# Final Report

Determining the Operability Limits of Chemical Herders

Richard Byrne, Paul D. Panetta, Hualong Du, and Alexandria Podolski
Applied Research Associates, Inc.

Report For

U.S. Department of the Interior
Bureau of Safety and Environmental Enforcement (BSEE)
Sterling, VA

March 2018

*This study was funded by the Bureau of Safety and Environmental Enforcement (BSEE), U.S. Department of the Interior, Washington, D.C., under Contract Number E16PX00022.*

## ACKNOWLEDGMENTS

We wish to thank Lauren Ferris, Professor Donglai Gong, and John Oldfield from The College of William & Mary, Virginia Institute of Marine Science for assistance setting up the experiment and Kevin Panetta for setting up the experiment and the viscosity measurements

## DISCLAIMER

The contents of this report do not necessarily reflect the views and policies of the Bureau of Safety and Environmental Enforcement (BSEE), nor does mention of the trade names or commercial products constitute endorsement or recommendation for use.

## Table of Contents

# EXECUTIVE SUMMARY

The purpose of the work is to study the commercially available herders, ThickSlick 6535 and Siltech OP40, for several crude oils to establish a baseline understanding of how the properties of the oil influence herder effectiveness over a range of temperatures found in seawater.

The proposed ASTM 1m$^2$ tray Herding Agent Effectiveness Test was adapted to carry out a large scale herder-oil test matrix. The test was instrumented with high resolution video based oil slick area monitoring and continuous acoustic based slick thickness measurement capability. Experimental iterations were used to optimize the procedure for repeatability within tests using the same herder–oil–temperature combination. The resultant test apparatus was used to evaluate a 14 oils, the two herders, OP-40 and ThickSlick at the nominal 5°C and 20°C temperatures using triplicate repetitions for the combinations tested. The oils used were analyzed for density, Saturates, Asphaltenes, Resins and Aromatics (SARA), sulfur content and viscosity. Data was reduced and compiled in tabular and plot formats. Video and raw thickness data were saved in a structured format for further evaluation. The continuous sampling and relatively high temporal resolution of the area and direct slick thickness measurement enabled both localization of maxima and minima and visual confirmation of the measurement error with high confidence.

Herder effectiveness criteria included maximum thickness, overall time integration of thickness, and thickness 60 minutes after herder application. Comparison plots of the effectiveness metrics vs. oil properties were used to confirm a strong dependence on viscosity and differences between the herder types. The ability to hold the oil at thickness over time had a strong negative correlation with temperature for OP-40 and little effect on ThickSlick even after viscosity effects were eliminated.

In addition the slick thickness and temperature corrected crude density were used to compute spreading force for the oil using a similar formulation as Fay [8], Garrett [9], Langmuir [10] and Buist et al. [11]. This quantity was then recast as a static containment force by reversing the sign. Comparisons between the containment force and the oil properties were examined to find a high correlation with the percent Aspaltenes in the crude and a loss of containment force over time for OP-40 proportional to temperature.

The multiple test point averaged time versus slick area and time versus slick thickness plots are included in Appendix A for every tested point.

# 1. OVERVIEW AND OBJECTIVE

Chemical herders are used to contract surface oil into smaller, thicker slicks by changing the balance of interfacial forces acting on the edge of the oil. By decreasing the surface tension between the oil and the water, the oil will contract into a thicker slick over a smaller area so that it can be more effectively cleaned up, especially for burning or skimming operations. Herders are applied along the perimeter of the slick and form a thin monolayer on the surface of the water from which the oil quickly retracts due to smaller external forces acting on the oil allowing the intermolecular attraction in the oil to draw it together. Because the intermolecular forces are unique to the oil composition the effectiveness of a herder is highly dependent on the oil present.

There is a strong relationship between the thickness the oil will reach under the influence of herders and the viscosity of the oil. There is also influence of other properties, such SARA (Saturates, Aromatics, Resins, and Asphaltenes) component makeup the sulfur content, and temperature on the efficacy of herders.

The purpose of the work is to study the commercially available herders, ThickSlick 6535 and Siltech OP40, for several crude oils with varying properties in a repeatable way to establish a baseline understanding of how oil properties and the influence of temperature affects herder effectiveness. This goal was accomplished through development of a lab experiment based on previously used methodologies that reduce the mixing effects found in nature to isolate the oil herder interaction and using a large oil-herder test matrix. The ultimate goal was to gain a scientific understanding of the operational characteristics of herders which can be used to inform decisions in response situations.

Over the years there have been many experiments to measure the efficacy of herders in various conditions including labs, the Army Cold Region Research and Engineering Laboratory (CRREL), Ohmsett, and in the open water [11]. They have shown varying degrees of effectiveness using a coarse estimate of the thickness based on a measurement of the area, knowledge of the density and volume of the oil assuming conservation of volume. While informative, that process can produce errors of ~10% in the thickness of the slick and can miss the time when the maximum thickness occurs and the dynamic changes in the thickness over time and thus the crucial information to gauge the effectiveness of herders [5].

This work is based on the proposed ASTM, 1 meter square tray test standard [5] with the addition of multiple controls, additional monitoring and higher temporal data acquisition. The test is essentially releasing a small amount of oil on the surface of a few inches of saltwater, allowing the oil to spread and then adding herder. The contraction of the oil and the amount of time the oil is held are of note. In addition to the one meter tray, the quantity of herder applied, the one hour duration of the test and the precautions used to insure uncontaminated sea water are all adopted directly from the ASTM procedure. The primary change in this experiment is the use of continuous measurement of the surface area of the slick using image analysis of high resolution video and direct and continuous measurement of the thickness of the slick using acoustic techniques. The change is significant because it boosts the sampling rate from a few times an hour to thousands of times an hours and adds direct thickness measurement instead of inferring thickness from the coverage area. Other changes, mostly geared towards repeatability are described in the experimental procedure section.

The direct and continuous measurements of thickness and area multiple times a second allow identification of the precise time of the maximum oil thickness, the rate of oil retraction, and the rate at which the oil spreads out again as the herder loses its effectiveness among other metrics. These high resolution measurements also allow the calculation of the repeatability of the experiments to a high degree providing better ability to discern pattern from error.

After iterating on the experimental design for repeatability a significant oil-herder test matrix was carried out over a course of months using a range of oil crude oils in the light, medium and heavy categories. The two commercially available herders used were ThickSlick 6535 and Siltech OP-40. The experiments performed to date are shown in the Table 1 with the oils ordered by viscosity.

Table 1: List of oils, herders and temperatures. Each check mark represents at a minimum three repeated experiments using the same combination of herder-oil and temperature range. Grey checks had fewer repetitions as noted

| | Warm (Avg 20°C) | | Cold (Avg 4°C) | |
|---|---|---|---|---|
| **Oil** | OP-40 | ThickSlick | OP-40 | ThickSlick |
| Agbami | ✓ | ✓ | ✓(2) | ✓(1) |
| Hibernia | ✓ | ✓ | | |
| Anadarko | ✓ | ✓ | ✓ | |
| ANS | ✓ | ✓ | ✓ | |
| Ewing Bank | ✓ | ✓ | ✓ | |
| Endicott | ✓ | ✓ | ✓ | |
| Alpine | ✓ | ✓ | ✓ | |
| IFO 120 | ✓ | ✓ | ✓ | |
| Doba Chad | ✓ | ✓ | | |
| Rock | ✓ | ✓ | ✓ | |
| Platform Gina H14 | ✓ | ✓ | | |
| Platform Gina (fresh) | ✓ | ✓ | | |
| Harmony | ✓ | ✓ | | |
| Canadian Sour | ✓ | ✓ | | |

The high temporal rate of data acquisition allowed for the accurate, precise, and objective evaluation of the herder effectiveness using several metrics including the increase from the minimum thickness just before the herder was applied to the maximum thickness after the herder was applied, the time to reach maximum thickness, and rate of change in the thickness (decrease in thickness) as the herder effect wears off. The area of oil on water measurement also has several similar metrics such as the minimum area after the oil contracts due to herder application and the rate of change of the area (increase in area) as the herder effect wears off. Details of these and other metrics will be described in subsequent sections.

# 2. MEASUREMENT METHODOLOGY

## 2.1. PURPOSE

The purpose of this study was to systematically test the function of herders across several oil types, and draw relationships between herder function, and the physical and chemical properties of the oil treated. The experiment was designed to measure the degree and time profile of the oil contraction in a repeatable way. The experiment did not have the same mixing nor scale as an in-situ application but was focused on measuring small differences between the ways different herders and oils respond in order to establish baseline research data. The measurement methodology was designed to delineate the ideal behavior for oil herder interaction which will potentially provide information about herder efficacy in operational environments. The methodologies developed can be expanded to consider weathering, wind, and waves to better predict efficacy in operational environments.

## 2.2. Apparatus

The herder experimental apparatus, shown in Figure 1, consisted of an enclosed, ventilated space with removable Plexiglas panels for easy access. Each panel had a small hole through which a tube attached to an air compressor with a low velocity air flow could be used to direct the location of an oil slick to keep it from contacting the walls of the tray. The enclosure housed a 1 meter x 1 meter tray which held approximately 1 inch of water during the experiment. The position of these 8 syringes along with the syringe pump used to dispense the herder are shown in Figure 2. Before water was added to the tray, it was covered with a plastic liner to prevent contamination between experiments. After synthetic seawater was added to the tray, a circular containment ring made of plastic was lowered into the water and filled with oil as shown in Figure 3. The ring was lifted allowing the oil to expand and form a slick on the surface of the water. Before the slick could contact the side of the tray, 160 μL of herder was dispensed onto the surface of the water via 8 syringes by a syringe pump. Figure 3 also shows the contracted slick after the application of the herder.

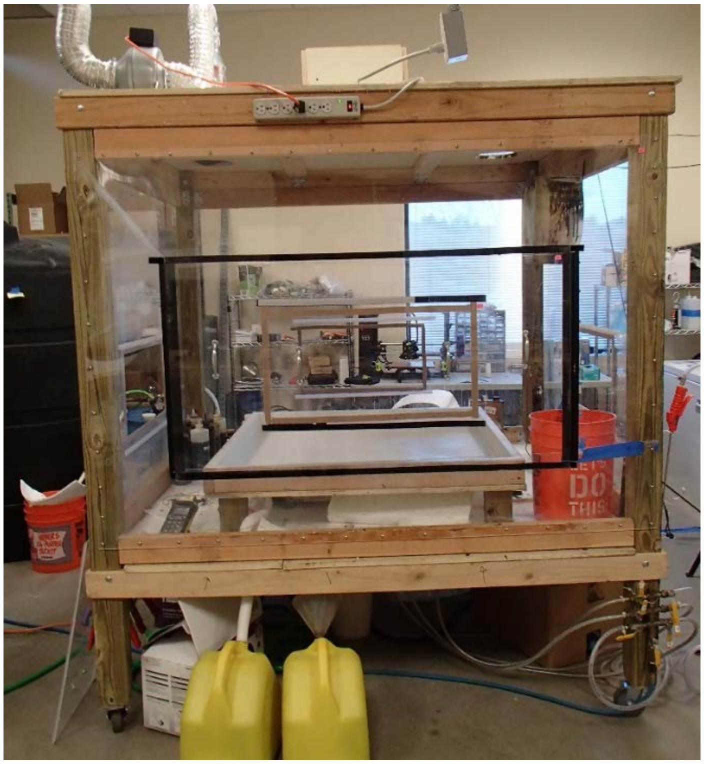



Figure 1: The herder test apparatus

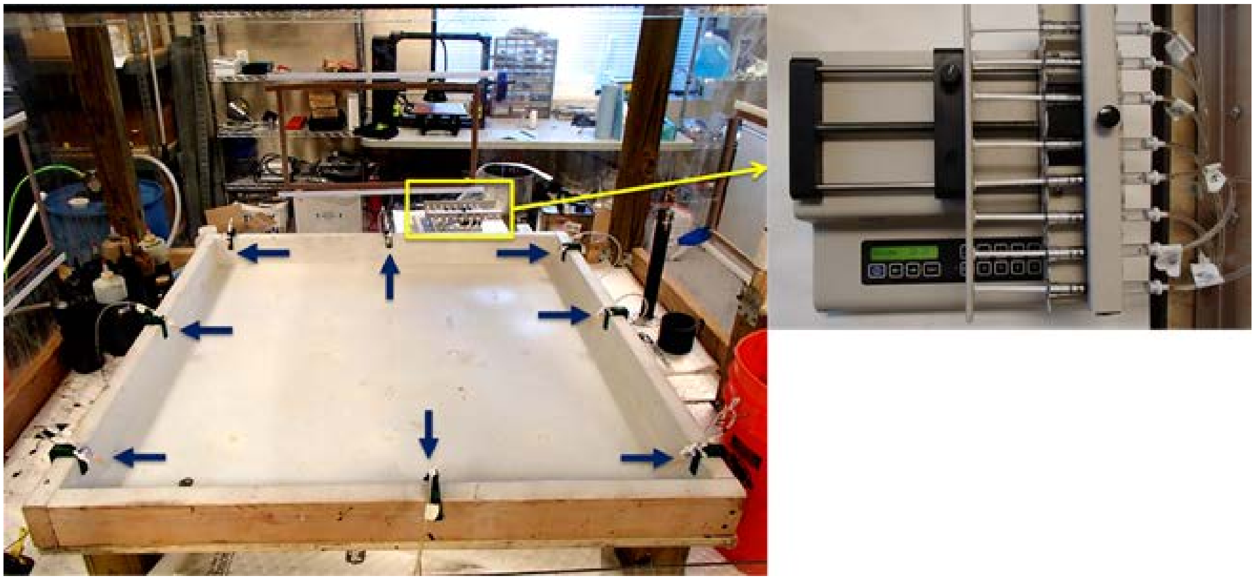


Figure 2: Herder needle placement shown left. Needles show locations of herder nozzles. Syringe pump shown right.

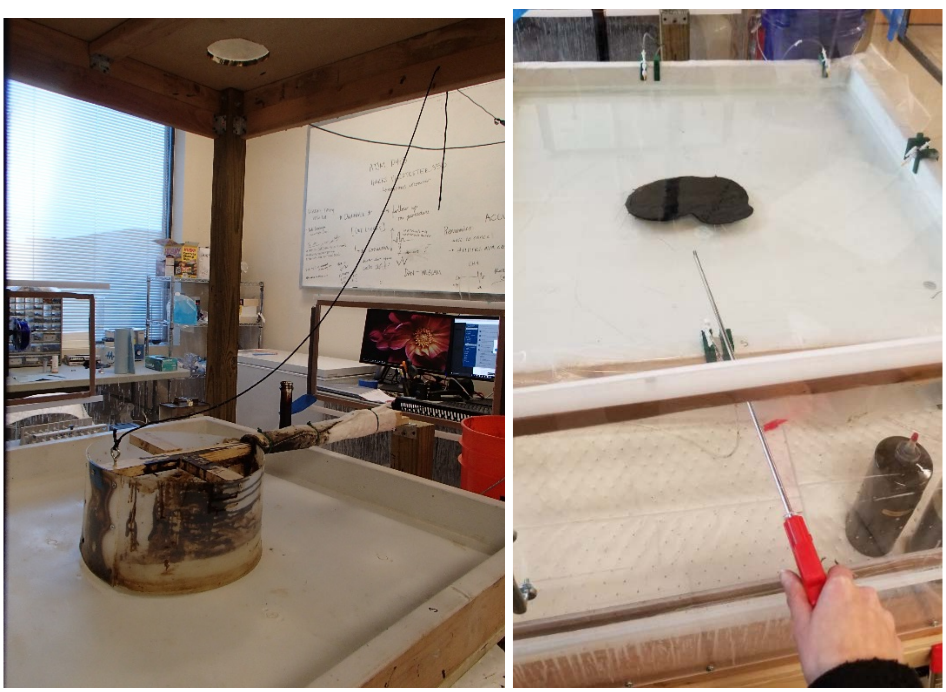
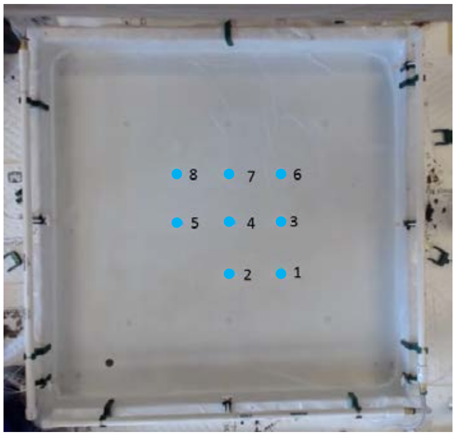


Figure 3: oil containment ring left, tube with low volume air flow right

After the initial contraction, the slick thickness and area data were collected using and ultrasound transducers and video respectively for 60 minutes during which the pressurized air was used to direct the slick away from the wall of the tray and over the transducers, the position of which are shown in Figure 4. The proposed ASTM standard used 1 Liter of oil for the experiment. Initially an attempt was made to follow this proposed standard, however, often the slick contacted the wall of the tray and became distorted, decreasing experimental repeatability. These runs were ultimately discarded and the procedure adjusted to use less oil. For this study the oil volume was decreased to a 230 ml target amount, as this volume resulted in a smaller, more controllable slick. Some experiments resulted with a small percentage of oil on the wall, however, the experiments with less than 5% were generally kept.




• Transducer

Figure 4: Acoustic transducer positions

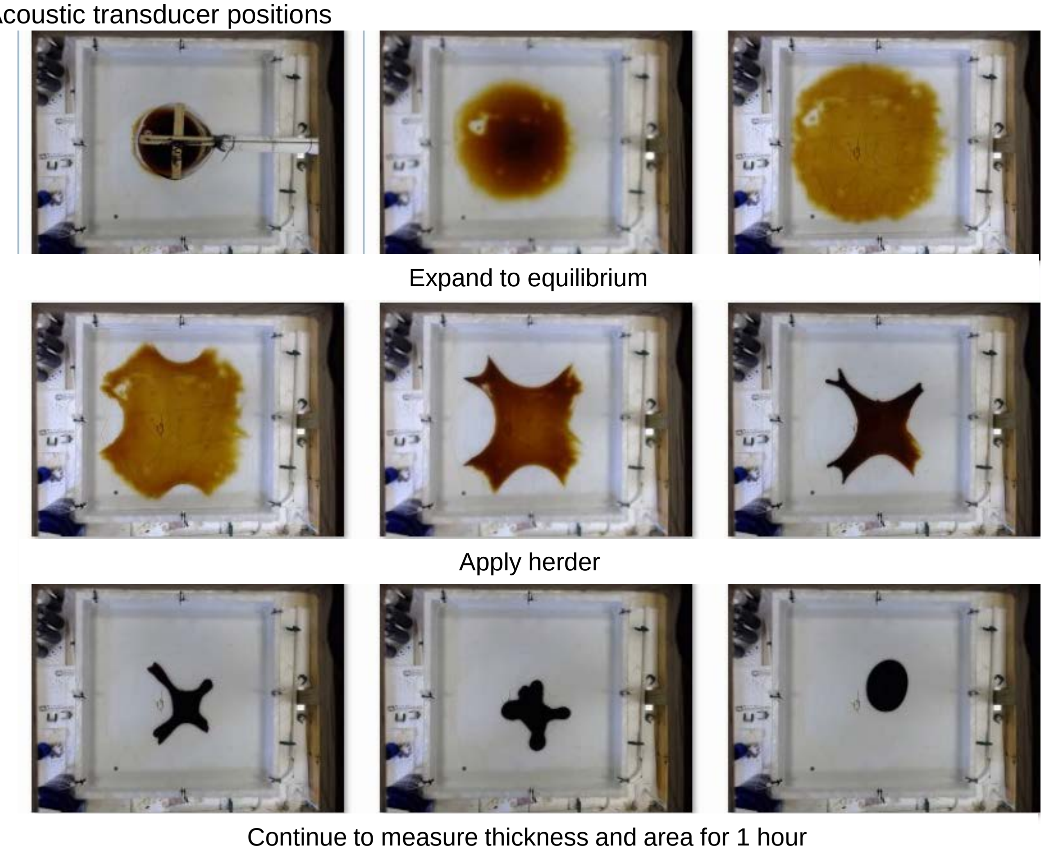



Figure 5: Progression of the experiment from top down view of the oil slick.

The overall progression of the experiment is shown in Figure 5 reading left to right, top to bottom. The top row shows the expanding oil after the containment ring is lifted, a two to three second time span. The middle row shows the contraction of the oil after herder is applied which also happens in a few seconds and the bottom row, happening over the course of minutes, shows the oil gradually forming a circle.

At the end of the experiment, the oil was removed from the top of the water and the plastic liner was perforated just above a drainage hole located in the corner of the tray. The hole led to a 5 gallon waste storage container where waste water was collected before being transferred to a larger storage tank.

There was some variability in temperature which was measured during the experiment. The water temperature during the warm experiments was typically between 18°C and 24°C. The cold temperature tests followed the same procedure as the warm tests, however both the water and oil were chilled prior to the experiment to 5°C ±3°C. Additionally, ice packs were used to line the bottom of the tray under the plastic liner as seen in Figure 6. The temperature was measured multiple times during the cold test and remained constant with ±3°C. Because the temperature as not held constant during the tests, the oil viscosity and density lab characterizations made at at 5°C and 20°C were adjusted to the actual test temperatures using two points on ASTM viscosity interpolation/extrapolation tables D341-17 [13] and interpolation for density based on ASTM D1250-08 [14].

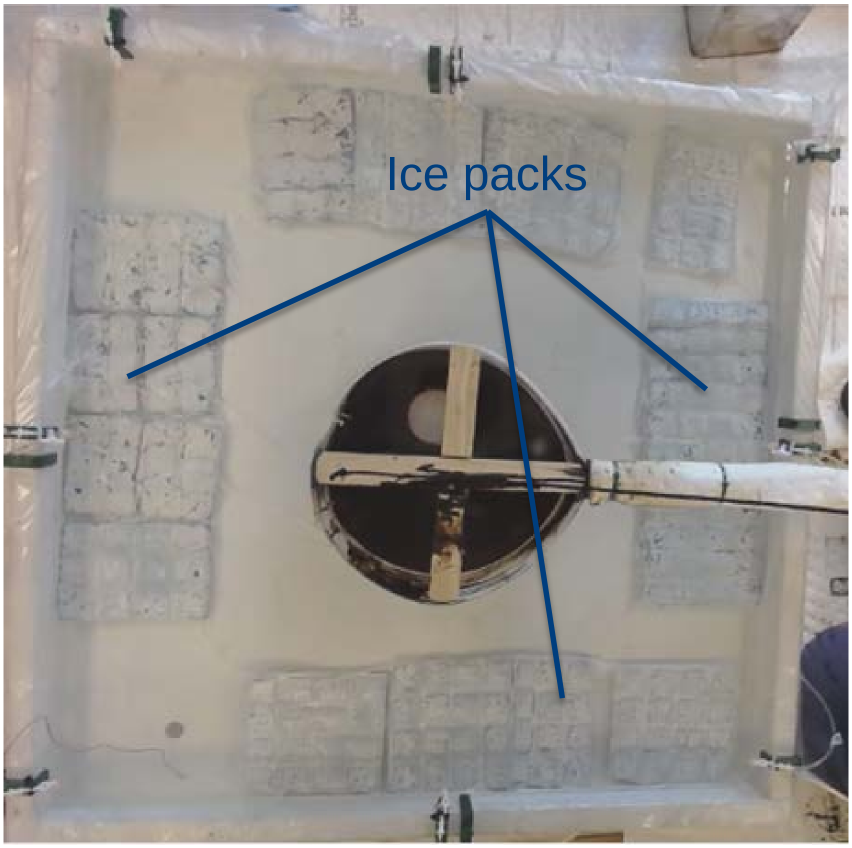



Figure 6. Configuration of test apparatus for cold temperature measurements.

## 2.3. AREA MEASUREMENT

The area was determined by using an overhead camera which takes images of the entire tray. The camera takes 30 frames per second (fps) in the first 100 seconds and then trails down to 5 fps for the remainder of the experiment yielding video files that are roughly 30 Mb. The video was analyzed using a custom algorithm that squares off and rectifies the 1 meter x 1 meter surface of the water to an exact 480 pixel x 480 pixel image. The program dynamically determines the threshold for oil to an intensity value just between the dark oil and the light background and colors all pixels dark below the threshold and light above.

The resultant image shown on the left in Figure 8 is displayed to make sure the oil is properly represented and the threshold converts oil to black and background to white. The largest error is when the expanding oil had faster spreading sheen of much lighter intensity. The algorithm interpolated somewhere in the middle of the sheen. The sheen quickly disappeared however once herder were applied.

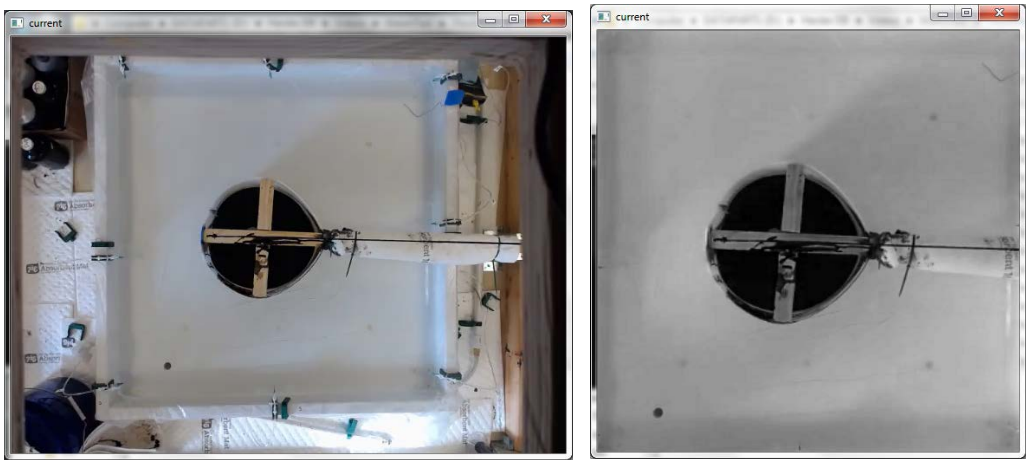


Figure 7: Original video on left and water surface transformed to 480 x 480 pixels

The dark pixels were counted for each frame and using the conversion between 480 pixels x 480 pixels and 1 meter x 1 meter area the oil area is determined.

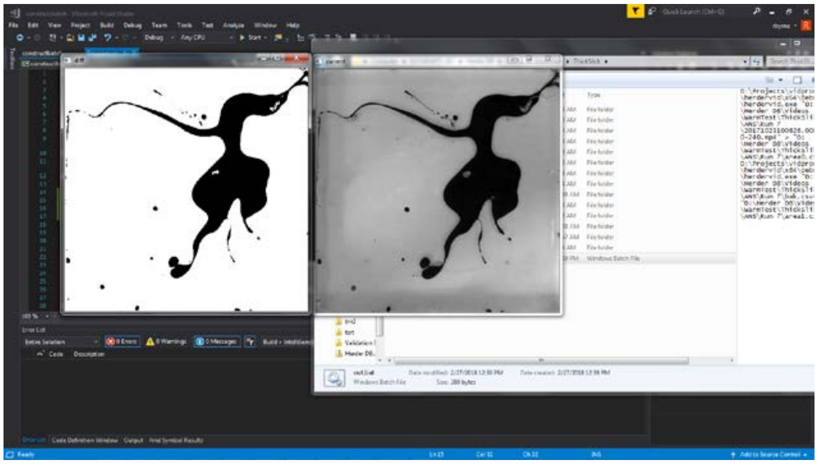


Figure 8: Area extraction program with actual oil (right) and pixels used for counting (left)

## 2.4. Acoustic Thickness Measurement

The thickness of the slick was determined by measuring the transit time of an acoustic wave through the slick and back to the acoustic transducer. Acoustic data from Harmony at warm temperature is shown in Figure 9 after OP-40 was added. The left figure is an acoustic "sonar" like image showing the reflections from the bottom and top of the slick between 100 seconds and 120 seconds after the herder was added. The right figure shows the amplitude of a single acoustic "ping" 120 seconds after the herder was added.

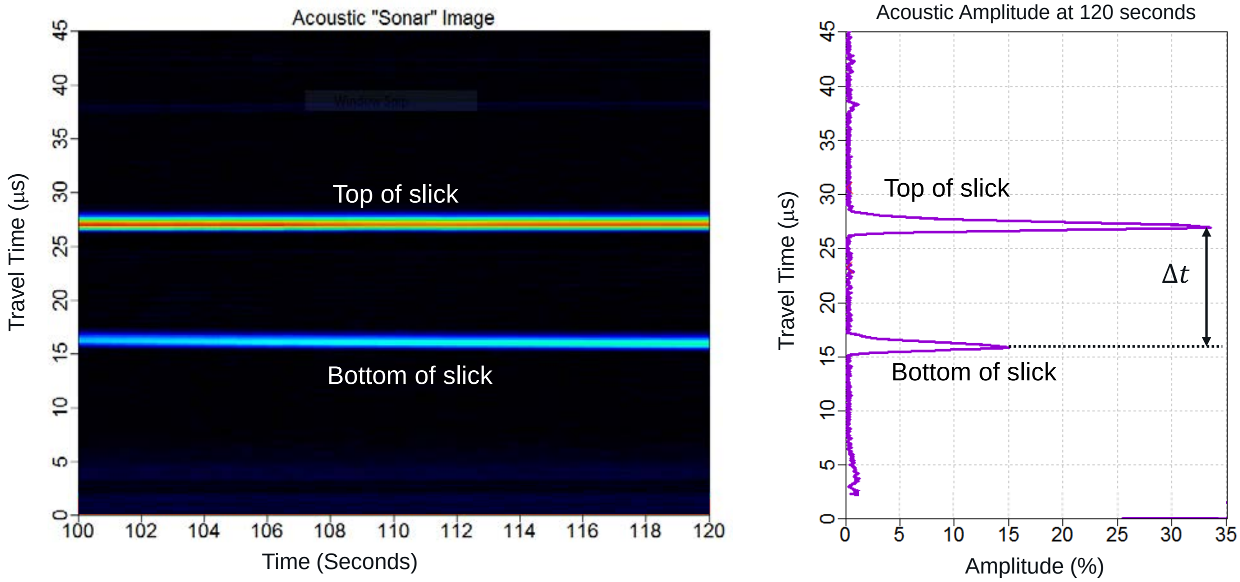



Figure 9.  Harmony at warm temperature

The thickness is calculated from the equation below by multiplying the thickness by half the difference in travel time between the bottom and top of the slick. In this case the slick was 8.2 mm thick 120 seconds after the herder was applied. Acoustic data was collected every 0.2 seconds during the first 2 minutes to capture the dynamics of the interaction of the herder with the oil and every 2 seconds for the remainder of the test.

$$Thickness = \frac{v \cdot \Delta t}{2}$$

Where,

$$v = speed\ of\ sound$$
$$\Delta t = travel\ time\ between\ echoes$$

## 3. HERDER EFFECTIVENESS METRICS

The simultaneous measurement of area and thickness at a continuous high data rate provided an opportunity to extract numerous parameters related to the dynamic interactions of the oil with the herders. The high fidelity and time density of the measurements created the capability to determine the effectiveness of herders that did not exist prior to this work. Using these data we were able to extract the following parameters which are part of the database:

- Minimum thickness prior to herder application and Maximum area prior to herder application
    - Although the thickness and area were recorded at all times the maximum thickness and minimum area, consistently occurred at the same time and were mostly constrained by the tray size in this experiment. These two parameters indicate how much spreading of the oil was allowed before the herder was applied.
- Maximum thickness achieved after herder application and Minimum area achieved after herder application
    - As a rule both the maximum thickness and minimum area occurred at the same time in the experiment indicating the point of maximum herder influence when the oil is most confined and the slick thickest. The more important of the two for operational relevance is the maximum thickness.
- Thickness range and area range: The difference between the minimum thickness and the maximum thickness and the difference between the maximum area and minimum area before and after herder application.
    - The ability to find the maximum or minimum thickness or area was only possible because of the high acquisition rate of the data.
- Transition time to maximum thickness and minimum area
    - As both herders act fairly quickly the distinctly different rates were enumerated using this metric. The transition time is slower for large scale in-situ use and it is yet to be seen how the time in the laboratory translates to open water.
- The thickness achieved at any given time and specifically at 15, 30, and 60 minutes after the application of the herder
    - In isolation these parameters can advise whether the oil under the influence of the herder (in calm conditions) is thick enough to be ignited or skimmed.
    - When compared to the initial or maximum thickness these parameters could be used as a measure of the effectiveness of the herder. Also, thickness parameters can be used to estimate the net interfacial force between herders and oil.
- Relaxation of thickness and area as measured by the decrease in the thickness and increase in area as a function of time
    - This metric is used to determine the rate at which the herder is losing its strength at any time. This metric is the slope of the thickness or area as a function of time over a 10 minute window to show the overall trend as opposed to a spot or localized slope.
- The area under the thickness vs. time curve

- This metric combines a measure of the ability of the herder to boost the thickness of the crude and the ability of the herder to hold that thickness over a significant time into a single metric as illustrated in Figure 10.

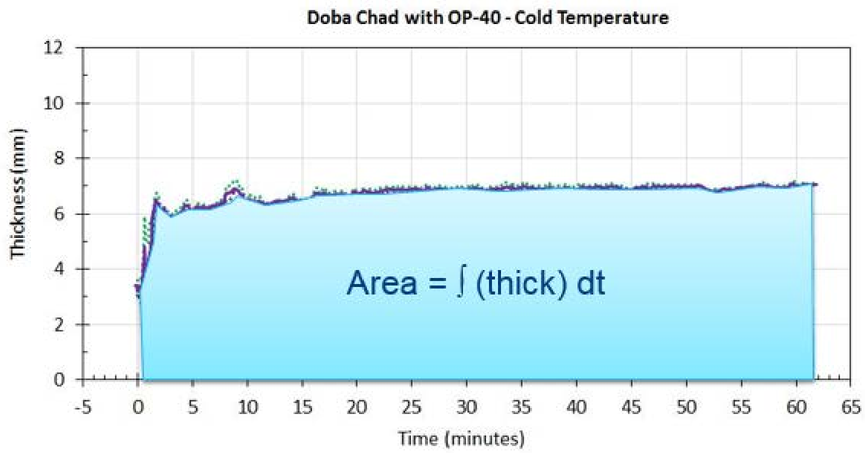



Figure 10. Area under thickness curve

## 4. VALIDATION OF MEASUREMENT METHOD

To determine the reproducibility of the measurement procedure and validate the process over a large viscosity range, multiple nominally identical tests were performed with Ewing Bank with viscosity 28.95 cP with the herder ThickSlick, and Endicott, which has a viscosity of 273 cP, with the herder OP-40 at warm temperatures. Based on the large size of the testing apparatus and access to ambient air conditions, the temperatures for these measurements were 16.5°C ±1.3°C for Ewing Bank and 28°C ±1°C for Endicott.

The thickness from measurements for Ewing Bank crude oil are shown in Figure 11. For these tests the herder was applied at time zero and data was collected for 62 minutes. The minimum thickness ranged between 1.1 mm to 1.3 mm before the herder was applied and achieved a maximum thickness ranging between 3.1 mm and 3.3 mm after the herder was applied. These values along with several other metrics are shown in Table 2. The area of the slick for four trials is are shown in Figure 12. The average of the maximum thickness and the range show a small standard error 1% and 3% respectively. In addition, the average thickness for all the runs plotted plus and minus the standard error shown in Figure 13 while the average slick area and standard error (dotted line) is shown in Figure 14.

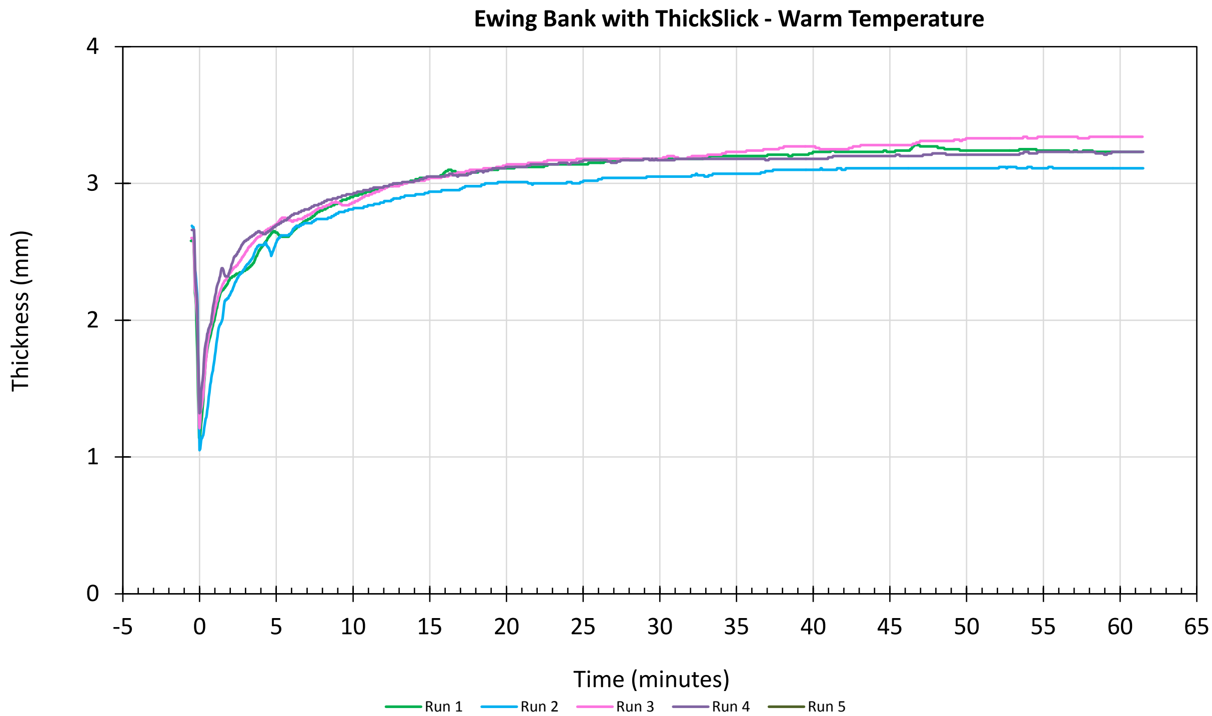



Figure 11. Thickness as a function of time for Ewing Bank with ThickSlick at warm temperatures for multiple runs.

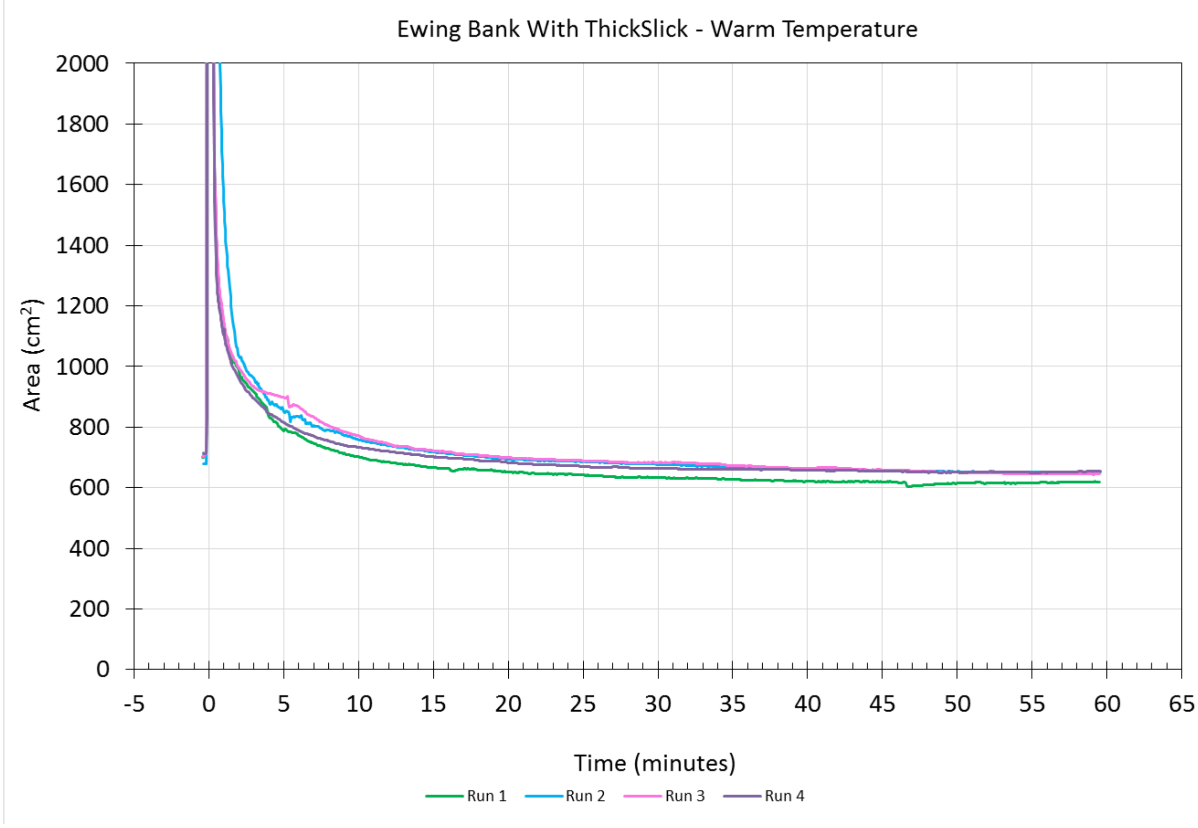



Figure 12: Area as a function of time for Ewing Bank with ThickSlick at warm temperatures for multiple runs.

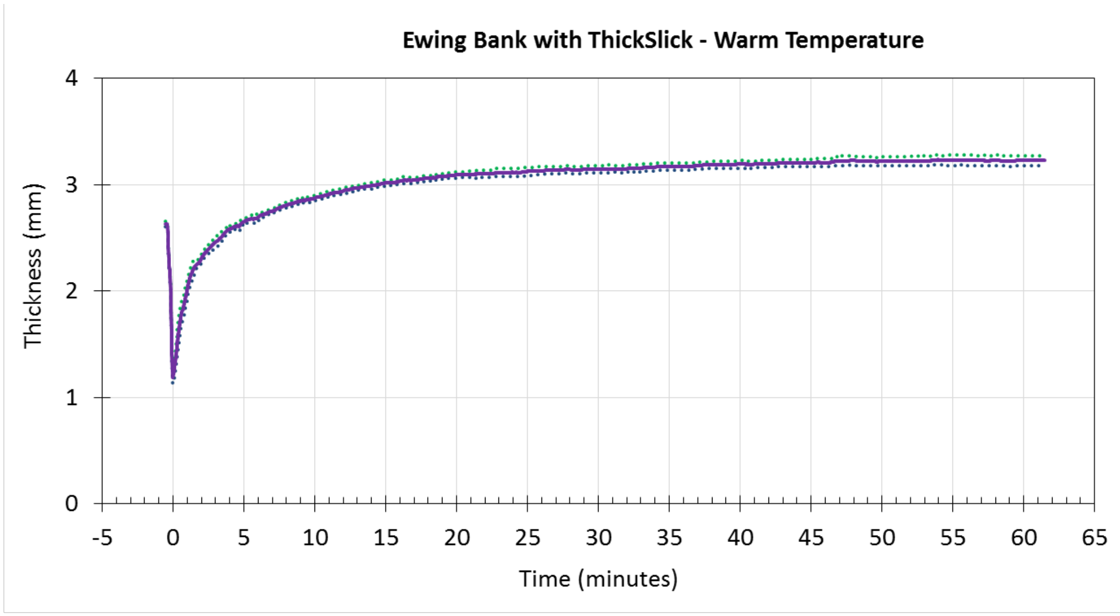



Figure 13: Average thickness with computed band for standard deviation

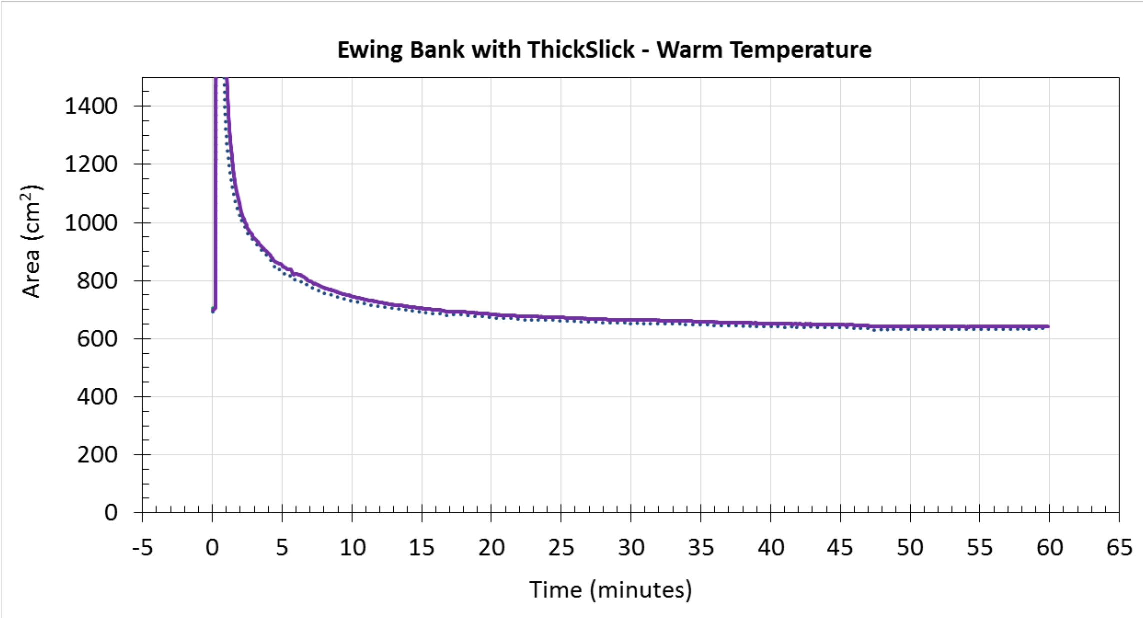


Figure 14: Average area with computed band for standard deviation

Table 2: Ewing Bank with ThickSlick Metrics for 4 runs

| **Run #** | **Maximum Thickness (mm)** | **Minimum Thickness (mm)** | **Range (mm)** | **Minimum Thickness Position (Seconds)** | **Max Thickness Position (Seconds)** | **Time Difference (Seconds)** | **Thickness (mm) 60 min after herder application** |
|---|---|---|---|---|---|---|---|
| 1 | 3.3 | 1.1 | 2.1 | 33 | 2835 | 2802 | 3.2 |
| 2 | 3.1 | 1.1 | 2.1 | 31 | 3207 | 3176 | 3.1 |
| 3 | 3.3 | 1.2 | 2.1 | 32 | 3356 | 3324 | 3.3 |
| 4 | 3.2 | 1.3 | 1.9 | 31 | 3366 | 3335 | 3.2 |
| 5 | | | | | | | |
| | | | | | | | |
| **Average** | 3.2 | 1.2 | 2.1 | 32 | 3191 | 3159 | 3.2 |
| **Stdev** | 0.09 | 0.11 | 0.11 | 1 | 248 | 249 | 0.09 |
| **Standard Error** | 0.05 | 0.06 | 0.05 | 0.51 | 124.10 | 124.51 | 0.05 |
| **%** | 1% | 5% | 3% | 2% | 4% | 4% | 1% |

One of the important attributes of herders is their ability to allow the oil to maintain a thickness above a level that is actionable for remediation methods especially for burning and skimming over a time period that is relevant to operational time scales. From the graph of the average thickness vs. time in Figure 13 it can be seen that the slick increased from ~1 mm to over 3 mm and slowly continued increased over the 60 minute test.

To capture the dynamic nature of this process the change in thickness over time or holding power over a 10 minute period starting at 10 minutes is computed. The data are plotted with the time value at the center of the 10 minute window and represent the change in thickness over that 10 minute period. These values provide a direct measure of the holding power of the herder and the changes to that holding power in time provides information about how long the herder alters the interfacial surface tension to allow the oil to stay at a given thickness. In the case of Ewing Bank with ThickSlick at ~20°C, Figure 15, the thickness increased in the 10 to 20 minute period rapidly and continued to slowly increase for the entire test.

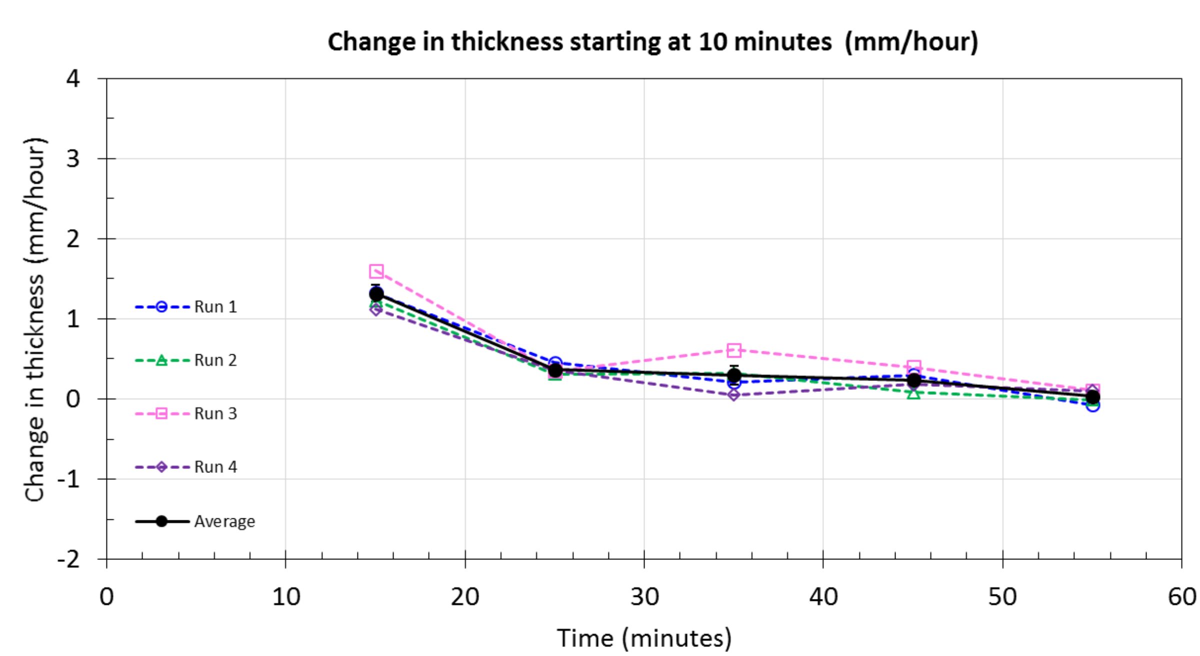


Figure 15: Ewing Bank – Thickslick change in thickness for all 4 runs and average

The second validation data set looks at thickness only, used Endicott crude with OP-40 herder at room temperature. Five runs to validate the measurement method were performed as shown in Figure 16, Figure 17, and Figure 18 where the thickness as a function of time for each run, the average thickness, and the change in thickness over time are plotted respectively. The metrics and statistics are summarized in Table 3. In general, Endicott showed a similar trend in thickness vs. time for each run but much different than that of Ewing Bank and ThickSlick. Instead of increasing thickness the full 60 minutes this oil-herder combination reached a maximum thickness nearly immediately, declined for 15 minutes, levelled off for 30 minutes, then declined again.

The self-similarity of each run for both oil-herder combinations but wide contrast between the two sets supports the ability of this experimental set up to discern the dynamic interactions of the oils with herders and allows a deep study in various environments.

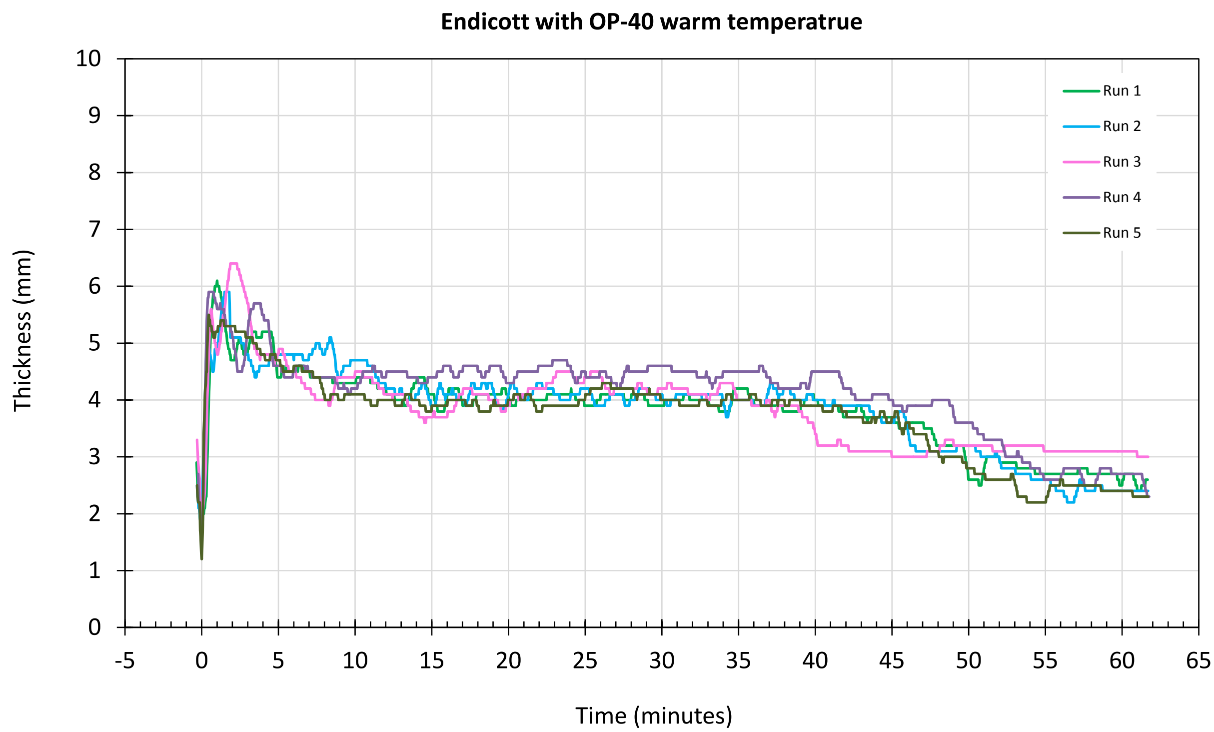



Figure 16: Thickness vs. time for all 5 Endicott, OP-40 warm temperature runs.

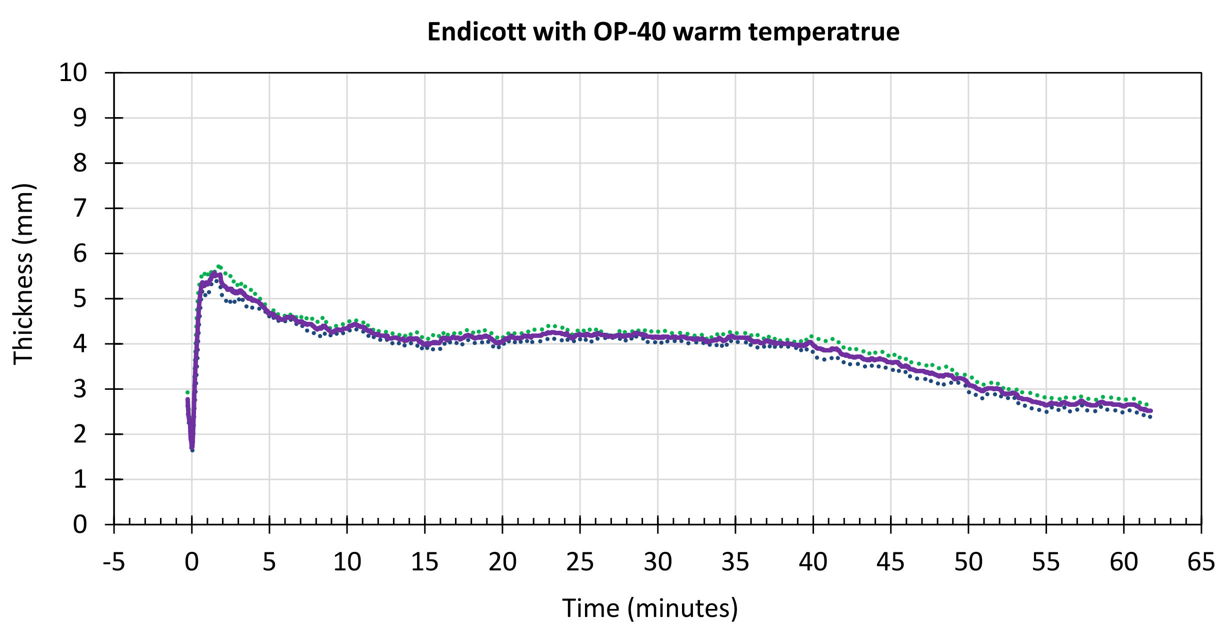



Figure 17: Average thickness vs. time from all Endicott / Op-40 warm temperature runs with standard deviation.

Table 3: Endicott and OP-40 metrics for all 5 runs

| Run # | Maximum Thickness (mm) | Minimum Thickness (mm) | Range (mm) | Minimum Thickness Position (Seconds) | Max Thickness Position (Seconds) | Time Difference (Seconds) | Thickness (mm) 60 min after herder application |
|---|---|---|---|---|---|---|---|
| 1 | 6.1 | 1.7 | 4.3 | 20 | 80 | 61 | 2.6 |
| 2 | 5.9 | 1.8 | 4.2 | 16 | 125 | 109 | 2.4 |
| 3 | 6.4 | 1.8 | 4.6 | 18 | 145 | 127 | 3.1 |
| 4 | 5.9 | 1.6 | 4.3 | 14 | 47 | 33 | 2.7 |
| 5 | 5.5 | 1.2 | 4.2 | 18 | 46 | 29 | 2.4 |
| | | | | | | | |
| **Average** | 6 | 1.6 | 4.3 | 17 | 89 | 72 | 2.6 |
| **Stdev** | 0.33 | 0.25 | 0.16 | 2 | 45 | 45 | 0.29 |
| **Standard Error** | 0.15 | 0.11 | 0.07 | 0.9 | 20.15 | 19.96 | 0.13 |
| **%** | 2% | 7% | 2% | 5% | 23% | 28% | 5% |

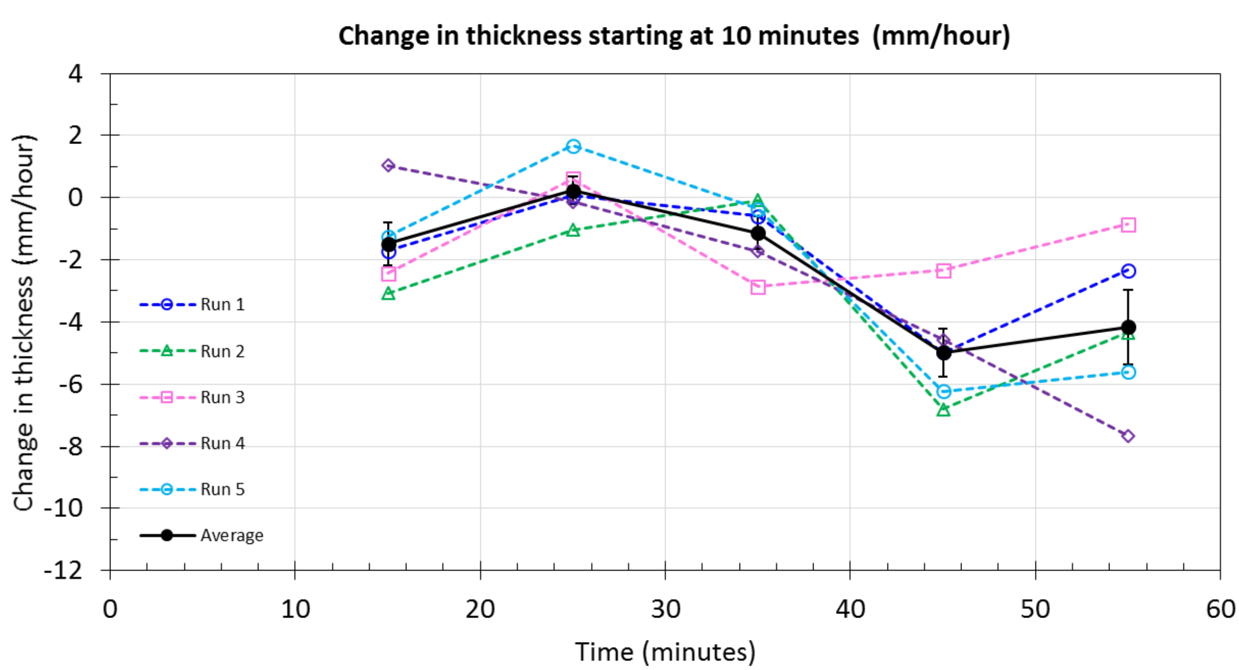


Figure 18: Endicott change in thickness

A comparison of the holding power of the herders is shown in Figure 18 for Endicott OP-40 and Figure 15 for Ewing Bank ThickSlick. The plot is of the rate of change of thickness over a 10 minute window. A positive value indicates the thickness was increasing, negative it was decreasing. The five data points at 10 minute intervals show agreement run to run for the combinations but a huge difference between the oil-herder types. Ewing Bank shows a positive value for all five points meaning the herder is holding and even gaining strength while Endicott is essentially zero or below zero for all 5 points meaning the oil is relaxing the entire experiment after the initial thickness maximum occurred within minutes of the herder being applied.

These validation measurements show an experimental design that has low enough random error and high enough systematic repeatability to discern between key herder effectiveness metrics for various oil herder pairs.

### *Volume*

Since the volume should remain constant over the duration of the experiment unless some mechanism changes the overall volume of the oil, such as evaporation it is a key element which can used to validate runs and for quality assurance. The area at every time element multiplied by the thickness represents the volume of crude oil floating on the surface of the water (See Figure 19). During the first 5 minutes of the run the volume typically oscillated due to variations of thickness across the slick so that the measured thickness may not have been representative of the average in the slick in this time. Figure 20 shows a typical pattern of how the oil retracted in 99% of the runs, starting very spread out and eventually, within 5 minutes forming a circle in the center of the tray.

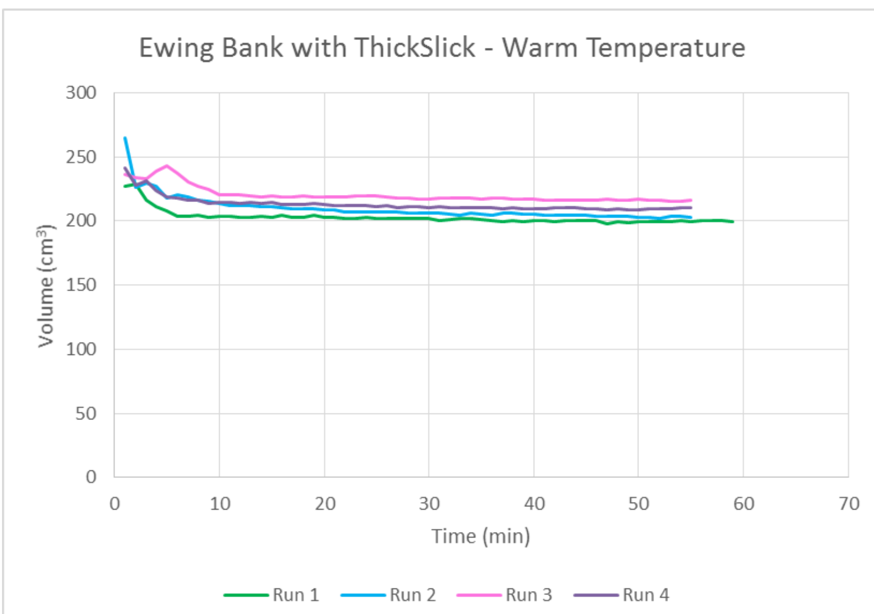



Figure 19: Volume derived from thickness x area

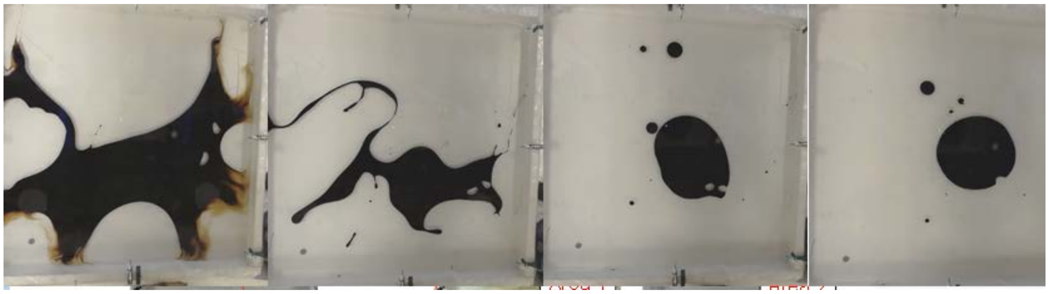


Figure 20: Left two frames are in first 5 minutes of run, then run stabilizes shown by two images on right, taken > 5 min

The standard error for thickness as a function of time is produced using the statistics between the four runs of the Ewing Bank oil is shown in Figure 21. The error is highest in the time the slick is first acted on by herders and in transition when it contracts quickly. The volume error for the averaged value was less than 10%.

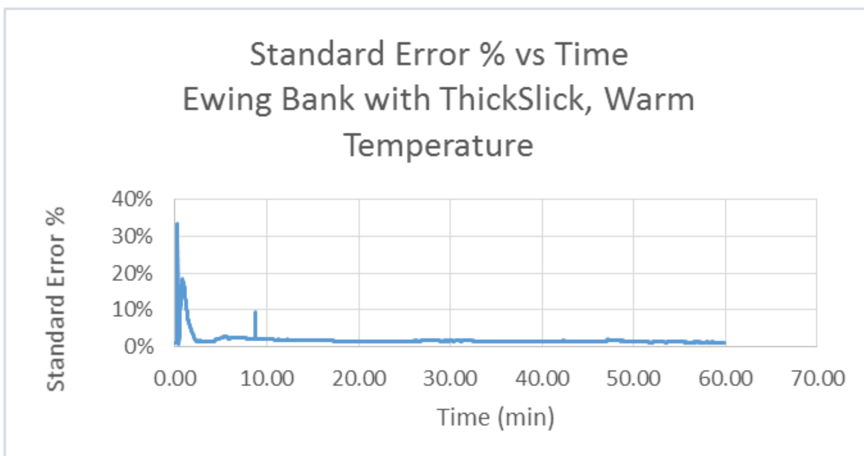



Figure 21: Standard error computed at each time step from variation between runs shows higher uncertainty in first 5 minutes

## 5. OIL AND HERDER PROPERTIES

The study used the two commercially available herders ThickSlick 6535 and Siltech OP40 featured in the U.S. Environmental Protection Agency, Original Equipment Manufacturer Regulations and Implementation Division Technical Product Bulletin's #S-5 and #S-6 respectively. The two herders listed are likely to be considered for use in actual spill events and have been included in previous studies making the results of this study relevant to the wider community.

The 14 oils used included 5 light oils, 2 medium oils and 7 heavy oils based on dynamic viscosity. Light oils were those with viscosities < 100 cP and heavy oils had viscosities > 500 cP as shown in Table 4. The density was determined using ASTM 5002, and the viscosity was determined using ASTM D7042 which is accurate for lighter oils up to 500 cP.

Table 4: Oil viscosity and density from laboratory analysis. U-unobtainable.

| # | Oil Name | Viscosity @20˚C Dynamic Viscosity cP | Viscosity @5˚C Dynamic Viscosity cP | Density @20˚C g/mL | API Gravity @20˚C | Viscosity Classification |
|---|---|---|---|---|---|---|
| 1 | Agbami | 2.00 | 7.00 | 0.788 | 48.1 | light |
| 2 | Hibernia | 8.57 | 18.81 | 0.852 | 34.6 | light |
| 3 | Anadarko | 10.57 | 20.96 | 0.916 | 23.0 | light |
| 4 | ANS | 25.00 | 43.00 | 0.860 | 33.0 | light |
| 5 | Ewing Bank | 28.95 | 92.30 | 0.897 | 26.2 | light |
| 6 | Endicott | 256.0 | 1376 | 0.929 | 20.8 | medium |
| 7 | Alpine | 317.0 | 1268 | 0.918 | 22.6 | medium |
| 8 | IFO 120 | 1035 | 4531 | 0.954 | 16.8 | heavy |
| 9 | Doba Chad | 1657 | 7780 | 0.925 | 21.5 | heavy |
| 10 | Rock | 2617 | 14170 | 0.961 | 15.7 | heavy |
| 11 | Platform Gina H14 | 2928 | 15460 | 0.962 | 15.6 | heavy |
| 12 | Platform Gina (fresh) | 3244 | 15140 | 0.961 | 15.7 | heavy |
| 13 | Harmony | 3422 | U | 0.945 | 18.3 | heavy |
| 14 | Canadian Sour | 3460 | 17760 | 0.971 | 14.2 | heavy |

The viscosity versus density for these oils shown in Figure 22 generally follows the typical relationship for crude oil, those with higher viscosity are more dense. The data points at 5°C have a higher viscosity than those at 20°C for the same density. The lines shown in the plot are arbitrary trend lines to point out the interesting outlier which is Anadarko crude. This oil sample was tested to have an unusually high density to viscosity ratio which may be useful in separating which property is the driver for some herder-oil interactions.

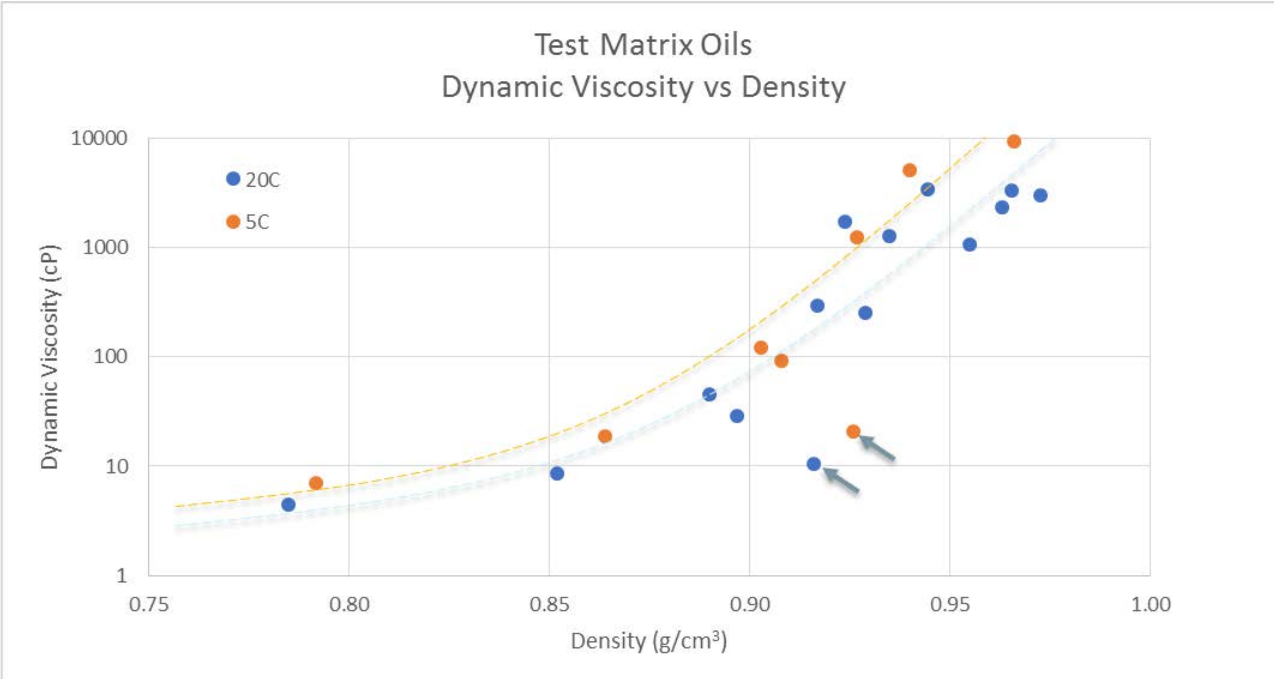


Figure 22: Dynamic viscosity vs. density for oils in the study. Arrows show Anadarko as outlier.

The oil samples were tested for Saturates, Asphaltenes, Resins and Aromatics (SARA) using a Iatroscan TLC-FID (Thin Layer Chromatography and Flame Ionization Detector) standard method IP-469. The IP-469 method determines all four compound classes by adsorption chromatography which in the case of asphaltenes may under predict by 20% especially for the lighter oils [12]. Retaining the oil samples and evaluating the methodology and results in this ongoing study using a more accurate test for asphaltenes such as IP-143 may be valuable. The sulfur content was measured using ASTM D4294. The components are shown in Table 5 and Figure 23.

Table 5 : SARA properties of oils

| # | Oil Name | Saturates % m/m | Aromatics % m/m | Resins (Polar I) % m/m | Asphaltenes (Polar II) % m/m | Sulfur Content wt % |
|---|---|---|---|---|---|---|
| 1 | Agbami | 63.5 | 32.1 | 3.6 | 0.8 | 0.00 |
| 2 | Hibernia | 45.0 | 42.4 | 9.4 | 3.2 | 0.57 |
| 3 | Anadarko | 44.5 | 41.2 | 13.3 | 1.0 | 0.65 |
| 4 | ANS | 27.2 | 52.3 | 14.4 | 6.1 | 1.36 |
| 5 | Ewing Bank | 24.7 | 51.4 | 18.9 | 5.0 | 2.44 |
| 6 | Endicott | 29.4 | 47.3 | 14.7 | 8.6 | 1.62 |
| 7 | Alpine | 58.0 | 40.3 | 1.7 | 0.1 | 0.23 |
| 8 | IFO 120 | 22.9 | 44.9 | 23.1 | 9.1 | 0.95 |
| 9 | Doba Chad | 50.0 | 33.7 | 14.3 | 6.0 | 0.15 |
| 10 | Rock | 14.3 | 39.3 | 23.6 | 22.8 | 4.06 |
| 11 | Platform Gina H14 | 15.9 | 51.2 | 18.2 | 14.7 | 3.98 |
| 12 | Platform Gina (fresh) | 13.7 | 43.7 | 24.0 | 18.6 | 3.64 |
| 13 | Harmony | 16.5 | 40.8 | 28.2 | 14.5 | 4.60 |
| 14 | Canadian Sour | 12.9 | 56.5 | 19.4 | 11.3 | 4.12 |

The dominant identified driver on herder performance is viscosity and/or density since they are highly correlated. The SARA components and sulfur were measured to determine help determine if viscosity is the sole property that controls herder effectiveness or if one or more of the SARA components or sulfur are primary or secondary factors that contribute to herder effectiveness.

A few key observations are below:

- For the light and medium crude oils:
  - Agbami, Alpine, have high saturates relative to their position in the viscosity order
  - Alpine has low resins and low asphaltenes
  - Anadarko has a high density:viscosity ratio
- For the heavy oils
  - Doba Chad has high saturates relative to its position in the viscosity order.
  - Doba Chad and IFO 120 have low sulfur relative the slightly heavier oils
  - The five heaviest oils are similar in their properties.

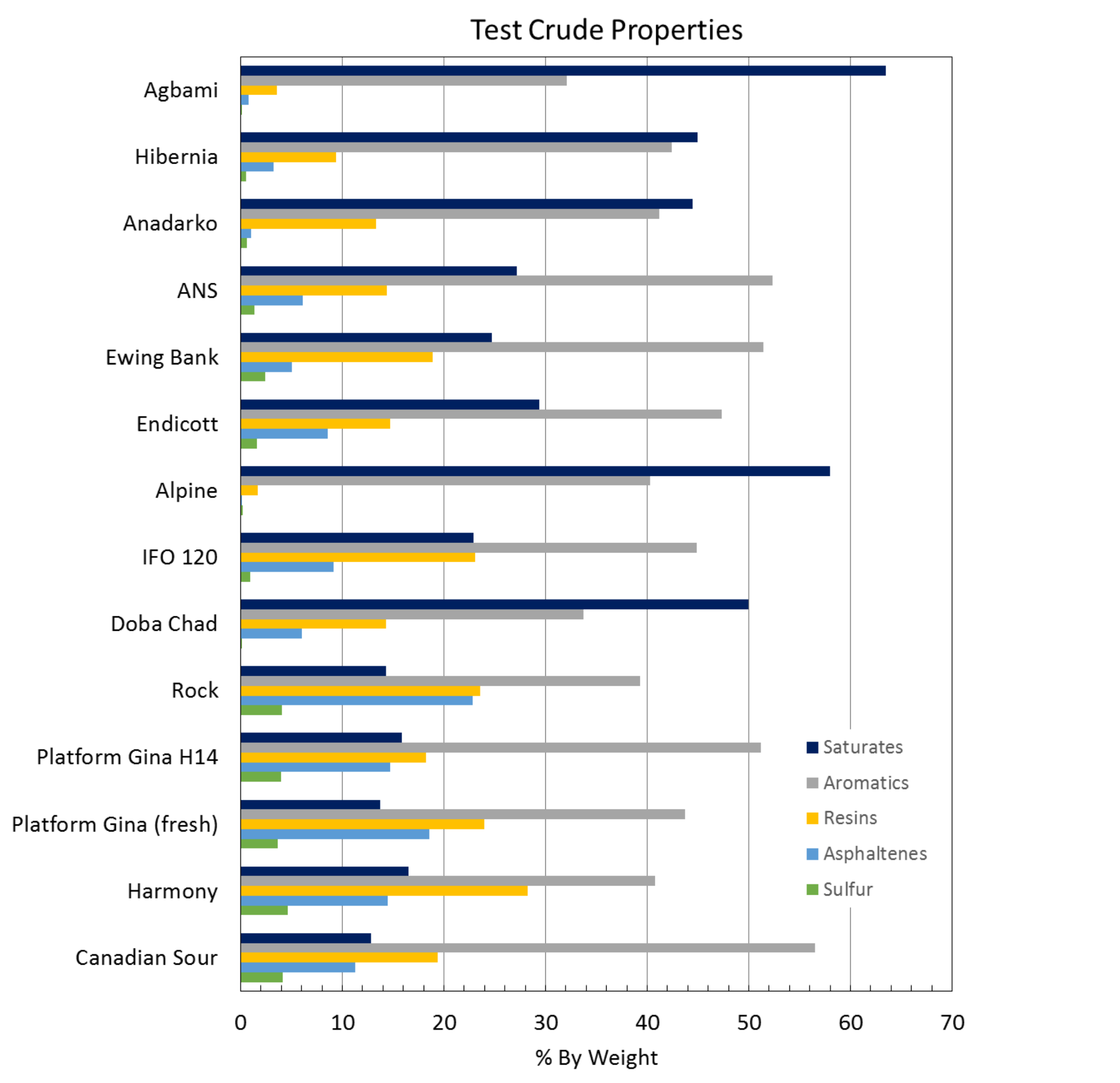



Figure 23: SARA and sulfur % by weight for test crude oils ordered in increasing viscosity.

### 5.1.1. Temperature corrections to viscosity and density

Since the crude oil properties were tested at the fixed temperatures of 5°C and 20°C but the experiments were performed at temperatures which varied from 5°C and 20°C the viscosity and density needed to be corrected to the temperature of the oil for each test performed. The viscosities measured at 5°C and 20°C were used to determine the corrected viscosity through the ASTM D341 Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum Products process [13]. This process uses two viscosity temperature points to either extrapolate or interpolate the viscosity at a third temperature. Density was corrected using density-temperature relations in ASTM D1250-04 [14]. The correction is relatively small as the tests were performed over a small range as shown in Figure 24 and Figure 25 for viscosity and density respectively.

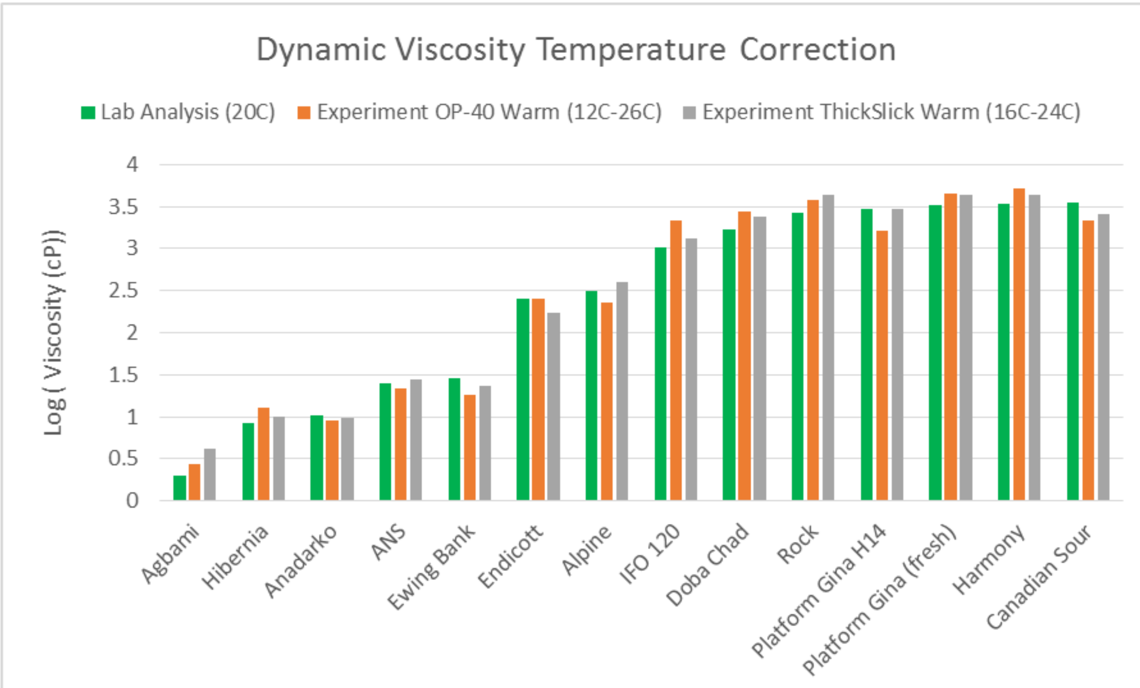


Figure 24: Viscosity for warm tests using the ASTM D341 to determine viscosity at test temperatures.

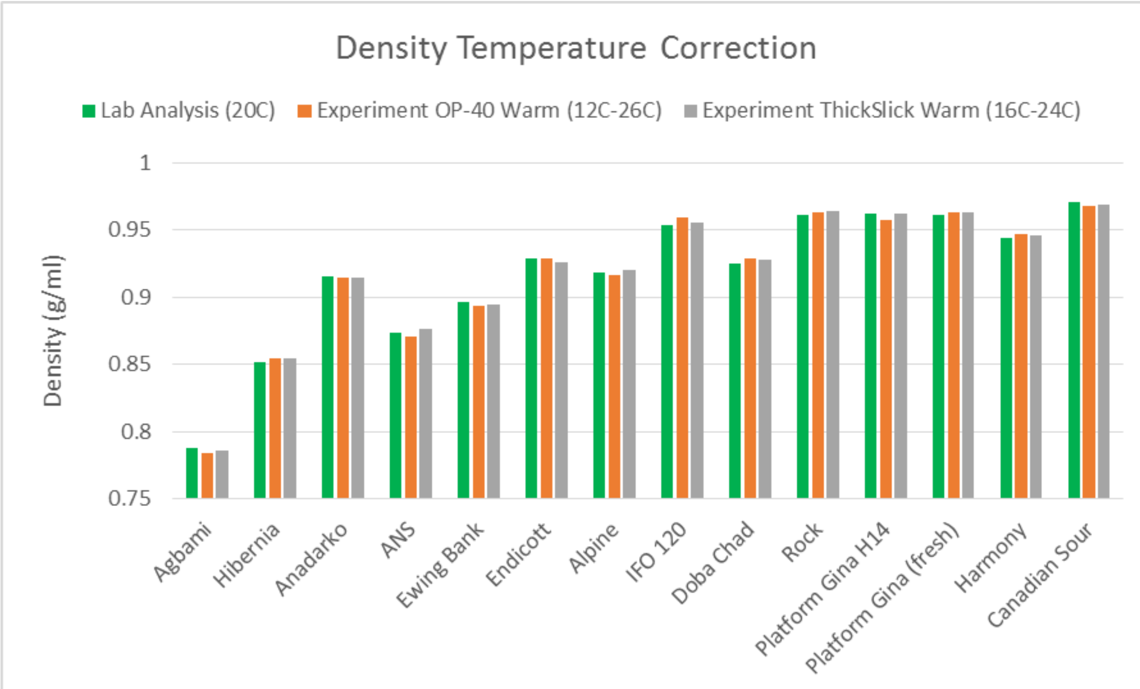


Figure 25: Density at warm temperatures using ASTM D1250 – 04 [14].

## 6. HERDER EFFECTIVENESS RESULTS

We performed 149 experiments using combinations of OP-40 or ThickSlick herder, one of 14 crude oils at room temperature or near freezing temperature. These tests resulted in 37 unique combinations as seen in Table 6.

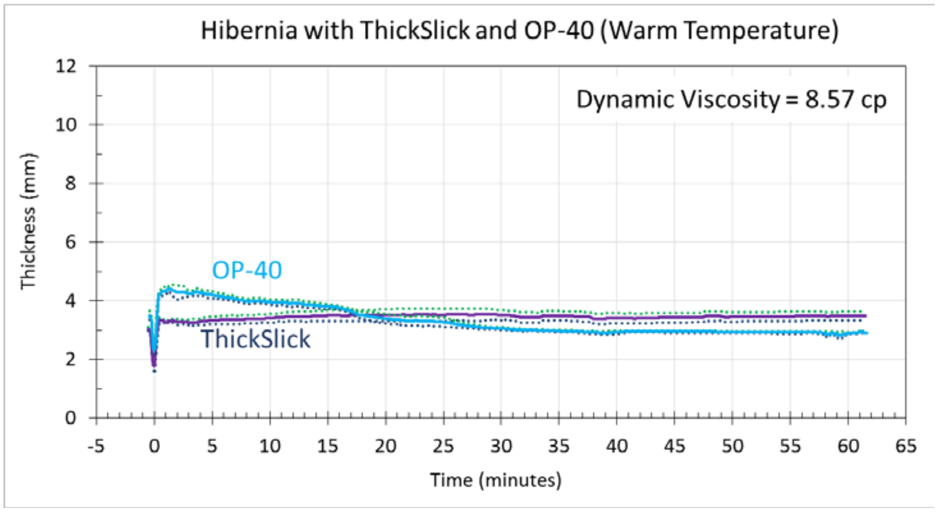
Table 6: Test matrix combinations

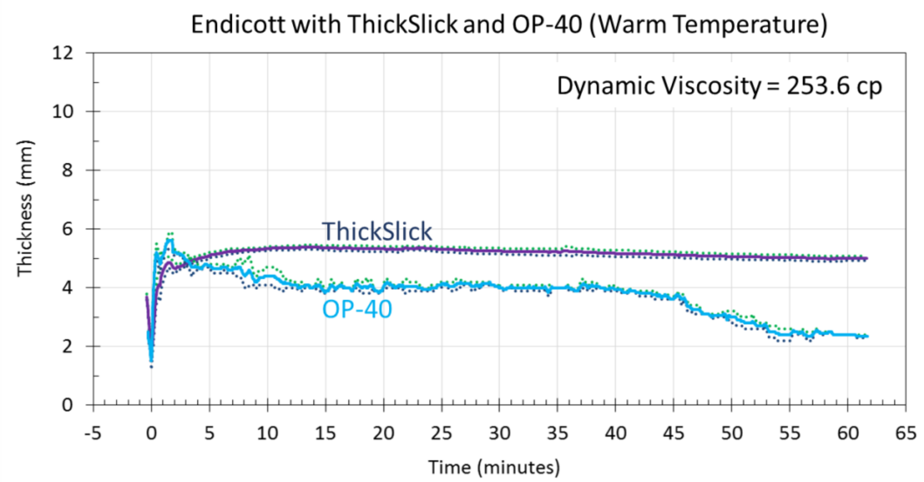
| | **Warm (Avg 20°C)** | | **Cold (Avg 4°C)** | |
|---|---|---|---|---|
| **Oil** | OP-40 | ThickSlick | OP-40 | ThickSlick |
| Agbami | ✓ | ✓ | ✓(2) | ✓(1) |
| Hibernia | ✓ | ✓ | | |
| Anadarko | ✓ | ✓ | ✓ | |
| ANS | ✓ | ✓ | ✓ | |
| Ewing Bank | ✓ | ✓ | ✓ | |
| Endicott | ✓ | ✓ | ✓ | |
| Alpine | ✓ | ✓ | ✓ | |
| IFO 120 | ✓ | ✓ | ✓ | |
| Doba Chad | ✓ | ✓ | | |
| Rock | ✓ | ✓ | ✓ | |
| Platform Gina H14 | ✓ | ✓ | | |
| Platform Gina (fresh) | ✓ | ✓ | | |
| Harmony | ✓ | ✓ | | |
| Canadian Sour | ✓ | ✓ | | |

On average each herder-oil-temperature combination was tested 4 times. However, some were run more or less depending on the circumstances of the test. The intention was to run all combinations in triplicate to strengthen the statistics and provide the opportunity to reject bad runs. The additional runs were due to some combinations being run more than 3 times to develop validate the measurement method and some to replace runs where the equipment malfunctioned or excess oil stuck to the wall of the tray leaving too little in the center. For the test matrix all runs were in triplicate except the cold run for Agbami where OP-40 (2 runs) was reduced due to a bad run. Due to there being just one test in the cold temperature range for ThickSlick this result is not used in the statistical correlations to follow but the thickness-time and area-time results are shown in Appendix B: Figure 69.

### 6.1. THICKNESS RESULTS

The thickness of the slicks were monitored throughout the experiment. Figure 26 shows the thickness as a function of time for a light (Hibernia), medium (Endicott) and heavy (Rock) crudes at the warm temperatures. The graphs are ordered from lowest viscosity to highest viscosity and are plotted on the same scale for easy comparison. From the lowest to highest viscosity, the maximum thickness achieved due to the herder trended higher. The most viscous oils achieved the highest thickness. This trend is shown which shows the maximum thickness for all oil-herder combinations as a metric for herders effectiveness will be described in section 6.3.



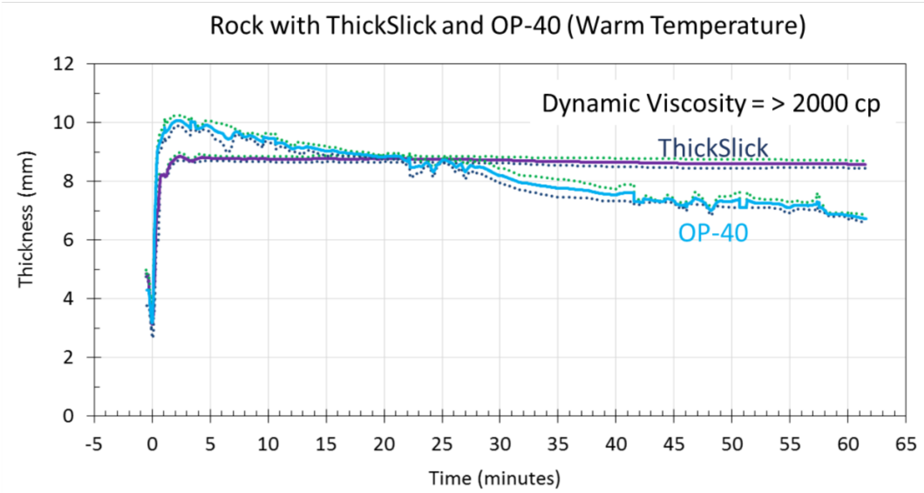



Figure 26: Thickness vs time plots for 60 minutes following application of herders OP-40 and ThickSlick on 3 different viscosity oils

Figure 26 shows in each case, regardless of viscosity of the oil, OP-40 caused the slick to increase quickly and allowed the oil to reach a maximum thickness in less than 5 minutes while ThickSlick caused the oil to achieve lower thickness initially and took longer to achieve the maximum thickness. ThickSlick however, held the slick at that elevated thickness for a longer period of time. This behavior was a pattern for most all the oils in the experiment which can be seen in Appendix A.

The slope of the thickness as a function of time was used to understand the relative holding power of the herder. To directly quantify the changes in thickness and area as a function of time after application of the herders, the slope of those parameters were calculated over a 10 minute time span starting 10 minutes after the application of the herders and starting after the maximum thickness was achieved. The slope of the curves 10 minutes after the herders were applied offers a more direct comparison between the relaxation and sometimes the failure of the herder to maintain a thicker slick.

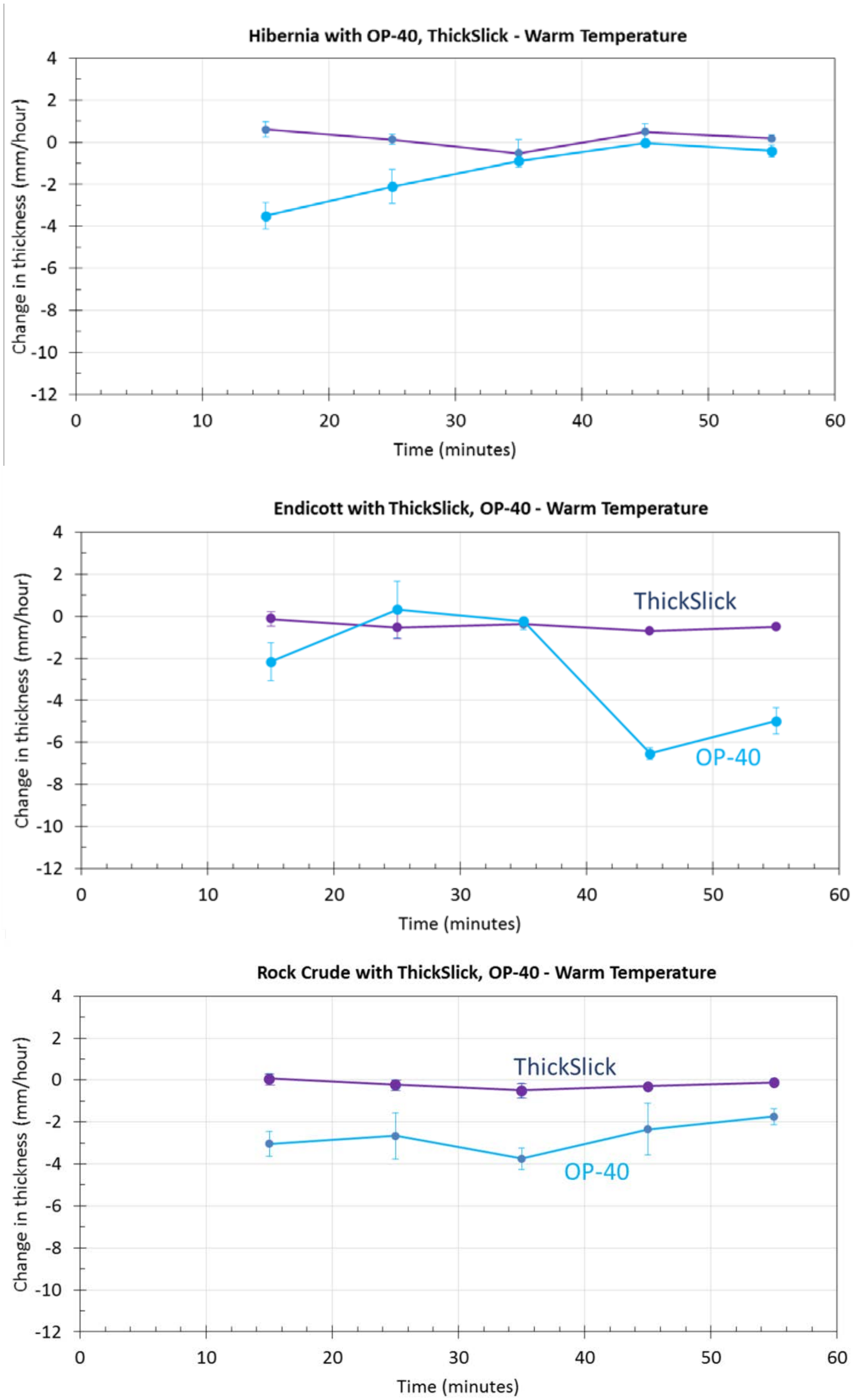
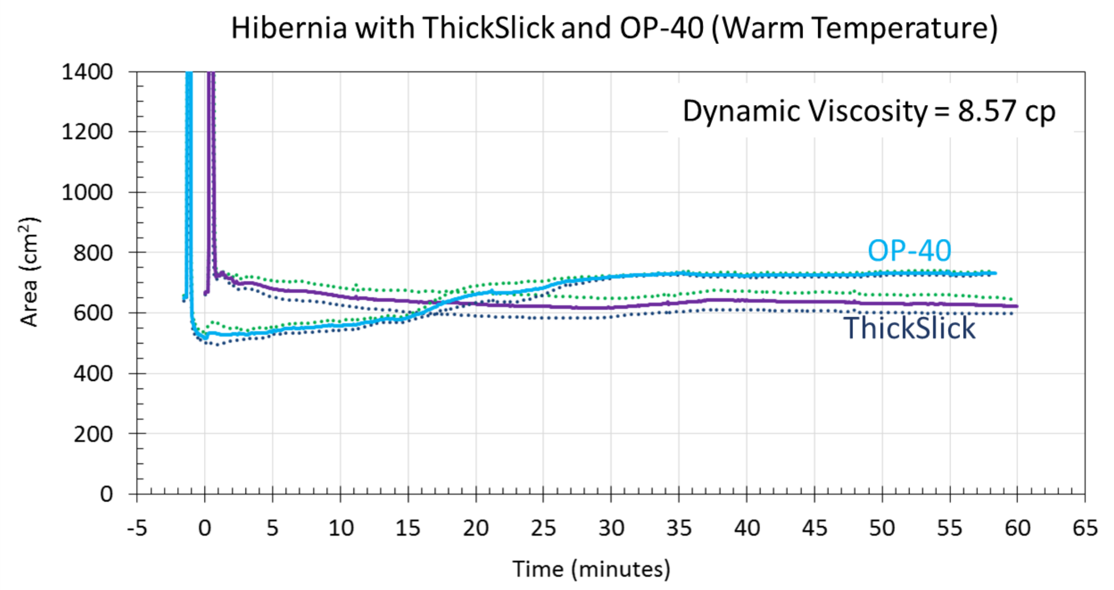


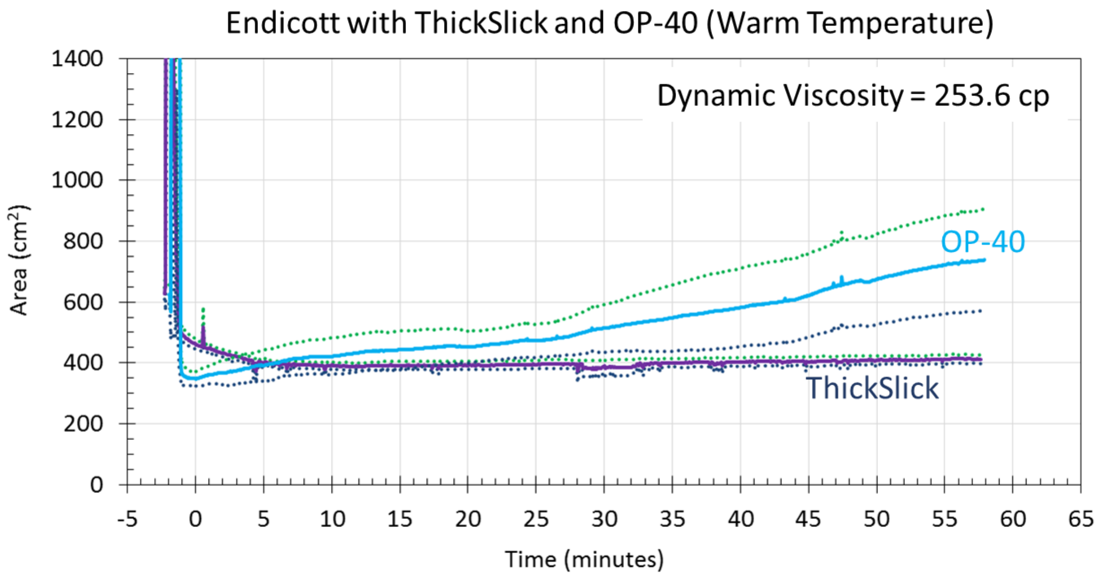
Figure 27: Average rate of change of thickness over 10 minute periods

Values above 0 mm/hour indicate an increasing thickness and values below 0 mm/hour indicate a decreasing thickness. For OP-40, in all cases, the slope of the thickness as a function of time was generally below the value for ThickSlick but oscillates more wildly indicating that slick thickness decreased in time more rapidly when OP-40 was applied. The most notable and important features are the large negative values, in the light (Hibernia), medium (Endicott), and heavy (Rock) oils implying that the thickness of the slick decreased rapidly. The breakdown is notable in the first 10-20 minute region for the Hibernia-OP-40 and during the 40 minutes after herder application for Endicott OP-40.

## 6.2. AREA RESULTS

The area was also measured over time at 30 times a second and then at a slower rate of 5 Hz after 100 seconds. The area as a function of time correlates nicely with the thickness as a function of time. Artifacts in one should appear in the other if they have to do with state of the slick, if the artifacts are not coincident the oil could have drift to the edge of the transducers causing an isolated thickness variation or a variation is isolated to the area could be caused by the pressurized air used to reposition the oil.





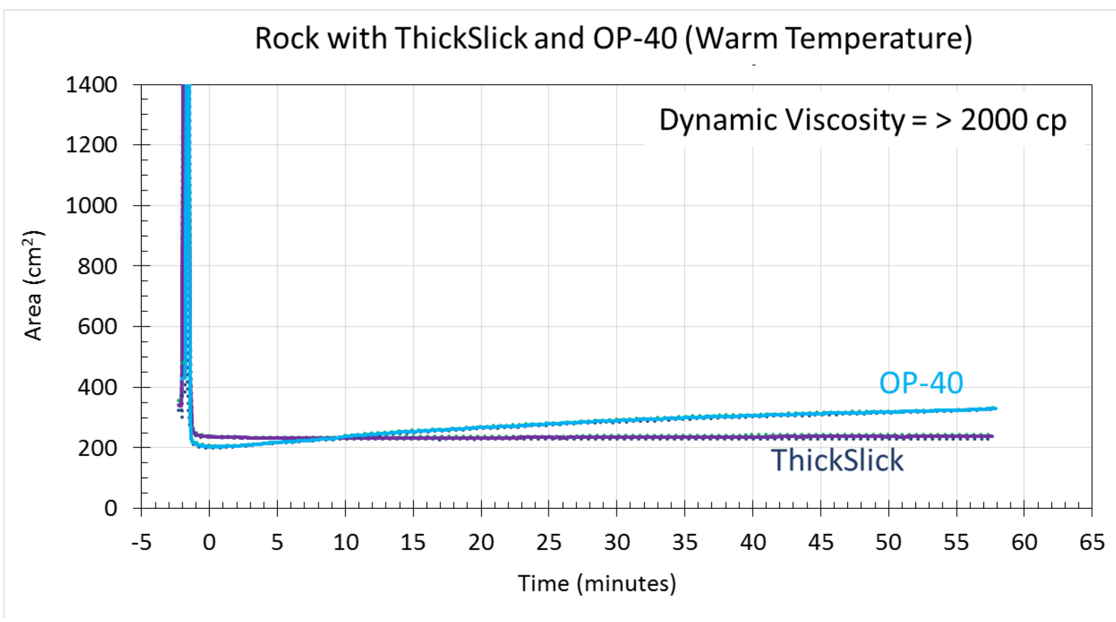




Figure 28: Area vs time plots on left and thickness vs time on right for 60 minutes following application of herders OP-40 and ThickSlick on 3 different viscosity oils.

The high temporal resolution of the data allowed a quantitative measurement of combinations of metrics that could not previously be obtained including integration of many aspects of the thickness curve. Specifically, the herder effectiveness calculated as the area under the thickness curve after the herder was applied, as shown in Figure 10 could now be accurately calculated and used to objectively compare the effectiveness of herders. This calculation of the herder effectiveness provided a parameter that was influenced by both the maximum thickness achieved as well as the holding power of the herder.

## 6.3. HERDER EFFECTIVENESS

A number of metrics of herder effectiveness are described in Section 3, Herder Effectiveness Metrics. The further analysis here will focus mostly on the thickness metrics and the result of the integration under the thickness curve over the full 60 minutes. The maximum thickness represents the initial contraction of the oil after the herder is applied, if burning or skimming can start immediately maximum thickness is the most important metric for herder effectiveness. If burning of skimming is delayed the ability of the herder to maintain thickness for 30, 60 minutes becomes a more informative metric.

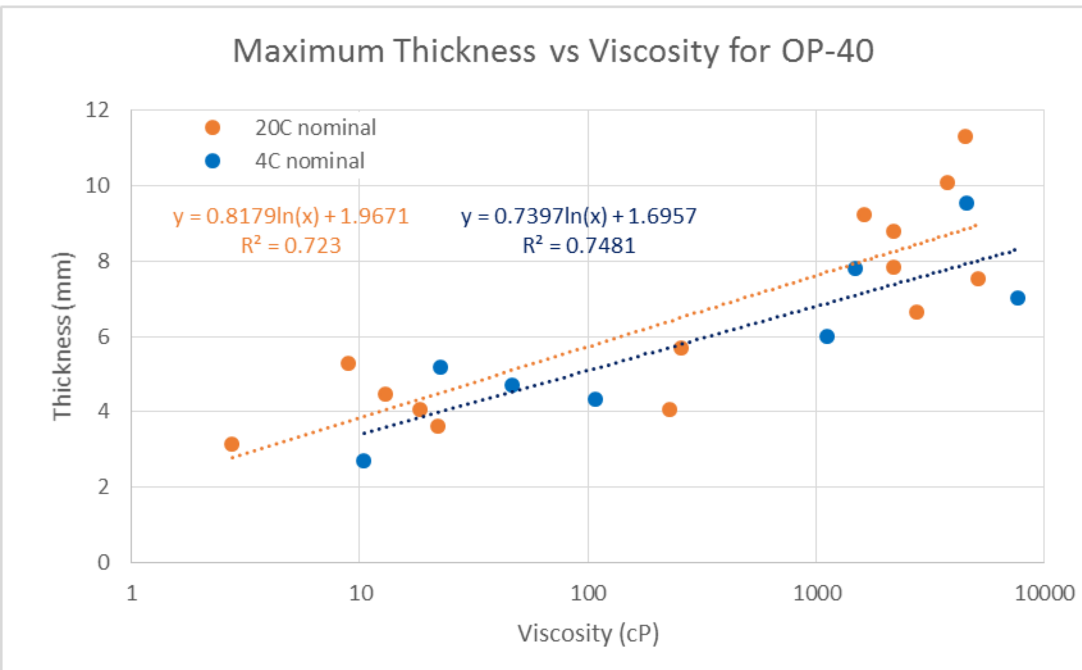



Figure 29: Maximum thickness after application of herder for different temperature levels for OP-40

Figure 29 shows the maximum thickness the slick reaches after the application of OP-40. With OP-40 there were two temperature ranges warm and cold. The relationship between thickness and viscosity was fairly consistent between the two temperatures, with the thickest slicks achieved at the warmer temperatures. Note the log scale on the x axis, thickness versus the log of viscosity trends closer to linear than thickness vs viscosity.

Figure 30 shows the comparison between OP-40 and ThickSlick for the warm temperature tests. The maximum thickness achieved using OP-40 has a consistently higher compared to ThickSlick but the two herders had a very similar increase in maximum thickness as a function of viscosity noted by the similar slopes for each curve fit.

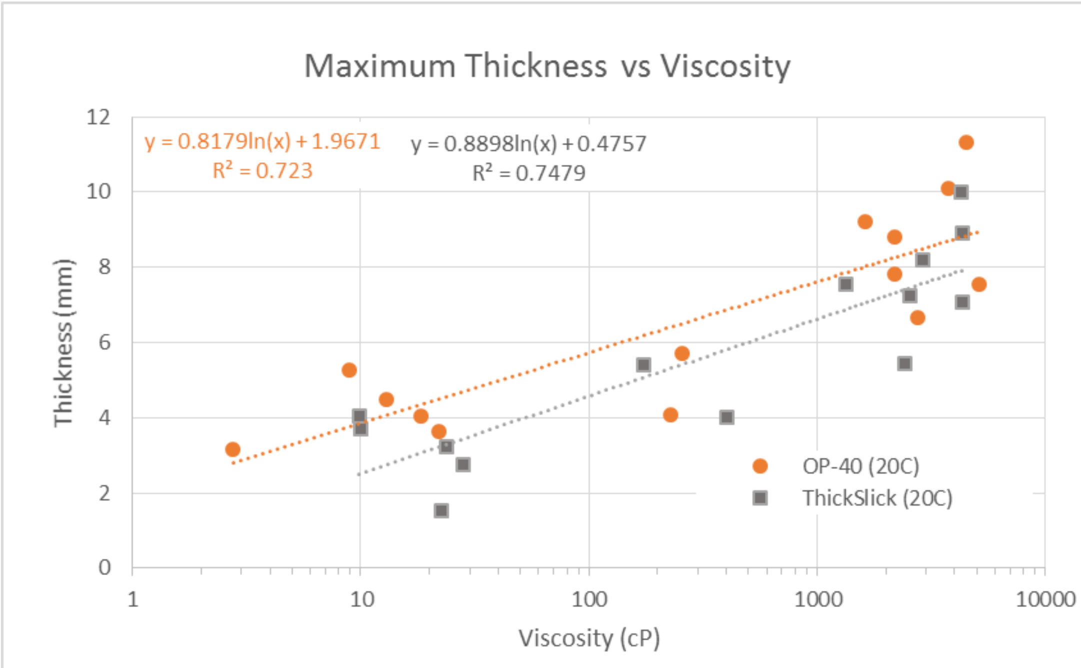



Figure 30: Maximum Thickness after application of herder for ThickSlick and OP-40 for the nominal 20C tests.

The thickness after 60 minutes for OP-40 warm and cold tests shown in Figure 31 shows a similar trend as the maximum thickness except the cold temperature plot has higher thicknesses than the warm temperature tests in contrast with Figure 29. The same trend can be illustrated by showing a cross plot of the maximum thickness versus the thickness at 60 minutes (Figure 32). The slope of the line shows the fractional decrease in thickness from the maximum to the thickness at 60 minutes. The green line shows a slope of 1 meaning there was no decrease. The thickness using ThickSlick has a slope of nearly one while OP-40 for the warm temperature tests shows a fractional decrease in thickness of 0.639 over 60 minutes. The cold temperature tests for OP-40 showed a small fractional decrease of 0.862. The comparison between the thickness after 60 minutes for OP-40 and ThickSlick in Figure 33 shows the thickness after 60 minutes using ThickSlick was higher than the OP-40 implying that ThickSlick allowed the slick to maintain the elevated thickness longer.

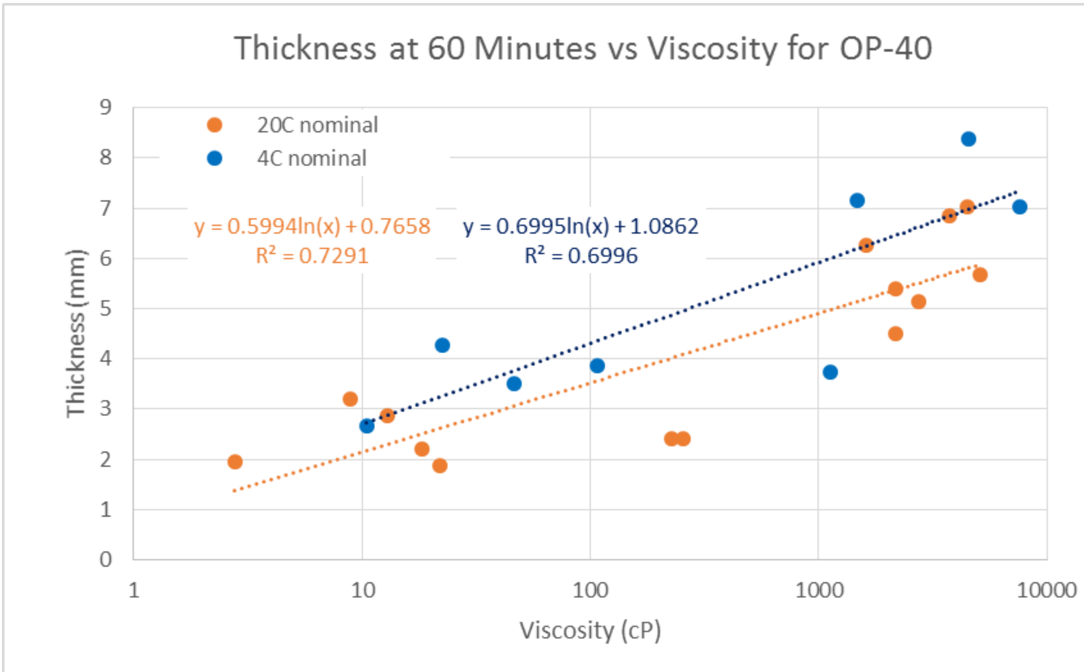



Figure 31: Thickness 60 minutes after herder application for OP-40 including all those tested at cold temperature

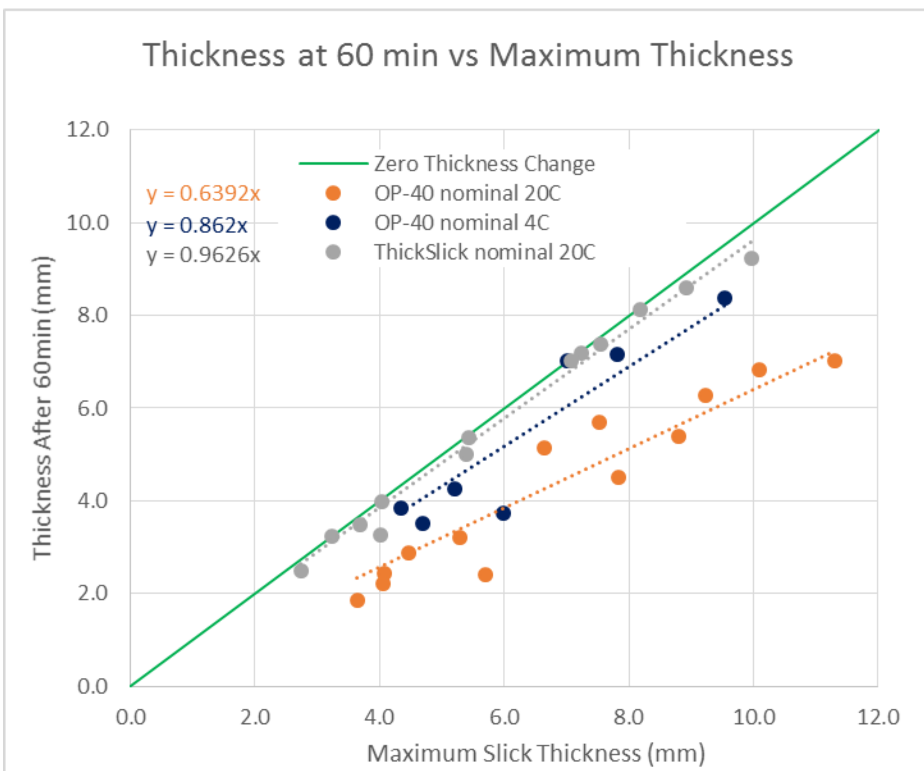



Figure 32: Slick thickness at 60 minutes versus maximum thickness.

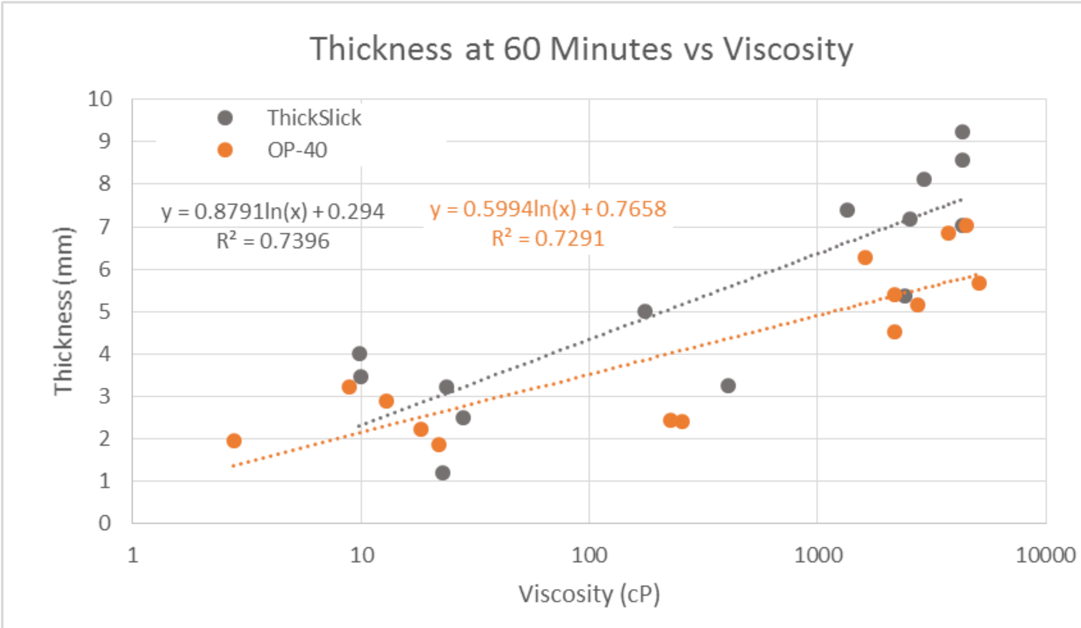


Figure 33: Thickness at 60 minutes for both herders warm tests

The trend that OP-40 achieved a higher initial thickness than ThickSlick, but ThickSlick allows the oil to holds the elevated thickness longer can be deduced from the shape of the thickness vs time plots as shown in Appendix A. The cross plot of maximum thickness vs thickness at 60 minutes, Figure 32, shows the OP-40 average loss of thickness to be > 30% while ThickSlick loses less than 5%. The comparison of the cold and warm trends for OP-40 show that the higher temperature has a faster decline.

The area under the thickness vs. time curve provides a herder effectiveness metric that combines both the maximum thickness and the duration of elevated thickness as shown in Figure 34

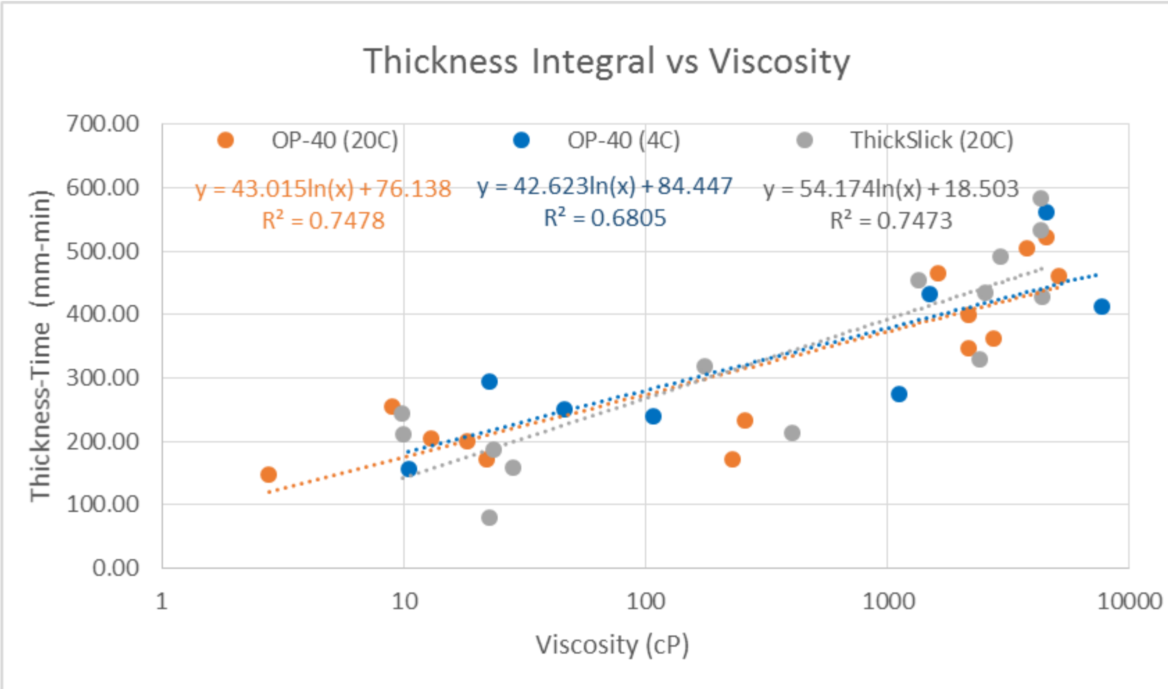



Figure 34: Thickness integration over full 60 minutes for all herders and all temperatures

The thickness integration plot for ThickSlick at warm temperature and OP-40 at both warm and cold temperatures. Figure 34, suggests the overall herder effectiveness over the full 60 minutes is close between the two the herders and is not much different for OP-40 for cold or warm temperature. This metric shows the initially higher thickness of OP-40 relative to ThickSlick is cancelled out by the faster decline of the OP-40 thickness over the course of 60 minutes when integrating over the entire time.

### 6.3.1. Herder Effectiveness Based on Interfacial Force

The Garret and Barger [9] formulation for the thickness of a static oil lens on water lens is a useful starting point to describe the behavior of a finite amount of oil after the application of herders. The equation describes the thickness, h, as function of $F_o$, the spreading force of oil on water, $F_m$, the spreading force of the monolayer on water, which can be the herder on water, $\rho_w$, and $\rho_o$, the density of water and oil, and g, the acceleration due to gravity.

$$h^2 = -\frac{2(F_o - F_m)\rho_w}{g\rho_o(\rho_w - \rho_o)} \qquad [1]$$

The density variables can be grouped under the variable P,

$$P = \frac{\rho_w}{\rho_o(\rho_w - \rho_o)} \qquad [2]$$

and the quantity $F_c$ can be defined as,

$$F_c = -F_S = (F_m - F_o) \qquad [3],$$

where $F_s$ is the spreading force defined by Langmuir [10]. The introduction of $F_c$ is for convention so the quantity acts in the same sign direction as the herder-oil effectiveness and will be referred to as the containment force from here on, as the net force required to hold the oil a static thickness h..

Rearranging the terms from [1] arrives at,

$$\frac{gh^2}{2P} = (F_m - F_o) = F_c \quad [4]$$

The left side of equation 4 is comprised of the thickness and the density exclusively, the right side is the summation of the interfacial forces, a direct indication of the force holding the oil slick together. In the context of this study the equation states that the net interfacial forces from the oil-herder interface supply enough force to hold the oil at height *h*.

If the quantity $\frac{gh^2}{2P}$ is computed for each oil-herder combination in the experiment it can be used as way to measure $F_c$, the containment force, which is dependent on the chemistry of the oil, salt water, and herders.

In this study the density for each oil is determined using laboratory analysis at multiple temperatures and the thickness of the slick is measured directly multiple times a second. Using the density of the oil and saltwater to compute P and the thickness as the variable h in equation 4 the net containment force $F_c$ can be computed throughout the experiment. The quantity is the best representation of what is happening at the molecular level so is well suited to compare to the oil properties such as the SARA components, the % sulfur by weight, the viscosity, and density in an attempt to identify primary and secondary drivers of herder effectiveness.

### 6.3.2. Maximum Thickness

The maximum thickness attained by the slick, which typically occurs just after the herder is applied is defined as, *h,* in equation 1 for each test along with the temperature corrected densities for salt water and oil to compute P. The two herders have similar correlations with Asphaltenes in regards to the maximum thickness achieved except the curves are offset to reflect the higher initial containment force for OP-40 shown in Figure 35.

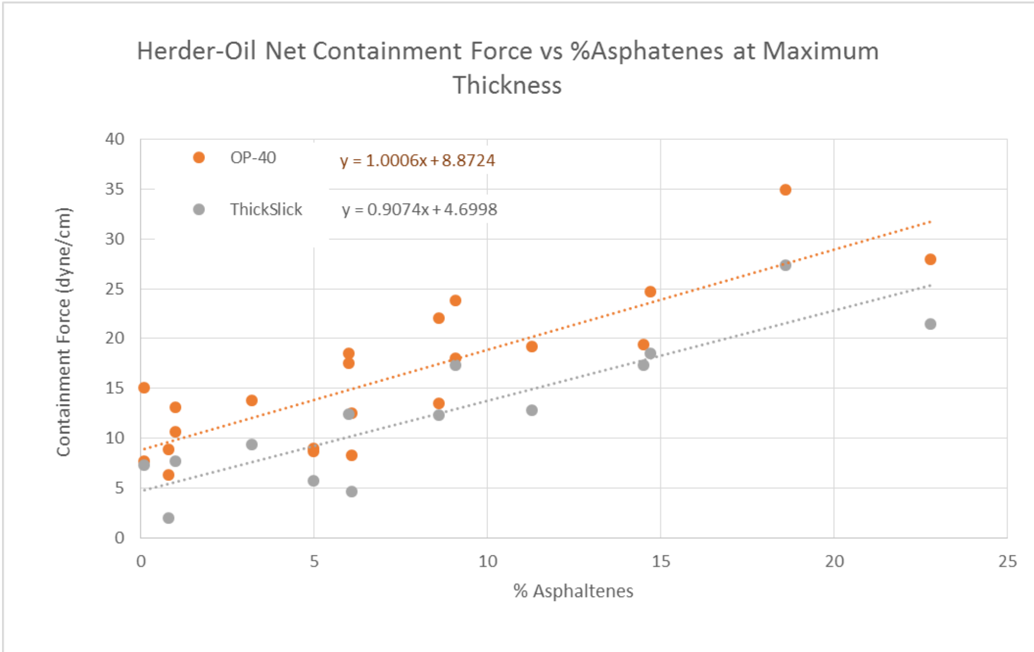



Figure 35: Containment force vs % Asphaltenes for both herders

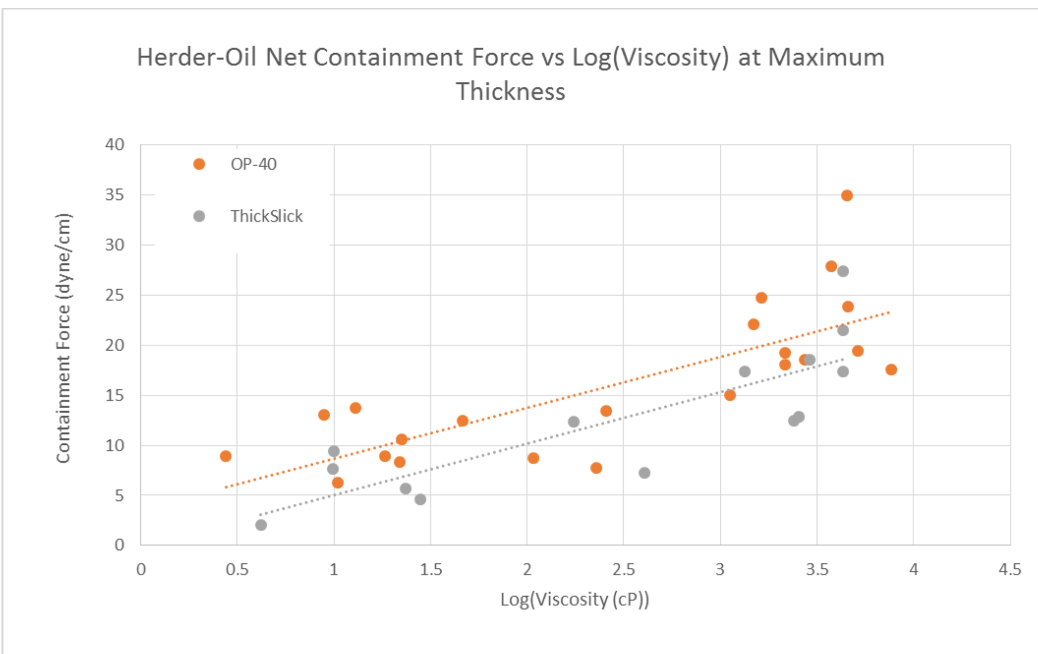



Figure 36: Containment force vs Log(Viscosity) at maximum thickness for both herders

Figure 37 shows the relationship between containment force and Asphaltenes for both warm and cold temperatures for OP-40. The two linear trend lines show a decent agreement with data. Since the cold temperature points have a steeper slope there could be a temperature effect in addition to the possible effect of the Asphaltene content.

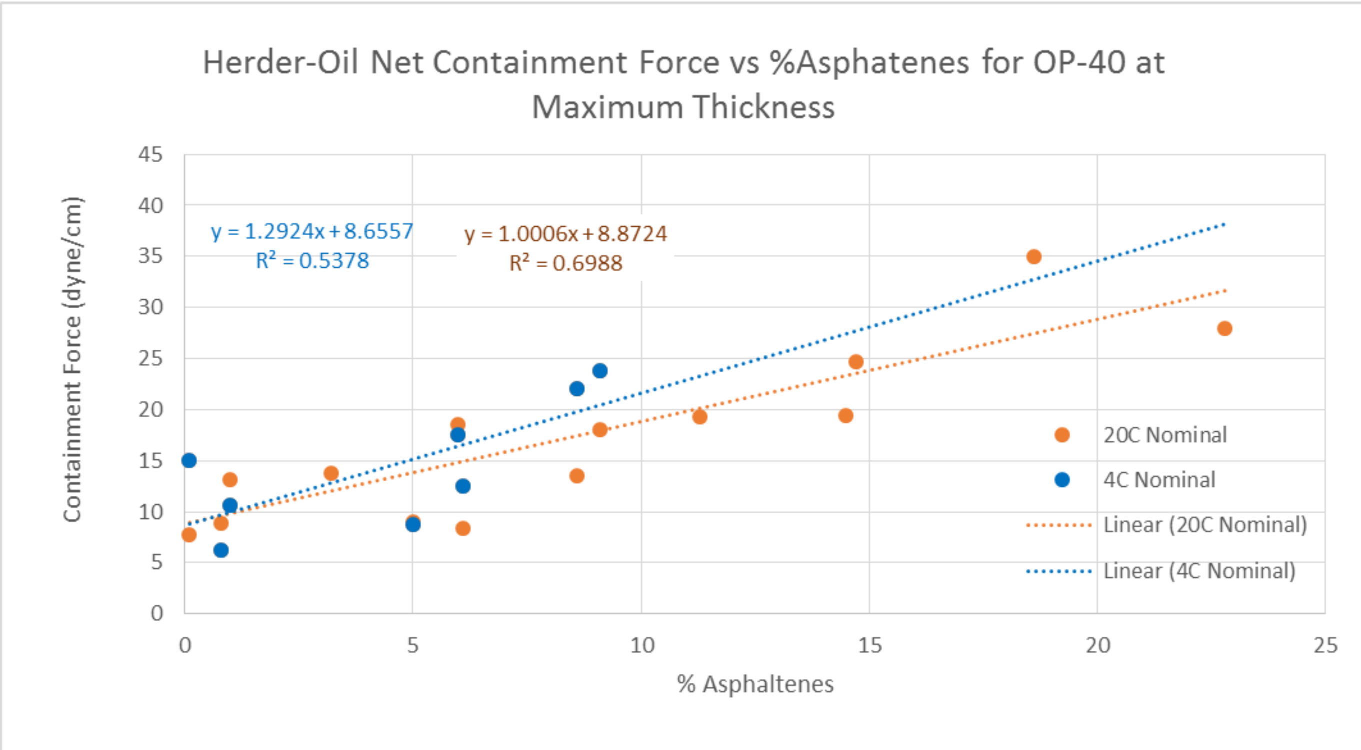


Figure 37: Containment force vs % Asphaltenes for OP-40 at Maximum Thickness

The net containment force, $F_c$, is then correlated with other properties and shown in Table 7. The highest correlation for OP-40 and ThickSlick is that of Asphaltenes. It is even higher than viscosity. The correlation is just that, a statistical relation that shows when variables trend together. The SARA components and viscosity also have strong correlations between them as shown the far right column of Table 7: Correlation of the net containment force, $F_c$, for Oil-OP40, Oil-ThickSlick and log of dynamic viscosity at maximum thickness to oil properties. Since the SARA components have strong correlations with viscosity it is difficult to separate how much and which of the SARA quantities affect the interfacial forces and how much the viscosity of the oil contributes to the same. The fact that the % Asphaltenes has a higher correlation than the viscosity with $F_c$ means there is more likely a real chemical mechanism involving Asphaltenes effecting herder effectiveness, or at least the containment energy.

Table 7: Correlation of the net containment force, $F_c$, for Oil-OP40, Oil-ThickSlick and log of dynamic viscosity at maximum thickness to oil properties.

| Linear Correlation Coeficient R | OP-40 (Warm Temp.) | OP-40 (All Temp.) | ThickSlick | Log(Viscosity) |
|---|---|---|---|---|
| Log(Viscosity) | 0.76 | 0.77 | 0.83 | 1.00 |
| API | -0.65 | -0.66 | -0.76 | -0.85 |
| Density | 0.68 | 0.69 | 0.78 | 0.87 |
| Saturates | -0.65 | -0.60 | -0.70 | -0.63 |
| Aromatics | 0.01 | 0.07 | 0.06 | 0.09 |
| Resins | 0.68 | 0.63 | 0.74 | 0.68 |
| Asphaltenes | 0.88 | 0.84 | 0.88 | 0.77 |
| Sulfur | 0.67 | 0.57 | 0.67 | 0.63 |

To truly decouple the actual cause and effect, if possible with a relatively small sample size we need to use multivariable correlation analysis techniques used in big data analysis which will be considered for future work.

### 6.3.3. Relaxation of Herder-Oil Containment Force Over Time

The change, generally a decrease, in the containment energy over time as the monolayer supplied the by the herder dissipates is measured and correlated to the quantities in Table 8. The change is computed by substituting thickness at 60 minutes and at 15 minutes into equation [4] to compute $F_c$ for each and then subtracting $F_c$ at 60 minutes from that at 15 minutes.

Table 8: Correlation of the % change in net containment force for Oil to OP-40, Oil to ThickSlick between 15 minutes and the end of the 60 minute test.

| Linear Correlation Coeficient R | OP-40 (All Temp.) | ThickSlick |
|---|---|---|
| Log(viscosity) | -0.18 | -0.21 |
| API | 0.04 | 0.46 |
| Density | -0.04 | -0.44 |
| Saturates | -0.31 | 0.56 |
| Aromatics | 0.31 | -0.49 |
| Resins | 0.17 | -0.60 |
| Asphaltenes | 0.21 | -0.27 |
| Sulfur | 0.31 | -0.43 |
| Temperature | 0.74 | -0.09 |

The OP-40 shows very low correlations except for temperature. Throughout the experiment the OP-40 is clearly closer to breakdown of the interfacial containment than the ThickSlick and whatever mechanism contributes to the breakdown is being explored with this exercise. The table shows the OP-40 containment force degrading significantly faster proportional to temperature. The first thing that comes to mind is a reaction rate based effect or a mixing effect as both of which increase with temperature. ThickSlick has a very low correlation with temperature. The temperature effect on both herders can be seen in Figure 38.

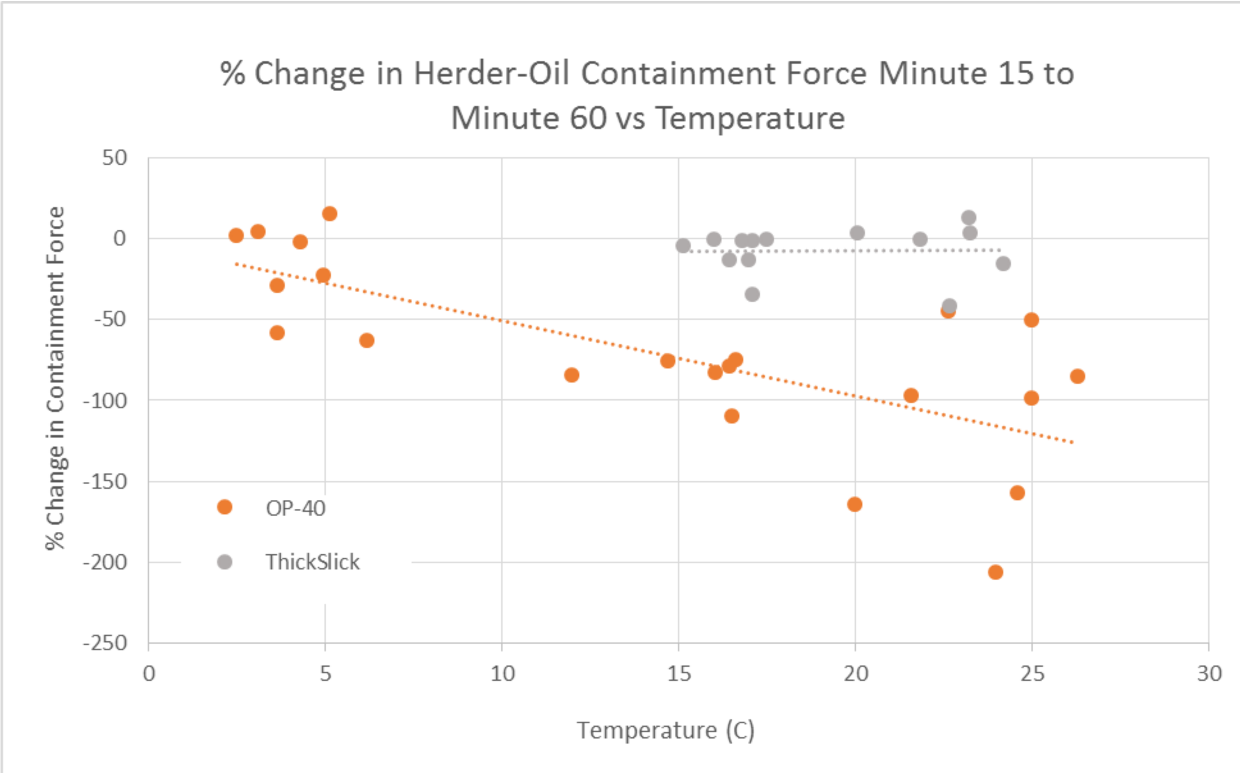


Figure 38: Change in containment energy from 15 minutes to 60 minutes versus temperature

The ThickSlick correlation with saturates or resins is not notable. The plot shown in Figure 39 shows a central scatter zone with no real pattern and a few outliers. The same two showing a large negative change in containment force are outliers in both plots and if removed take away any significant pattern. There clearly would need to be a specialized selection of oils that are both high in both resins and saturates and a selection that are low in both to prove a relationship with ThickSlick. Using a lower amount of ThickSlick to get a larger percent change as it wears off would help create more informative statistics.

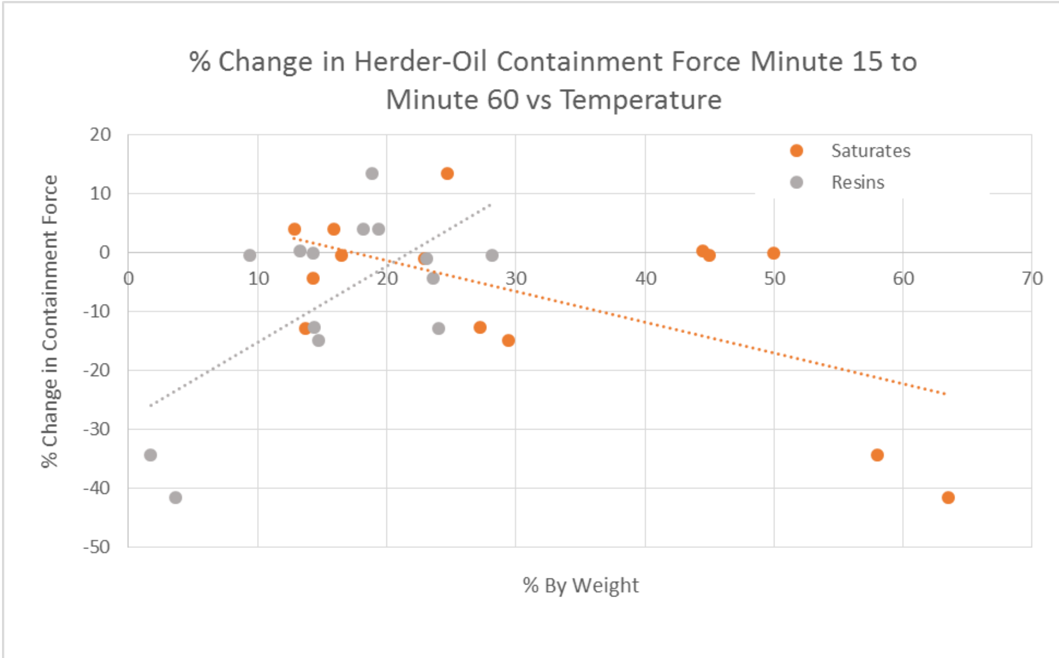


Figure 39: Change in containment force 15 minutes to 60 minutes versus saturates and resins for ThickSlick.

# 7. CONCLUSION

The experimental procedure based on the proposed 1m$^2$ tray ASTM standard was refined to increase repeatability for the same oil-herder combination. Through a series of trial and error experiments, the procedures outlined here show a reduction in the amount of oil for testing, a more consistent application of oil using an oil containment ring, and a manual air blowing technique to keep the oil from attaching to the tray sides. The automated direct acoustic thickness measurement, 0.2 Hz to 2 Hz and continuous area computation at 5 Hz to 30 Hz allowed detailed tracking of the slick and a high confidence level in the standard error for the runs. The density of the data allowed an accurate determination of variables indicative of herder effectiveness and create numerous quantitative metrics to enumerate the herder effectiveness for instance maximum slick thickness, which relies on a high enough density of data to locate the maximum thickness which may have not been missed with coarse data acquisition. .

In all there were 149 runs using the 14 oils and 2 herders. The matrix was divided into runs using room temperature water and oil that averaged 20°C and runs using cooled oil and water averaging a temperature of 4°C. Notable findings were that ThickSlick created a lower initial thickness than OP-40 consistently but maintained that thickness for a longer time. OP-40 relaxed faster over time. The patterns can be seen in APPENDIX B.

Other conclusions show viscosity as the primary driver for herder effectiveness as defined as the maximum thickness obtained and the ability to hold the thickness over time. The value of the highest containing force for each herder has a strong correlation with the % Asphaltenes, and the ability to hold the thickness over time for OP-40 is related strongly to temperature, where the herder holds better for longer at cold temperatures.

## 7.1. FUTURE WORK

Future studies introducing wind and waves into the tank would be valuable. The experiment used a slight puff of air to keep the sample off the sides of the tray. The same technique could be used to blow the sample back and forth at different rates for the full hours. The constant video monitoring and feedback would be used to automatically control the air streams. The vibration could be used to generate small sating waves. The large scale environment at Ohmsett could ultimately be used to test wind and waves on the herder-oil interaction with the notable addition of the high speed thickness and area measurement.

Since the viscosity and density of oil correlates with the SARA components it is difficult to decouple the effect of viscosity from Asphaltenes for example with linear correlation alone. A careful multivariable statistical analysis of the data may be able to clarify the true dependencies between SARA, sulfur, viscosity and density to herder effectiveness.

Using the herder dosage of 160 μl for both of the herders created a mono layer that was very stable for ThickSlick and less stable for OP-40 over the 60 minutes. It would be useful to repeat the test matrix using a lower amount of the ThickSlick in order to induce mono-layer breakdown earlier. The rate and timing of the breakdown could be then studied to identify if any of the oil properties and components studies here affect the ThickSlick – oil combination effectiveness over time.

As the major effort in this project was in refining the experimental apparatus to achieve repeatability there is a huge opportunity in follow-on lab testing using this apparatus. Follow on testing using the process here is relatively inexpensive for the amount of added information supplied. More herder oil interaction would strengthen the database and increase the ability to statistically decouple the correlations between SARA components from the viscosity effects.

## 8. REFERENCES


1. Venosa, A.D., Holder, E., 2011. Laboratory-Scale Testing of Dispersant Effectiveness of 20 Oils Using the Baffled Flask Test. U.S. Environmental Protection Agency, March 2011.

2. Fingas, Merv. Review of the North Slope Oil Properties Relevant to Environmental Assessment and Prediction. Spill Science, Edmonton, Alberta, Canada, June 2010

3. USEPA, TECHNICAL PRODUCT BULLETIN #S-5, “THICKSLICK 6535”. OEM REGULATIONS IMPLEMENTATION DIVISION, LISTING DATE: JUNE 29, 2012

4. USEPA, TECHNICAL PRODUCT BULLETIN #S-6, “Siltech OP-40”. OEM REGULATIONS IMPLEMENTATION DIVISION, LISTING DATE: JUNE 29, 2012

5. SL Ross Environmental Research Ltd. REVIEW OF ASTM STANDARDS FOR OIL SPILL RESPONSE EQUIPMENT. U.S. Department of the Interior Bureau of Safety and Environmental Enforcement, February 17, 2015

6. Fingas, Merv. Review of Oil Spill Herders. Spill Science, Edmonton, Alberta, 2014

7. Buist, I. and P. Meyer, Research on Using Oil Herding Agents for Rapid Response In-situ Burning of Oil Slicks on Open Water, AMOP, p. 480-505, 2012

8. Fay, J.A., 1971. Physical processes in the spread of oil on a water surface. In International Oil Spill Conference, American Petroleum Institute 1971(1), 463-467.

9. Garrett, W., Barger, W., 1970. Factors affecting the use of monomolecular surface films to control oil pollution on water. Environ. Sci. Technol. 4 (2) February 1970.

10. Langmuir, I., 1933. Oil lenses on water and the nature of the monomolecular expanded films. J. Chem. Phys. 10 November 1933.

11. Buist, I., S. Potter, T. Nedwed and J. Mullin, Herding Surfactants to Contract and Thicken Oil Spills in Pack Ice for In-situ Burning, Cold Regions Science and Technology, (67) 41306, p. 3- 23, 2011

12. http://www.intertek.com/petroleum/testing/sara/

13. ASTM D341-17, Standard Practice for Viscosity-Temperature Charts for Liquid Petroleum Products, ASTM International, West Conshohocken, PA, 2017, www.astm.org

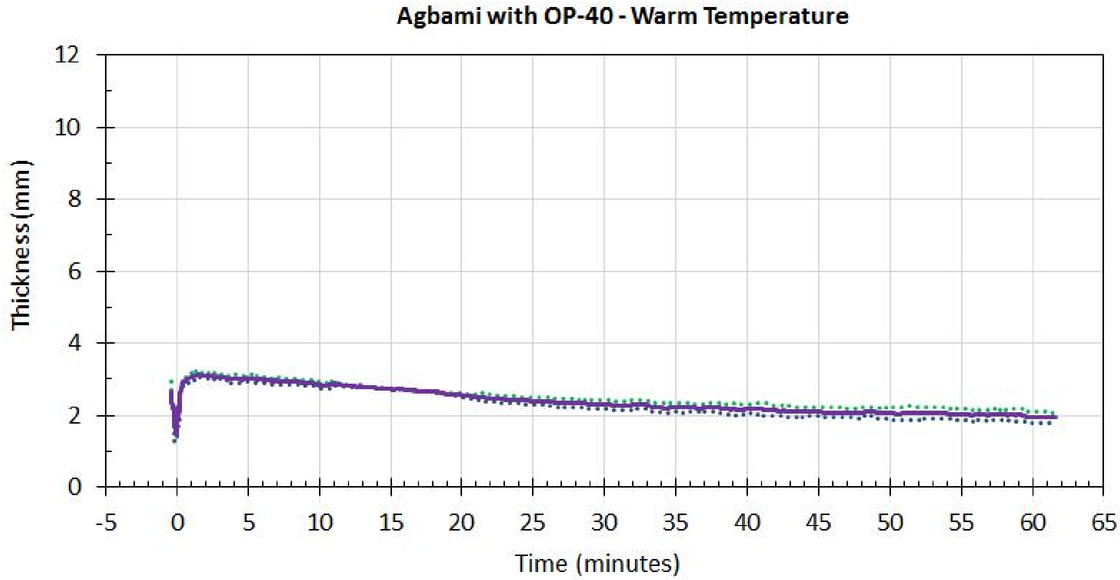
14. ASTM D1250-04, Standard Guide for Use of the Petroleum Measurement Tables, ASTM International, West Conshohocken, PA, 2004, www.astm.org

# 9. APPENDIX A: THICKNESS AND AREA RESULTS FOR EACH TEST

The data below show the average thickness and the standard error for multiple replicate tests as a function of time for the 14 oils tested in this project at the warm temperatures which averaged 20°C ± 4°C and cold temperatures which averaged 4°C ±2°C with Siltech OP-40 and ThickSlick 6535.

### HERDER RESULTS AT WARM (20°C) TEMPERATURES

In general OPO-40 caused the oil in reach a higher thickness than Thickslick, but ThickSlick allowed the oil to hold the achieved thickness longer than OP-40, with OP-40 releasing its hold in the 30 to 40 minute range. The higher viscosity oils achieved a thicker slick than the low viscosity oils.



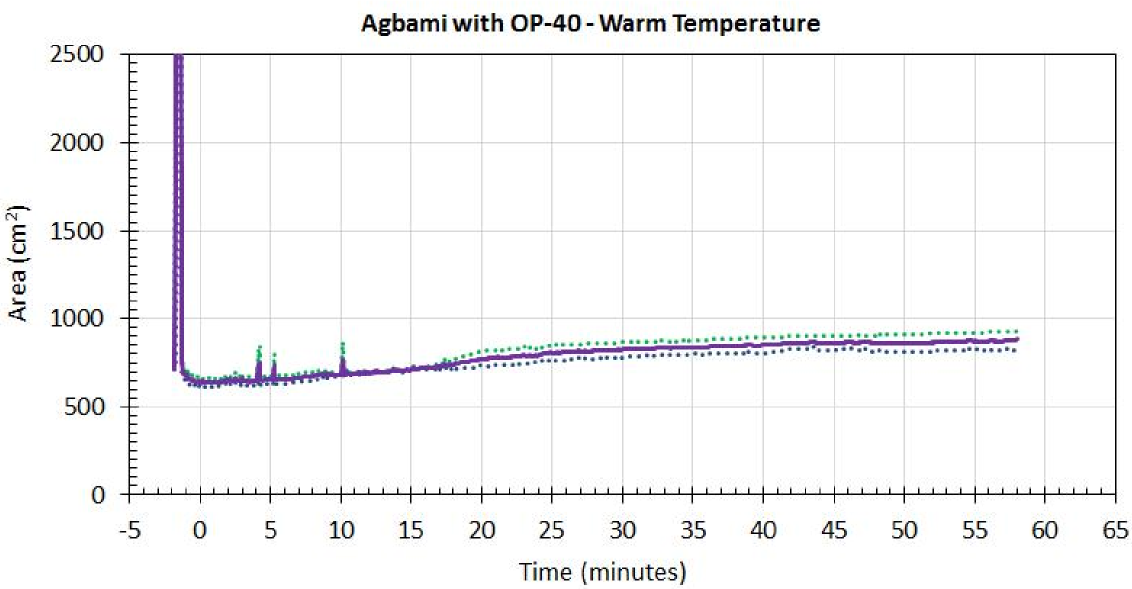




Figure 40: Agbami with OP-40, Warm Temperature, Thickness and Area

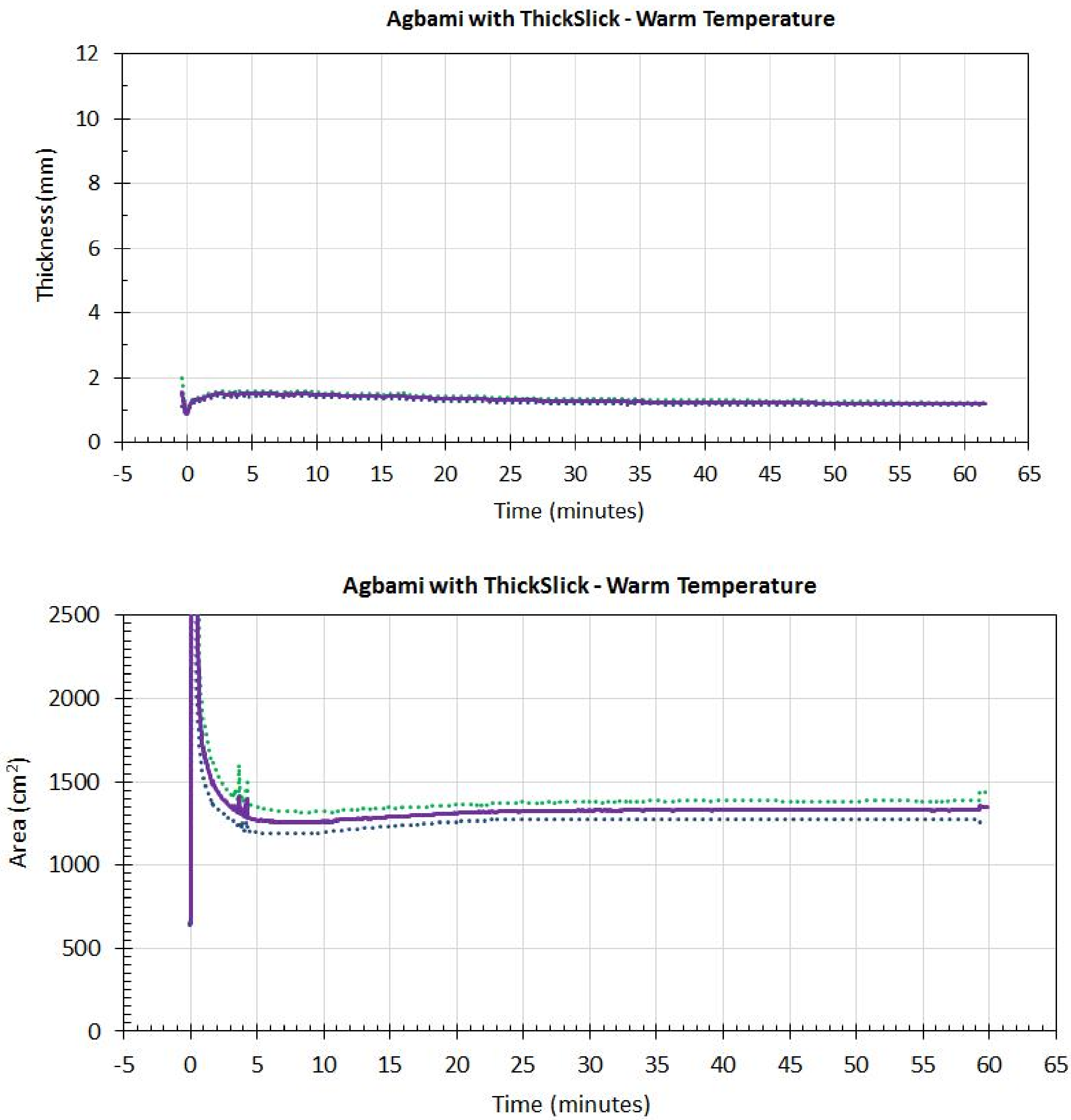



Figure 41.  Agbami with ThickSlick, Warm Temperature, Thickness and Area

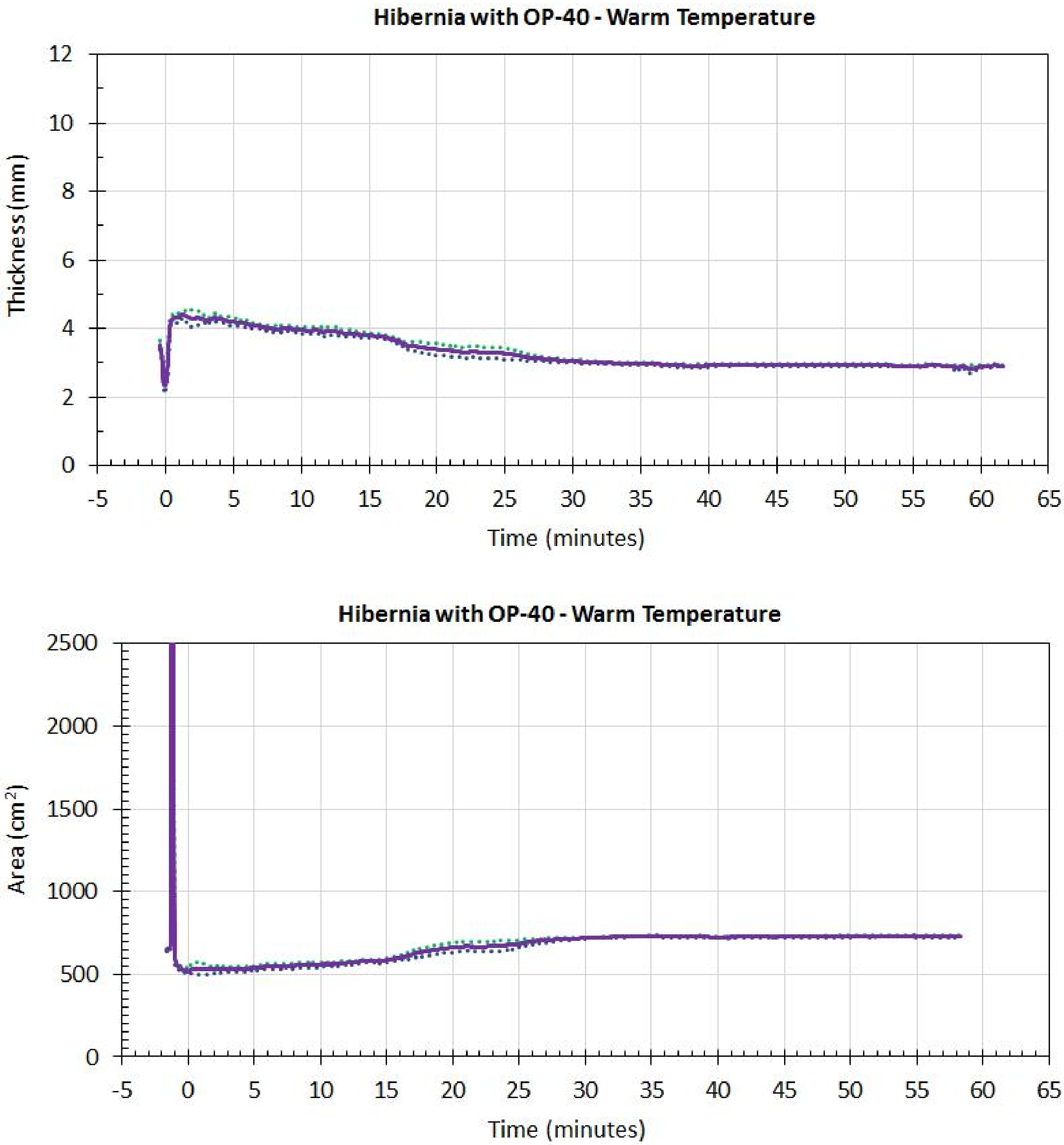
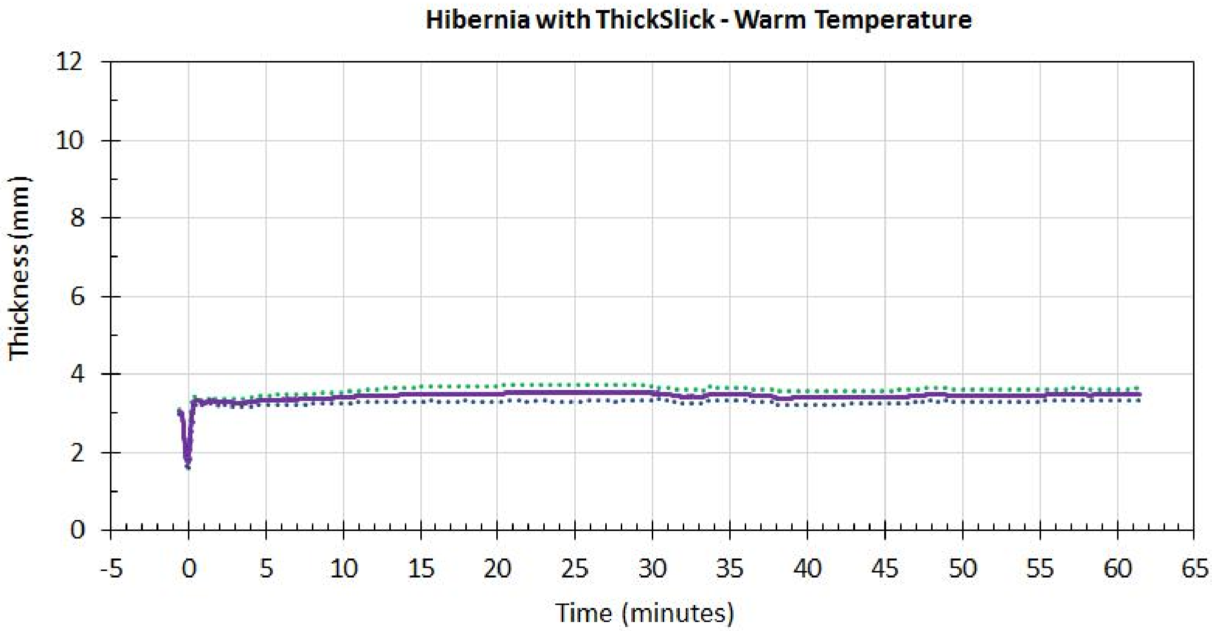



Figure 42: Hibernia with OP-40, Warm Temperature, Thickness and Area



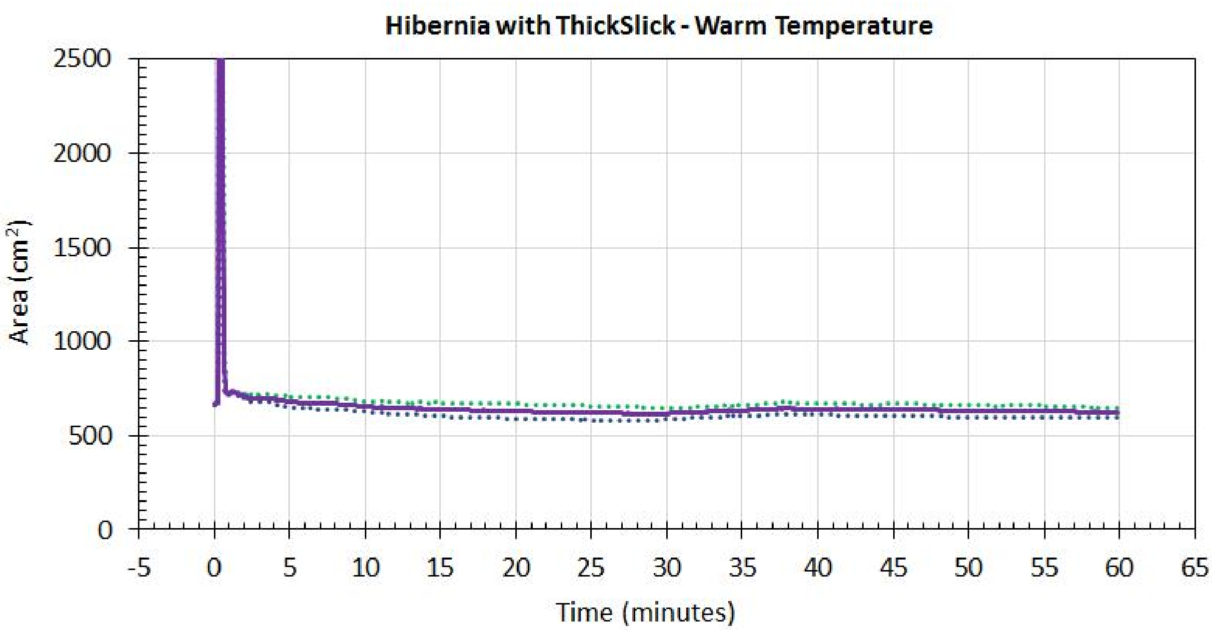
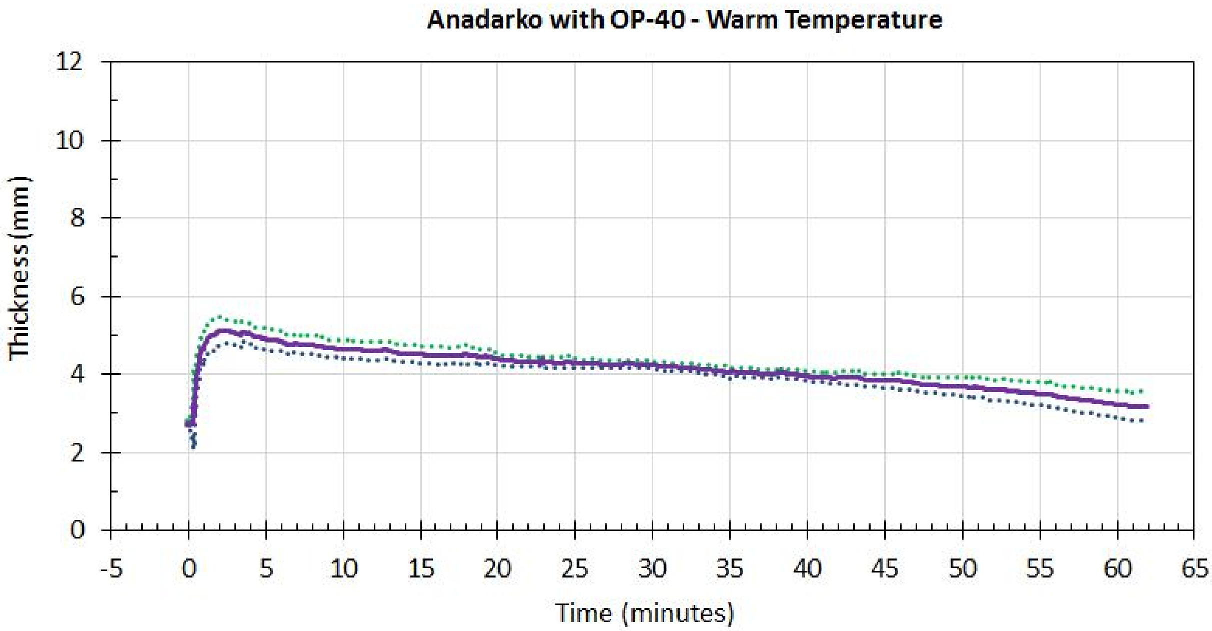




Figure 43. Hibernia with ThickSlick, Warm Temperature, Thickness and Area



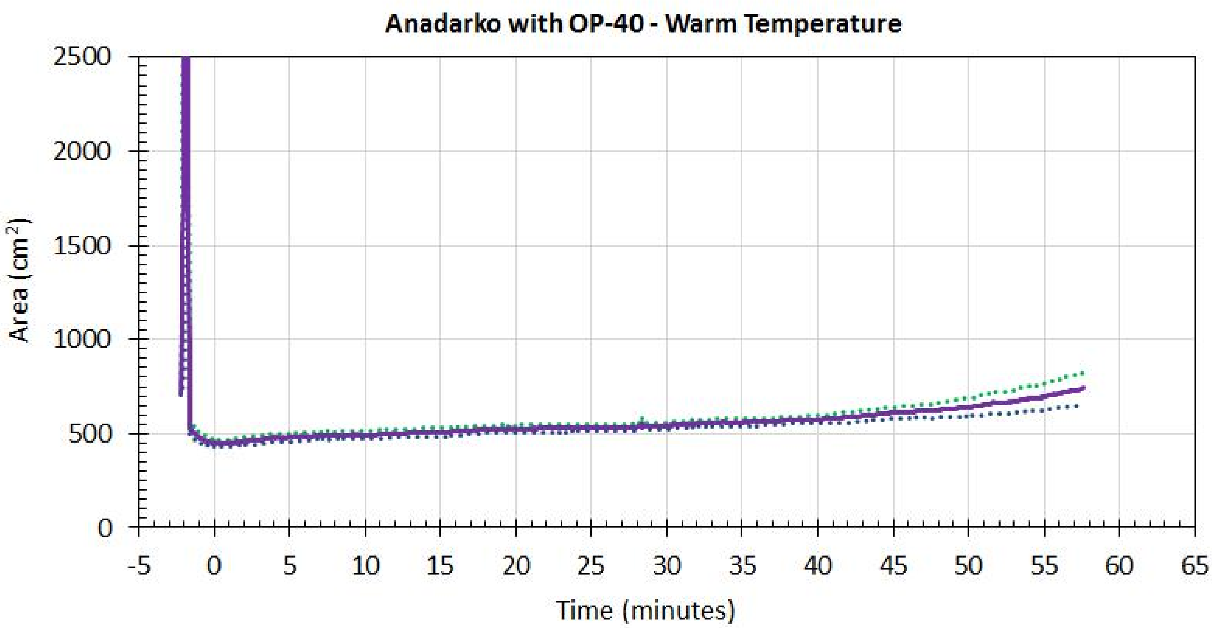
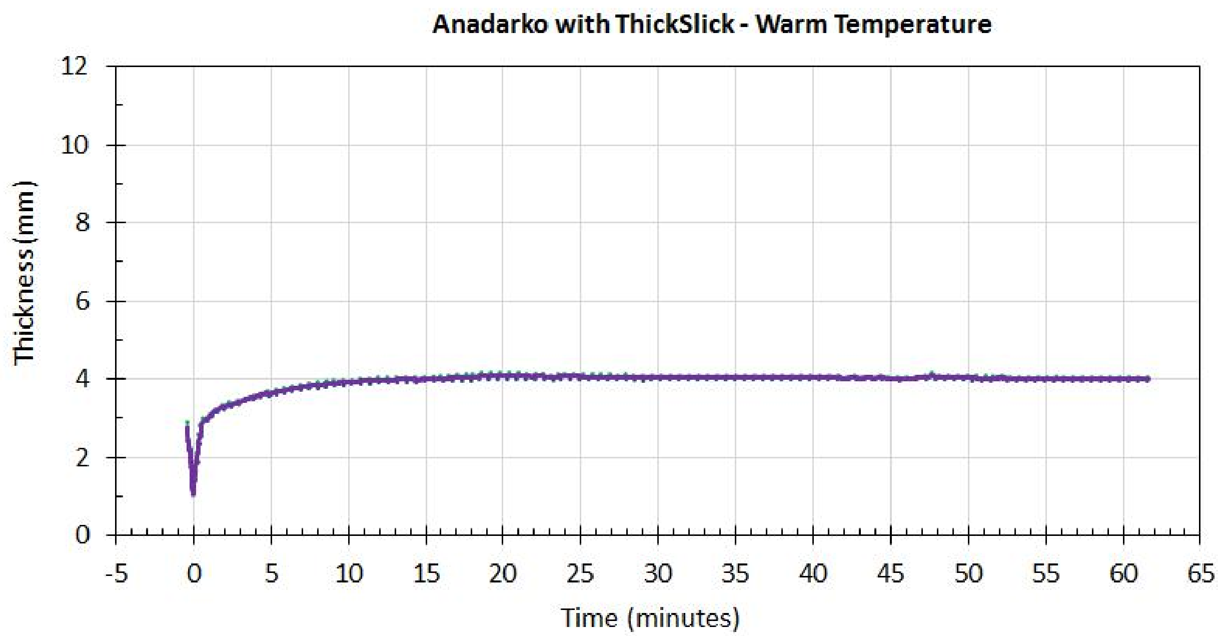




Figure 44: Anadarko with OP-40, Warm Temperature, Thickness and Area



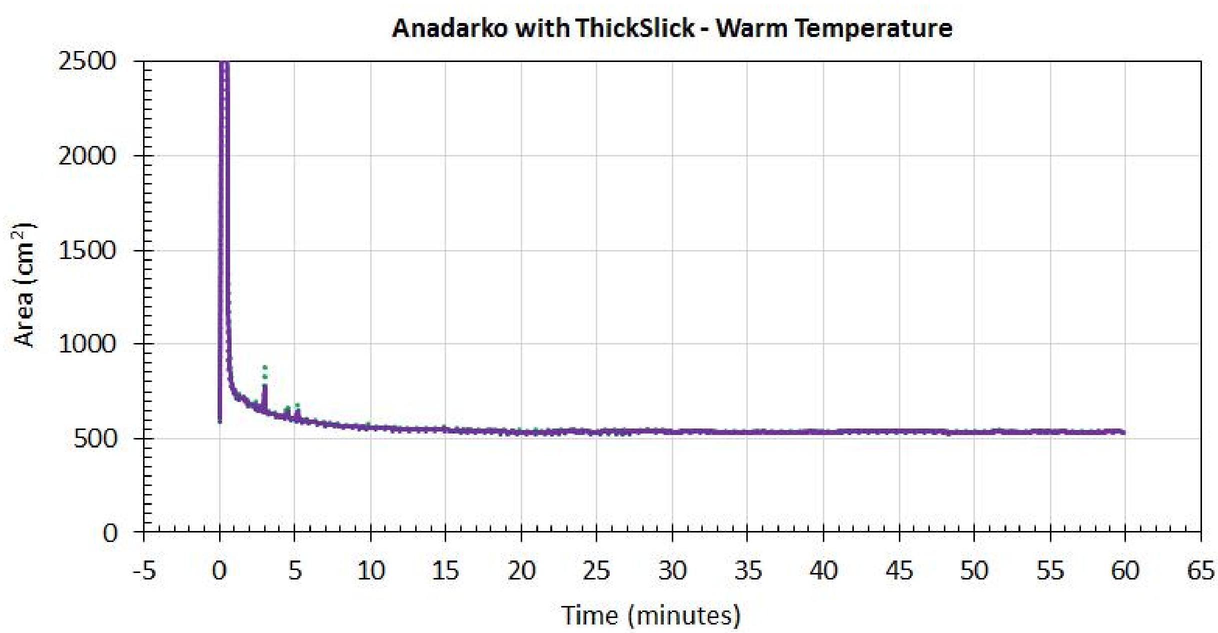
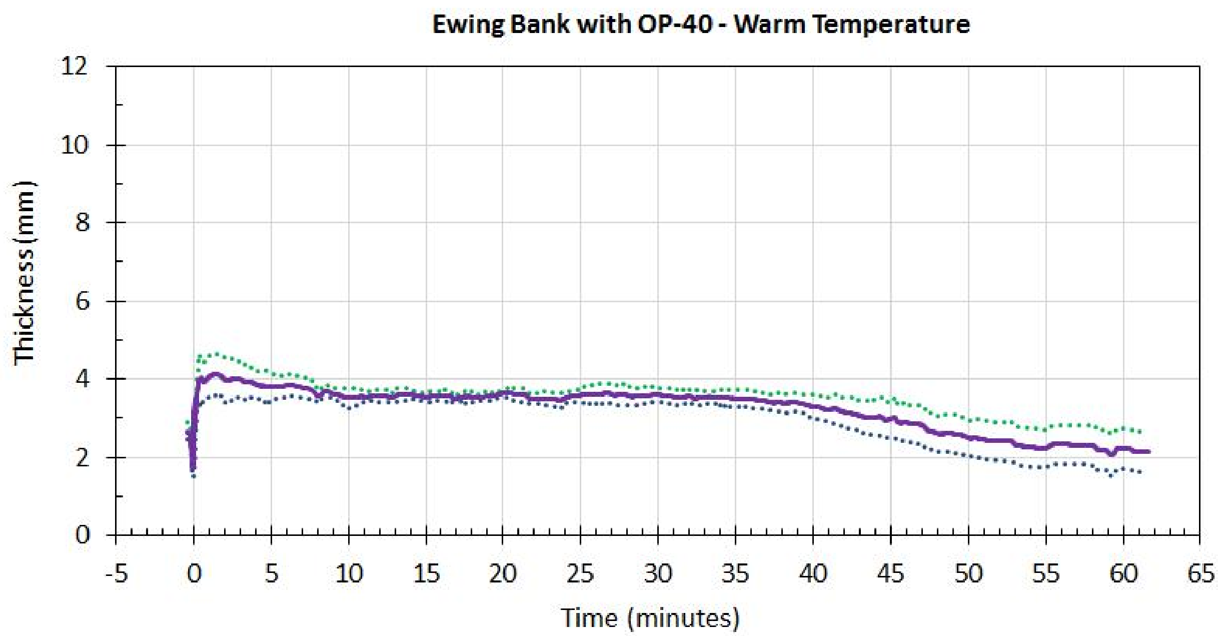




Figure 45.  Anadarko with ThickSlick, Warm Temperature, Thickness and Area



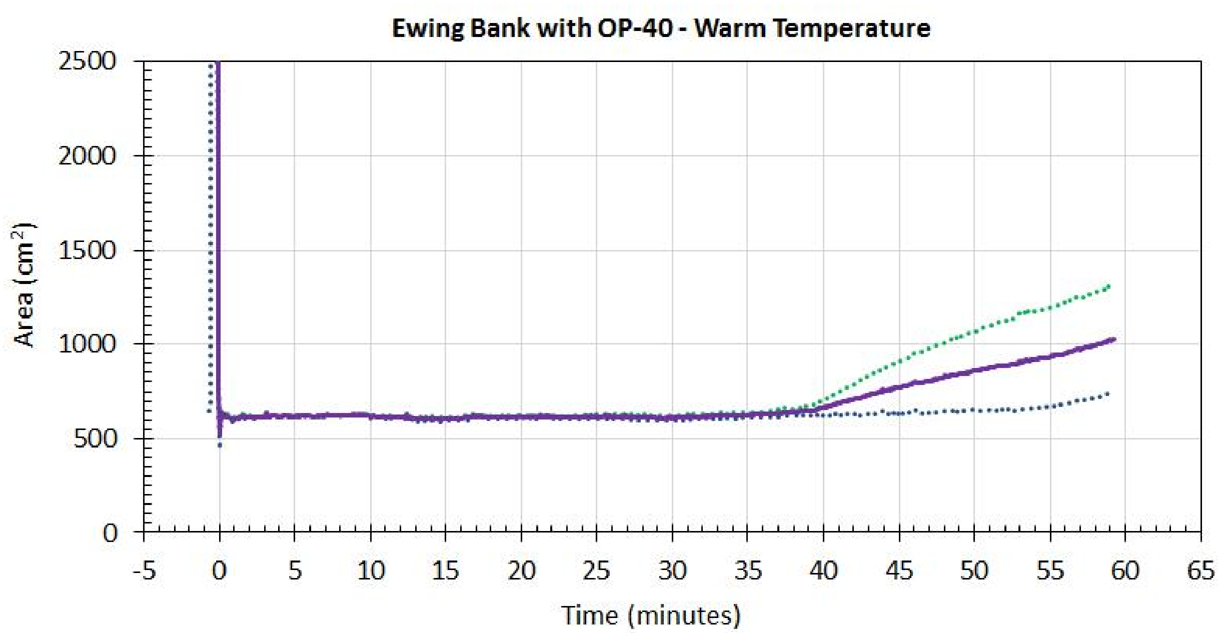




Figure 46: Ewing Bank with OP-40, Warm Temperature, Thickness and Area

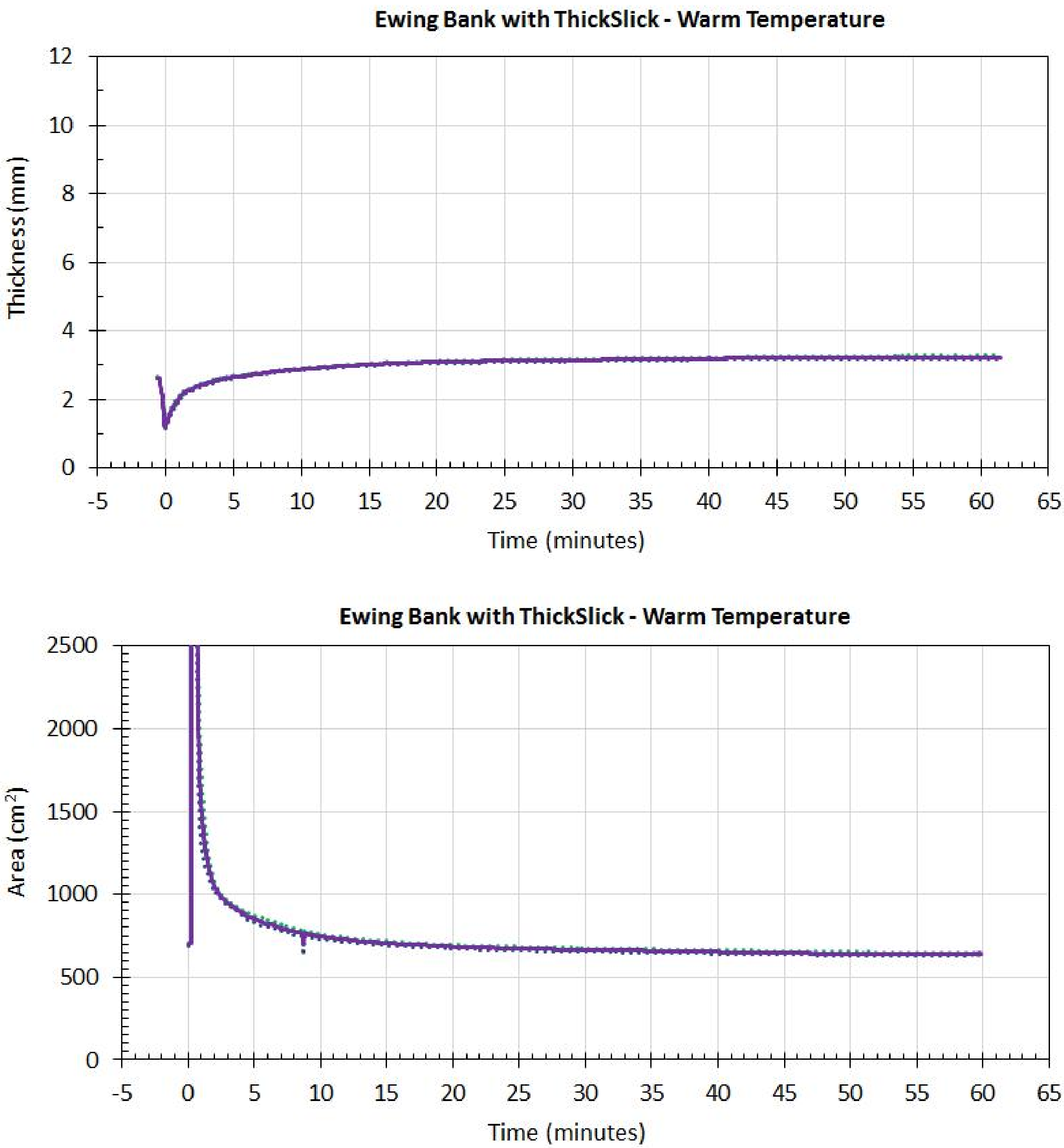
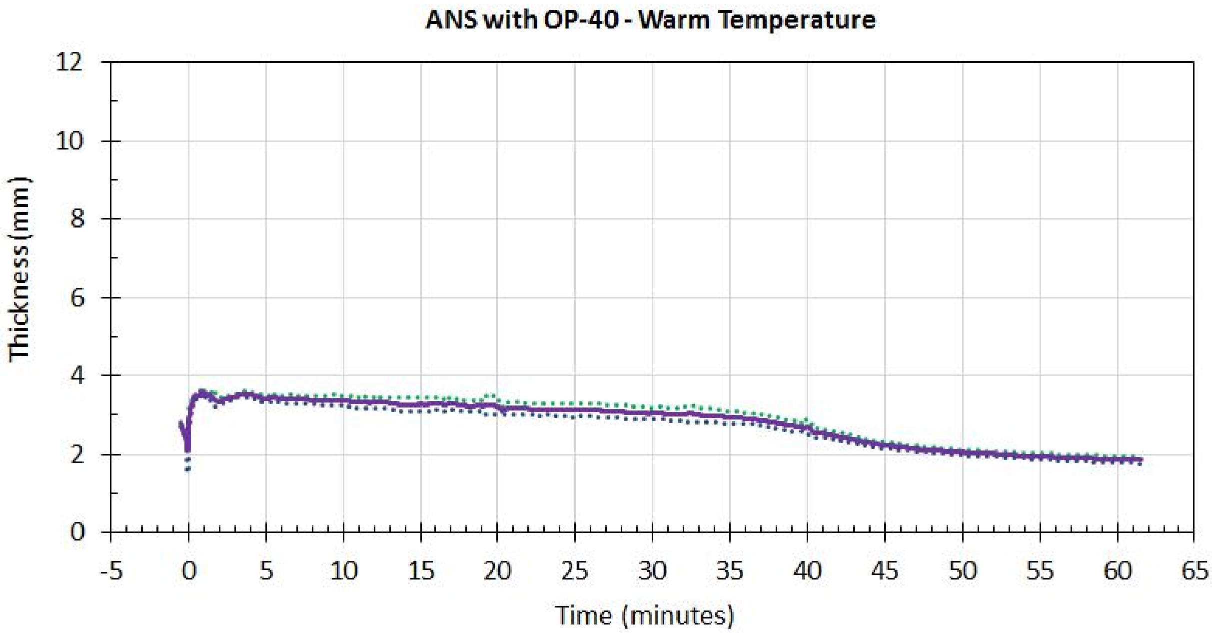



Figure 47. Ewing Bank with ThickSlick, Warm Temperature, Thickness and Area Plot



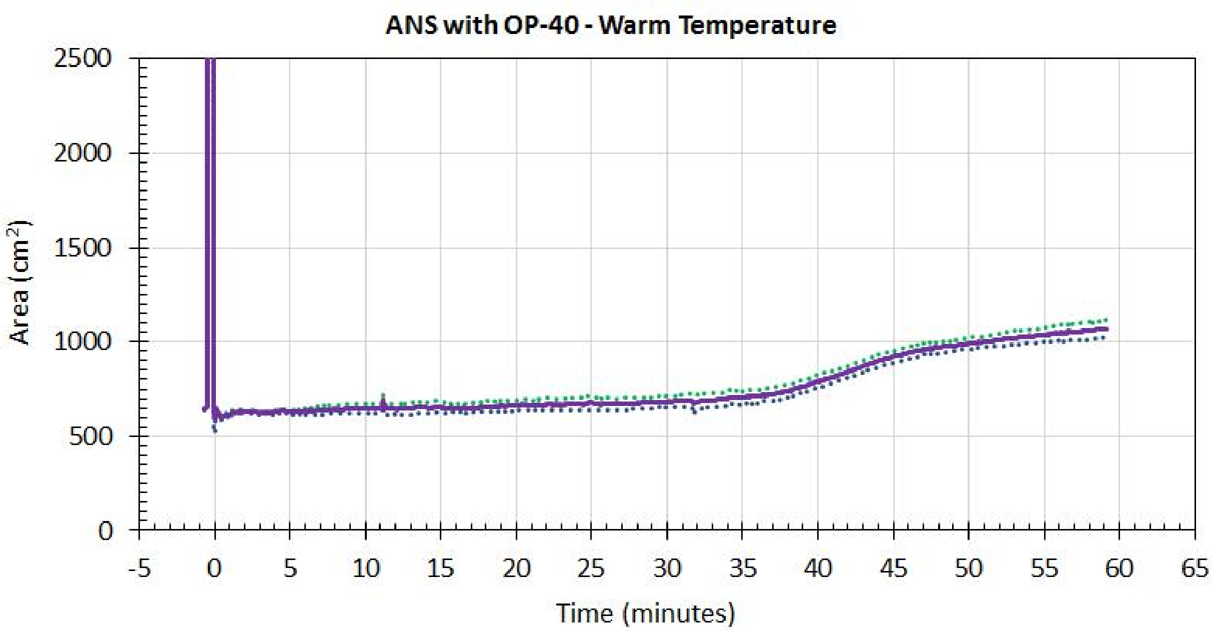
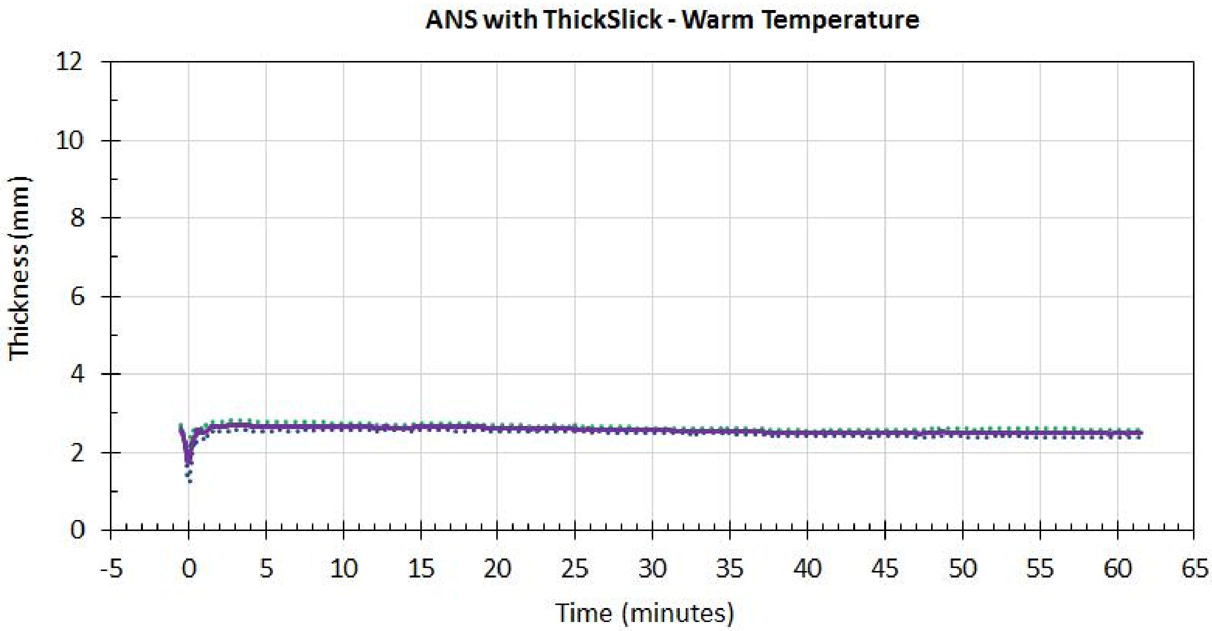




Figure 48: ANS with OP-40, Warm Temperature, Thickness and Area Plot



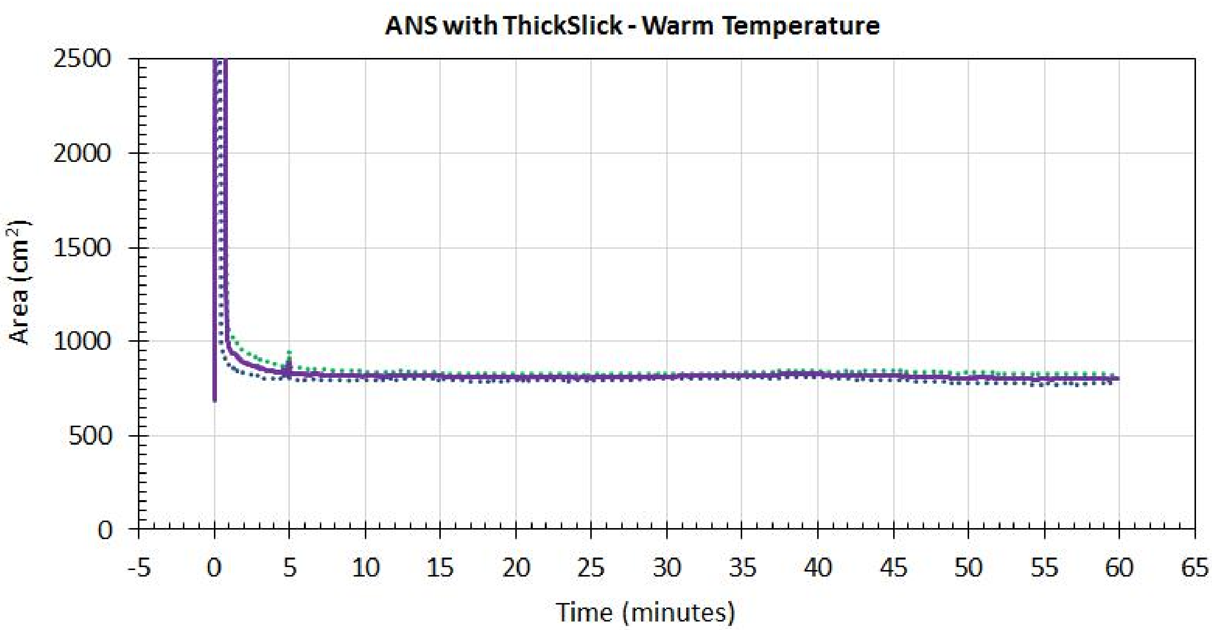
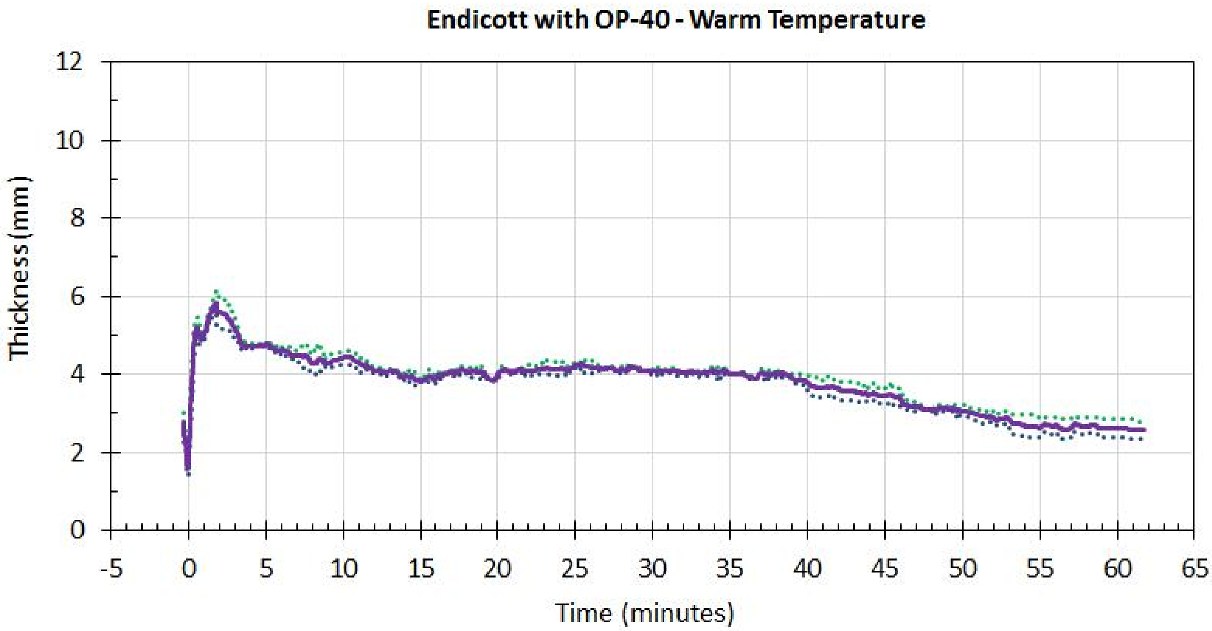




Figure 49. ANS with ThickSlick, Warm Temperature, Thickness and Area Plot



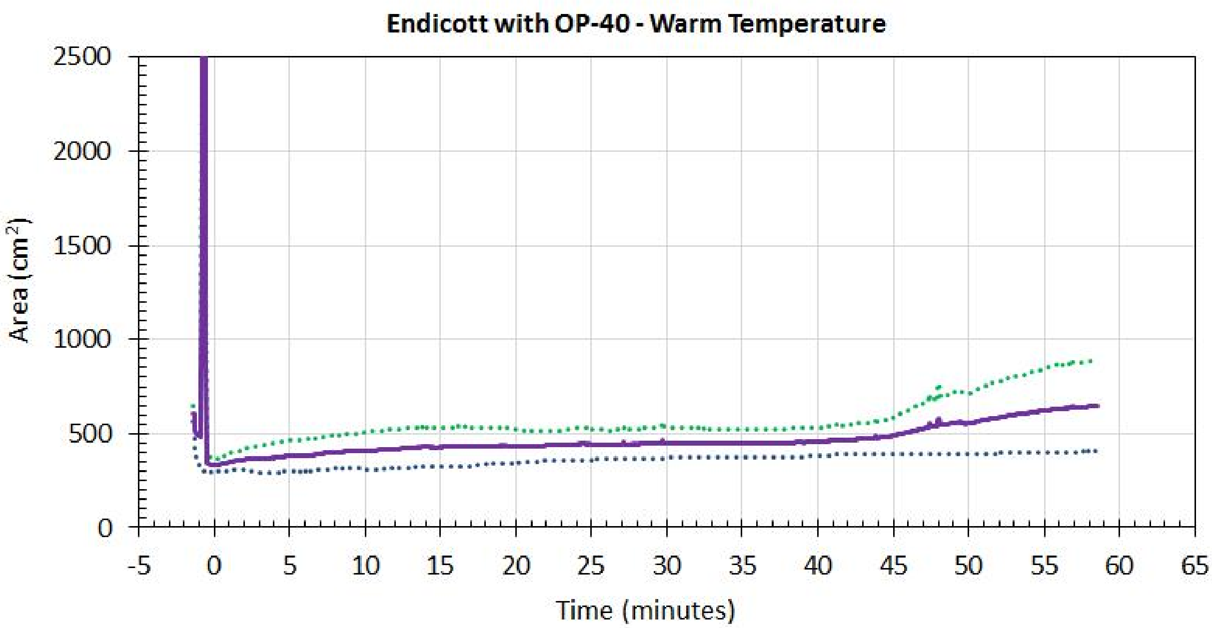
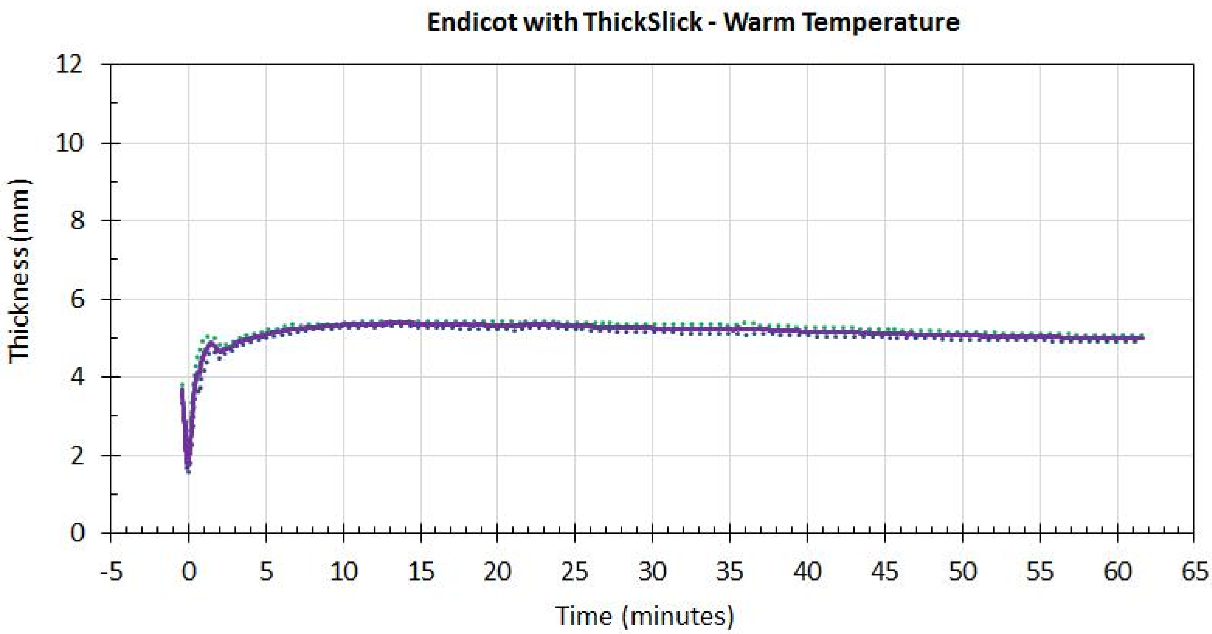




Figure 50: Endicott with OP-40, Warm Temperature, Thickness and Area Plot



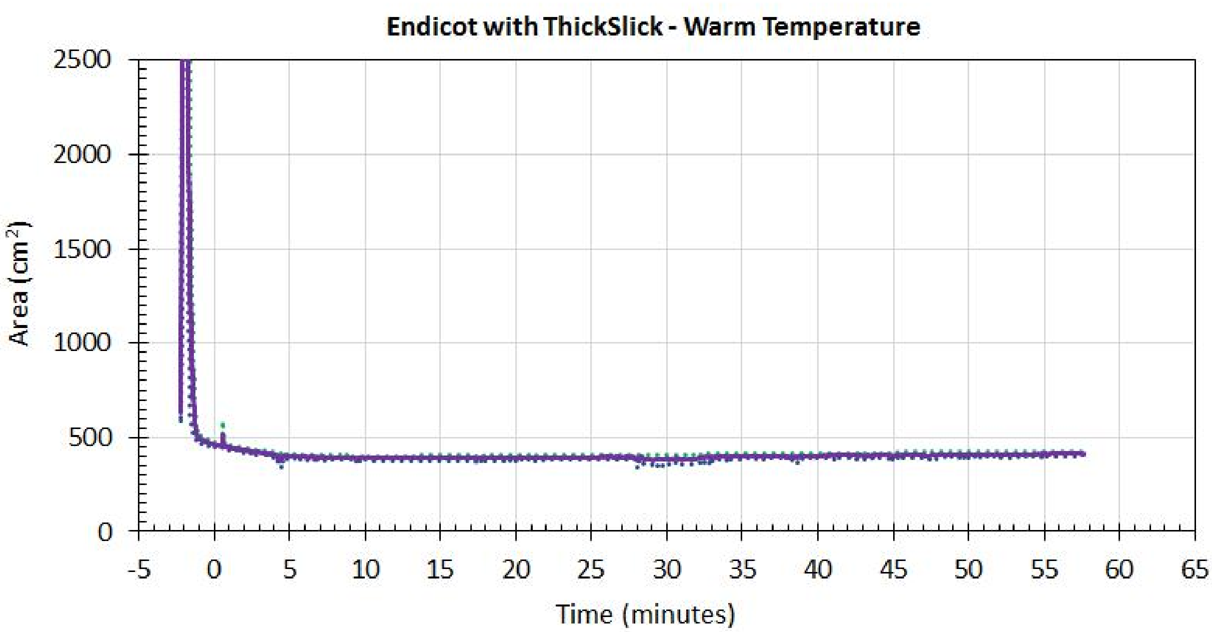
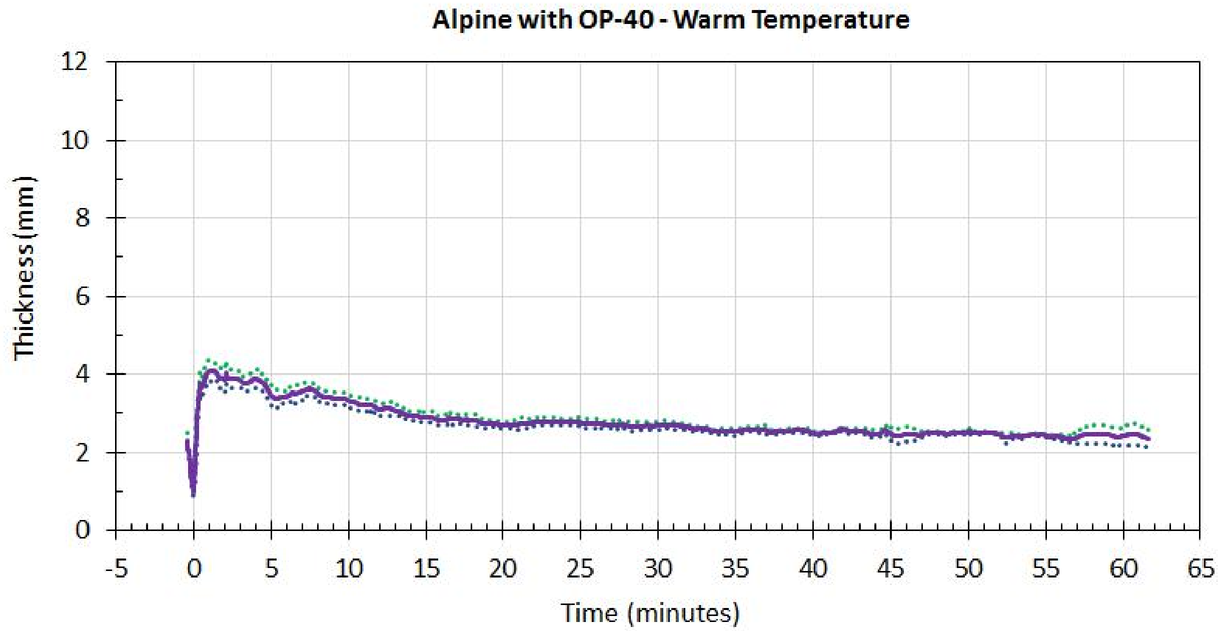




Figure 51. Endicott with ThickSlick, Warm Temperature, Thickness and Area Plot



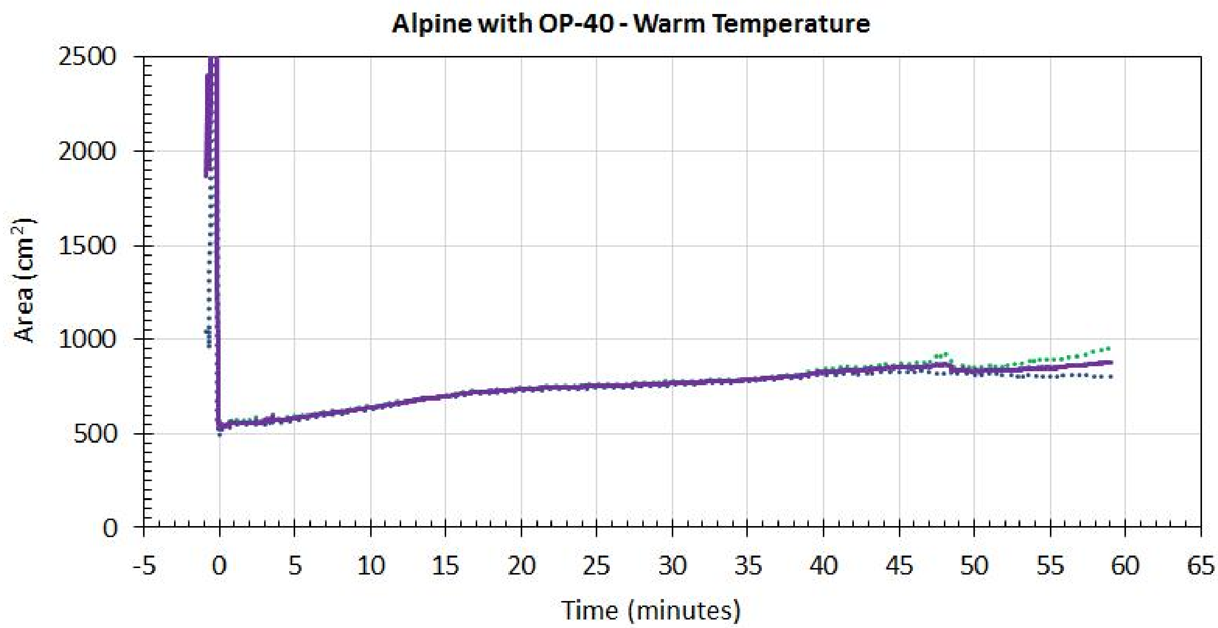
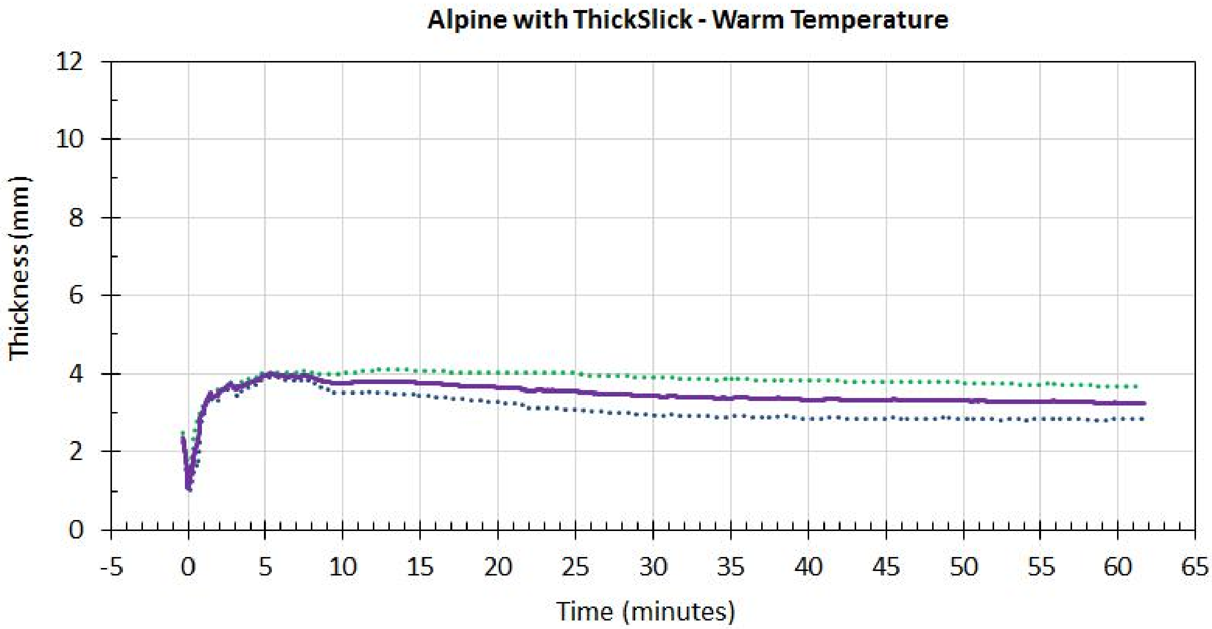




Figure 52: Alpine with OP-40, Warm Temperature, Thickness and Area Plot



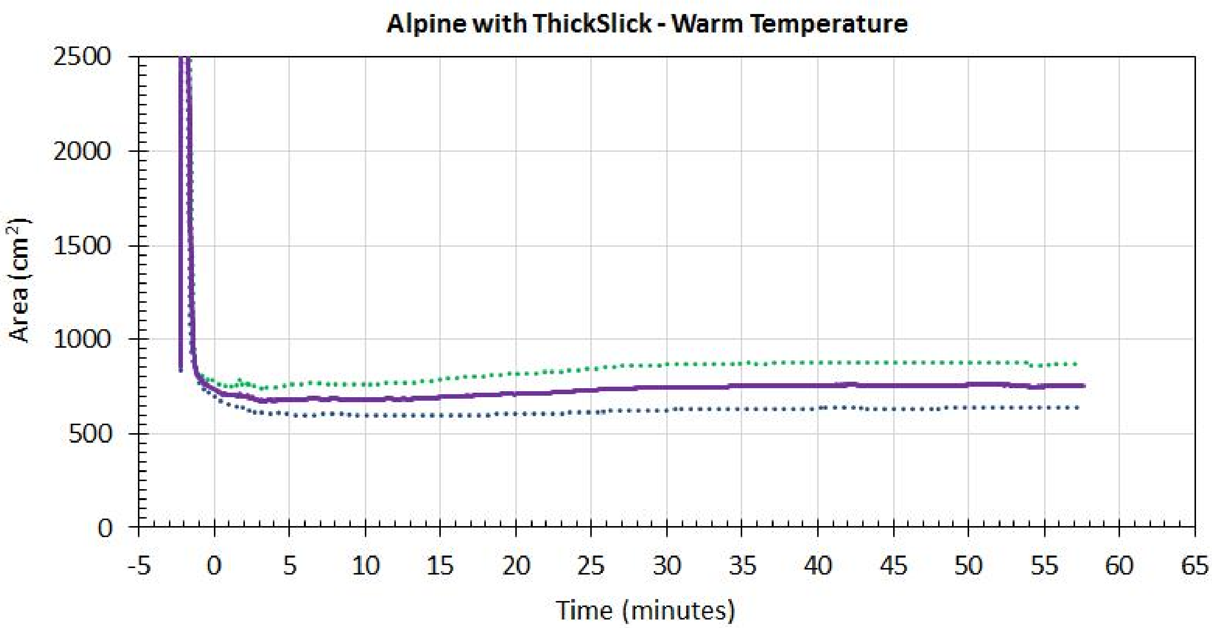
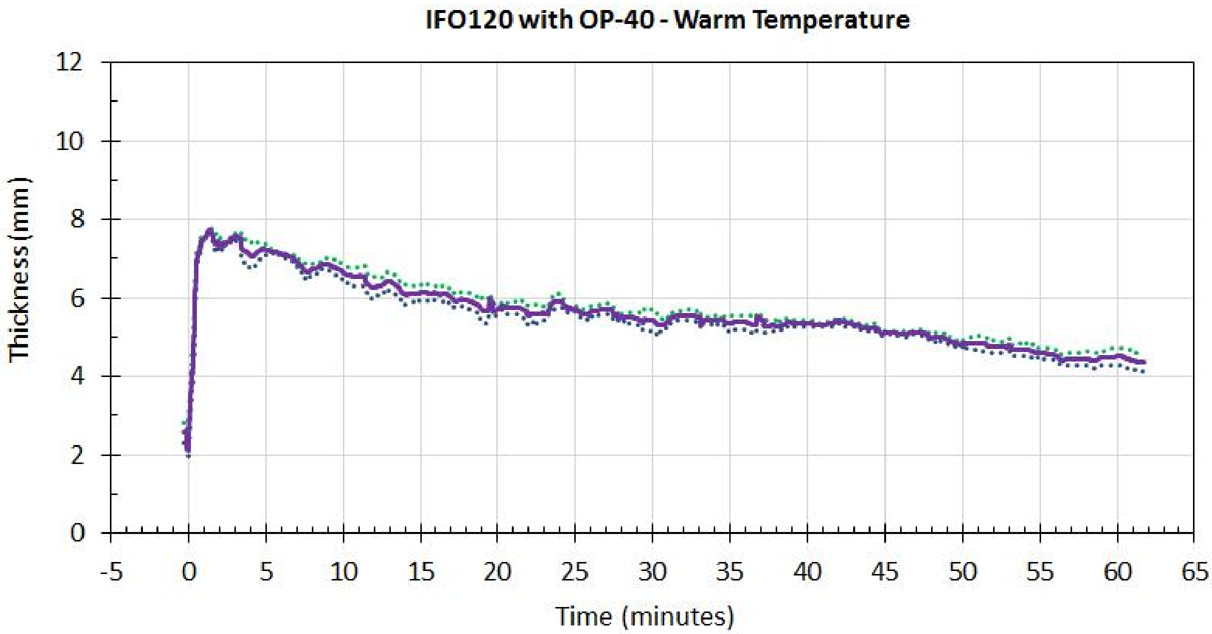




Figure 53. Alpine with ThickSlick, Warm Temperature, Thickness and Area Plot



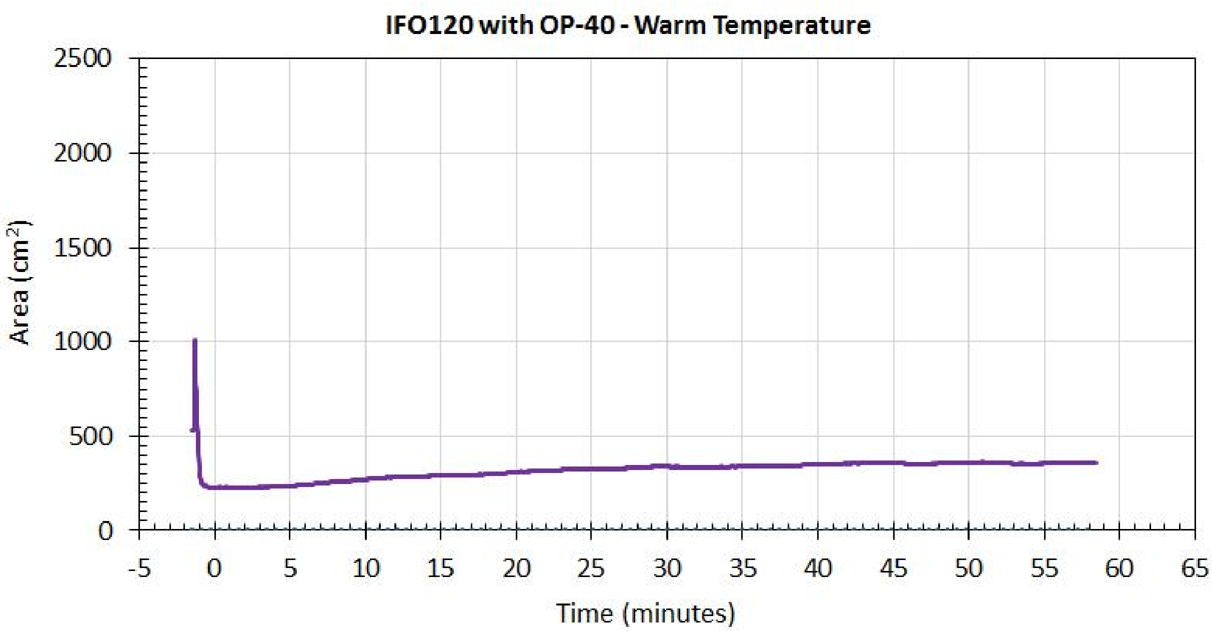
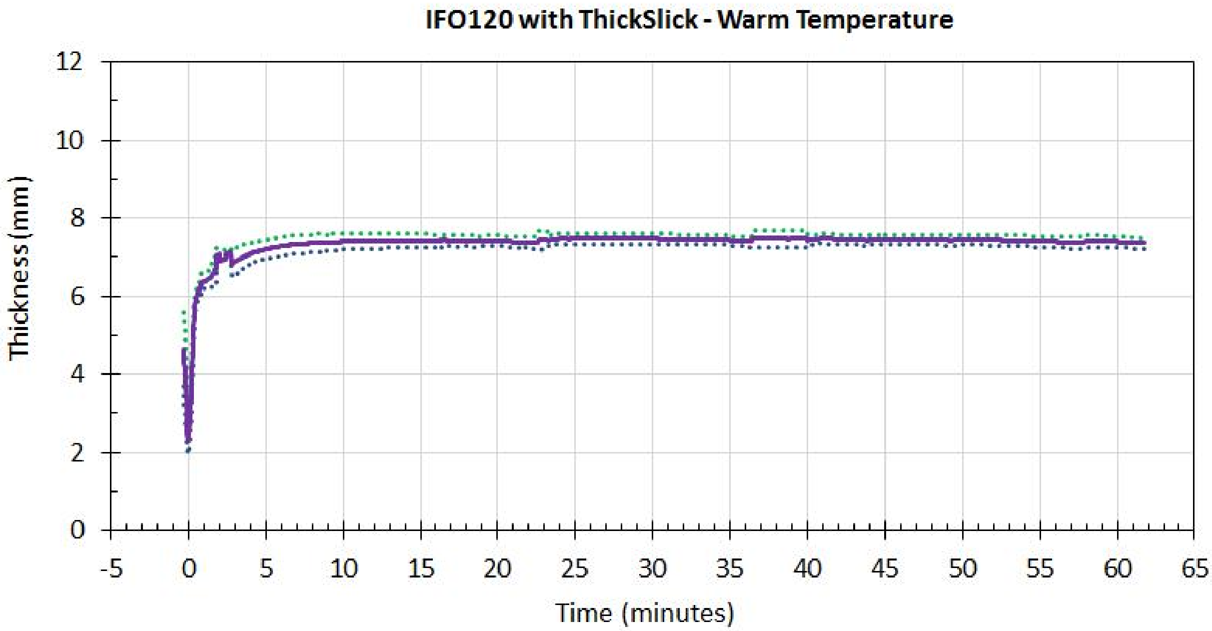




Figure 54: IFO120 with OP-40, Warm Temperature, Thickness and Area Plot



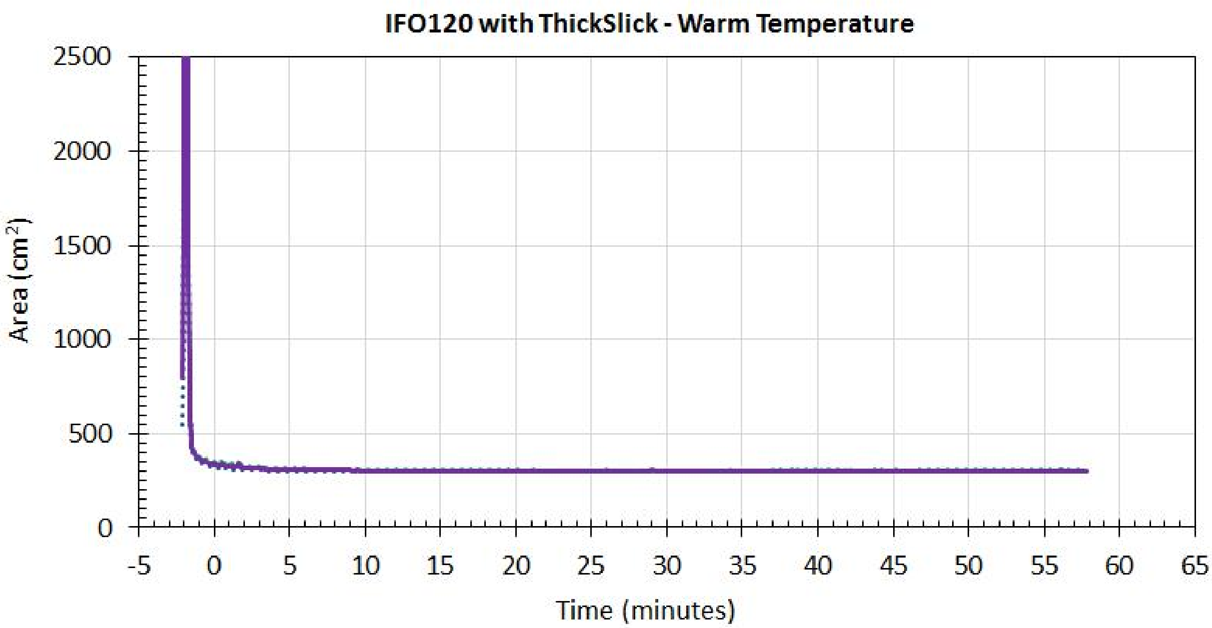
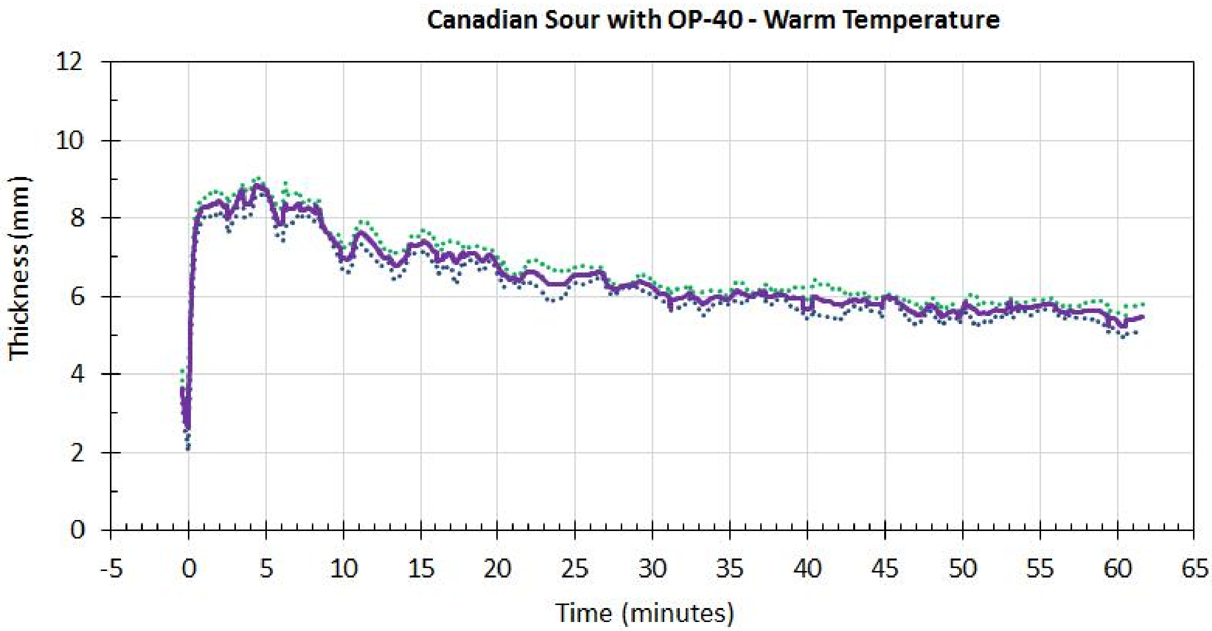




Figure 55. IFO120 with ThickSlick, Warm Temperature, Thickness and Area Plot



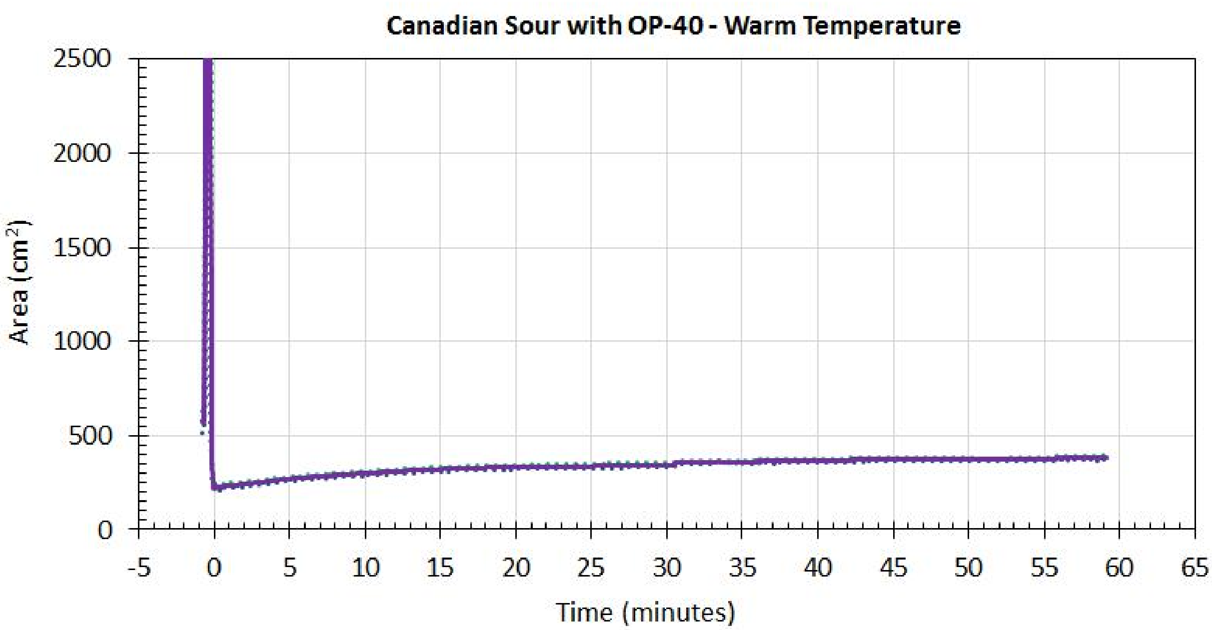
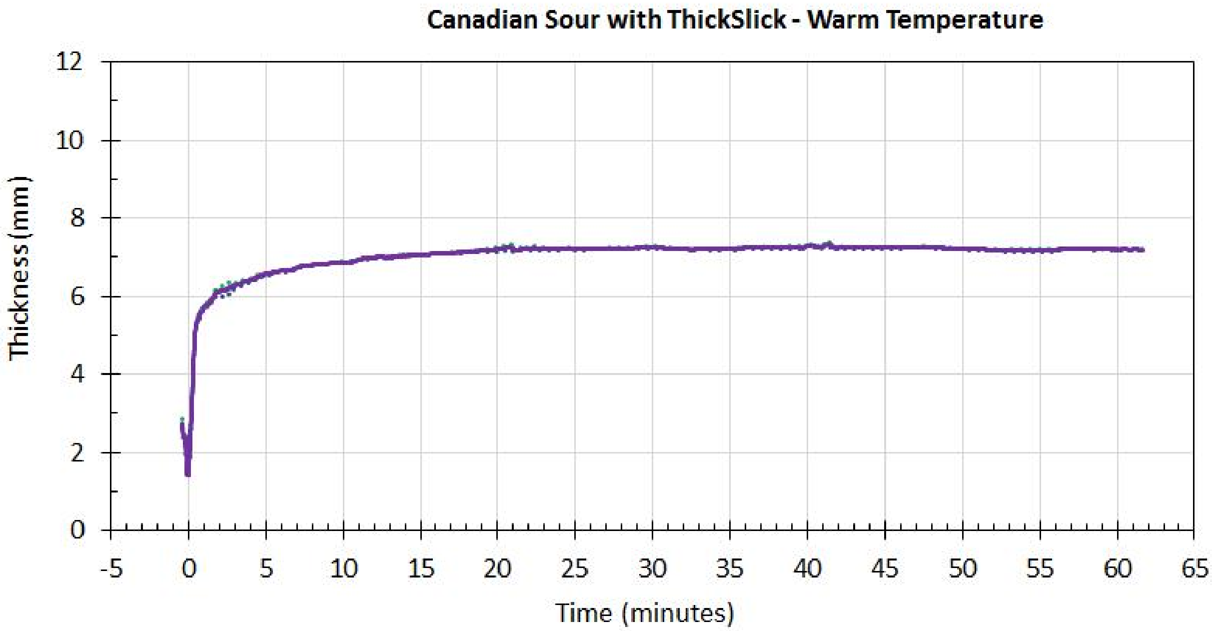




Figure 56: Canadian Sour with OP-40, Warm Temperature, Thickness and Area Plot



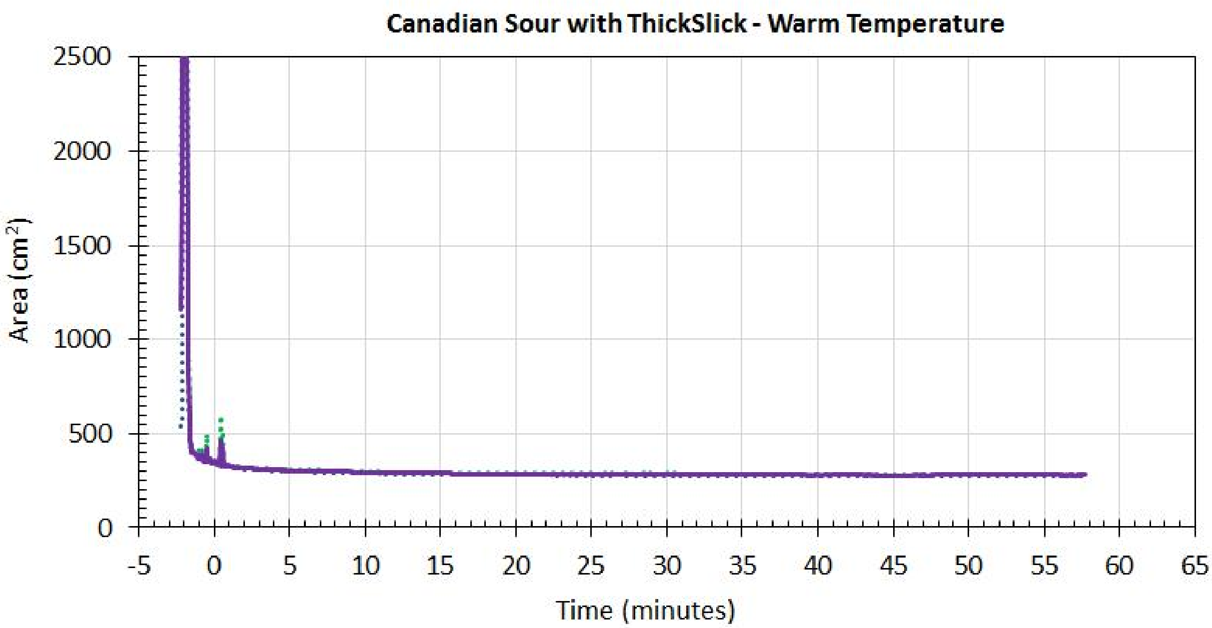




Figure 57. Canadian Sour with ThickSlick, Warm Temperature, Thickness and Area Plot

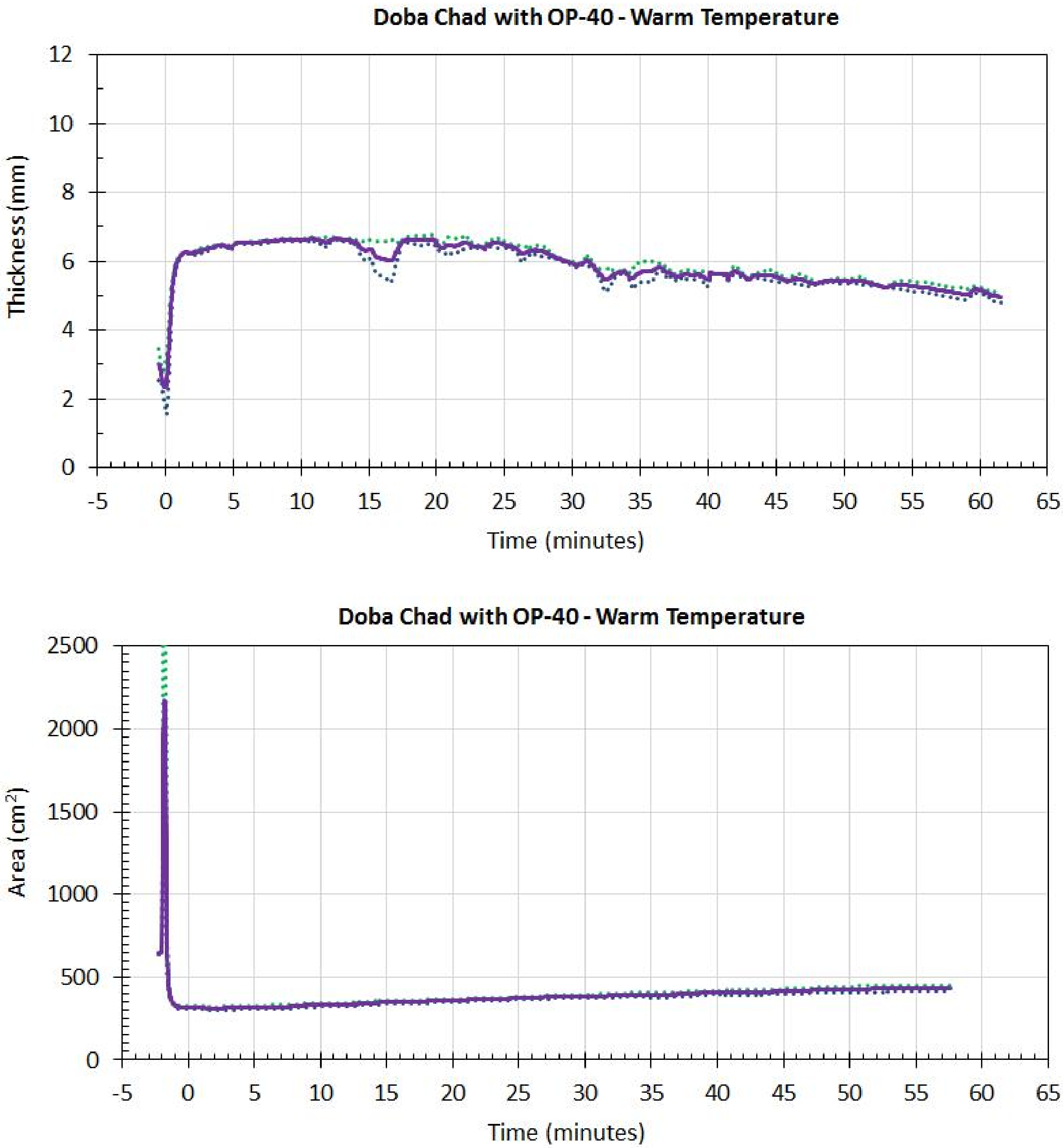


Figure 58: Doba Chad with OP-40 Warm Temperature, Thickness and Area Plot

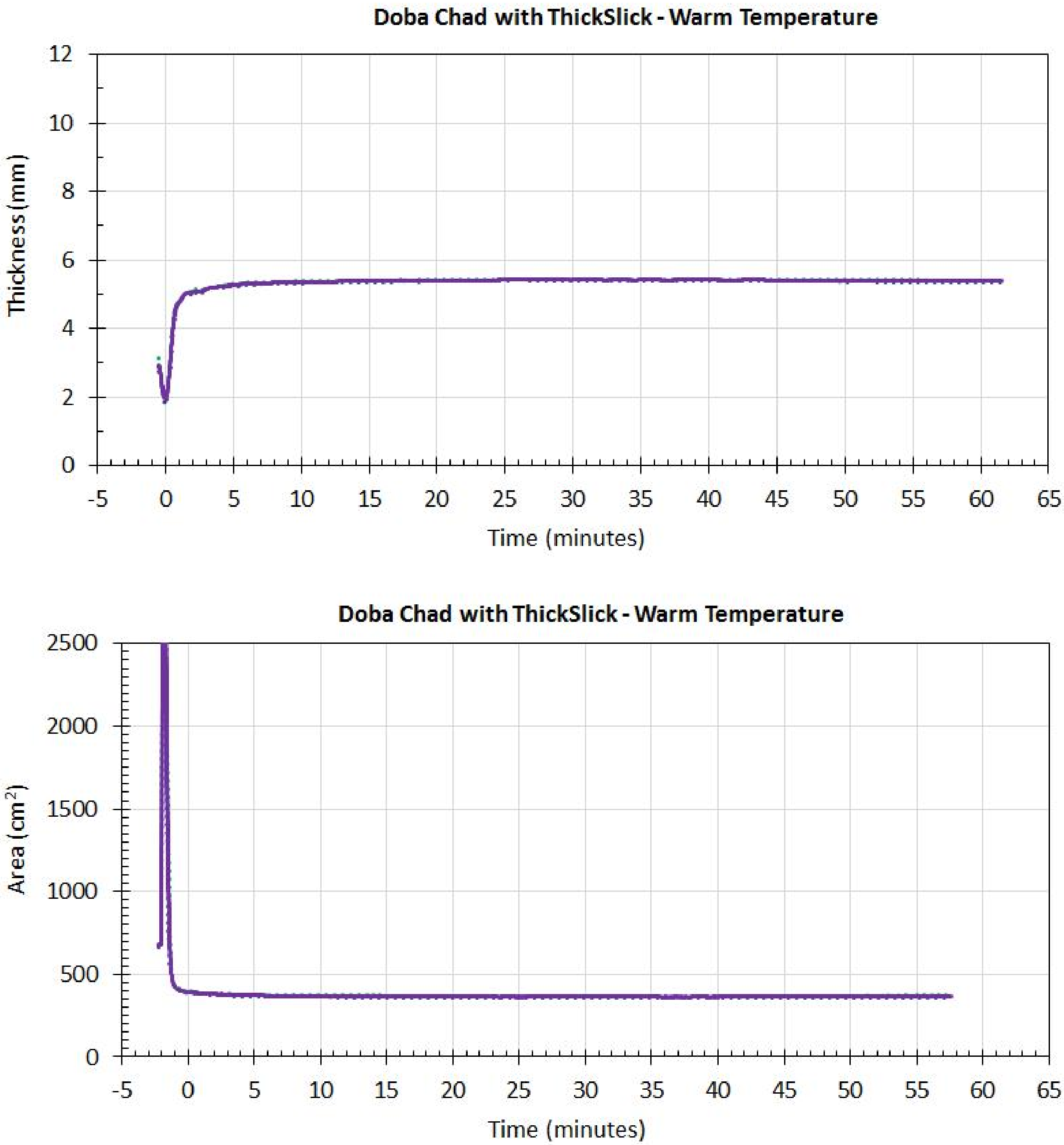
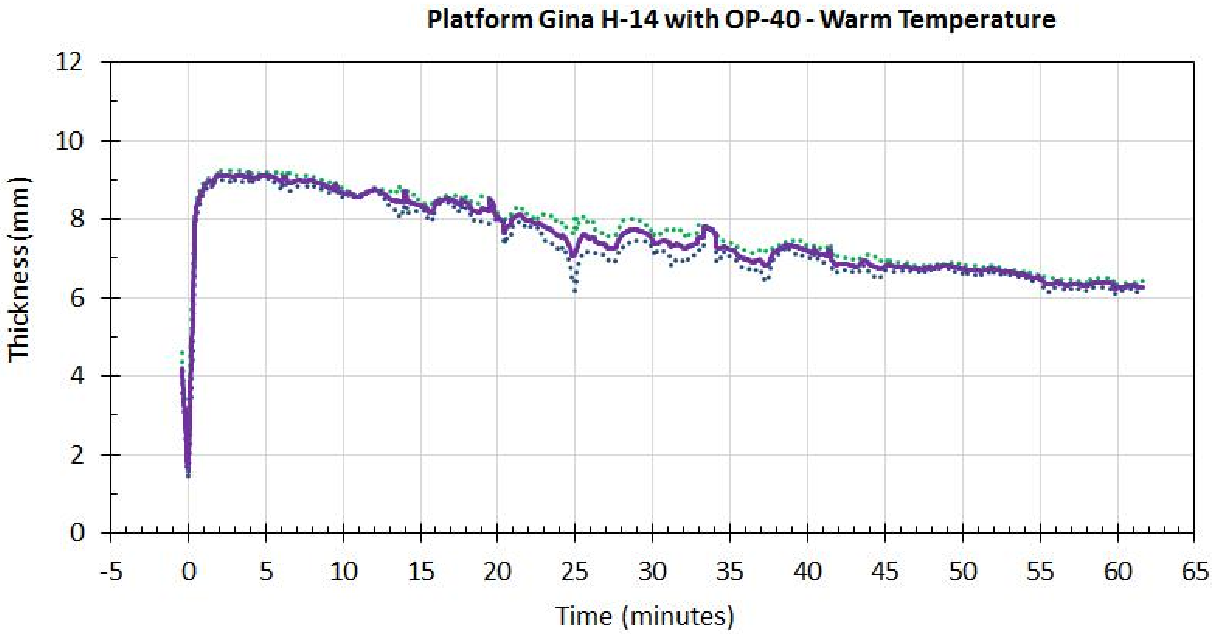



Figure 59. Doba Chad with ThickSlick, Warm Temperature, Thickness and Area Plot

.



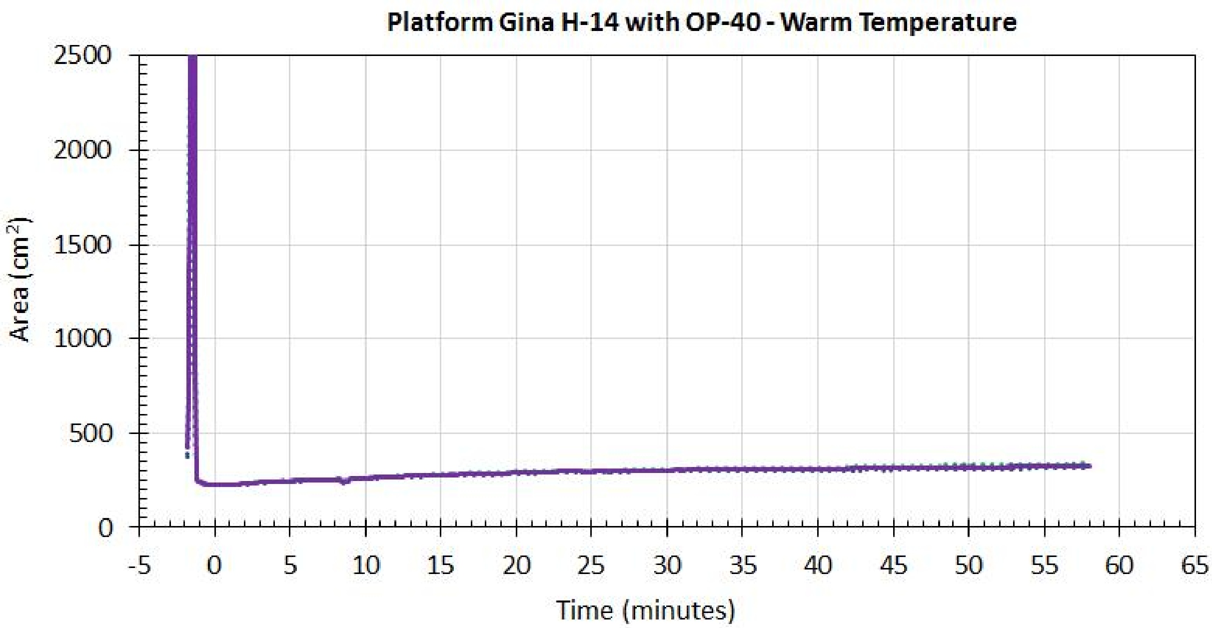




Figure 60: Platform Gina H-14 with OP-40, Warm Temperature, Thickness and Area Plot

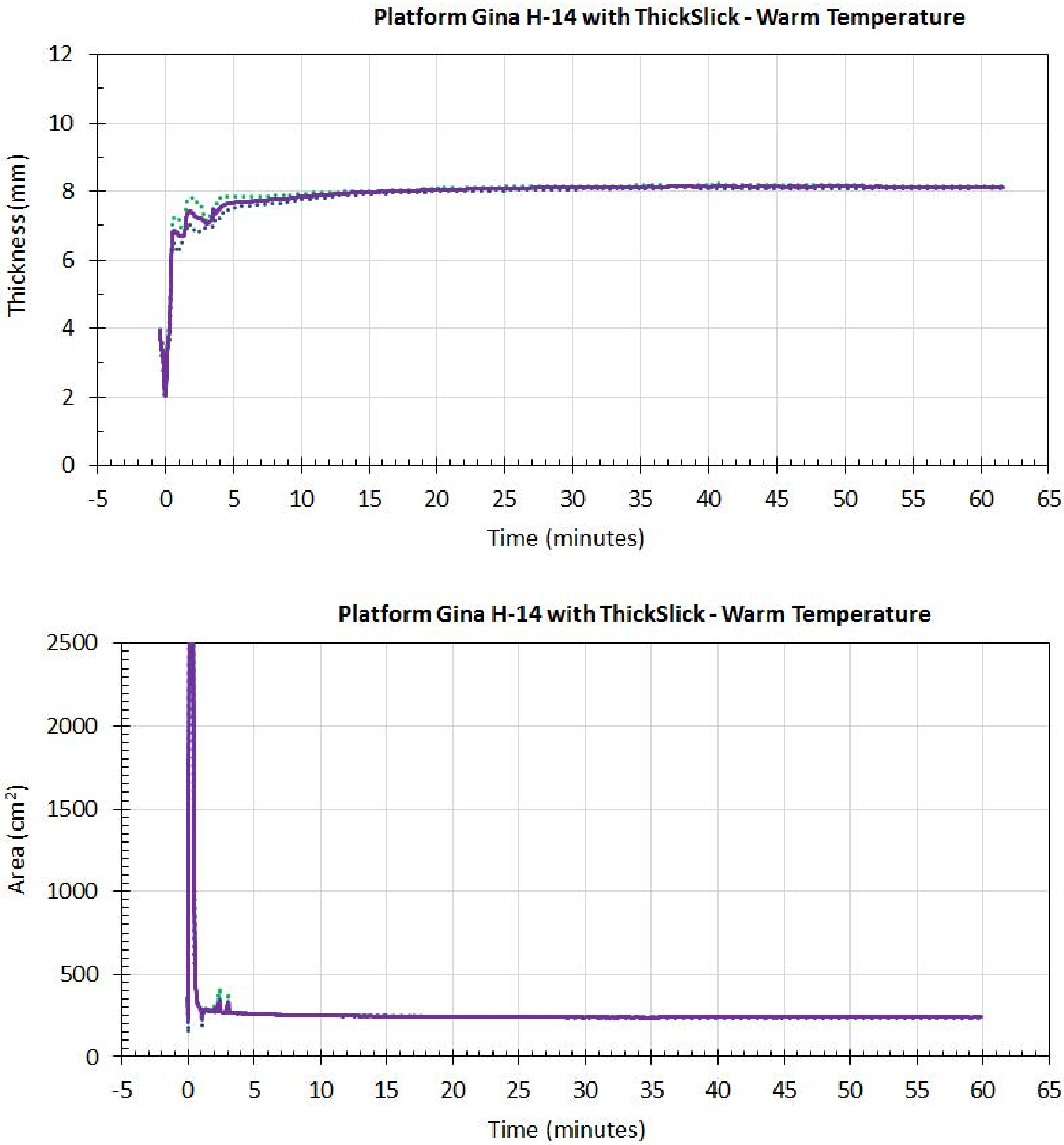
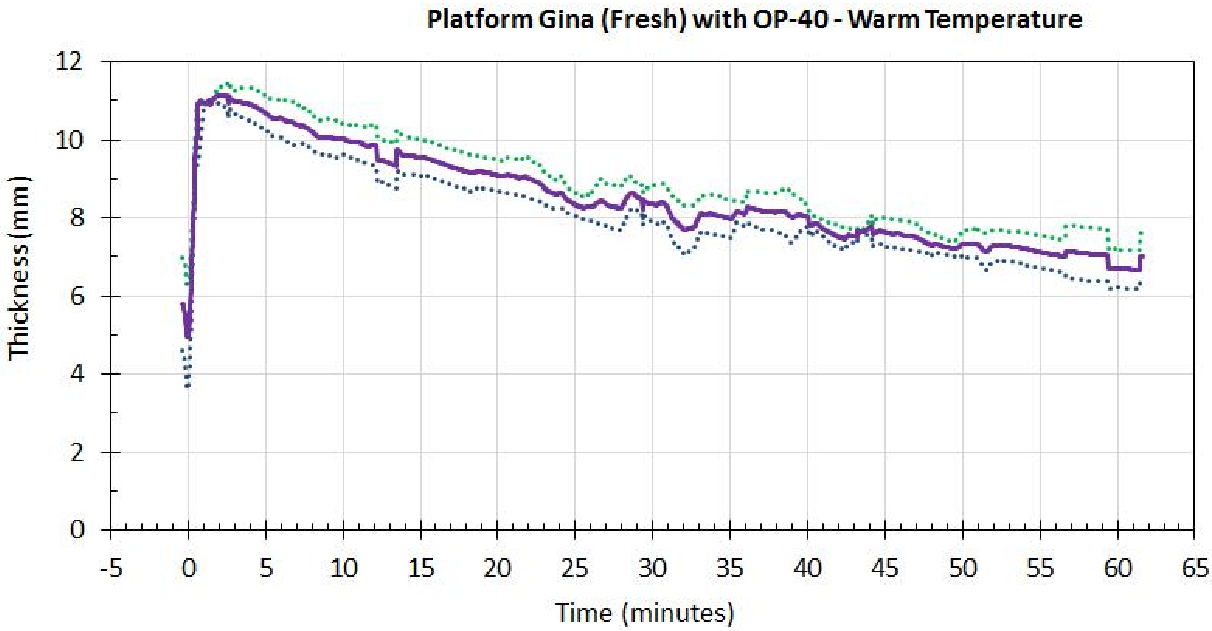



Figure 61. Platform Gina H-14 with ThickSlick, Warm Temperature, Thickness and Area Plot

.



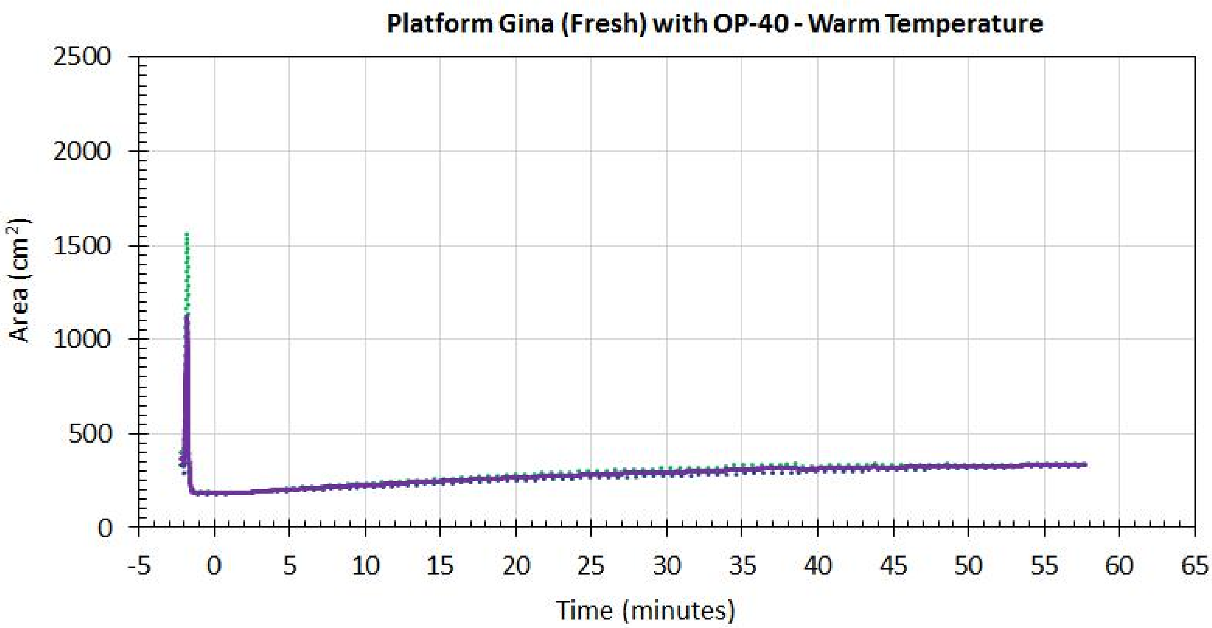
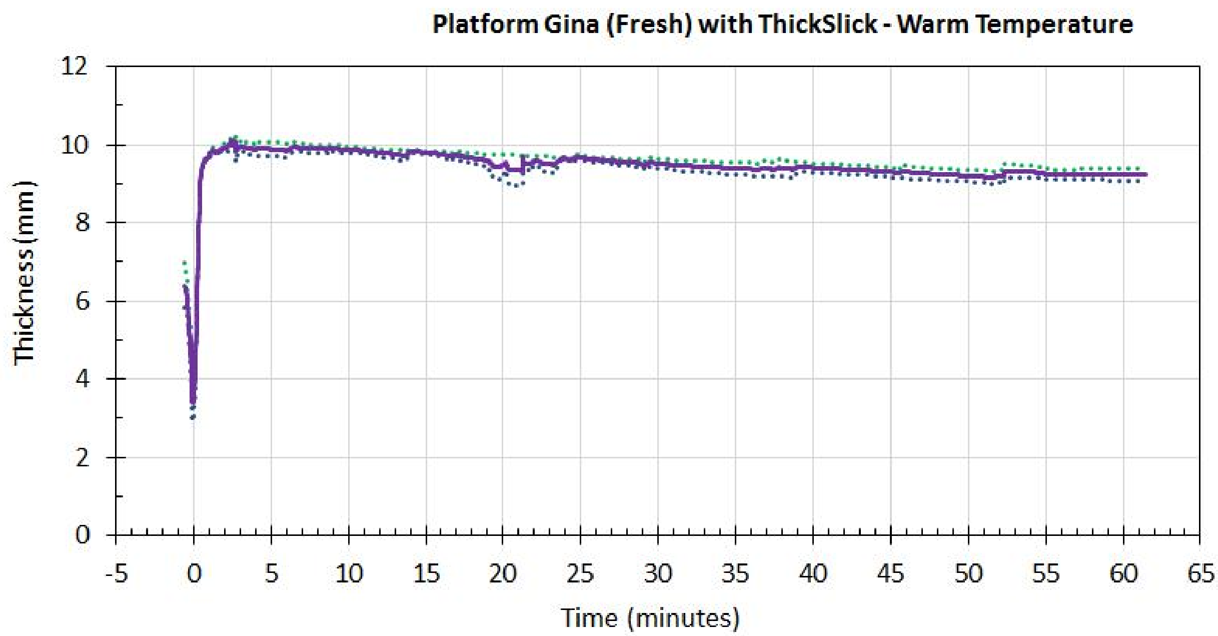




Figure 62: Platform Gina (Fresh) with OP-40, Warm Temperature, Thickness and Area Plot



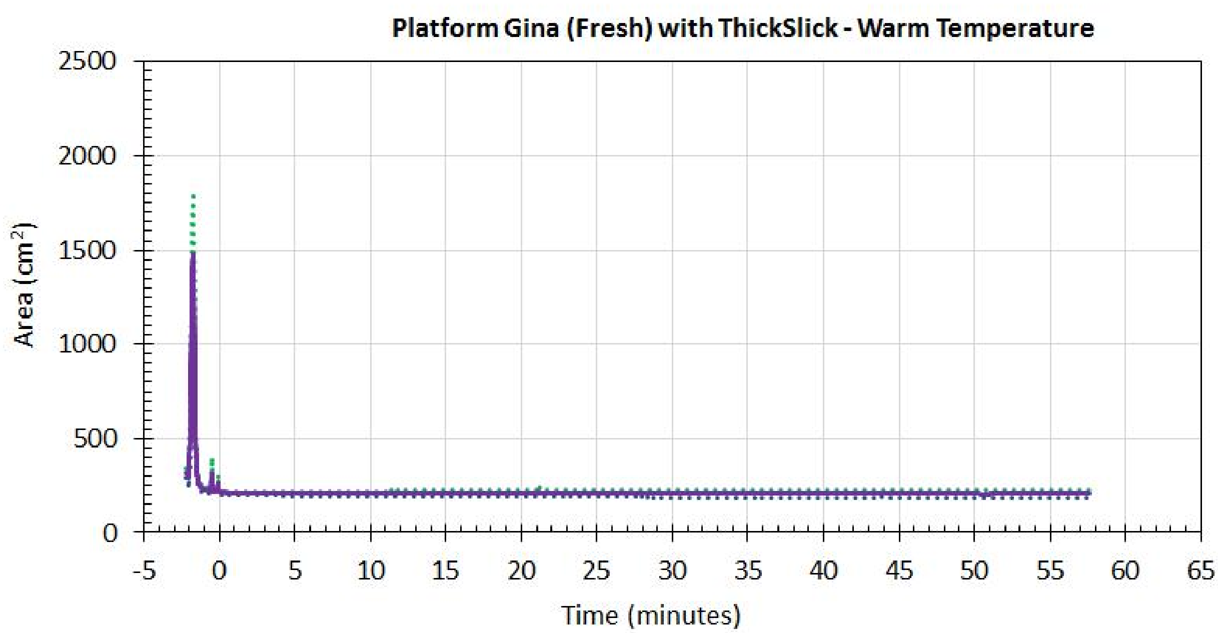
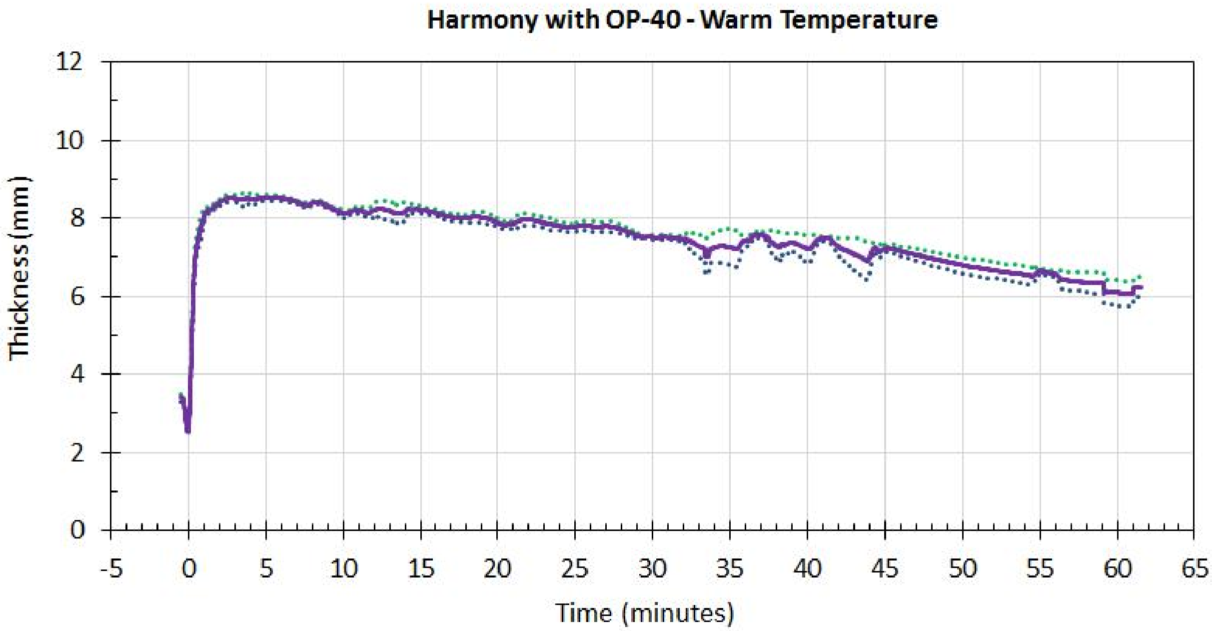




Figure 63. Platform Gina (Fresh) with ThickSlick, Warm Temperature, Thickness and Area Plot

.



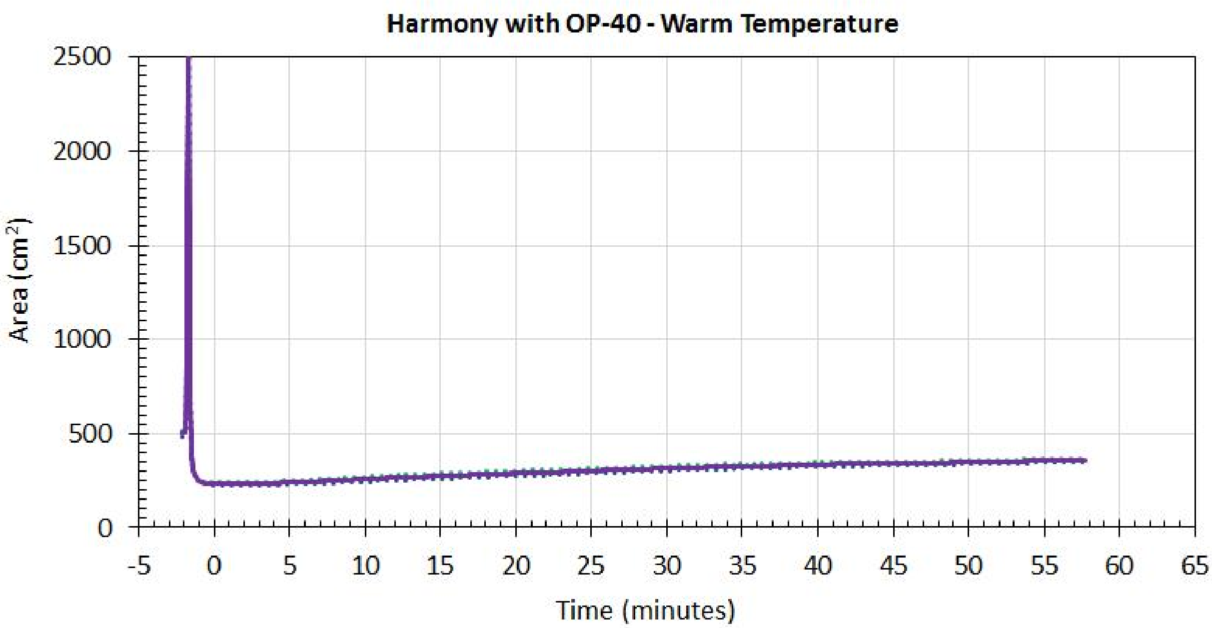




Figure 64: Harmony with OP-40, Warm Temperature, Thickness and Area Plot

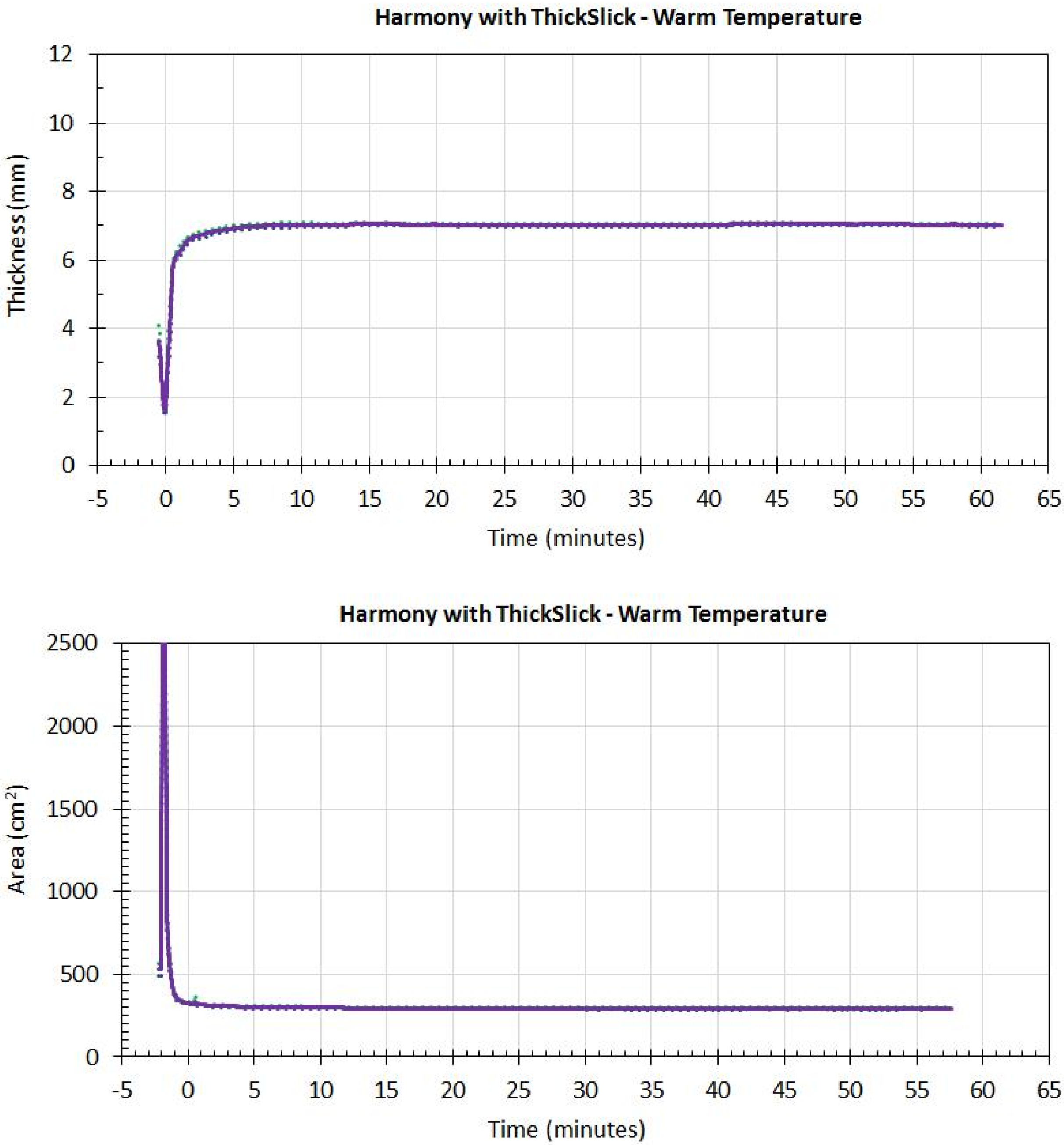



Figure 65. Harmony with ThickSlick, Warm Temperature, Thickness and Area Plot

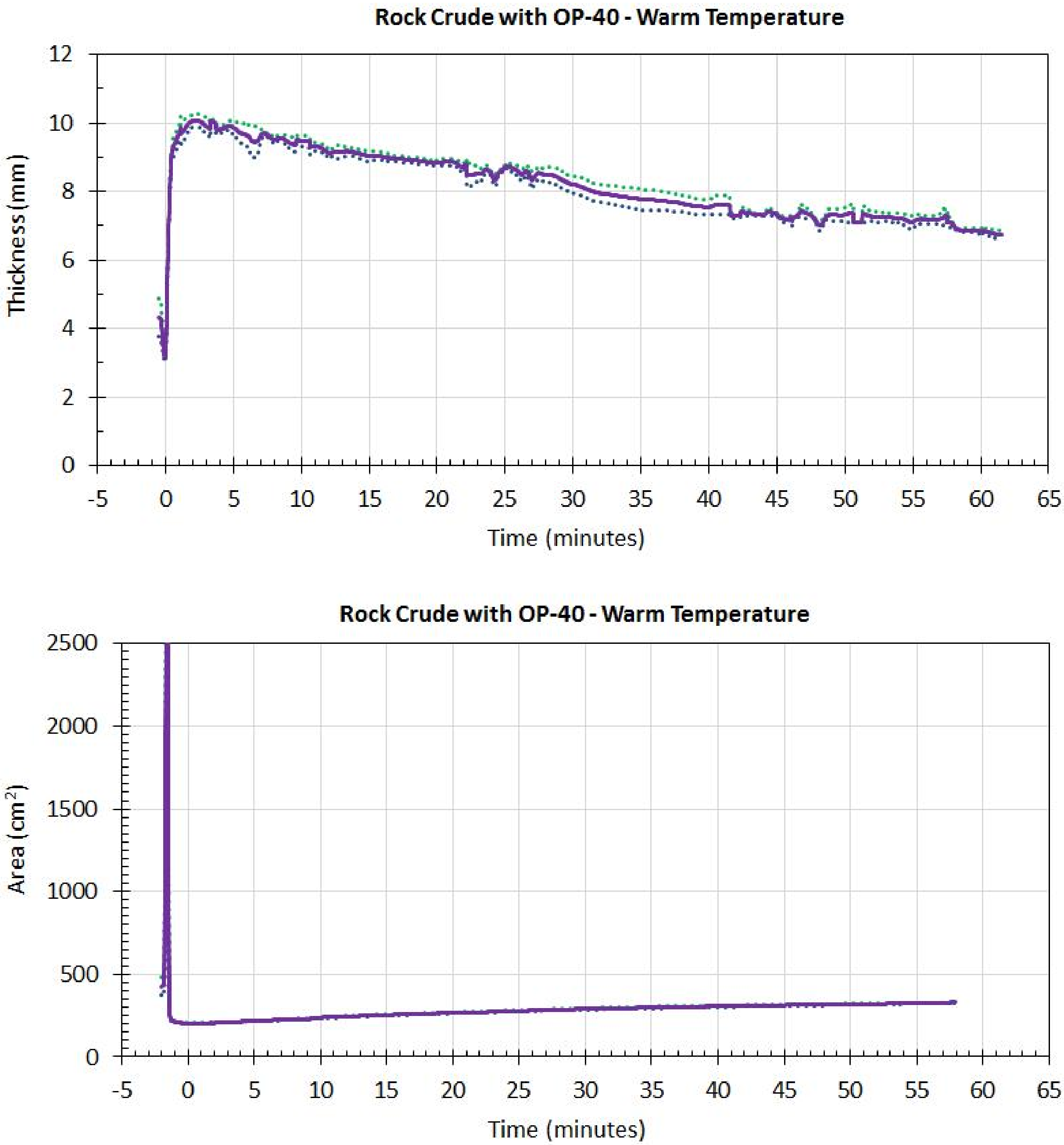



Figure 66: Rock with OP-40, Warm Temperature, Thickness and Area Plot

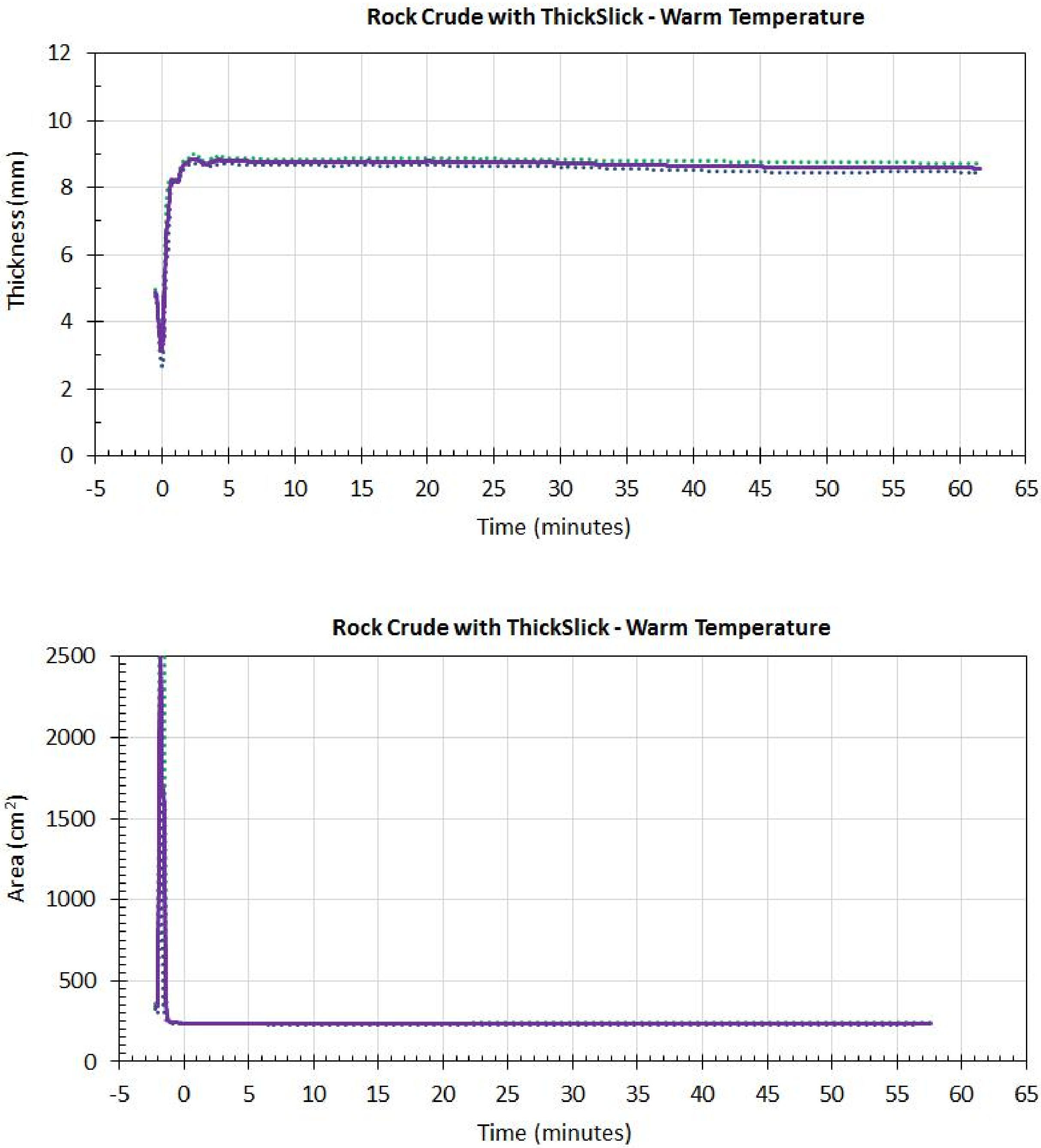
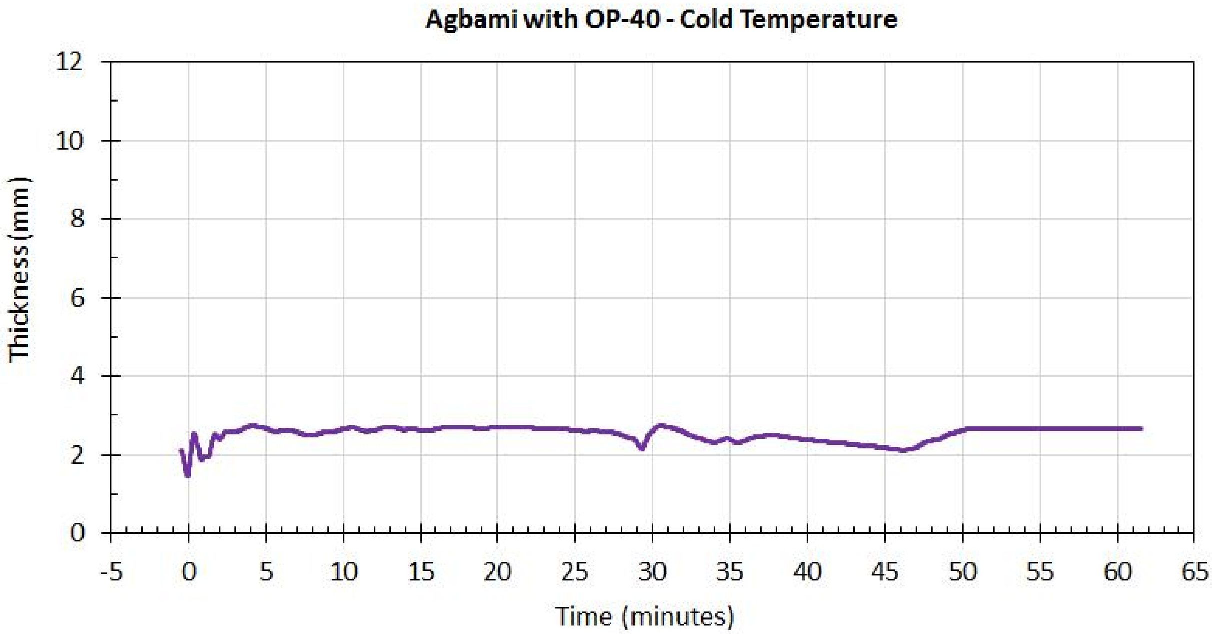



Figure 67. Rock with ThickSlick, Warm Temperature, Thickness and Area Plot

### HERDER RESULTS AT COLD (4°C) TEMPERATURES

A the effectiveness of the herders were tested on a subset of the oils with Agbami being the only oil tested at cold temperatures with both OP-40 and ThickSlick.



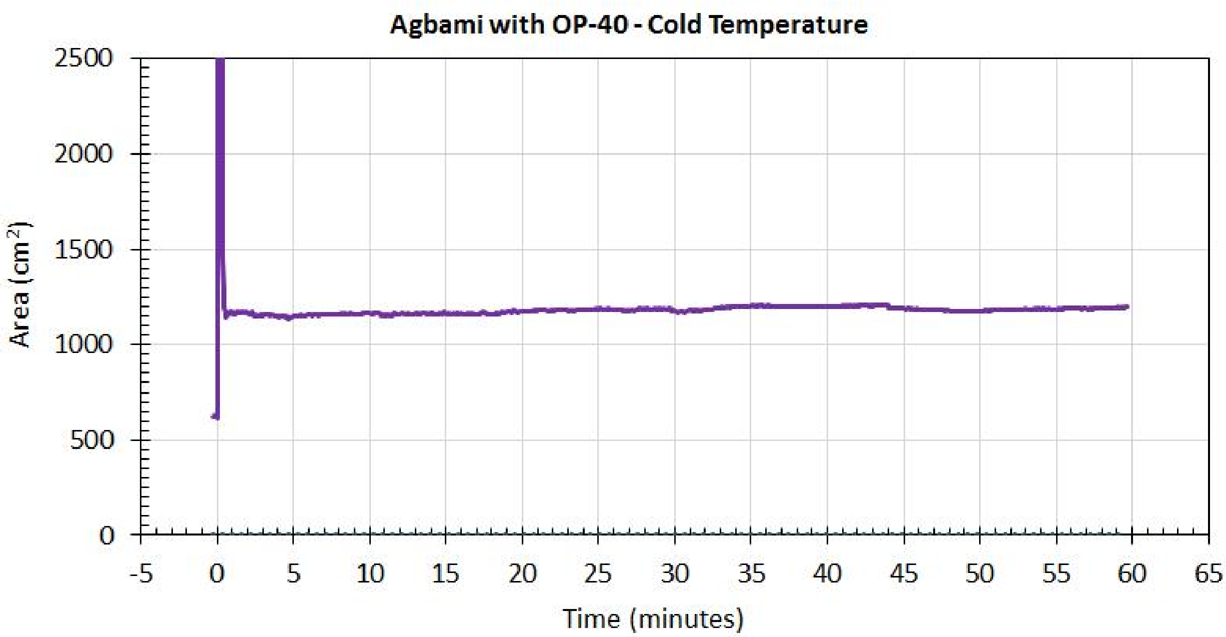




Figure 68: Agbami with OP-40, Cold Temperature, Thickness and Area

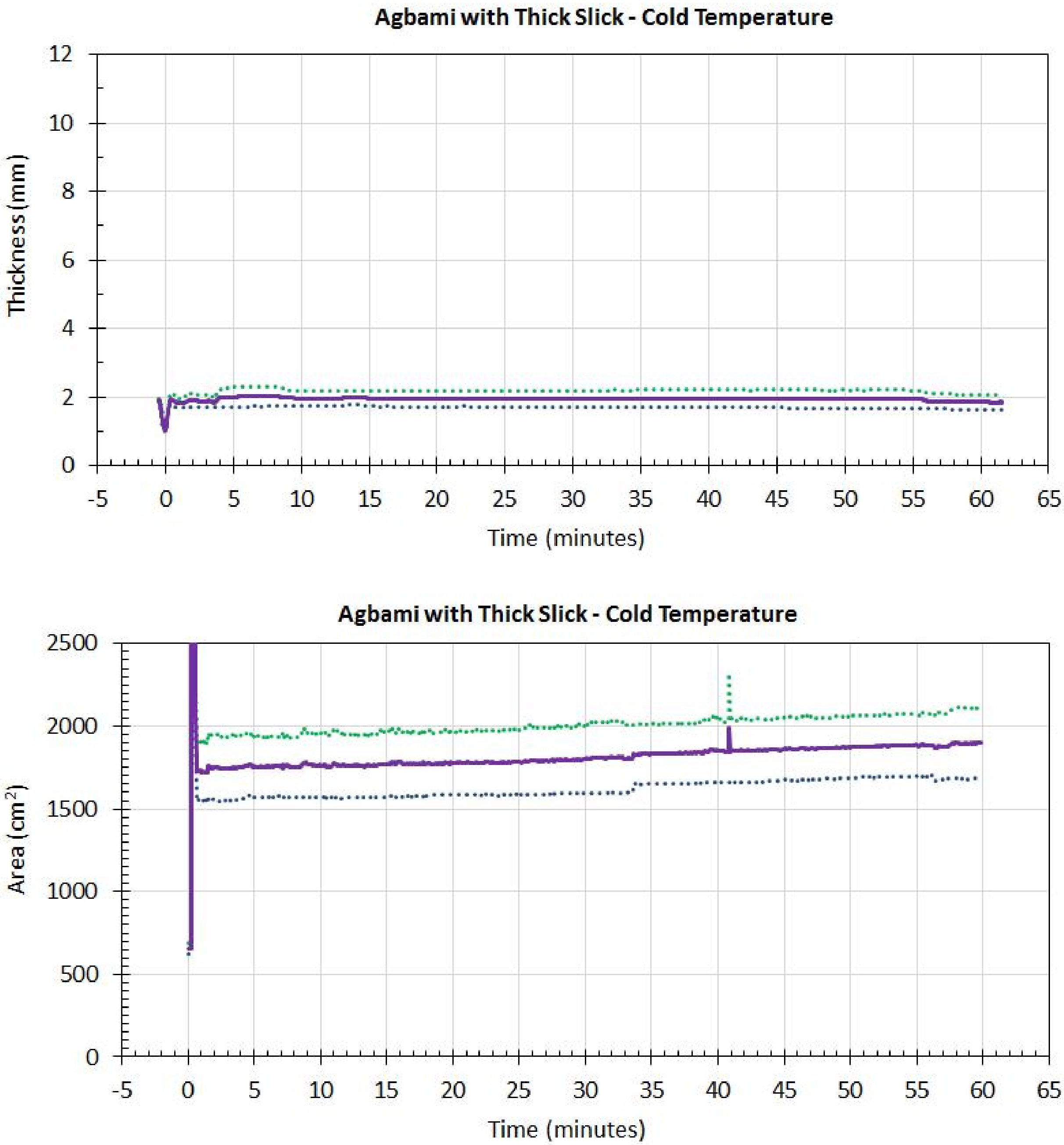



Figure 69: Agbami with ThickSlick, Cold Temperature, Thickness and Area

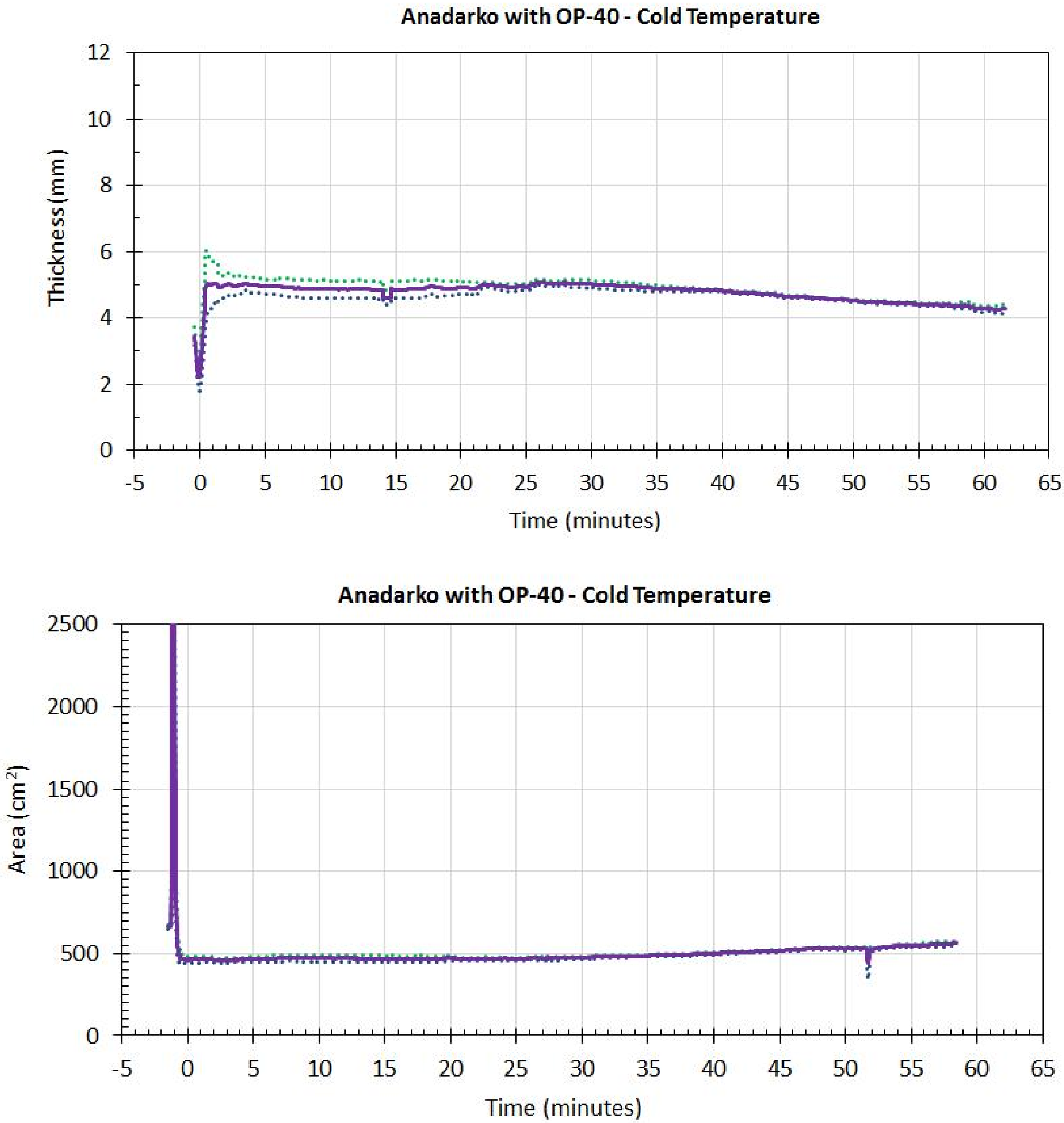



Figure 70: Anadarko with OP-40, Cold Temperature, Thickness and Area

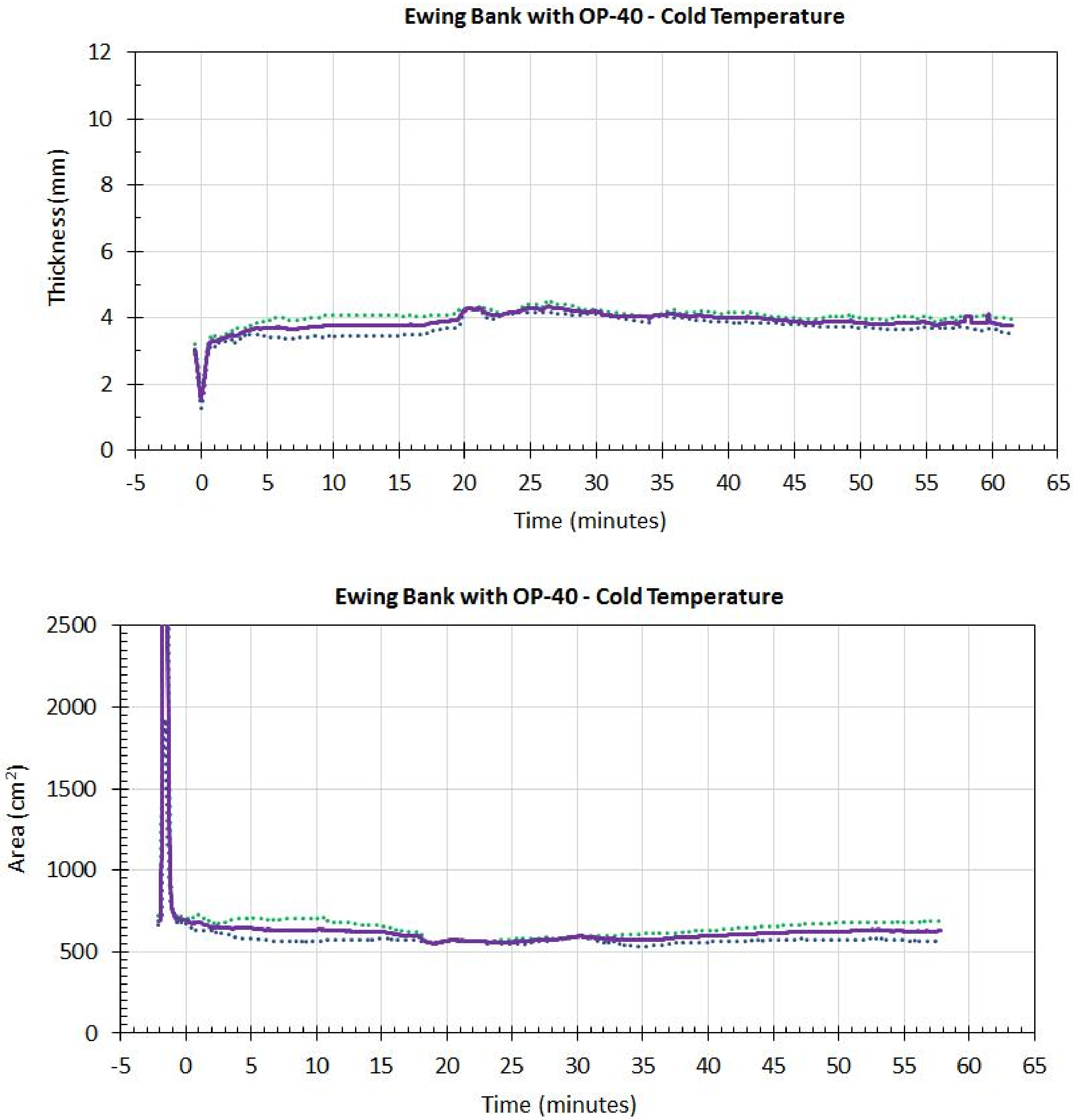
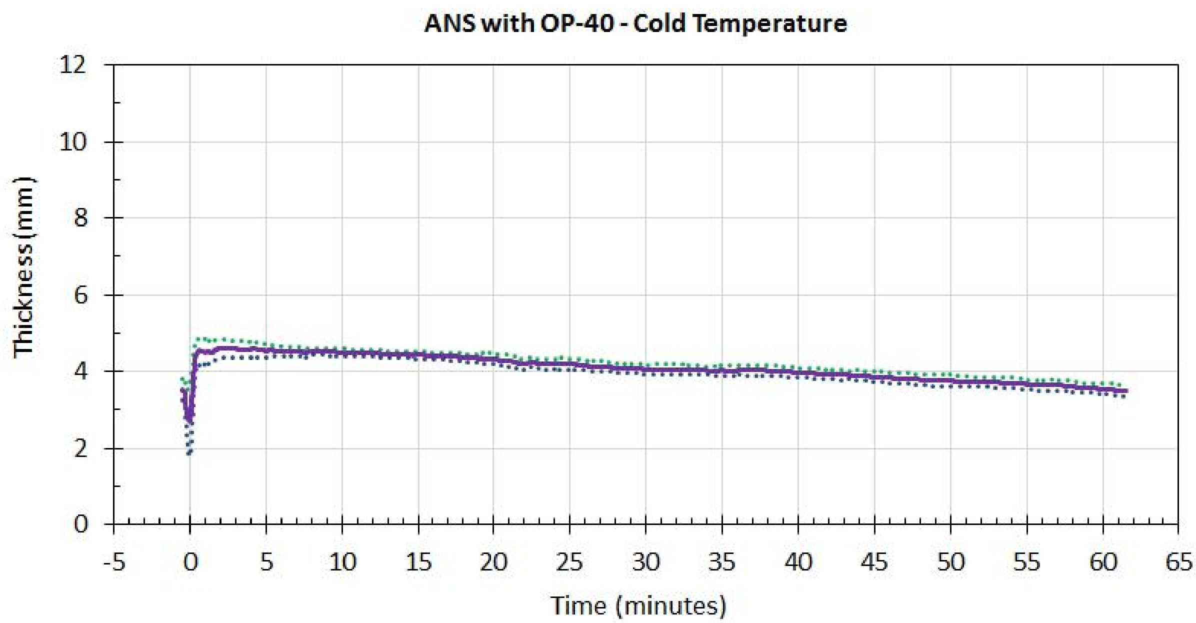



Figure 71: Ewing Bank with OP-40, Cold Temperature, Thickness and Area



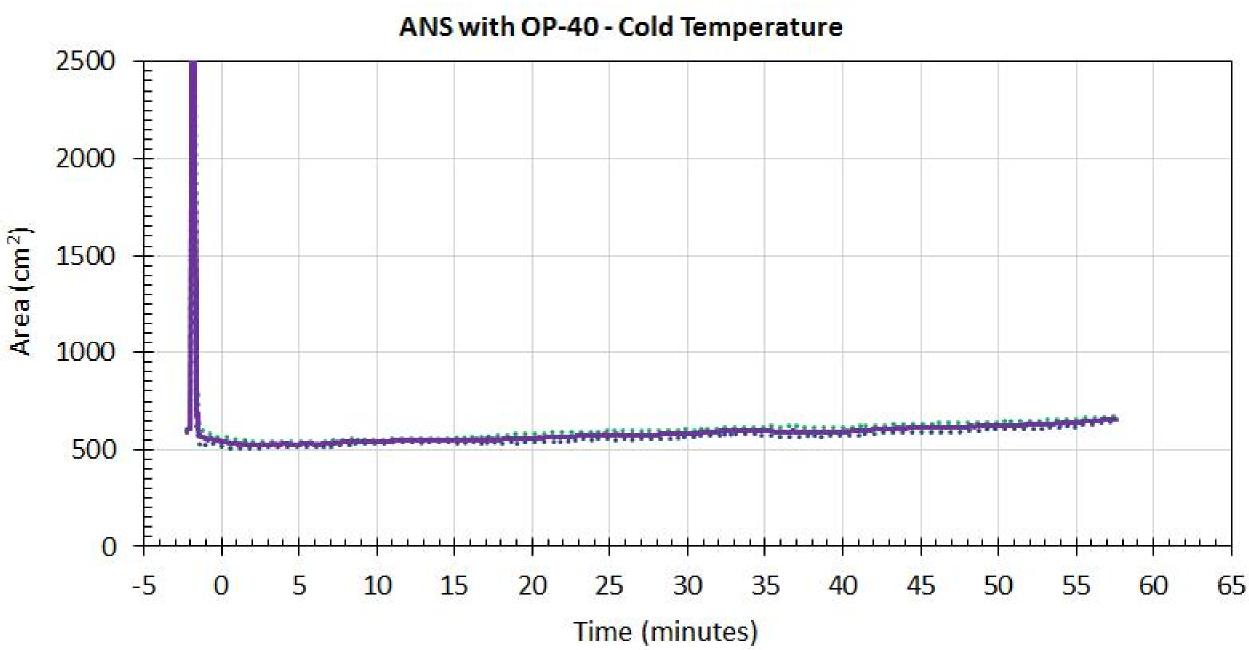
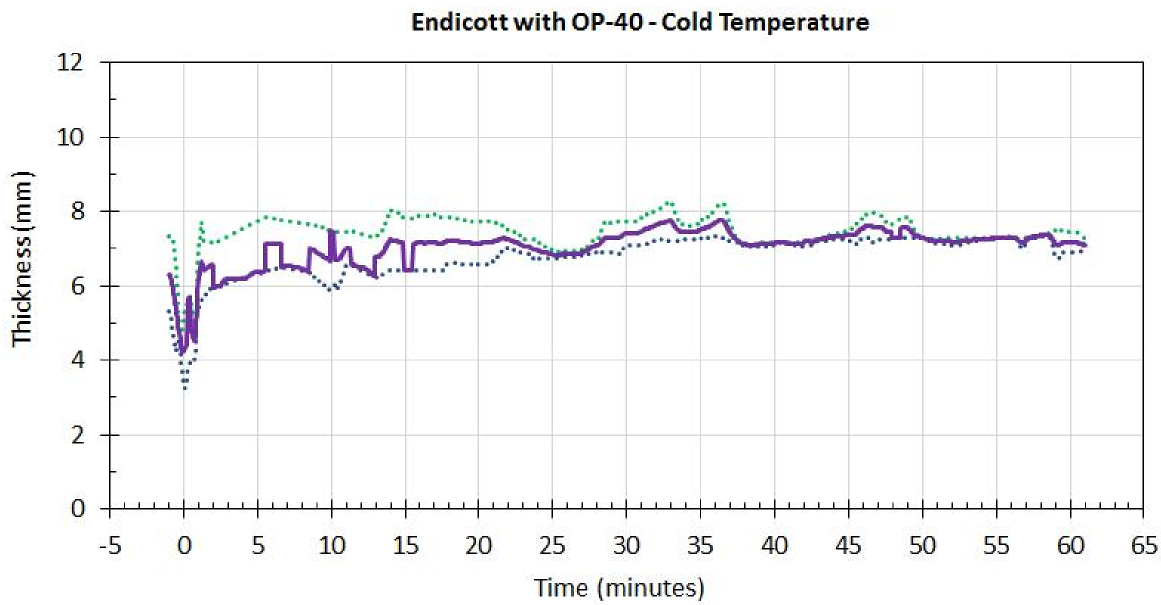




Figure 72: ANS with OP-40, Cold Temperature, Thickness and Area



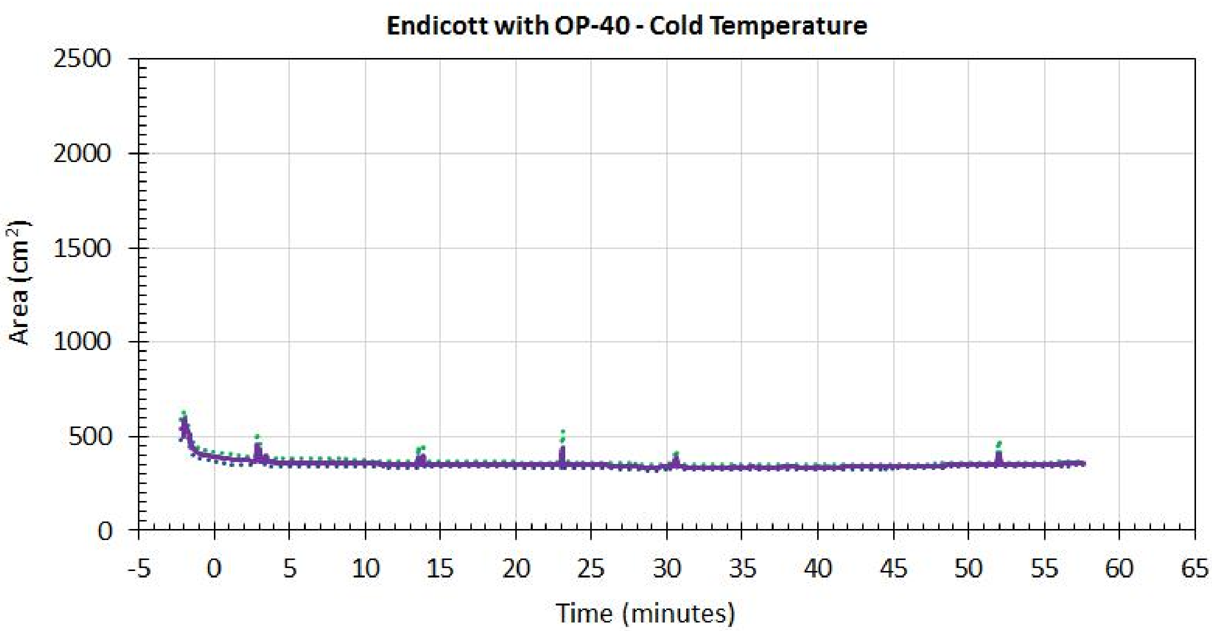
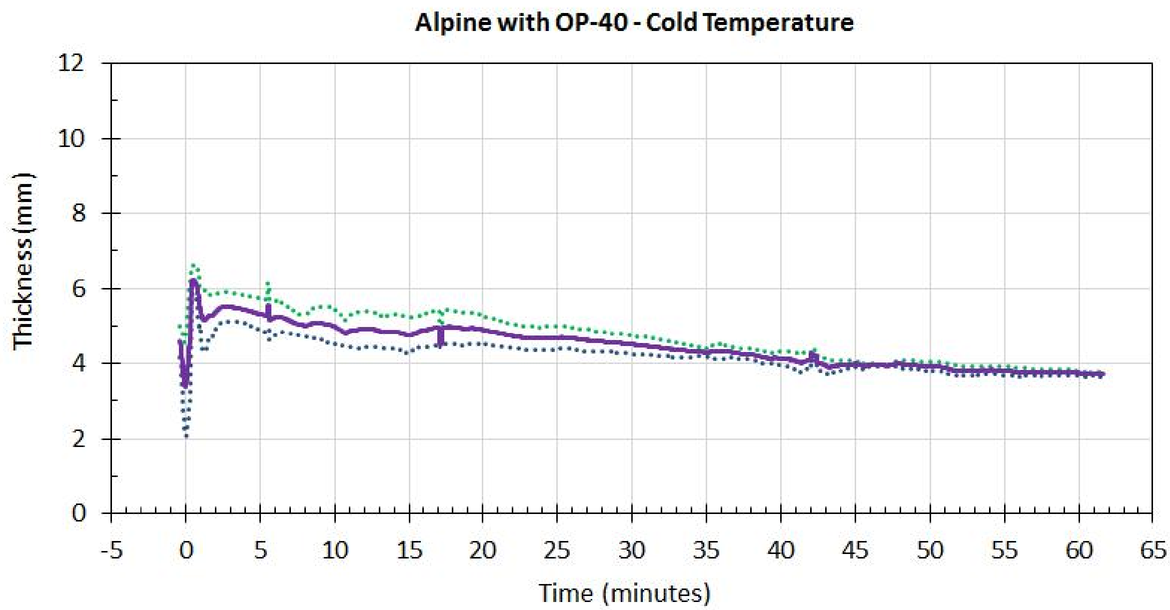




Figure 73: Endicott with OP-40, Cold Temperature, Thickness and Area



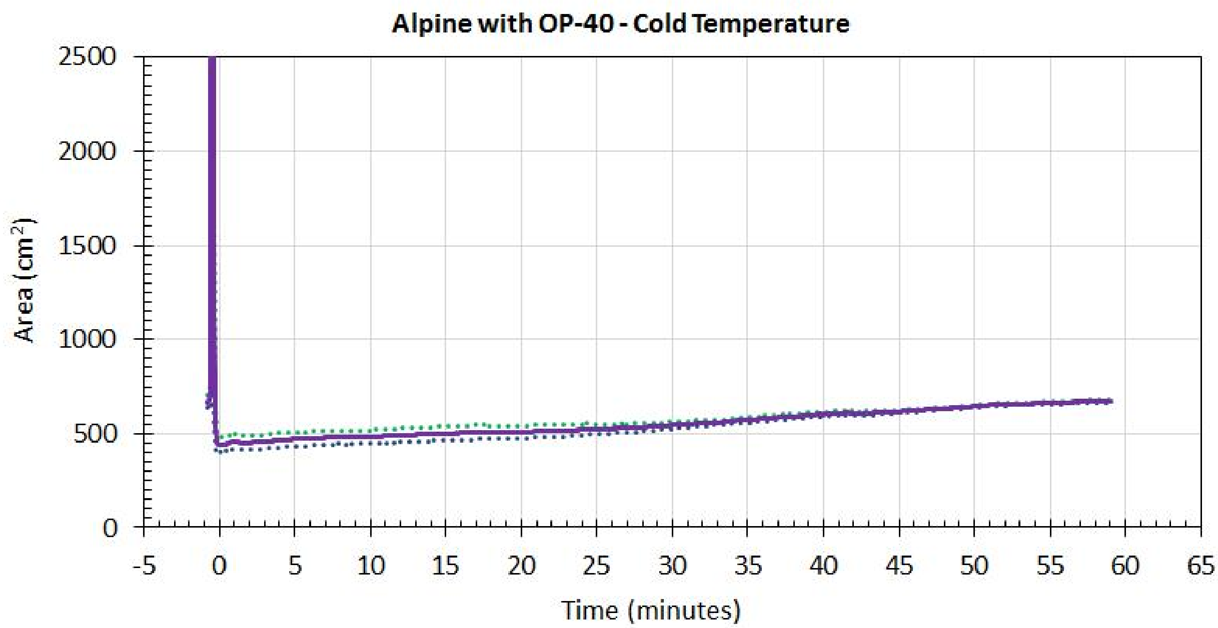
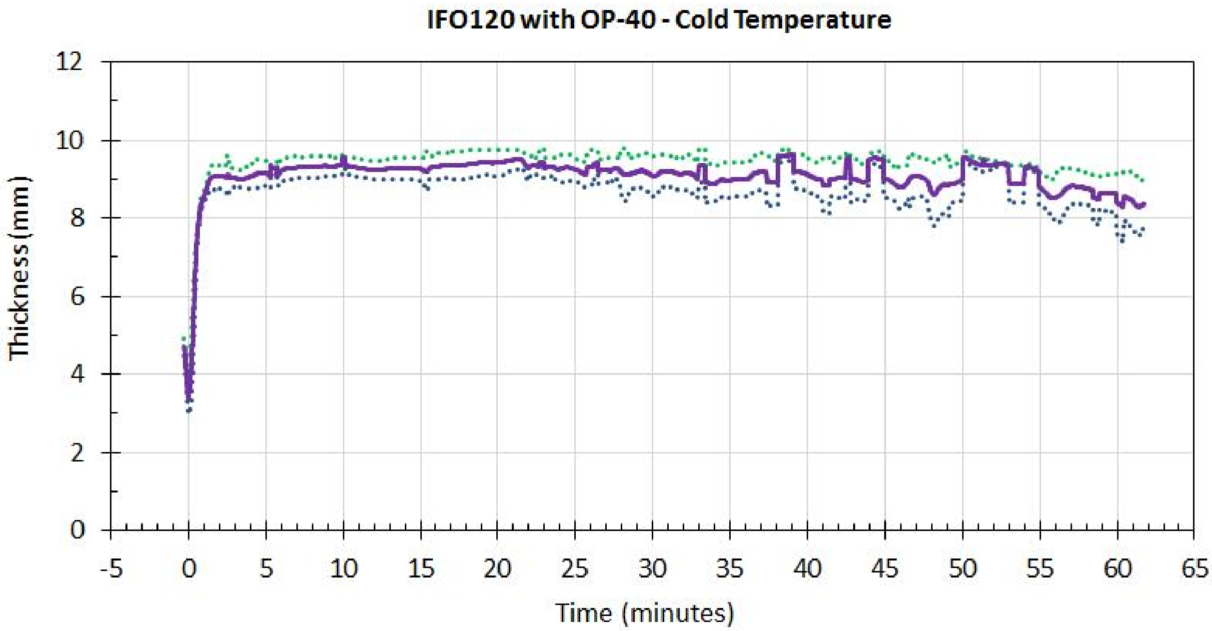




Figure 74: Alpine with OP-40, Cold Temperature, Thickness and Area



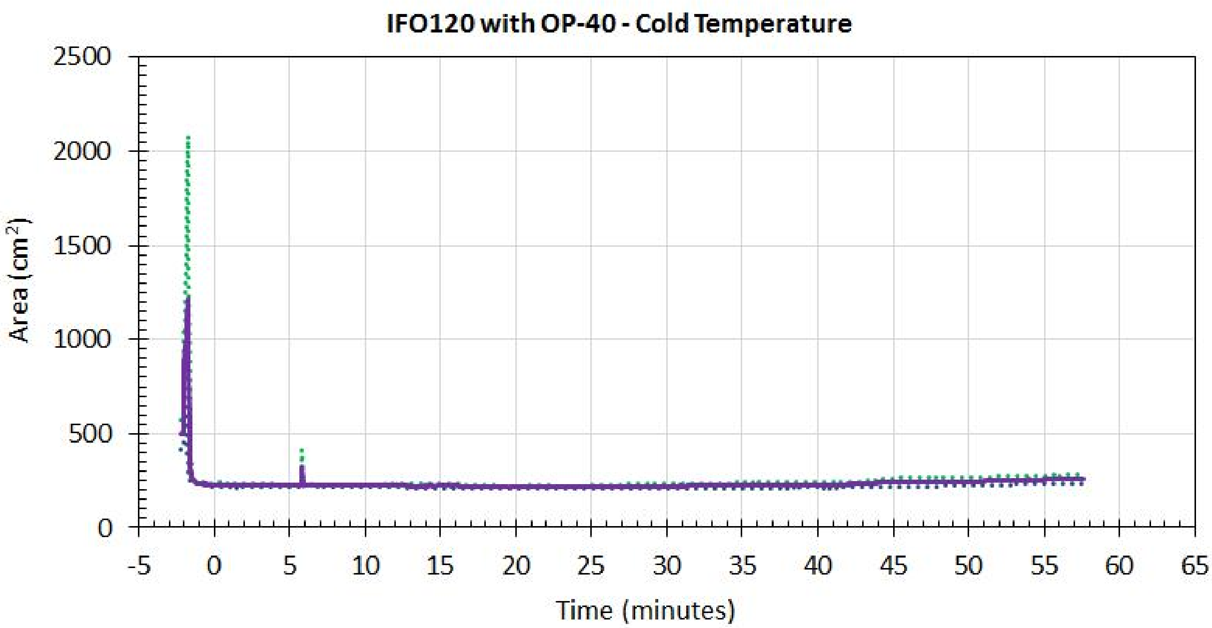




Figure 75: IFO 120 with OP-40, Cold Temperature, Thickness and Area

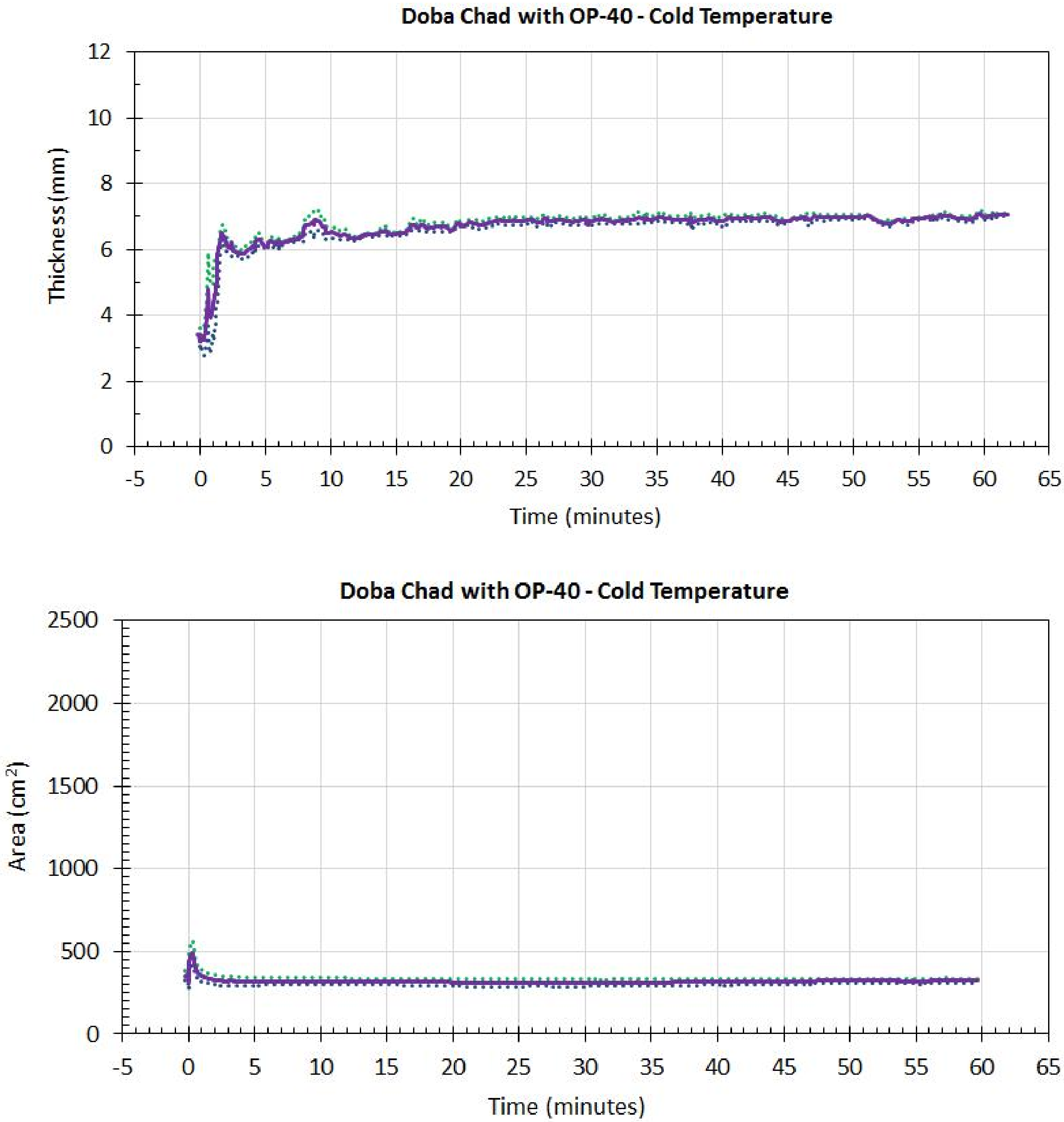



Figure 76: Doba Chad with OP-40, Cold Temperature, Thickness and Area

# 10. APPENDIX B: PROCEDURE

**Experiment Procedure**

1. Mix 685 g of Instant Ocean into 5 gallons of water until salt dissolves completely.
2. Allow salt water to reach desired temperature.
3. Set the regulated pressure in the air compressor to 25psi for the air blower.
4. Set dispense volume of the multi syringe pump to 20 $\mu$L.
5. Add a pea sized amount of ultrasound gel to each transducer.
6. Spread 1mm thick plastic liner over tray, and secure the edges. Smooth the seal between the drop cloth and the gel, ensuring there are no air bubbles.
7. Fill tray with 5 gallons of water mixed with Instant Ocean; it should be approximately 1-2 cm deep in the 1m tray.
8. Place 8 herder dispensing needles: one at each corner, and one in the middle of each side. Make sure the stopcocks are in the closed position and there is no herder dripping from the needle tip.
    - ✶ Note: Ensure there are no air bubbles in the dispensing needle and/or the line; if necessary, bleed the herder lines by deploying the herder several times in a different container before a run until all needles disperse herder simultaneously.
9. Position thermocouple in the corner of the tray, and tape into place
10. Take a sample of the water once it has fully drained from car buoy and test the surface tension of this sample using a capillary tube. A measurement between 0.0350 J/m^2 and 0.0500 J/m^2 is an acceptable range.
11. Lower the plastic ring, approximately 33cm in diameter, into the water.
12. Slowly pour 230 mL of oil into the ring.
    - ✶ Note: Pour less viscous oil using cone, holding cone just above the surface of the water. Pour viscous oil over a piece of solid plastic angled so it barely touches the surface of the water. Pour slowly so oil does not touch the plastic liner.
13. Open the herder dispersant needles. Make sure to wipe away any escaping herder droplets.
14. Measure and record the start temperature.
15. Close all ducts and windows, sealing any potential gaps with tape to prevent any additional air flow to help control the movement of the slick.
16. Check transducer signals; if necessary adjust the gain so the signal fills approximately 75% of the screen.
17. Begin data collection of images and acoustic signals.
18. Slowly pull up the ring and allow oil to spread to equilibrium size. The edges of the slick should almost touch the edges of the tray.

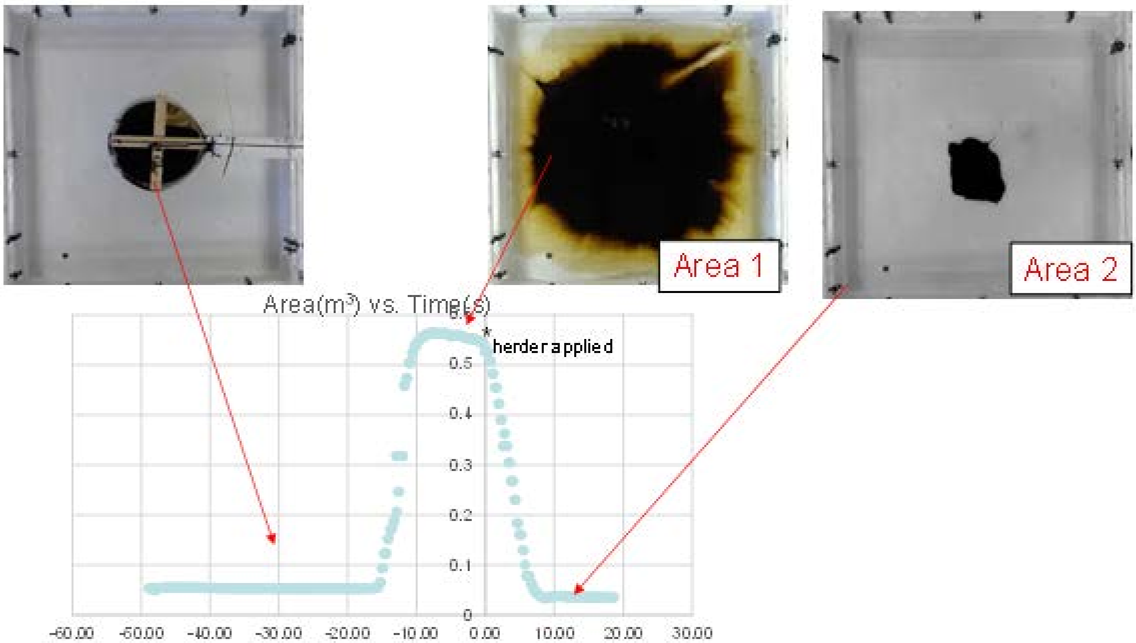


Figure 77: Illustration of what is happening in tray steps 18-20

1. Administer 160 μL of herder (20 μL from each dispensing needle) approximately 30 seconds after beginning data collection. Once herder is administered, remove dispensing needles so no additional herder drips during the experiment.
2. Allow oil to reach a stable shape. If necessary, use the air gun to gently push the oil slick back towards the center of the tray, ensuring that at least one transducer is covered at all times.
3. Upon experiment completion, measure and record final water temperature.

**Clean Up Procedure**

- Once data collection is finished, open air ducts to outside ventilation and wait for approximately 3 minutes as fumes begin to dissipate.
- Open windows on herder apparatus.
- Soak up oil with absorbent pads.
- Connect drainage tube to a storage tank.
- Poke a hole in plastic liner above drainage tube and allow water to begin draining
- Once all water has been drained, wrap up all absorbent pads in the tray liner and store this waste in a sealed container for appropriate disposal.
- Wipe up any moisture left in the tray.
- Place down protective absorbent pads and then clean the oil ring.
- Change out any absorbent pads lining the area around the tray that are oil soaked.

**Cold Procedure Changes**

- Line the edges of the tray with 4-8 frozen ice packs.

- Use 10 gallons of salt water chilled to 5°C.
- Fill to approximately 3 cm-4 cm deep.