



International Oil Spill Response Technical Seminar

# Research on Development and Effectiveness Evaluation Technology of New Environment-friendly Oil Spill Dispersant

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## Abstract

Reasonably using oil spill dispersant has become one of the important emergency means intended to handle offshore oil spill accidents. With the worldwide nonstop occurrence of offshore oil spill accidents, the effect and toxicity influence of oil spill dispersant have seized popular attention. In particular, oil spill dispersant used in deepwater oil spill accidents urgently needs undergo evaluation of its underwater jetting effect. In this paper, the authors summarized the present condition and existing problems of researches on formula development, sea-surface and underwater application effect evaluation of oil spill dispersant. In addition, the authors gave a description about the progress made in the researches on new environment-friendly oil spill dispersant carried out by their laboratory and in the effect evaluation technology of sea-surface and underwater application of oil spill dispersant.

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## 1. Introduction

In recent years, with worldwide implementation of increasingly more hydrocarbon production activities, subsea pipeline cracking, offshore oil drilling platform leakage, or some other reasons have led to frequent occurrence of

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underwater oil spill accidents. Subsea spilled oil has severely impaired both marine environment and mankind in the entire process in which it enters water body undersea all the way to sea surface. For example, in the oil spill accident happened to a drilling platform named Deepwater Horizon in Mexico in April 2010, about 700,000 tons of crude oil leaked. The crude oil leaked and entered water body at the water depth of 1,500 m, and then formed a suspending plume zone at the depth between 1,000 m and 1,200 m; moreover, about 50% of crude oil rose to sea surface under the influence of buoyancy (Jane Lubchenco, et al, 2012), significantly damaging water body and marine organisms. With the further deepened exploration and development of gas and oil in South China Sea, offshore drilling platforms have advanced to the deepwater zone where subsea pipelines are constantly extended and thus lead to a relatively high risk of deepwater oil spill.

Surfactant, as the major component of oil spill dispersant, is able to remarkably decrease the interfacial tension between spilled oil and seawater and the viscosity of spilled oil, turning it to stable oil-in-water emulsion that will be rapidly dispersed in seawater due to its accelerated biological degradation, reducing the hazardous impact of spilled oil on marine environment.

Reasonably using oil spill dispersant has become one of the important emergency means intended to handle offshore oil spill accidents. For offshore oil spill accidents, oil spill dispersant is usually sprayed via either vessel or plane. However, the sea-surface spraying effect of oil spill dispersant cannot be quantitatively evaluated mainly because of: (1) Uncertainty of environmental conditions such as sea wave and temperature; (2) Difficult accurate evaluation by current technology of area and thickness of sea-surface oil films dispersed by oil spill dispersant. For an underwater oil spill accident like that happened to Deepwater Horizon in Mexico, Remote Operated Vehicles (ROV) was used to jet 3,000 m<sup>3</sup> of oil spill dispersant at seabed oil spill starting spot. This is the first large-scale underwater jetting of oil spill dispersant for oil spill accident in the world. However, few researches on underwater application technology and effect of oil spill dispersant are reported so far.

In this paper, on the basis of summarizing present research situation of oil spill dispersant development and the evaluation technology of its sea-surface and underwater application effect, the authors gave a description about the researches on these aspects carried out and progress made by their laboratory.

## **2. Development of New Environment-friendly Oil Spill Dispersant**

Since 1960s, the international community started the research and development of chemical oil spill dispersant. In 1967, a great volume of oil spill dispersant was used to handle the spilled oil from the Torrey Canyon oil spill accident; due to its high toxicity, the oil spill dispersant severely damaged the marine ecological environment. Hence, many scholars began to focus on the researches of low-toxic oil spill dispersant. Generally speaking, the oil spill dispersant products have undergone three development stages by types of surfactant and solvent (Su, 1992): For the first generation of products, the major component is anionic surfactant and the major solvent light aromatic hydrocarbon; for the second generation, the major component is nonionic surfactant with lower toxicity (mainly ether surfactant); for the third generation of concentrated products, its D-sorbitol, fatty acid, and other raw materials come from agricultural and sideline products, and the solvent is polyethyleneglycol so that the oil spill dispersant products are much less toxic.

The performance indicators of oil spill dispersant mainly include emulsification rate, biodegradability and biotoxicity. Through comparatively analyzing existing oil spill dispersant products in China, we found that they are mostly prepared using chemical surfactant serving as major component. Although they do have a great emulsification capability, their biodegradability and biotoxicity are not ideal.

In view of this situation, we launched the research on new efficient environment-friendly oil spill dispersant by starting with the international exploration focus-biosurfactant and its application. Firstly, we chose and cultured high-yielding strains of biosurfactant in addition to sampling bed mud and water body. After fermenting these

strains, we extracted biosurfactant with high emulsification performance. According to the main assessment indicators such as emulsification rate, biotoxicity and biodegradability, and through designed orthogonal experiment, we determined the oil spill dispersant formula dominated by biosurfactant.

Currently, the test over the efficient environment-friendly oil spill dispersant developed by us performed by the North China Sea Environmental Monitoring Center, State Oceanic Administration shows that its performance indicators meet relevant national standards. This oil spill dispersant can be used in oil spill accidents by domestic offshore oil platforms, ports and vessels and has a very promising application prospect.

### **3. Research on Evaluation Technology of Sea-surface Application Effect of Oil Spill Dispersant**

#### *3.1. Research progress of sea-surface application effect of oil spill dispersant*

The effect of oil spill dispersant used to handle offshore oil spill accident is influenced by many factors, such as oil type, oil spill dispersant type and environmental conditions (Fiocco and Lewis, 1999). Internationally, small indoor experiments are usually used to implement performance comparison of oil spill dispersant and study impacts of environmental factors. The typical examples are SFT (Fingas et al., 1987), BFT(Sorial et al, 2004a; Sorial et al, 2004b; Venosa et al, 2011), EXDET (Becker et al., 1993) and WSL (Martinelli, 1984) tests carried out by EPA. Such experiments are simple, cheap and controllable, but their results are inaccurate(Fingas, 2008) since they cannot reflect on-site sea condition. Fortunately, the wave flume simulation experiment developed in recent years can make up for the former's defects in addition to owning the former's merits, so that it has become an effective means to determine the effect of oil spill dispersant. For example, Li et al. (2008) used wave flume for their comparative study in which the effect of oil spill dispersant emulsifying MESA crude oil under regular wave and breaking wave conditions is investigated; Trudel et al. (2010) used OHMSETT wave flume to investigate the viscosity restriction of Corexit 9500 oil spill dispersant emulsifying crude oil. For the oil spill accident happened to the Deepwater Horizon in Mexico in 2010, the BP oil spill dispersant evaluation team used SL Ross wave flume to comparatively test the emulsification rates of oil spill dispersants and screened out those suitable for underwater environment (Ahnell et al, 2010).

Regarding researches on sea-surface application effect of oil spill dispersant, foreign countries started relevant researches abroad since 1990s which, however, were rarely seen in China. Daling et al. (1990) tested the emulsification rates of 3 kinds of crude oil emulsified by oil spill dispersant and their oil droplet diameter distribution, and afterwards built up a mathematical empirical model describing the relation between emulsification rate and oil droplet diameter distribution according to the test results. McCay et al. (2001) carried out the simulation research on sea-surface spilled oil behavior and water body concentration under the influence of oil spill dispersant by assuming that the emulsification rate of oil spill dispersant is respectively 25%, 50% and 75% and utilizing the 3D oil spill incidence model SIMAP. The research findings show that the used oil spill dispersant can change the oil-water entrainment rate and the oil droplet size distribution and promote the dispersion of oil droplets towards water body so as to lower oil evaporation rate and increase the oil concentration in water body. Chandrasekar et al. (2006) investigated the influence of many factors (e.g. oil type, oil spill dispersant type, salinity, temperature, weathering degree and rotating speed) on emulsification rate of oil spill dispersant through small indoor experiments, and built up a multi-factor empirical equation describing the relation between emulsification rate of oil spill dispersant and many influential factors.

#### *3.2. Research on simulation experiment of sea-surface application effect evaluation of oil spill dispersant*

According to required oil spill dispersant type used for emergency handling of offshore oil spill accidents and required technical conditions of applying oil spill dispersant, our lab built the simulation experiment device used for evaluating sea-surface application effect of oil spill dispersant. The device is called Wave Flume for Offshore Oil Spill Simulation Experiment, as shown in Figure 1. Its physical dimensions are 5 m×0.3 m× 0.4 m (length × width × depth). The both ends of wave flume are provided with wave generators and wave dampers; the generator can

generate waves with maximum wave height of 0.15 m and adjustable frequency. The flume has the temperature regulation function which supports a temperature range from 5 to 30°C.



Fig.1. Wave Flume for Offshore Oil Spill Simulation Experiment

The experiment starts with injecting seawater into the wave flume until the water depth reaches 0.25 m. A restrictor ring is then placed in the central zone of the flume; a 100 ml injector is used to inject a certain volume of crude oil into sea surface. Next, oil spill dispersant is injected into oil surface by a specific dispersant-to-oil ratio. Next, the wave generation system of the wave flume is started to mix oil, oil spill dispersant and seawater for 20 minutes.

The emulsification rate and oil droplet diameter distribution are chosen as evaluation indicators of oil spill dispersant application effect. The horizontal area of the wave flume is designed with 5 water body sampling cross-sections which are arranged 0.4 m apart. Each cross-section is provided with 2 sampling points at different depths where automatic samplers are used to sample 100 ml of water body at different times (2, 5, 10 and 20 minutes). After extracted by dichloromethane, the water samples are measured by UV-vis spectrophotometer to determine the concentration of dispersed oil in water sample and further the emulsification rate of oil spill dispersant emulsifying experimental crude oil. Meanwhile, a microscope camera is used to collect and analyze diameter data of dispersed oil droplets in water body.

#### **4. Research on Underwater Application Effect Evaluation Technology of Oil Spill Dispersant**

##### *4.1. Underwater oil spill theory*

Underwater blowout oil spill mainly involves three important featured stages (Figure 2): Jet zone, plume zone and surface interaction zone (Fannelop and Sjoen,1980). Jet zone refers to an area in which underwater spilled oil ejects in the form of jet from oil spill opening and rises at the initial speed caused by pipeline or formation pressure. The jet zone stands for the initial stage of underwater oil spill. Plume zone refers to an area in which spilled oil rises in the form of plume at a slower speed under the influence of buoyancy playing an increasingly dominating role. The plume stage lasts much longer, specifically from the end of the jet stage to the plume rising to sea surface. The behavioral features of underwater plume are highly related with oil droplet diameter formed during the plume stage, specifically, oil droplets with smaller diameters are more possible to form underwater plume (Yapa et al, 2012). The plume remarkably influenced by buoyancy and transverse flow has a serious impact on the behavior and incidence

of deepwater underwater spilled oil. In the surface interaction zone, due to the influence of the external environmental factors (e.g. wind, wave), spilled oil drifts, disperses or weathers.

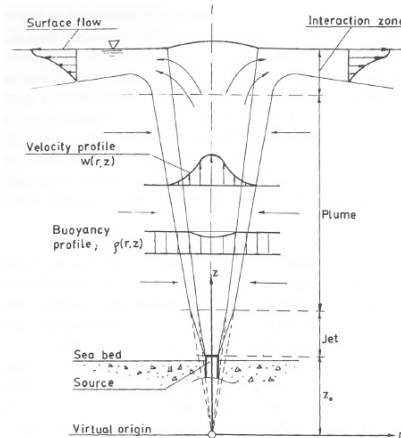


Fig.2. Stages of Underwater Blowout Oil Spill (Fanneløp and Sjøen, 1980)

For deepwater underwater oil spill, after crude oil ejects from underwater oil spill spot, spilled oil entrains surrounding water body. Due to the greater density compared to oil, the surrounding water body is constantly entrained into buoyant jet which consequently grows bigger in both volume and density. Now, the oil droplets in the buoyant jet gather up with water body and then migrate as a whole in the form of mixture. The migration of the main body of plume is related with the shape, size and density of oil droplets. As high-density seawater is constantly entrained, the plume grows further bigger in density; when the plume rising to a low-density seawater environment, a stable state is achieved between the plume and the surrounding water body; now, the oil droplets tend to disperse. At a certain stage, the impetus of the plume completely disappears, and the plume floats up under the influence of its own buoyancy (Rye et al, 1997; Yapa et al, 1999). Smaller oil droplet diameter leads to oil droplets taking a longer time to rise to sea surface. Meanwhile, the oil droplets begin to disperse horizontally under the influence of transverse flow. The stages of deepwater underwater plume behavior are as shown in the following figure (Zheng et al, 2003).

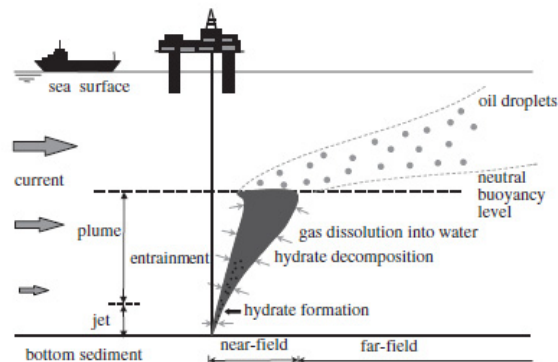


Fig.3. Stages of Deepwater Underwater Blowout Oil Spill (Zheng, 2003)

Spraying deepwater underwater oil spill dispersant is considered to be able to disperse spilled oil at underwater oil spill spot and thus change the diameter distribution of oil droplets and further influence the behavioral process and incidence of underwater spilled oil. However, regarding the effect prediction model of underwater application of oil spill dispersant, foreign study is currently in its infancy stage, while no relevant study has been seen in China.

For the oil spill accident happened to the Deepwater Horizon in Mexico, Paris et al. (2012) simulated the behavior and incidence of the components of petroleum hydrocarbon in water body by using the hydrodynamic and random buoyant particle tracking coupling model, and also simulated the far-field conveyance process of oil starting at the invasion depth. The simulation result indicates that oil spill dispersant can only slightly reduce the volume of crude oil rising to sea surface (1%~2%) under the assumed condition that underwater oil spill dispersant was well mixed with oil, but it can significantly increase the oil content in the plume at the depth of 1,000 m (10%~25%) .

#### 4.2. Experimental research

In order to investigate the effect of oil spill dispersant jetted to disperse underwater spilled oil, our lab built underwater application simulation experiment device of oil spill dispersant according to the underwater oil spill characteristics and oil spill dispersant jetting needs. The underwater simulation experiment flume for oil spill dispersant is as shown in Figure 4. The flume is a completely transparent glass channel with the physical dimensions of 2 m×1 m× 1 m (height × length × width), able to hold 2 m<sup>3</sup> of seawater. The flume bottom is provided with a crude oil jetting orifice and an oil spill dispersant jetting opening, allowing to simulate oil spill dispersant spraying under the underwater oil spill condition.

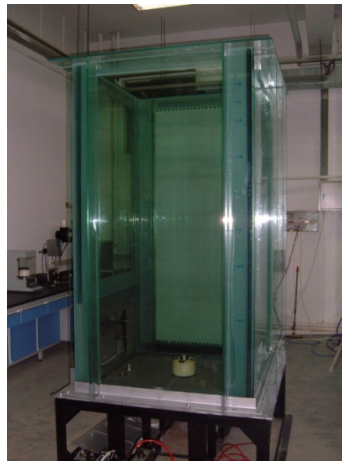


Fig.4. Underwater Simulation Experiment Flume for Oil Spill Dispersant

However, what should also be considered is that the built experiment device is a 2 m-high atmospheric-pressure experiment unit, so it is basically infeasible to simulate the underwater (especially deepwater) crude oil blowout process with it. This research, therefore, mainly aims at the stage of underwater oil spill in which spilled oil ejects, breaks and then forms oil droplets.

The underwater simulation experiment system of oil spill dispersant is as shown in Figure 5. The underwater simulation experiment system of oil spill dispersant consists of experiment flume, experiment water preparation flume, spilled oil ejection unit, oil spill dispersant jetting unit and data acquisition unit.

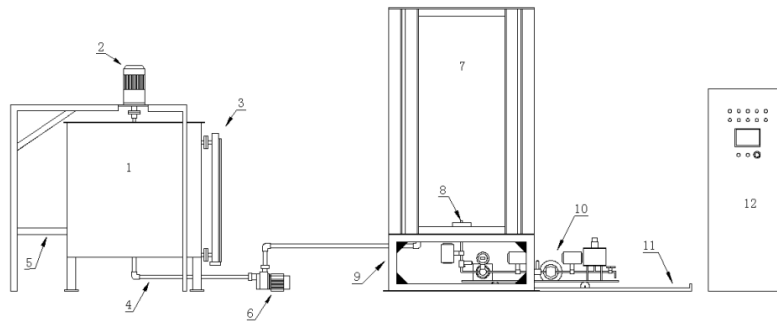


Fig.5. Underwater Simulation Experiment System of Oil Spill Dispersant

The experiment starts with injecting artificial seawater into experiment flume until the water depth reaches 1.7 m. The oil tank is then filled with experiment crude oil which ejects from the flume bottom into water body with the help of the pressure pump. Next, an oil spill dispersant jetter is used to jet oil spill dispersant over the oil spill opening via a conduit to allow the dispersant-to-oil ratio (DOR) to reach a specific value. The ejection effect of crude oil is as shown in Figure 6.



Fig.6. Underwater Ejection Effect of Crude Oil

At the height 1.5 m from the flume bottom, a camera is used to shoot the major profile of spilled oil from a side of the flume. At the adjacent side of the flume, a microscope camera is used to shoot diameter data of oil droplets. Next, data are extracted from the oil droplet diameter information pictures and analyzed before determination of oil droplet diameter distribution in experiment water body. After an experiment cycle, water samples are collected to determine oil concentration and surface tension data.

#### 4.3. Discussion

As the underwater application effect of oil spill dispersant is influenced by many factors such as oil type, crude oil ejection conditions, oil spill dispersant type and consumption, it's necessary to choose representative crude oil according to specific characteristics of sea area, and carry out application effect evaluation simulation researches of

oil spill dispersant in the cases of different oil spill dispersant spraying positions and different dispersant-to-oil ratios on the basis of screening oil spill dispersant type.

The oil droplet diameter distribution formed during the initial stage of underwater oil spill is the important factor influencing the migration of underwater spilled oil. However, the international community has currently reached no definitive conclusion of the impact of pressure on the diameter distribution of underwater spilled oil. Therefore, it's needed to carry out evaluation researches on underwater application effect of oil spill dispersant under high pressure condition to investigate the impact of deepwater pressure condition on oil droplet diameter distribution.

The evaluation model of underwater application effect of oil spill dispersant is built according to the results of underwater application effect simulation experiment of oil spill dispersant being carried out by our lab. Furthermore, the above-mentioned model is coupled with the prediction model of underwater spilled oil behavior to realize simulated prediction of underwater spilled oil behavior and incidence under the influence of oil spill dispersant.

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