



## ON THERMODYNAMIC EFFECTS ASSOCIATED WITH MARINE OIL SPILLAGES UNDER LOW TEMPERATURES

M.P. Lobachev and K.E. Sazonov  
Krylov Shipbuilding Research Institute  
St.Petersburg, Russia

### ABSTRACT

Quite a lot of theoretical and experimental studies have been already dedicated to oil spillage behaviour in both open sea waters and under the ice. However, most of them were so far aimed at considering the process of oil propagation under these or other conditions exclusively from the point of view of hydrodynamics and ignored any effects associated with temperature dynamics. Arctic and ice-covered waters have temperatures of about 0 °C. Therefore, any spillage in such environment involves a temperature gradient of at least 40 °C. Such a drop produces a significant impact upon physical processes involved in oil spreading. The paper discusses various aspects related to considerations of thermodynamic effects in the analysis of spilt oil behaviour in cold seas.

### 1. INTRODUCTION

The open water oil spill spreading process is usually divided into three phases (Fay, 1971): gravity-inertia, gravity-viscosity and viscosity-surface tension. The phases are named for their respective prevailing forces. When we consider oil spreading under the ice, the equivalent of the gravity force is the buoyancy. Additionally, we can discard the viscosity-surface tension phase. By the end of the spreading history, while the oil film becomes thinner, surface tension forces are dominating, and the spill eventually stops advancing because tension and buoyancy forces reach equilibrium (Yapa and Chowdhury, 1989).

In (Izumiyama at all, 1998) gravity, viscosity and surface tension forces are assumed to be governing factors during all spill life phases. The authors do not consider only one stage: the gravity-inertia phase. Under this approach it turns out that though the final radius of the spill is dictated by the balance of buoyancy and surface tension forces, the time interval necessary to achieve this radius is markedly affected by the viscosity-to-surface tension ratio, not by just the viscosity only like follows from formulae suggested in (Yapa and Chowdhury, 1989).

In (Izumiyama at all, 1998) they have derived an expression for the oil spill radius at a constant flow rate:

$$R = \left[ \frac{k_0}{\pi^3} \right]^{1/8} \cdot \left[ \frac{\Delta \rho g Q^3}{\mu_0} \right]^{1/8} \cdot f(\alpha) \cdot t^{1/2} \quad (1)$$

where:  $f(\alpha) = (\alpha - \sqrt{\alpha^2 + 2\alpha + 1})^{1/8}$  and  $\alpha = 2\pi k_0 \frac{\sigma_n^2}{\Delta \rho g \mu_0 Q}$

Here  $Q$  – rate,  $\sigma_n$  – surface tension coefficient,  $\mu_o$  – oil kinematics viscosity coefficient at the environment water temperature,  $\Delta\rho$  – difference between oil and water mass density,  $g$  – gravity acceleration.

For the constant volume phase it is:

$$\bar{r} - \bar{r}_0 + \ln \left| \frac{1 - \bar{r}}{1 - \bar{r}_0} \right| = -4\alpha(\alpha^* - 1) \quad (2)$$

where:  $\bar{r} = \left[ \frac{R}{R_f} \right]^4$ ;  $\bar{r}_0 = \left[ \frac{R_0}{R_f} \right]^4$ ;  $t^* = \frac{t}{t_0}$ .

Here  $R_0$  is the spill radius at the instant the oil source exhausts (i.e. at the start of the constant volume phase);  $t_0$  is the respective elapsed time from the initial instant of the event; the factor is  $k_0=0.5$ ;  $R_f$  is the final radius of the oil spill found from the same formula as in (Yapa and Chowdhury, 1989):

$$R_f = \left[ \frac{1}{2\pi^2} \right]^{1/4} \cdot \left[ \frac{\Delta\rho}{\sigma_n} \right]^{1/4} \cdot V^{1/2} \quad (3)$$

The formula suggested in (Izumiyama at all, 1998) for the ratio of the spill radius at the end of the constant flow rate phase to the final radius,  $\frac{R_0}{R_f}$  is:

$$\frac{R_0}{R_f} = (2\alpha)^{1/8} \cdot f(\alpha)$$

Fig.1 shows  $t_{0.9}^*$  intervals found from  $t_{0.9}^* = \frac{t_{0.9}}{t_0}$  as a function of the  $\alpha$  parameter. In this case the  $t_{0.9}$  time is the interval during which the oil spill reaches its  $0.9R_f$  radius.

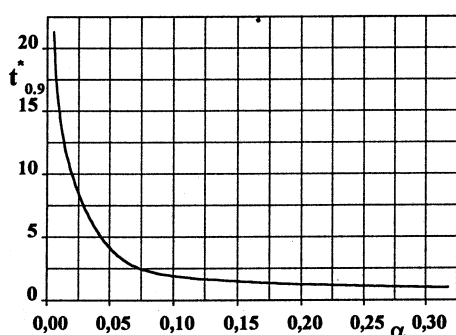


Fig.1 Spill spreading time to  $R=0.9R_f$  versus  $\alpha$ .

It may be clearly seen that at high  $\alpha$  parameters, i.e. at low viscosity values  $\mu_0$  or low flow rates  $Q$ , the  $0.9R_f$  radius is achieved during a time interval comparable with the duration of the constant flow rate phase. At the same time if either the viscosity or the flow rate is high, the time necessary for the spill to spread to the radius of  $0.9R_f$  (or, accordingly,  $R_f$ ) abruptly becomes much longer. (A similar conclusion can be after some additional deliberations drawn from (Yapa and Chowdhury, 1989) though the result will not be so compact and representative.) Thus, for practical applications involving spillages of high-viscosity oils or

catastrophic accidents it is relevant to find not only the final spill radius but as well the  $R_f$  radius corresponding to the end of the constant flow rate phase. This radius is a factor

which governs dynamics of oil spill behaviour under realistic conditions for some initial period after the accident.

However, under realistic conditions this value (the  $R_0$  radius) may be affected not only by factors discussed in above-mentioned references. So far we have considered only the isothermal formulation but it is known that on Arctic lines oil is heated. The heating is realized before oil pumping in pipeline or tanker. During oil transportation by tankers the oil temperature remains at specified level. Therefore, in case of an accident the spilt oil is sure to have a temperature at least 40 °C above the ambient. As may be judged by data from (Izumiyama at all, 1998), (Danielson and Thomason, 1997), oil viscosity is very dependent on the temperature. This dependence may be especially strong for various oil mixtures (Danielson and Thomason, 1997). Other oil characteristics (including surface tension) may as well be temperature-dependent though not to such a great extent. In addition to that, surface tension is significantly affected by the presence of surface-active substances. Nonuniform oil spill surface temperatures combined with nonuniform surfactant concentrations may cause global currents (Marangoni effect) which could in their turn lead to sizeable changes in the oil spreading pattern. At the moment, however, we are not discussing these issues. The present paper covers only temperature-driven viscosity variations due to which in the subject problem this parameter becomes a value varying all over the oil spill volume. As far as can be judged by even the most simplistic case of flow between two parallel planes, three-dimensional viscosity irregularities may lead to very unconventional manifestations (Aristov, 1998).

## 2 SCHEME OF OIL SPREAD UNDER THE ICE AND SIMPLIFYING ASSUPTIONS

It is possible to use the ways developed in (Landau and Lifshitz, 1969), (Levich and Krylov, 1969), (Brons, 1994) in order to derive the general equations and conditions on oil/water division surface in general formulation. However complexity of the task although some simplifications allows to apply only numerical methods for its solution. It is labour-intensive process. That's why for evaluation of temperature influence importance it is desirable to conduct an additional analysis at the maximum simplified formulation.

The oil flow pattern under the ice is schematically depicted in Fig.2.

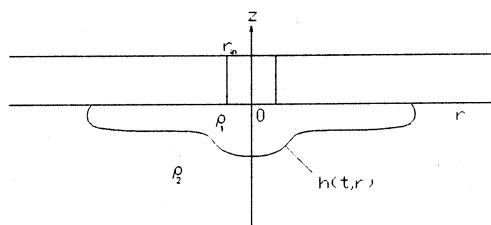


Fig.2 Oil flow under the ice.

A spillage of heated oil immediately initiates heat exchanges with the environment. E.g., in way of the spill the ice starts melting. However, thanks to very low oil thermal conductivity, surface temperatures fairly soon equalise with the ambient level. Therefore, the melt ice volume turns out to be rather small. Thus, at least in the beginning of our

considerations we may ignore melting at the ice/oil boundary and assume that the spill surface adjacent with the ice cover has the same temperature as the latter.

Considering the inherent high oil viscosity, for the sake of initial tentative evaluations we may ignore the convective heat transfer. We may also skip the first phase of the spillage event history and assume the thickness of the spill to be uniform all over its area. Then we can essentially regard the oil spill as a disk with a specified pattern of heat exchange with the environment. Every point of this assumed disk communicates with the environment for its own time interval. The area of the spill side surface is minor, and therefore its heat exchange

contribution is irrelevant. The thus established temperature distribution will be true everywhere except in a zone along the spill rim. The width of this zone is about the thickness of the spill.

Taking into consideration mentioned simplifications the estimation of oil spill radius may be found at first approximation from formulas indicated in introduction. At that let's assume that these formulas may be used also for case of variable oil viscosity in area (in spite of it isn't absolutely true). Such approach can be used for preliminary evaluations.

### 3. TEMPERATURE EFFECT EVALUATIONS

In this case tentative assessments can be made utilizing the solution for a cooling unrestricted plate uniformly heated at  $t=0$  to a temperature of  $T_{in}$  and immersed in a medium which has a constant temperature  $T_0$ . The  $\alpha$  factor of heat transfer from the plate surface into the environment is assumed to have no time variations. The  $z$  axis is perpendicular to side surfaces, the origin of the grid is at the middle of the plate. It has been mentioned before that oil temperature at the ice/oil boundary may be taken same as that of the ice. However, here we assume that at this division surface there also is heat transfer to the environment with the same factor  $\alpha$ . This enables us to use an already available solution and to check whether it was correct to claim that oil surface temperature would soon cool to the ambient level.

Nondimensional temperature in the  $z$  plane at the  $t$  instant can be found (Luikov, 1967) from:

$$\Delta \bar{T} = \frac{T - T_0}{T_{in} - T_0} = \sum_{n=1}^{\infty} A_n \cos(\beta_n z / \delta) \exp(-\beta_n^2 Fo), \quad (4)$$

$$A_n = \frac{2 \sin \beta_n}{\beta_n + \sin \beta_n \cos \beta_n}.$$

where:  $\beta_n$  are roots of the characteristic equation  $\text{ctg} \beta = \frac{1}{Bi} \beta$ ; the Fourier number is  $Fo = at / \delta^2$ ; the Bio criterion is  $Bi = \alpha \delta / \lambda$ ; the plate thickness is designated as  $2\delta$ ;  $\lambda$  is temperature conductivity.

At  $Bi \geq 100$  the plate surface temperature  $T_w$  is virtually equal to the ambient temperature and is:

$$\Delta \bar{T} = \sum_{n=1}^{\infty} \frac{4(-1)^{n+1}}{(2n-1)} \cos\left[\frac{(2n-1)\pi z}{2\delta}\right] \exp\left[-\frac{(2n-1)^2 \pi^2}{4} Fo\right]. \quad (5)$$

For the purposes of the subject task it is  $Bi \geq 100$  for the greater part of various kinds of crude oil at the constant flow rate phase. Or at least  $Bi \geq 50$ . Therefore, tentative assessments can be calculated with the latter formula.

Let us now find temperature profiles for a specific oil spill. Spill sizes will be estimated with (1) and (2) known to have been derived ignoring any viscosity variations. Let the flow rate be  $Q=0.1\text{m}^3/\text{sec}$ ; the constant flow rate phase duration  $t_0=1.8 \cdot 10^4$  sec (5 hr); the initial oil temperature  $T_{in}=313$  °K (40 °C); the ambient temperature  $T_0=273$  °K (0 °C); oil viscosity at the initial temperature  $\mu_{in}=0.1\text{Pa sec}$ ; the surface tension  $\sigma=0.1\text{N/m}$ ; the difference between

oil and water densities  $\Delta\rho=0.1 \text{ kg/m}^3$ ; the temperature conductivity  $\alpha=0.088 \cdot 10^{-6} \text{ m}^2/\text{sec}$ ; the thermal conduction  $\lambda=0.143 \text{ W/(m C)}$ ; the heat transfer may be taken like for still water  $\alpha=580 \text{ W/(m}^2 \text{ C)}$ . Actually, all these coefficients are very variable but for tentative estimations we can use data on any sort of crude oil.

Computations for these inputs with formula (1) give  $R_0=105.5\text{m}$ . The final radius is  $R_f=200.3\text{m}$ . Thicknesses are respectively  $h_0=0.0514 \text{ m}$  and  $h_f=0.0143\text{m}$ .

In order to find the temperature at an arbitrary radius  $r$ , the  $t$  interval during which the subject section is in contact with the environment may be established from:  $\frac{t}{t_0} = \left(\frac{r}{R_0}\right)^2$

Fig.3 shows the oil spill median plane temperature profile by the end of the constant flow rate phase. The same Figure offers ratios of viscosities associated with these temperatures to the initial viscosity value. When finding viscosities as temperature functions it was assumed that viscosity follows  $\mu = A \exp(b/T)$ .  $A$  and  $b$  factors were taken from data available in (Izumiyama at all, 1998):  $A=4.65 \cdot 10^{-8} \text{ Pa}\cdot\text{sec}$ ,  $b=4.24 \cdot 10^3 \text{ K}$ . The formula derived for  $\mu/\mu_{in}$  was:

$$\mu / \mu_{in} = \exp \left[ b \left( \frac{1}{T} - \frac{1}{T_{in}} \right) \right]. \quad (6)$$

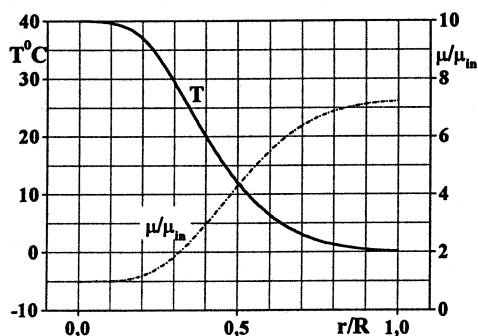


Fig.3 Temperature and viscosity distributions for the spill median surface by the end of the constant flow rate phase.

the spill radius is  $0.25, 0.50, 0.75 R_0$  and  $R_0$ . Respective elapsed time values are  $1.126 \cdot 10^3 \text{ sec}$ ,  $4.502 \cdot 10^3 \text{ sec}$ ,  $1.013 \cdot 10^4 \text{ sec}$ ,  $1.8 \cdot 10^4 \text{ sec}$ . All values were plotted versus the  $r/R$  ratio in order to make it possible to compare different final radii  $r/R$

It may be noticed that there are sizeable variations in both the temperature and the viscosity. Thus, it may be said that heat effects associated with oil spreading are significant. Spill surface temperature calculations with formula (4) indicate that it is practically same as the ambient level. This indirectly supports the assumption made for boundary conditions: at least at the ice/oil boundary oil temperature may be taken equal to ice temperature.

Temperature and viscosity variation dynamics associated with oil spreading can be evaluated by computations for different instants starting with the beginning of the event. Figs.4 show profiles of similar values as in Fig.3 but for the instants when

Computations for  $R > R_0$  indicate to an extremely fast drop of the temperature all over the oil spill area. Therefore, heat-associated effects are relevant only during the constant flow rate phase.

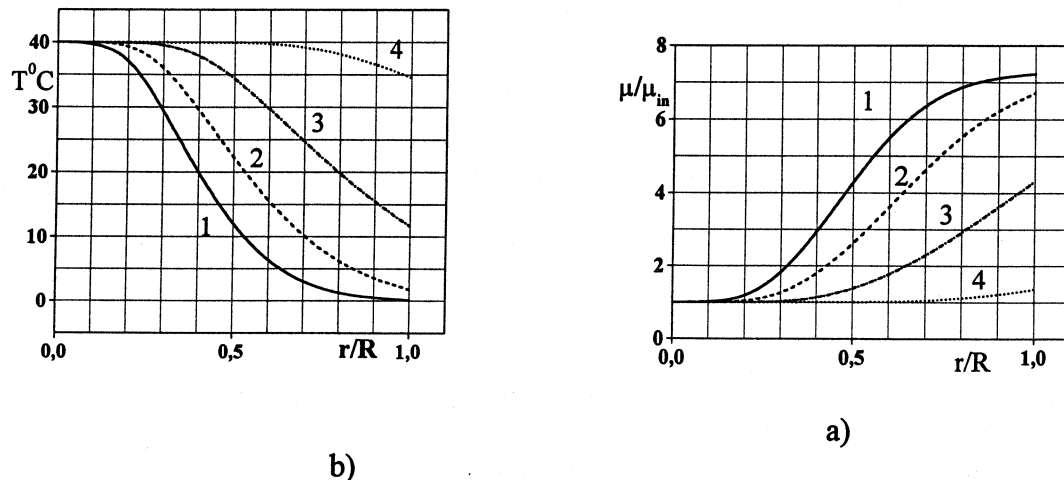


Fig.4 Temperature a) and viscosity b) distributions for the spill median surface at different time instants. 1 -  $R = 0.25R_0$ ; 2 -  $R = 0.5R_0$ ; 3 -  $R = 0.75R_0$ ; 4 -  $R = R_0$ .

Formulae (4), (5) also enable to compute temperature and (with (6)) viscosity distributions for the spill thickness. Fig.5 offers temperature and  $\mu/\mu_{in}$  plate thickness profiles (from the median line) for  $r=0.25R_0$  by the end of the constant flow rate phase. One may easily see that these values are quite nonuniformly distributed over the oil spill thickness.

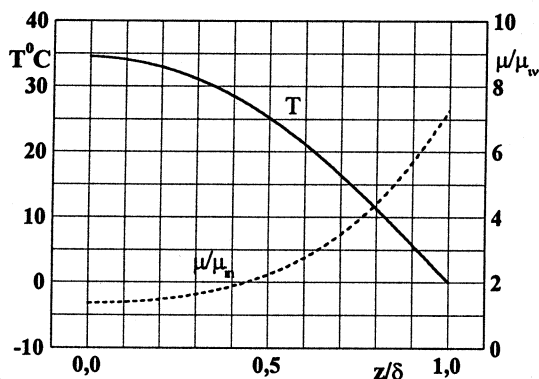


Fig. 5 Spill thickness temperature and viscosity profiles at  $r=0.25R_0$  by the end of the constant flow rate phase.

Other radii show similar patterns with gradual leveling of all parameters (Fig.6). Such viscosity profiles with higher values closer to a solid surface usually lead to slower flow at the wall and to pushing stream lines away from the surface. Considering the obvious viscosity growth in the axial direction noticeable in previous plots, one may well expect that the oil spill thickness should increase compared to the isothermal case. That would make it impossible to use traditional analytical approaches (Yapa and Chowdhury, 1989), (Izumiyama et al., 1998) and would mean inevitable application of numerical methods.

#### 4. CONCLUSIONS

The above-described theoretical analysis shows the influence of thermodynamic effects upon oil spreading in ice-covered water is various at different process stages.

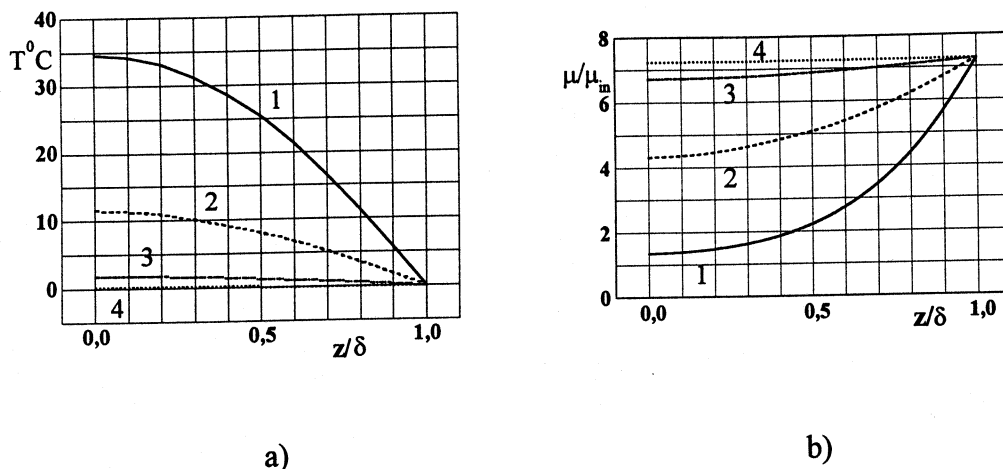


Fig.6 Spill thickness temperature a) and viscosity b) profiles at different radii by the end of the constant flow rate phase. 1 -  $r/R_0 = 0.25$ ; 2 -  $r/R_0 = 0.5$ ; 3 -  $r/R_0 = 0.75$ ; 4 -  $r/R_0 = 0.25$ .

Thermodynamic effects upon oil spreading parameters are most sizeable during the constant flow rate phase. These effects are especially marked for high-viscosity oils. In comparison with the isothermal case there is such change of oil viscosity in area that it can lead to a significant increase in the oil spill thickness. This aspect may be sometimes quite important, especially in accidents in littoral waters or narrow passages.

When the spill enters its constant volume phase, the contribution of thermodynamic effects recede. Low-viscosity oils reach this phase fairly quickly and by that time their spills are rather thin. These circumstances lead to very fast vertical heat exchanges and the spreading oil cools down to the ambient temperature. Highly-viscous oils spread at the constant volume phase very slowly. Therefore, though the time required for equalising the temperatures is significant, compared to the total duration of the event it is short and thermodynamic processes associated with this phase may be ignored.

It should be, however, said that these conclusions are so far only tentative. More detailed investigations into absolutely nonlinear aspects like viscosity variability across the oil spill, temperature effects upon surface tension characteristics or phase transitions in the spreading oil may yet reveal quite interesting and surprising effects.

## 5. REFERENCES

- Aristov S.N. 1998. Stationary Flow of Variable-Viscosity Fluid. Papers of the Academy of Sciences, v.359, No.5, pp.625-628 (in Russian)
- Brons M. 1994. Topological fluid dynamics of interfacial flows. Phys. Fluids 6:2730-2737.
- Danielson T. J. and Thomason W.H. 1997. Influence of Crude Oil Properties on Northern Gateway Terminal Transportation Systyem. Proc. Int. Conf. RAO-97, St. Petersburg, pp. 379-385.
- Fay J. A. 1971. Physical processes in the spread of oil on a water surface. Proc. Joint Conf. On Prevention and Control of Oil Spills. American Petroleum Institute, Washington D.C., pp.463-467.

- Izumiyama K., Uto S., Narita S. & Tasaki R. 1998. Effects of Interfacial Tension on the Spreading of Oil under an Ice Cover. Proc. Of the 14<sup>th</sup> Int. Symposium on Ice. Potsdam, New York, USA, pp. 419-426.
- Landau L.D. and Lifshitz E.M. 1969. Fluid Mechanics. Oxford: Pergamon. 3rd ed.
- Levich V.G. and Krylov V.S. 1969. Surface-tension-driven Phenomena. Annu. Rev. Fluid Mech. 1:293-316.
- Luikov A.V. 1967. Theory of Thermal Conduction. Vuishay Shkola, Moscow, 599 p (in Russian).
- Yapa P.D. and Chowdhury T. 1989. Oil Spreading under Ice Covers. Proc. Of 1989 Oil Spill Conference, pp. 161-166.