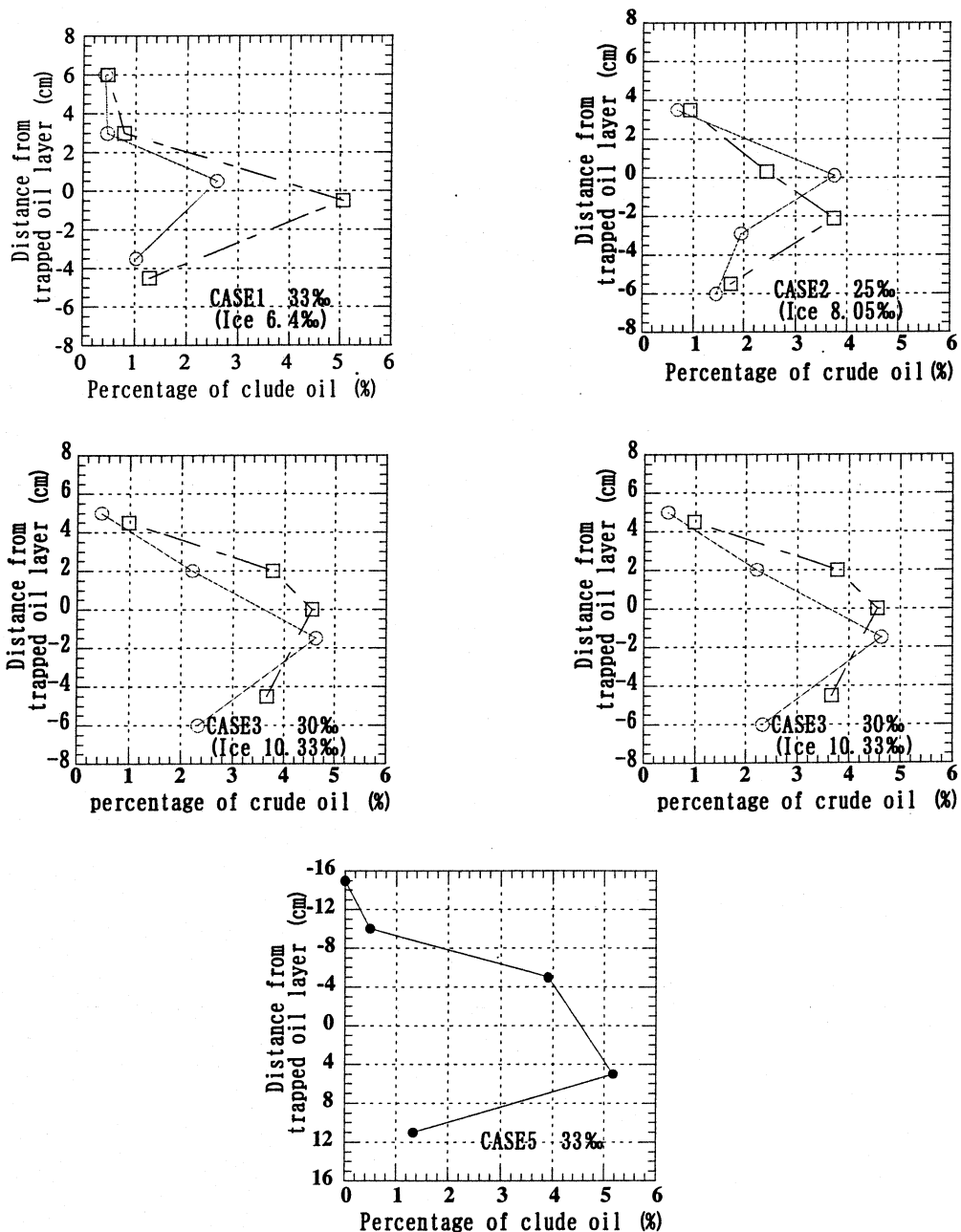


Figure 14. Percentages of crude oil in the ice layers

The results showed that the crude oil trapped in the ice penetrated through the ice, although less than 1% of the oil penetrated to the top layer. The reason for the high percentage of oil found in the portion of ice that was below the depth at which the oil was injected in tank B was thought to be as follows: due to the small size of the tank, ice formation following the injection of oil was not sufficient and therefore the oil was not completely trapped in the ice.

The results of past experiments have shown that the coefficient of water permeability is dependent on the salt concentration and water temperature (Saeki et al, 1986). The relationship between the permeability coefficient of the ice and the percentage of oil in the portion of ice that was above the depth at which the oil was injected in the present experiments is shown in Table 2.

Table 2. Permeability coefficient of the ice

	Salinity of Ice (%)	Permeability coefficient (-5°C) (cm/sec)
CASE1	6.40	0.0013
CASE2	8.05	0.0022
CASE3	10.33	0.0035
CASE4	8.71	0.0026

		Permeability Coefficient (cm/s)	
		Just after oil trap	4 weeks after oil trap
1 st layer	2.1	0.000012	0.00000048
2 nd layer	2.9	0.000038	0.000018
3 rd layer	3.0	0.0002	0.000038
4 th layer	2.7		0.000055
5 th layer	4.1		0.0006

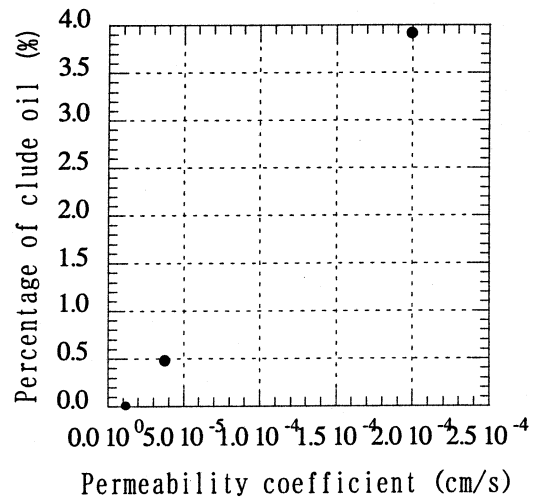
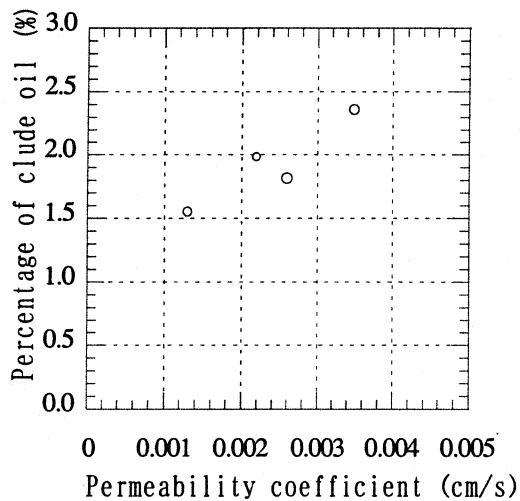


Figure 15 Relationship between the permeability coefficient of ice and percentage of oil in the ice (left, cases 1~4; right, case 5)

The results show that there is a strong correlation between the permeability coefficient of the ice and the percentage of oil in the portion of ice that was above the depth at which the oil was injected.

5. CONCLUSIONS

- 1) Iranian crude oil flowing on seawater evaporates at almost the same rate at a low temperature (such as in the Sea of Okhotsk in winter) and at a normal temperature. If the oil is exposed to the atmosphere, almost 80% of the evaporation is completed within about 50 hours, and the components with high volatility completely evaporate within 300 hours.
- 2) The evaporation rate of Iranian crude oil at a low temperature (oil temperature of about 0°C) decreases proportionally to the approximate -1.0 power of the elapsed time and becomes constant at about 300 hours after exposure to the atmosphere.
- 3) The viscosity of Iranian crude oil at a low temperature (oil temperature of about 0°C) increases at an almost constant rate for about the first 300 hours after the start of evaporation, then suddenly increases by two fold after 300 hours, and finally reaches a constant value of about 22 dPa·s. The viscosity of the oil at a low temperature is about 10-fold greater than that at a normal temperature during the first 300 hours after the start of evaporation.
- 4) Only 3~5% of the oil trapped beneath an ice sheet penetrates through to the lower ice layer and less than 1% penetrates through to the surface layer. There is a strong correlation between the percentage of oil in the ice and the coefficient of water permeability.

If an oil spill were to occur in the Sea of Okhotsk during winter and emulsification of the oil did not occur, there would be little increase in the viscosity of the oil trapped under the ice due the lack of evaporation, and the oil could be recovered in a state of relatively low viscosity. On the other hand, if the oil was not recovered soon after the spill, the oil would not only become sandwiched in the ice but would also penetrate through the ice, making recovery of the oil extremely difficult. Thus, efforts should be made to immediately recover oil that has been spilled in sea covered with ice. Moreover, the penetration of oil through the ice is thought to affect the rate of diffusion of oil flowing under an ice sheet.

6. REFERENCES

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