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Modified Wood Flour: A Multifunctional Agent to Support In Situ Burns

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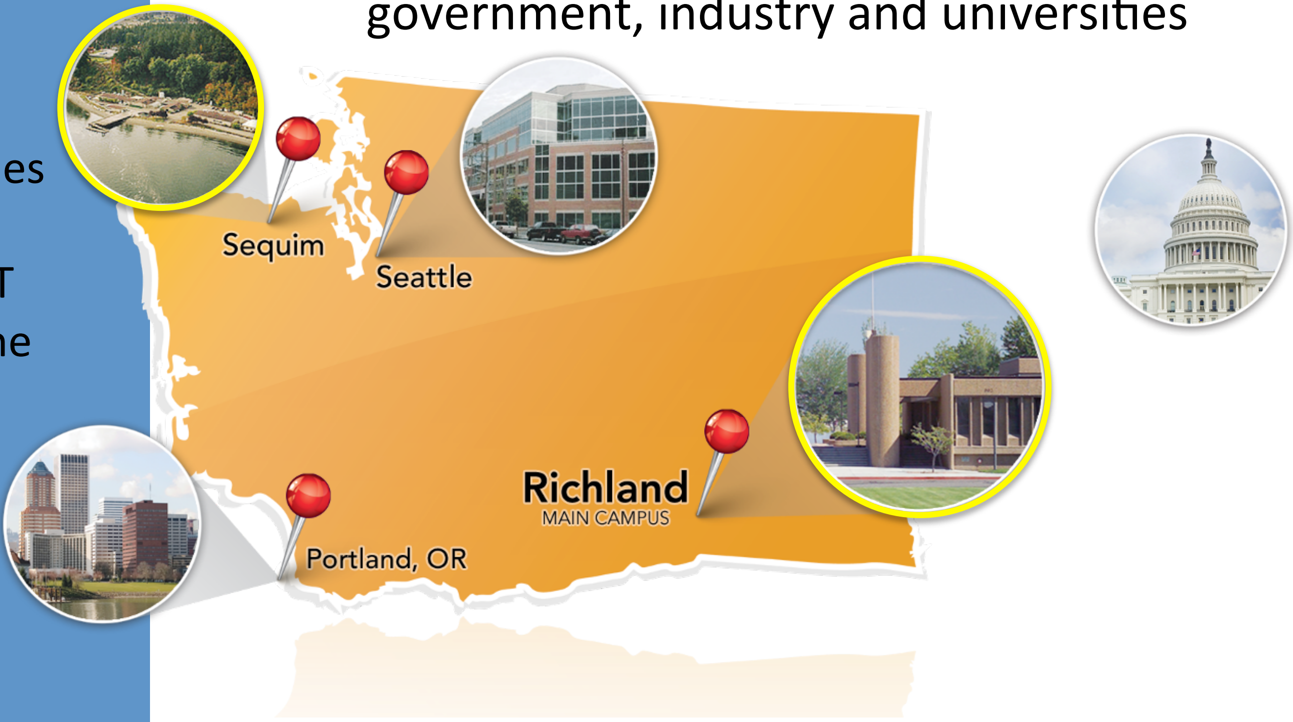
Pacific Northwest National Laboratory

- Big problems, mission-driven
- High-risk, potentially high-reward
- Large, long-term, multidisciplinary research
- Maintain capabilities and facilities for DOE’s mission, S&T community, and the nation

Scientific advances = Economic Growth and Competitiveness

- US Department of Energy, Office of Science
- Proudly operated by Battelle since 1965
- More than 4,400 staff
- Unique capabilities
- Mission-driven collaborations with government, industry and universities



Project Overview

- Objective:
  - Conduct a series of controlled tests to identify or develop materials to facilitate in situ burning of crude oil in conditions found in the Arctic
  - Functional despite cold, ice, wind, or waves

- Aims:
  - Identify or create a material that combines effects (e.g., herding, sorption, other) for dynamic operation
  - Use of material doesn’t preclude other operations
  - Longer lasting effect than with liquid chemical herding agents
  - Fast acting: ability to initiate a burn shortly after application
  - Environmentally friendly
  - Low cost

Summary of Tests and Findings

- Tests:
  - Screening and down-selection of COTS, modified COTS, and new materials
  - Operation in icy water
  - Mid-scale in situ burning
  - Scaled demonstration at the Joint Marine Test Facility
  - Support for biodegradation

- Findings:
  - A chemically modified wood flour (fine sawdust) worked best across several performance metrics
  - It doesn’t result in significant contraction of a slick
  - But it enables burning of thinner slicks and keeps the slick together
  - Enables crude to burn more intensely in cold/icy water
  - Resultant ash and tar is more buoyant
  - It maintains viability of microorganisms

Chemical Herding Agents

- Well-reviewed, for example by SL Ross Environmental Research in a series of reports for BSEE
  - Herding agents have higher spreading pressures than crude oil, allowing these to spread quickly into a surfactant monolayer
    - Very little herding agent is needed, ~ $50 g/m^2$
  - The herding agent reduces tension on the water surface, allowing an oil slick to contract and thicken
  - Oil slick thickness greater than 3mm is typically required for burning
  - Efficient burns can rapidly (in minutes) remove ~90% of oil from the ocean surface

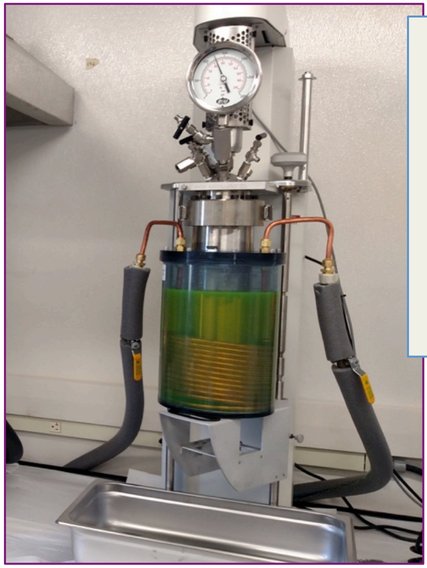
- Interestingly, the sea surface microlayer, a naturally occurring surfactant in the ocean, does not appear as a consideration in many lab or field tests

Challenges and Inspiration

- Challenges with chemical herding agents
    - Mode of action is to thicken an oil slick for ISB, but no other benefit
    - Dissipate in ~1 hour, but contraction of oil in cold water is slower (up to 1 hr needed)
    - Poor performance with wind (≥2m/s; 4.5 mph) or waves
    - Mixed results when ice is present
    - Concerns about toxicity, though small quantities are used

- Technical inspiration
    - Work designing and testing coatings for antifouling/anticorrosion protection
        - Hydrophobic, oleophilic, oleophobic, icephobic surface modifications
    - Stabilization of microorganisms on lignocellulose for long term (months-years) viable storage and transport under various conditions
    - Prior experience with bioremediation, including oil

Bench to Midscale Oil Research at PNNL-Marine Sciences Laboratory



High Pressure, Low Temperature Research for OCS: Parr reactors rated to 3000 PSI (2 km depth)

Custom Wave Tank

Shore break extension

Ports to connect to external chiller

Freezer Laboratory

Operates at -10°to -15°C

Starting Material

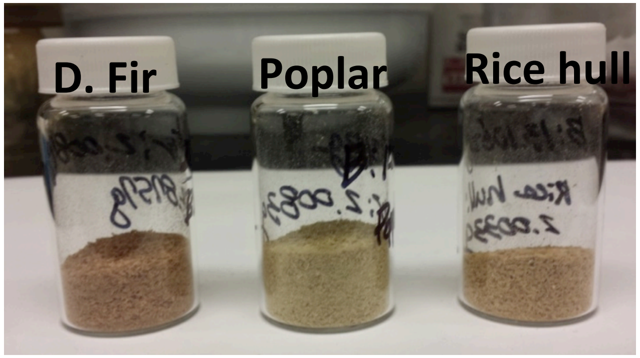
- Screened a number of base materials
  - Silicates
  - Lignocellulosic material

Test materials candidates

- Fir (soft wood)
- Poplar (hard wood)
- Rice hull (high silica content)
- Various mesh sizes

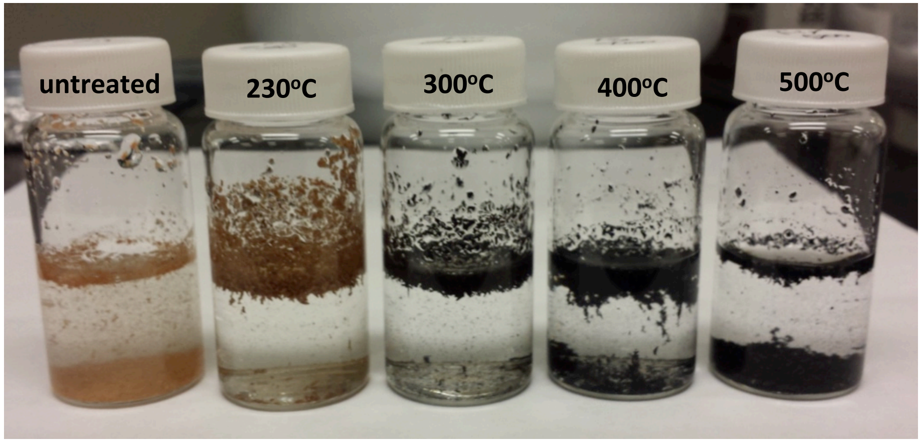
Additives

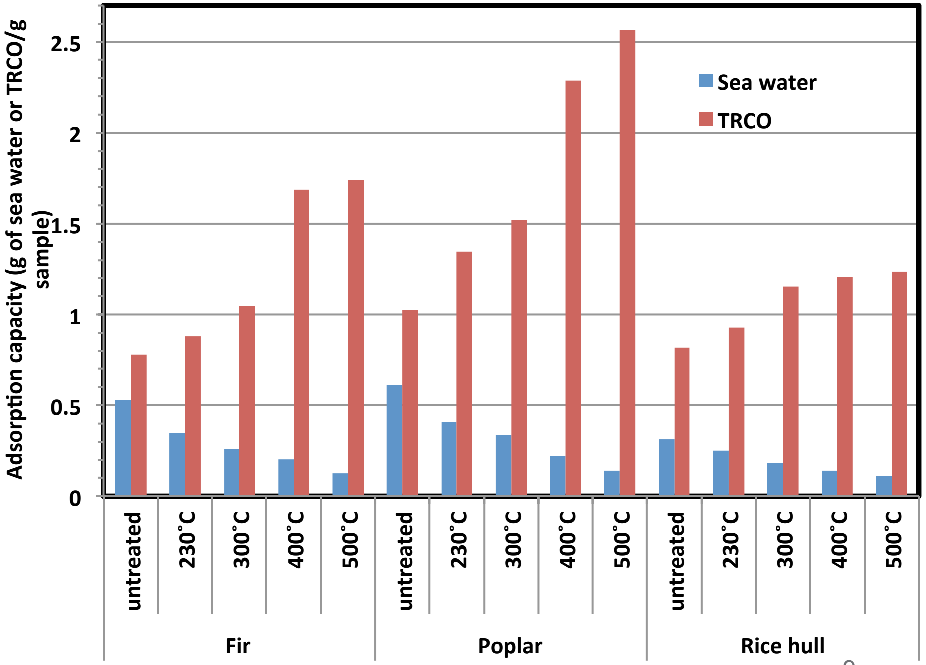
- Thermal treatment
- Oleic acid
- Acetylation
- USN herding agent



What Didn’t Work

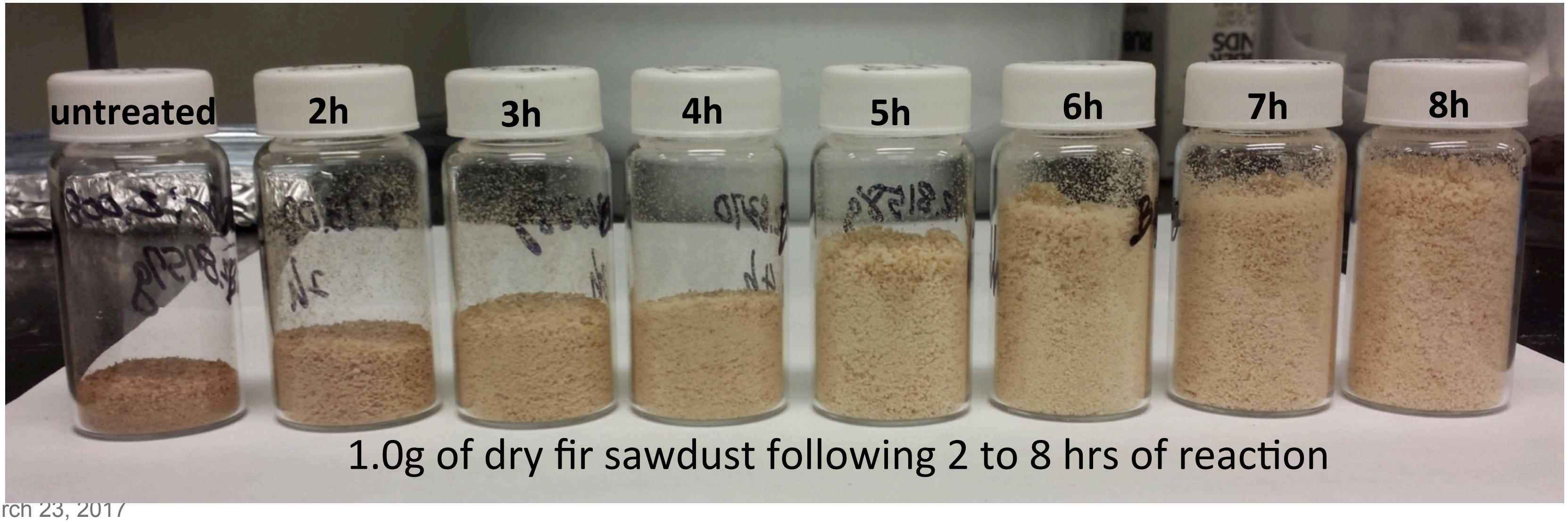
- Silicates
  - Quickly ruled out due to costs and buoyancy (of cheap materials)
- Lignocellulose: anaerobic thermal treatment, acetylation
  - Poor balance of buoyancy and sorption
- Tests:
  - Oil adsorption (incipient method on samples kept at 43% RH)
  - Moisture adsorption
  - Buoyancy





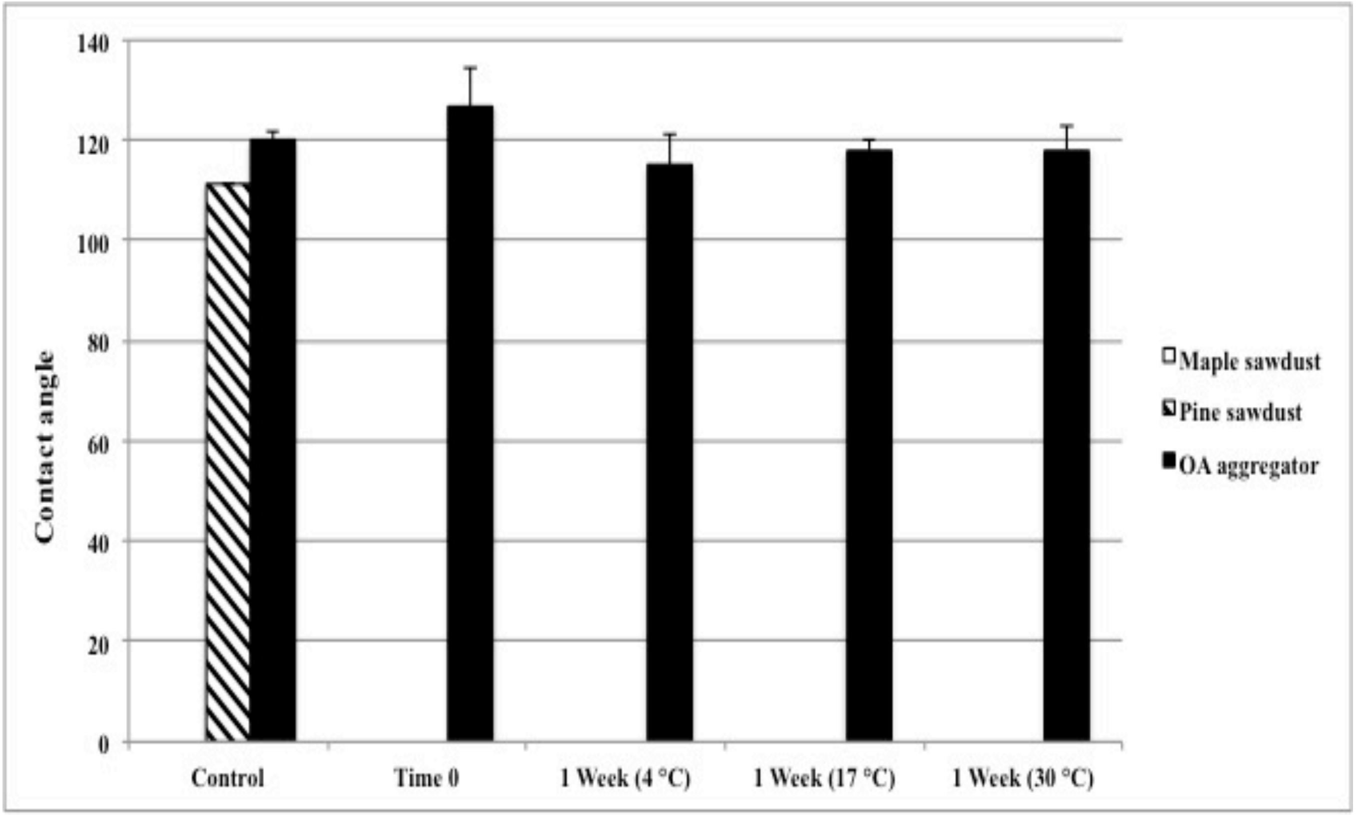
Most Promising

- Sawdust chemically modified with fatty acids
  - Softwoods (pine, Douglas fir) outperformed hardwoods (poplar and maple)
  - Pine 40-60 mesh (0.43 – 0.25 mm) wood flour performed the best
    - Buoyant >3 mos, adsorbs ~5x wt crude oil and <0.2x seawater, icephobic
  - Reaction times optimized, process still ‘laboratory scale,’ up to kg of material produced

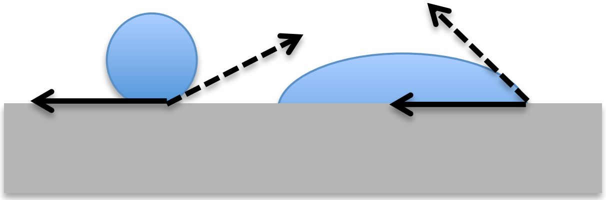


1.0g of dry fir sawdust following 2 to 8 hrs of reaction

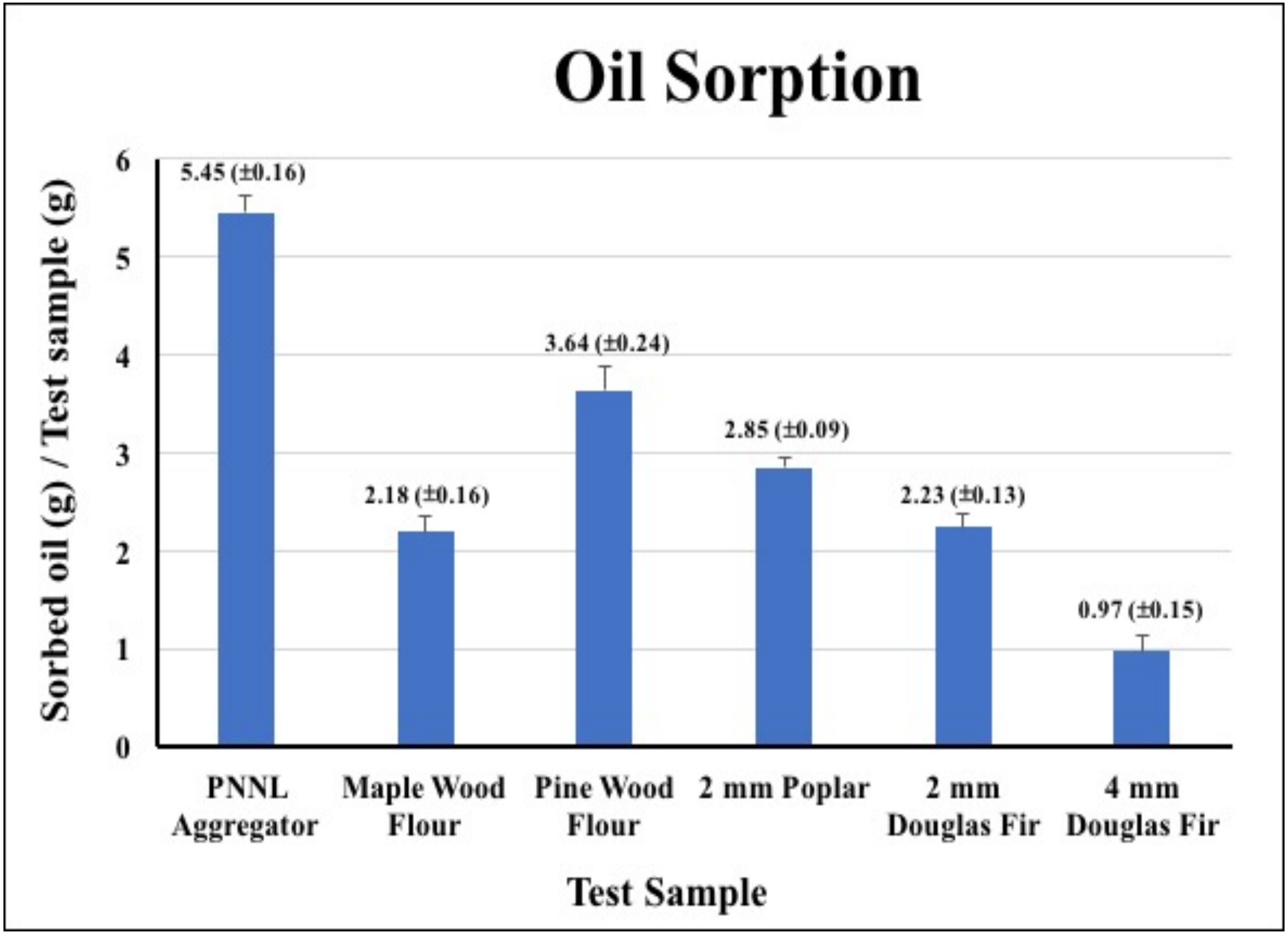
Hydrophobicity: Contact Angle



- Contact angles >90° are considered hydrophobic.
- Contact angles >120° are considered highly hydrophobic
  - Teflon has a contact angle of ~110°

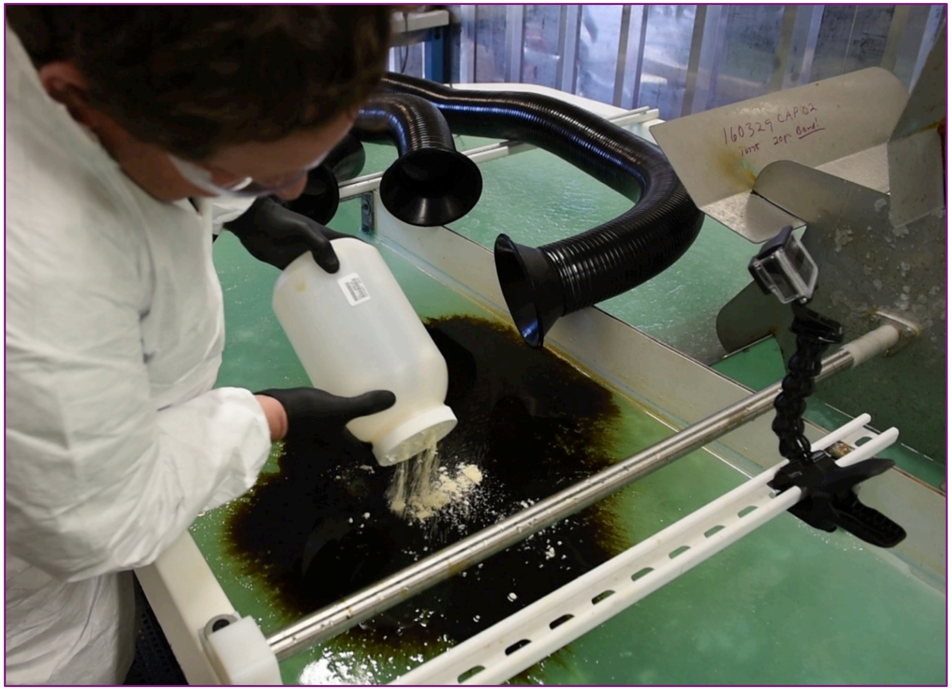


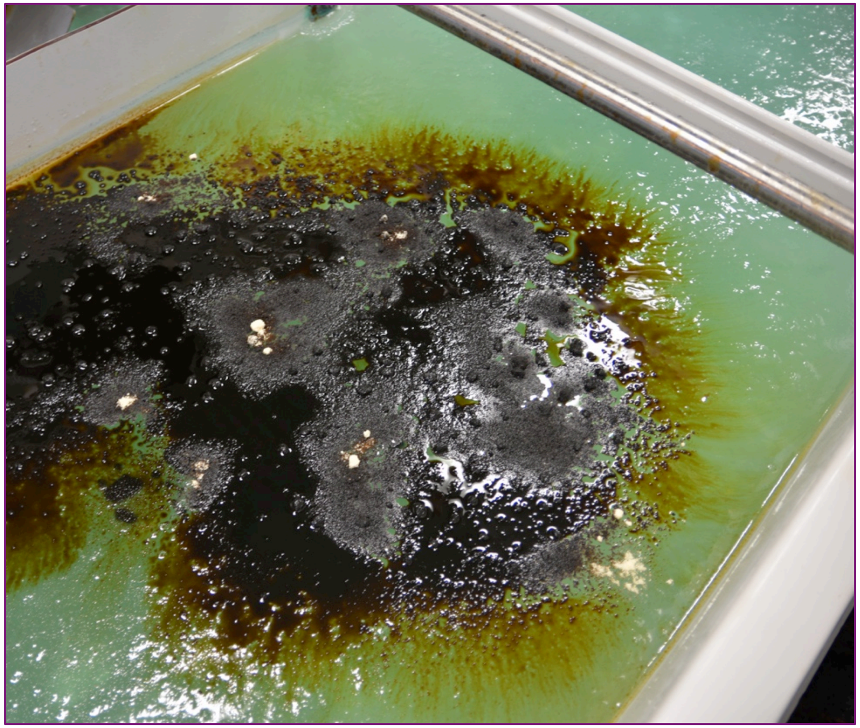
Oil Sorption



Ice Tests

- Freezer laboratory (no burning)
  - -15°C air with circulating seawater chilled to -20°C
  - Frazil ice through coagulated and harder forms or brash ice
  - Outdoor tests in static tanks





Burn Tests at JMTF

- Conducted 6 burn tests at JMTF in October, 2016
  - First experimental burn since Hurricane Katrina damaged the facility
- Scheduling opportunity preceded tests in Sequim
- Optimized the aggregator:oil ratio and method of application on-site

- Used a small, 6 x 6 section of the 30’x100’ tank
- Burns with 4 and 8 liters of ANS or Macondo crude
- High humidity and air temperature (88°F, heat index 98°+)

Findings from the Burn Tests at JMTF

- Aggregator soaks into the oil quickly
- Too much aggregator and any excess floated on top of the oil-soaked aggregator
    - Oddly, very slow transfer of oil from particle to particle– the aggregator holds onto the oil “greedily”
    - Too much aggregator suppressed the burns
- It kept the slicks from spreading when applied around the edge of the slick, but very little contraction occurs
- Aggregator that fell into the larger tank ‘swept’ the surface clean

Burn Tests

- Range of burn tests conducted in Sequim, 20^{o} to 50^{o}F (-6.6^{o} to 10^{o}C)
- Burn tests in Sequim
  - 20 cm to 2.4 m diameter burn pans
  - Up to 6 L oil per burn

500 mL oil only with sea ice
Low intensity burn

500 mL oil with sea ice and
1/10 aggregator
Higher intensity burn

Burn Residues

- Burn residues: ash and tar, no sheen
  - Residues include unburned aggregator
  - Residues from burns with aggregator remain buoyant for days with gentle or vigorous shaking


Oil only residue after 1 week shaking at 200 rpm

Oil + aggregator residue after 2 weeks rocking

Oil + aggregator residue after 2 weeks shaking at 200 rpm

Burn Results

- Able to burn slicks <1 mm thick
- Able to ignite within 5 min of application
- Applying the aggregator around perimeter and over the top works well
- Aggregator appears to act as a wicking agent; it is effective at separating the oil from the water during the burn
- The aggregator itself is mostly unburned
- Ratios greater than 1:7 (aggregator:oil) suppress the burn
- It may not be the ratio of aggregator to oil (mass:mass) that matters, but aggregator to surface area
  - Assessing data to determine if it is application rate per unit surface area, or a combination
  - Ratios of <1:12 mass:mass (lower limit uncertain) work well
- Burn temperatures up to 900^{o}C
  - Can increase by up to 100^{o}C using a variant with powdered accelerant
- Without accelerant, we had difficulty igniting weathered crude (>20% loss)

Microbiology

- Explored use of aggregator to stabilize, store, and transport pre-cultivated bioremediation organisms
  - Any oil:aggregator mix that escapes the ISB site prior to ignition may be degraded
    - Aggregator keeps the slick at the surface and provides surface area for microbial growth to facilitate biodegradation

- Findings
  - Aggregator itself is non-toxic to microorganisms
  - It maintains the viability of a mixed community (fungi and bacteria) for at least several weeks, even at elevated (32^{o}C) temperatures
    - Tested at 4^o, 22^o, and 32^{o}C
  - The aggregator also appears to become colonized by seawater organisms that may degrade it over time

Conclusions

- The product is still in its early phases (TRL3-4)
- There appear to be some benefits in facilitating burns and maintaining a cohesive slick
  - Need to further explore the impact of wave and wind energy
  - Data analysis wrapping up to determine precise burn efficiencies
- Need to further refine application ratios (mass:mass or mass:area)
- Inclusion of an accelerant may help to burn weathered oil
- Engaging end users to determine additional questions or challenges
- Stabilization of microorganisms achieved
- PNNL providing funding to optimize chemical synthesis
  - Unclear what the actual cost would be at scale

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