Clean Technologies and Environmental Policy, April 2016, Volume 18, Issue 4, pp 1141 − 1150
DOI:10.1007/s10098-016-1107-1

Development of a Testing Protocol for Oil Solidifier Effectiveness Evaluation

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Abstract

Chemical countermeasures for oil spill remediation have to be evaluated and approved by the U.S. Environmental Protection Agency before they may be used to remove or control oil discharges. Solidifiers are chemical agents that change oil from a liquid to a solid by immobilizing the oil and bonding the liquid into a solid carpet-like mass with minimal volume increase. Currently,they are listed as Miscellaneous Oil Spill Control Agent in the National Contingency Planand there is no protocol for evaluating their effectiveness. An investigation was conducted to test the oil removal efficiency of solidifiersusing three newly developed testing protocols. The protocols were qualitatively and quantitatively evaluated to determine if they can satisfactorilydifferentiate effective and mediocre products while still accounting for experimental error.The repeatability of the three protocols was 15.9%, 5.1% and 2.7%.The protocol with the best performance involved measuring the amount of free oil remaining in the water after the solidified product was removed using an ultraviolet–visible spectrophotometer and it was adopted to study the effect of solidifier-to-oil mass ratio, mixing energy, salinity, andbeaker size (i.e., area affected by the spill) on solidifier efficiency. ANOVAswere performed on the data collected and results indicated that the beaker size increased spreading, whichreduced removal efficiency. Mixing speedappears to impart a ceiling effect with no additional benefit provided by the highest level over the middle level. Salinity was found to be mostly an insignificant factor on performance.

Key Words

Oil spill; Oil solidifier; Crude Oil; Salinity; Protocol; Effectiveness.

1. Introduction

Solidifiers used in oil spill response are typically high molecular weight polymers that have a large oleophilic surface area. They react with oil to form a cohesive, solidified mass that floats on water. The U.S. Environmental Protection Agency (EPA) and ExxonMobil Research and Engineering conducted research on the potential use of solidifiers in a scenario where the vessel was loaded to capacity was in imminent danger of sinking or breaking up (Goldstein et al., 1974). The strategy was to solidify the oil in the vessel to prevent its release to the water. However, several limitations such as availability of equipment for injecting and mixing the contents of the tank and the large amount of products required for solidifying the cargo were identified. ExxonMobil Research and Engineering initiated another program in the 1990s to identify solidifiers that potentially could be used to protect shorelines from oil spills (Dahl et al., 1996). Although past evaluations of solidifiers concluded that the cost of application to large spills would be prohibitive due to the large amount of material required to solidify the entire spill (Fingas et al., 1990), they concluded that the amount of solidifier can be significantly reduced if only the leading edge of a spill in calm water such as a harbor or lake was solidified. The motivations for using solidifiers are to recover oil from smaller areas quickly, to prevent the spread of slicks, to recover thin sheens and to protect areas and wildlife on a rapid basis.

Since then different laboratory effectiveness tests have been developed for solidifiers. Fingas et al. (1993) tested three different solidifiers by adding the product (at 1 minute intervals) to oil under constant stirring conditions until the oil solidifies. The solidifier that performed better in laboratory tests was tested again on a larger scale. They found that it was necessary to double the amount used in the laboratory to solidify oil in a real spill. Ghalambor (1996) investigated the performance of 23 solidifiers to remove three crude oils. The solidifiers were tested under static and dynamic (200–400 rpm) conditions and the heat released during the solidification reaction was measured by a solution calorimeter. This study found that the level of solidifier consumption varied for different crude oils. DeLaune et al. (1999) tested a commercial solidifier (Nochar A650) on open water to remove South Louisiana crude oil. The effectiveness test consisted of applying one part solidifier to two parts crude oil and letting them react for 4 days. At the end of the contact time, the researchers found that over

70% of the crude oil was solidified. 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 solidifiers were used to remove Prudhoe Bay crude oil under laboratory conditions. The concentration of crude oil remaining on the artificial seawater ranged from 16% to 43% for solidifiers tested with a Solidifier-to-Oil-mass-Ratio (SOR) of 1:4. These results generally agree with the work done by DeLaune et al. (1999). Cardello (1996) investigated the use of oil spill solidifiers for land applications by evaluating the final consistency and solidification time for SORs from 1:1 to 1:4. Rea (1991) tested seven pure polymer or cross-linking chemicals with diesel fuel. A penetrometer test to determine hardness/toughness of the solidified product was conducted in order to verify relative degree of solidification. There was little differentiation between the various polymers in terms of penetrometer data over the time.

It should be noted that all researchers felt that the disappearance of free oil method did not result in good repeatability. Analytical means in any test system is a major concern. Penetrometers and viscometers were used to determine an end point for noting the presence of liquid oil by several researches (Rea 1991; Fingas 1995). These methods did not yield consistent results and sampling a heterogeneous material proved to be difficult. Even though various effectiveness tests have been performed, there is a lot of variability based on oil type and test conditions. The performance of solidifier products is expected to depend upon a number of incident-specific variables including oil type, oil amount, and weather conditions such as the state of the sea, and air and sea temperature. Walker et al. (1999) reviewed the effectiveness and environmental considerations for non-dispersant chemical countermeasures and reported that the effectiveness decreases for emulsified, weathered, thick, or heavy oils due to the difficulty of mixing the product into viscous liquids. They reported also that salinity has no effect on the solidification of oil which agrees with studies by Pelletier and Siron (1999) Walker et al. (1995) and Fingas (2008).

The evaluation and pre-authorization of solidifier products is essential since it will serve as a strategic planning tool for regional response teams and state or federal coordinators. Additionally, understanding the environmental considerations and the role of solidifier and oil properties will help

101 determine the desirability and appropriateness of using solidifiers for oil spill remediation. One of the
102 outcomes of this research will be in the form of a standardized effectiveness testing protocol that is
103 reproducible and provides information that can be used to predict effectiveness in the field.
104 Additionally, the effect of protocol variables such as solidifier type, oil type, SOR, salinity, mixing
105 energy and surface area on removal efficacy were studied at multiple levels. The data collected from
106 these experiments were used to perform an Analysis of Variance (ANOVA) on each oil type to
107 determine the most sensitive variables. Only significant variables will be used for future experimental
108 work. The new effectiveness test for solidifiers presented herein may eventually be used to screen
109 productsprior to use in order to differentiate effective and mediocre products.

110 **2. Materials and Methods**

111 Nochar A650(Nochar, Inc., Indianapolis, IN, USA), Waste-Set #3200®(Environmental &
112 Fire Technology, LLC, Grand Rapids, MI, USA), C.I.Agent(C.I.Agent Solutions, LLC, Louisville,
113 KY, USA), Rubberizer(ClearTec™, San Diego, CA, USA), and HTP(American Products Enterprises
114 Corp., Woodstock, GA, USA) were used in the solidification experiments. These five commercial
115 solidifiers (referred to randomly as S1, S2, S3, S4, and S5; i.e., the labels assigned should not be
116 construed to refer to the solidifier order named above) were evaluated for their effectiveness in
117 removing oilat room temperature. Three crude oils were used for these experiments, namely Arabian
118 light crude (ALC), Prudhoe Bay crude (PBC), and Intermediate Fuel Oil 180 (IFO180), which are
119 light, medium, and heavy oils, respectively, according to their reported API gravity. PBC is a medium
120 weight EPA/American Petroleum Institute (API) standard reference oil. It has been thoroughly
121 characterized in previous EPA and API studies. The physical properties of the three crude oils used
122 are listed in Table 1.

123 **Table 1. Properties of Oils Used**

Oil Name	Measured Dynamic Viscosity at 22 °C cP	Measured Density at 22 °C g mL^{-1}	API Gravity	Oil Category by API Gravity*

Arabian Light	14	0.867	31.71	Light
Prudhoe Bay	30	0.898	26.07	Medium
IFO 180	1414	0.957	16.36	Heavy

**General crude oil categories: Heavy (API < 22.3°), Medium (22.3° ≤ API < 31.1°), and Light (API ≥ 31.1°).*

Artificial seawater, modified GP2 (Bidwell and Spotte, 1985), was used as one of the exposure media. The pH value of the artificial seawater was 7.6 ± 0.1, and the testing temperature was at ambient laboratory conditions (22 ± 1°C).Milli-Q water was used as the exposure mediumfor experiments that required freshwater.Methylene chloride (dichloromethane, DCM, pesticide quality) 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 UV-Visible spectrophotometry. The experiments were carried out in silanized beakers to minimize adherence and spreading of oil on the walls of the glassware(Armaregoet al., 2009).

2.1.Experimental Procedure

A volume of 0.25 mL of oil was added to silanized beakers containing 80 mL of water. A syringe was used to dispense the PBC and ALC oils. However, because IFO180 was too viscous to be dispensed with a syringe, a Brinkmann Eppendorf repeater pipettor capable of dispensing 2 µL to 5 mL, depending on the tip selected, was used for dispensing 0.25 mL of the heavy oil. Oil volume was kept constant in the experiments, while the mass of the solidifier was changed depending on the SOR. Each of the solidifiers was added to a slick of crude oil on water and after stirring the mixture for a contact time of 30 min, the solidifier and solidified oil were removed and analyzed. The removal of the solidified mass and analysis was performed using three distinct setups in order to identify the best method suited for measuring effectiveness of the solidifier product.

2.1.1. Protocol 1

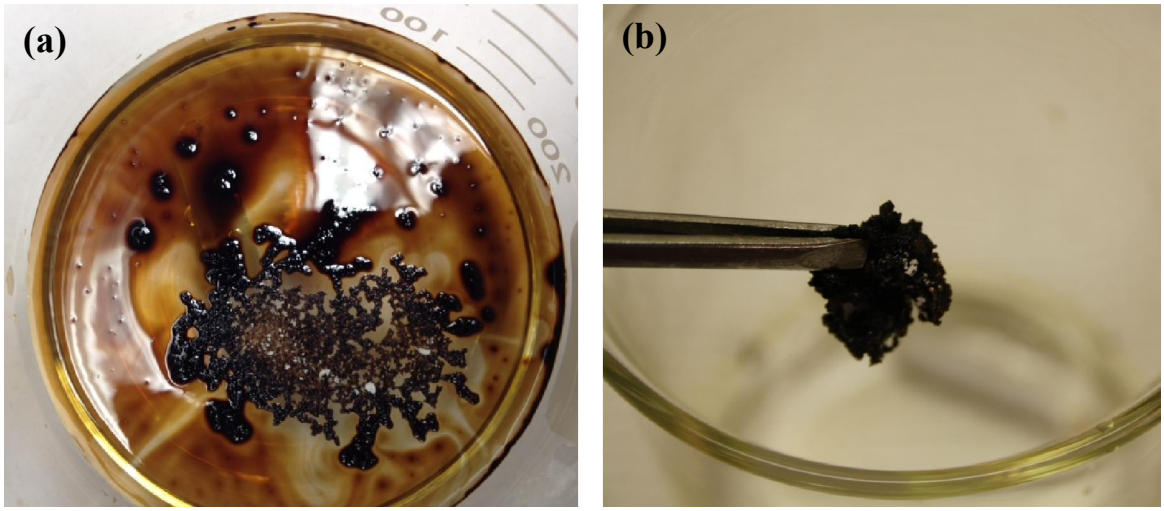
In the first method, the oil and solidifier were added at a SOR of 1:4. Oil volume was kept constant in the experiments (0.25 mL), while the mass of the solidifier was changed depending on the oil used (Supplementary Material, Table 1). At the end of the contact time, the solidified product was

removed with a spatula, dried for a day and weighed. The percent recovery of oil was calculated by measuring the weights of the oil and solidifier added initially and the weight of the final solidified product formed. The experiments were conducted in triplicate in 400 mL silanized beakers with the mixing speed set at 60 rpm.

2.1.2. Protocol 2

The second protocol consisted of removing the solidifier and solidified oil with tweezers as seen in **Fig. 1**at the end of the contact time. Some of the unsolidified oil adhered onto the solidified mat formed, and hence was removed by attachment (and not true solidification). The water with the remaining oil was transferred from the beakers to 250 mL separatory funnels. The beakers were rinsed with 20 mL DCM and the solution was added to the funnels and extracted. This was performed three times so that the final volume of the DCM extract was 60 mL. All experiments were carried out in triplicate and the residual crude oil remaining on the water after the solidified oil was removed was quantified by UV–Visible spectroscopy. A diode-array Agilent 8453 UV-Visible Spectrophotometer was used to analyze the extracts. This instrument was set to conduct complete sample scans over the range of wavelengths. Absorbance measurements at 340, 370, and 400 nm were used to calculate the area under the absorbance curve for the standards and samples (Srinivasan et al., 2007). The concentrations of the sample extracts were calculated using the trapezoidal rule (Supplementary Material, Equation 1). This method was performed with all 5 solidifiers and 3 oils for 1:4 SOR at 60 rpm and it represented oil removed conjointly by true solidification and attachment.

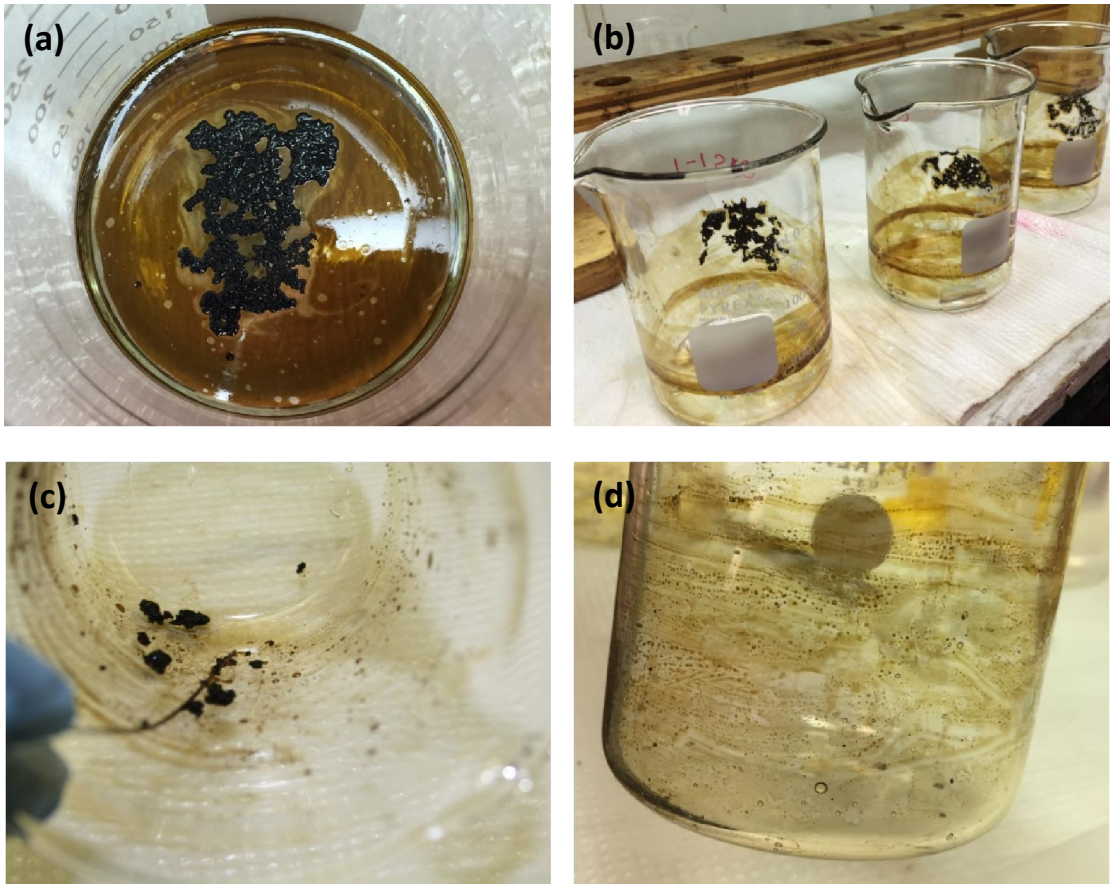
Fig.1. Experimental setup showing (a) top view of oil slick and solidifier in a 400 mL beaker with fresh water; (b) solidified product being removed with tweezers after contact time



2.1.3. Protocol 3

In the final method, after stirring the mixture for a contact time of 30 min, the solidified mass was gently moved to the side of the beaker (**Fig. 2b**) and the water and remaining oil was transferred to 250 mL separatory funnel. The solidified mass (i.e., solidifier + solidified oil + attached unsolidified oil) on the sides of the beakerwas moved around the walls of the beaker with a thin metal rod (**Fig. 2c**). Therefore, any oil that was not truly solidified into the polymer matrix remained in the beaker (**Fig. 2d**). Next, the beaker was rinsed with 20 mL DCM three times and then extracted. The oil in the extract was quantified with UV-Visible Spectrophotometer as in the previous method. This process was developed in order to measure the oil removed by true solidification alone and not by attachment.

Fig.2. Experimental setup showing removal by solidification alone



2.2. Fractional Factorial Design

Preliminary tests revealed that contact time and oil volume did not significantly affect performance and were thus fixed at values convenient for testing purposes (Rosales et al., 2010). A fractional factorial experiment was designed to determine variables that contribute to the performance of solidifiers in removing crude oil from surfaces using the protocol that performed the best. The factors and levels of each of the factors were the following: Beaker Size (400 and 800 mL Beaker), Salinity (0 ppt and 35 ppt), Mixing Speed (0 rpm, 60 rpm, and 120 rpm), and SOR (1:2, 1:4 and 1:8). The response factor was the percent of oil removed by the solidifier from the aqueous phase. This represents the percent of oil removed from the water at room temperature and was a direct measure of solidifier effectiveness.For each oil-solidifier combination the analysis was performed separately. SAS Proc GLM (King, 1995) was used to perform the statistical analyses, with each of the 4 variables, and the 6 two-way interactions between them. An analysis of interactions was done to determine whether two-way interactions occur that will vary the result obtained by any factor

independently. Within this experimental design, only two-way interactions were considered. Three-way and higher interactions were considered to be negligible.

3. Results and Discussion

In earlier studies, product efficiency was measured analytically by weighing the final product, determininghardness with a penetrometer, visually checking for the presence of an immobile oil slick and lack of sheen on exposed water surfaces or by measuring theraise in viscosity(Fingas, 2008).The experimental design and analytical technique used to quantify the oil removal efficiency often dictate the results and is therefore important to identify the most representative protocol.

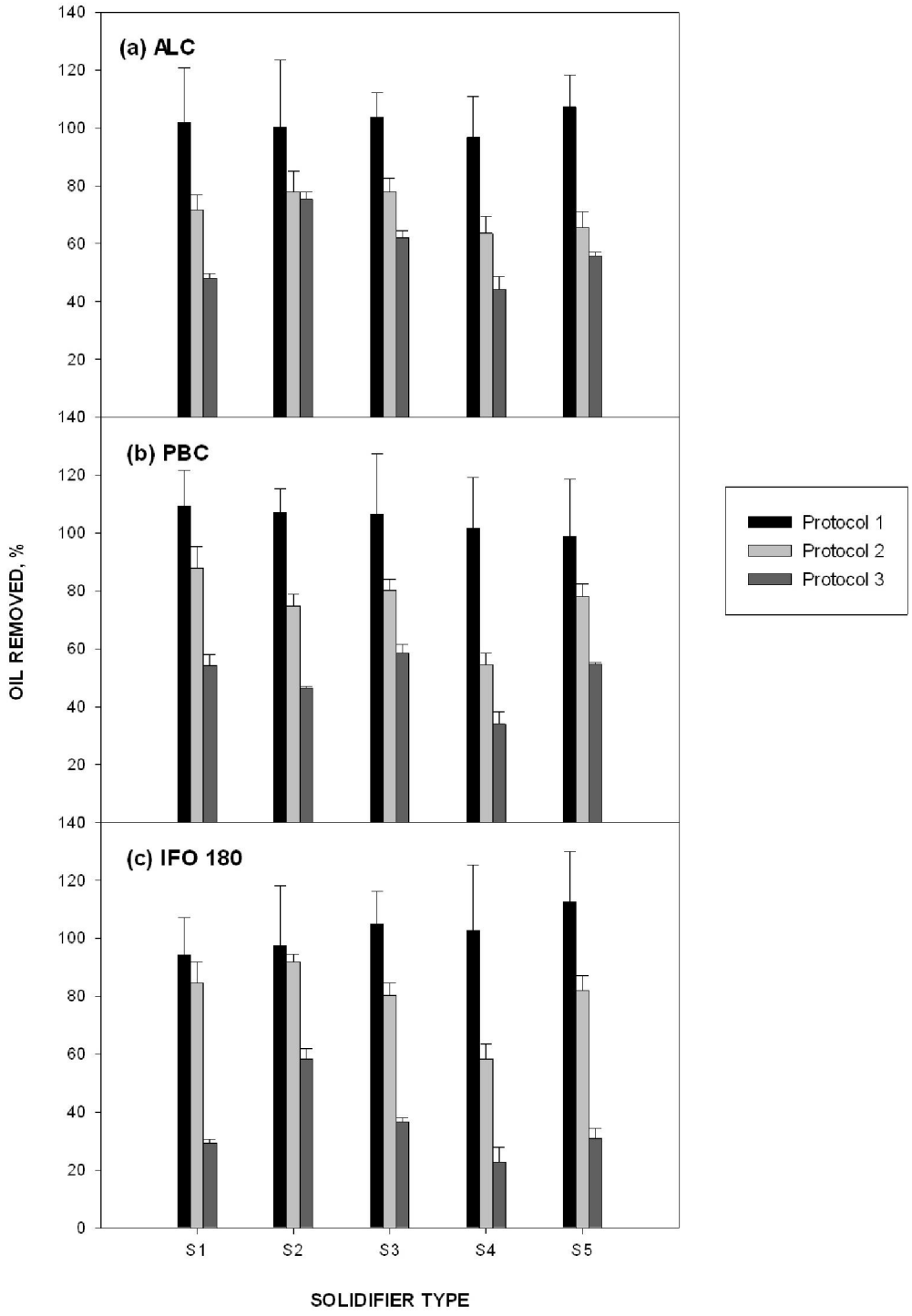
3.1. Comparison of Experimental Protocols

The percent of oil recovered by the 5 solidifiers ranged between 94.3% and 112.6% while following Protocol 1 as shown in Fig.3. It was observed that the final weight was higher than the weight of oil and solidifier combined in some instances, meaning that it included the weight of water. Although the final product was dried for 24 hours, water was entrapped in the solidified mass removed from the beakers. Therefore, measuring the oil removed as a weight percent was not an effective method for quantifying removal efficiency. Furthermore, by visual inspection, it was evident that such a high percent of oil recovery did not truly occur since a large amount of residual oil remained in the beakers and the weight percent removal calculated did not accurately reflect product efficiency.The percent of oil removed byProtocol 2 was 1.3, 1.5 and 2.4 times higher than Protocol 3 for the light, medium and heavy oil respectively. While the percent of oil removed by removed by solidification and attachment combined (Protocol 2) and solidification alone (Protocol 3) was comparable for the light and medium oil, it was almost twice as much for the heavier oil. Due to the increased viscosity of IFO 180, more oil was removed by attachment in comparison to the light and medium oil.

While developing a protocol for measuring solidifier effectiveness, it was important that the procedure successfully showcases differences that exist in product performances. The products differed from each other by about 14.4% in Protocol 3, while it was less apparent in Protocol 1 and 2

(5.0% and 10.7% respectively).An analysis of variance was performed with the results obtained from the three protocols, and the distinctionsinproduct efficiencies were not significant for Protocol 1and 2 ($p=0.688$ and $p=0.264$ respectively) while it was significant for Protocol 3($p=0.042$). In Protocol 1 and 2, the dissimilarities among the product efficiencies could bedue to random sampling variability and not necessarily due to actual differencesthat exist between the products.Protocol 3 managed to distinguish the product performance which will therefore assist in ranking them in order of effectiveness.The final protocol that will be adopted should differentiate the effective and mediocre products while still considering experimental error.The repeatability error which takes into account the inherent error of the method quantifying a product's efficiency was15.9%, 5.1% and 2.7% for Protocol 1, 2, 3 respectively.Therefore the closeness of agreement for a given sample that was analyzed by the same operator was better with Protocol 3 than Protocol 1 and 2.Good repeatability will provide higher confidence in the response factors used for the fractional factorial design experiment.

237 **Fig. 3. Oil Removal Efficiency Using Three Different Protocols**



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3.2. ANOVA Result

Experimental variables were evaluated at multiple levels using Protocol 3 to determine their effect on oil solidification and to establish optimal levels to be included in the final protocol. There were a total of 3 oils and 5 solidifiers resulting in 15 oil and solidifier combinations. The total number of experimental samples prepared for each oil-solidifier combination was 108 (2 beaker size x 2 salinity x 3 mixing speed x 3 SOR x 3 replicates). The results from the parametric study were evaluated by statistical analysis of variance.

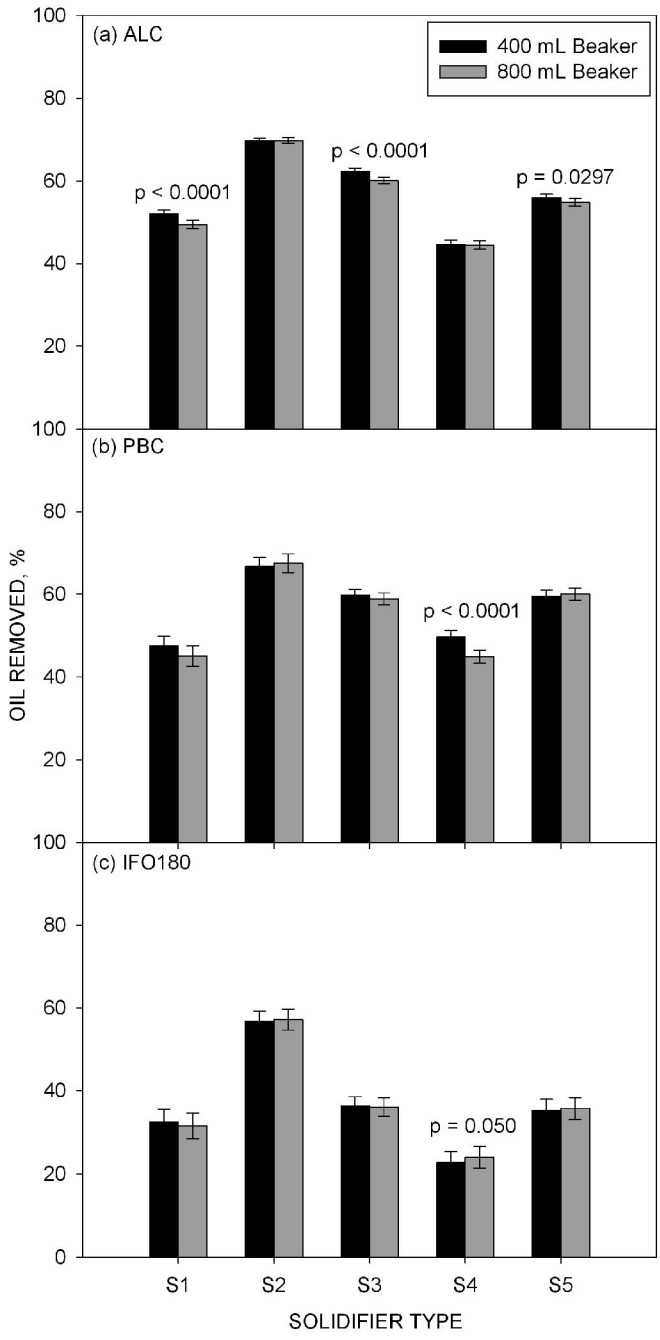
3.2.1. Main Effects

Proc GLM was used to test the level of significance of each factor studied; this method uses the F-test for performing the ANOVA. The analysis helped to quantify the main and interaction effects of the factors considered in the study using SAS software. The response (percent oil removed) was set at 95% confidence limit. The probability (p) was compared with α=0.05 (95% confidence limit) to evaluate the main effects and interaction effects of factors on percent of oil removed.

Fig. 4 shows the results for percentage oil removed with the 5 solidifiers and 3 oils. In case of ALC, the percent oil removed waslower with the 800 mL beaker for all the solidifiers. The differences in the mean values among the two beaker sizes werestatistically significant for S1, S3 and S5. For PBC, this was a significant factor only for S4, whereas, in the case of the heavy oil IFO 180, none of solidifier's removal efficiency was affected by beaker size. The size of the beakerdetermines the depth and surface area of the water and the thicknessof the oil slick. The surface area was found to be 41.74 cm^2 and 69.40 cm^2 for the 400 mL and 800 mL beakers, respectively. The thickness was calculated as volume (0.25 mL oil) divided by surface area. The thickness of the crude oil was 0.060 mm and 0.036 mm for the 400 mL and 800 mL beakers, respectively and this oil thickness was comparable to what was reported by Allen and Dale (1996),who reported that the typical equilibrium thickness in temperate waters is around 0.0254 mm.The increase in surface area and lower oil thickness associated with the 800 mL beaker caused the light and medium oil to spread more, resulting in lower removal rates. For the heavier and thicker oil, this did not appear to occur. This

266 correlates with the findings by Fieldhouse and Fingas (2009), who reported a need for a higher dose
267 of solidifier as the thickness of the slick decreases.

268 **Fig. 4. Effect of Beaker Size on Solidification**



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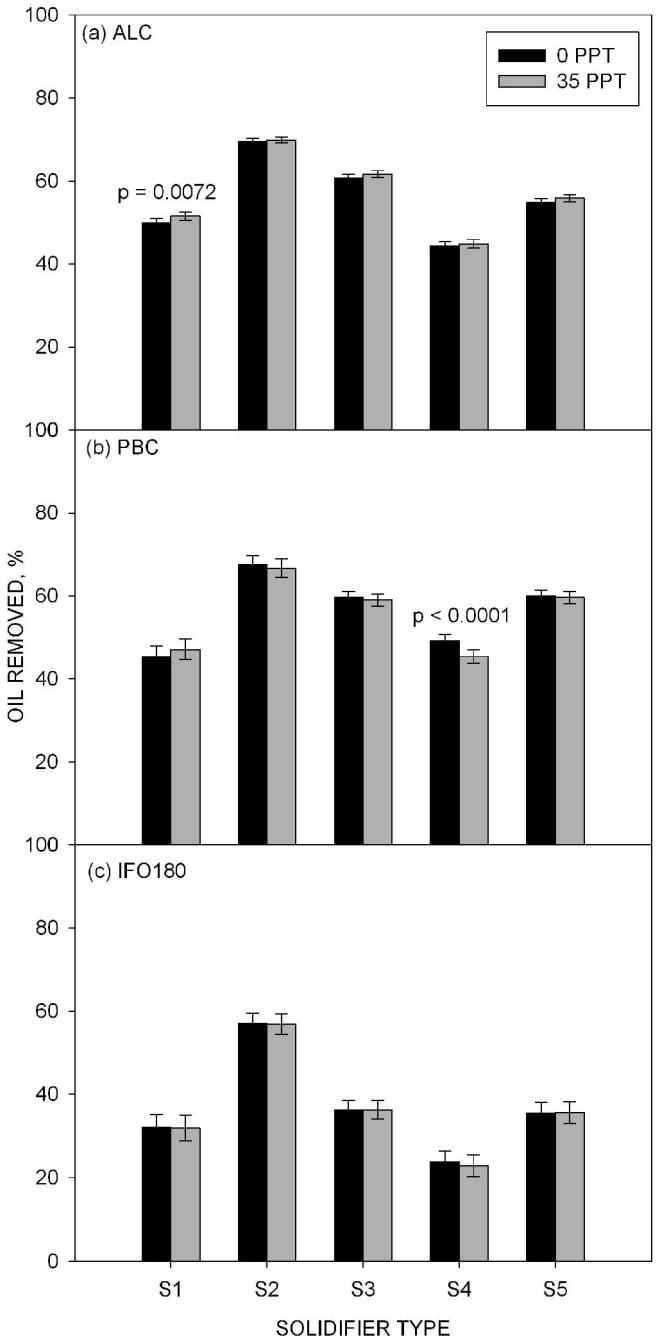
The effect of salinity on the 15 oil-solidifier combination is shown in Fig. 5. Salinity was found to be an insignificant main effect overall. However, it had a small but statistically significant effect on S1 while using ALC and S4 while using PBC. There was no observable trend, and these results indicate that salinity of the water may not be as important as with dispersants which is similar to the findings reported by Pelletier and Siron (1999).

Fig. 5. Effect of Salinity on Solidification



277 The effect of mixing speed on solidifier effectiveness is presented in Fig. 6. Mixing speed had
278 a statistically significant effect on solidification of PBC ($p < 0.05$ for all 5 solidifiers). Ceiling effects
279 on mixing speed were observed with no additional benefit provided by the highest level over the
280 middle level for this factor. Thus, the middle level can be considered to be the maximum value
281 needed to achieve the best response for this oil type. Mixing speed does not appear to affect the light
282 and heavy oils as much as the intermediate oil. During experiments with the light oil, excessive
283 mixing broke the solidified oil matrix and made it difficult to remove the product while with the
284 heavy oil, thesolidifier products remained unreacted at the end of the contact time and did not mix
285 with the oil completely. Due to this incomplete solidification, the heavy oils experienced lower
286 removal rates. This compares with the findings by Fieldhouse and Fingas (2009), who reported that
287 the heavier oils did not solidify properly and that the product simply remained on the surface not due
288 to the lack of mixing but due to physical constraint. They also reported that as the viscosity of the oil
289 increased, longer contact time and increased dosage were required. Mixing may play an important
290 role in regards to oil type, and solidifiers are generally considered to be more effective with lighter
291 oils (Fingas, 2008). Although the medium oil benefited from the mixing, this effect was not observed
292 for the light crude and heavy oils. The two crude oils and the heavy fuel oilgave similar responsesfor
293 all 5 solidifier products,which correlatewith changing viscosities.

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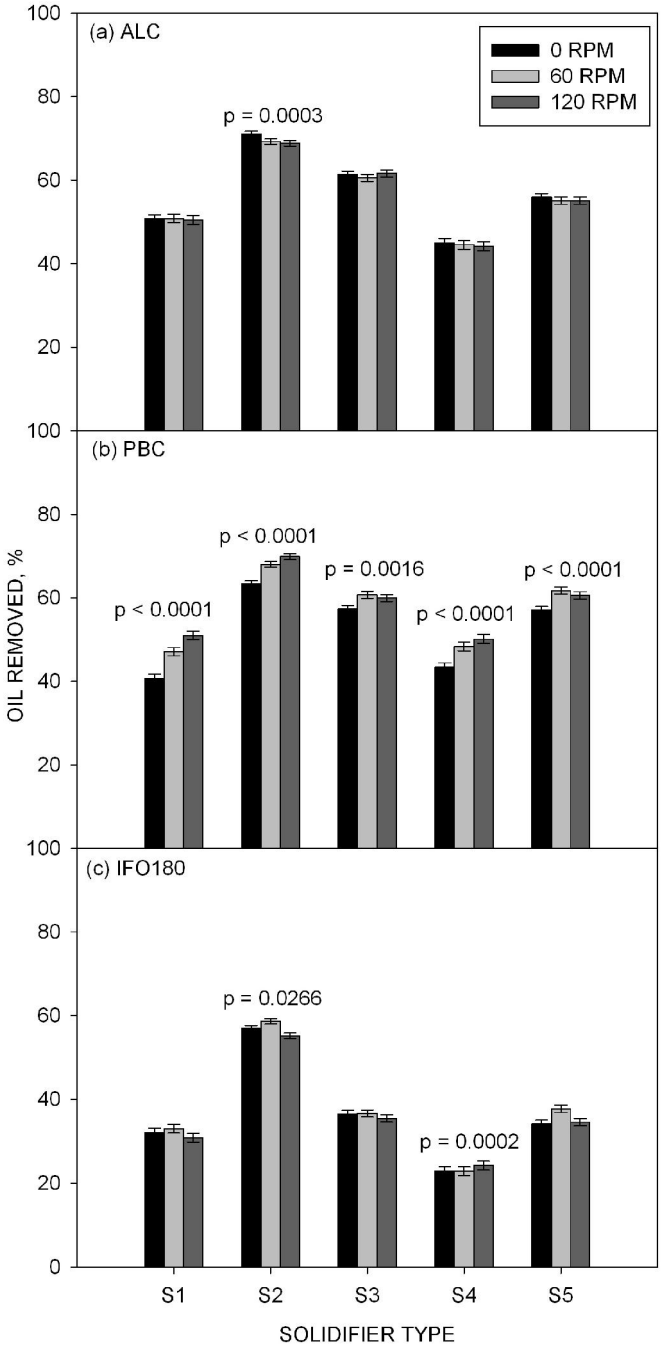
295 **Fig. 6. Effect of Mixing Speed on Solidification**



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298 Fig. 7 shows results of SOR on oil removed by each solidifier. Positive correlations were
299 observed for SOR with the highest application rates yielding the highest oil recovery. It is important
300 to note that there is no restriction on SOR except what is reasonable from an economic standpoint.
301 The removal rates were over 70% for the light and medium crude oils but only 40% for the heavy oil
302 at an SOR of 1:2. These results were comparable to the study by DeLaune et al. (1999), who reported
303 a removal efficiency of over 70% at an SOR of 1:2 while for South Louisiana crude oil and the
304 commercial solidifier Nochar A650. The removal rates for the light and medium oils were similar for
305 all three SORs. However, the removal rates were consistently lower for the heavy refined oil. The
306 viscosity of the three oils was measured with a Brookfield digital viscometer and was found to be 15
307 cP, 30 cP and 1414 cP for the light, medium, and heavy oils, respectively, at 22 ^{o}C, as shown
308 previously in Table 1. This strongly suggests that the light, low viscosity oils were more readily
309 solidified and that the heavier, viscous oils have difficulty blending with the solidifier product.
310 Overall, SOR was found to be the most important factor for solidification of floating oil, and in
311 addition, it affected the potency of the other factors significantly.

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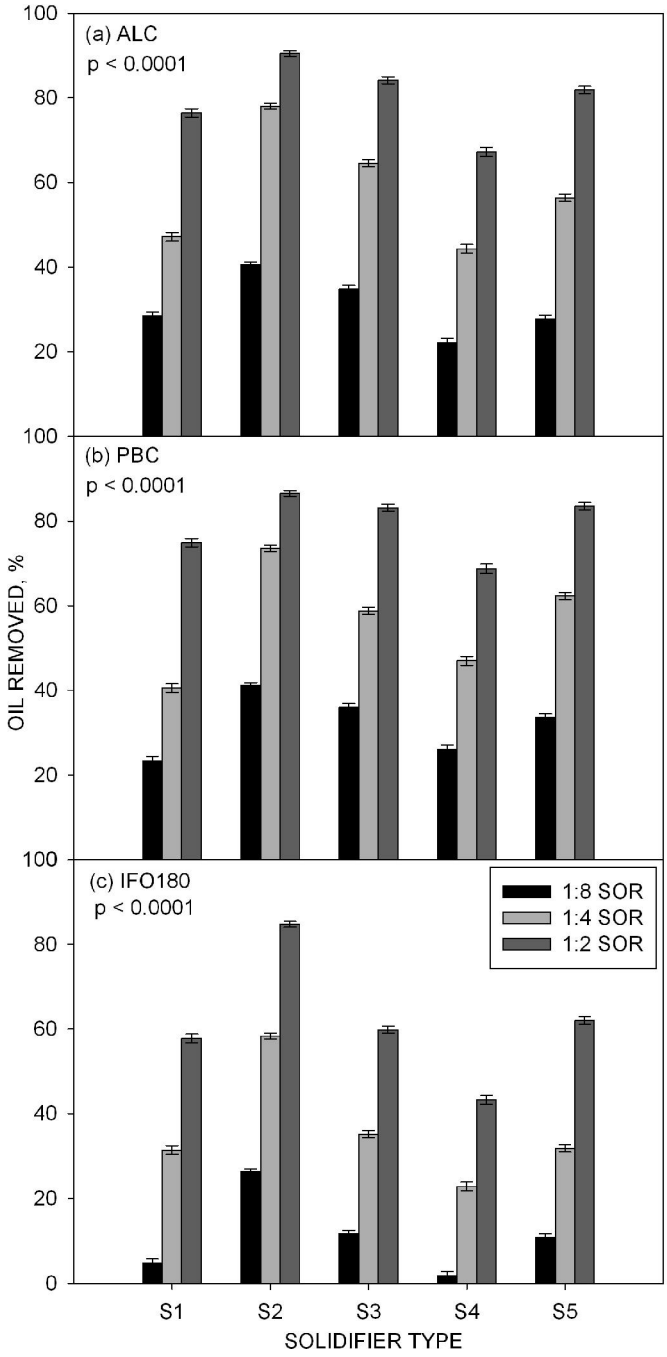
Fig. 7. Effect of SOR on Solidification



3.2.2. Two Way Interactions

An analysis of variance was done to determine whether any two-way interactions that may occur might vary the results obtained by any factor separately. A significant interaction means thatthe effect of one input variable varies at differing levelsof another input variable.Within this experimental design,only two-way interactions were considered.Significant two way interactions were determined for each oil-solidifier combination (Supplementary Material, Table 2). The overall number of

significant two-way interactions was higher for the light and medium oils. Many of the two-way interactions included SOR as one of the variables as expected. We concluded that SOR was an important factor not only for solidification of floating oil itself but it can also significantly affect the strength of the other factors at lower application rates. The removal efficacy while testing with the heavy oil remained consistently low with all parameters remaining insignificant except SOR.

4. Conclusion and Summary

In order to develop a laboratory protocol to test the effectiveness of commercial solidifiers in remediating oil spills on water, 3 experimental procedures were evaluated to determine if they would accurately quantify product performances and if the methodology itself was repeatable. While Protocol 1 and 2 did not have high accuracy or repeatability, Protocol 3 was successful in measuring product effectiveness and was found to be consistent and reproducible with standard deviation values under 5%. Results from the factorial experiment revealed that the effect of beaker size or surface area was more pronounced while using the light crude oil and salinity of the water did not affect removal efficiencies significantly for any of the oils. The removal efficiencyof the products increased by varying the mixing speed from 0 to 60 rpm butno benefit occurred by increasing the mixing speed from 60 to 120 rpm. Although mixing speed played an important role when the medium crude oil was tested, it did not impact the solidification efficiency much while using light and heavy oils. Removal rates for light and medium crude oils were similar under most conditions. This was likely due to similarities in the densities and viscosities of those tested oils. The numbers of statistically significant main effects and two-way interactions were higher for the light and medium oils and the removal rates remained low and unaffected by most variables for the heavy oil. The solidifier products remained unreacted at the end of the contact time due to difficulty in mixing while using the heavy oil. The effect of protocol variables on the light, medium, and heavy oils was considered in order to understand the solidifiers' performances under various environmental conditions and different oil spill scenarios. From a practical standpoint, the only variables that gave meaningful differences were product type and SOR. S1, S3 and S5 were lightly packed white powders and appeared to be similar in texture and consistency. While using ALC and PBC, the removal rates were around 80%, while

with IFO 180, it was around 60% at 1:2 SOR. S2 had the highest removal capacity with 90%, 87% and 85% for ALC, PBC, and IFO 180 respectively at 1:2 SOR. S4 removed the least amount of oil with 68%, 69% and 43% efficiency for ALC, PBC, and IFO respectively at 1:2 SOR. The differences in oil removal efficiency with change in product type and oil type were less noticeable at the high SOR of 1:2. However, at 1:8 SOR, S2, the best performing product removed 40% of ALC and PBC but only 25% of IFO 180. The worst performing product, S4 removed around 25% of ALC and PBC while removing only 2% of IFO 180. There is no restriction on SOR except what is reasonable from an economic standpoint. These results could aid in evaluating and choosing products with the highest oil removal efficiency.

In general, optimal removal rateswere obtained while using Protocol 3 with a 400 mL beaker at 60 rpm using fresh water. Therefore, the protocol will call for each product's removal efficiency under these standardized conditions at the intermediate SOR of 1:4. This protocol will provide a standard for the U.S. EPA in solidifier product evaluation prior to listing on the National Contingency PlanProduct Schedule. Round robin testing will also be performed before pass-fail decision rules are established and final recommendations for the testing protocol can be published in the Federal Register. Countries that do not currently have a list of approved solidifiers or solidifier product approval regulations, and whose relevant regulatory authority wishes to develop such an approved list can utilize this test method or accept products that have been approved under this testing protocol, for inclusion on their own approved solidifier list.

Acknowledgments

This research was supported in part by U.S. EPA's National Risk Management Research Laboratory, Cincinnati, OH under Contract No. EP-C-11-006. The use of trade names or commercial products is for identification only and does not imply endorsement by any agency of the U.S. Government.

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