Crude Corrosivity Investigations
Enbridge Pipelines

CCQTA/COQA Meeting

Kananaskis, Alberta

June 19-20, 2012

Trevor Place

Purpose of this presentation

- Enbridge is always pleased to share our operational experiences. I hope that any information I can share will be useful to the CCQTA and/or individual stakeholder organizations and companies.

- Enbridge interest in crude corrosiveness substantially predates the recent furor over diluted bitumen versus conventional .

- The recent focus on crude corrosivity (especially that of dil-bit) underscores the importance that we, as an industry, need to collectively get our ducks in a row on this issue

- To this end, I would like to present some of the work Enbridge has undertaken over the past several years. I hope that your awareness of these works might assist the CCQTA and/or any of those here today to focus any work you are doing appropriately.

- Learn from our successes and mistakes…

  (or at least…) make your own “new” mistakes!

Summary of Enbridge experience

- Internal corrosion is VERY isolated.
- Low water cut crude oils are generally non-corrosive (this includes diluted bitumens)
- Internal corrosion may occur at locations where the trace amounts of water and sediment (<0.5% v/v) accumulate and persist
- Enbridge rigorous inspection history indicates slow moving heavy oil pipelines are relatively more prone to internal corrosion than pipelines carrying other products
- In response to this threat, Enbridge began a systematic internal corrosion mitigation program in the early 1990's to specifically target slow moving heavy oil pipelines
- Enbridge has come to understand that the principal determinant of corrosion on our system is product type and flow regime - these factors affect sediment deposition and can lead to under-deposit corrosion
- Location factors (not product corrosivity) determines corrosion incidence and severity
- The morphology of internal corrosion observed on the Enbridge system is readily identified using high resolution MFL inspection tools
- Cleaning and inhibition programs may be required under flow conditions insufficient for safe transit of potential corrosive materials
- These mitigation processes are effective (>90% reduction)

Pipeline Sediments

- Shifted focus to pipeline sediment in 2005
- Investigated sediment stratification/deposition during transport[1,2,3,4,5,6]
- Initiated a joint industry project in 2007/8 with several chemical vendors and ARC (AITF)[7]
- Still some ongoing work with AITF on long term sludge corrosivity[8,9]
- AITF/GE initiated PiCom – a joint industry project investigating corrosive sludges from an active treatment perspective
- Enbridge focus has been on the development of corrosive conditions (accumulation and persistence of corrodents) as opposed to the measurement of corrosivity as a distinct parameter
- There is ALWAYS room for improvement, and Enbridge would like to include commodity specific factors (such as a relative corrosivity) to augment our existing processes.

1. Unpublished internal Enbridge/AITF study "Toroid wheel"
2. "Understanding and Mitigating Under-Deposit Corrosion in Large Diameter Crude Oil Pipelines – A Progress Report", IPC2008-64562
3. "Understanding and Mitigating Large Pipe Underdeposit Corrosion", Materials Performance, January 2009
4. "Modeling of Solids Deposition for a Heavy Crude Oil Pipeline Using enpICDA™", RIO IBP1290-11
5. "Parametric Study of Solids Deposition in a Heavy-Oil Pipeline", NACE C2012-01679
6. "Computational Fluid Dynamics Study of Solids Deposition in Heavy Oil Transmission Pipeline", Corrosion Journal, June 2012
7. "Evaluating Corrosion and Inhibition Under Sludge Deposits in Large Diameter Crude Oil Pipelines", NACE C2010-10143
8. "Development of a Test Protocol for the Evaluation of Underdeposit Corrosion Inhibitors in Large Diamter Crude Oil Pipelines", NACE C2011-11263
9. *Long Term Sludge Corrosivity Study* – anticipated 2013

1995 CANMET Study

- **60 Enbridge (IPL) crudes were evaluated**
  - Density (680-930 kg/m^3)
  - Water content (33-3764 ppm)
  - Acid number (0.01-3.92 mg KOH/g)
  - Total sulphur (0.06-4.82 %)
  - Select ions by inductively coupled plasma (ICP)
  - Near-IR spectra for classification of crude groups
  - Coupon exposure followed by evaluation of iron concentration change in the crude after coupon exposure
  - Electrochemical analysis (7 fluids tested)

- **Extremely low corrosion rates were obtained**
  - Most fluids (>50) did not yield measurable corrosion rates
  - <1E-2 mpy in two fluids (by iron uptake, ICP)
  - <1E-3 mpy in four fluids (by Tafel analysis)

- **Confirmed assumptions about the non-corrosiveness of crude oil**

Crude Corrosivity Measurement

- **Few hydrocarbon corrosivity test methods accepted by industry**
  - **TM0172: 'Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines'**

    'Verifying Residual Inhibitor Effectiveness in Petroleum Products'
  - **Add 300ml oil to beaker (38C)**
  - **Insert rod coupon and stir (0.5 hrs @1000RPM)**
  - **Add 30ml distilled water and stir (3.5 hrs)**
  - **Remove coupon, wash with solvents and visually evaluate:**

Corroded Area	Rating
0	A
<0.1%	B++
<5%	B+
5-25%	B
25-50%	C
50-75%	D
75-100%	E

CON's and PRO's:

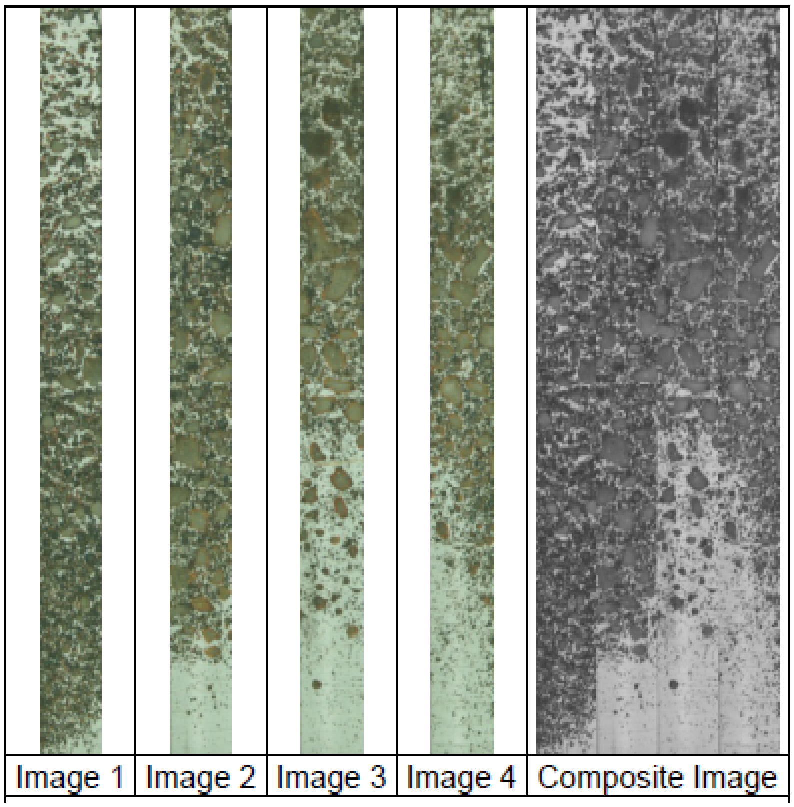
- **Stirring rate does not create full vertical mixing**
- **Evaluation sensitive only below 5%**
- **Not really suitable for uninhibited crude products**

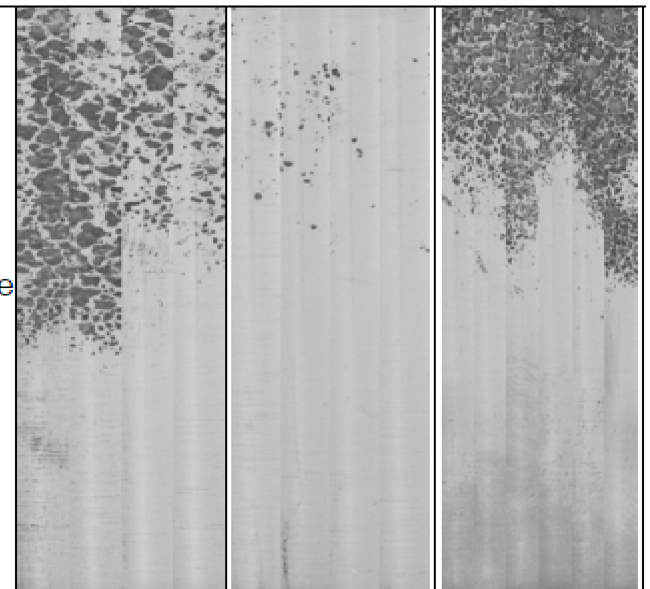
But…

- **Rapid and low tech**
- **Partly addresses type of emulsion formed**
- **Partly addresses effect of crude on the water**
- **Partly addresses the issue of wettability**

TM0172 (modified) w/ Optical Analysis[10]

- **Angled stirrer (for improved vertical mixing)**
- **Use of baffles (instead of expensive Berzelius beaker)**
- **Use of sealed beaker (to avoid evaporation of light ends)**
- **Digital optical analysis (quantitative assessment)**



Composite Image			
Visual Rating	C	B+	C
Digital % Analysis	22.2%	0.7%	26.1%
Digital Rating	B	B+	C

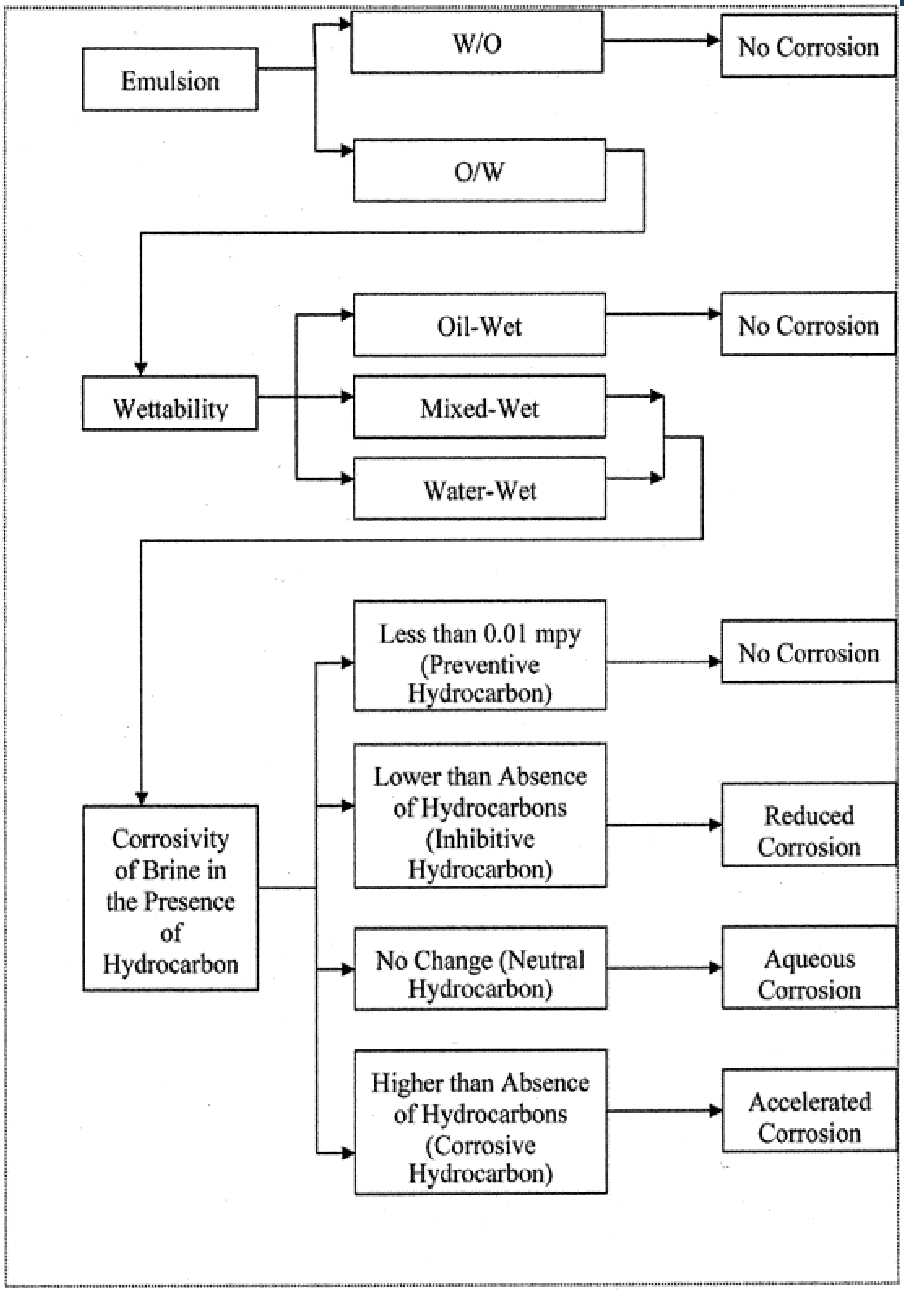
10 'Digital Analysis of Rod Coupons for NACE Test Method TM0172 "Determining the Corrosive Properties of Petroleum Cargos"', IPC2012-90311

ASTM G205 (December 2010)

- Principal authorship by CanMet
- Guideline document (not a test method)
- First corrosivity test specifically addressing crude oils
- Evaluates 3 parameters:
  - Type of emulsion formed and emulsion inversion point
  - Wettability: ability of the crude to form a protective film on a surface
  - Effect of crude on the corrosiveness of a standard brine

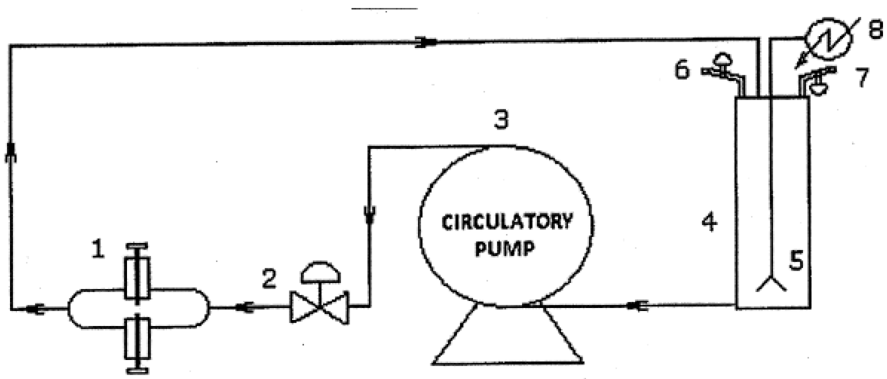
- Enbridge engaged Cormetrics, Ammonite, and CanMet to perform testing of various crudes on the Enbridge system
  - Moved apparatus from Ontario to Alberta (Summer 2011)
  - Performed several stages of testing with periodic modifications to the procedures presented in G205 (Summer 2011 – Spring 2012)

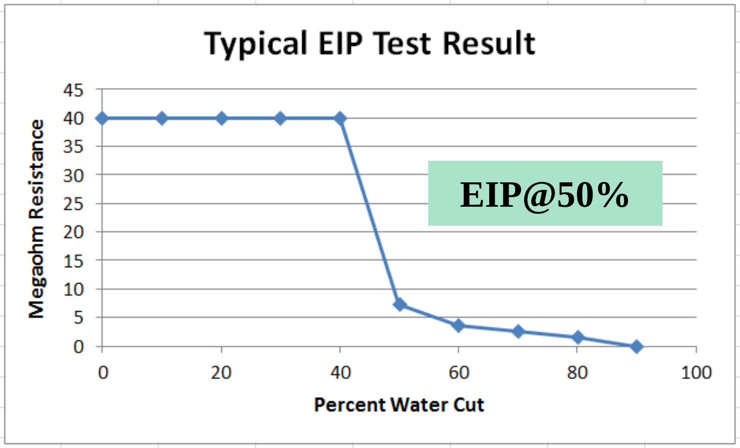
G205-10 Flow Chart



- **Emulsion Inversion Point (EIP test)**
- **Wettability of crude**
- **Effect on standard brine**

Emulsion Inversion Point Test

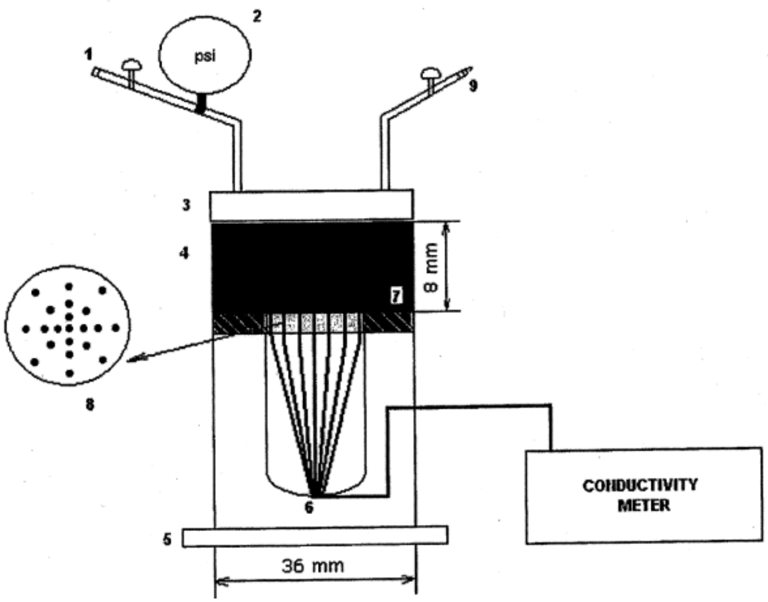




- **Equipment Modifications**
  - Changed piping (added drain leg)
  - Changed pump and impeller (to handle more viscous crudes)

- **Procedural modifications**
  - Dispensed with purging requirements (this flashed off too many light ends and produced a different crude altogether)
  - Shortened run time at each water addition (to prevent formation of stable emulsion)

Wettability Test



Wettability Test (CWA) using Polarity Switch with readings at 10 second intervals

Pin Identity	Average Resistivity Reading with 50% Crude/50% Brine (ohms)	Pin Identity	Average Resistivity Reading with 50% Crude/50% Brine (ohms)
A1	20,171,750	E1	711,000
A2	overload	E2	20,149,950
A3	overload	E3	overload
B2	38,150,000	F2	overload
B3	overload	F3	420,000
C1	20,010,730	G1	21,603,000
C2	20,030,275	G2	21,155,000
C3	3,085,000	G3	25,345,000
D2	20,030,035	H2	20,146,650
D3	20,020,390	H3	24,045,000

- **Equipment modifications**
  - Made cell more serviceable (to permit easier cleaning between tests)
  - Added spacer ring (to improve coverage of headpins)
- **Procedural modifications**
  - Changed purge method (to avoid disturbing fluids)
  - Modified reading intervals (to shorten measurement cycle)
  - Eliminated problematic switcher
  - Bi-polar resistance measurements (to avoid polarization of reference pin)
  - Increased brine volume (to improve coverage of headpins)
  - Run test at different pressures*
- **Improvements still required**
  - Test criteria need to be validated
  - What resistance = water wetted surface?
  - How many conducting pins to determine 'oil wet', 'water wet', or 'mixed wet'? (G205 suggests <4 pins=OW, 5-15=MW, >16=WW)

"Determination of the Effect of Crude Oil on the Corrosiveness of the Aqueous Phase" (G205 – 8.3)

G205 (paragraph 8.3.1) "Under water wet conditions, the corrosivity of the aqueous phase may be altered by the dissolution of ingredients from the crude oil. The effect of crude oil on the corrosiveness of the aqueous phase can be determined either *by pretreating the coupons with crude oil, and then conducting the experiment in the aqueous phase* (typically 3% NaCl) or conducting the experiments in the presence of both the crude oil and aqueous phase." Test Method D665, Guide G170, Practice G184, Test Method G202, and NACE TM0172 are suggested

- **CanMet originally used a Rotating Cage (RC) test, which involved pretreating a flat coupon with oil, rinsing the coupon in distilled water, and then running standard autoclave in clean brine.**
  - **CGR < 0.01 mpy = "preventative hydrocarbon"**
  - **CGR(crude) < 0.85CGR(control) = "inhibitory hydrocarbon"**
  - **CGR(crude) > 1.15CGR(control) = "corrosive hydrocarbon"**
  - **CGR(crude) ~ CGR(control) = "neutral hydrocarbon"**

- **Cormetrics adapted this procedure using a Rotating Cylinder Electrode (RCE), which produced very nominal changes in test results over a wide variety of crudes.**
- **Upon further consideration, the CanMet method is simply an "oil film persistence" test and NOT a measure of the effect the crude oil has on the aqueous phase.**

- **In discussion with Ammonite/Cormetrics and CanMet, a substantial variation to this procedure was agreed upon (as follows):**

Corrosivity of Brine* (*contacted by crude)

- **Equipment modifications**
  - Smaller RCE cells utilized to permit testing in duplicate using smaller volumes
  - Different reference cells and purge tubes
- **Procedural modifications**
  - Modify test duration from 12-16 hours
  - Modify purge gas from N2 to CO2
  - Increase RCE temp from 25C to 40C
  - Use brine extracted from the EIP apparatus at the 50% water cut point to represent 'crude contacted brine'
  - Coupons are not pre-treated in oil (*so as to not obfuscate the "effect of crude on corrosiveness of brine" with "oil film persistency")
  - RCE is run in duplicate in the 'crude contacted brine' and compared to a single RCE run for original brine
- **Improvements still required**
  - As we are deviating from standard tests, need consensus from industry (CCQTA?)

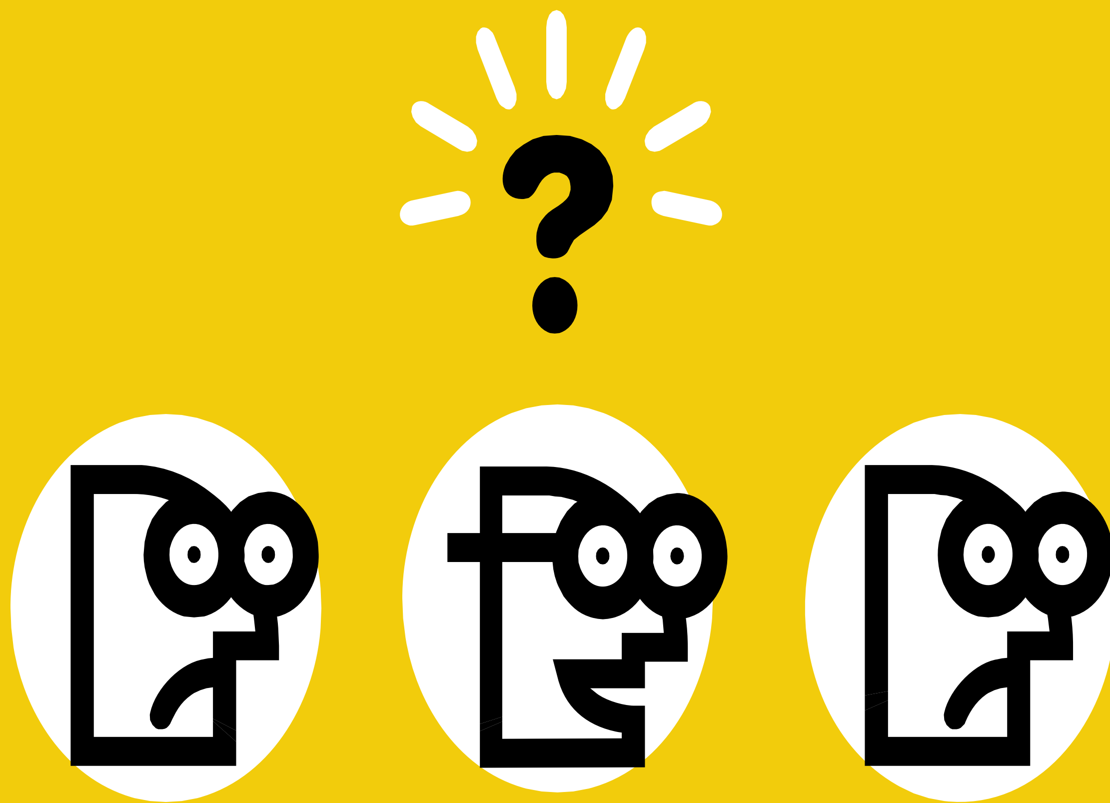
Corrosivity of Brine* (*contacted by crude)

ENBRIDGE

- **Example data (dip and rinse)**
  - Thirteen (13) crudes tested using original CanMet dip and rinse method
  - BRINE BLANK = 188 mpy (12mpy S.D. on 17 samples)
  - CRUDE (Min) = 120 mpy
  - CRUDE (Max) = 169 mpy
  - CRUDE (Avg) = 153 mpy (13mpy S.D.)

- **Example data (using crude contacted EIP brine)**
  - Four (4) crudes tested
  - BRINE BLANK = 188 mpy (12mpy S.D. on 17 samples)
  - CRUDE (Min) = 2.26 mpy
  - CRUDE (Max) = 8.43 mpy
  - CRUDE (Avg) = 4.24 mpy (2.91 mpy S.D.)

- **Improvements still required**
  - Running a blank in white kerosene for comparison
  - Looking for consensus from peer group (CCQTA?)
  - Looking for guidance on interpretation of results.



It's QUESTION TIME !!