# Dilbit Crude Oil Properties, Weathering Behavior, and Spill Countermeasures

E. Taylor[1], G. Challenger[1], J. Rios[1], M. McCarthy[2], C. Brown[3], and J. Morris[4]

[1]Polaris Applied Sciences, Inc., Bainbridge Island, WA, USA
[2]Mac McCarthy, Inc., Edmonds, WA, USA
[3]Colpat Pipeline Consulting Inc., Sherwood Park, Alberta, Canada
[4]Witt-O'Brien's, Seattle, WA, USA

# Learning Outcomes

- Dilbit and oil sand crude exports are not new and their properties are encompassed within the range of petroleum products handled and shipped worldwide
- Dilbits undergo rapid evaporative weathering but remain buoyant on water for days unless mixed with sediment, similar to many oils
- Countermeasures for medium to heavy crude oils are appropriate for response to dilbit releases
- Ongoing and planned research initiatives continue to provide knowledge on dilbit characteristics and spill countermeasures.

# Presentation

- Dilbit studies
- Gainford Tests
  - Oil properties and weathering
  - Spill countermeasures tests
  - Skimmer tests
- Comparisons with Other Testing
- Conclusions

# Dilbit Studies

- Literature review of 2010 showed limited detailed studies (mainly laboratory and bench-scale tests) had been completed that characterize the fate and behavior of heavy crude oils
- Imperial Oil, SL Ross, WCSS, Environment Canada, NRCan had undertaken select studies on dilbit physical properties and mechanical countermeasures
- Spill response: Westridge (Burnaby, BC) and Marshall (MI)

# Recent Dilbit Tests

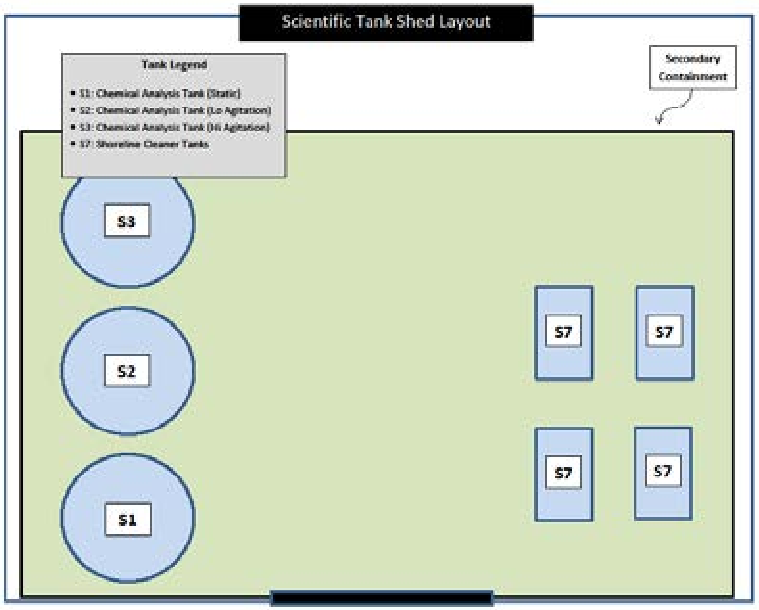
- SLRoss 2005 – Dilbit physical properties and weathering for modeling
- SLRoss 2011 – Flume test; dilbit on freshwater with plunge
- KM Gainford Test 2013 – Dilbit on brackish (estuarine) water, skimmers, dispersants, burning and shoreline cleaning agents
- API/SLRoss 2013 – Diluted oil sands crudes on freshwater, over artificial stream bed, and sediment/soil penetration

# Recent Dilbit Tests

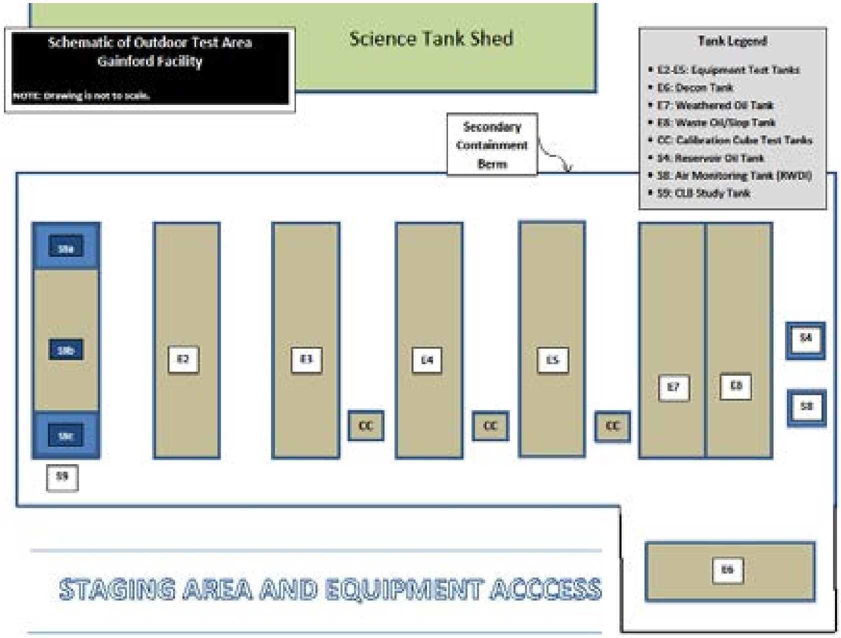
- Government of Canada (2013) –and dilbit physical and chemical properties, synthetic evaporation, weathering and behaviour, sediment mixing, and chemical dispersants
- Government of Canada (2013-2014) – wave tank studies of dilbit weathering and behaviour, fine sediment interaction, and chemical dispersants in saltwater (with freshwater influx)
- Ongoing R&D and Expert Panels (NRC and RSC)

# Gainford Tests

- Meso-scale tests for 10 days under simulated wave and wind conditions that may be more typical of the marine setting of Burrard Inlet, and a research plan that consisted of :
  - Characterisation of properties and behaviour of representative dilbit oil samples naturally weathered under varied physical conditions:
    - Cold Lake Winter Blend (CLWB) and
    - Access Western Blend (AWB)
  - Testing of mechanical equipment as products weathered on the surface of the water over a 10-day period;
  - Testing the efficacy of non-mechanical countermeasures, such as
    - in-situ burning,
    - chemical dispersants, and
    - shoreline cleaning agents



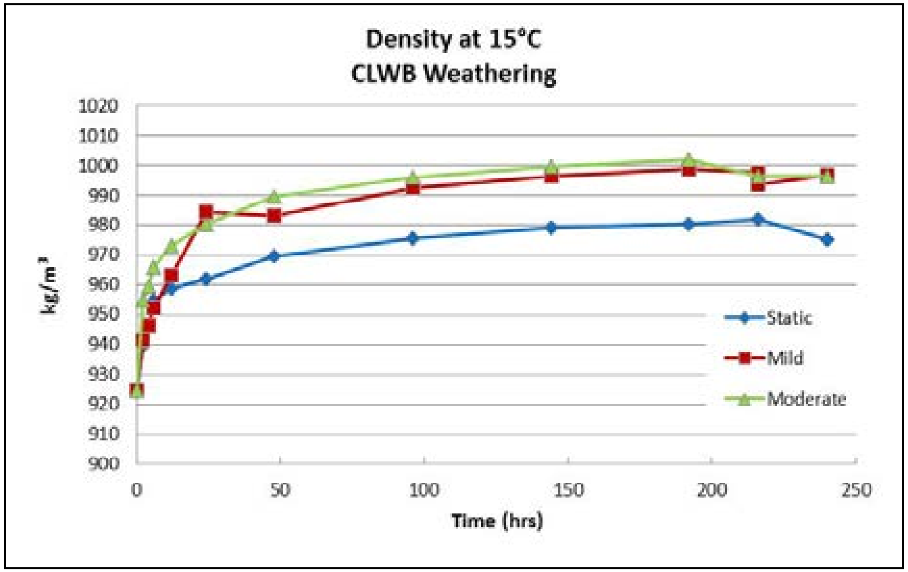
Scientific Tank Shed Layout
Tank Legend
S1: Chemical Analysis Tank (Static)
S2: Chemical Analysis Tank (Lo Agitation)
S3: Chemical Analysis Tank (Hi Agitation)
S7: Shoreline Cleaner Tanks
Secondary Containment
S3
S2
S1
S7
S7
S7
S7

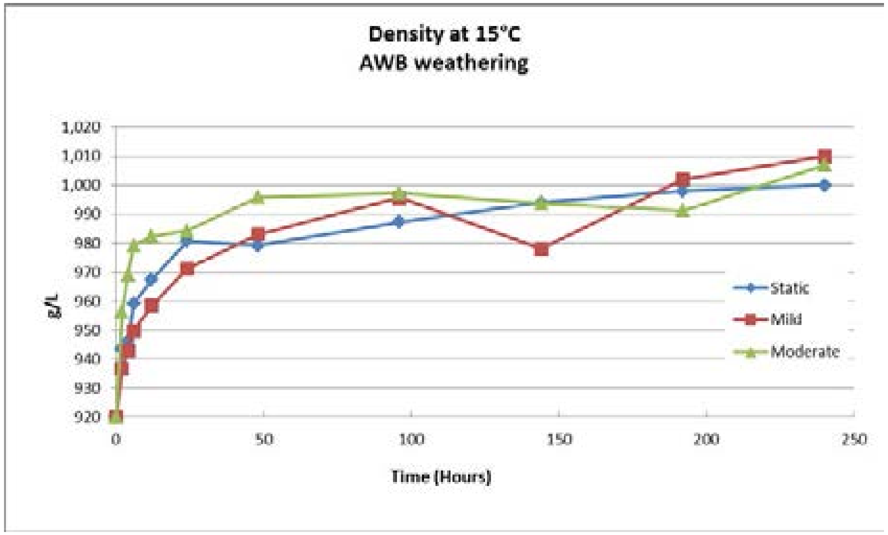



Schematic of Outdoor Test Area
Gainford Facility
NOTE: Drawing is not to scale.
Science Tank Shed
Secondary Containment Berm
Tank Legend
E2-E5: Equipment Test Tanks
E6: Decon Tank
E7: Weathered Oil Tank
E8: Waste Oil/Slop Tank
CC: Calibration Cube Test Tanks
S4: Reservoir Oil Tank
S8: Air Monitoring Tank (KWDI)
S9: CLB Study Tank
E2
E3
E4
E5
E7
E8
CC
CC
CC
S4
S8
S9
E6
STAGING AREA AND EQUIPMENT ACCESS

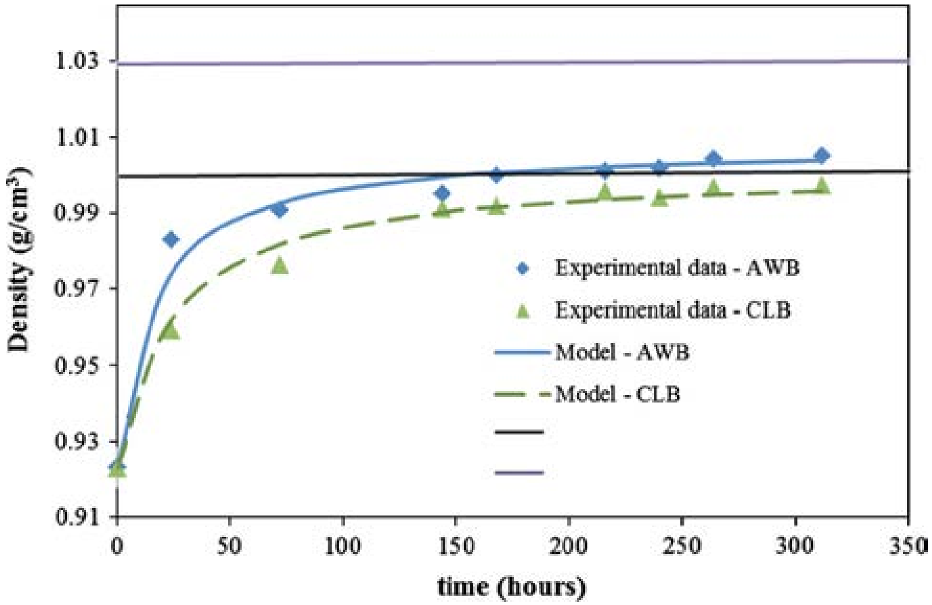
# Density

Gainford

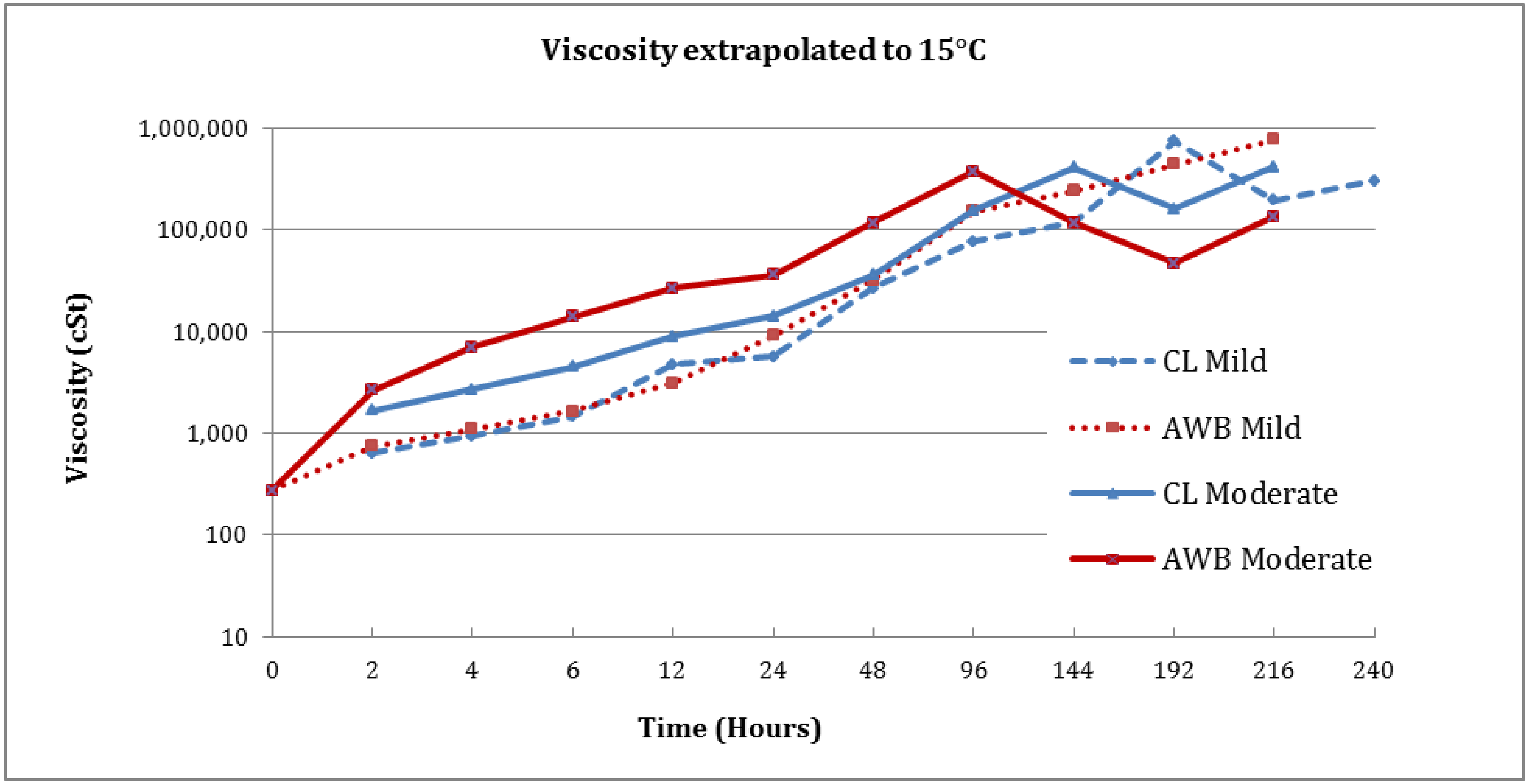


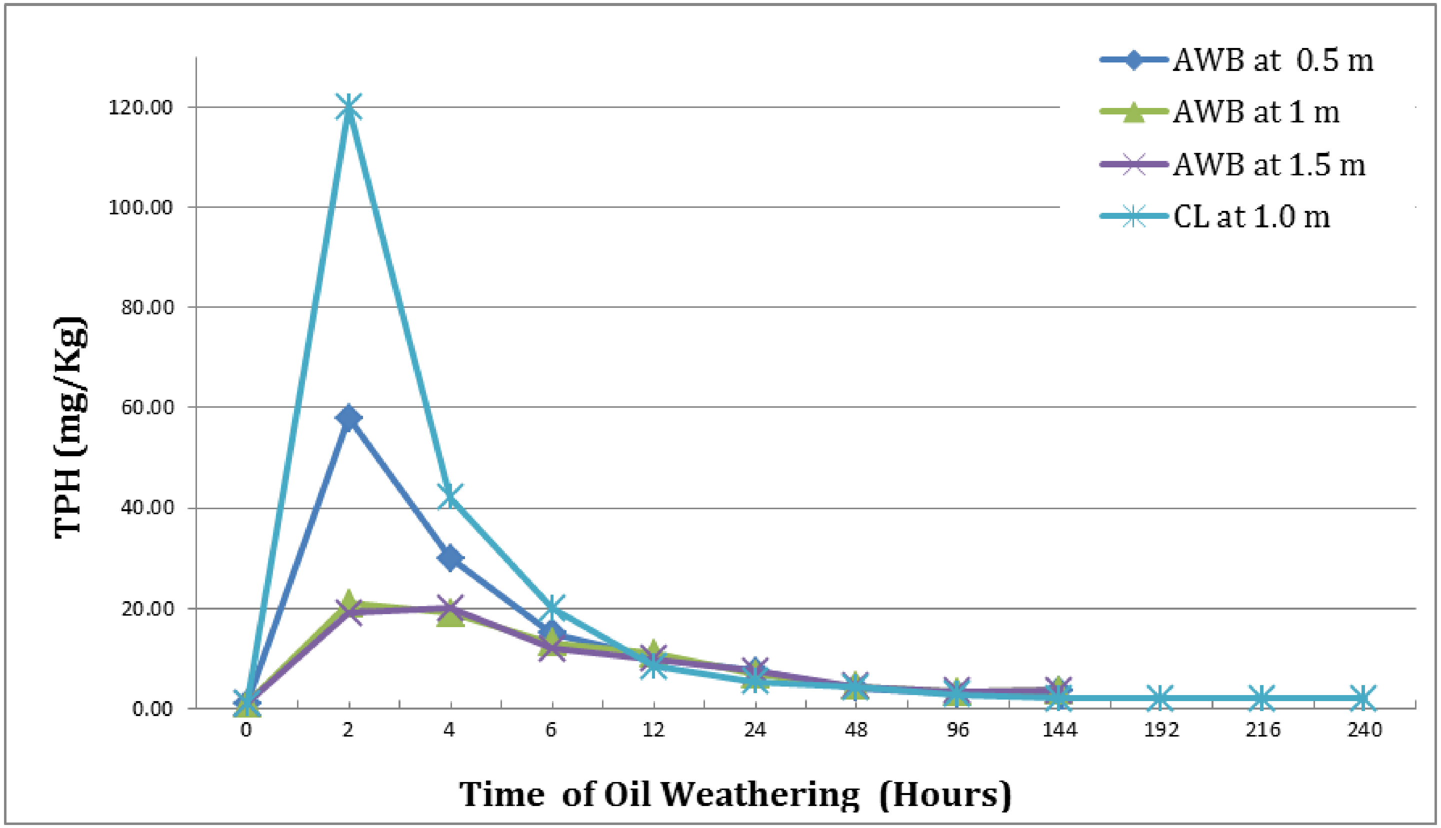

King et al., 2014



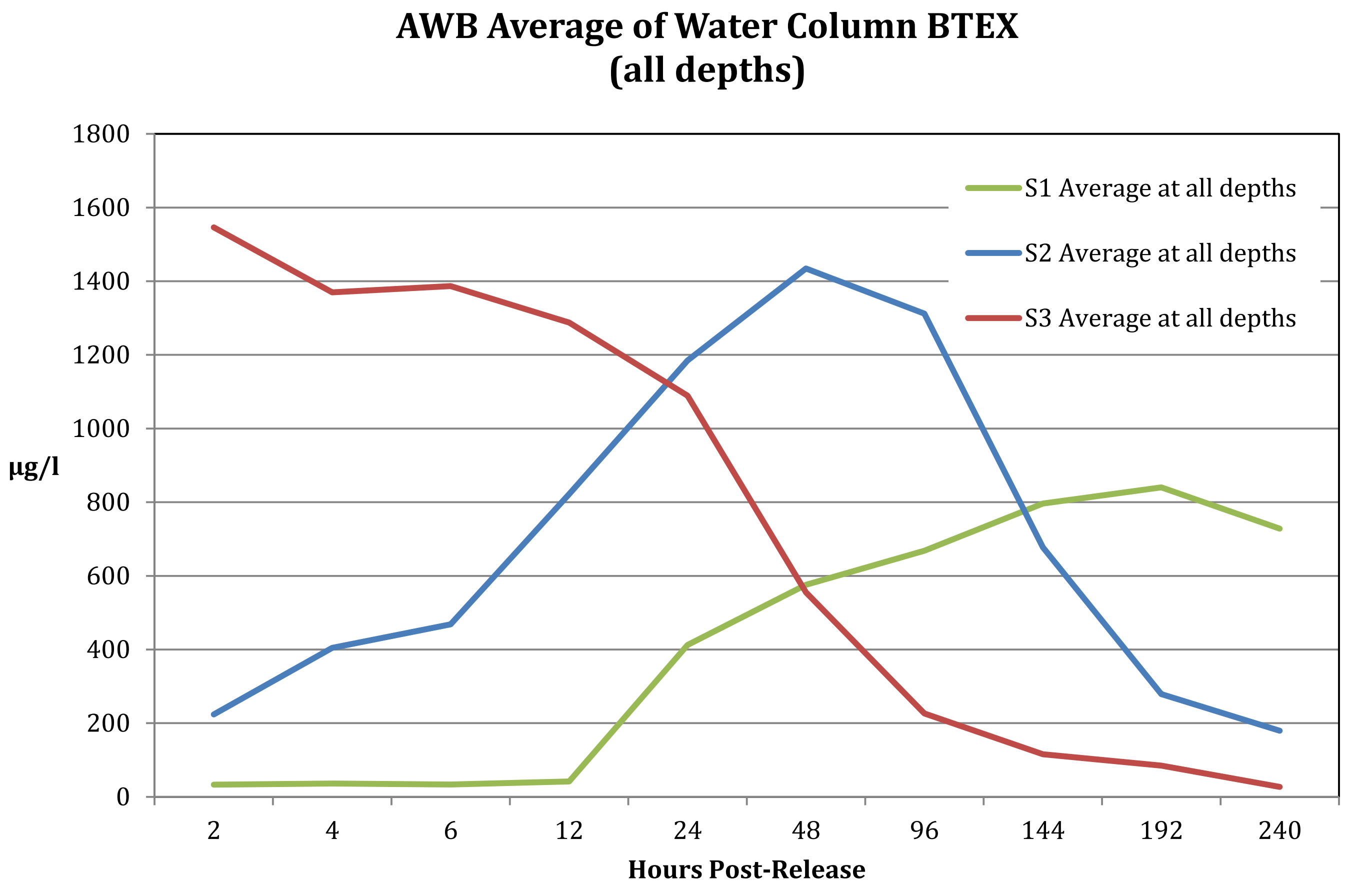
# Viscosity of Weathered Dilbit



# TPH in the water column



# BTEX in water column



# Emissions

- Light hydrocarbons emission rates declined by >80% in 6 hours.
- Emissions of all combined chemical groups declined
  - by >80% after 12 hours
  - and >90% after 3.4 days


| Chemical Group | Time to Achieve Emission Rate Reduction by | | |
|---|---|---|---|
| | > 80% | > 90% | > 95% |
| Light Hydrocarbons | 6 h | 12 h | 175 h |
| Volatile Organic Compounds | 12 h | 66 h | 82 h |
| Volatile Organic Hydrocarbons | 12 h | 82 h | 175 h |
| Total Reduced Sulphurs | < 6 h | < 6 h | < 6 h |
| Total Hydrocarbons (Detected) | < 6 h | 6 h | 30 h |
| Total Volatile Organic Hydrocarbons (Detected) | 12 h | 30 h | 37 h |

# Equipment Tests

- Aquaguard RBS Triton 60 DI3 - a brush skimmer driven by a diesel/hydraulic power pack
- Desmi DBD-5 system - a diesel/hydraulic powered skimmer fitted with an oleophilic brush-drum assembly
- Lamor MultiMax LAM 50/3C Brush Skimmer - a conveyor belt type oil skimmer with three stiff-brush-chains

**ASTM Standards**

- F-631:Standard Guide for Collecting Skimmer Performance Data in Controlled Environments
- F-2008:Standard Guide for Qualitative Observations of Skimmer Performance
- F2709-08: Standard Test Method for Determining Nameplate Recovery Rate of Stationary Oil Skimmer Systems

# Equipment Results

| Date of Test | Approx. Elapsed Time from Oil Release that Test was Conducted (Hrs.) | Duration of Peak Test | Density of Oil Sample (lab result; Absolute; kg/m3 @ 15 °C) | Viscosity of Oil Sample (lab result: cSt extrapolated to 15 °C)* | Number of Skimmers Tested | Range of Water Content in Oil Sample from Cal. Cubes (lab result; %) | | Range in Rate of Oil Recovery (liters/sec.) | | Range of % of Oil Content in Cal. Cube | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | High | Low | High | Low | High | Low |
| 13-May | 4 | 2 min | 925.2^ | 220 | 3 | 22.0 | 5.7 | 0.86 | 0.21 | 33 | 19 |
| 15-May | 46 | 4 min | 952.4^ | 1252 | 3 | 11.8# | 8.2 | 0.59 | 0.58 | 95 | 81 |
| 17-May | 96 | 4 min | 970.1 - 985.1 | 6603 - 15523 | 3 | 50.4 | 24.1 | 0.70 | 0.31 | 98 | 79 |
| 19-May | 144 | 4 min | 982.5 - 989.9 | 7982 – 17234* | 3 | 47.5 | 20.0 | 0.71 | 0.40 | 94 | 28 |
| 21-May | 192 | 4 min | 986.2 - 993.0 | 15903 – 30304 | 3 | 49.0 | 26.2 | 0.82 | 0.25 | 95 | 79 |
| 22-May | 216 | 4 min | 975.1^^ | 9642 | 2 | 17.0 | 13.2 | 0.26 | 0.12 | 97 | 73 |
| | | | | | | | | | | | |

# Results

- **Equipment Testing**
  - Maximum recovery rates for oil weathered for up to 8 days ranged from of 0.59-0.86 l/s (2.12-3.1 $m^3$/hr) before notably dropping to 0.26 l/s (0.94 $m^3$/hr) on Day 9.
  - Under the test conditions, the weathered CLWB behaved no differently than other crude oils and was mechanically recoverable by the skimming units tested.
  - Equipment performance would have been improved by the use of drum and disc skimming attachments initially to better recover the low viscosity oil, then changing to use the brush/belt attachments after a few days of weathering.

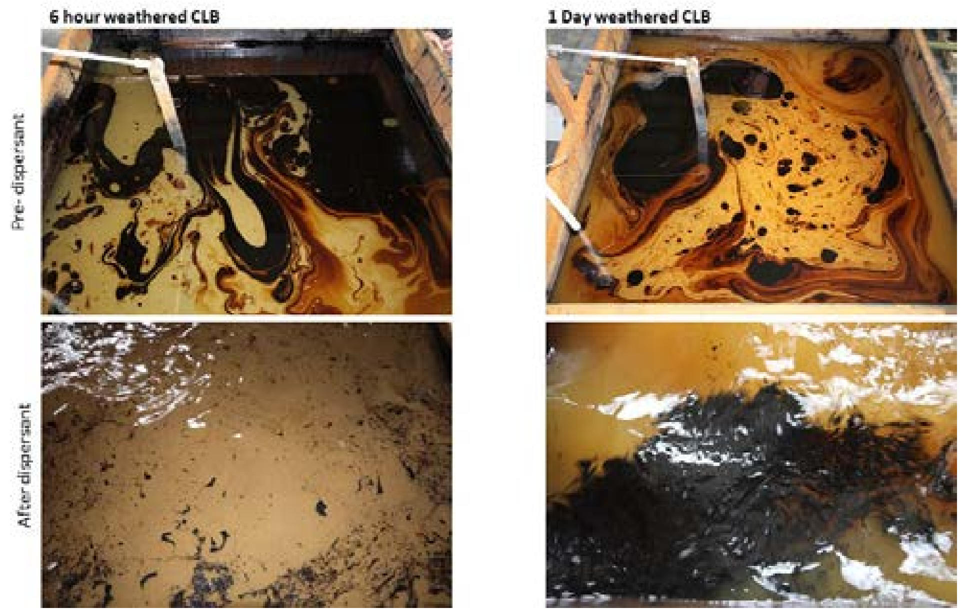
# Chemical Dispersants

**Gainford**

- The visual observations of the dispersant test revealed that Corexit 9500 was marginally effective on CLWB weathered to 6-hour

**Govt of Canada**

- Baffled flask tests showed promise but likely limited to first 12 hrs



# Controlled Burning

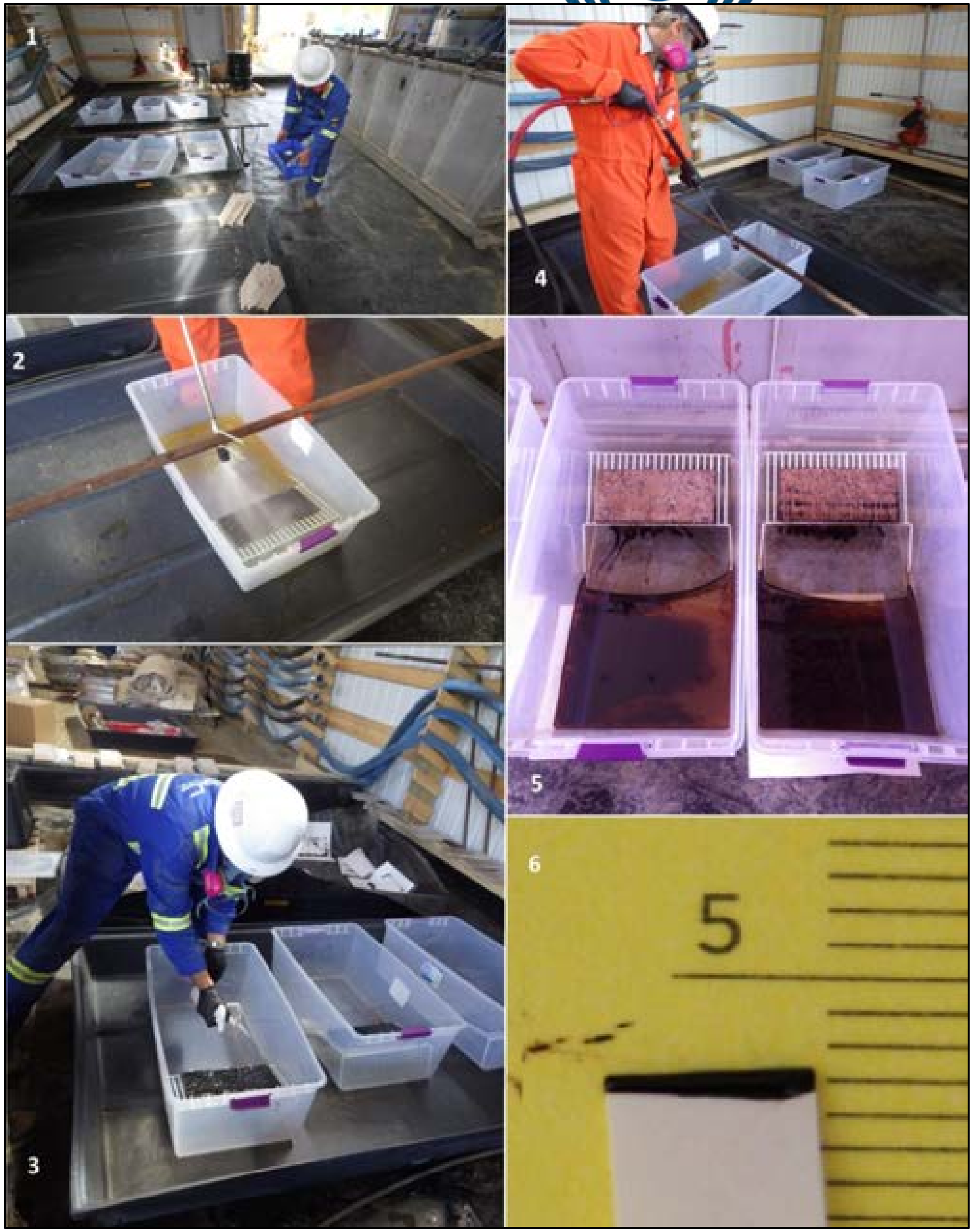
**Gainford**

- 6-hour weathered CLWB dilbit was effective - approximately 70 percent of oil removed through burning
- Approximately 50 percent of 24-hour weathered CLWB dilbit was removed, but only after sustained effort to ignite

# Substrate Washing Tests

**Gainford**

- Granite tiles oiled on porous (non-polished) surface
- Fan spray approximately 25 cm wide
- Tip at 22.5 cm from the tile surface
- Pressure: 0.21 – 0.31 MPa; 30-45 psi
- Treatment for 30 seconds (approximately 11 passes with the wand) and approximately 3 L of water



# Results

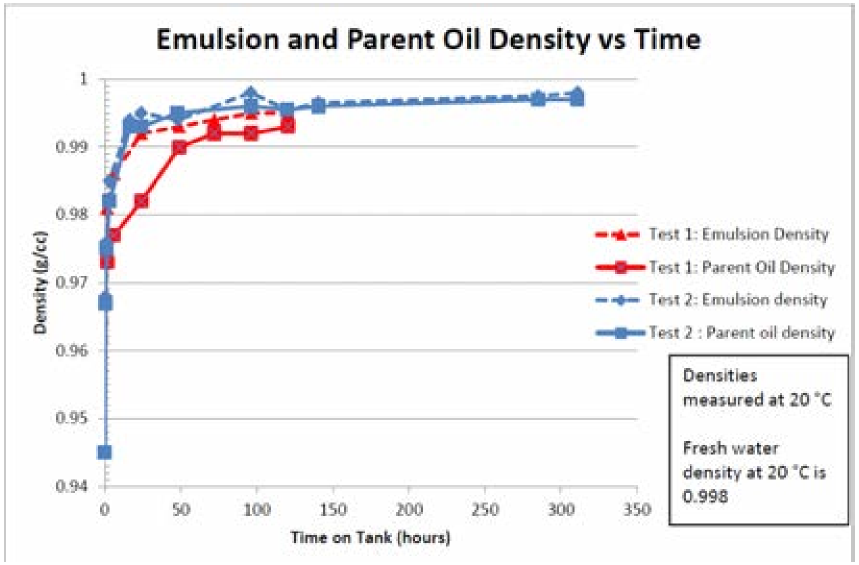
- **Shore cleaning agent**
  - The thickness of the oil on tiles after 24 hours varied from 0.5 mm (weathered 24 hours) to up to 2 mm (5 days weathering)
  - Flushing alone was ineffective at removing most of the bulk oil
  - The time oil weathered on water before being placed on the tile was less important than the time the weathered oil was exposed to air
  - Oiled tiles were effectively cleaned with Corexit 9580 after air drying exposed to 96 hours (sunlight) to 120 hours (shade), regardless of starting with CLWB weathered on water for 1, 3, or 5 days

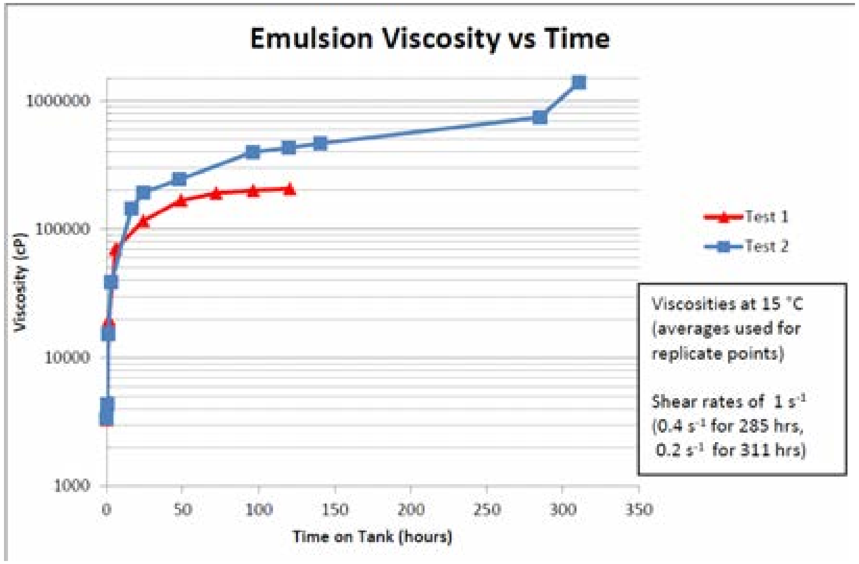
# SLRoss (2012) Flume Study

- Natural weathering of CLB in continuous circulation on 15°C freshwater and subjected to a simulated waterfall, which had an overwash effect.
- A small part of the oil slick (<1% to <5% by observation) was seen to submerge and hang in the water column as either neutrally buoyant droplets or blobs
- At the end of the tests approximately 15% of the recovered oil was collected from the tank walls 10 cm below the water surface. This oil is assumed to be that which accumulated from the near neutrally buoyant drops that were present during the test.
- Approximately 85% of the oil in tests was found either at the surface or stuck to the side walls within 10 cm of the surface.
- No oil was found to sink or stick to the lower portion or bottom of the flume.

# SLRoss (2012) Flume Study

- UV light exposure appeared to accelerate oil weathering forming a thin surface crust
- Oil and water emulsions formed but were unstable.



# API Highlights/Observations

- Testing by SLRoss encompassed
  - 3 diluted oil sands crudes (2 dilbits, 1 dilsynbit)
  - 2 heavy conventional crudes
- Flume tests were done in warm (20°C) and cold (2°C) water conditions and *both* for freshwater and saltwater (32 ppt)
- River bed tests (flow over 3 bed types: sand, gravel, cobble)
- Oil penetration tests into porous media (sand, sand-gravel, loam)

# API Highlights/Observations

- The measured densities for all emulsion samples of crudes and oil sands crudes (except for one) never exceeded 0.999 in 5 days of testing
  - Some oil deposits were observed at the bottom of the flume tank after 5 days for one of the oil sand products tested
- The oil sands products generally evaporated more quickly than the conventional heavy crude oils resulting in a more rapid increase in viscosity and density

# API Highlights/Observations

- The surface behavior of all of the oils on the recirculating flume was quite similar
- Good mobility of the surface oil was observed up to the point where the oil viscosity reached approximately 20,000 cP
- The viscosities of the three diluted bitumen products emulsions reached about 100,000 cP within:
  - about 24 hours of exposure (20°C tests)
  - approx. 6 hours (2°C water tests)

CLEAN PACIFIC™

# API Highlights/Observations

- The fresh conventional heavy crude oils and the oil sands products formed either meso-stable or entrained emulsions. None of the oils formed emulsions when evaporated.
- No significant difference in the oil penetration results obtained from the dilbit oils versus the conventional heavy crude oils.
- The degree of streambed *(FW environment)* oiling appeared to increase with increasing evaporated oil density and increasing bottom roughness

KINDER MORGAN CANADA INC.

# Dilbit Comparison with Other Oils

| Oil Property | Units | Oil Types | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Gasoline | Diesel | Light Crude | Dilbit[1] | Heavy Crude | Intermediate Fuel Oil | Bunker C | Crude Oil Emulsion |
| Density | $Kg/m^3$ at 15°C | 720 | 840 | 780 to 880 | 824 to 941 | 880 to 1000 | 940 to 990 | 960 to 1040 | 950 to 1000 |
| API Gravity | | 65 | 35 | 50 to 30 | 39 to 18 | 30 to 10 | 20 to 10 | 15 to 5 | 15 to 10 |
| Viscosity | mPas at 15°C | 0.5 | 2 | 5 to 50 | 270.5* to 265,263 ** | 50 to 50,000 | 1,000 to 15,000 | 10,000 to 50,000 | 20,000 to 100,000 |
| Flash point | °C | -35 | 45 | -30 to 30 | <-35**m to 58*m | -30 to 60 | 80 to 100 | >100 | >80 |
| Solubility in Water | ppm | 200 | 40 | 10 to 50 | - | 5 to 30 | 10 to 30 | 1 to 5 | - |
| Pour Point | °C | NR | -35 TO -1 | -40 to 30 | -30**m to 15**m | -40 to 30 | -10 to 10 | 5 to 20 | >50 |
| Interfacial Tension | mN/m at 15°C | 27 | 27 | 10 to 30 | 27*m to 150*m | 15 to 30 | 25 to 30 | 25 to 35 | - |

Modified from Fingas (2001);
[1]Values provided include weathered dilbit from tests; NR= not relevant;
* Calculated for AWB; ** Calculated value for CL;
*m Measured value of AWB; **m Measured value of CL

# Learnings / Key Messages

- No two-phase separation into bitumen and diluent
- Off-gassing of light-ends could have safety implications for responders/ public, as with any crude oil
- Both AWB and CLWB dilbits remained floating during weathering tests; no sinking was observed for the dilbits tested
- Both AWB and CLWB weathered dilbits surpassed viscosities of 10,000cSt within 48 hours and exhibited strong tendency to form a more continuous thick mat rather than a thin sheen on water.
- Countermeasures for medium to heavy crude oils are appropriate for response to dilbit releases