# Onboard Flotation System for Spilled Oil Clean up at Sea

F. Shi [1, 2], Y. Duan [1], Y. Soong [1], M. Gray [1]

[1] National Energy Technology Lab., Pittsburgh, PA, [2] AECOM, South Park, PA, fan.shi@netl.doe.gov, yuhua.duan@netl.doe.gov, yee.soong@netl.doe.gov, mac.gray@netl.doe.gov

## ABSTRACT

Oil spill response is a top priority for the oil and gas industry and instrumental for obtaining a license to operate. It is a demanding task in any environment, but Arctic regions present particularly difficult challenges. The U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL) has performed research taking unique flotation skills and equipment previously used for coal preparation and repurposing them to investigate oil separation under Arctic conditions. Commercial flotation equipment has been used to ensure that all device specifications meet industrial standards and are ready for commercialization. The study involved experiments to measure oil separation using a flotation process at simulated Arctic conditions. NETL has successfully demonstrated the feasibility of using a flotation process for rapid separation of crude oil under Arctic and Gulf of Mexico (GOM) conditions. Oil separation efficiency with different surfactants, temperature, and ice conditions has been investigated for batch Denver cell and continuous column operations. Authentic crude oils and surrogate seawater have been used in all experiments. The largest advantage of using the flotation process is that it provides high oil/water ratio product, thus significantly reducing the storage requirement for oil spill waste water. Oil separation in the presence of ice has been tested. The hydrophobicity difference between oil-contaminated ice (hydrophobic) and cleaned ice (hydrophilic) enables easier separation of oily ice particles from water using the flotation method. Overall, the flotation process has successfully demonstrated excellent oil separation from seawater under simulated Arctic conditions.

***Keywords***: oil spill response, flotation, separation, arctic conditions, gulf of mixico

## 1. INTRODUCTION

An oil spill is a form of pollution and typically refers to the unintentional release of liquid petroleum products (e.g., crude oil) into the environment. Spills can happen during oil drilling or transportation and pose a threat to the local environment. Oil spills at sea typically spread for hundreds of nautical miles in a thin oil slick, and cleanup and recovery is generally much more difficult than on land, especially in the Arctic, because extreme environmental conditions may prevent human response. A large thin slick area can quickly form by the spread of spilled oil on seawater. Figure 1 shows a general schematic of an oil spill dispersion process on seawater. Different response strategies may be employed depending on where the spill occurs, where the slick is moving, and the different types of equipment available. In all cases, the earlier the slick is contained and the oil concentrated, the easier the recovery operations will be.

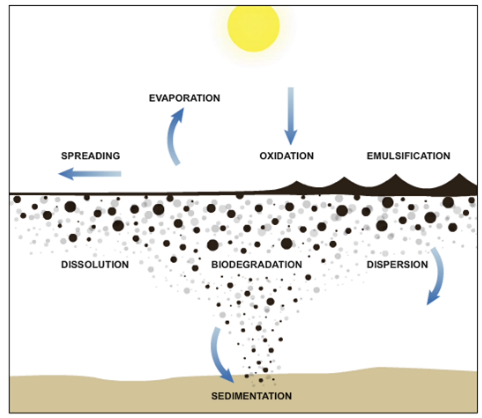


**Figure 1** Schematic of oil spill dispersion process on sea. [1]

Traditional oil recovery technologies face challenges in the ice-covered waters of the Arctic operating environment. Another issue is the storage, transfer, and disposal of the recovered oil/ice/water mixture. After this mixture is recovered, there is a lack of infrastructure available in the Arctic to allow offload of the recovered product. Therefore, the ability to separate the water from the oil after recovery will allow for more efficient storage.

The objective of this study is to initiate the development of a prototype flotation system for the treatment of recovered spilled oil/water/ice mixture under Arctic conditions. With proper flotation device designs and optimized operating parameters, a froth flotation scheme for separating spilled crude oils from Arctic seawater seems very likely to meet EPA's discharge regulation [2].

## 2. EXPERIMENTAL

### 2.1. Materials

ASTM sea salt mix was used in the standard practice (ASTM D1141-98)[3] to prepare substitute ocean water. Authentic crude oils, including two arctic crude (ANS, and North Star), and pacific and GOM crudes (Ewing bank and Harmony) were provided by U.S. Department of Interior's Bureau of Safety and Environmental Enforcemen (BSEE). Five frothers, including three glycol ethers based Custo527, FloMin F660 and FloMin F672, Methyl isobutyl carbinol (MIBC) and 2-Ethylhexanol (2-EH), were used in the flotation tests. Commercial demulsifiers, Dow Chemical's water clarifiers, were tested.

## 2.2. Experiment systems

*Benchtop D-12 Denver Cell*

A bench-top flotation device, a D-12 Denver cell (METSO), was used for proof-of-concept and screening surfactants and to investigate the effects of bubble size, ice content, and other operating conditions. It is considered as a single-stage batch mode flotation cell. The size of each batch ranged from 250 mL to 2,000 mL. A compressed air supply at 40 psig was recommended. Operating temperature was controlled by a recirculating chiller.

*3" Flotation column*

A pilot-scale 3" laboratory flotation column system was purchased from ErieZ. To minimize the heat exchange between the flotation column and the environment, a heavy-duty insulation blanket was installed. The 3" flotation column was an ideal tool for evaluating the flotation characteristics of oily, cold seawater with or without ice. Test sample results and operating parameters were directly scaled up to determine full-sized column flotation cell performance and requirements.

## 2.3. Analyitic methods

The TD-500D (Turner Designs) is a dual-channel, handheld fluorometer designed for quick measurements of crude oil and refined hydrocarbons in water. The dual-channel design makes the TD-500D applicable to a wide range of hydrocarbon types and concentration ranges [4]. For most crude oils the linearity limit is well beyond 1000 ppm.

Due to the high salt content of the aqueous portion of the flotation samples, a GC method with solid phase extraction (SPE) using a 3 ml Discovery SPE column was developed to ensure the ability to quantify the amount of the gycol-based frother in the water without interferences from the salt. An Agilent 6890 GC-FID equipped with a 60 m Stabil wax-DA capillary GC-column was used for quantitation with a 200 °C injector temperature and 1 µl injection at 10:1 split ratio.

Standard Test Method D4928—12 "Water in Crude Oils by Coulometric Karl Fischer Titration" [5]—was followed for water content measurement of water samples from flotation experiments.

# 3. RESULTS AND DISCUSSIONS

## 3.1. Gas holdup measurement

Gas holdup is one of the most important parameters characterizing the hydrodynamics of a flotation process. Gas holdup measurements for different frother conditions in seawater at the freezing point were investigated in Denver cell as shown in Figure 2. As shown, gas holdups of all four frothers in freezing seawater at -2 °C were similar to those results from 5 °C. Overall, among all four frothers, F660 showed the highest gas holdup in seawater at very low frother dosages. F660 also showed a low residual concentration during flotation operation. Therefore, F660 has been selected for further flotation investigations, unless otherwise mentioned.

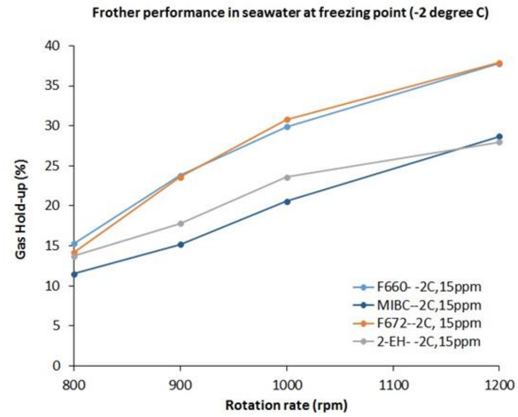


**Figure 2**. Gas holdups in freezing seawater at -2 °C.

## 3.2. Crude oil tests in Denver Cell

Flotation tests for all four crude oils were performed in a Denver cell at varied temperatures, as shown in Table 1. For baseline tests without frother, residual oil in water varied significantly, probably due to high turbulence in cell.

**Table 1**. Experiment Results of crude oils at different operating conditions

| Crude | Temp (°C) | Frother | Frother (ppm) | Residual oil (ppm) | Residual water (%) |
|---|---|---|---|---|---|
| NS | -2-5 | n/a | - | <80.0 | - |
| | | F660 | 15 | <15 | <20 |
| ANS | -2-5 | n/a | - | <30 | <10 |
| | | F660 | 5 | <2 | <10 |
| | | | 15 | <5 | <10 |
| | | Custo527 | 5 | <10 | <10 |
| | | | 15 | <2 | <15 |
| Ewing Bank | 30 | - | 0 | <1 | <5 |
| | | F660 | 15 | <2 | <15 |
| | | Custo527 | 15 | <2 | <15 |
| Harmony | 30 | - | 0 | <1 | <5 |
| | | F660 | 15 | <1 | <10 |
| | | Custo527 | 15 | <1 | <15 |

For NS tests, oil content was as low as 13.3 ppm in the water sample which already met the EPA's 15 ppm disposal standards. However, water in oil products was more than 10%. The high-water content in oil was primarily due to the difficulty in collecting oil froth at a high turbulence in Denver cell. For ANS tests, a second frother, Custo527, was used to compare to F660. Typical contact time between oil and water was less than 5 minutes, depending on oil collecting speed. As expected, residual oil in all of water samples was found less than 15 ppm. Also as expected, water content in most oil samples was less than 15%. It was found that at a low frother dosage (i.e., 5 ppm), most values of water in oil were less than those with a high frother concentration. The difference was primarily because of the entrapment of tiny bubbles generated at a relatively high frother concentration.

Flotation of two non-Arctic crude oils (Ewing Bank and Harmony crude oils) were investigated at 30 °C. Three frother conditions were applied: a baseline (no frother), 15 ppm of F660, and Custo527, respectively. Similar to the results of Arctic crude oils tests, less than 15 wt% of water in oil products was found, while only trace amount of residual crude in the treated seawater (< 2 ppm). All residual concentrations of non-arctic crude oil after flotation operations met the EPA's 15 ppm disposal standards. Therefore, flotation operation has been proven to be capable of removing different crude oils successfully from seawater, even at warm temperatures.

*Emulsified arctic oil test*

Results of flotation of emulsified ANS crude are shown in Figure 3. The concentrations of emulsified ANS dropped dramatically in the first 10 minutes of flotation, even without frother. After 20 minutes of flotation, less than 20 ppm of oil was found in the treated water in the presence of frothers. The oil concentration decreased gradually below 15 ppm after 60 min of flotation. When no frother was used, less than 5 ppm of oil was found after 60 min flotation. This could possibly be attributed to the difference of bubble size generated with and without frothers. In a Denver cell, due to high turbulence, oil attached small bubbles generated by the frother can be easily back-mixed into bulk water, and hence the final oil concentration was higher than that of flotation of "big" bubbles without frother. In addition, Denvel cell flotation also showed excellent performance in removing crude oil from oil contaminated ice.

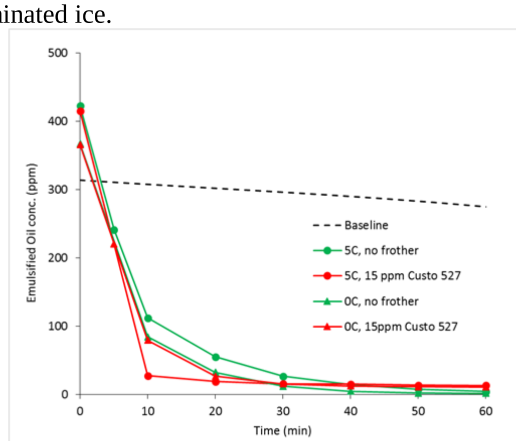


**Figure 3**. Flotation results of emulsified ANS crude oil.

Overall, the concept of using flotation operations to separate ANS crude oil from seawater near Arctic conditions was successfully proved in a Denver cell. The flotation can also separate emulsified oil as well as oil contaminated ice at simulated Arctic temperatures. All treated water samples have met the EPA's regulation (<15 ppm) for discharged water from vehicles at sea.

## 3.3. Crude oil tests in 3" flotation column

To investigate the effectiveness of a continuous column flotation process for crude oil cleanup, ANS crude oil was tested at varied conditions. Oil feed rate was up to 200 mL/min. Water co-feed rate was up to 100 ml/min. To reach the steady-state operation, a typical flotation column test lasted up to 45 mins, unless stated otherwise. Results are summarized in Table 2.

As shown in Table 2, there was less than 15 ppm of non-emulsified oil in all water samples. Oil samples contained less than 10% of water when there was no co-feeding water (crude conc. > 90%), while water content can go as high as 50% in presence of water co-feeding.

To investigate the effectiveness of frother and water clarifier for crude oil cleanup, ANS crude oil was tested with 10-50 ppm of Dow clarifier in seawater near freezing point. Water in oil froth was as low as 10% in 10 ppm of Dow clarifier experiments. By changing oil residence time in column, we believed that a better oil froth sample with less water can be obtained. Clean water samples were found containing less than 10 ppm of oil.

**Table 2.** A summary of ANS Oil column flotation

| Crude Conc. (%) | Temp. (°C) | Frother (ppm) | Demulsifier (ppm) | Residual oil (ppm) | Residual water (%) |
|---|---|---|---|---|---|
| >90 | 5 | 0 | 0 | <15 | <10 |
| 60-70 | -2-5 | 0 | 0 | <15 | <50 |
| | 5 | 15 | 0 | <15 | <30 |
| | -2-5 | 0 | 10-50* | <10 | <15 |
| | -2 | 15 | 0 | <5 | <10 |
| 0.05 | -2-5 | 0 | 0 | <100 | n/a |
| | | 0 | 10 | <30 | n/a |

*Emulsified Arctic oil test*

To investigate continuous flotation processes for the emulsified Arctic oil, ANS emulsion solutions similar to the previous Denver Cell batch operation were prepared. The same preparation procedure was followed to prepare at least 30 liters of a stable solution of ~500 ppm emulsified ANS oil in seawater. Different from Denver cell tests, only Dow clarifier was used. For all flotation tests, oil emulsion concentration was about 500 ppm (0.05%), as shown in Table 2. Water samples were taken after 30 minutes of flotation operation. Results were also summarized in Table 3. More than 80% of oil emulsion was removed from water after flotation treatment. With the addition of a small amount of Dow clarifier, oil emulsion was reduced to as low as 15 ppm. It was also noticed that temperature played a negative effect on the removal of oil emulsion primary due to the low efficiency of Dow clarifier at temperatures below the freezing point.

Overall, flotation column operation was able to successfully remove both non-emulsified and emulsified crude oil from seawater near Arctic conditions. In addition, flotation column processes also successfully demonstrated the separation of oil and oily ice from clean ice and seawater.

*Process modelling*

Scale-up simulations are critical for studying how geometry changes affect flow, and so results mostly track liquid velocity along various axes. As Figure 4 lays out[7], we initially focused on adjusting flow rates, heights, radius and sparger configurations for low-turbulence operation with enough mixing inside a column. As a result, a reduction in gas flow rate does not reduce the liquid velocity by the same proportion. This relationship is also present in the downward liquid velocities near the column walls. Four gas spargers were added to the bottom of the column in a cross pattern. All spargers had inlet openings that were a fifth of the area of the original single sparger. This allowed the inlet gas velocities to be equal to the original inlet velocity. As Figure 4e shows, the velocity distribution across the diameter is broader than with a single sparger, although significant horizontal fluctuations to the peak velocity are still present.

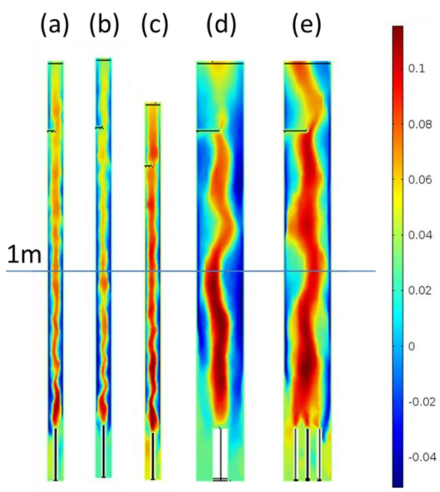


**Figure 4**. Liquid velocities of scale-up changes to the (a) initial column by (b) reducing flow, (c) reducing height, (d) increasing radius, and (e) multiplying spargers. The figure on the right is the legend in m/s.

## 4. SUMMARY AND RECOMMENDATION

Separation of crude oil from seawater was successfully demonstrated in both batch Denver cell and con Continuous flotation column operations at varied conditions. Results showed that residual crude in bulk discharged seawater was less than 15 ppm, which met EPA's discharge standard. Water in oil was as low as 10 wt %.

A technology transfer goal of NETL is intended to facilitate the commercialization of energy-related technologies with promising commercial potential that are developed at its facilities. This goal is part of a broader set of initiatives to foster stronger partnerships among government facilities, private sector companies, and other entities involved in bringing energy-related technologies to the marketplace. The collaboration on the current project with BSEE has greatly assisted in the maturation of this flotation technology that will potentially remediate oil spills in Arctic, as well as in the Gulf of Mexico, Atlantic Ocean, and Pacific Ocean. Although significant research and development advances have been made over the duration of this project, the current Technical Readiness Level (2-3) [6] could be further increased to attract interest by outside commercial entities. It is suggested that this relatively modest increase in TRL be conducted under a further collaboration with industry and government.

## DISCLAIMER

This study was funded by the U.S. Department of the Interior, Bureau of Safety and Environmental Enforcement through Interagency Agreement E15PG00032 with the Department of Energy, National Energy Technology Laboratory.



## REFERENCES


1. Seapro responder handbook, http://www.seapro.org/responderhandbook.htm, as of May 10, 2015.
2. EPA Discharges Permitted under MARPOL, http://www.epa.gov/oem/content/reporting/oilexem.htm , as of May10, 2015, as of Dec. 10, 2016.
3. ASTM D1141-98(2013), "Standard Practice for the Preparation of Substitute Ocean Water," ASTM International, West Conshohocken, PA, 2013, www.astm.org.
4. Oil content analyzer, TD-500D users' manual, 2016, (Tuners Design, USA).
5. Shi, F., Gu, X., and Chiang, S.H., "A Study of Hydrodynamic Behaviors in a Multi-stage Loop-Flow Flotation Column," Fluid/Particle Separation Journal, 2002. 14(3): 185-198.
6. DOE G 413.3-4, U.S. Department of Energy Technology Readiness Assessment Guide, 2009.
7. L. Chong, Y. Lai, M. Gray, Y. Soong, F. Shi, Y. Duan, "Molecular Dynamics Study of the Bulk and Interface Properties of Frother and Oil with Saltwater and Air", J. Phys. Chem. B, 2017, DOI: 10.1021/acs.jpcb.6b13040