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Report

Dispersion of Emulsified Oils at Sea - Laboratory Study

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Executive Summary

In September 1997, a series of field trial experiments were carried out by the National Environmental Technology Centre (NETCEN) to investigate the effectiveness of dispersants on emulsified crude oils and a residual fuel oil. Laboratory test work was planned in the programme of work to build on the results of the field trial.

The field trial concluded that the emulsified crude oil slicks of Alaska North Slope and Forties Blend were rapidly dispersed after spraying with Corexit 9500 and Dasic Slickgone NS dispersants, indicating that the time window for dispersant application can be longer than previously considered (IMO/UNEP, 1995).

The different chemical composition of the two crude oils, and in particular the higher asphaltene content of the Alaska North Slope crude oil, did not have a significant effect on the relative dispersibility. Both of the weathered crude oils were dispersed completely and efficiently. Thus studies linking dispersibility and composition were not appropriate. However the rate and extent of water uptake did not proceed in a continuous linear fashion in the Alaska North Slope slick, therefore the laboratory test programme attempted to isolate the reasons for this variance.

In the field trial, the IFO-180 fuel oil was partially dispersed by spraying with only 600 litres of Corexit 9500 after it had been on the sea for 4 hours. Operational problems prevented further application of dispersant at this early stage of weathering. When further dispersant application was possible the following day, it was effective only to a very limited extent due to a significant increase in the viscosity of the residual fuel oil in the fuel oil emulsion. Thus, while the field trial results indicated that heavy fuel oils such as IFO-180 might be amenable to dispersant treatment, the results were not conclusive. Laboratory test work was undertaken to provide additional information on the likely viscosity limits of fuel oil dispersibility.

Alaska North Slope crude oil - Emulsion Stability

During the field trial experiment, the emulsification of the Alaska North Slope crude oil did not proceed as a continuous process. The water content of the emulsified Alaska North Slope crude oil only reached a maximum of approximately 40 % volume after 10 hours and then declined to a mean value of around 30 % volume (a range of 25 % to 35% volume).

There are several possible reasons for the observed behaviour. The weather during the field trial was particularly warm and sunny. Photo-oxidation may have caused chemical changes within the Alaska North Slope crude oil and this could have caused differences in emulsion stability with time. It is also possible that the emulsion that had formed was being broken by the heat from the sun, built up again overnight in the cooler conditions and then was broken down again before it was sprayed with dispersant.

The laboratory study programme for the Alaska North Slope crude oil was based on determining the potential effect of specific chemical and physical processes on the stability of the emulsified oil. More specifically, the study was conducted to determine how photo-oxidation

and thermal cycling alters the physical and chemical properties of Alaska North Slope oil residues and emulsions, and whether these effects explain the observed emulsification behaviour of Alaska North Slope in the field.

Analysis of the surface oil samples collected during the Alaska North Slope field experiment demonstrated that a change in chemical composition of the Alaska North Slope did occur as the oil became weathered (over 55 hours). The oil showed an increase in the resin and asphaltene content, which may have been the result of photo-oxidation. However, laboratory simulations of photo-oxidation were unsuccessful in altering the chemical composition of the Alaska North Slope to the extent observed in the field.

The sunny weather conditions of the field trial meant that considerable variations in surface emulsion temperature were measured. To test whether these temperature changes had resulted in the reduced water uptake, thermal cycling tests were undertaken to simulate the day and night changes in temperature experienced by the oil at sea. Alaska North Slope crude oil emulsions were placed in a water bath simulating sea temperature at 18°C, and the air temperature was varied by a maximum of 20°C. The emulsions studied did not break as a result of the thermal cycling. Therefore it is unlikely that the change in temperature between day and night would effect the emulsion stability considerably and we do not believe that this was the reason for the non-linear emulsification observed in the field.

In summary, comparing the Forties Blend and ANS slicks on the field trial, the ANS crude oil formed higher viscosity and more stable emulsions than the Forties blend. This is partly due to the higher asphaltene content measured in the ANS compared to the Forties blend. However, the low water content of the ANS emulsions appears to be due to changes in composition caused by photo-oxidation during weathering. The resin content of the weathered ANS crude oil increased more rapidly due to photo-oxidation than the increase in asphaltene content. It appears that the tendency for asphaltene precipitation diminished on weathering due to the changing ratio of these oil components, rather than increased. This could explain the nonlinear emulsification observed for the ANS slick during the field trials. The emulsions of both the Forties blend and the ANS were completely dispersed in the AEA 1997 field trials.

IFO-180 Fuel Oil - Viscosity Limits

Since the field trial results of the dispersibility of fuel oils were not conclusive, the most effort was spent on this aspect of the test work. The laboratory study was undertaken using the WSL rotating flask method. Dispersibility was defined by the WSL result obtained; on the basis of previous comparisons between effectiveness in the field and in laboratory tests, values above 15% were used to indicate that the oil was dispersible and values of less than 15% were taken to indicate that the oil was not dispersible. However, the relationship between laboratory test results and effectiveness in the field has not been fully established, therefore the resultant effectiveness values should be used as an indication of likely dispersibility not as definitive dispersibility limits. Definitive dispersibility can only be determined through experimental field trials carried out at sea.

The study indicated that IFO-180 fuel oil emulsions with a viscosity of 22,000 cP and IFO-380 fuel oil emulsions with a viscosity of 26,000 cP are dispersible with Corexit 9500 in laboratory test conditions. Dasic Slickgone NS does not disperse the same emulsion of IFO-380 fuel oil

and will only disperse IFO-180 emulsions at high dose rates (1:10 and 1:25) when tested under the same conditions.

The comparison of the laboratory test results with the results of the sea trial seem to provide a correlation that indicates:

- At low wind speeds (< 5 ms $^{1)}$ the IFO-180 fuel oil which was used in the sea trials was dispersible using Corexit 9500 after the oil had weathered on the sea surface for 4 hours and lost 4% of its volume by evaporative loss.

- At low wind speeds (< 5 ms') the IFO-180 fuel oil that had weathered on the sea surface for 24 hours (and lost 8% of its volume by evaporative loss) would have been on the border line of effective dispersibility with Corexit 9500. This confirms the observations made at the field trials.

- The laboratory test results indicate that at higher wind conditions (> 5 ms') both the IFO180 fuel oil which weathered for 24 hours and the IFO-380 fuel oil from the same source (Ellesmere Refinery) are likely to be dispersible using Corexit 9500 in the field. The IFO380 fuel oil is not likely to be dispersible in the field using Dasic Slickgone NS.

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