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SL Ross Environmental Research Ltd.
Danish Centre for Energy and the Environment

RESEARCH SUMMARY: HERDING SURFACTANTS TO CONTRACT AND THICKEN OIL SPILLS FOR IN-SITU BURNING IN ARCTIC WATERS

ABOUT THE JIP

Over the past four decades, the oil and gas industry has made significant advances in being able to detect, contain and clean up spills in Arctic environments. To further build on existing research, increase understanding of potential impacts of oil on the Arctic marine environment, and improve the technologies and methodologies for oil spill response, in January 2012, the international oil and gas industry launched a collaborative four-year effort – the **Arctic Oil Spill Response Technology Joint Industry Programme (JIP)**.

Over the course of the programme, the JIP will carry out a series of advanced research projects on six key areas: dispersants, environmental effects, trajectory modeling, remote sensing, mechanical recovery and in situ burning. Expert technical working groups for each project are populated by the top researchers from each of the member companies.

JIP MEMBERS

The JIP is managed under the auspices of the International Association of Oil and Gas Producers (IOGP) and is supported by nine international oil and gas companies – BP, Chevron, ConocoPhillips, Eni, ExxonMobil, North Caspian Operating Company (NCOC), Shell, Statoil, and Total – making it the largest pan-industry programme dedicated to this area of research and development.

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CHAPTER 1. EXECUTIVE SUMMARY

In-situ burning (ISB) is an oil spill response option particularly suited to remote, ice-covered waters. The key to effective ISB is to ignite an oil slick that is more than 3 mm thick. If ice concentrations are high, the ice itself can limit oil spreading and keep slicks thick enough to burn. However, in drift ice conditions and in open water, oil spills can rapidly spread and become too thin to ignite. Fire-resistant booms can collect and keep slicks thick in open water but even light ice conditions make the use of booms challenging.

A multi-year research project was initiated in 2004 and continues in 2014 to study oil-herding surfactants as an alternative to booms for thickening slicks in light ice conditions for ISB (Buist *et al*, 2014). Table S1 summarizes the experimental work that has been completed to date.

Herding agents thicken oil slicks that have spread too thinly to support combustion. This is accomplished by spraying a small amount of surfactant around the perimeter of the slick. The surfactants are not applied to the oil but to the water surface immediately adjacent to the slick. Once applied, the surfactants will spread to ultimately form a monomolecular layer that significantly reduces the surface tension of the water. The reduced water surface tension reverses the oil spreading tendency and a thin slick will rapidly re-thicken. The surfactants do not need a boundary to “push” against and work equally well far offshore.

Only a very small amount of surfactant (5 L per linear kilometer of slick perimeter) is needed to herd slicks because only a monomolecular layer is needed. This amount of surfactant could be one to two orders of magnitude less than the amount of surfactant needed to disperse the slick.

Small-scale laboratory experiments were completed in 2003 and 2005 to examine the idea of using herding agents to thicken oil slicks among loose pack ice for the purpose of ISB. Encouraging results prompted further mid-scale testing in 2006 and 2007 at the US Army Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire; at Ohmsett, the National Oil Spill Response Research & Renewable Energy Test Facility in Leonardo, New Jersey; and, at the Fire Training Grounds in Prudhoe Bay, Alaska.

The non-proprietary hydrocarbon-based herder formulation (now called ThickSlick 6535) used in these experiments proved effective in considerably contracting oil slicks in brash and slush ice concentrations of up to 70% coverage. Slicks in excess of 3 mm thick, the minimum required for ignition of weathered crude oil on water, were routinely achieved. Herded slicks were ignited and burned equally well in both brash and slush ice conditions at air temperatures as low as –17°C. The burn efficiencies measured for the herded slicks were only slightly less than the theoretical maximums achievable for equivalent-sized, physically contained slicks on open water.

Successful mid-scale field trials of the technique were carried out in the Barents Sea off Svalbard in the spring of 2008 as one facet of a large joint industry project on oil spill response in ice, co-ordinated by SINTEF. These larger field experiments involved one release of 630 L of fresh Heidrun crude onto water in a large lead. The free-drifting oil was allowed to spread for 15 minutes until it was far too thin to ignite (0.4 mm), and then the hydrocarbon-based herder was applied around the slick periphery. The slick contracted and thickened for approximately 10 minutes at which time the upwind end was ignited. A 9-minute long burn ensued that consumed an estimated 90% of the oil.

From 2007 to 2009 experiments were carried out at lab scale and larger scale at CRREL comparing the efficacy of herding agents formulated with silicone-based surfactants, herding agents formulated with second-generation fluorosurfactants and the hydrocarbon-based herder previously developed and tested. The results showed that the fluorosurfactant-based herders did not function better than the hydrocarbon-based herder; however, the new silicone surfactant formulations considerably outperformed the hydrocarbon-based herder. More recently (2009), experiments were conducted to determine if herding agents could 1) improve skimming of spilled oil in drift ice; 2) clear oil from salt marshes; and 3) improve the efficiency of dispersant application operations.

Ohmsett experiments in 2010 on the use of herders as a rapid-response technique for use in open water showed that herders on open water

- Restrain a slick for more than 45 minutes in calm waters,
- Restrain a slick in a non-breaking swell condition, but the constant stretching and contracting of the herded slick elongates and slowly breaks it into smaller segments.
- Breaking or cresting waves rapidly disrupt the herder's monomolecular layer and the oil slick resulting in many small slicks.

Two herding agents (ThickSlick 6535 and SilTech OP-40) have been placed on the U.S. Environmental Protection Agency (EPA), National Oil and Hazardous Substances Pollution Contingency Plan (NCP) Product Schedule for consideration for use in U.S. waters and were commercially available as of June 2012. Samples of these herders have also been submitted to Environment Canada for consideration for use in Canadian waters.

An application system consisting of a pump, controls and reservoir has been designed to be placed inside an appropriately equipped helicopter. It incorporates a reel-able hose that is used to lower the application nozzle to the correct height above the water for herder application. Dry land, static trials were conducted in September 2013 and helicopter flight trials are planned for 2015. A back-pack sprayer system for herder application from a small vessel is available off-the-shelf, with only minor modifications required for cold-temperature use.

Initial biodegradation tests indicate that ThickSlick 6535 will biodegrade rapidly. OP-40 will biodegrade more slowly. Toxicity testing required for listing with the U.S. EPA found that ThickSlick 6535 was "practically non-toxic" (as defined the U.S. EPA aquatic toxicity ranking system). OP-40 had somewhat greater toxicity.

Based on over 10 years of development, industry is now pursuing full-scale commercial application of herders. This technique will allow response to Arctic spills in drift ice conditions and open water using a rapid response system (helicopters) that minimize equipment needs and personnel to remove the majority of a herded slick from the marine environment. Further the technique uses a very small amount of "practically non-toxic" surfactants that rapidly biodegrade.

Table S1: Summary of research on herders in the last 10 years.

Year	Location	Herders	Oils	Scale	Results
2003	SL Ross lab	EC 9580	ANS, Pt. McIntyre, Northstar, Chayvo	I m^2 pans	• 1-mm oil slicks herded to 2 to 4 mm • Sheens not herded to ignitable thickness • Water salinity not important • Oil composition important • Ice pieces did not interfere
2004 & 2005	SL Ross lab	OC-5 USN EC 9580	ANS Cook Inlet Gas Oil	I m^2 pans 10 m^2 pool Wind/wave tank	• Best herder - USN • 1-mm oil slicks herded to 3 to 4 mm • Could ignite and burn herded slicks • Wind/waves break up herded slick
2005	CRREL Basin	USN	Hydrocal	81 m^2	• USN effective up to 70% ice cover • Frazil ice restricted spreading of herder • Herder worked at -21°C • Choppy waves broke up herded slick
2006	Ohmsett	USN	Blend Ewing Bank/ Arab Medium	1000 m^2	• USN effective • Free slicks in ice herded to ≈3-4 mm • Swell waves did not break up herded slicks
2006	Prudhoe Bay Pool	USN	Kupurak	25 m^2	• USN effective in brash and slush up to 30% cover • Frazil ice restricted spreading of herder • Choppy waves broke up herded slick • Slicks that could not be ignited initially, were herded and successfully ignited and burned • Burn efficiencies near theoretical maximums for mechanically contained slicks of same thickness • Removal rates same as contained slicks • Burning slicks did spread slightly, then re-herd after extinction
2007 & 2008	SL Ross lab	PF151N Sylgard Silsurf Siltech Silube	ANS Kuparuk No. 2 Fuel Oil Chayvo	1 m^2 10 m^2 DFP	• PF-151 no better than USN • Silsurf A004-UP best in static tests • Silsurf best in Dynamic Film Performance • Herder applied to oil degrades herder on water performance • Dose of 150 mg/m^2 represents saturation for silicone herders
2008	SL Ross lab	USN Various solvents	ANS	1 m^2	• Increasing amount of solvent reduces gel point of USN • Best solvent is 2-ethyl 1-butanol

Year	Location	Herders	Oils	Scale	Results
2008	Barents Sea	USN	Heidrun	Large lead Slick initially 1700 m^2	• 630 L crude released from ice edge • Spread for 10 minutes, then apply USN from boats • Ignited with gelled gasoline in baggies 23 minutes after release • Burned for 9 minutes • 90+% removal efficiency
2008	SL Ross lab & CRREL	Silsurf A108, A004-D & B2-P3-A50	Kuparuk	25 m^2	• A108 best herder • Herded thicknesses of 5 to 6 mm • Herding ability of silicone surfactants declined slowly over time
2008 & 2009	SL Ross lab and Ohmsett	USN	ANS Pt. McIntyre Marine Gas Oil Kuparuk Oseberg	2 - 4000 m^2	• Herding a slick in drift ice improves weir skimmer recovery rates, but not oleophilic skimmer recovery rates • The improvement for weir skimmers does not approach their performance in thick slicks contained by booms. • Herders do not keep oil out of salt marshes • Skimmers can improve the operational efficiency of vessel-based dispersant application, but detract from aerial dispersant operational efficiencies
2010	SL Ross lab	USN		Spray tests	• Straight stream nozzle best for herder application in cross-wind • SSC 0002 nozzle selected • Backpack sprayer identified for small boat application
2011	SL Ross lab and Ohmsett	USN OC-5 A108 A004-D	Kuparuk ANS No. 2 Fuel Oil	1 m^2 10 m^2 DFP wind/wave tank 4000 m^2	• Silicone herders retained small burning slicks • A108, A004-D and USN were best three • A108 noticeably better than A004-D and USN • Monolayer of herder will last at least 45 minutes in calm conditions • Monolayer survives for considerable time in swell, but slick fragments • Breaking waves rapidly disrupt herding
2013	DESMI-AFTI	Water & Canola as surrogates		Spray tests	• Static tests of helicopter application system using person lift • Similar spray drop sizes as produced in SL Ross lab

CHAPTER 2. INTRODUCTION

This report summarizes the results of a ten-year research program by SL Ross Environmental Research on the feasibility of using oil herding surfactant chemicals to contract oil slicks spilled on water among drift ice (sometimes called broken ice). This research has been jointly funded by industry and government, (ExxonMobil, The US Department of the Interior, Agip Kashagan North Caspian Operating Company, Sakhalin Energy Investment Company, Statoil ASA and The Joint Industry Program on Oil Spill Contingency for Arctic and Ice Covered Waters headed by SINTEF). The intention of the herding is to thicken the slicks sufficiently to allow them to be ignited and burned *in situ* without the need for mechanical containment.

In-situ burning is a countermeasure that has only been used operationally once for an offshore marine oil spill, although it has been tested for other spills. Its successful use during the Gulf of Mexico Deepwater Horizon response increased interest in further investigating its potential value as a technique to manage spilled oil. In the 2010 incident, controlled burning of spilled oil with fire booms eliminated between 220,000 and 310,000 barrels of oil that could have otherwise reached shorelines and other sensitive resources in the Gulf of Mexico. Between April 28th and July 19th, 2010, over 400 burns were initiated. Burns continued throughout this period in daily-approved ISB Burn Areas, typically within 5 to 25 kilometres of the Deepwater Horizon spill source.

These burns were conducted using response vessels pulling fire-resistant booms. This technique is fully developed and systems to apply it in an emergency are stockpiled worldwide. Herding agents promise a significant advance over ISB with booms because the burn operations can be conducted completely with a single helicopter to both apply surfactants to the water surface and then drop an incendiary device on the herded slick. This will allow ISB to become a rapidly applied technique that can treat large areas because operations are carried out at the speed of helicopters rather than boats. These benefits are particularly important for remote Arctic locations.

Arctic spill scenarios could potentially include sea conditions ranging from open water, various concentrations of drift and pack ice and solid or near solid ice cover. ISB has a potential role in each of these situations, with tactics selected to suit the specifics of the scenario.

In-situ burning has been considered a viable, primary spill response option for oil spills in arctic waters since offshore drilling began in the Beaufort Sea in the 1970s. Field trials at that time demonstrated on-ice burning of spilled oil offered the potential to remove almost all of the oil present on an ice surface with only minimal residue. Since then, a great many studies and trials have been undertaken to investigate and document burning of crude oil slicks (both fresh and emulsified) in cold open water, slush ice, drift ice, pack ice and on solid ice. Laboratory and field experiments spanning the past 40+ years have led to a good understanding of the science of burning under a variety of ice conditions and the importance of such factors as minimum ignitable slick thickness for various oil types and states of weathering, wind and wave limits for successful burning, and the maximum water, ice and snow contents that can be tolerated for a successful burn (Buist *et al*. 2013).

The behaviour of oil spilled in ice covered waters largely dictates whether in-situ burning is possible for a given spill and is governed principally by the ice concentration in the case of drift or pack ice. Conventional oil spill response options to deal with spills in drift and pack ice are limited and likely to result in highly variable removal values, depending on a variety of natural conditions and logistical constraints. In some conditions, it may only be possible to track the oil until it is released from the ice the following spring and then ignite and burn it.

The key to effective ISB is thick oil slicks (above 3mm). Solid ice and concentrated pack ice can assist and enable effective ISB by keeping slicks to the required thickness, also in these high ice concentrations, initially thin slicks can be herded against ice edges by the wind and thickened enough to ignite and burn efficiently. In loose drift ice conditions oil on the water can rapidly spread to become too thin to ignite. Fire-resistant booms can collect and contain thick slicks in open water; however, field deployment tests of booms and skimmers in pack ice conditions in the Alaskan Beaufort Sea in 2000 (Bronson *et al.*2002) and fire boom testing in the Barents Sea in 2009 (Potter and Buist, 2010) highlight the limitations of booms in even very open drift ice. Laboratory- and mid-scale tank tests found that if slicks were in the 2- to 5-mm thick range in pack ice (greater than 6 to 7 tenths coverage), even with no possibility of physical booming, effective burns could be carried out (Buist *et al*. 2003).

The focus of herder research has thus been on their application in drift ice conditions (1 to 6 tenths ice cover) in which slicks can spread fairly rapidly. As mentioned, another advantage of using herders in drift ice conditions is the possibility that the entire operation could be carried out using helicopters, or possibly even remote control aircraft, to spray herders on the water around slicks and then ignite the thickened oil with aerially deployed igniters. This type of a totally aerial response could be much faster, more effective, safer and less complicated than conventional icebreaker-based countermeasures in arctic waters.

CHAPTER 3. THEORY

A spill of crude oil spreads on a calm water surface due to the balance of a number of forces (Fay 1969). When the oil is very thick it spreads rapidly due to the influence of gravity that is resisted by the inertia of the oil (denoted as the gravity-inertia spreading regime which usually only lasts for seconds or minutes). As the oil thins gravity is still the dominant spreading force but it is resisted by the viscosity of the underlying layer of water being accelerated by the oil. This is called gravity-viscous (G-V) spreading. Finally, when the oil becomes relatively thin (a few millimetres or less), the spreading force is the net surface tension of the oil, air and the surrounding water and the resistance is viscosity (surface tension-viscous spreading, or ST-V).

Complicating this final spreading regime is the fact that, in reality, the thick oil will be surrounded by thin oil sheens that may have different surface and interfacial tensions than the thick oil. Fay's treatment of spreading allows calculation of the thickness at which the transition from G-V spreading to ST-V spreading takes place (denoted sometimes as the "equilibrium thickness"):

$$h_c = \sqrt{\frac{\sigma}{(\rho - \rho_o)g}} \qquad \textbf{(1)}$$

Where: h_c ≡ critical transition thickness [cm]

ρ_o ≡ density of oil [g/cm^3]

ρ ≡ density of water [g/cm^3]

σ ≡ spreading coefficient, or net surface tension [g/cm s^2]

$= \gamma_w - \gamma_o - \gamma_{o/w}$

γ_w, γ_o ≡ surface tension of water and oil [dynes/cm = mN/m]

$\gamma_{o/w}$ ≡ interfacial tension between water and oil [dynes/cm = mN/m]

g ≡ acceleration of gravity [cm/s^2]

Fay (1969) also proposed an equation for the maximum length scale of a slick; based on the presumption that diffusion of soluble components through the oil slick into the water column eventually causes the spreading coefficient (or net interfacial tension) to decline to 0. This equation, rewritten to estimate final slick thickness, is:

$$h_\infty = \left(\frac{\rho^2 \nu D^3 V^2}{\sigma^2} \right)^{1/8} \qquad \textbf{(2)}$$

Where: h_∞ ≡ final slick thickness [cm]

V ≡ Volume of oil [cm^3]

D ≡ Molecular diffusivity of oil [cm^2/s]

≈ 1 x 10^{-4} cm^2/s

ν ≡ kinematic viscosity of water [cm^2/s]

Fay and Hoult (1971), noting that Equation 2 predicted final slick thicknesses an order of magnitude greater than observed at sea, proposed the following modification:

$$h'_\infty = \left(\frac{\rho^2 \nu D^3 s^6 V^2}{\sigma^2} \right)^{1/8} \qquad \textbf{(3)}$$

Where: s ≡ solubility of natural surfactants from oil in water

Langmuir (1933), proposed that the thickness of a lens of non-spreading oil on water can be calculated from:

$$h^2 = \frac{-2F_S \rho_w}{g\rho_o(\rho_w - \rho_o)} \qquad \textbf{(4)}$$

Where: F_S ≡ Spreading force [dynes/cm = mN/m]

$= \gamma_w - \gamma_o - \gamma_{o/w}$

Garrett and Barger (1970) rewrote Equation 4 to allow for the calculation of the thickness of an oil lens contained by a monolayer of surface-active herding agent on the water surrounding the oil lens:

$$h^2 = \frac{-2(F_o - F_m)\rho_w}{g\rho_o(\rho_w - \rho_o)} \qquad \textbf{(5)}$$

Where: F_o ≡ Spreading pressure of oil on water [dynes/cm= mN/m]

$= \gamma_w - \gamma_o - \gamma_{ow}$

F_m ≡ Spreading pressure of monolayer on water [dynes/cm= mN/m]

Numerical values of F_m are obtained experimentally with interfacial tensiometers using the following relationship from Canevari (1973):

$$F_m = \gamma_w - \gamma_{w/m} \qquad \textbf{(6)}$$

Where: $\gamma_{w/m}$ ≡ surface tension of water with monolayer on it [dynes/cm= mN/m]

CHAPTER 4. EARLY RESEARCH

The use of specific surface-active chemicals (surfactants), sometimes called oil herders or oil collecting agents, to clear and contain oil slicks on the surface of open water is well known (Garrett and Barger, 1972; Rijkwaterstaat, 1974; Pope *et al*., 1985; MSRC, 1995). These agents have the ability to spread rapidly over a water surface into a monomolecular layer as a result of their high spreading coefficients, or spreading pressures. The best herding agents have spreading pressures in the mid-40 mN/m range, whereas most crude oils have spreading pressures in the 10 to 20 mN/m range. Consequently, small quantities of these surfactants (applied at a rate of at least 5 L per linear kilometre of slick edge or, alternatively, 50 mg per square metre of open water surface) will quickly clear thin films of oil from large areas of water surface, contracting the oil into thicker slicks.

Herders sprayed onto water surrounding an oil slick result in formation of a monolayer of surfactants on the water surface. These surfactants reduce the surface tension of the surrounding water considerably (from about 70 mN/m to 20-30 mN/m). When the surfactant monolayer reaches the edge of a thin oil slick it changes the balance of interfacial forces acting on the slick edge and allows the interfacial tensions to contract the oil into thicker layers. Herders do not require a boundary to “push against” and work even in unbounded open water. A conceptual drawing of the herding process is shown in Figure 1.

Although commercialized in the 1970s as a tool to enable skimming without booms, herders were not used offshore because they only worked in very calm conditions: physical containment booms were still needed to hold or divert slicks in wind speeds above 2 m/s, and breaking waves disrupted the herder layer. Thus, skimming operations could not be completed before the herders had dissipated and the slicks re-spread. In-situ burning, however, does not have these limitations because once ignited even slicks covering large areas only require 10 – 20 minutes to burn.

For application in loose pack ice (which calms wind waves), the intention is to herd freely-drifting oil slicks to a burnable thickness, then ignite them. The herders will work in conjunction with the limited containment provided by the ice to allow an extended window of opportunity for burning. Note, however, that given the appropriate conditions, herders will work in ice-free, open water.

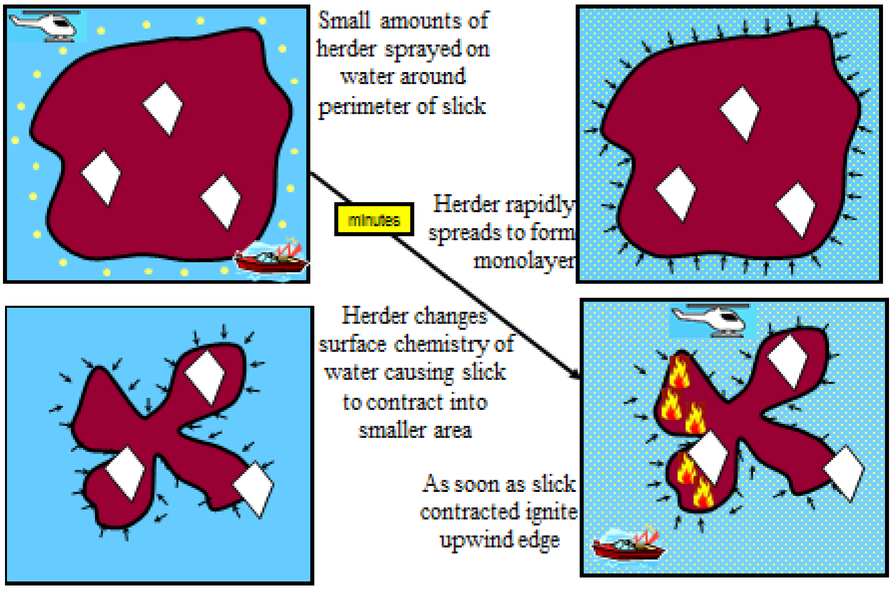

Figure 1. Conceptual drawing depicting the herding process in pack ice.

CHAPTER 5. PRELIMINARY SCREENING TESTS

A very small scale (1 m^2) preliminary assessment of a shoreline-cleaning agent with oil herding properties was carried out in late 2003 to assess its ability to herd four crude oils (ANS, Pt. McIntyre, Northstar and Chayvo) on cold water and between ice floes (SL Ross 2004). The tests involved releasing small amounts of oil onto plastic film-lined 1 m^2 pans of cold tap water (Figure 2), some containing different ice types (blocks vs. cubes), allowing the oil to spread to equilibrium and then taking digital photographs at 30-minute intervals from directly above the pan before and after addition of the herder.

Figure 2. 1-m^2 pans used for preliminary screening tests.

The photos were analysed by computer to determine slick areas.[1] EC9580 (a commercial product designed as a shoreline cleaner that exhibits slick herding abilities) was used as the herding agent. Its measured spreading pressure on cold tap water was 38 mN/m. This is somewhat lower than the values reported for past herders, OC-5 and Shell Herder; however, the experimental results were promising:

- After 60 minutes the herding action of EC9580 was essentially complete.
- EC9580 acted much more rapidly at 25°C than at 2°C, but the end result, in terms of total area reduction, was about the same.
- Water salinity did not considerably affect the action of EC9580. The herder was only slightly more effective on saline water than on tap water.
- EC9580 reduced the total area covered by non-contiguous slicks to the same extent as contiguous slicks, but did not cause non-contiguous slicks to recombine.

[1] Overhead digital photography and computer analysis of slicks in the images was used to measure thick slick areas in all the tests described in this paper. See SL Ross 2007 for details. Thick slick area was converted to average slick thickness (with an error estimated at ± 10%) using the volume of oil released. Any visible sheen generated by the oil slicks prior to herder application was not included in the area calculations, i.e., the pre-herding areas reported are of the thick portion of the slick only. The post-herder calculations are also of the thick area only.

- Using the shoreline cleaner on cold water (2°C) greatly reduced the area of sheens (10 to 100 µm thick) of fluid oils, but the thickness of the herded oil was only in the 1-mm range, not thick enough to ignite.
- On thicker (≈1 mm) slicks, the shoreline cleaner effect was much more promising and could herd slicks to thicknesses of 2 to 4 mm.
- Although the presence of ice slightly retarded the effectiveness of the herding agent, it still considerably thickened oil among ice.
- The composition of the oil appeared to play a strong role in determining potential efficacy: oils that gelled or did not spread readily on cold water could not be herded.

The results of these experiments were consistent with those reported by Pope *et al*. 1985 for three commercial herders acting on slicks of fresh Alaskan crude oils on cold water (85 to 95 % reduction in area of thin films; up to 50% reduction in area of 1 to 3 mm oil layers and minimal reduction of thicker [4 to 6 mm] layers). The slightly better performance of the commercial herders used by Pope *et al*. 1985 may be because of their higher spreading pressure (ca. 45 mN/m) compared with Corexit 9580 and/or changes in the composition of Alaskan crude oils over 20 years. The test results reported were also consistent with the cold-water tests in small pans reported by Garrett and Barger 1972, who showed that small, 1.5-mm slicks of used motor oil on 2°C water herded to thicknesses of 3 to 4 mm for 3 hours by the best herding agent formulations.

CHAPTER 6. SMALL-SCALE TESTING

The encouraging results from the preliminary testing led to a second series of small-scale tests in 2004 and 2005 (SL Ross 2005). The goals of this experimental work were to:

1. Undertake some additional small-scale (1 m^2) experiments on different herder formulations to see if surfactants with higher spreading pressure could obtain considerably better results than Corexit EC9580 with sheens and/or 1-mm slicks.
2. Conduct larger scale (10 m^2) quiescent pan tests to explore scaling;
3. Carry out small-scale (2 to 3 m^2) wind/wave tank testing to investigate wave and wind effects on herding efficiency; and,
4. Perform initial, small-scale *in situ* ignition and burn testing.

6.1.1 1 m^2 Pan Tests

Additional small-scale tests were performed to evaluate the effectiveness of chemical herders that had spreading pressures greater than Corexit 9580. Two different herder recipes were tried: OC-5 (with a spreading pressure of 40 mN/m) and the best of the herders on cold water evaluated by the US Navy's Naval Research Laboratory (Garrett and Barger, 1972). This latter herder, denoted as USN, was produced by blending 65% (v/v) Sorbitan monolaurate (Span 20) and 35% 2-ethyl butanol. Its measured spreading pressure on cold salt water was 41 mN/m. These tests involved releasing small amounts of fresh Alaska North Slope (ANS) crude into 1 m^2 pans of near-freezing 35‰ (parts per thousand) artificial seawater, some containing different ice types (2.7 kg of small cubes or four 2.7-kg blocks), allowing the slicks to spread to equilibrium and then taking overhead digital photographs at different intervals before and after addition of a herder. The photos were analysed by computer to determine slick areas. The USN herder proved to be the better of the three, both initially (after 1 min) and over a one-hour time span (Table 1).

Table 1. Results of 1 m^2 pan tests with three herders on ANS crude in different ice types.

			Oil volume	Thickness of Oil (mm) after apply herder			
Test No.	Agent	Conditions	(mL)	@ 0 min	@ 1 min	@ 30 min	@ 60 min
1	EC 9580A	warm water	1	0.1	0.9	1.3	1.3
3	EC 9580A	warm water	1000	3.0	3.4	1.9	1.7
7	EC 9580A	cold water	1000	1.9	3.0	1.8	1.7
12	EC 9580A	cubes	1000	1.9	2.8	1.8	1.7
14	EC 9580A	blocks	1000	2.2	3.7	2.8	2.8
2	OC-5	warm water	1	0.1	1.3	1.4	1.2
4	OC-5	warm water	1000	2.0	3.5	2.5	2.6
8	OC-5	cold water	1000	2.0	3.5	2.5	2.6
11	OC-5	cubes	1000	1.8	2.6	2.0	2.2
13	OC-5	blocks	1000	2.5	3.6	2.1	1.8
5	USN	warm water	1	0.02	0.6	1.4	1.5
6	USN	warm water	1000	2.0	4.1	2.9	3.1
9	USN	cold water	1000	1.8	4.1	3.7	4.2
10	USN	cubes	1000	1.6	3.3	3.1	3.7
15	USN	blocks	1000	2.3	3.9	3.7	3.6

6.1.2 10 m^2 Pool Tests

The 10-m^2 tests were performed in a rectangular wooden frame (3 m x 3 m x 9 cm high) lined with a sheet of plastic film (Figure 3). The lined frame was filled with approximately 2 cm of 0°C artificial 35‰ seawater. For some tests ice (blocks or cubes) was placed in the frame. At the beginning of each test the desired volume of ANS crude oil was placed on the water near the middle of the pan and allowed to spread to equilibrium. An overhead picture of the oil slick was then taken. After this, the herder was added around the edges of the pan in ten discrete doses from a micropipette. Overhead pictures were taken at 1 minute, 30 minutes, and 60 minutes after the addition of the herder. One additional test was conducted with Cook Inlet crude and one with Gas Oil (diesel) including ice blocks.

Figure 4 shows a plot of slick thickness versus time for all the tests over the first hour and for one test that was left overnight. All of the final herded slick thickness values were greater than 3 mm, and thus could have been easily ignited. Final herded thicknesses were about 15% to 20% higher on cold, open water than in the presence of ice blocks. The increased thickness measured the next morning may have been due to the water warming to 5° to 7°C. Pre-treatment of the water with the herder before adding the oil resulted in higher final slick thickness in ice blocks (4.0 mm vs. 3.5 mm). The Cook Inlet crude was herded to the same final thickness as the ANS crude (3.5 mm). The Gas Oil slick was herded to a final thickness of 4.2 mm.

Figure 3. 10-m^2 pan.

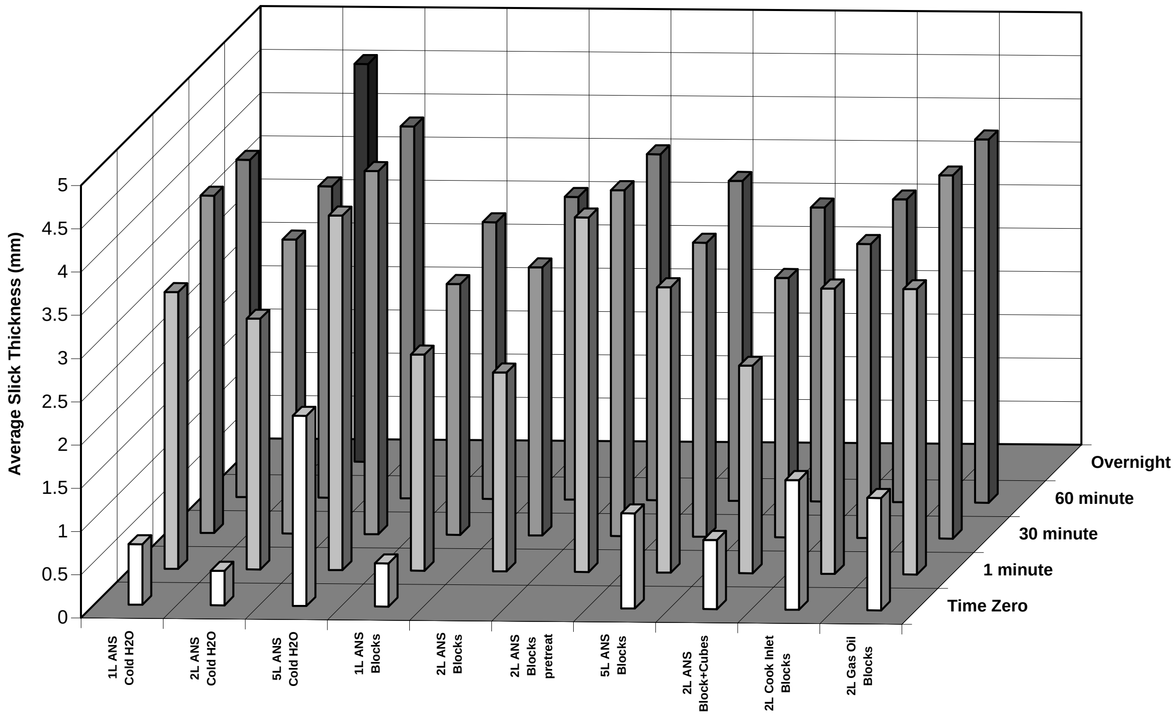

Figure 4. Results of 10-m2 pan tests.

6.1.3 Wind/Wave Tank Tests

The next series of small-scale experiments involved placing fresh ANS crude onto 2 to 3 m^2 of the surface of an 11 m x 1.2 m x 1.2 m (L x H x W) wind/wave tank containing 35‰ artificial seawater water at 0°C (Figure 5). The tests were conducted to study wind and wave effects on herding and preliminary small-scale *in situ* ignition and burn testing. A test area was created by isolating an area of water surface with floating barriers stretched from one side of the tank to the other.

Figure 5. Wind/wave tank rigged for burn tests.

Tests were carried out on open water, with floating 2.7-kg ice blocks and with grounded ice blocks.

The results of the tests in the wind/wave tank showed that:

- Herding tests in the deeper wind wave tank in calm conditions produced results similar to those in the shallow pans.
- A 1.5 to 1.7 m/s wind was capable of balancing the effect of the USN herder on an oil slick on water. With free-floating ice, the wind pushed the ice and herded slick to a barrier, where it accumulated. The final oil thickness between the ice blocks was estimated to be 5 to 6 mm in this situation.
- The USN herder, applied on one side, could slowly clear oil from between grounded ice blocks, even upwind as long as the wind speed did not exceed 2 m/s.
- Oil slicks contracted by the USN herder were successfully ignited and burned in open water and in the presence of ice blocks. The burn efficiencies measured (Table 2) were similar to those measured for physically contained slicks of the same dimensions. The presence of ice blocks in one burn test appeared to slightly reduce the oil removal efficiency.
- The presence of waves did not appear to detract from the immediate effectiveness of the herder on a slick; however, over time, opposing wind and wave action did cause the single slick to break up into smaller slicklets. Breaking waves dispersed the herder into the water.

Table 2: Results of Wind/Wave Tank Burning Tests

Test	Herder	Ice	Initial Oil		Residue	Removal Efficiency	
			(mL)	(g)	(g)	Mass %	Volume %
31	Pretreated with herder	Open water	400	365.0	151.2	58.6	64
32	Pretreated	Open water	200	183.1	92.8	49.4	56
33	After oil spread	Open water	200	188.5	93.7	50.3	56
34	Pretreated	Blocks	400	351.3	212.6	39.5	47

6.1.4 MID-SCALE TESTING

The next series of tests involved larger scales and more realistic conditions (SL Ross, 2007). This entailed:

1. A two-week test program at a scale of 100 m^2 at CRREL in the fall of 2005.
2. Experiments carried out at Ohmsett in February 2006 to explore the use of herders on spreading oil slicks in free-drifting ice fields at a scale of 1000 m^2.
3. Burn experiments at the scale of 30 m^2 in a specially prepared pool containing broken sea ice in the fall of 2006 at Prudhoe Bay, AK.

6.2 Testing at CRREL

The first series of mid-scale experiments with the USN herder was conducted in a large, indoor refrigerated ice tank at the US Army CRREL Ice Engineering Research Facility in Hanover, NH during November and December of 2005 (Buist *et al*. 2006). The main features of this facility are:

- Basin dimensions of 37 m long x 9 m wide x 2.4 m deep.
- The basin is in a large refrigerated room with air temperature control down to -24°C.
- The water in the basin is doped with 10‰ of urea.
- The basin includes two towing carriages and dedicated instrumentation and data acquisition systems.

For these experiments, low-volatility lubricating oil (Hydrocal) was used in order to eliminate any potential problems with crude oil vapours in the enclosed CRREL facility. Earlier screening experiments had shown that the USN herder would work as well on water doped with 10‰ urea as it did on 35‰ salt water (SL Ross 2007).

Once an ice sheet had been grown in the basin, an area at one end of the basin was cleared and it was divided into 9 m x 9 m sections using small oil booms built specifically for the experiment (Figure 6). The booms were attached to the wall of the basin using specially designed clamps and connectors to ensure that no oil or herder leaked onto the adjacent clean water. For some tests, dropping the air temperature to -21°C and spraying the water surface with a snowmaking machine created frazil ice.

The target coverage of ice was created inside each area using slabs cut from the main ice sheet on the tank, and then a pre-measured volume of oil, calculated to result in a 1-mm average slick thickness over the open water area, was poured onto the water surface between the floes. A video camera mounted above the center of each test area was used to obtain overhead images. The digital still images from the video were used to calculate the area of the thick portion of the slicks over time. Once the oil had stopped spreading among the ice and a digital video image had been acquired, the USN herder was applied to the water around the edge of the slick at a dose of 50 mg per square metre of open water surface using a 3-mL syringe. Video images were captured for a period of one hour after herder application. It was noted that the herder itself solidified in the syringe at the colder air temperatures (-7° to -21°C) which necessitated keeping the syringe warm until it was needed. The key experiment variables included:

- Ice coverage (10, 30, 50 and 70% surface coverage);
- Ice type (brash or frazil);
- Air temperature (0° or -21°C);
- Waves (calm or small waves)

In total, 17 experiments were conducted over the two-week test period. To summarize the CRREL results:

- The U.S. Navy cold-water herder formulation proved effective in considerably contracting Hydrocal oil slicks in brash ice concentrations of up to 70% ice coverage. Slick thicknesses well in excess of 3 mm were routinely achieved (Figure 7).

Figure 6. CRREL test basin layout.

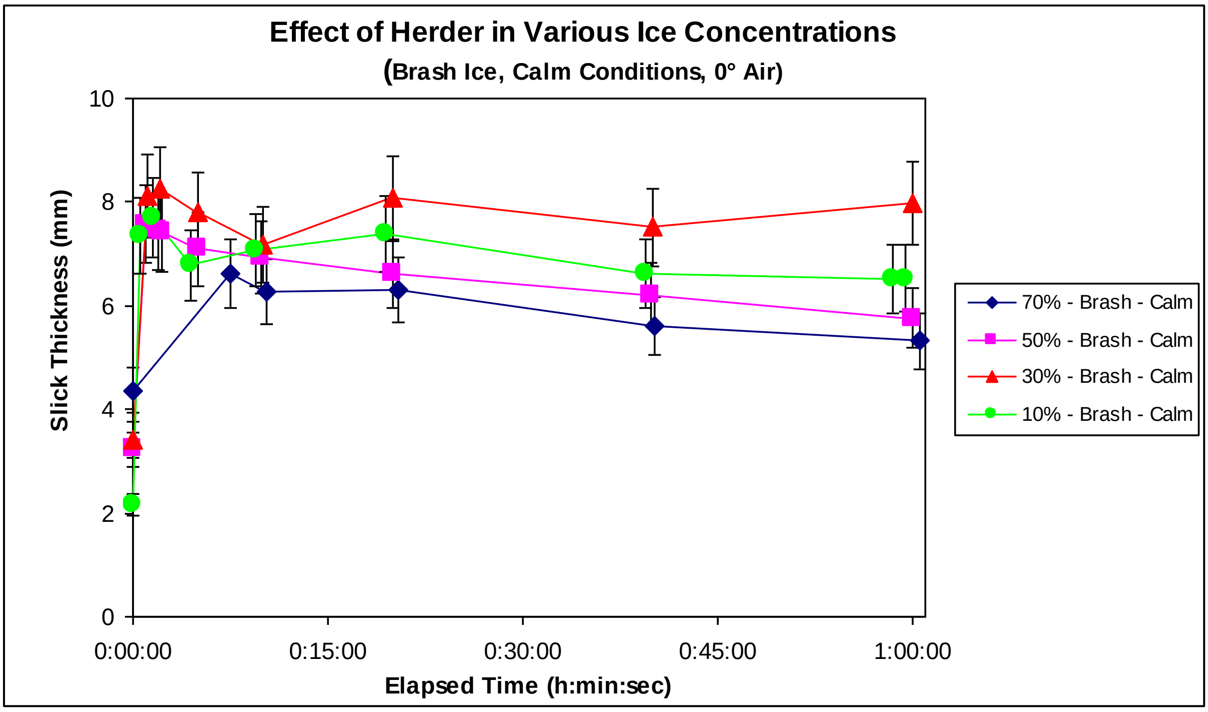

Figure 7. Herded slick thickness in various brash ice concentrations at the CRREL basin.

- The presence of frazil ice (new ice crystals forming on the water surface in very cold air temperatures) restricted the spreading of both the Hydrocal oil and the herder.
- The herded Hydrocal thickness declined slowly over the 1-hour experiments.
- The herder seemed to work as well on water at air temperatures of -21°C as it did at 0°C.

- Short, choppy waves in pack ice caused a contiguous herded Hydrocal slick to break up into small slicklets.

6.3 Testing at Ohmsett

The second series of mid-scale experiments with the USN herder was conducted at Ohmsett, in Leonardo NJ, during February 2006 (Buist *et al*. 2006). The purpose of these was to experiment with herders at the scale of 1000 m^2 using free-drifting slicks and ice pieces. The middle portion of the Ohmsett tank (203 m x 20 m x 3.4 m deep) was divided into two 20 m x 50 m test areas using containment booms attached to the sides. The booms were sealed tightly to the tank walls using clamped boom slides to allow them to move with waves. The ice was supplied by CRREL in the form of 1 m x 1 m x 20 cm slabs grown from urea-doped water to simulate sea ice. Each test involved placing 40 slabs in the test area, with 10 of the slabs quartered with an axe to provide a range of ice sizes. The tank salt water was maintained below 0°C using a large industrial chiller. The test oil was a 50:50 blend of Ewing Bank (26 °API density) and Arab Medium (30 °API density) crude oils. For two tests, evaporated crude was used. All but the first test employed two initial containment systems: a section of boom was used to contain the ice pieces just down-drift of a floating plastic ring that held the oil at a thickness of approximately 3 mm. First, the boom holding the ice pieces was released, allowing the ice to drift. Once the ice was determined to be at full speed in the prevailing wind, the oil was released to drift into the ice field. When the oil slick was in the ice field (Figure 8), the USN herder was applied using hand-held spray bottles.

A portable lift was used to take overhead pictures of the slick. The digital images were analysed to give slick areas and thickness over time. Figure 9 summarizes the results.

Test 1 involved releasing 20 L of fresh crude oil and ice from the circular containment ring simultaneously. The slick quickly accelerated out of the ice field and spread over the open water area. The herder was applied approximately one minute after the release. The test procedure was subsequently changed to that described above.

For Test 2, 22 L of fresh crude was released from the containment ring two minutes after the ice was released. The herder application started two minutes later. The wind speed averaged 2.9 m/s. The slick was herded to an average thickness of approximately 2 mm over the 8½-minute experiment.

In Test 3, the volume of fresh oil was increased to 60 L. The wind averaged only 1 m/s. The herder application commenced about 7 minutes after the oil was released. The herder contracted the slick and maintained a slick thickness of 3 mm over the time of the experiment. With the greater oil volume (and perhaps the lower wind speed) the slick did not break into small slicklets as in Test 2; rather, it elongated into several “streamers” which resulted from the herder contracting individual “arms” of the initial slick.

Test 4 involved the release of 60 L of 11% evaporated crude. The wind speed was 1.6 m/s. Herder application commenced 2½ minutes after the oil was released and was completed about 5 minutes later. The experiment ended about 6 minutes after the herder application finished, when the slick reached the tank wall. The herder initially contracted the slick to a thickness of more than 4 mm, but then streamers began to form as the slick drifted and the average thickness declined to 3 mm by the end of the experiment. Test 4 had a higher initial (unherded) thickness than Test 3, probably because the evaporated oil spread less than the fresh.

For Test 5, after 60 L of 11% evaporated crude was released into the ice and allowed to spread, the wave generator was started at a low setting to generate a 20-cm high swell with a 7-s period. The herder was applied after the waves had started, approximately 3½ minutes after the oil was released from the containment ring, and was finished 4 minutes later. The experiment ended 7 minutes after that. The herder contracted the slick to a thickness of 7 mm and, within the estimated measurement error, maintained it throughout the experiment period. It is possible that the wave action distributed and maintained the monomolecular layer of herder better than in calm conditions, leading to the greater thickness of oil than Test 4.

Figure 8. Herder test in drifting ice at Ohmsett.

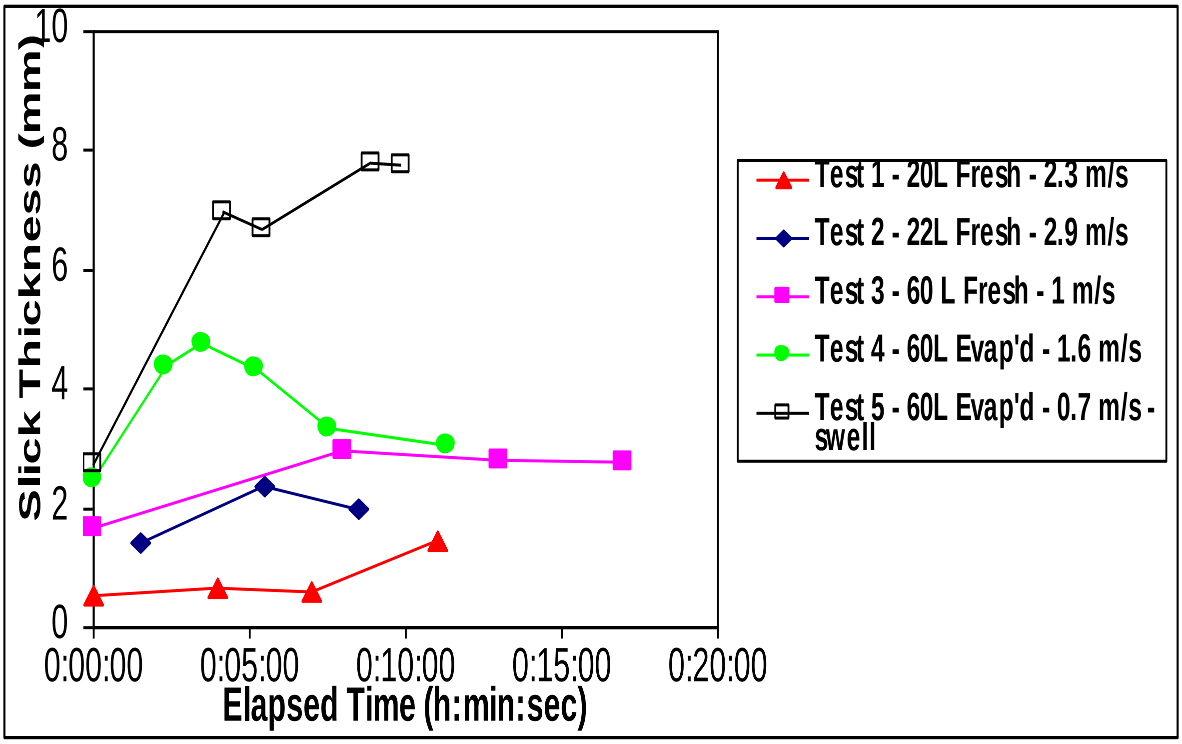

Figure 9. Ohmsett test results.

6.3.1 Burn Testing at Prudhoe Bay

The third and final series of mid-scale experiments with the USN herder was performed at the Fire Training Grounds in Prudhoe Bay, AK in November 2006 (Buist *et al*. 2007). These tests contrasted from the previous basin tests in that the oil was ignited and burned after the herding.

The experiments were conducted in a shallow, lined, grade-level pool (Figure 10). The pool was constructed using large timbers to form walls with a liner draped over the timbers. The portions of the liner exposed to radiant heat from fire were covered with corrugated metal sheeting to protect them from melting. Disused fabric fire boom was placed inside the perimeter of the basin walls, under the overhanging corrugated metal, to protect the liner from direct contact with burning oil. Fresh water drawn from a frozen lake nearby was used to fill the pool each morning. After each day's testing, the test pool was drained. The dimensions of the pool were approximately 6 m x 6 m x 30 cm deep. Roughly 3 m^3 of water was used to fill the pool to a depth of 8 cm. A windbreak, designed to nearly eliminate wind in order to prevent the slicks from drifting quickly to an edge, surrounded the pool. The windbreak achieved wind speed reductions of well over 90%. Saline ice was grown in a pit at the test site and placed in the pool to simulate brash ice fields for some of the experiments. Snow was used to simulate slush ice in another experiment.

Figure 10. View of test pool at Prudhoe Bay from above.

Immediately prior to each experiment, the ice slabs and pieces were distributed evenly inside the test pool and any make-up ice added. Next, the pre-weighed volume of Kuparuk crude oil was poured onto the water and allowed to spread. Once the oil had stopped spreading an overhead digital photograph was taken. Digital video of each experiment was also taken. Then, USN herder was added drop-wise from a 3-mL syringe to the water surrounding the slick from the edge of the test pool. It proved necessary to keep the herder warm in the -10 to -20°C temperatures, as it had at CRREL. Once the herding action had stopped, a second digital photo was taken.

Once the post-herding photo was taken, plastic baggies containing gelled gasoline were distributed in the slick and then ignited with a propane torch attached to a pole. The torch was also used to ignite other areas of the slick directly. An observer timed the burn, recording the percentage of the slick area covered by flame as a function of time. After the burn, the residue was recovered manually using pre-weighed sorbent pads that were placed in pre-weighed oily waste bags. The bags were reweighed after 24 hours in a heated trailer, following decanting as much free water as possible, to determine burn oil removal efficiency and rate. For many experiments, a post-burn photo was also taken. The test variables included:

- Ice coverage (0, 10 and 30% surface coverage);
- Ice type (brash or slush);
- Oil volume (7.5 and 15L); and,
- Herder application time (post-spill or pre-spill).

Two of the tests involved placing the oil on the water, allowing it to spread, then attempting to ignite the slick without applying herder.

Two additional experiments were conducted to investigate the effects of floating brash ice (as opposed to the normally grounded ice pieces) and the effects of small waves. In total, 20 experiments were conducted over the one-week test period.

Figure 11 shows the thickness of the oil on the test pool for each of the experiments:

- When the oil had spread to equilibrium and before the herder was applied; and,
- After the slick had finished contracting after the herder had been added.

The data showed that:

- The USN herder proved effective in considerably contracting the crude oil slicks in brash and slush ice concentrations of up to 30% ice coverage. Slick thicknesses in excess of 3 mm were routinely achieved.
- The presence of frazil ice restricted the spreading of the oil and the herder effectiveness.
- Short, choppy waves caused the herded slick to break up into small slicklets.
- Longer, non-breaking waves did not appear to cause the herded slick to break up.

Figure 12 illustrates the *in situ* burn oil removal efficiency results as a function of ice coverage. In two tests (5 and 6), the oil was allowed to spread and was not herded. Repeated attempts to ignite these slicks failed. To summarize:

- Otherwise unignitable crude oil slicks that were contracted by the USN herder could be ignited and burned *in situ* in both brash and slush ice conditions at sub-zero air temperatures as low as –17°C.
- Slicks that were not herder could not be ignited.
- As the volume of oil increased, the removal efficiency increased. Oil removal efficiencies for herded slicks averaged 50% for 7.5-L slicks and 70% for 15-L slicks.
- The type of ice (brash *or* slush) did not considerably affect the removal efficiency.
- Generally, it was not possible to reignite re-herded residue.
- Steeper, cresting waves detracted from the burn efficiency while longer, non-breaking waves did not.
- The removal efficiencies measured for the herded slicks were comparable to but slightly less than the theoretical maximums achievable for equivalent-sized, physically contained slicks on open water (Figure 13).
- The oil removal rate for the slicks was in the range expected for equivalent-sized, physically contained slicks on open water.

It was observed that in most experiments the area of the slick increased somewhat as the flames spread to engulf the entire slick; then, as the fire died down, the residue contracted. This behavior was most pronounced for the slicks involving pre-spill application of the herder.

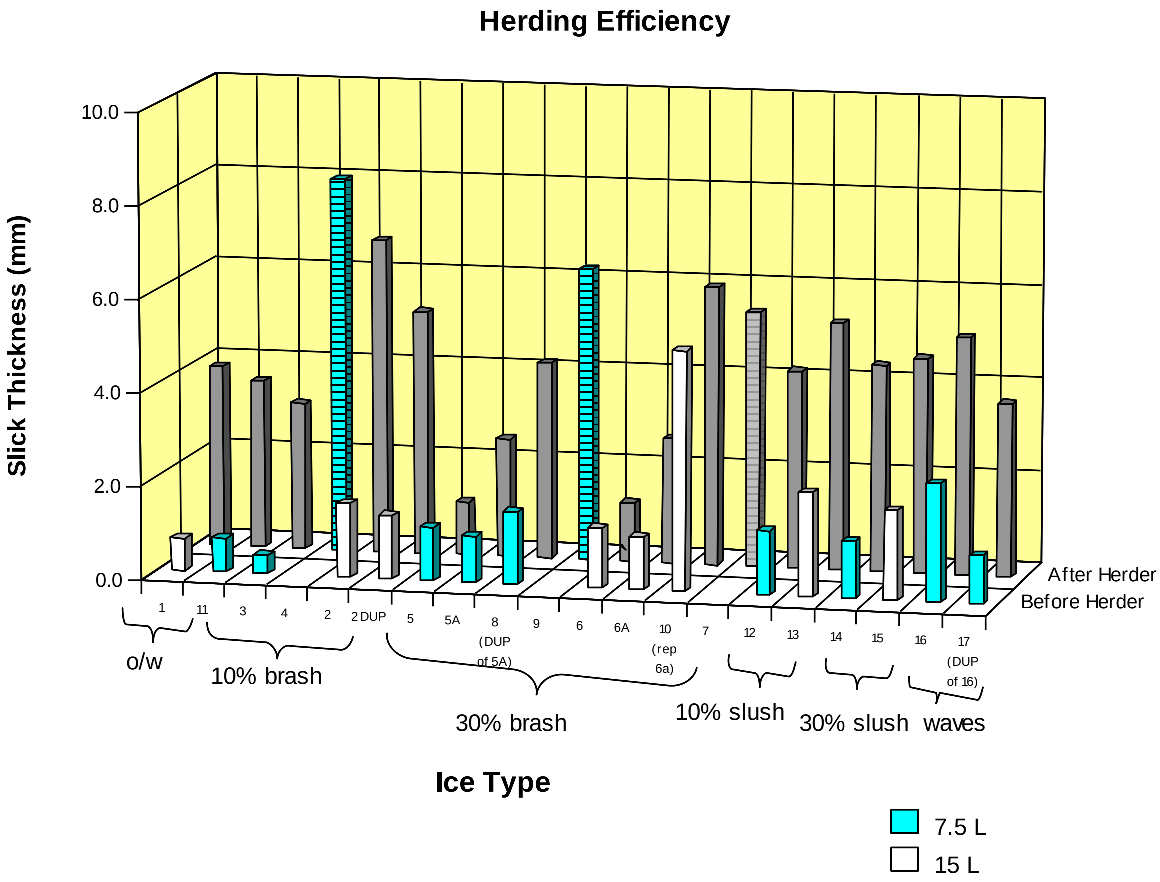

Figure 11. Slick thickness before herder and after slick contracted.

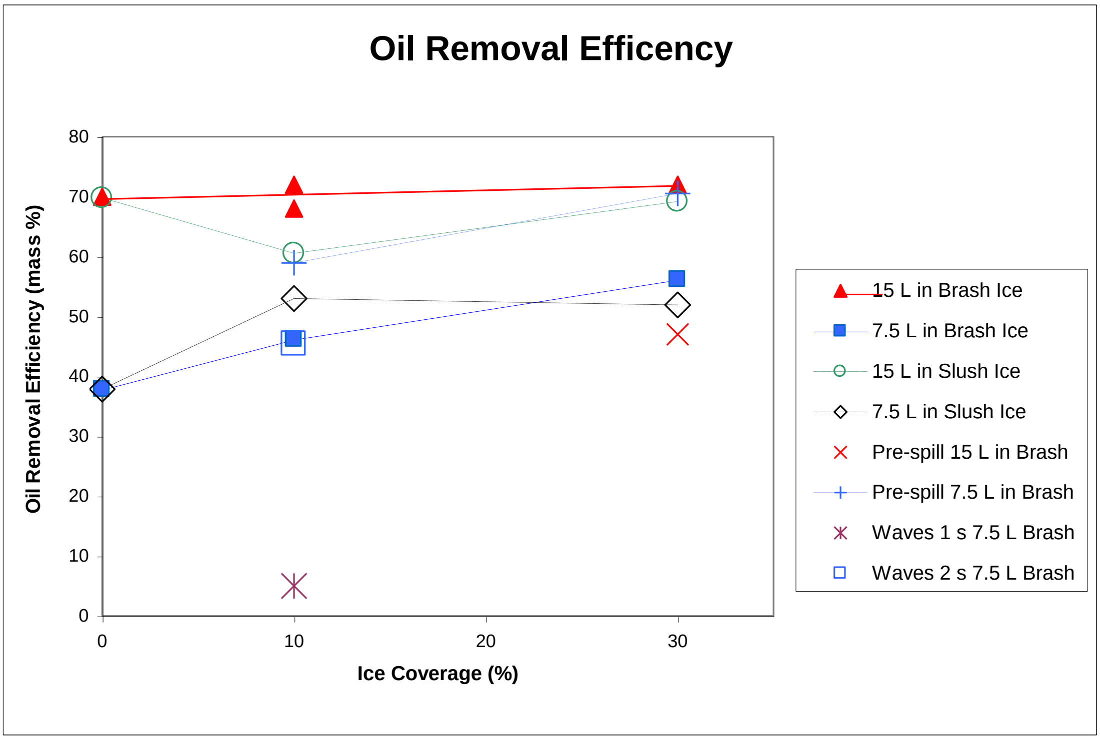

Figure 12. *In situ* burning oil removal efficiency test results.

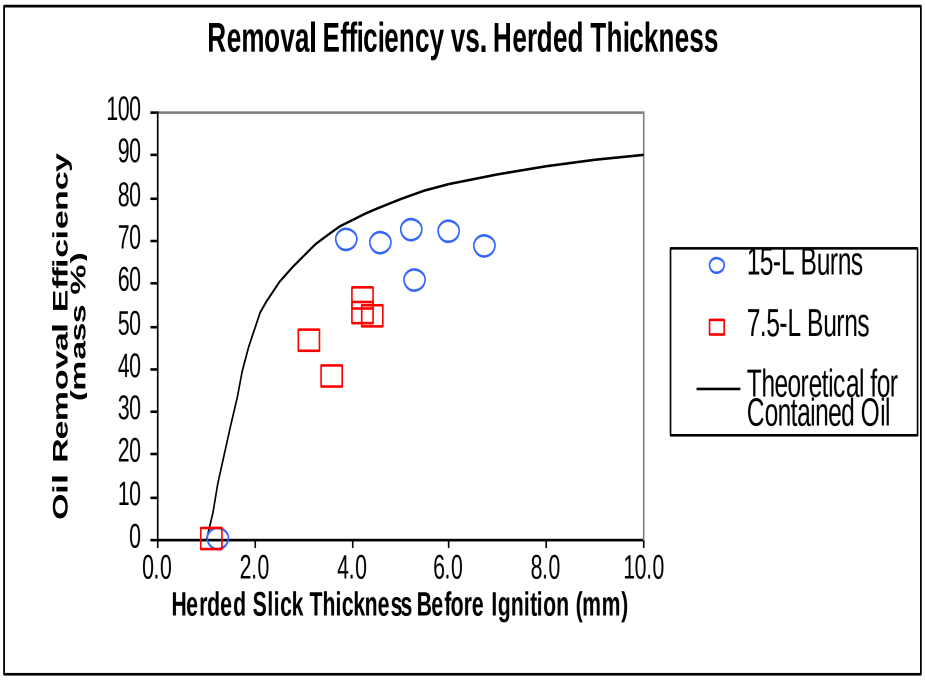

Figure 13. Comparison of measured oil removal efficiencies with theoretical.

CHAPTER 7. FIELD EXPERIMENTS IN THE BARENTS SEA

In the spring of 2008, two experimental spills of Heidrun crude oil were carried out in the Barents Sea to field test the use of the USN herding agent to thicken oil spills in drift ice for burning (Buist *et al*. 2010b). The experiments were part of a larger experiment that took place off Svalbard from May 18 to 28, 2008 (Sørstrøm *et al*. 2010). Figure 14 shows the general location of the two herder and *in situ* burning experiments that took place on May 22 and May 24, 2008.

The first experiment on May 22 involved 102 L of fresh Heidrun crude released into a monolayer of USN herding agent that had just been placed on the water. This slick was unexpectedly carried by currents to a nearby ice edge where the oil was ignited and burned. Approximately 80% of the oil was consumed in the ensuing burns.

The second test on May 24 involved releasing 630 L of fresh Heidrun crude oil from the side of a large ice floe into very open drift ice. The wind speed was 4.4 m/s measured at the surface. The crude was allowed to spread until the thick portion stopped growing (as judged from a helicopter) and was still a contiguous slick.

At this point oblique aerial digital photographs were taken at an altitude of about 100 m to record the size of the thick portion of the unherded slick. Then, herder was applied on the water around the slick periphery using pressurized garden sprayers (3L of the USN herder were applied in total) and the contraction of the slick was monitored and recorded from the helicopter.

Next, the slick was ignited by hand from a small boat positioned at the upwind edge of the free-floating herded slick. One 1-L baggie of gelled gasoline was placed in the slick near the upwind edge and ignited with a torch.

Digital video of the ignition and burn was taken from the helicopter in order to document burn times and areas. Once the slicks had extinguished, aerial photographs were taken to document the residue area, and samples were taken to estimate the residue thickness. Then, personnel in small boats recovered as much of the residue as possible with pre-weighed sorbent materials in order to obtain an estimate of the oil removal efficiency. The recovered burn residue was placed in pre-weighed plastic garbage bags for decanting, drying, re-weighing and disposal.

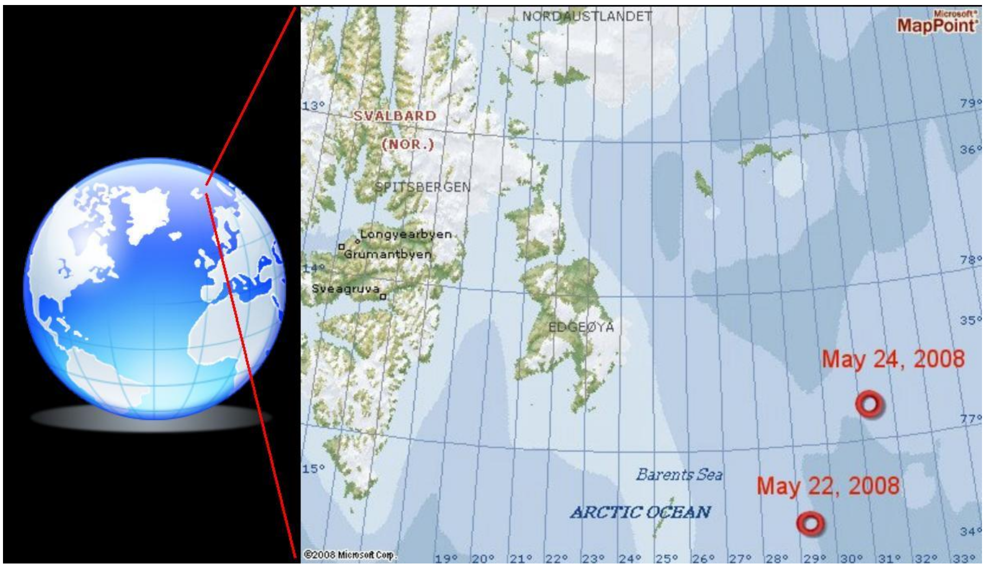

Figure 14. Map of general location for May 22 and 24, 2008 herder experiments.

The known GPS positions of the two boats in the photographs and the helicopter (including its altitude at the time of a photograph) were used to calculate the vertical angle of the photographs in order to correct the perspective of the pictures of the slicks for digital thick slick area analysis. The resulting thick slick area was converted to average thickness using the initial spill volume. The error in thick slick thickness determined using this method is likely on the order of ± 10%. Burn efficiency and burn rate were calculated for each experiment.

Figures 15 through 26 document the chronology of the experiment. The oil was released over a 2.5-minute period. It was allowed to spread on the water in the lead for approximately 15 minutes, and then the herder was applied between the edge of the floe and the slick. This was followed by herder application along two sides of the slick by personnel in one boat and along the third side of the slick from the second boat. Table 3 gives the slick areas (and slick thicknesses) calculated from the aerial images for the experiment.

Table 3: Estimated May 24, 2008 slick areas from aerial photo analysis.

Photo Time	Description	Thick Slick Area (m^2)	Average Slick Thickness (mm)
17:24:50	Max. spread (Figure 17)	1658	0.4
17:34:48	Herder applied to 3 sides of slick (Figure 20)	403	1.6
17:37:41	Just after ignition (Figure 22)	153	4.1

The first igniter was placed on the upwind edge of the herded slick 23 minutes after the oil release and the burn finally extinguished 9 minutes later after a large, intense burn traveling the length of the herded slick. As much as possible of the residue and unburned oil was recovered using the small boats with pre-weighed sorbent pads, short sections of sorbent boom and a full section of sorbent boom; however, it was obvious from the helicopter that the entire residue was not recovered. Figure 27 shows the amount of residue and unburned oil on the water after the burn. Table 4 presents the data collected for the burn. The estimate of burn efficiency based on the amount of oil released and residue recovered is 94%, but this is likely high, based on the residue and sheen seen in Figure 27.

Figure 15. Oil release begins.

Figure 16. Oil release ends

Figure 17. Max. oil area.

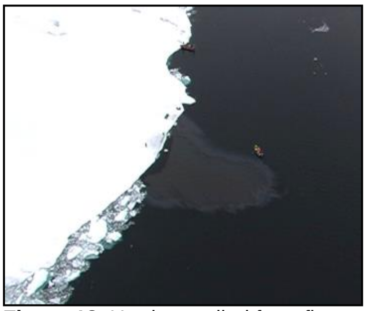

Figure 18. Herder applied from floe.

Figure 19. Herder applied from 1st boat.

Figure 20. Herder from 2nd boat.

Figure 21. Slick before ignition.

Figure 22. Ignition at upwind end.

Figure 23. Burn of upwind slick.

Figure 24. Extinction of upwind.

Figure 25. Burn of downwind portion.

Figure 26. Burn extinguished.

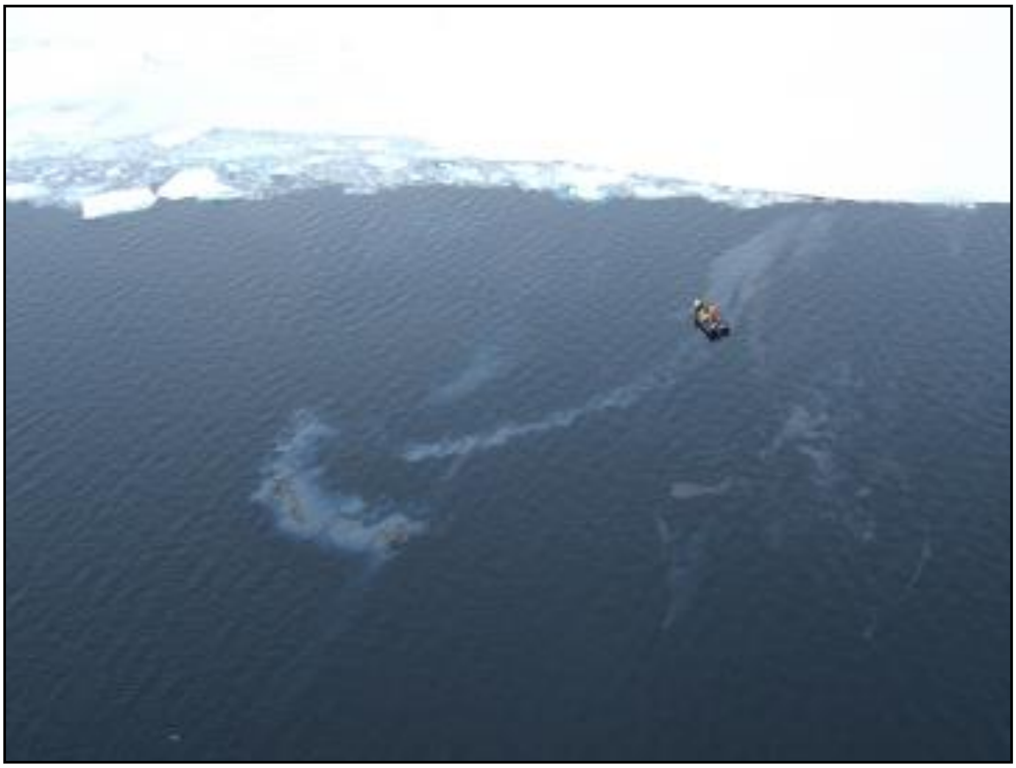

Figure 27. Residue remaining after large burn.

Table 4: Burn data collected on May 24, 2008.

Burn #	Ignition (min:sec)	Time to Flame Coverage (min:sec)			Extinction (min:sec)	Comments
		50%	100%	50%		
Upwind	0:00 (17:36:40)	1:50	2:07	3:48	4:02	Upwind area ≈ ½ of total; upwind extinguished as downwind ignited
Downwind	-	4:07	5:23	7:05	8:56	Formed long, narrow fire
Residue Collection						
	Weight of Oily Sorbent After 24 hours Decant (kg)		Weight of Clean Sorbent (kg)		Residue Weight (kg)	Burn Efficiency (mass %)
Both Burns Combined	79.0		46.2		32.8	94

The total burn times (from 50% flame coverage after ignition to 50% flame coverage prior to extinction) measured from the video for the two burns were 2 minutes and 3 minutes. Previous research has established that for *in situ* crude oil fires on water greater than 3.5 m in size, the nominal burn rate is 3.5 mm/min (Buist *et al*. 2013). Considering that the measured thickness of the slick at ignition was 4.1 mm, burn times of 2 and 3 minutes indicate that further thickening of the slick occurred after ignition. This could have been caused both by the continuing chemical action of the herder (earlier laboratory tests showed the herder could thicken Heidrun crude to more than 5 mm (Buist *et al*. 2010b) and the effects of air being drawn into the fire by the hot, rising combustion gases inducing a surface water current that herded the slick (Buist and Twardus, 1985).

CHAPTER 8. BETTER HERDER FORMULATIONS

Several projects were undertaken to improve the effectiveness of herders for use in drift ice conditions (Buist *et al*. 2010a).

8.1 Improved Cold Weather Handling

The USN herder was observed to gel in the syringe used to apply it during tests when air temperatures were below 0°C. The possibility of modifying the solvent (type or amount) in the hydrocarbon herder formulation to improve its handling at sub-zero temperatures was explored using bench- and small-scale experiments. The results indicated that the best way to improve the cold-weather handling of the USN herder is to increase the amount of 2-ethyl 1-butanol solvent (freezing point -114°C). The gelling point of the USN herder can be reduced from -4° to -13°C by increasing the amount of 2-ethyl 1-butanol solvent by a factor of 3.5, from a ratio of the active ingredient, Span 20 to solvent of 65/35 to a ratio of 35/65. The increase in the amount of solvent does not appear to decrease the effectiveness of the Span 20 (the experiments to confirm this were conducted with equal amounts of Span 20 (Buist *et al*. 2010a).

8.2 Better Herding Surfactants

There have been significant advances in surfactant technology since the 1970's. Two classes of "superwetter" surfactants – second-generation fluorosurfactants and silicone-based surfactants could enhance herding of oil slicks on water. These new surfactants can reduce the interfacial tension of water to 20 mN/m and lower, producing spreading pressures in the 50 mN/m range, a significant improvement over the hydrocarbon-based USN herder (spreading pressure in the 40 mN/m range).

In 2007 and 2008, small-scale experiments were carried out comparing the efficacy of herding agents formulated with silicone-based surfactants, formulated with second-generation fluorosurfactants, and the USN herder. The fluorosurfactant-based herders did not perform any better than the USN herder. In static tests, a silicone-surfactant based herder produced considerably higher initial herded slick thicknesses but these declined back to the thickness of the USN herder over the one-hour test period. Discussions with the manufacturer of the silicone-based surfactant resulted in other silicone surfactant formulations to test.

In 2009, experiments were conducted with three new silicone-based surfactant herder formulations (A108, A004-D and B2-P3-A50): first, at small-scale; and second, at a much larger scale at CRREL (Buist *et al*. 2010a). The small-scale experiments resulted in the selection of the first two new silicone-based surfactants for larger-scale testing. The purpose of the larger-scale experiments was to repeat the herding part of the tests conducted with the USN herder at Prudhoe Bay, AK in the fall of 2006 (see pg. 17 above).

A test pool was set up on a 15-cm thick sheet of freshwater ice grown on the Ice Engineering Test Basin at CRREL (Figure 28). The test area was approximately 5.3 m x 5.3 m x 15 cm replicating the inside dimensions of the test pool at Prudhoe Bay in 2006 (see Figure 10). The test pool walls were constructed with timbers and the pool was lined with white polyethylene (Visqueen) sheeting. Blocks of ice were used to replicate the ice conditions used in the Prudhoe tests. Clean water from the basin was used to fill the test area to a depth of 5 to 10 cm for each individual experiment. An overhead digital video camera was used to record the spread of the oil and subsequent herding for later analysis. Each test lasted approximately one hour. At the end of each experiment, the crude oil was sorbed off the water surface, the ice blocks and water were removed and the plastic liner was replaced to ensure a pristine test pool water surface for the next test. The new white Visqueen plastic sheeting was rinsed with clean water prior to its placement in the pool to ensure that it did not release surfactants that may have affected the spreading of the oil.

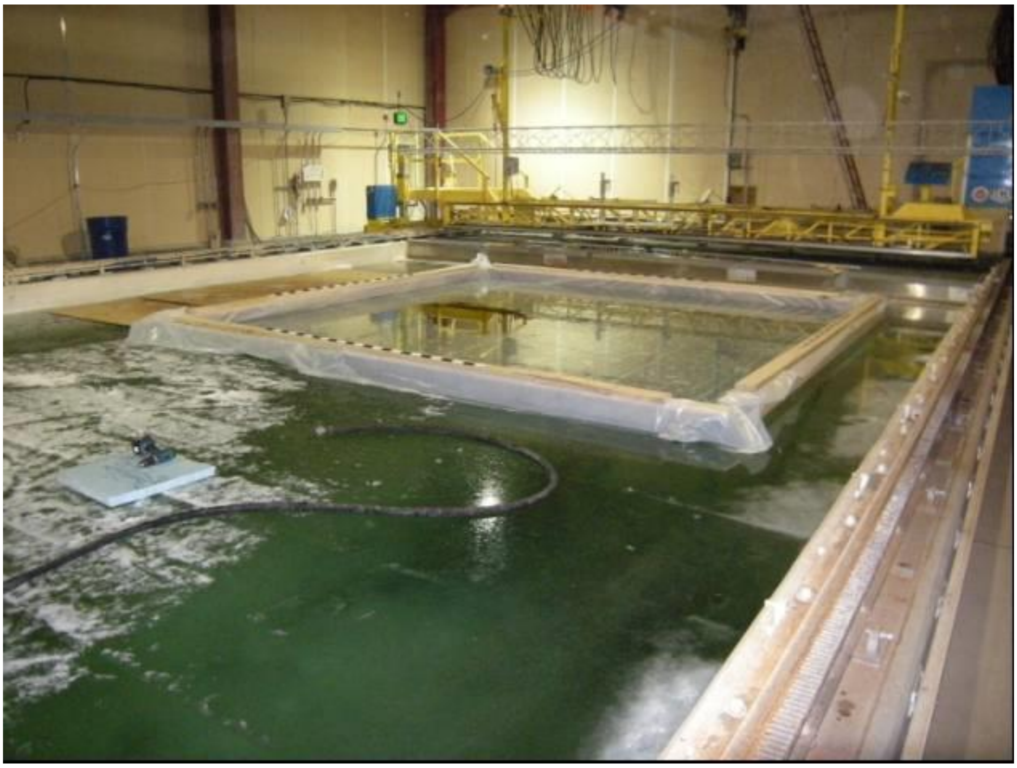

Figure 28. Test pool on ice at CRREL.

The pool water surface tension was measured before each test to ensure that an uncontaminated interface was present. The test oil was Kuparuk crude, the same as used in the experiments in Prudhoe Bay.

The test matrix variables were:

- One crude oil (fresh Kuparuk)
- Two oil volumes (7.5 L and 15 L)
- Three brash ice areal coverages (0, 10 and 30% ice cover)
- Two silicone-based herders (A108 and A004-D) applied at 150 mg/m^2

The results for the large-scale tests at CRREL are given in Figure 29. The results from the 2006 tests at Prudhoe Bay with the USN herder are also shown for comparison. The areas of the slicks at Prudhoe Bay were only measured once, with the time of the photograph ranging from approximately 2 to 7 minutes after the USN herder had been applied. These slicks were then ignited.

In Figure 29 the results from the CRREL tests on open water are given with solid lines, in 10% ice cover with dashed lines and in 30% ice cover with dotted lines. The performance of both silicone herders declined slowly over time, more so with the 7.5-L slicks than the 15-L slicks. With the 7.5-L slicks, the A108 herder proved better than the A004-D in all cases; with the 15-L slicks the A108 herder proved better than the A004-D in 30% ice cover, but produced almost identical results in 10% ice cover.

Figure 30 compares the initial herding achieved by the three herders. The initial slick thickness values for the CRREL data set is the average of the 1, 2 and 5-minute measurements.

In general, both silicone herders performed considerably better than the USN herder in similar conditions. The only exceptions being the 7.5-L test with the USN herder in 30% ice cover where it outperformed the A004-D herder and the 15-L test with the USN herder in 10% ice cover where it equalled the performance of both silicone herders.

Based on the CRREL test results and comparison with the Prudhoe Bay test data, A108 proved to be the best silicone based herder of the three tested. It considerably outperformed the USN herder in most tests with similar conditions.

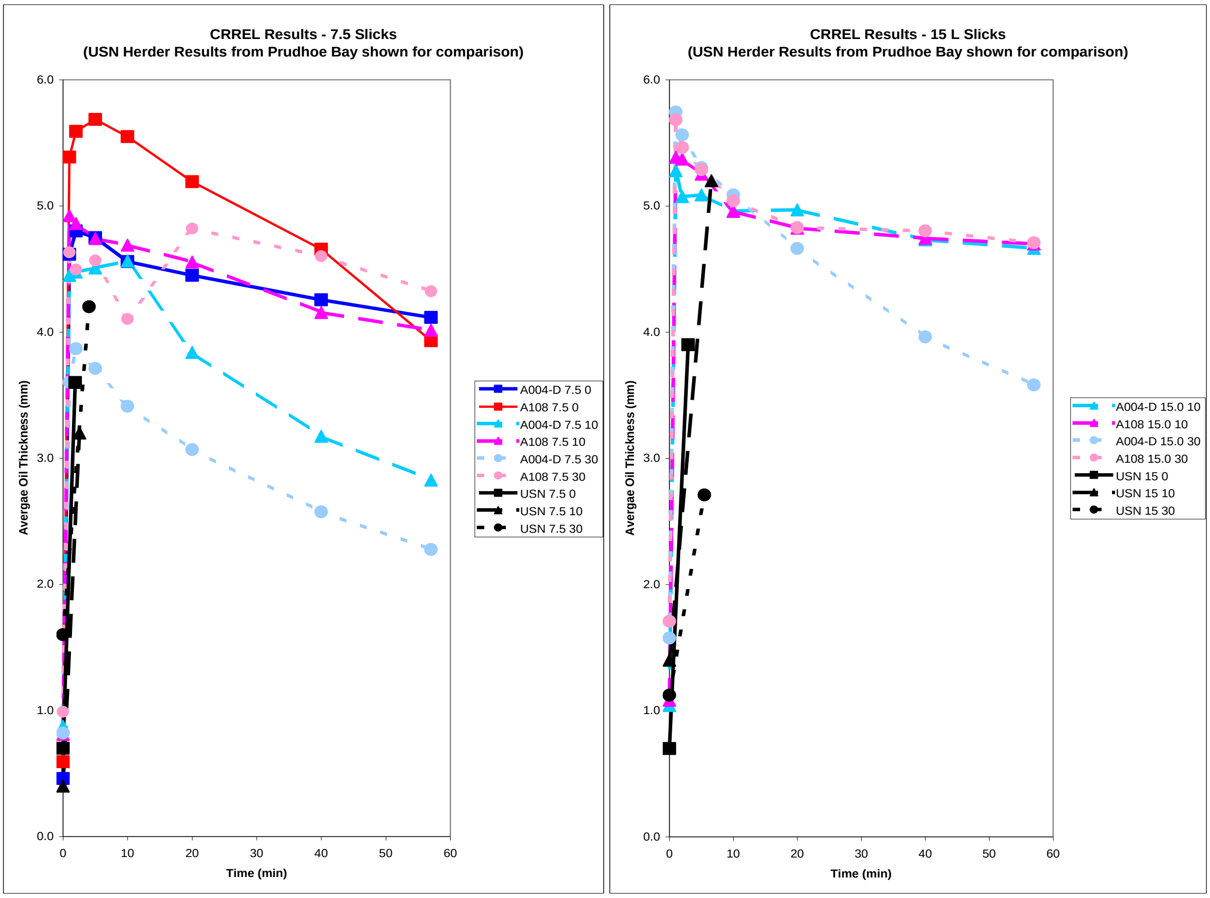

Figure 29. CRREL results with 7.5 L and 15 L slicks

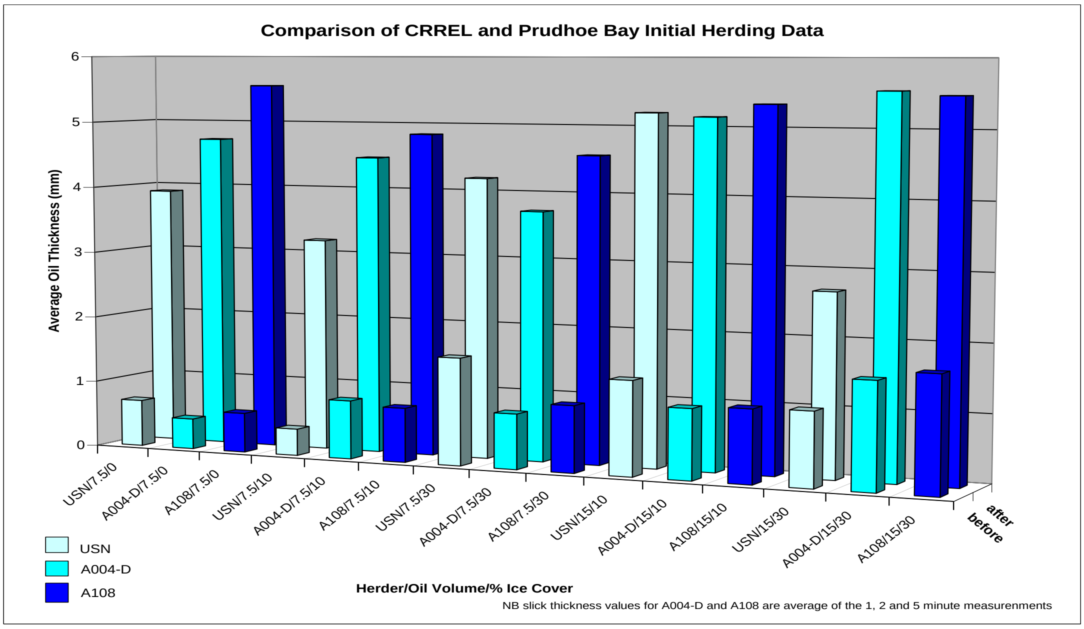

Figure 30. Comparison of initial herding results from CRREL tests with Prudhoe Bay results.

CHAPTER 9. COMMERCIALIZATION OF HERDERS

In the fall of 2011 work began on getting experimental herders listed in the U.S. EPA's National Contingency Plan (NCP) Product Schedule so that they could be used during spill response operations in U.S. waters. This process involved submitting samples to a certified laboratory for proscribed testing and the submission of the data required for listing (U.S. CFR 300.915 Subpart J). The proscribed testing includes a *Test to Distinguish Between Surface Collecting Agents and Other Chemical Agents*. For a herder to be listed as a Surface Collecting Agent, at least 75% of 5 mL of the candidate herder must resurface after being inverted 5 times in a graduated cylinder with 95 mL of distilled water and then allowed to settle for one hour.

A 4-L sample of the ThickSlick 6535 (previously named USN) and a 4-L sample of the silicone herder Siltech OP-60 (previously named A108), were sent to an accredited laboratory in Louisiana and subjected to the required tests, plus some additional cold-weather rheology measurements.

The ThickSlick 6535 passed the *Test to Distinguish Between Surface Collecting Agents and Other Chemical Agents*; however, the Siltech OP-60 did not, forming a cloudy suspension/solution that did not separate in the specified hour of settling. A second silicone surfactant (OP-40, previously known as A004-UP) was then chosen as a substitute for Siltech OP-60. Siltech OP-60 has passed the *Test to Distinguish between Surface Collecting Agents and Other Chemical Agents* in the manufacturer's laboratory and has been lab-tested previously and shown to be a good herder (SL Ross, 2008).

Table 6 presents the laboratory test results for the ThickSlick 6535, Siltech OP-60 and OP-40. The ThickSlick 6535 had a significantly lower toxicity than both the Siltech OP-60 and OP-40. The ThickSlick 6535 had a much lower toxicity than No. 2 fuel oil (i.e., had a much higher LC50); however, the 1:10 mix of the ThickSlick 6535 and the No. 2 fuel oil was more toxic than the No. 2 fuel oil by itself. The 1:10 mixtures of Siltech OP-60 and OP-40 exhibited the same trend. These herders are not intended to be applied onto the oil; rather, they are intended to be applied to the water around the perimeter of the oil and should not mix with the oil. Even if herders were accidentally sprayed onto a slick, the dosage would be considerably less than 1:10 (the recommended field application rate for herders is 150 mg/m^2, more than 30 times less than the design application rate for dispersants that the toxicity test was originally designed for). The analytical results for the two herders that passed the *Test to Distinguish Between Surface Collecting Agents and Other Chemical Agents* (ThickSlick 6535 and OP-40) show that both will float on water and are relatively low viscosity fluids at room temperature. When cooled, the ThickSlick 6535 will congeal at -2°C and freeze at -24°C: the OP-40 will congeal at -59°C and freeze at -71°C. Neither undergoes any phase separation during cooling. Both ThickSlick 6535 and OP-40 are partially miscible in water. Both of their flash points exceed 180°F (82°C).

The two herders that passed the tests have been placed on the US EPA list and are now commercially available. These two can be used, with the Federal On Scene Commander's concurrence, for spill response operations in U.S. waters. Samples of all three herders have been sent to Environment Canada, along with all the EPA test data, for their consideration for use in Canadian waters. Small quantities (200 L) of the two herders listed on the NCP Product Schedule have been produced and are stockpiled at DESMI-AFTI in Buffalo, NY.

Table 6. Summary of EPA NCP Listing Required Test Results

TEST		ThickSlick 6535	Siltech OP-60	Siltech OP-40
	Units	**Results**	**Results**	**Results**
NCP Category		Surface Collecting Agent	Not passed the tst	Surface Collecting Agent
Toxicity tests				
Herder				
M. bahia 48-hr LC50	ppm	286	4.76	6.83
M beryllina 96-hr LC50	ppm	138	15.9	3.33
No.2 Fuel Oil				
M. bahia 48-hr LC50	ppm	2.43	2.43	6.43
M beryllina 96-hr LC50	ppm	37.6	37.6	40.5
10:1 No.2 Fuel Oil / Herder				
M. bahia 48-hr LC50	ppm	1.53	4.38	3.27
M beryllina 96-hr LC50	ppm	5.91	10	9.7
Reference Toxicant-Sodium Dodecyl Sulfate				
M. bahia 48-hr LC50	ppm	8.23	8.23	8.68
M beryllina 96-hr LC50	ppm	3.02	3.02	2.33
Analytical tests				
Key Findings Summary				
Flash Point		>180 °F (82°C)	>180 °F (82°C)	>180 °F (82°C)
Pour Point		21.2 °F (-1.7°C)	37.4 °F (3°C)	-74.2 °F (-59°C)
Viscosity	cSt	24.7	38.55	8.27
Viscosity @100°F	SUS*	118	184	53
Specific Gravity@60°F		0.974	1.056	0.988
Surface Collecting Agent Test		PASS	FAIL	PASS
Phase Separation		None	None	None
Freezes at		11.2°F (-24°C)	12.2°F (-11°C)	-95.8°F(-71°C) ((-71°C)
Solubility		Partial Miscibility	Total Miscibility	Partial Miscibility
pH		6.45	7.5	10.1

* Saybolt Universal Seconds

CHAPTER 10. BIODEGRADATION TEST

Figure 42 shows the results of preliminary biodegradation tests with the two US EPA approved herders, ThickSlick 6535 and Siltech OP-40. ThickSlick 6535 biodegraded to >10% on Day 1 and to 60% by Day 5 (readily biodegradable). Siltech OP-40 reached only 10% on Day 16 and 19.34% on Day 28 (the end of the test), which is considered as hardly biodegradable. As is the case with the toxicity testing of herders in the previous section, the methodologies and species employed for these biodegradation tests are not likely to be applicable to herder use in Arctic waters.

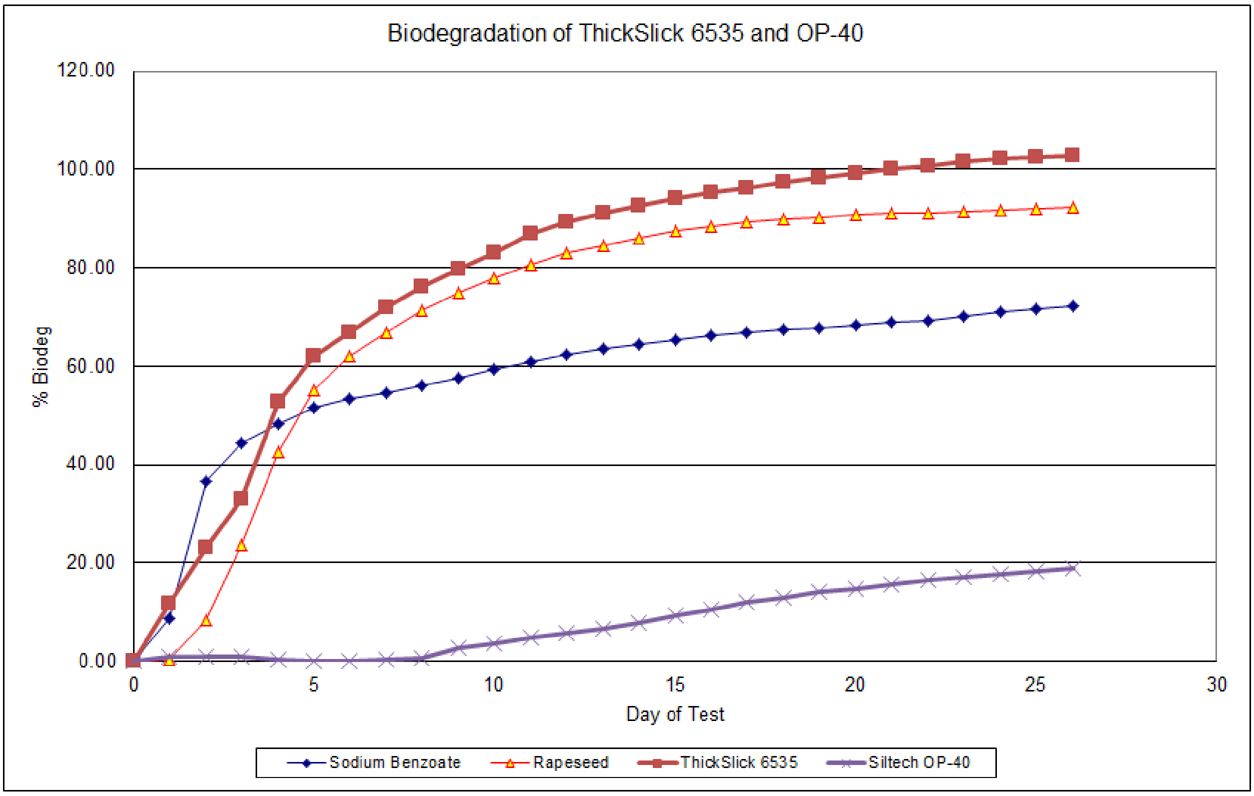

Figure 42. Biodegradation curves for ThickSlick 6535 and Siltech OP-40

CHAPTER 11. HERDERS TO IMPROVE OTHER MARINE SPILL RESPONSE OPERATIONS

A two-year research project was completed in 2009 (Buist *et al*. 2010c) that studied whether herders can assist with other areas of spill response that have inherent restrictions on effectiveness, specifically:

- The use of herding agents in pack ice to enhance mechanical recovery of spilled oil with skimmers;
- Using herders to clear oil from marsh areas; and,
- Applying chemical herders around oil slicks on the open ocean to improve the operational effectiveness of subsequent dispersant application.

11.1 Skimming in Drift Ice

The main problem with using mechanical recovery systems in drift ice conditions is that the booms, deployed to collect and concentrate oil for effective skimming, also collect and concentrate ice pieces that quickly render the skimmers ineffective (Bronson *et al*. 2002). The research on using herding agents to thicken slicks for *in situ* burning has shown that they can considerably contract and thicken oil slicks among ice, without concentrating the surrounding ice. This could be beneficial to mechanical recovery. In fact, as a skimmer removes oil from the centre of a herded slick, the action of the herding agent may cause the slick to continuously contract towards the skimmer, eliminating the need to move the skimmer around to contact all the oil. On the other hand, it has been observed that the surfactant in the USN herding agent renders sorbent pads less hydrophobic and their water retention increases considerably. This could be a significant detriment to oleophilic skimmers such as drums, discs and rope mops whose recovery surfaces contact herding agent. Experiments to study the use of herders to improve skimmer operations in drift ice were carried out in the laboratory and at Ohmsett using both weir and oleophilic skimmers.

The first series of laboratory tests involved 54 individual dip tests to determine if common materials used in oleophilic skimmers (PVC, aluminum and stiff brush bristles) would be detrimentally affected by contact with the USN herding agent prior to contacting the oil (ANS and Kuparuk crudes and No. 2 Fuel Oil) to be recovered on room temperature water of different salinities (0, 15 and 30‰). The overall average reduction in adherence of oil to the material dipped in herder was 19% for the PVC and 5% for the aluminum. There was no significant difference in the adherence results for the stiff brush.

The next series of laboratory experiments was carried out in an indoor wind/wave tank filled with 30‰ salt water at 0°C using the same oils. The experiments involved measuring the performance of both a small surrogate weir skimmer and a small disc skimmer mock-up with and without herding agent applied to the slick to be skimmed. Generally, herding improved the Oil Recovery Rate (ORR – the volume of oil recovered per unit time) and the Oil Recovery Efficiency (ORE – the fraction of oil in the recovered fluid) performance of the weir skimmer by factor of two to three. No significant improvement was noted with the disc skimmer. The ORE for the disc skimmer was actually worse with the application of herder because the disc contacted, and recovered, more water than when the oil was not herded.

The final series of experiments was conducted at Ohmsett using real skimmers: a small weir skimmer (DESMI Termite) and a small oleophilic disc skimmer (Morris Industries MI-2). The general test procedure was to put 1.2 m x 1.2 m x 20 cm slabs of freshwater ice supplied by

CRREL into a 32-foot diameter boom circle with the desired ice piece size distribution (see Buist *et al*. 2002 for the prescribed size distribution), then move it to the upwind part of the tank. Next, the boom was released and allowed to accelerate to its terminal drift speed. Once this was reached, the oil (ANS crude, Pt. McIntyre crude or Marine Gas Oil) was placed in the boom circle, allowed to spread, photographed, herder applied (if required) and skimming started. Skimmer performance data was measured using standard Ohmsett test protocols. Figure 31 shows a typical test.

Figure 32 shows the ORR results for the weir skimmer and Figure 33 gives the same for the oleophilic disc skimmer. The addition of herder improved the performance of the weir skimmer by factors of 3 to10: however, the oil thicknesses produced by the herder were too low to permit maximum performance of the weir skimmer (the highest ORR achieved was 15 L/min whereas the skimmer pump is rated at 500 L/min). No significant improvement was measured in the performance of the disc skimmer.

Figure 31. Overhead view of disc skimmer test with 10% ice before and after herding.

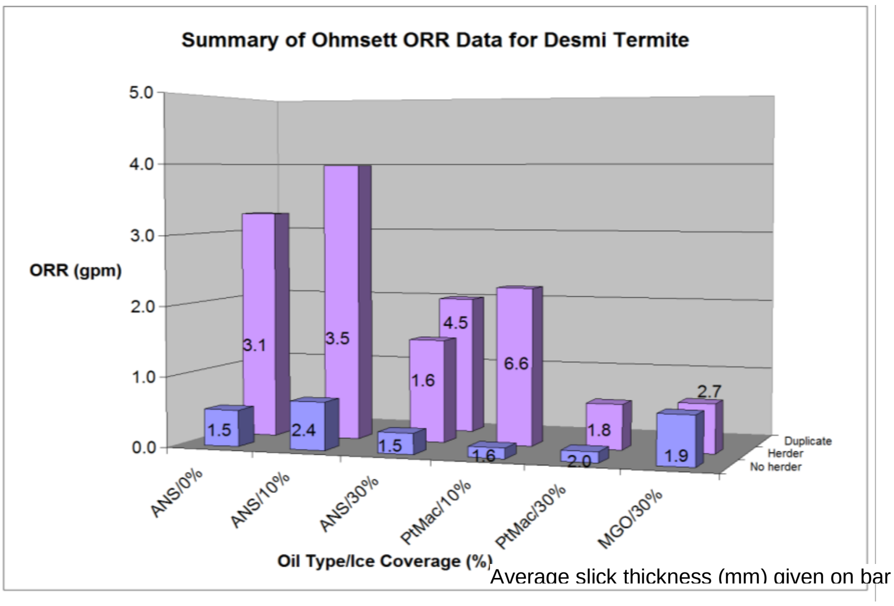

Figure 32. ORR results for weir skimmer experiments.

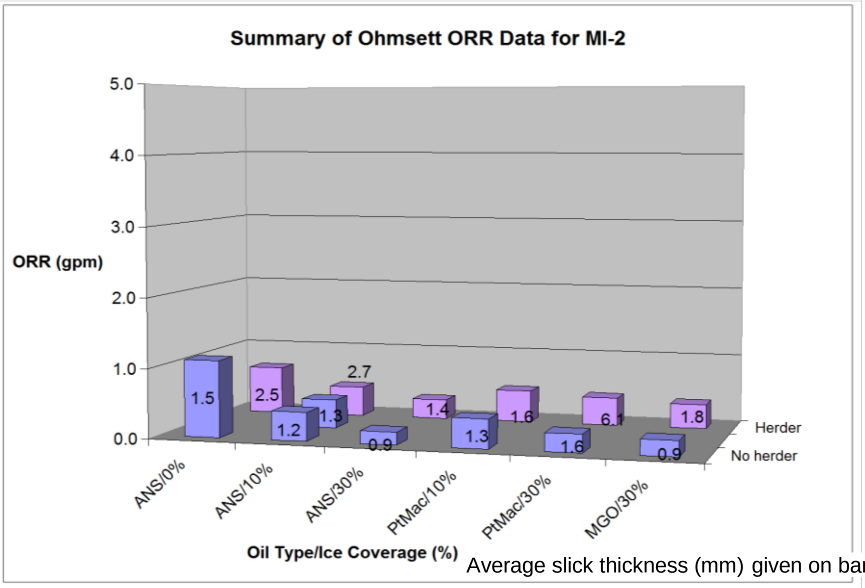

Figure 33. ORR results for oleophilic disc skimmer.

11.2 Herders to Clear Salt Mashes

A series of preliminary small-scale experiments was also undertaken in the fall of 2008 in small plastic pans to determine the feasibility of using herders to clear oil slicks from salt marshes. The experiments utilized similar local fresh water marsh plants as surrogates for salt marsh species and involved ANS and Kuparuk crudes and No. 2 Fuel Oil on water with different salinities (0, 15 and 35‰) at three temperatures (0°, 10° and 20°C). In none of the experiments did the herder clear the oil completely from the marsh plants. In some tests the herder caused the oil slicks to contract in size sufficiently to considerably reduce the oiled area of the marsh; however, even in these cases, there remained a ring of oil at the waterline around the originally oiled stalks of the marsh plants. A short series of tests to simulate oil entering a salt marsh on a rising tide indicated that pre-applying herders might prevent plant oiling.

In all cases, after herder had been added, the slick thickness was great enough to support ignition. This is a significant finding, since even though the herder did not clear the oil out of the marsh plants, it could contract the oil sufficiently to allow *in situ* burning, an accepted oil removal practice for salt marsh environments (Myers 2006).

11.3 Herders to Improve Operational Efficiency of Dispersants

One of the identified weaknesses of chemical dispersants is that they consistently either under-dose or over-dose real oil slicks due to the inherent large variability in oil thickness at sea. Dispersant drops that fall on thin oil or sheen tend to penetrate through to the underlying water and are wasted. In addition, the surfactants in dispersants also act as herders causing sheens or thin oil slicks to rapidly contract resulting in much of the dispersant being wasted as it falls directly on water.

Dispersant drops that fall on thicker slicks will mix with the slick, if conditions are right. However, it is impossible to visually determine the thickness of the “black” portions of a slick, making accurate dosing with dispersant difficult - thin portions of the slick are overdosed and thick portions are under-dosed. The application of a herding agent around the periphery of a slick just prior to it being treated with dispersant would cause the slick to contract into much thicker oil, covering a much smaller area with a more uniform, and predictable, thickness. This could allow more precise application of dispersant to a smaller area of oil at a more predictable dosage.

Herders will contract free-spreading oils with thicknesses ranging from <1 µm to 1+ mm into slicks of ~1 to 4 mm thickness, eliminating the sheen overdosing problem and allowing better dosing for the thick slick. This offers the possibility of considerably improving dispersant targeting. Slicks that have spread to «1 mm thickness could be shrunk and thickened with a chemical herder applied by a helicopter-slung bucket delivery system, or vessel-based delivery system, then treated with dispersant from ships or aircraft. Another possibility is the application of herding agents around slicks in calm seas to prevent them from spreading until the wind picks up and breaking waves (necessary for effective chemical dispersion) appear.

Experiments were conducted at Ohmsett in the fall of 2009 to compare dispersant application on herded slicks at rates representative of aerial spraying vs. boat spraying. The tank water salinity was 35‰ and the temperature ranged from 15 to 20°C. The general test procedure used at Ohmsett was to rig the tank for dispersant testing, lay down a slick of crude oil on the tank using the Main Bridge oil discharge system (Figure 34), and allow the oil slick to spread until it reached an equilibrium thickness, then apply herder to contract the slick (Figure 35). Dispersant was applied next, either with a hand wand at a rate to simulate vessel-based application or with a spray bar mounted on the Main Bridge at a rate to simulate aerial application from a C-130. After the dispersant application, the waves were started (Figure 36) and left on for 30 minutes, during which time a laser particle size analyser and an *in situ* fluorometer were towed through the oil droplet cloud. The standard technique of sweeping the tank surface and collecting the surface oil once the waves were turned off was used to estimate overall dispersant effectiveness.

Just prior to each experiment, the test area was swept with sorbent to remove any surfactant that had resurfaced. Experiments were also run with no herder as controls. Four tests involved fresh Oseberg crude and three involved artificially evaporated Oseberg crude.

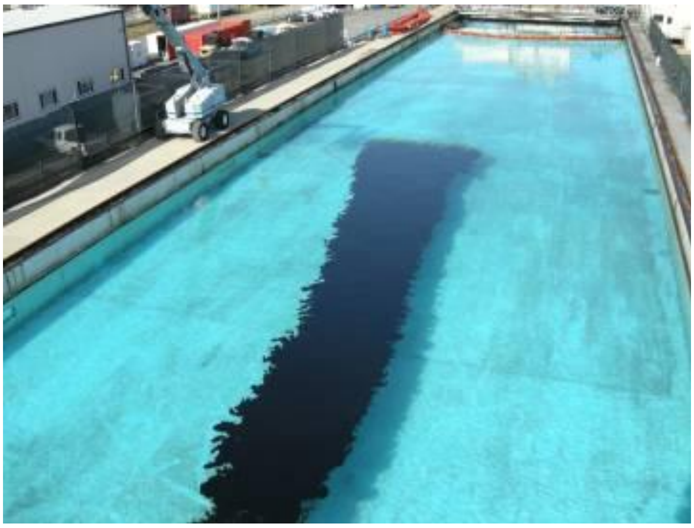

Figure 34. Oil spreading after release.

Figure 35. Herded oil.

Figure 36. Oil beginning to disperse after treatment and waves on.

Table 5 presents the dispersed oil data. Three observations can be made from Table 5:

1. Comparing aerial application of dispersant with and without herder (Test 2 vs. Tests 3 and 4 and Test 6 vs. Test 7), the herder did not detract from dispersant effectiveness;
2. Herding a slick prior to applying dispersant from a vessel, improves dispersant effectiveness with weathered oil (Test 5 compared to Tests 6 and 7); and,
3. Herding a slick prior to spraying dispersant by an aircraft reduces operational efficiency, i.e. the total amount and the ratio of dispersant applied to the same amount of oil (Tests 2 vs. 3 / 4 and Tests 6 vs. 7). In other words, herding a slick before applying dispersant from an aircraft results in more dispersant being wasted by landing on water instead of oil.

Table 5. Dispersant application data and measured effectiveness.

Herd-Disperse at Ohmsett

	Oil Volume & Evap'n	Total Dispersant and Application	Dispersant Hitting Target	DOR	Comments	Visual Estimates (from Video)	Dispersant Effectiveness (Surface oil recovered)
	(L)	(L)	(L)				(%)
Test 1 20_10_2009 **Herded**	94.0 **Fresh**	4.1 **Vessel**	4.1	1:23	Hand wand	All dispersant applied hit oil	99
Test 2 21_10_2009 **Herded**	63.9 **Fresh**	2.9 **C-130**	~0.48	1:90 to 1:280	Wide slick DOR versus narrow slick DOR	Approx. 1/6 of dispersant spray hit oil. 1:130 DOR	99
Test 3 21_10_2009 **Not herded Control**	63.1 **Fresh**	2.3 **C-130**	~0.77	1:40 to 1:110	Wide slick DOR versus narrow slick DOR	Approx. 1/3 of dispersant spray hit oil. 1:80 DOR	86
Test 4 (Repeat 3) 22_10_2009 **Not herded Control**	77.0 **Fresh**	2.4 **C-130**	~2.04	1:35 to 1:38	1:35 by thickness estimate	Approx. 85% of dispersant hit oil. 1:38 DOR	94
Test 5 22_10_2009 **Herded**	72.8 **Evap'd**	4.6 **Vessel**	3.0	1:22	Hand wand	90% of oil hit by 3 L of dispersant	98
Test 6 23_10_2009 **Herded**	70.7 **Evap'd**	2.4 **C-130**	0.22	1:320	1:325 by thickness 1:321 by ~% disp hitting oil	Slick was wind herded prior to herder application	67
Test 7 23_10_2009 **Not herded Control**	75.9 **Evap'd**	2.8 **C-130**	0.89	1:100 to 1:240	Wide (10' at start) DOR versus Narrow (4' at end) DOR	1:85 by ~amount of dispersant hitting oil	66

CHAPTER 12. HERDERS IN OPEN WATER

Herders were studied in the 1970s as an open water oil spill response technique but the goal was to provide containment for mechanical recovery. In this application herders were limited to relatively calm conditions because the herder itself dissipated quickly in higher seas, allowing the slick to respread. Field tests of herders on open water with a 25-gallon fuel oil slick in Chesapeake Bay (Garrett and Barger, 1972) and a 5-ton crude oil slick in the North Sea (Rijkwaterstaat 1974) have shown them to retain their efficacy for several hours in winds of up to 6 m/s (12 knots) and up to 2-m (6-foot) seas, providing the herder monolayer is periodically replenished.

The dissipation of the herder monolayer in open water occurs over periods of tens of minutes: not enough time to allow skimming of the herded slick. *In situ* burning is a process that requires only minutes to implement using minimum logistics and equipment that can be rapidly delivered to a remote site by a helicopter. Once ignited, the air being drawn into a large *in situ* oil fire by the combustion process will also contain the burning slick and thicken it further (Buist and Twardus 1985; Buist *et al.* 2010a). Thus, there is great potential for *in situ* burning enhanced by chemical herders to be a very effective rapid response technique in ice-free waters – both in polar and temperate regions.

A research program was carried out in 2011 for the US Department of the Interior's Bureau of Safety and Environmental Enforcement (BSEE) that investigated the suitability of herders as a rapid-response in situ burning tool for open water (SL Ross 2012, Buist and Meyer 2012). The research was conducted in two parts: the first involved laboratory testing to identify the best herding agent(s) for warmer water conditions; the second involved experiments at Ohmsett to quantify the persistence of the herder monolayer in waves.

A series of comparative experiments was undertaken at the SL Ross lab with hydrocarbon-based and silicone-based herding agents in 1-m^2 pans, a 10-m^2 pan, small pans mounted on a rocking shaker and the SL Ross wind/wave tank to determine the best of several candidate herders for use on warmer water. Overhead digital photographs were taken and analyzed by computer to determine the herder effectiveness in the pan tests. The wind/wave tank tests were videotaped. The results showed that:

- In the laboratory herding tests the Silsurf A108, Silsurf A004-D and USN herders performed best.
- The two silicone-based herders retained a small burning crude oil slick and achieved burn efficiencies as good as or better than the USN herder.
- The Silsurf A108 herder performed noticeably better than the Silsurf A004-D and USN herders in all test conditions during the Ohmsett tests.

Surfactant film persistence (i.e., how long the monolayer generated by a specific herding agent will last) as a function of sea state and to what degree periodically replenishing the film can counteract this was investigated in an 8-day test program at Ohmsett. The experiments took advantage of the facility's newly upgraded wave making capabilities. Overhead digital video and photographs were taken to qualitatively compare and determine the persistence of the herding agents in calm conditions, a swell and breaking waves. A total of 11 experiments were completed with three herding agents (USN, Silsurf A108 and Silsurf A004-D) in the three wave conditions: 9 tests as per the test protocol plus an additional duplicate test and a control (no herder). Based on visual observations of the tests the following conclusions can be drawn:

- The monolayer of each of the herders will survive for more than 45 minutes in a calm sea.

- The presence of breaking or cresting waves rapidly disrupts the herder monolayer and the oil slick resulting in many small slicklets.
- The monolayer survives for considerable periods of time in a swell condition, but the constant stretching and contracting of the herded slick results in elongating the oil slick and slowly breaking the slick into smaller segments.
- The Silsurf A108 performed noticeably better than the other two herders in all tests.

CHAPTER 13. APPLICATION SYSTEMS DESIGN AND TESTS

The primary usage being considered for herders is the thickening of relatively small individual slicks of oil (on the order of 10's to 100's of meters in size) in an Arctic environment in the presence of drift ice where wave conditions are relatively calm. To be effective the herders need to be applied at about 5 liters per kilometer of slick perimeter (SL Ross, 2007). An important characteristic of delivery systems will be good droplet size control in order to limit the production of fines that might drift onto the slick. The herder should be applied onto the water surface around a targeted slick, as contamination of the slick itself with herder will reduce its ability to contract into a thicker state for efficient burning.

To meet these basic requirements, two primary modes of application are considered feasible. The herder could be applied from a small boat that travels slowly around the perimeter of the oil slick at a speed that does not mix the herder into the water; or, it could be applied from a helicopter at a speed and altitude that minimizes rotor downwash influences on the herder spray and nearby slick. For the purpose of application system design it was assumed that small boat application would be completed at a speed of 2 to 5 knots (i.e., no wake).

When applying dispersant from a bucket slung under a helicopter the recommended altitude is 10 to 15 m and the recommended speed is 25 to 50 knots directly into the wind, in order to minimize effects of the rotor wash on the droplets of dispersant (Fiocco and Lewis, 1999). When applying herder, the helicopter would fly at a forward speed of approximately 10 to 20 knots, slower than when applying dispersant, because of the need to maneuver around individual slicks. The altitude of the helicopter while applying herder would likely be higher than while applying dispersant in order to reduce the rotor wash effect on the water surface. Field tests will be required to confirm these assumptions.

To achieve minimal over-spray and negligible penetration of product into the water column the herder will have to be applied with a large enough drop size to curtail crosswind drift and small enough drop size to limit penetration into the water column. Experience with chemical dispersant application systems has shown that spray drops smaller than about 0.3 mm tend to drift significantly and drops in excess of 1 mm tend to penetrate through oil slicks into the water below.

In dispersant application a wide spray-swath is desired whereas with herders, a narrow spray width is preferred. The slower speeds envisioned for herder application by helicopter and the different air flow patterns from a helicopter platform versus a fixed-wing aircraft should result in less herder atomization due to wind shear and a tighter drop distribution from a nozzle positioned beneath the helicopter.

A "straight stream" type of nozzle is well suited to this purpose. At the low speeds proposed for application from a small surface boat the flow from a straight stream nozzle should not atomize into small droplets and will result in a very narrow spray band striking the water with negligible herder drift (Buist and Belore 2011).

The required application flow rates for the range of application speeds that would likely be used for the boat and helicopter application modes are summarized in Table 7. The SSC 0002 nozzle appears to be a reasonable choice based on flow rate and likely drop size characteristics. Multiple nozzles (five to ten) would be required for the helicopter spray system but a single nozzle would be adequate for the boat application system at 2 knots.

Table 7. Application Speeds and Nozzle Requirements versus Spray Speed

Spray Speed [knots] (m/s)	Required Flow [gpm] (L/s)	# of 0002a nozzles @60 psi
	Boat Application	
[2] (1.0)	[0.24] (0.015)	1.0
[5] (2.6)	[0.61] (0.039)	2.5
	Helicopter Application	
[10] (5.1)	[1.2] (0.077)	4.9
[20] (10.2)	[2.4] (0.154)	9.8

[a]The first two digits of the nozzle identifier refer to the fan angle (00 or 0° in this case). The remaining digits refer to the flow rate of the nozzle in tenths of gpm when operated with water at 40 psi (0002 refers to 0.2 gpm of water at 40 psi).

Experiments conducted at the SL Ross lab, simulating spraying from a helicopter and a small boat confirmed that the SSC 0002 straight stream nozzle was suitable for herder application (Buist and Belore, 2011). A commercial backpack sprayer (Figure 37) was deemed to be appropriate for small boat application in temperate conditions: heating and insulation of the backpack sprayer will be required for Arctic use.

Figure 37. Commercial backpack sprayer recommended for small-boat application system.

13.1 Helicopter Herder Application System Initial Testing

The DESMI AFTI herder application system (Figure 38) has been designed to transport and apply either OP-40 or ThickSlick 6535 from the open rear door of a commercial helicopter. The storage tank is insulated and carries up to 20 gallons (75 L) of herder. Its features include:

- 28 V electrical system using aircraft quality components
- Two modules which are easily handled by two or 3 persons
- Aluminum frames with the reel module having an extendible reel
- 100 feet (30 m) of insulated Stratoflex stainless steel hose with Teflon liner

- Powered reel
- Air powered pump and air compressor for purging of lines
- Self-contained 28 V battery plus 28 V accessory cord for attachment to aircraft power
- Complete electrical circuit protection with integral circuit breakers
- Multiple nozzles (up to seven) to adjust flow rate

Figure 38. Mark I Helicopter Herder Application system

An initial series of tests involved deploying the full length of the 100-foot hose on the ground, operating the pump with water and measuring the flowrates through the nozzles. Figure 39 shows the nozzle body with seven SSC 0002 nozzles spraying water. Proper operation of the air purge system, storage reel and other components was also confirmed.

Figure 39. Applicator spray nozzle configuration.

The second series of tests involved lifting the Mark I Helicopter Herder Application system and an operator to a height of 46 feet (14 m) using a person lift (Figure 40). These tests involved operating the pump with tap water and recording the spray pattern generated by the nozzles. The winds at this time had increased to 21 mph (34 km/h), gusting to 29 mph (47 km/h), which is the upper limit for safe operation of the person lift. The third series of tests involved a short test from a 15-foot (5 m) height (due to the gusty winds) of the application system spraying a surrogate fluid.

Figure 40. Applicator raised 46 feet above ground

Canola oil (with a viscosity of ≈ 70 mPas at 20°C) was determined to be a good substitute for the OP 40 herder at colder temperatures. This test involved operating the pump with the surrogate fluid drawn directly from a small drum and recording the spray pattern generated by the nozzles on Kromecoat cards. In order to minimize the spray of Canola onto the surrounding area, all but one of the nozzles was wrapped in a garbage bag placed in a bucket suspended from the nozzle body. The flow from the one uncovered nozzle was directed into an inflatable plastic swimming pool.

As can be seen from Figure 41, the flow from the one nozzle (on the order of 0.4 L/min, or 0.12 gpm) began to break up into droplets within a foot or two of the nozzle. Comparison of Kromecoat cards passed through the Canola spray and from laboratory tests in 2010 spraying ThickSlick 6535 in a 20-knot crosswind revealed roughly similar drop sizes.

Figure 41. Flow of Canola oil from single nozzle.

CHAPTER 14. SUMMARY

A multi-year project, from 2003 until the present, undertaken by SL Ross Environmental Research evaluated the concept of enhancing *in situ* burning using chemical herders in light to medium ice concentrations. Experiments included small-scale pan tests, medium- and large-scale basin tests, and field trials.

Two experimental burns of free-drifting oil slicks in drift ice were successfully completed in the Barents Sea. The first experiment involved 102 L of fresh crude released into a monolayer of USN herding agent that had just been placed on the water where approximately 80% of the oil was consumed in the ensuing burns. The second experiment involving the release of 630 L of fresh crude onto water in a large lead. A9-minute long burn ensued that consumed an estimated 90% of the oil.

Small-scale experiments were carried out comparing the efficacy of herding agents formulated with silicone-based surfactants, formulated with fluorosurfactants, and the USN herder. The fluorosurfactant-based herders did not perform considerably better than the USN herder. In static tests, a silicone-surfactant based herder initially produced considerably higher herded slick thicknesses but declined back to the thickness of the USN herder over the one-hour test period. Subsequent mid-scale experiments at CRREL showed that a silicone-based surfactant, A-108, proved to be the best silicone based herder of the three tested. It considerably outperformed the USN herder in most tests with similar conditions.

The cold-weather results indicated that the best way to improve the handling of the USN herder is to increase the amount of 2-ethyl 1-butanol solvent. The increase in the amount of solvent does not appear to decrease the effectiveness of the active ingredient.

In 2011 a research program was carried out to explore the use of herding agents for in situ burning in open water conditions as a rapid-response technique for oil spills offshore. The research was conducted in two parts: the first involved laboratory testing to identify the best herding agent(s) for warmer water conditions; the second involved experiments at Ohmsett to quantify the persistence of the herder monolayer in waves.

DESMI-AFTI worked in conjunction with S.L. Ross Environmental Research to get approval to use herders in North American waters. The proscribed test data from an accredited laboratory in Louisiana on three candidate herding agents (also called surface collecting agents) was submitted to the U.S. EPA for approval to list them on the National Contingency Plan (NCP) Product Schedule. Two herders have been placed on the list and are now commercially available. These two can be used, with the FOSC's concurrence, for spill response operations in U.S. waters. Samples of all three herders have been sent to Environment Canada, along with all the EPA test data, for their consideration. Quantities (200 L) of the two herders listed on the NCP Product Schedule have been produced and are stockpiled at DESMI-AFTI in Buffalo, NY. At present, there are no other jurisdictions that have approved herders for use in their waters. Canada is expected to introduce regulations to approve the use of spill-treating agents offshore, including herders, in the very near future.

An application system, consisting of a pump, controls and reservoir has been designed to be placed inside an appropriate helicopter. It incorporates a reel-able hose that is used to lower the application nozzle to the correct height above the water for herder application. Dry land, static trials were conducted in September 2013 and helicopter flight trials are planned for 2015. A back-pack sprayer system for herder application from a small vessel is available off-the-shelf, with only minor modifications required for cold-temperature use.

14.1 FINDINGS:

- Small-scale pan tests found that the best hydrocarbon-based herder formulation for cold conditions was one developed in the early 1970s by the U.S. Navy (65% Span-20 and 35% 2-ethyl 1-butanol).
- Medium- to large-scale basin tests found that the USN cold-water herder considerably contracted fluid crude and refined oil slicks on cold open water, in brash ice and in slush ice concentrations of up to 70% ice coverage.
- Slick thicknesses in excess of 3 mm, the minimum required for ignition of weathered oil *in situ*, were routinely achieved.
- Results show that the monolayer of the most effective herders will survive for more than 45 minutes in a calm sea. The presence of breaking or cresting waves rapidly disrupts the herder monolayer and the oil slick resulting in the production of many small slicklets from the herded slick and the re-spreading of the oil to thin slicks. The monolayer survives for considerable periods of time in a swell condition, but the constant stretching and contracting of the herded slick results in elongating the oil slick and slowly breaking the slick into smaller segments.
- Burn tests showed that otherwise unignitable crude oil slicks that were contracted by the USN herder could be ignited and burned in situ in both brash and slush ice conditions at air temperatures as low as –17°C. Measured oil removal efficiencies for herded slicks averaged 50% for 7.5-L slicks and 70% for 15-L slicks. The efficiencies measured for the herded slicks were only slightly less than the theoretical maximums achievable for equivalent-sized, physically contained slicks on open water. The type of ice (brash or slush) did not considerably affect the burn efficiency.
- Generally, it was not possible to reignite re-herded residue. Steeper, cresting waves detracted from the burn efficiency while longer, non-breaking waves did not. The oil removal rate for the slicks was in the range expected for equivalent-sized, physically contained slicks on open water.
- Limitations to the chemical herder were found in two test conditions and for sheens. The herder effectively contracted sheens into small areas but did not thicken them enough to burn. The presence of new ice crystals (frazil ice) that rapidly formed on the water surface in very cold air temperatures restricted the effectiveness of the herder. This limitation may not be significant because it was observed that the frazil ice kept slicks from spreading on their own. Short, choppy waves caused a herded slick to break up into small patches that may limit propagation of a flame, although this may be an artefact of the relatively small volumes of oil used in the experiments. Longer, non-breaking waves, simulating a swell in pack ice, did not appear to cause a herded slick to break up, and in fact may have assisted the process by promoting spreading of the herder over water to the slick's edge.
- The use of herders in drift ice conditions could potentially improve the Oil Recovery Rate and Oil Recovery Efficiency performance of weir skimmers by factors of 2 to 10; however, the oil thicknesses produced by the herder were too low to permit maximal performance of the weir skimmer. No significant improvement was measured in the performance of a disc skimmer in herded slicks compared to unherded slicks.
- In terms of using herders to clear oil from salt marshes, the herder did not clear the oil completely from the marsh plants in any of the tests. In some tests the herder caused the oil slicks to contract in size sufficiently to considerably reduce the oiled area of the marsh; however, even in these cases, there remained a ring of oil at the waterline around the originally oiled stalks of the marsh plants. In all cases, after herder had been added, the

slick thickness was great enough to support ignition. This is a significant finding, since even though the herder did not clear the oil out of the marsh plants; it could contract the oil sufficiently to allow in situ burning.

- For the case of using herders to improve operational efficiency of chemical dispersant application offshore:
  - The use of herders on an oil slick did not detract from the effectiveness of chemical dispersant application.
  - Using herders to contract slicks on open water can improve the operational efficiency of dispersants applied by vessels. This may help with dispersant operations in ice where the additional mixing energy of propeller wash is needed, and in remote Arctic areas lacking large airport facilities to support aerial dispersant operations.
  - Herding a slick to be sprayed with dispersants from aircraft could reduce operational efficiency by making the slick much smaller than the swath width of the dispersant sprayed from the plane, thus wasting large amounts of the dispersant. This may not be an issue for larger, thicker slicks at sea.
- Preliminary biodegradation tests indicate that ThickSlick 6535 will biodegrade rapidly. OP-40 will biodegrade more slowly.

14.2 CONCLUSIONS

The findings of this research indicate that oil spill responders should consider utilizing herders as a method of enhancing *in situ* burning in light to medium ice concentrations and in salt marshes, where spilled oil can rapidly spread and use of fire containment booms is impractical. Further, research has shown that herders can be a tool for open water ISB given the appropriate conditions. As with most oil spill response techniques, a rapid response will improve the chances of success when using herders for *in* situ burning

Specifically: -

1. Herding agents work best on relatively fresh crude oil and light distilled product slicks that are still of relatively low viscosity and remain ignitable.
2. Slicks that have gelled or significantly emulsified and viscous residual fuel oil slicks would not be good candidates for herder use.
3. The use of herders can improve weir skimmer efficiencies in drift ice conditions, but not to the point where these devices operate at maximum capacity.
4. Herding agents may also offer a way to improve the operational efficiency of chemical dispersant application from ships.
5. When considering the ignition of herded slicks in drift ice the usual visibility/VFR, daylight and slick ignition limitations (wind ≤10 m/s; water content ≈< 25%) on ISB operations would apply (SL Ross 2011).
   i. The persistence of the herder monolayer on the water surface is also a consideration: breaking waves will dissipate the herder monolayer in minutes allowing the slick to respread.
   ii. Although there is little information on the occurrence of breaking wind-generated waves in drift ice, the open water criteria is that waves begin to break fairly frequently at wind speeds of 3.6 to 5 m/s (Beaufort Force 4).
   iii. The effect of drift ice on wave growth and breaking is also a consideration. Oil released from the ice edge on the lee side of a large lead was successfully ignited and burned in

a 4.4 m/s wind, measured with a hand-held anemometer at ice level (Buist et al. 2010b).

iv. There is insufficient data at present to draw conclusions as to the upper wind limits for effective herding of oil slicks in various drift ice concentrations.

v. It seems reasonable that in low drift ice concentrations (1/10th) there will be little change from the general rule for the onset of breaking waves in open water. In higher concentrations, there will likely be a significant wave dampening effect of the ice and thus higher wind speed limits, (up to the ignition limit of 10 m/s) for the successful application of herders for ISB.

14.3 NEXT STEPS:

The next steps for herder research for Arctic ISB include:

- Determining the window-of-opportunity for herder effectiveness as a function of oil weathering (evaporation, emulsification, increasing pour point, etc.) and environmental conditions (temperature, slush ice and waves) in laboratory and test tank experiments;
- Field trials involving the use of helicopters to apply both herders and igniters in order to establish the feasibility of aerial application;
- Studying the likely fate of herders applied in Arctic waters; and,
- Evaluating the potential environmental impacts of herder use in Arctic conditions.

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