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Effect of Salinity on the Effectiveness of Solidifiers for Crude Oil Spill Remediation

Devi Sundaravadivelu[1], Makram T. Suidan [2]*, Albert D. Venosa[3], Pablo I. Rosales [4]

[1] University of Cincinnati, College of Engineering and Applied Science, Environmental Engineering Program, Mail Location 0012, Cincinnati, OH 45221, USA

[2] American University of Beirut, Faculty of Engineering and Architecture,Room 308, P.O.Box 11-0236 Riad El Solh, Beirut1107 2020, Lebanon

[3]U.S. Environmental Protection Agency, National Risk Management Research Laboratory, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA (retired)

[4]University of Cincinnati, Advanced Materials Characterization Center, Cincinnati, OH 45221, USA

* Corresponding author. Tel.: 011 961-1-347 952; Fax: 011 961-1-744 462; E-mail address: msuidan@aub.edu.lb (M.T. Suidan).

ABSTRACT 300048:

A laboratory investigation was conducted to test the effectiveness of solidifiers with fresh water and artificial seawater using Prudhoe Bay Crude oil. Experiments were designed to study the effects of salinity, solidifier type, solidifier-to-oil mass ratio (SOR), mixing energy and beaker size using five solidifiers.

The U.S. Environmental Protection Agency is developing a protocol for testing the effectiveness of solidifiers in a laboratory setting. This involves measuring the amount of free oil remaining in the water after the solidified product is removed using an ultraviolet–visible spectrophotometer. For these experiments, 0.25 mL of oil was added to salinized beaker containing 80 mL of water. Milli-Q water and sterile GP2 seawater were used as the exposure media. The mass of the solidifier was changed depending on the SOR. Each of the solidifier was added to a slick of crude oil on water. After stirring the mixture for 30 minutes, the solidifier was removed. The water with the remaining oil was transferred from the beaker to 250 mL separatory funnel. The solution in the funnel was extracted three times with 20 mL of dichloromethane and the final volume adjusted to 60 mL. The extracted samples were analyzed for oil content with an Agilent 8452 ultraviolet–visible spectrophotometer. All experiments were carried out in triplicate. An analysis of variance (ANOVA) was performed on the data collected, which helped quantify the main and interactive effects of the variables. Salinity of the water was mostly found to be an insignificant factor. Results indicated that SOR and solidifier type are the most important variables affecting removal efficiency.

INTRODUCTION:

Solidifiers are typically high molecular weight, dry hydrophobic materials that have a porous matrix and a large oleophilic surface area. They react with oil to form a cohesive, solidified mass that floats on water. Solidifiers often consist of polymerization catalysts and cross linking agents. Tests have reported that most solidifiers work but require large amounts of agents to solidify the oil effectively. It has been reported that 16% to over 200% by weight (solidifier–oil mass ratio) is required to solidify crude oil (Fingas et al., 1993, 1995). The effectiveness of the products varies widely; however, the aquatic toxicity of all products tested is below the threshold of measurement (Fingas et al., 2008). The use of solidifiers for oil spill remediation can be useful especially in sensitive areas where the use of chemical is not ideal.

Different laboratory effectiveness tests have been developed for solidifiers. Fingas et al. (1993) tested the effectiveness of three different solidifiers by adding the product at one minute intervals to oil under constant stirring conditions until the oil solidifies. They found that it was necessary to double the amount used in the laboratory to solidify oil in a real spill. Rosales et al. (2010) conducted a screening study on the use of five different solidifiers as a response tool to remove crude oil slicks on seawater. The concentration of crude oil remaining on the artificial seawater ranged from 16% to 43% for solidifiers tested with a solidifier to oil ratio (SOR) of 1:4. These results generally agree with the work done by Delaune et al. (1999) who reported a 70% removal of crude oil using 1:2 SOR. Dahl et al. (1996) studied the effectiveness of solidifier using three different crude oils. The solidifier was added till no visible oil remained. The SOR ranged between 1.5 to about 3.5.

Even though various effectiveness tests have been performed, there is a lot of variability based on oil type and test conditions. Better knowledge of a solidifier’s performance under various environmental conditions will help in the development of protocols for testing the appropriateness of using solidifiers while responding to oil spills. Several experiments have been conducted to measure the effect of salinity on other oil spill countermeasures such as dispersants. Generally the efficiency of dispersants increase with increase in salinity for most oil–dispersant combinations as reported by Chandrasekar et al. (2006). However, the effect of salinity on solidifiers has not been widely studied.

National Oil and Hazardous Substances Pollution Contingency Plan (NCP) Product Schedule governs the use of Miscellaneous Oil Spill Control Agent (MOSCA), surface washing agents (SWA), dispersants and bioremediation agent. Currently, nine of the twenty one MOSCA listed are solidifiers and there are no effectiveness values summarized unlike dispersants or SWA. The application rates for the solidifier products reported in the NCP vary in terms of test conditions used for measuring their effectiveness such as oil type, salinity, mixing energy, and volume of oil used, as there are no protocols in place for evaluating the effectiveness of solidifiers. Standardized method for measuring and reporting solidifier efficiency is crucial as this would aid in making informed decisions in the event of a spill and enhance the likelihood of a successful clean-up operation.

OBJECTIVES:

The goal of this work was to measure the efficiency of commercial solidifiers and develop a preliminary effectiveness testing protocol that is reproducible and provides information that can be used to predict effectiveness in the field. Also, the effect of protocol variables namely salinity, solidifier type, solidifier-to-oil mass ratio (SOR), mixing energy and surface area on solidifier effectiveness was studied. The work presented here shows the methodology that was chosen to create reproducible and repeatable conditions for a valid testing protocol and discusses the effect of the five variables.

MATERIALS AND METHODS:

Five commercial solidifiers (referred to as S1, S2, S3, S4, and S5) were examined at three different SORs in this study for their effectiveness. Prudhoe Bay Crude (PBC), medium weight EPA/American Petroleum Institute (API) standard reference oil was used in the study. Artificial seawater, modified GP2 (Bidwell and Spotte, 1985), was used as one of the exposure media with a salinity of 35 ppt. Milli-Q water was used as the exposure media for experiments that required fresh water. Methylene chloride (DCM) was used for preparation of oil in DCM stock standards and for extraction of aqueous samples. Oil in DCM standards and samples were analyzed directly by ultraviolet–visible spectrophotometery.

Experimental Procedure: The effectiveness of a solidifier was determined by the amount of free oil remaining in the water after the solidified product was removed from the solution. The experimental procedure was based on the study by Rosales et al. (2010).A volume of 0.25 mL of oil was added to salinized beakers containing 80 mL of water. Oil volume was kept constant in the experiments, while the mass of the solidifier was changed depending on the SOR. The experiments were carried out using an SOR of 1:2 (0.112 g solidifier–0.223 g crude oil), 1:4 (0.056 g solidifier–0.223 g crude oil), and 1:8 (0.028 g solidifier–0.223 g crude oil). Each of the solidifiers was added to a slick of crude oil on water in a 400 mL or 800 mL beaker as shown in Fig. 1. After stirring the mixture (at 0, 60 or 120 rpm) for a contact time of 30 minutes, the solidifier and solidified oil were removed with tweezers. The water with the remaining oil was transferred from the beakers to a 250 mL separatory funnels. The remaining solution in the funnels was extracted three times with 20 mL of DCM and the final volume adjusted to 60 mL.

All experiments were carried out in triplicate. The resulting data were plotted as the average of triplicate samples; the acceptance criterion for the triplicate samples was initially set at a Standard Deviation of $\leqslant$5%. All residual crude oil concentrations remaining on the water after the solidified oil was removed was measured by ultraviolet–visible spectroscopy. A diode-array Agilent 8453 ultraviolet–visible spectrophotometer was used to analyze the extracts. Once the parametric study with five solidifiers and PBC was completed, an evaluation of the experimental parameters was carried out by statistic analysis of variance.

Fig. 1 Experimental setup showing (a) top view of oil slick and solidifier in a 400 mL beaker with fresh water; (b) triplicate samples mixing at 60 rpm for 30 min; (c) solidified product being removed with tweezers after contact time.

Fractional Factorial Design: For this work, a fractional factorial experiment was designed to determine variables that contribute to the performance of solidifiers in removing crude oil from surfaces under the developed preliminary protocol. The response factor was the percent of oil removed by the solidifier from the aqueous phase. This represents the fraction of oil removed from the water at ambient laboratory conditions and is a direct measure of solidifier effectiveness. Table 1 lists the five factors with fixed conditions and the five factors that were tested at multiple levels. This resulted in 5 one-way interactions and 10 two-way interactions. All experiments were performed in triplicate, which resulted in 180 experimental conditions and 540 total experimental units.

SAS Proc GLM was used to perform the statistical analyses, with each of the five solidifiers, each of the five variables, and all two-way interactions between the variables. Three-way and higher interactions were considered to be negligible. Because significant differences were expected between the five solidifiers, analyses were also performed for the five solidifiers separately to confirm the conclusions found in the combined model. The results of the separate analyses yielded similar conclusions as the combined model.

Table 1: Factors and levels for fractional factorial experiment.

Factors	Levels
Time	30 min
Oil Volume	0.25 mL
Water Volume	80 mL
Temperature	22 ˚C
Oil	PBC
5 solidifiers	S1, S2, S3, S4, S5
2 beaker size	400, 800 mL
2 salinities	0, 35 ppt
3 mixing speed	0, 60, 120 rpm
3 SOR	1:2, 1:4, 1:8

RESULTS AND DISCUSSION:

Preliminary tests revealed certain variables that did not significantly affect protocol performance and were fixed at values convenient for testing purposes (Rosales, et. al., 2010). Those variables were fixed at the following levels: contact time (30 min), oil volume (0.25 mL), and water volume (80 mL). All remaining variables were evaluated at multiple levels to determine their significance to solidify and to establish optimal levels. The General Linear Model Method from the ANOVA was used to test the level of significance of each factor studied; this method uses the F-test for performing the ANOVA. If the resulting p-value from the F-test is smaller than the α-level selected, the association is statistically significant (Srinivasan et al., 2007). ANOVA performed helped to quantify the main and interaction effects of the factors considered in the study using statistical analysis software. The response (percent dispersion) was set at 95% confidence limit. The probability, P, is compared with α=0.05 (95% confidence limit) to evaluate the main effects and interaction effects of factors on percent of oil recovered.

Table 2: Main and Two Way Interactions in the Combined Model

Factor	P value
Solidifier	p < 0.0001
Beaker size	p = 0.0081
Salinity	**p = 0.1210**
Mixing speed	p < 0.0001
SOR	p < 0.0001
Salinity * Solidifier	p = 0.0164
Salinity * Beaker size	**p = 0.0516**
Salinity * Mixing speed	**p = 0.0749**
Salinity * SOR	p = 0.0007
Solidifier * Beaker size	p = 0.0025
Solidifier * Mixing speed	p = 0.0087
Solidifier * SOR	p < 0.0001
Beaker size * SOR	p < 0.0001
Mixing Speed * SOR	p < 0.0001
Beaker size * Mixing speed	p < 0.0001

P value < 0.05 = Significant factor

Main Effects in the Combined Model: Table 2 shows the 5 main interactions and the 10 two way interactions from the combined model. P-values denoting significant differences among the multiple levels for each factor are also given. All factors were found to be significant with the exception of salinity (p = 0.121). Solidifier type, beaker size, mixing speed and SOR were found to significantly affect response across the levels. An expected difference in oil recovery is observed depending on the type of solidifier and the amount of solidifier added. Positive correlations were observed for SOR with the highest application rates yielding the highest oil recovery. It is important to note that there is no restriction on SOR except what is reasonable from a cost and toxicological standpoint. However, ceiling effects were observed for mixing speed with no additional benefit provided by the highest level over the middle level for this factor. Thus, the middle level can be considered to be the maximum value needed to achieve the best response. The average removal efficiency was marginally higher with the 400 mL beaker (56.6%) than the 800 mL beaker (55.3%).

Two Way Interactions in the Combined Model: An analysis of interactions was done to determine whether any two way interactions that may occur might vary the result obtained by any factor separately. While salinity was found to be an insignificant factor, it was necessary to evaluate if other factors may affect salinity in any way. To do this, the two-way interactions between salinity and the other four factors were evaluated. Of the four interactions only [Salinity * Mixing Speed] (p = 0.0749) and [Salinity * Beaker Size] (p = 0.0516) were found to be insignificant. [Salinity * Solidifier] and [Salinity * SOR] were found to be statistically significant. To determine if the solidifiers performed better in fresh water or saline water, the results of the [Salinity * Solidifier] interactions were studied. For S2, S3, S4 and S5, there was a slight decrease (average of 1.4%) in removal efficiency when using the artificial seawater. Based on these results, we can say that, generally the removal rate is slightly higher while using fresh water. When we look at the interactions between [Salinity * SOR], the mean removal efficiency while using fresh water found to be somewhat higher. When we look at the 6 other two way interactions, they are all found to be statistically significant too. Most of these two-way interactions include either solidifier type or SOR as one the variable. Thus, we can conclude that solidifier type and SOR are the most important factors, and additionally, they affect the potency of the other factors significantly.

Main and Two-way Interactions in the Separate Analysis: When a separate analysis was performed on each of the five solidifiers, the results obtained were very similar to the combined model. Beaker size was an insignificant factor for most solidifiers. However, there was a higher removal rate (3%) with the 400 mL beaker for S1 and S4. Salinity was found to be an insignificant factor except for S4. The removal efficiency was a bit higher while using fresh water with all the solidifiers, but this was especially significant for S4. Mixing speed was found to be a significant factor with all the solidifiers. But the ceiling effect that was observed in the combined model was present in the separate analysis too. For example, with S5, the removal efficiency was 57%, 61% and 60% for a mixing speed of 0 rpm, 60 rpm and 120 rpm respectively. The SOR was a very significant factor for all solidifiers and there was a positive correlation wherein higher efficiency was achieved by adding additional solidifier.

Table 3: Main and Two-way Interactions in the Separate Analysis

Factor	**P value for**				
	S1	**S2**	**S3**	**S4**	**S5**
Beaker size	0.0122	**0.319**	**0.1112**	<.0001	**0.3846**
Salinity	**0.0728**	**0.348**	**0.2766**	<.0001	**0.4933**
Mixing speed	<.0001	<.0001	<.0001	<.0001	<.0001
SOR	<.0001	<.0001	<.0001	<.0001	<.0001
Salinity * Beaker size	0.0153	**0.3372**	0.0176	**0.5768**	**0.956**
Salinity * Mixing speed	**0.2387**	0.0026	0.0038	<.0001	<.0001
Salinity * SOR	**0.1801**	<.0001	<.0001	0.0024	0.003
Beaker size * SOR	<.0001	<.0001	**0.1079**	**0.0534**	<.0001
Mixing Speed * SOR	<.0001	<.0001	0.0341	<.0001	<.0001
Beaker size * Mixing speed	<.0001	<.0001	0.0027	0.0189	**0.9572**

P value < 0.05 = Significant factor

The two way interaction between [Salinity * Beaker Size] was found to be insignificant in the combined model. However, this was not the case for S1 and S3 in the separate analysis. There was around 2% decrease in efficiency while using the artificial seawater. Also, [Salinity * Mixing Speed] was not significant in the combined model. But in the separate analysis, it was significant for all solidifiers except S1. For S2, S3, S4 and S5, the removal efficiency is a little higher while using fresh water. In conclusion, the removal efficiency is marginally higher while performing the experiments with fresh water in a 400 mL beaker at a mixing speed of 60 rpm which overall agreed with the conclusions obtained in the combined model.

CONCLUSION AND SUMMARY:

In order to develop a method to test the effectiveness of commercial solidifiers in cleaning up oil spills on water, five variables at multiple levels were evaluated using a fractional factorial design. In general, salinity was found to be an insignificant factor. Solidifier type and SOR were the most significant variables. Thus, using this method one can measure each product's recommended application rate under predetermined laboratory conditions and compare their performances. This preliminary testing method is found to be consistent and reproducible with standard deviation values under 5%. While reproducibility of operators has to be considered in the future evaluation of this method, the current experimental procedure is able to systematically evaluate commercially available solidifiers under laboratory conditions. The impact of protocol variable may be more pronounced while using heavier oils. Hence, future experiments will be conducted using a heavier weight refined oil, and additional solidifiers.

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