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Studies in support of the regulation of dispersant use in the Kazakhstan Sector of the Caspian Sea (KSCS)

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ABSTRACT 299800:

The use of oil spill dispersants is often regulated by national authorities to ensure that products approved for use as dispersants on spilled oil in national waters are of reasonable effectiveness and of low inherent toxicity. KING (Kazakh Institute of Oil & Gas) undertook a study to assess the use of oil spill dispersants on spilled oils in the Kazakhstan sector of the Caspian Sea (KSCS) to support decision-making for such regulations in the RoK (Republic of Kazakhstan).

The KSCS has some characteristics that are unlike open ocean conditions in other parts of the world; the salinity is much lower than in the open sea. The shallow waters of the northern Caspian Sea have very low salinity (9 psu (practical salinity units) or less) due to the inflow of freshwater from the River Volga, and are frozen in winter. The deeper water in the southern part of the KSCS has a salinity of up to 14 psu. The effectiveness of oil spill dispersants is known to be affected by water salinity.

Different countries around the world have developed different test methods to assess dispersant effectiveness. The project examined the options and decided to modify the WSL (Warren Spring Laboratory) LR 448 dispersant effectiveness test method, as used in the UK. The method was adapted by KING and testing was conducted by Karaganda State University (KSU) to test a variety of dispersants under Caspian Sea conditions. Dispersant effectiveness testing should be conducted with a test oil that is representative of oils that might be spilled in the area being considered. Kashagan crude oil was distilled to 200°C to simulate the evaporative loss that would occur shortly after the oil was spilled at sea and the residue used as the test oil in the dispersant effectiveness testing.

Several commercially-available dispersants were tested using the modified LR 448 method with the 200°C+ Kashagan test oil under a variety of conditions with salinities ranging from 0 psu to 35 psu and at temperatures of 5°C and 25°C. The results indicate that some internationally recognized dispersants could be suitable for use in the KSCS.

INTRODUCTION:

The relevant departments of national governments in many countries around the world regulate the potential use of oil spill dispersants on spilled oil in national waters. These regulations often consist of two sets of regulations:

1. Product approval regulations, which describe which dispersants would be approved to be used, and;
2. Dispersant use regulations, which describe where and when the approved dispersants could be used on spilled oil in national waters.

The aim of product approval regulations is generally to ensure that:

i. Any dispersant that could be used on spilled oil in national waters is likely to be reasonably effective, and:
ii. Any dispersant should not be of relatively high inherent toxicity, or should not cause an increase in the potential toxic effects that could be caused to marine organisms by exposure to dispersed oil.

These regulations set standards that a dispersant must conform to before it will be approved for use. Effectiveness testing and toxicity testing is conducted to ensure that candidate dispersants meet the standards for minimum acceptable effectiveness and do not exceed a maximum acceptable toxicity.

Different countries have developed different effectiveness test methods and toxicity test methods. This paper concentrates on the effectiveness method developed for use to assess the effectiveness of dispersants in the conditions that might occur in the Kazakhstan Sector of the Caspian Sea (KSCS).

The Kazakhstan Sector of the Caspian Sea

The KSCS has some characteristics that are unlike open ocean conditions in other parts of the world. The waters of the northern Caspian Sea are shallow (an average depth of 4 metres with a maximum of 8 metres) and have very low salinity, from 0 to 9 psu (practical salinity units) due to the inflow of freshwater from the River Volga. The northern Caspian Sea is frozen in winter, but can reach temperatures of 25°C or more in the shallows in summer. Further south in the KSCS, the depth increases to over 200 metres with salinities up to 14 psu. The salinity of the entire Caspian Sea is illustrated in Figure 1.

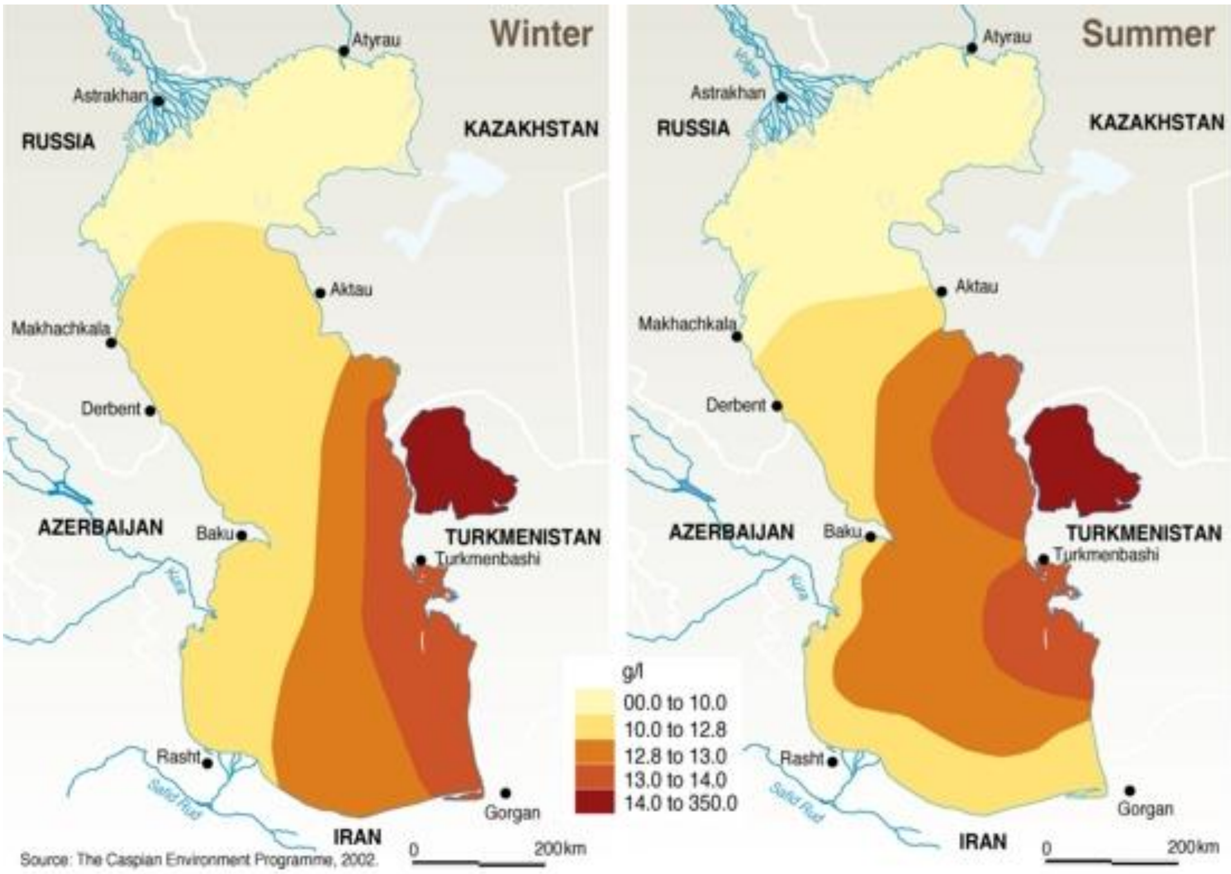

Figure 1. Salinity of the Caspian Sea (The Caspian Environment Programme, 2002)

Testing of dispersant effectiveness

Many different laboratory methods have been devised to measure the effectiveness of dispersants (Clayton et al, 1992). The basic principles of all the methods are similar and simple:

i. Dispersant is added to a sample of a test oil.
ii. The dispersant-treated oil is mixed with sea water with a particular method and intensity of agitation for a period of time.
iii. An aliquot (sub-sample) of the dispersed oil in water is taken.
iv. The proportion of the original oil that has dispersed into the water is measured.
v. The effectiveness, normally expressed as a percentage, is calculated.

The major differences between the individual effectiveness test methods are the test oil used and the method, intensity and duration of agitation.

Test oil and test variables

Ideally, the test oil used in dispersant effectiveness testing for product approval purposes should be relevant to the oil spill risk. If the major oil spill risk is from offshore exploration and production activities, it might be possible to select a crude oil that is ‘typical’ of offshore oil production. However, spilled crude oils can rapidly ‘weather’ (lose volatile components by evaporation and form water-in-oil [w/o] emulsions) and this causes a dramatic change in their physical properties. Different degrees of evaporative loss and levels of w/o emulsification would be needed to simulate or represent the state of the oil after different periods of weathering. If the major oil spill risk is from passing oil tanker or cargo ship traffic, the selection of a relevant test oil is more difficult because the type of oil that could be spilled will be unknown. If a crude oil is to be used as a test oil, choosing the crude oil may be difficult, as a wide range of crude oils may be traded as cargoes. Ships use a range of fuel oils ranging from MGO (Marine Gas Oil) used to power high-speed diesel engines to IFO (Intermediate Fuel Oil) grades of HFO (Heavy Fuel Oil) that power very large slow-speed diesel engines. Which would be the most appropriate test oil for dispersant effectiveness testing? The prime purpose of a test oil for dispersant approval purposes is that it should produce results that differentiate candidate dispersants.

Method, intensity and duration of mixing in effectiveness test method

The methods of mixing employed in dispersant effectiveness methods include:

- End-over-end flask rotation in the WSL (Warren Spring Laboratory) LR 448 method (MMO), used in the UK and Norway.
- A sub-surface oscillating hoop in the IFP (Institut Français du Pétrole) method (Bocard and Castaing. 1987), used in France and Norway.
- A stream of air impinging on the water surface in the MNS (Mackay-Nadeau-Steelman) method (Mackay et al., 1978) used in Norway
- A shaker table used in the SFT (Swirling Flask Test) (EPA, 2003) and Baffled Flask Test (Venosa et al, 2002) used in the USA

Work has been conducted to try and establish which of these methods most closely correlates with the mixing conditions that occur at sea. However, there are two points to consider:

i. The sea-state can vary from no wave action in a flat calm sea to mountainous waves in storms and hurricanes. Any, or all, of the test methods might more closely resemble one sea-state than another, but none can be said to be a good simulation of the mixing and dilution processes that occur at sea.

ii. It is currently not possible to accurately quantify dispersant effectiveness on spilled oil at sea. There is therefore no quantified data-set to which results obtained in the different laboratory tests can be correlated.

Significance of the results obtained in laboratory test methods

Effectiveness testing of dispersants for product approval purposes is designed to provide discrimination between candidate dispersants, under the conditions of the test. A somewhat arbitrary ‘pass mark’, of for example 60%, is used to distinguish between an acceptable and an unacceptable level of effectiveness. Such laboratory testing does not accurately simulate dispersant use on spilled oil at sea. The results obtained from the laboratory tests produce that indicate the relative effectiveness of different dispersants, not an indication of the absolute effectiveness of dispersant use at sea. A dispersant that is approved on the basis that it produces a result of above 60% in the particular test method with the specified test oil may produce very high levels, or very low levels, of dispersion of oil at sea. The effectiveness of a dispersant used on spilled oil at sea will depend on the type of oil spilled (and the state of weathering of the spilled oil) and the prevailing conditions (primarily sea state, but also temperature and salinity).

Previous studies on dispersant effectiveness in low salinity waters

There have been several studies on the effectiveness of dispersants in low salinity or freshwater. Wells and Harris, 1979, tested four dispersants using the MNS method and found that all were much more effective in seawater than in freshwater. Lehtinen and Vesala, 1984 found reduced effectiveness with three dispersants (one marine and two freshwater) as salinity and temperature decreased. Payne et al, 1985, using the swirling flask test method, also found that the effectiveness of four commercially-available dispersants was lower at lower salinities. Belk et al, 1989 tested, using the WSL LR448 method, four dispersants (unnamed) and some formulations developed as freshwater dispersants. The freshwater formulations worked reasonably well in freshwater, but not as well at higher salinity. Brandvik and Daling, 1992 found that a dispersant designed for low salinity, Inipol IPF, was better than other dispersants at low salinity, but that its effectiveness was poor below 12.5 psu. Blondina et al, 1999, used a modified swirling flask method to investigate the effectiveness of two dispersants, Corexits 9527 and 9500, with ten oils and salinities from 0 psu to 35 psu. George-Ares et al, 2001 described how the effectiveness of Corexit 9500 dispersant could be improved in freshwater by the addition of calcium chloride. Fingas and Ka'aihue. 2005a. found that currently available dispersants have a very low effectiveness or are sometimes even completely ineffective in freshwater. Dispersant effectiveness studies have previously been conducted for the Azerbaijan sector of the Caspian Sea (Abbasova et al. 2005). This work concluded that some commercially-available dispersants would be of reasonable effective in waters with a salinity of 12 psu.

A literature review including the use of dispersants in fresh and brackish waters, published in 2010 (SL Ross, 2010), summarised the findings of numerous tests conducted since the late 1970s as: *The consistent significant finding of all of these tests is that dispersant designed for use in marine environments (water salinity in the 30 to 35 psu range) are considerably less effective when the salinity falls below about 20 psu or above 40 psu.* This could imply that dispersants for use in low salinity water, such as the Caspian Sea, would need to be especially formulated for such use as commercially-available dispersants designed for marine use (the majority of commercially-available dispersants) would be of low effectiveness.

MATERIALS AND METHODS USED:

After a consideration of the effectiveness methods used around the world, it was decided to use a modified WSL LR448 procedure. Accepting that no laboratory test method can be a precise simulation of the conditions at sea, the WSL LR448 method was preferred on the basis of its relative simplicity and ease of operation.

Test oil

Effectiveness testing for approval purposes in the UK uses two tests oils; A MFO (Medium Fuel Oil) with a viscosity of 2,000 cP at 10°C and a blend of the MFO with MDO (Marine Diesel Oil) to produce a viscosity of 500cP at 10°C. These oils would not be appropriate for approval testing in the RoK.

Kashagan crude oil was selected as being an appropriate test oil. In order to provide a degree of simulated weathering, several distillation residues to temperatures of 200°C, 220°C and 250°C, and denoted as 200°C+, 220°C+ and 250°C+, were prepared. Because of the wide range of seas temperature possible in the northern Caspian Sea, it was decided that effectiveness testing would be conducted at two temperatures, 5°C and 25°C. Dispersant use on oil spilled onto or under a continuous ice-sheet would not be feasible or desirable, but dispersant use amongst broken ice on a cold sea could be feasible. The physical properties of the residues were determined at these two temperatures. The 220°C+ and 250°C+ residues became solid at 5°C indicating that their Pour Points were higher than this temperature. The 200°C+ Kashagan residue was used as the test oil

Test conditions used

Normal ocean salinity (33 psu - practical salinity units) is not relevant to dispersant use in the KSCS where the salinity ranges from almost 0 psu in the extreme north to 13 or 14 psu in the southern KSCS (see Figure 1). However, for the purposes of test development, it was decided to test dispersants with a full range of salinity from 0 psu (freshwater) to 35 psu.

Apparatus

No commercial supplier of the apparatus used in the WSL LR448 test procedure currently exists. Design drawings, photographs and videos of the apparatus used at SINTEF were supplied and the workshop at KSU constructed the apparatus shown in Figure 1.

The glass flasks with the required dimensions (which are critical for the repeatability and reproducibility of the results from method) were fabricated by the glassblower at KSU.

Figure 2. Modified WSL LR448 apparatus at KSU

Dispersants tested

Ten dispersants selected where from among those dispersants that are commercially-available and have been approved for use in several countries (Table 1).

Dispersant	Approved for use in (selected examples)
Corexit 9500	France (marine use), UK, USA
Inipol IP-90	France (marine use)
Inipol IPF	France (freshwater use)
Dasic Slickgone NS	France (marine use), UK, Cyprus, Norway
Dasic Freshwater Dispersant	France (freshwater use), UK
Finasol OSR 51	UK
Finasol OSR 52	Cyprus, France, UK, USA
Bioversal HC	Italy, Spain
FLD-1	China
FLD-2	China

Table 1. Dispersants used in this study

France is the only country that specifically approves dispersants for use in at sea (marine) or for freshwater use (Merlin et al, 1991). All the other countries test for dispersant effectiveness using full salinity (33 or 35 psu) seawater. A dispersant treatment rate of 1 part dispersant to 25 parts of test oil, the same as used in many approval tests (for example in France and the UK) was used in this work.

Test method

The dispersant efficiency tests were carried out in a temperature controlled cabinet. All test materials were kept in the cabinet for 24 hours prior to the commencement of the test. The separating funnel was placed in the motor-driven rack and 250 ml of synthetic seawater of the required salinity was added. 5 ml of the test oil was placed onto the surface of the seawater using a syringe and the clock was started. After one minute, 0.2 ml of the dispersant to be tested was added using a micro-syringe. The dispersant was added to the oil drop-wise, starting from the center of the oil lens so that the dispersant is distributed as evenly as possible. Stoppers were placed in the separating funnels and held in place with the retaining device. After 2.5 minutes, the rotation of the separating funnel was started and continued for 2 minutes. When the rotation was stopped, the separating funnels were allowed to stand undisturbed for 1 minute. The stoppers were removed and 50 ml of oily water was run off into a measuring cylinder in no longer than 10 seconds. 50 ml of the sample from the measuring cylinder was placed in a 100 ml separating funnel. The measuring cylinder was washed twice with 10 ml of chloroform which was added to the 100 ml separating funnel. The stoppered funnel was shaken for 1 minute. After the phases had completely separated the chloroform layer was run off into a 100 ml volumetric flask through a filter paper No. 1 placed in a glass funnel (into which 1.5 g of anhydrous sodium sulphate has been placed). The filter paper and sodium sulphate were thoroughly washed with chloroform and then chloroform was added up to the mark on the volumetric flask. The flasks were stoppered and well shaken. The absorbance of the sample solution was measured using a quartz cell of 10 mm to a wavelength of 580 nm. The amount of oil in the sample was determined by comparison with a calibration curve and the effectiveness calculated as a percentage of the amount of oil used in the test.

RESULTS AND DISCUSSION:

Results of tests conducted at 25°C and with a range of salinity

The effectiveness results obtained with eight of the dispersants using the 200°C+ Kashagan residue at 25°C and a range of salinities are presented in Figure 3.

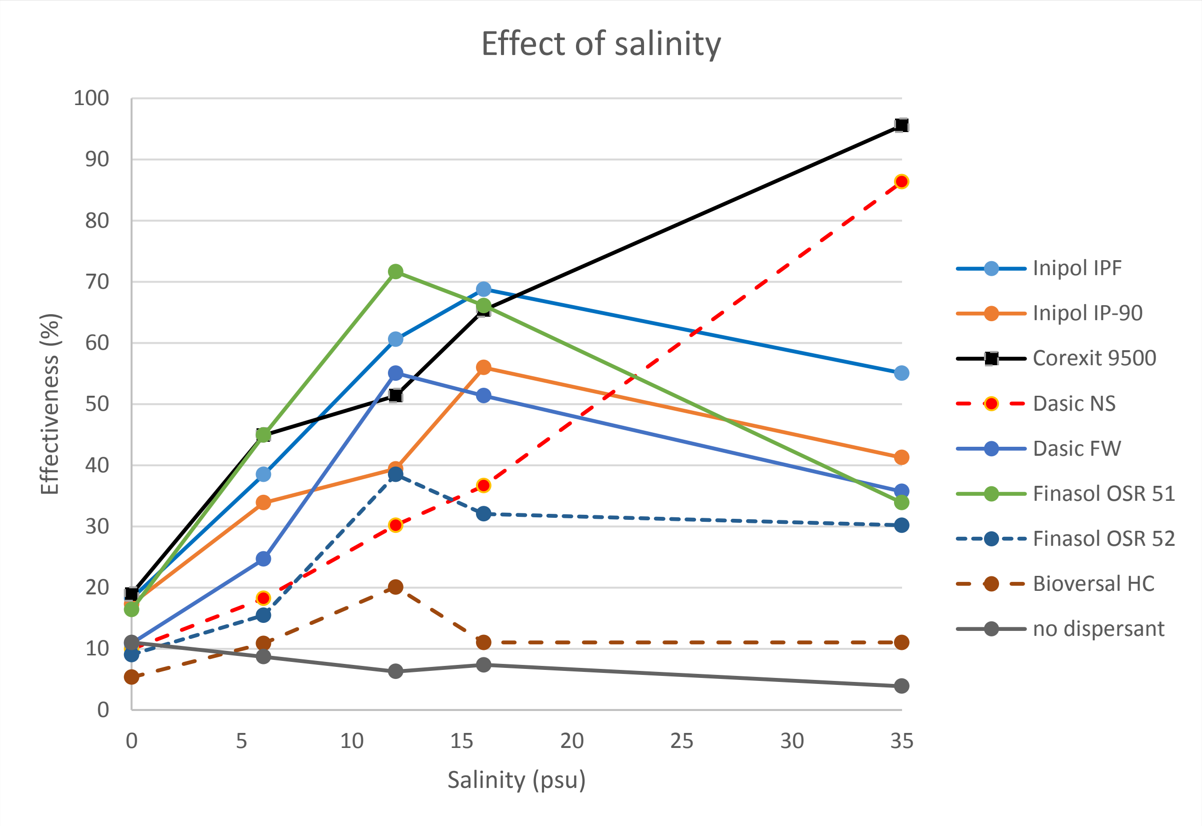

Figure 3. Dispersant effectiveness results from testing at 25°C

There is a very wide range of effectiveness obtained with the different dispersants at full oceanic (35 psu) salinity and all dispersants cause much lower effectiveness in freshwater (0 psu salinity). However, while two dispersants (Corexit 9500 and Dasic Slickgone NS) exhibited an almost liner reduction in effectiveness with reducing salinity, the other dispersants had a peak of effectiveness at intermediate salinities of 16 or 12 psu. This trend is consistent, although more marked, with the some of the results obtained by Blondina et al, 1997, who found that the variation in dispersant effectiveness with salinity was dependent on the dispersant and the test oil. The two dispersants approved for freshwater use in France (Inipol IPF and Dasic Freshwater Dispersant) has peaks of effectiveness at 16 psu and 12 psu salinity, but where of low effectiveness in freshwater. Finasol OSR 51, Inipol IP-90, Finasol OSR 52 and Bioversal HC also exhibited similar peaks of effectiveness at intermediate salinity values, but the effectiveness of Bioversal HC was very low.

Results of tests conducted at 5°C and with a salinity of 16 psu

Nine of the ten dispersants were tested with the 200°C+ Kashagan residue at 5°C at a salinity of 16 psu. The effectiveness results obtained are presented in Figure 4.

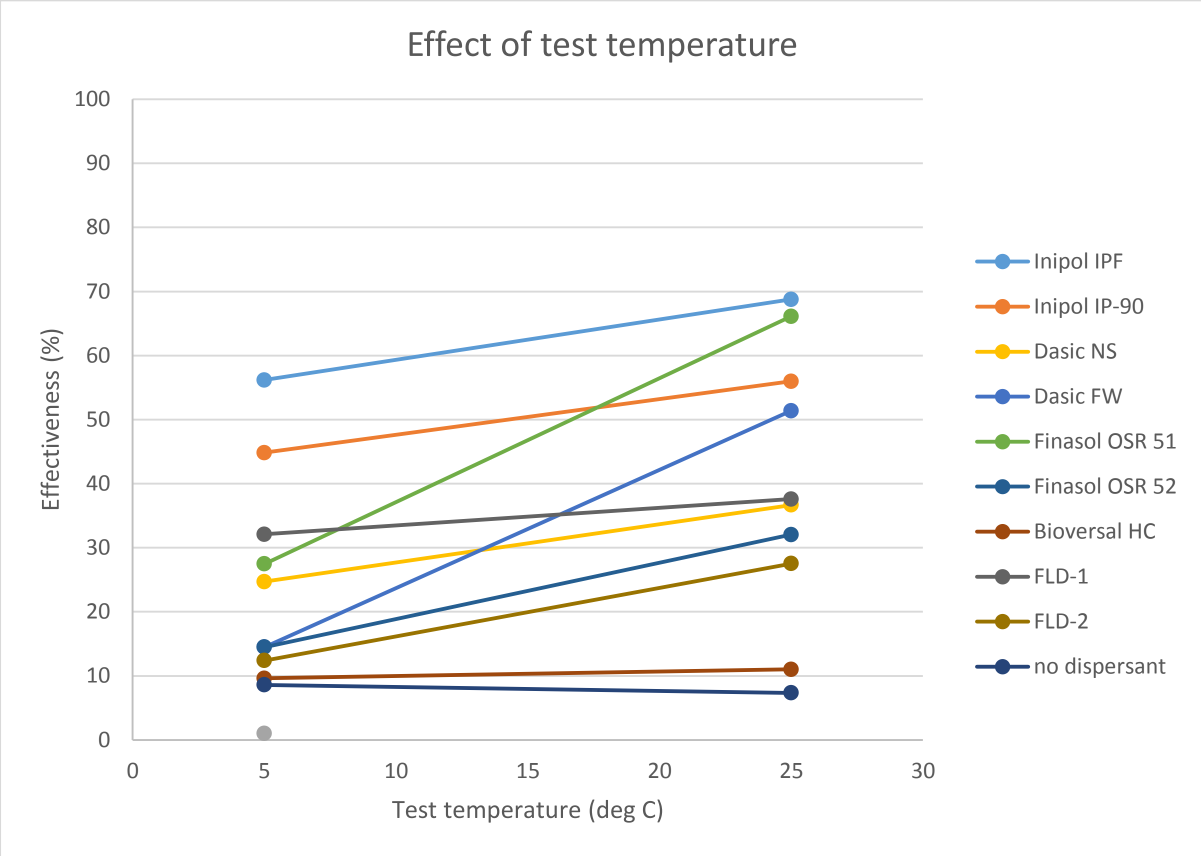

Figure 4. Dispersant effectiveness results from testing at 5°C and 25°C

All of the dispersants tested produced lower effectiveness values at 5°C than at 25°C, although in many cases the reduction at the lower temperature was not large.

Discussion

Dispersant effectiveness results for conditions that considered relevant to waters of the KSCS, a salinity range of 6 to 16 psu, are shown in Table 2. In order to more clearly distinguish between the relative effectiveness of the dispersants, effectiveness values in excess of 60% are **bold underlined** and in excess of 40% are in **bold**.

Test temperature	At 25°C			At 5°C
Salinity	**6 psu**	**12 psu**	**16 psu**	**16 psu**
Corexit 9500	**45**	**51**	**65**	n.d.
Inipol IP-90	34	39	**56**	**45**
Inipol IPF	38	**61**	**69**	**56**
Dasic Slickgone NS	18	30	37	25
Dasic Freshwater Dispersant	25	**55**	**51**	15
Finasol OSR 51	**45**	**72**	**66**	27
Finasol OSR 52	15	38	32	15
Bioversal HC	11	20	11	10
FLD-1	n.d.	n.d.	38	32

FLD-2	n.d.	n.d.	28	12
No dispersant	9	6	7	9

Table 2. Dispersant effectiveness results at 0 to 16 psu at 25°C and at 16 psu at 5°C

The purpose of testing was not to select only one dispersant from all of the dispersants tested, but was to categorize them into groups that could be recommended, considered acceptable or not recommended for use in the KSCS. On the basis of effectiveness values exceeding 60% and 40%, Finasol OSR 51 is the most effective dispersant at 25°C, followed by Inipol IPF and Corexit 9500. Dasic Freshwater Dispersant achieved a result of 55%, but produced lower results at both higher and lower salinities. Several dispersants produced effectiveness values below 40% at all salinities when tested at 25°C. Inipol IPF was also the most effective dispersant tested at 5°C (but note that Corexit 9500 was not tested at this temperature).

On this basis, the dispersants were categorised into the three groups:

Recommended: Finasol OSR 51, Inipol IPF and Corexit 9500

Acceptable: Inipol IP-90 and Dasic Freshwater Dispersant

Not recommended: Finasol OSR 52, Dasic Slickgone NS, Bioversal HC, FLD-1 and FLD-2

A report describing the method development and the results obtained has been submitted to the RoK Ministry of Environment and Water Resources for their consideration in developing dispersant product approval regulations for Kazakhstan.

CONCLUSIONS:

An internationally recognised dispersant effectiveness test method has been modified for testing dispersants in conditions of low salinity that are relevant to the KSCS. The results show that some commercially-available dispersants, which are already approved for use in other parts of the world, produce reasonable effectiveness results when tested with 200°C+ Kashagan residue at 25°C or 5°C and in salinities ranging from 6 psu to 16 psu. Results obtained from laboratory effectiveness testing methods cannot accurately predict dispersant performance at sea because this will depend on many factors, but the results are good indicators of likely relative performance. The modified method has been suggested to the RoK Ministry of Environment and Water Resources as possibly being the basis for product approval regulations to be developed for Kazakhstan.

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