

Final Project Report for the Base Period

(including Tasks 1 and 2)

Project Title: Temporary Oil Spill Storage and Recovery in Alaskan Arctic Environments Using New PETROGEL™ Technology

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Acknowledgements

This study was funded by the Bureau of Safety and Environmental Enforcement (BSEE), U.S. Department of the Interior, Washington, D.C., under Contract E14PC00002.

December 1, 2015

Executive Summary:

The objective of this BSEE project is to advance the Petrogel technology with a focus on the practical evaluation of Petrogel materials for oil spill recovery and cleanup under Alaskan Arctic sea conditions in conjunction with Alaskan North Slope (ANS) crude oil. This project was divided into two periods, including the base period to advance Petrogel technology with an operational testing in Ohmsett's fast tank to validate the desirable Petrogel material for recovering ANS oil. With a Go decision, in the option period we will work with a toll manufacturer to prepare 250 lbs of Petrogel material, and BSEE will conduct simulated field testing in Ohmsett's Main Tank.

This report highlights major R&D experimental results from the base period between September 15, 2014 and November 30, 2015. The study involves two major Tasks. In Task 1, we focused on a systematic study to tailor Petrogel material, designing and synthesizing various polymer structures and morphologies, and evaluating their ANS oil absorption capacities and kinetics. The experimental results directed us to the most suitable Petrogel material (called i-Petrogel) for absorbing ANS oil under Arctic sea conditions. In addition to the absorption capacity and kinetics, the material design also included the consideration of the operational requirements during material handling, spreading, recovery, and pumping, as well as reusing the recovered oil/i-Petrogel adducts. For comparison, several commercial sorptions were also examined side-by-side, including melt-blown PP pads, PU foams, and cellulose products. At the end of Task 1, we successfully identified two specific i-Petrogel structures and compositions that can absorb ANS oil with the absorption capacity 30-40 times and fast kinetics. In Task 2, once two i-Petrogel structures were validated in the small-scale laboratory oil absorption testing, we performed a scale-up study with the target of developing a commercial process that can be used for the large production of i-Petrogel material with consistently high quality (i.e. polymer composition, molecular weight, purity, etc.). In the second half of Task 2, we successfully prepared >20 pounds Petrogel material in flake form, with two compositions of 1/1 and 3/1 rigid/soft polymer weight ratios (>10 pounds each). BSEE conducted an operational test on these two i-Petrogel samples under four testing conditions at the Ohmsett facility. The four tests were carried out in two (10'x10') fast tanks, containing 20 gallons of 10% weathered ANS crude oil that was poured over 75% filled seawater (salinity 29-33 ppt), to examine the effectiveness of the i-Petrogel absorbents in an ANS oil spill recovery. The tests were focused on oil absorption capacity, recovery of the resulting oil/i-Petrogel on the water surface by skimmers, and the pumping ability of the resulting oil/i-Petrogel adducts.

Overall, we have successfully conducted all proposed R&D tasks and achieved the milestones and targets proposed for the base period. The performance testing results in Ohmsett were very encouraging. They were consistent with the experimental results observed at the Penn State laboratory. The specific flake form of i-Petrogel, with a 1/1 rigid/soft polymer weight ratio, is capable of absorbing ANS oil about 40 times its weight. The absorption kinetics are fast; in the first 2-3 hours it is possible to achieve about 80-90% saturation. The resulting ANS oil/i-Petrogel viscous fluid, floating on the water surface, can be effectively recovered by an Elastec TDS 118 drum skimmer and pumped using a centrifugal pump. The water content in this recovered ANS oil/i-Petrogel fluid, ranging from 0 to 3 wt%, is dependent on fluid viscosity, drum rotation speed, and setting time. After setting the recovered ANS oil/i-Petrogel fluid for a few days, most of the gathered water was spontaneously phase-separated and removed. The dry ANS oil/i-Petrogel fluid can be refined as ANS crude oil using a regular distillation process.

Final Report (Base Period):

Project Description

In the base phase of this BSEE project, four major tasks and milestones were suggested in the proposal. They are listed below with the associated research activities. The detailed experimental results in each task were reported during the course of this R&D project. This final report highlights major technological advancements and accomplishments.

Task 1A: Develop Petrogel Structure and Morphology

Petrogel will be tailored to the specific structure consistent with the chemical make-up of ANS crude oil and Arctic weather conditions. In addition, form, size and shape of the polymer for ease of deployment and maximum absorption will be investigated.

Task 1B: Laboratory Testing and Evaluation

Parallel to the material synthesis, we will construct a small test tank to carry out oil sorption experiments under simulated Arctic conditions using ANS oil. Tests will include sorption capacity, rate of oil absorption, oil retention, and ease of application and recovery. Two commercially available oil sorbents will be tested along with Petrogel in order to provide material comparison. We will also verify Petrogel's refining capability using TGA-Mass spectroscopy to understand the effect of the Petrogel structure on the distillation process. We will also prepare a completed Material Safety Data Sheet during this task.

Task 2A: Study Petrogel Scale-up Process

We will conduct a scale up study with the target of preparing the selected form of Petrogel in a 10-20 pound quantity. At the end of this task, we hope to understand the most suitable scale-up procedure and reaction condition.

Task 2B: Evaluation at Ohmsett Facility

An operational test will be conducted on Petrogel at the Ohmsett facility in a small tank. This test will demonstrate whether Petrogel effectively absorbs ANS oil and whether it can be successfully collected with mechanical recovery equipment.

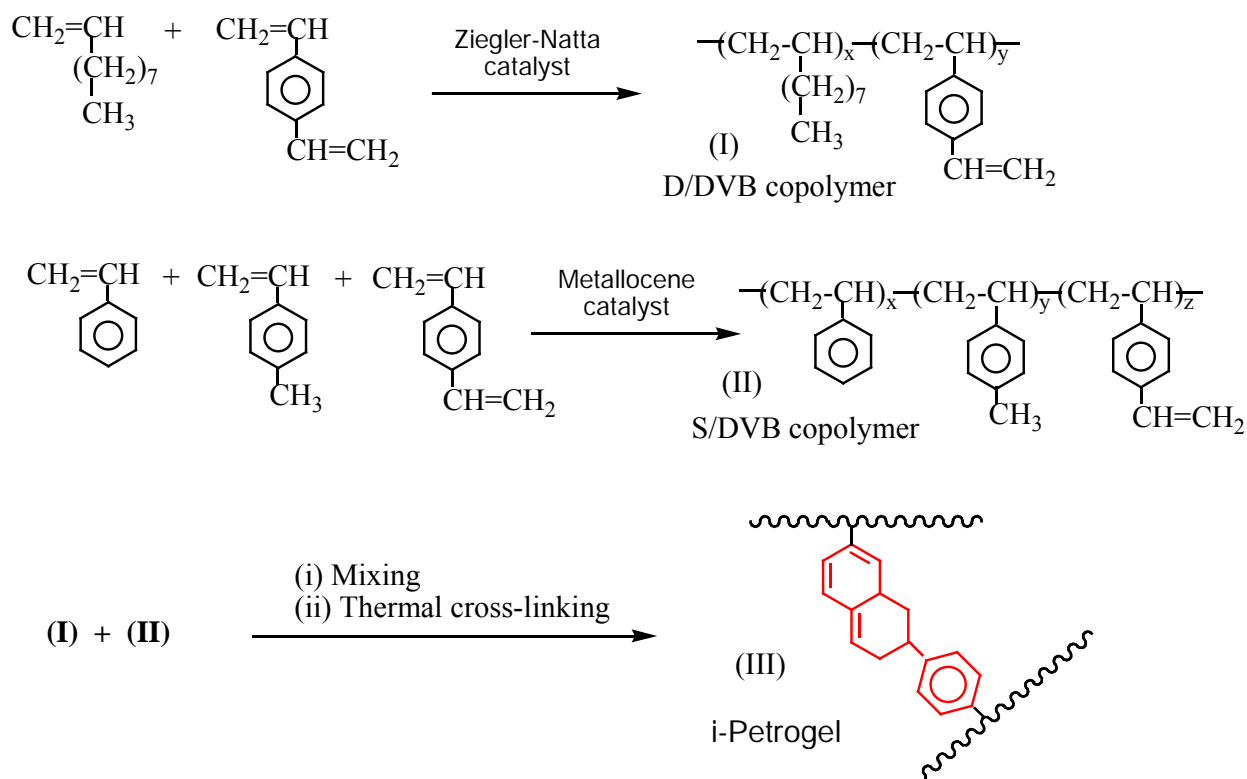
Design of New i-Petrogel Oil Superabsorbent

Before this BSEE project, the material of Petrogel was based on a random copolymer network structure (as illustrated in Figure 1, left). This copolymer structure contains aliphatic hydrocarbon monomer units (A) and aromatic hydrocarbon monomer units (B). They are randomly distributed along the polymer chains. A small amount of crosslinkers (X) are also incorporated in the polymer chain to form a network structure that allows the polymer to swell with the oil (hydrocarbon) molecules, without dissolving the polymer chains in the solution. A typical Petrogel polymer is a 1-octene/styrene/DVB (DVB: divinylbenzene) random terpolymer that is an elastic (soft) material with a low T_g and amorphous (dense) morphology. The oil absorption capacity (swelling ability) is inversely proportional to the crosslinking density. Due to its soft, somewhat sticky nature, this Petrogel material is difficult to form into stable foam, flake, or film products. Petrogel in pellet and particle forms has been shown to be very effective in absorbing refined oil products, such as toluene, xylene, gasoline, diesel, etc., with relatively low molecular weight and viscosity and narrow composition distribution of hydrocarbon molecules. However, it has a much lower absorption capacity and slower kinetics when absorbing large and complex hydrocarbon mixtures, typical of crude oils.

It is interesting to note that most of the reported IPN polymers were based on hydrophilic polymers "Hydrogels", prepared by acrylic monomers and the free radical polymerization mechanism (E. S. Dragan, "Design and applications of interpenetrating polymer network hydrogels. A review" Chemical Engineering Journal 2014, 243, 572-590; Waters, et al., *Macromolecules* 2011, 44, 5776; Owens III, et al., *Macromolecules* 2007, 40, 7306; Xia et al., *Langmuir* 2004, 20, 2094). Hydrogels swelled in aqueous solution have gained much attention due to their biomedical applications. However, it is rare to find corresponding IPN polymers based on olefinic monomers and the transition metal coordination polymerization mechanism (used in our i-Petrogel polymer preparation). There is no report on the hydrophobic IPN polymers used in oil spill recovery applications. We recently submitted a US patent application for this technology to protect the intellectual property.

Synthesis of New i-Petrogel Material

Both soft aliphatic and rigid aromatic copolymers were separately synthesized using two different catalyst systems. As illustrated in Equation 1, the aliphatic copolymer was prepared by a Ziegler-Natta mediated copolymerization reaction between high α -olefin (such as 1-decene) and divinylbenzene (DVB) to form the aliphatic (soft) D/DVB copolymer (I), and the aromatic copolymer was prepared by a metallocene-mediated copolymerization reaction between styrene monomer and divinylbenzene (DVB) to form the aromatic (rigid) S/DVB copolymer (II). As will be discussed later, we used a mixed styrenic monomer, including styrene and p-methylstyrene (p-MS), to prevent forming the semi-crystalline copolymer. Since the crystalline domains in the polymer matrix are not penetrable by hydrocarbon molecules, it is undesirable to have the semi-crystalline copolymers as the oil absorbent.



Equation 1. Synthesis mechanism to prepare i-Petrogel oil-superabsorbent.

Several systematic studies were conducted to find the best reaction conditions to prepare both copolymers (I) and (II). Table 1 summarizes two representative reaction sets, including 1-decene/divinylbenzene (D/DVB) copolymerization mediated by a heterogeneous Ziegler-Natta catalyst ($\text{TiCl}_3\text{.AA/Et}_2\text{AlCl}$) and styrene/divinylbenzene (S/DVB) copolymerization mediated by a homogeneous metallocene catalyst ($\text{C}_p^*\text{TiCl}_3/\text{MAO}$). Evidently, the Ziegler-Natta catalyst shows an effective incorporation of DVB units (crosslinkers) in poly(1-decene) copolymer chain with a mono-enchainment mechanism and high catalyst reactivity. GPC and DSC results indicate soft aliphatic copolymers with low T_g (< -50 °C), high molecular weight, and a rather narrow composition distribution. On the other hand, the preparation of aromatic S/DVB copolymer required some extensive investigation to find the suitable catalyst system to prepare a processible (soluble) copolymer. It is well known in polymer science to prepare S/DVB copolymers using free radical polymerization mechanism. However, the resulting S/DVB copolymers are crosslinked (unprocessible materials), because the DVB comonomer involves a double enchainment during the free radical copolymerization. Our objective was to prepare processible polymers (without crosslinking reaction during the polymerization), which allows the formation of polymer blends (mixtures) between soft copolymer (I) and rigid copolymer (II) before thermal crosslinking, as illustrated in Equation 1. Fortunately, we have discovered the reaction condition involving the $\text{C}_p^*\text{TiCl}_3/\text{MAO}$ metallocene catalyst, which can engage in a single enchainment of DVB units to form the processible aromatic S/DVB copolymer (II). However, this catalyst also produces semi-crystalline syndiotactic polystyrene (s-PS) polymer chains. To prevent the formation of semi-crystalline polymers, we used a mixed styrenic comonomer that contains about 1/1 mole ratio of styrene and p-methylstyrene (p-MS) mixture. The resulting S/DVB copolymer (II) is completely amorphous with a high T_g (> 100 °C). Overall, this $\text{C}_p^*\text{TiCl}_3/\text{MAO}$ mediated copolymerization reaction is highly effective in the preparation of aromatic rigid copolymers with high molecular weight, high polymer yield (catalyst activity), and similar comonomer reactivity ratio among three styrenic comonomers (i.e. styrene, p-methylstyrene, and divinylbenzene).

Table 1. Synthesis of aliphatic D/DVB and aromatic S/DVB copolymers using Ziegler-Natta and Metallocene catalysts.

Run	Polymerization Conditions ^a				Polymerization Results		
	1-decene (ml)	Styrene ^b (ml)	DVB (ml)	Temp/Time (°C/hr)	Yield (%)	A/B/X ^c (mol%)	Crosslinking (%)
A-1	10	0	0.5	25/3	69	97.87/0/2.13	100
A-2	10	0	0.3	25/3	90	97.89/0/2.11	100
A-3	10	0	0.2	25/3	95	98.06/0/1.94	100
A-4	10	0	0.1	25/3	91	98.66/0/0.34	100
A-5	10	0	0.05	25/1	84	99.40/0/0.66	94
A-6	10	0	0.02	25/1	92	99.40/0/0.60	93
B-1	0	10	0	25/0.5	69	0/100/0	0
B-2	0	10	0.05	25/1	94	0/99.5/0/5	100
B-3	0	10	0.1	25/1	92	0/98.9/1.1	100
B-4	0	10	0.2	25/1	90	0/97.7/2.3	100
B-5	0	10	0.3	25/1	90	0/96.4/3.6	100

^a Ziegler-Natta catalyst: $\text{TiCl}_3\text{.AA/AlEt}_2\text{Cl}$; Solvent: 50 mL toluene.

^b A mixed monomer containing styrene (50%) and p-methylstyrene (50%).

^c A: 1-decene aliphatic units; B: mixed aromatic units; X: DVB crosslinker units.

As illustrated in Equation 1, the resulting D/DVS (I) and S/DVB (II) copolymers were mixed in a homogeneous solution before casting into polymer films. The isolated polymer mixture was subjected to a thermal crosslinking reaction at $>200\text{ }^{\circ}\text{C}$ to form a crosslinked mixture, i-Petrogel (III) that has an interpenetrated network (IPN) molecular structure containing individual elastic (low T_g) aliphatic hydrocarbon blocks and rigid (high T_g) aromatic hydrocarbon blocks. They are interpenetrated and connected into a network structure through crosslinker (x) units. The molecule-scale connectivity offers new i-Petrogel materials with uniform morphology. Additionally, it is easy to fine-tune a complete range of aliphatic/aromatic composition to match the ANS oil composition. It also allows us to prepare film and foam products with high surface areas and short oil diffusion paths, which are proved to be essential for absorbing ANS crude oil containing a broad range of aliphatic and aromatic hydrocarbons. Overall, our project goal is to achieve rapid ANS oil absorption with high absorption capacity, which can stop spilled oil from "weathering" and provide a temporary oil storage mechanism for positioning the recovery equipment. In addition, the oil-swelled gel (free of water) can be easily recovered by skimmers and subsequently refined as regular crude oils.

Evaluation of New i-Petrogel Material

The ANS oil absorption capacity of each individual aliphatic D/DVB and aromatic S/DVB copolymer networks was not impressive and was less than that of the original Petrogel. The results clearly show slow ANS oil absorption kinetics, compared with those of toluene and diesel. The complex crude composition and high viscosity in the ANS oil require an absorbent with high surface area and a short oil diffusion path. Thus, a systematical study was conducted in the preparation of i-Petrogel material by varying the ratio of soft and rigid copolymer content and crosslinking density to identify the most suitable i-Petrogel structure for absorbing ANS oil. Figure 2 compares three ANS oil absorption profiles using three i-Petrogel-0.2 absorbents that are prepared from the same individual soft and rigid polymer chains containing 0.2 mol% DVB crosslinker units, with three different weight ratios (3/1, 1/1, and 1/3) between rigid and soft polymers. The ANS oil absorption evaluation were conducted at $25\text{ }^{\circ}\text{C}$ (top) and $0\text{ }^{\circ}\text{C}$ (bottom), respectively, using the ASTM F716-09 test method.

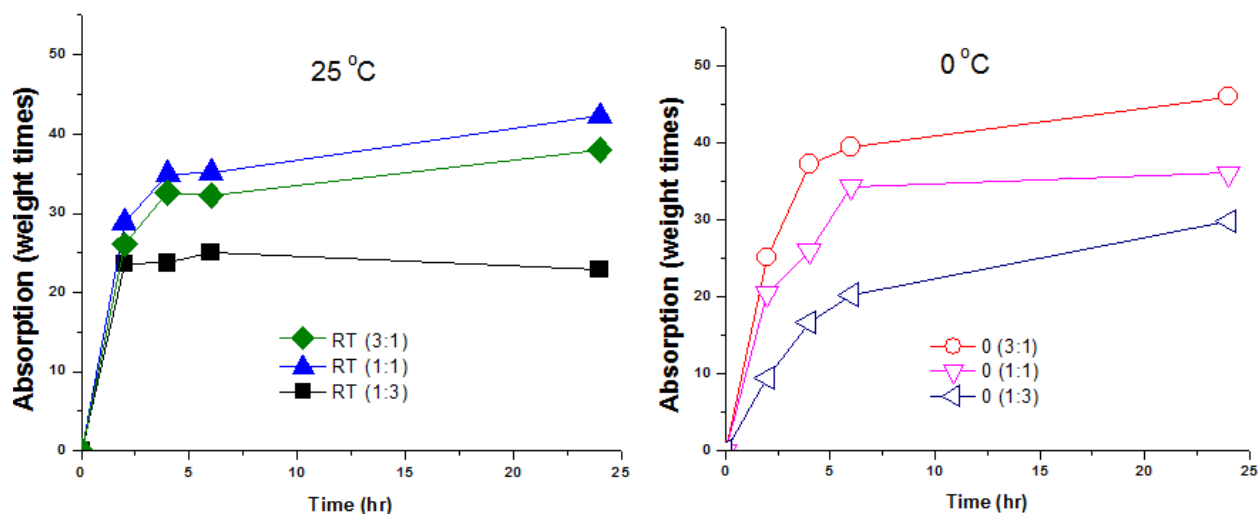


Figure 2. ANS oil absorption profiles at $25\text{ }^{\circ}\text{C}$ (left) and $0\text{ }^{\circ}\text{C}$ (right) for three i-Petrogel-0.2 absorbents with 3:1, 1:1, and 1:3 rigid and soft polymer weight ratios, respectively.

All three i-Petrogel absorbents show remarkably better ANS oil absorption capacities and kinetics than the corresponding individual aliphatic (soft) and aromatic (rigid) polymer networks. At ambient temperature (Figure 2, left), all three i-Petrogel-0.2 materials performed rapid ANS oil absorption kinetics, reaching more than 20 times the polymer weight in less than 2 hours. The i-Petrogel-0.2 with 1/1 wt. ratio reached 42 times after contacting with ANS oil for 24 hours. Furthermore, it is very interesting to observe the results in Figure 2 (right) when the ANS oil absorption is carried out at 0 °C. The i-Petrogel-0.2 with 1/1 wt. ratio reached 35 times, and the i-Petrogel-0.2 with 3/1 wt. ratio reached 45 times the oil absorption capacity. All of them became highly oil-swelled soft gels. It is interesting to note that the differences between the three absorption profiles may be associated with the recovery of the resulting i-Petrogel-0.2/ANS oil gel. Some of them, especially the 1/3 sample, after absorbing a large quantity of ANS oil became too soft to fully recover (isolated) from the water surface.

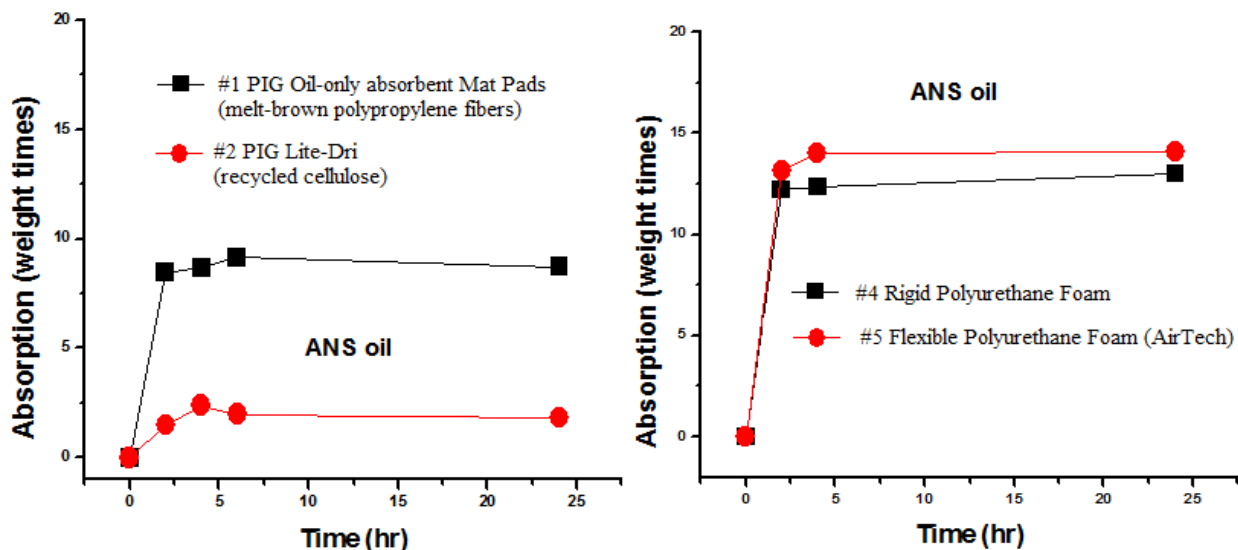


Figure 3. ANS oil sorption profiles for (left) #1 PIG melt-brown PP fiber and #2 PIG recycled cellulose and (right) #4 rigid PU foam and #5 flexible PU foam (ASTM F726-12 Test method).

For comparison, we have also evaluated several commercial oil-sorbents under similar sorption conditions at ambient temperature. They represent several material classes, including two most commonly used commercial oil sorbent materials (#1 melt-brown PP and #2 recycled cellulose) purchased from New PIG and two polyurethane foams (#4 rigid PU foam and #5 flexible PU foam) provided by AirTech a California-based company. Figure 3 shows the ANS oil sorption profiles of these four commercially-available oil sorbents. PIG melt-brown PP fiber pad (#1) shows very fast oil-sorption kinetics with a sorption capacity of about 10 times. This sorption profile is consistent with the **adsorption mechanism**, i.e. adsorbing oil molecules in its interstices via capillary action. Due to the weak oil-substrate interaction, this PP fiber-based adsorber also exhibits easy re-bleeding of adsorbed oil under a slight external force. PIG recycled cellulose (#2) shows poor oil absorption capacity (2-3 times). As discussed later, it also absorbs a significant quantity of water, causing the recovered solids to be unsuitable for calcinations; the majority will end up in landfills. On the other hand, both PU foams with open-pore morphology and high surface areas contain both hydrophobic (soft) and hydrophilic (rigid) segments along the polymer chain. Thus, they absorb both hydrocarbons and some water, and the water absorption capacity is dependent on the length of soft (polyol) segments (discussed later).

The fast kinetics of ANS oil sorption profiles, shown in Figure 4 (right), are consistent with the **adsorption mechanism**. The rigid PU foam (#4) shows about 12 times the oil adsorption capacity, while the soft (flexible) PU foam (#5) offers a slightly higher oil adsorption capacity, up to 15 times. The difference may be associated with the polyol segment, with the fact that the flexible PU foam has longer soft (hydrocarbon) segments. One key feature of this technology is the reusability of the PU foams. In other words, the adsorbed oil can be removed (recovered) by physical compression, and the recovered PU foams can be repeatedly deployed for many times before discarding as chemical waste.

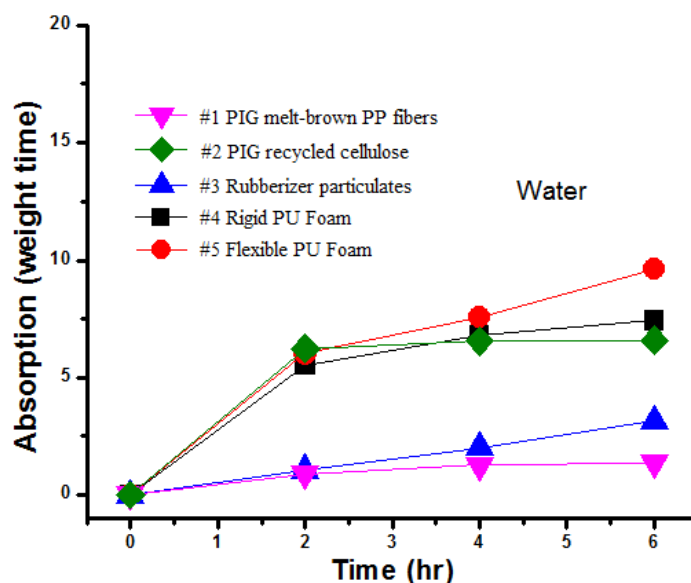


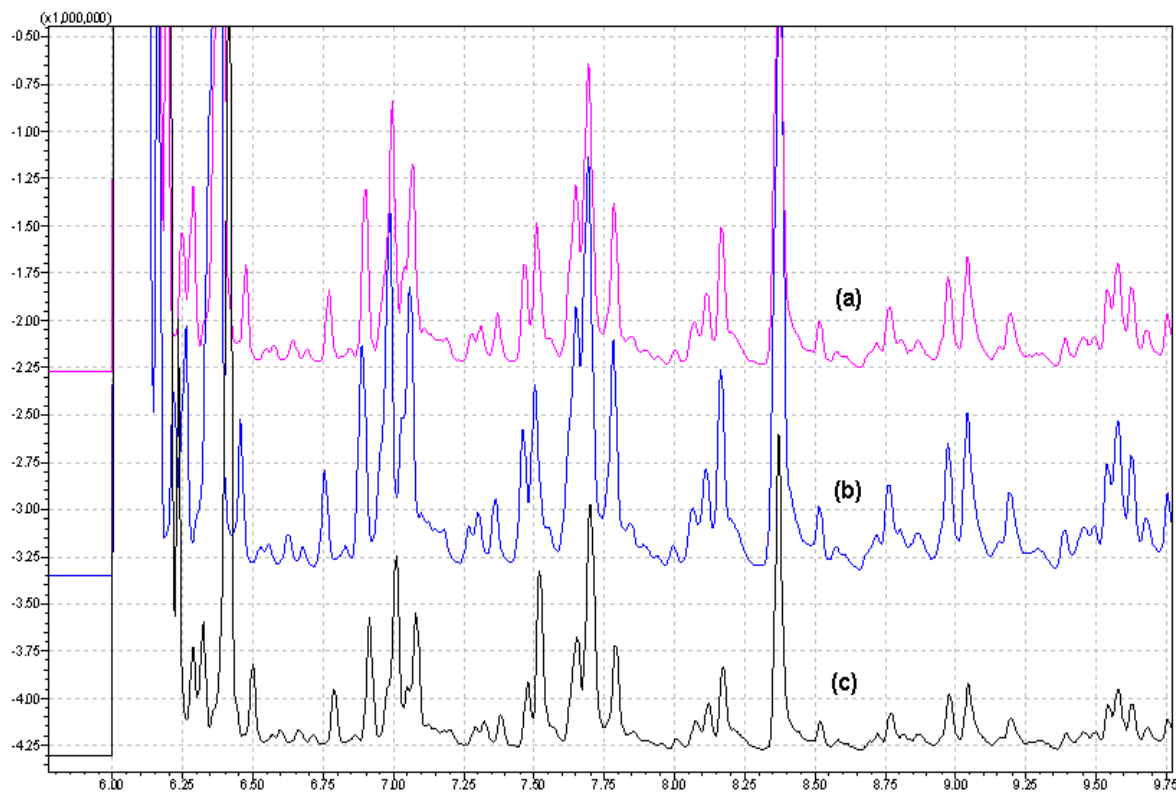
Figure 4. Water-sorption profiles for all 5 commercial oil sorbents.

Figure 4 shows the water-sorption profiles for these commercial oil sorbents. It's clear that there are two classes of commercial oil-sorbents in terms of water-sorption. Both PP fiber (#1) and EPDM Rubberizer (#3) are prepared from pure hydrocarbon polymers with hydrophobicity to prevent water sorption. On the other hand, the recycled cellulose (#2) and two polyurethane foams (#4 and #5) are quite hydrophilic with significant water-sorption capacity, more than 5 times of the polymer weight. Recovering oil with contaminated water is problematic; it is designed as a pollutant instead of an asset.

As discussed, a unique feature of i-Petrogel is its ability for recovery and reuse of the oil/i-Petrogel adducts. Because Petrogel doesn't absorb water and is less dense than water, after absorbing ANS oil, the resulting oil/i-Petrogel adducts float on the water's surface and is easy to see and recover. The recovered oil/i-Petrogel adducts contain >97% ANS oil and <3% polyolefin (hydrocarbon polymer). It is very interesting to understand the refining capability of these adducts. Figure 5 compares GC-Mass spectra of two resulting i-Petrogel-0.2 and i-Petrogel-0.02 (1/1 wt. ratio) gels (after fully absorbing ANS oil) with ANS oil itself. All three GC-Mass spectra are almost indistinguishable. They are essentially the same as the ANS oil mixture. The low percentage of i-Petrogel polymer in the gel mixture can be completely thermally decomposed to liquid hydrocarbon (oil) molecules. This combination of i-Petrogel's thermal degradation property and its selective oil absorption capability (without water) is very unique, and may offers an oil spill recovery process without secondary pollution caused by the disposal of recovered oil/water mixtures and solid wastes.

GC-MS

Pink: x-Petrogel-0.2 (1/1 wt ratio) with ANS oil
 Blue: x-Petrogel-0.02 (1/1 wt ratio) with ANS oil
 Black: ANS oil



Ret.Time	Name
6.234	Cyclohexane,1,4-dimethyl-
6.286	Cycloheptane,methyl-
6.323	Cyclopentane,1-ethyl-2-methyl-
6.416	Octane
6.5	Cyclohexane,1,4-dimethyl-
6.914	Heptane,2,6-dimethyl-
7.01	1-Pentene,3-ethyl-2-methyl-
7.08	Cyclohexane,1,1,2-trimethyl-
7.478	1-Octene,4-methyl-
7.52	Ethylbenzene
7.654	Octane,2-methyl-
7.7	Benzene,1,2-dimethyl-
7.791	Heptane,2,5-dimethyl-
8.173	Benzene,1,2-dimethyl-
8.371	Nonane
9.046	Tridecane,3-methyl-
10.286	Nonane
11.986	Nonane
13.525	Nonane
15.009	Octane,2,7-dimethyl-

Figure 5. GC-Mass spectra of (a) i-Petrogel-0.2 (1/1 wt. ratio)/ANS oil, (b) i-Petrogel-0.02 (1/1 wt. ratio)/ANS oil, and (c) ANS oil.

Overall, we have successfully developed a new class of i-Petrogel oil-superabsorbent (oil-SAP) that contains two interpenetrated and interconnected networks, including both aliphatic (soft) and aromatic (rigid) polymer networks. We have identified two potential i-Petrogel-0.2 compositions with 3/1 and 1/1 weight ratio between aromatic and aliphatic polymers. These new oil-SAPs demonstrate fast ANS oil absorption kinetics and the ability to reach the absorption capacities 42 and 35 times their weight after coming to contact with ANS oil for 24 hours at 25 and 0 °C, respectively. In addition, the resulting i-Petrogel-0.2/ANS oil mixture (soft gel) contains no water, and floats on the water surface for easy recovery. The GC-Mass results indicate a complete absorption spectrum of all ANS hydrocarbon molecules by i-Petrogel-0.2, and the recovered i-Petrogel-0.2/ANS oil mixture (soft gel) can be refined as the regular ANS oil. All combined experimental results indicate that i-Petrogel-0.2 (with 3/1 and 1/1 wt. ratios) shall be suitable for absorbing ANS oil under Alaskan arctic conditions.

Scale-up i-Petrogel Production

In Task 2, our R&D activities shifted to the material scale-up, focusing on two identified i-Petrogel-0.2 materials with 3/1 and 1/1 weight ratios between rigid S/DVB and soft D/DVB copolymers, respectively. In addition to learning the material scale-up process, the main objective was to prepare 10-20 pounds of these two i-Petrogel absorbents for an operational evaluation at the Ohmsett facility. As discussed, the preparation of i-Petrogel material involves two steps, including the first step learning how to scale-up the production of both rigid and soft polyolefin polymers and then investigating the reactive-compounding process to mix two polymers with a specific composition and *in situ* thermal-crosslinking reaction to form the desired i-Petrogel product with an interpenetrated polymer network (IPN structure).



Figure 6. (left) A drybox with inert atmosphere
(right) a pilot polymerization unit.

To carry out this polymer scale-up task, we first installed a pilot plant polymerization unit with the equipment for handling air-sensitive chemicals (catalysts and purified monomers). As shown in Figure 6, this system is centered at an autoclave (1 gallon) reactor with control units for chemical feeding, heating/cooling, and agitation. A drybox (with an inert atmosphere) was also

deployed to prepare catalyst and purify monomers. With this complete system, we routinely produced about one pound of polymer in each reaction cycle. This system can make 2-3 runs per day based on the availability of purified chemicals. Tables 2 and 3 summarize both soft D/DVB and rigid S/DVB copolymerization results obtained from this pilot plant system.

Table 2. Summary of 1-decene/DVB copolymerization to form various soft D/DVB copolymers.

Run No.	Reaction Conditions			Polymerization Results		
	1-Decene (L)	DVB (L)	Temp/Time (°C/hr.)	1-Decene (mol%)	DVB (mol%)	Yield (%)
A'-1	10	0.5	25/3	97.87	2.13	69
A'-2	10	0.3	25/3	97.90	2.10	90
A'-3	10	0.2	25/3	98.07	1.93	95
A'-4	10	0.05	25/1	99.34	0.66	84
A'-5	10	0.02	25/1	99.57	0.43	92

^a Catalyst: TiCl₃.AA/Et₂AlCl; Solvent: 3 L toluene.

^b DVB: divinylbenzene cross-linker.

Table 3. Summary of styrene/DVB copolymerization to form various rigid S/DVB copolymers.

Run No.	Polymerization Conditions ^a				Polymerization Results			
	S ^b (M)	DVB (ml)	Temp/Time (°C/hr)	Yield (%)	S/p-MS/DVB ^c (mol%)	T _g ^d (°C)	T _m ^d (°C)	ΔH (J/g)
B'-1	1	3	25/1	94	50.0/49.5/0.5	106	no	No
B'-2	1	6	25/1	92	49.5/49.4/1.1	107	no	no
B'-3	1	12	25/1	90	49.6/48.1/2.3	107	no	no
B'-4	1	18	25/1	90	48.6/47.8/3.6	108	no	no

^a Catalyst: C_p*TiCl₃/MAO; Solvent: 3 L toluene.

^b A mixed monomer containing styrene (50%) and p-methylstyrene (50%).

^c S: styrene; p-MS: p-methylstyrene; DVB: divinylbenzene cross-linker.

^d T_g and T_m were determined by DSC measurements using TA DSC-Q100 calorimetry at 10°C/min in second heating cycle.

Both scale-up reactions, including heterogeneous TiCl₃.AA/Et₂AlCl catalyst mediated 1-decene/DVB copolymerization and homogeneous C_p*TiCl₃/MAO catalyst mediated styrene/DVB copolymerization, were very successful in producing the desired soft D/DVB and rigid S/DVB copolymers with high polymer molecular weight, high yield, and mono-enchainment of DVB units to form both copolymers with good processibility. As shown in Table 2, a broad range of high D/DVB copolymers (M_w>330,000 g/mol) with various DVB crosslinker contents have been prepared without any detectable crosslinking reaction. The resulting D/DVB copolymers were entirely soluble in common organic solvents, such as hexane and toluene. Figure 7 shows the ¹H NMR spectrum of a D/DVB copolymer containing 2.13 mol% of DVB units (run A'-1). In addition to a chemical shift at 0.8 ppm, corresponding to CH₃ in the 1-decene units, and a band between 0.9 and 1.7 ppm, corresponding to CH₂ and CH in the polymer backbone, there are three bands around 5.2 and 5.7 ppm (CH=CH₂) and 6.7 ppm (CH=CH₂); and an aromatic proton band between 6.9 and 7.4 ppm (C₆H₄). The integrated intensity ratio between all three vinyl protons and the four phenyl protons determine the

vinyl/phenyl mole ratio, which is near unity. The experimental results confirm the mono-enchainment of DVB comonomers in forming the processible D/DVB copolymer.

On the other hand, in the styrene/DVB copolymerization reaction we applied the same strategy by mixing *p*-methylstyrene (*p*-MS) in the styrene feed stock, with the incorporated *p*-MS units preventing the crystallization of syndiotactic polystyrene chains. The incorporation of the high content of *p*-MS units in the S/DVB copolymer show a complete amorphous morphology, exhibiting only one thermal transition (T_g at about 106-108 °C) and no detectable melting peak in the DSC curve. As shown in Table 3, the composition of the S/*p*-MS mole ratio nearly follows the comonomer feed ratio, indicating a similar comonomer reactivity ratio that leads to the formation of the random copolymer. Evidently, both copolymerization reactions are scalable for mass production of *i*-Petrogel products.

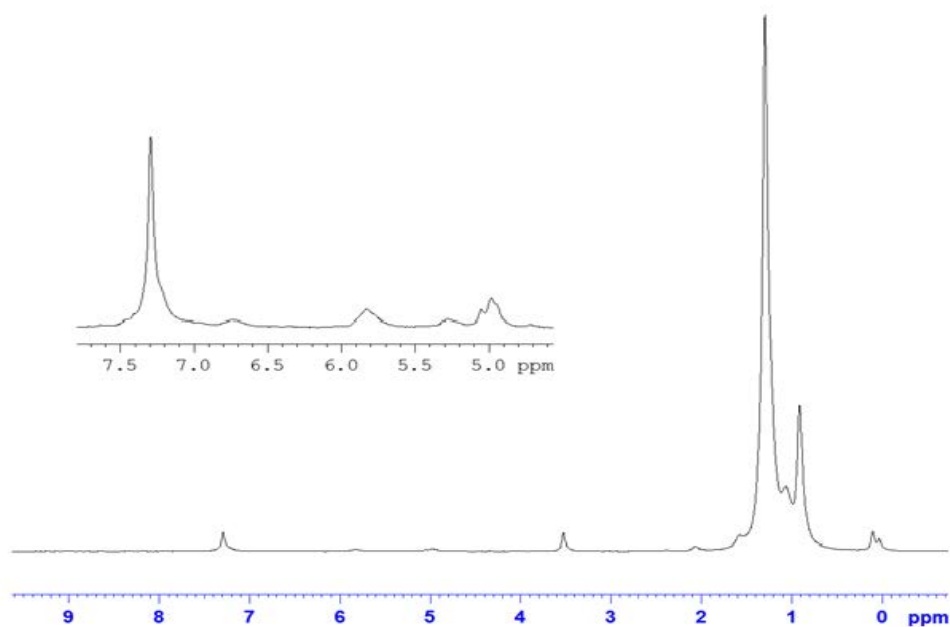


Figure 7. ¹H NMR spectrum of a D/DVB copolymer containing 2.13 mol% of mono-enchainment DVB units. (inset: expansion of the olefinic region)

In the subsequent reactive-compounding process to form the desired *i*-Petrogel material, the resulting rigid and soft polyolefin polymers were mixed in toluene solvent with a specific weight ratio. The homogeneous solution was casted into polymer films with a pre-determined thickness, controlled by the volume of solution. After evaporating the toluene solvent, the resulting solid films were thermally-treated for curing (thermal crosslinking reaction) to form the interpenetrated network (IPN) in the film matrix. As shown in Figure 8, *i*-Petrogel has an interpenetrated polymer network (IPN) molecular microstructure with two individual aliphatic (soft) and aromatic (rigid) polyolefin (hydrocarbon) polymer chains interlaced on a molecular scale. This IPN network cannot be separated unless chemical bonds are broken. The mechanical properties of this polyolefin IPN material can be easily tuned by the mixing ratio between soft and rigid polymers, as well as the DVB (crosslinker) content. As will be discussed, the resulting *i*-Petrogel material is tough, not sticky, and has the mechanical strength to form various structures and morphologies (i.e. films, foams, flakes, powders, etc.). For the operational test at the Ohmsett facility, the cured *i*-Petrogel films were chopped into flake pieces for easy handling.

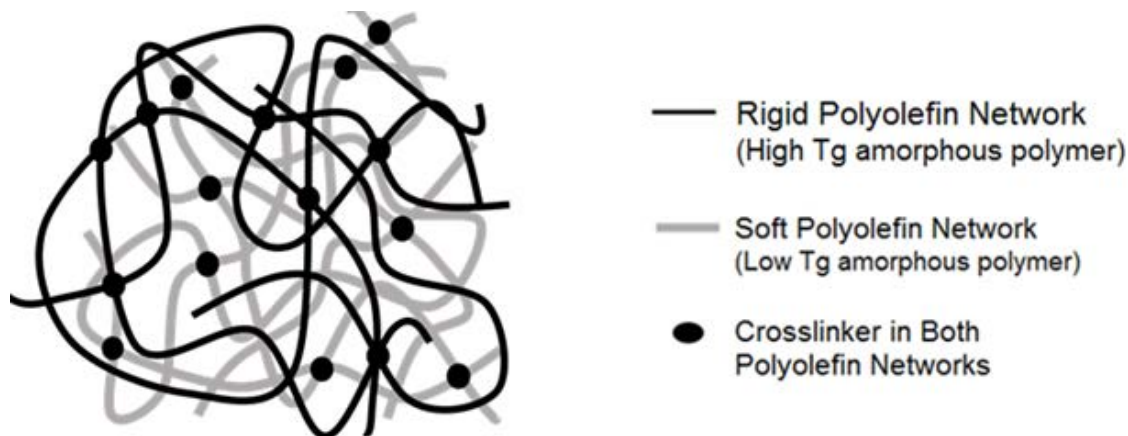


Figure 8. A schematic representation of the i-Petrogel material with an IPN molecular structure.

To understand the performance of the scaled-up i-Petrogel materials, we have prepared several i-Petrogel materials in flake form with similar rigid/soft copolymer compositions and compared their ANS oil absorption capacity and kinetics with those observed in small scale experiments. Table 4 summarizes two sets of the scaled-up i-Petrogel flakes. In the C' set, the flake samples were prepared by D/DVB copolymer (run A'-3) and S/DVB copolymer (B'-2) with 1-2 mol% DVB crosslinkers and the soft/rigid polymer weight ratios of 3/1, 1/1, and 1/3, respectively. In the D' set, the flake samples were formed by the D/DVB copolymer (run A'-5) and S/DVB copolymer (run B'-1) with about 0.5 mol% DVB crosslinkers and the soft/rigid polymer weight ratios of 3/1, 1/1, and 1/3, respectively. Table 4 also shows the ANS oil absorption capacity between two sets of the scaled-up i-Petrogel flakes and the corresponding four individual copolymers (control runs 1-4). All absorption tests were conducted under similar experimental conditions at 25 or 0 °C, following ASTM F716-09 (type II loose absorbent procedure). The absorption capacity was determined by measuring the weight ratio $W_t - W_0 / W_0$ between the absorbed oil to the original dried absorbent, wherein W_0 is the initial weight of the absorbent sample and W_t is the total weight of the absorbent-hydrocarbon gel after 24 hours.

Table 4. A Summary of ANS Oil Absorption Capacity Using Several Petrogel IPN Materials.

Run No.	D/DVB and S/DVB copolymers (weight ratio)	ANS Oil absorption Capacity	
		25°C	0°C
C'-1	A'-3/B'-2 = 3/1	22	30
C'-2	A'-3/B'-2 = 1/1	42	37
C'-3	A'-3/B'-2 = 1/3	37	45
D'-1	A'-5/B'-1 = 3/1	28	20
D'-2	A'-5/B'-1 = 1/1	47	32
D'-3	A'-5/B'-1 = 1/3	36	37
Control 1	A'-3	12	-
Control 2	A'-5	13	-
Control 3	B'-1	7	-
Control 4	B'-2	5	-

It is not surprising to see a low ANS oil absorption capacity for both individual soft D/DVB and S/DVB copolymer networks (control runs) due to the complex ANS oil composition and diffusion difficulties. On the other hand, all i-Petrogel flakes in both C' and D' sets show much better oil absorption performance. Figure 9 shows typical absorption kinetics (absorption capacity vs. time) at ambient temperature for an i-Petrogel flake (run C'-2) with 1-2 mol% DVB crosslinkers. This polyolefin interpenetrated network exhibits very fast absorption kinetics, nearly reaching the saturation level in 2-3 hours. After contacting with ANS oil for 24 hours, this i-Petrogel flake sample shows an absorption capacity of 42 and 37 times at 25 and 0 °C, respectively. It is also very interesting to see run C'-3, with a 3/1 weight ratio between the rigid S/DVB and soft D/DVB copolymer network, reaching 45 times the oil absorption capacity at 0 °C (icy condition). On the other hand, run C'-1 with a 1/3 rigid/soft weight ratio shows significantly less absorption capacity, which may be associated with the recovery problem of the resulting ANS oil/ i-Petrogel adduct. This sample after absorbing a large quantity of ANS oil becomes too soft to be fully isolated from the water surface. Similar experimental results were also observed in the D' set that involves S/DVB and D/DVB networks with about 0.5 mol% DVB crosslinker units and the same three different compositions of 3/1, 1/1, and 1/3 weight ratios between rigid and soft polymer networks. Again, runs D'-2 and D'-3 show good absorption capacity and fast kinetics at 25 and 0 °C and good recovery. Run D'-1, after fully absorbing ANS oil with a large volume expansion, becomes too soft to fully recovery. Overall, this scaled-up i-Petrogel material exhibits very similar oil absorption performance with the corresponding small scale i-Petrogel. They show ANS oil absorption capacity in the range of 35-40 times with fast kinetics, reaching the saturation level in 2-3 hours. Considering the recovery issue, the desired i-Petrogel shall be limited to 1/1 and 3/1 weight ratios between rigid S/DVB and soft D/DVB copolymers.

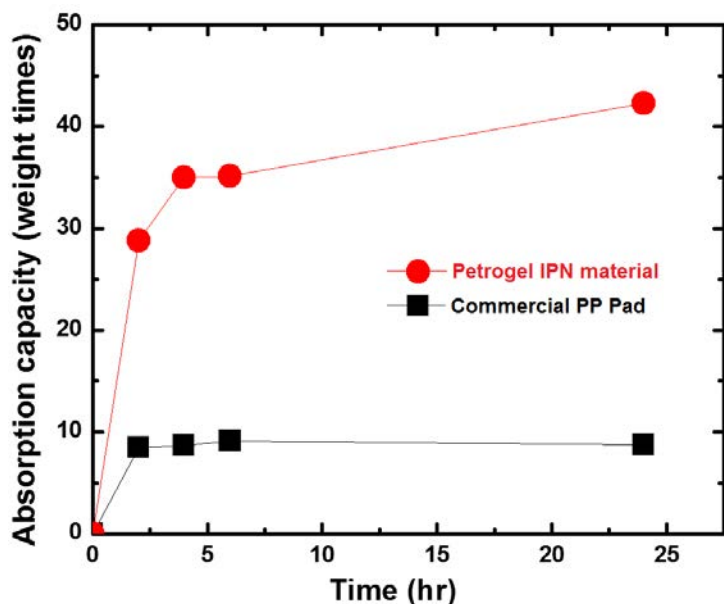


Figure 9. Comparison of ANS oil uptake vs. time between a scale-up i-Petrogel material (run C'-2) and a commercially available melt blown polypropylene pad.

Operational Test of i-Petrogel at Ohmsett Facility

Between October 5-8, 2015, BSEE conducted an operational test at the Ohmsett facility to evaluate oil spill recovery using two scaled-up i-Petrogel absorbents containing 1/1 and 3/1 weight ratio. They are the same i-Petrogel materials (runs C'-2 and C'-3 in Table 4), showing good ANS oil absorption capacities. This operational test was performed in two open tanks, containing seawater and the weathered Alaska North Slope (ANS) crude oil, using 20 pounds of i-Petrogel material (10 pounds each). The test focused on oil absorption capacity, recovery of the oil/polymer adducts on water surface by mechanical skimmers, and the ability of the resulting oil/polymer adducts to be pumped into a storage tank. The main objective was to identify the performance of i-Petrogel absorbent and understand the opportunities and barriers for large scale implementation of i-Petrogel technology in an oil spilled site on an open water surface.

Table 5. A summary of ANS oil testing conditions using two i-Petrogel absorbents.

Run	ANS oil (gallons)	i-Petrogel (lb)	ANS oil/i-Petrogel (weight ratio)	Testing time (hrs)	Skimmer type
Test 1	20	1/1 (3.75)	40	18 (overnight)	Elastec Drum Skimmer
Test 2	20	1/1 (5)	30	2 (day time)	Elastec Drum Skimmer
Test 3	20	3/1 (3.75)	40	18 (overnight)	Elastec Drum Skimmer
Test 4	20	3/1 (6)	25	4 (day time)	Vacuum pumping

As shown in Table 5, four tests were conducted with short and long oil exposure times for each i-Petrogel absorbent. For the oil absorption tests, a specified amount (20 gallons) of 10 % weathered Alaska North Slope (ANS) oil was added to a 10' x 10' x 3 foot deep portable frame water tank containing seawater (salinity=33ppt). The oil slick was about 8-9 mm thick and the tank was placed in the open air (outdoor). In order to understand the effect of the structure and composition of the materials on the oil absorption and recovery, two i-Petrogel flakes with 1/1 (C'-2) and 3/1 (C'-3) weight ratios between rigid and flexible polymers were evaluated under similar operational conditions. They were sprinkled onto the oil surface in the tank, evenly covering the surface. During the testing period, the outdoor weather was fair with clear sky and a temperature range between 50 (night) and 75 °F (noon). Both oil and water temperatures were monitored during the tests. At the end of absorption period, we gently agitated the surface with a stick for about 10 min to ensure complete contact between oil and i-Petrogel flakes. Two skimmers were applied, including an Elastec TDS 118 oleophilic drum skimmer (Tests 1-3) and a double diaphragm vacuum pump skimmer (Test 4) to study the recovery operation and efficiency. Several samples were isolated either directly from the testing surface or from the recovered oil by the skimmer.

Figure 10 shows several images during the Test 1 operation. First, 3.75 pounds of i-Petrogel with a 1/1 weight ratio (C'-2), shown in image (a), were uniformly spread onto the surface of 20 gallons of 10% weathered ANS oil (40/1 oil/polymer weight ratio), shown in image (b). The mixed ANS oil/i-Petrogel surface was left overnight (about 18 hours), without agitation (calm winds). After this spontaneous absorption period, the mixture shown in image (c) became a film-like gel material with a relatively uniform and bright surface and some swelled gel particles. They are viscous fluid floating on the water surface and can be physically picked up and recovered by simple sticks or nets. As shown in image (d), they can be effectively recovered by an Elastec TDS 118 oleophilic drum skimmer with various speeds. Although the high drum rotation speed (>20 rpms) increased the recovery rate, it also picked up some water drops along

with the recovered ANS oil/i-Petrogel fluid as shown in image (e). It is interesting to note that the viscous ANS oil/i-Petrogel fluid exhibits good adhesion to the HDPE drum surface and also provides a continuous oil/i-Petrogel fluid flow toward the rotating drums during the recovery. As shown in image (f), the recovered ANS oil/i-Petrogel fluid can also be pumped using a centrifugal or double diaphragm pump.

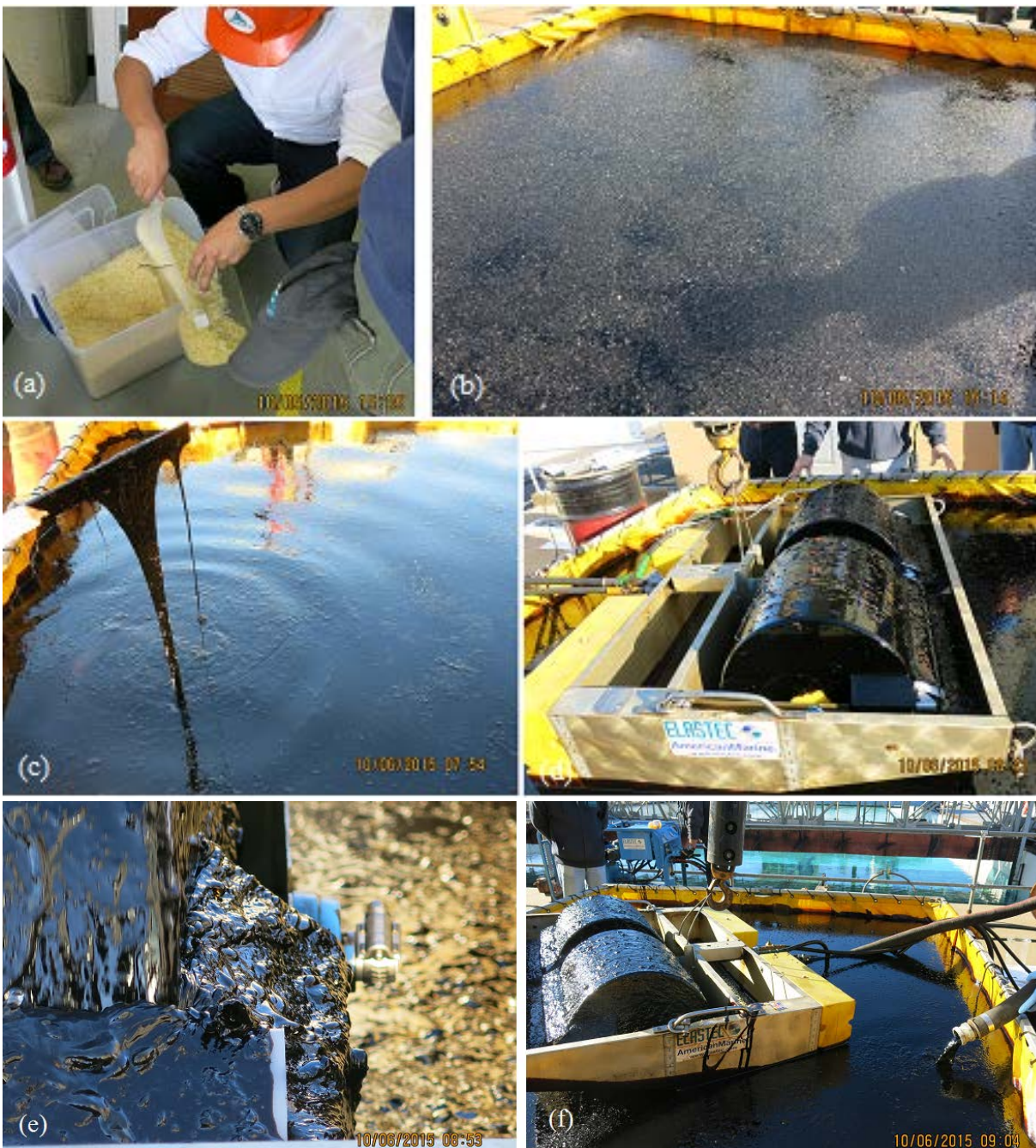


Figure 10. (a) The scaled-up i-Petrogel flakes with 1/1 weight ratio, (b) after spreading i-Petrogel flakes onto the oil surface, (c) after 18 hours absorption time, (d) recovery of ANS oil/i-Petrogel fluid by an Elastec TDS 118 oleophilic drum skimmer, (e) the recovered ANS oil/i-Petrogel fluid with high drum rotation speed, and (f) pumping of the recovered ANS oil/i-Petrogel fluid.

Figure 11 shows two images during Test 3 that was carried out under similar operation in Test 1, except using the i-Petrogel with a 3/1 weight ratio (C'-3). The same 3.75 pounds of i-Petrogel with a 3/1 weight ratio was spread onto the surface of 20 gallons of 10% weathered ANS oil (40/1 oil/polymer weight ratio), and the mixture was left overnight under similar weather conditions. Image (a) shows the ANS oil/i-Petrogel surface after 18 hours of spontaneous oil absorption. The resulting ANS oil/i-Petrogel adduct forms cohesive (sheet-like) gel that can be easily picked up and recovered by simple sticks or nets, as shown in image (b). However, the recovery by an Elastec TDS 118 oleophilic drum skimmer requires some physical assistance to move the sheet-like ANS oil/i-Petrogel adduct toward the rotating drums. In addition, the recovered viscous adduct also showed some pumping difficulties.



Figure 11. (a) The sheet-like ANS oil/i-Petrogel (3/1) adduct, (b) recovery of ANS oil/i-Petrogel sheet by a simple stick.

Some unexpected result was observed in Test 4: This test was conducted under the sunlight using the i-Petrogel with 3/1 rigid/soft polymer weight ratio and an unexpectedly high oil temperature (~ 120 °F) at noon time under strong sunlight. Instead of forming the cohesive sheet-like gel (as we expected), the oil/i-Petrogel adduct was a soft chunky gel. Evidently, the elevated temperature seems to reduce gel formation. In other words, the gel viscosity of oil/i-Petrogel adduct may be sensitive to temperature (>100 °F). This is a curious phenomenon, considering the desired material viscosity required at various operational stages.

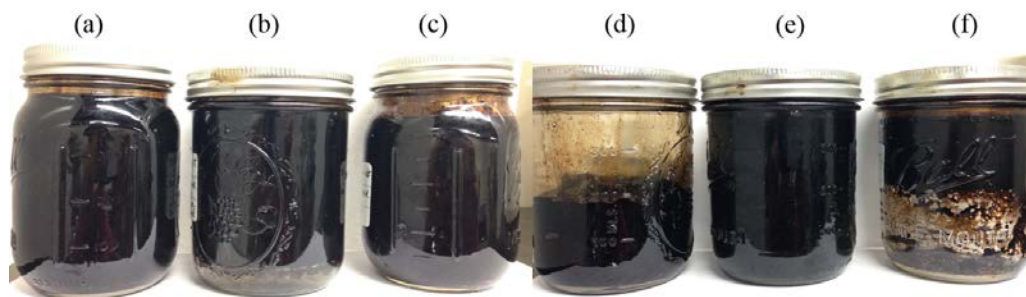


Figure 12. The recovered ANS oil/i-Petrogel samples from (a) the testing surface of Test 1 (18 h), (b) the drum skimmer recovered oil of Test 1 (18 h), (c) the drum skimmer recovered oil of Test 2 (2 h), (d) the testing surface of Test 3 (18 h), (e) the drum skimmer recovered oil of Test 3 (18 h), and (f) the vacuum pump recovered oil of Test 4 (4 h).

Figure 12 shows one set of the recovered ANS oil/i-Petrogel samples from this operational test. The first half (samples a, b, and c) uses i-Petrogel with a 1/1 weight ratio, and the second half (samples d, e, and f) involves i-Petrogel with a 3/1 weight ratio. Sample (a) was directly picked up from the testing surface in Test 1 (after 18 h absorption), and sample (b) was the same ANS oil/i-Petrogel fluid recovered by the drum skimmer. Sample (c) was the drum skimmer recovered ANS oil/i-Petrogel fluid after 2 hours of testing in Test 2. Samples (d) and (e) were the recovered sheet-like ANS oil/i-Petrogel adducts in Test 3 (18 h) from directly picking out or by the drum skimmer, respectively. Sample (f) was the vacuum pump recovered ANS oil/i-Petrogel adduct of Test 4 (4 h). The same set of the recovered ANS oil/i-Petrogel samples were provided to all three organizations – Penn State, BSEE, and Ohmsett – for further analysis. At Penn State, we focused on the water contents and refinery characteristics of these recovered samples.

Water content in the recovered samples were determined by two methods, including the phase-separated water and TGA-Mass measurements. As shown in Figure 12, the trapped water is slowly phase-separated from the recovered ANS oil/i-Petrogel fluids and they are clearly observed in the bottom of sample (b) and sample (f) bottles. We usually sampled the top layer of the ANS oil/i-Petrogel fluids for all the measurements. The first experiment was conducted by diluting the recovered ANS oil/i-Petrogel sample with dry toluene to reduce the material viscosity. As shown in Figure 13, the mixed solution was then placed in a burette for 24 hours to separate the trapped water and remove the contaminated water at the bottom of the burette. Table 6 summarizes the water contents in all samples after setting for 2 days and 2 months, respectively. The water contents in samples (a) and (b) were very low (<0.1 wt%). Other samples have significantly higher water contents, associated with the drum rotation speed, the viscosity of ANS oil/i-Petrogel fluid, and the setting time. Samples (d), (e), and (f), using i-Petrogel with a 3/1 weight ratio, trapped more water during the recovery and also proved more difficult in the phase separation, which may be associated to their high fluid viscosity. It is interesting to note that some different water content results were observed by the Ohmsett technicians, despite applying a similar measurement method. The deviation may be due to the sampling of experimental specimens from the mixed solutions, not the top of the recovered sample as was done in our case.

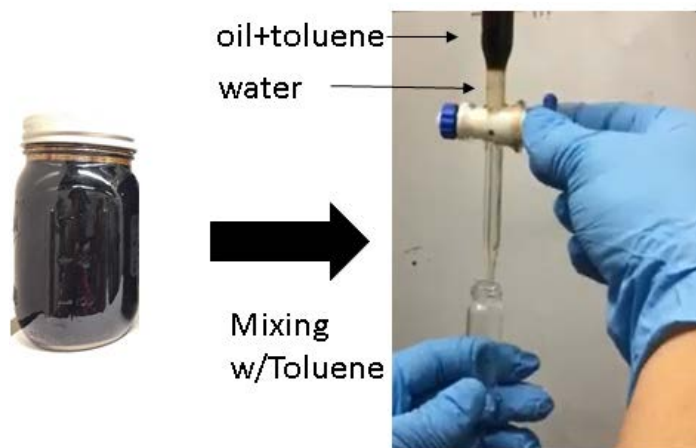


Figure 13. Schematic of the phase-separation method.

Table 6. Water contents in the recovered samples

Sample	Water Content (weight%)	
	after 2 days	After 2 months
a	0.01	0
b	0.1	0.07
c	2.8	1.2
d	4.6	2.8
e	4.4	3
f	7.4	4.5

The recovered sample (b) was also examined by TGA-MS with a heating rate of 10 °C/min from 50 to 600 °C. In addition to measuring the weight loss of the recovered sample by TGA, the resulting pyrolyzed products (H₂O, CO, and CO₂) were also monitored by a Mass spectrometer. As shown in Figure 14, sample (b) completely decomposed upon heating, with no detectable water during the pyrolysis.

***i*Petrogel 1:1 ratio, after ANS absorption(TGA-MS)**

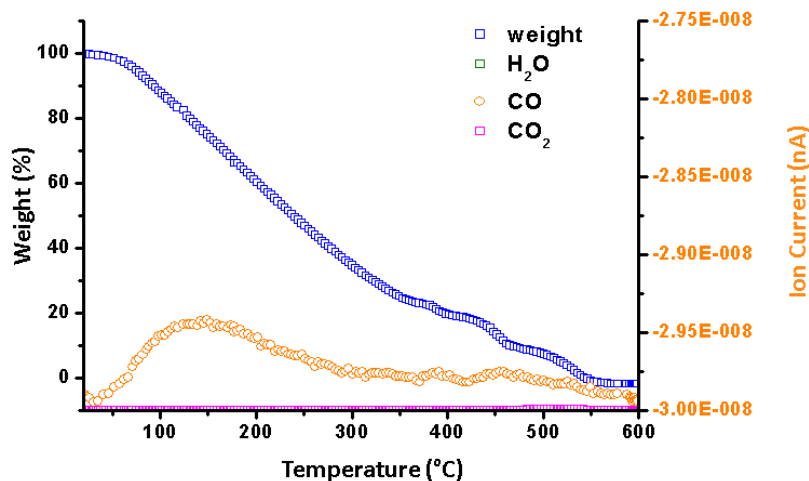


Figure 14. TGA-MASS results during the pyrolysis of the recovered sample b.

Conclusion/Recommendations

Based on the observation of the operational test at the Ohmsett facility and the test results in consistent with the experimental results obtained in our Penn State laboratory, we can draw several conclusion, discussed below:

- ***i*-Petrogel material:** We have identified the most suitable *i*-Petrogel IPN structure that can effectively and efficiently recover the spilled ANS oil on seawater surfaces. The material scale-up process, including polymer preparation and processing into various forms, has been developed for the mass production of various *i*-Petrogel products.
- **ANS oil absorption capacity and kinetics:** *i*-Petrogel oil-absorbent is capable of absorbing ANS oil 35-40 times the capacity under 25 and 0 °C. The absorption kinetics are fast in the first 2-3 hours to reach 80-90% saturation. The *i*-Petrogel with a 1/1 rigid/soft polymer weight ratio absorbs slightly more ANS oil to form the viscous ANS oil/*i*-Petrogel fluid. On the other hand, the *i*-Petrogel with a 3/1 rigid/soft polymer weight ratio forms the sheet-like ANS oil/*i*-Petrogel adduct.
- **Recovery by skimmers and pumping ability:** The Elastec TDS 118 oleophilic (HDPE) drum skimmer (with a smooth drum surface) showed effective recovery of the ANS oil/*i*-Petrogel viscous fluids in Tests 1 and 2, involving the *i*-Petrogel with a 1/1 rigid/soft polymer weight ratio. At a high drum rotational speed (with a high recovery rate), some water drops accompanied the recovered oil/*i*-Petrogel viscous fluid (sample b in Figure 9). The recovered oil/*i*-Petrogel fluid can be effectively pumped using the metered pump pallet from the skimmer sump to the storage tank. However, the (sheet-like) gel in Test 3 requires some

assistance to be picked up by the rotating drum skimmer. In addition, the recovered viscous adducts also show some difficulties during pumping.

- Water content in the recovered ANS Oil/i-Petrogel adducts: The water contents in the recovered sample is associated with the viscosity of the ANS oil/i-Petrogel fluid, the speed of skimmer drum rotation, and the sample setting time to allow for water phase separation. The trapped water contents in samples (a), (b), and (c), using the i-Petrogel (1/1 weight ratio) absorbent, are significantly less than those in samples (d), (e), and (f), using i-Petrogel with a 3/1 weight ratio.
- Reusing the recovered ANS oil/i-Petrogel fluids: Based on the GC-Mass measurements, the recovered ANS oil/i-Petrogel fluids (without water) show identical spectra with that of the original ANS oil. Combining with the TGA results of i-Petrogel polymer that is completely degraded to small organic molecules at <400 °C, the recovered ANS oil/i-Petrogel fluids shall be able to be refined as ANS oil using regular refining processes, preventing secondary pollution that is caused by the disposal of recovered materials.

Under this BSEE project, we have developed a practical i-Petrogel technology and identified the most suitable molecular structure for ANS oil spill recovery. Considering the combination of absorption capacity, absorption efficiency, kinetics, recovery, pumping, and refining capabilities, the i-Petrogel flake with an IPN structure and a 1/1 weight ratio between soft D/DVB and rigid S/DVB copolymers is the most suitable oil superabsorbent. In the option period we will work with a toll manufacturer to prepare 250 lbs of this Petrogel material, and BSEE will conduct simulated field testing in Ohmsett's Main Tank. In addition, there are several recommendations for further study to fully realize Petrogel potentials and speed-up the application for full scale (commercial) oil spill recovery operation, including:

- Using commercially-available polymers to prepare the i-Petrogel absorbent.
- Studying the best Petrogel form that can be dispersed in water and spread via airplanes (similar to dispersants).
- Carrying out the refining test on the recovered oil/Petrogel by regular distillation process.