Effect of Ashphaltene Stability on Fouling Rate and Fouling Morphology

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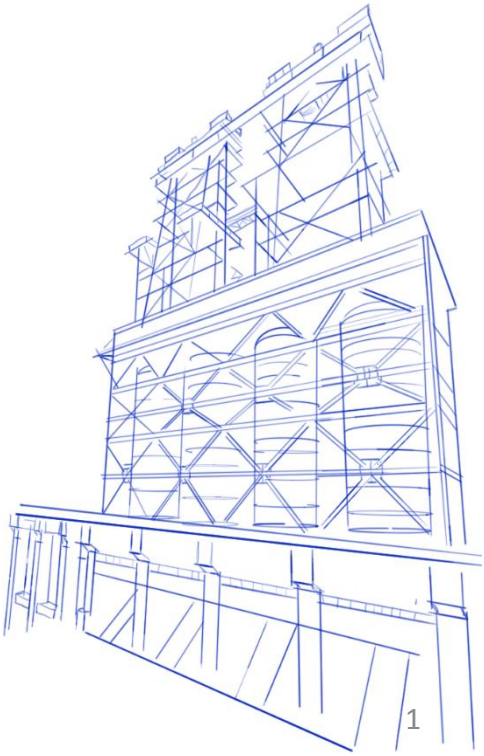
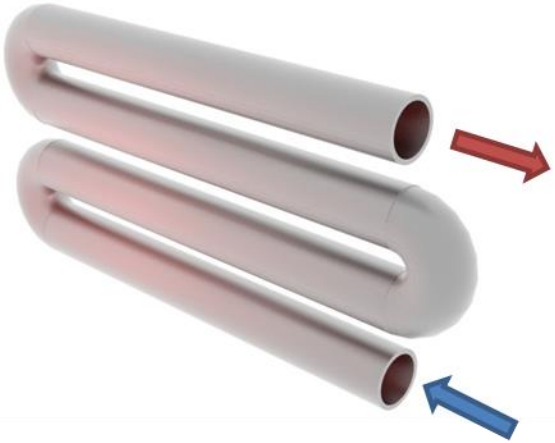
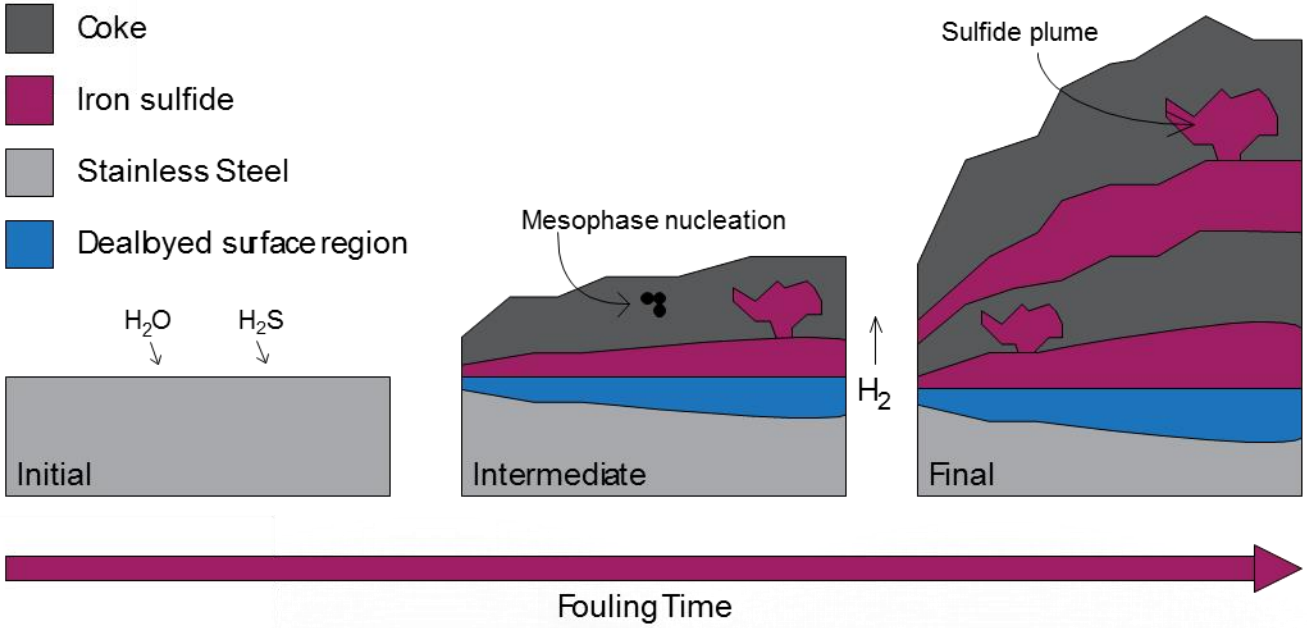
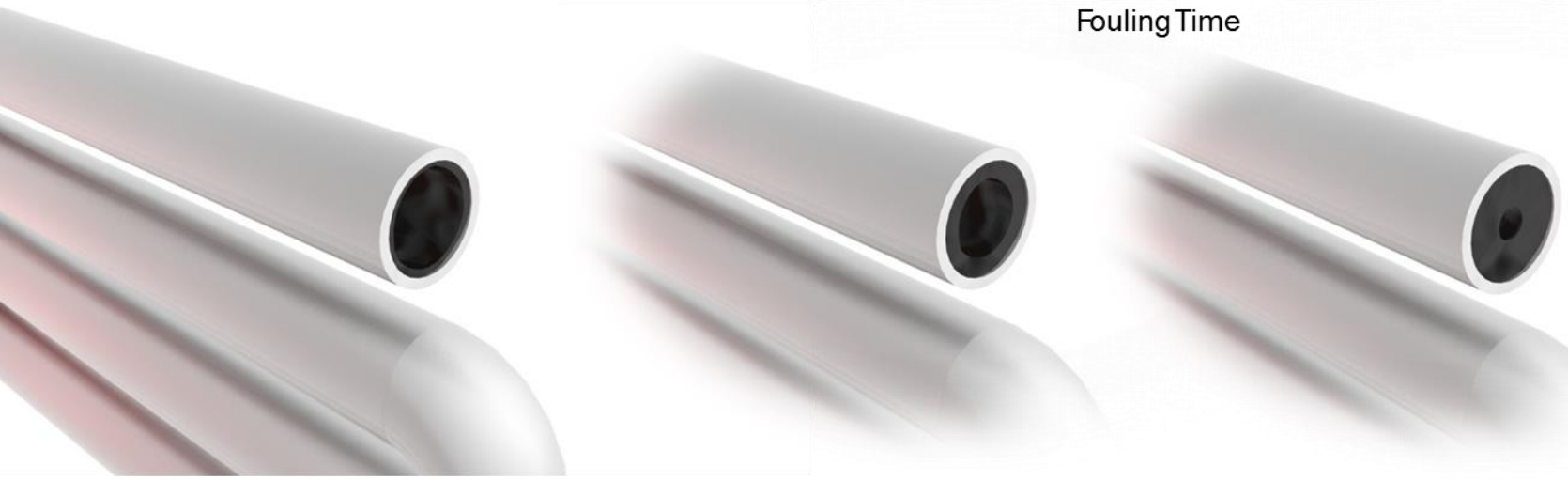


Heat Exchanger Fouling

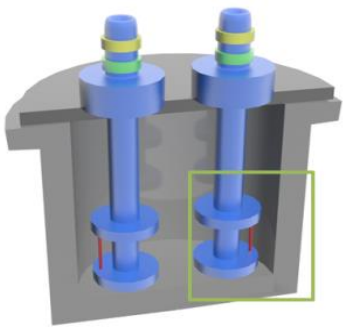


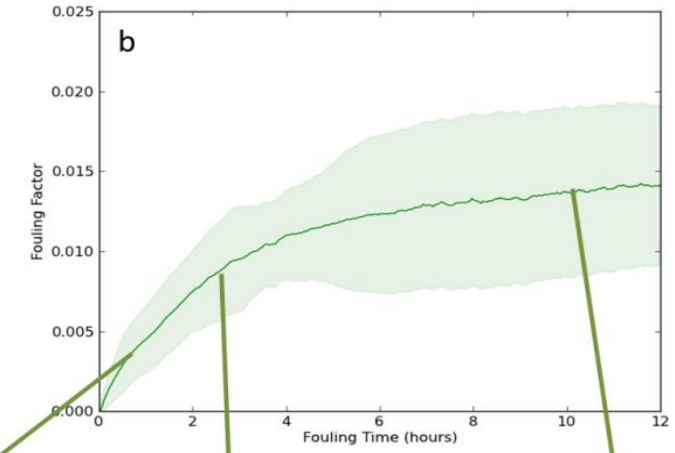


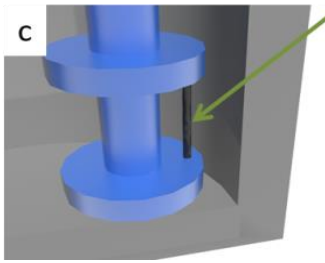


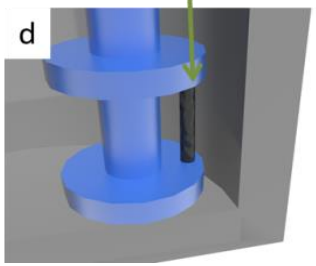
Hot Wire Fouling Test

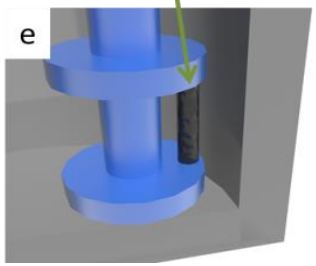
- Test Wire in Feedstock
  - Electrical heating
    - controls temperature
    - measure the heat flow from the wire
- Fouling Factor vs. Time
  - Based on thermal conductivity of the foulant

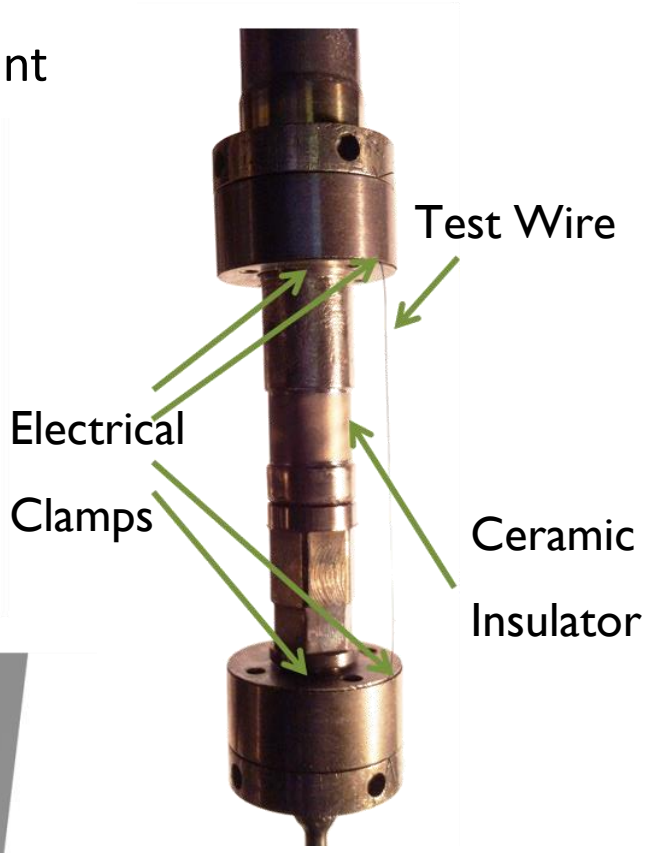




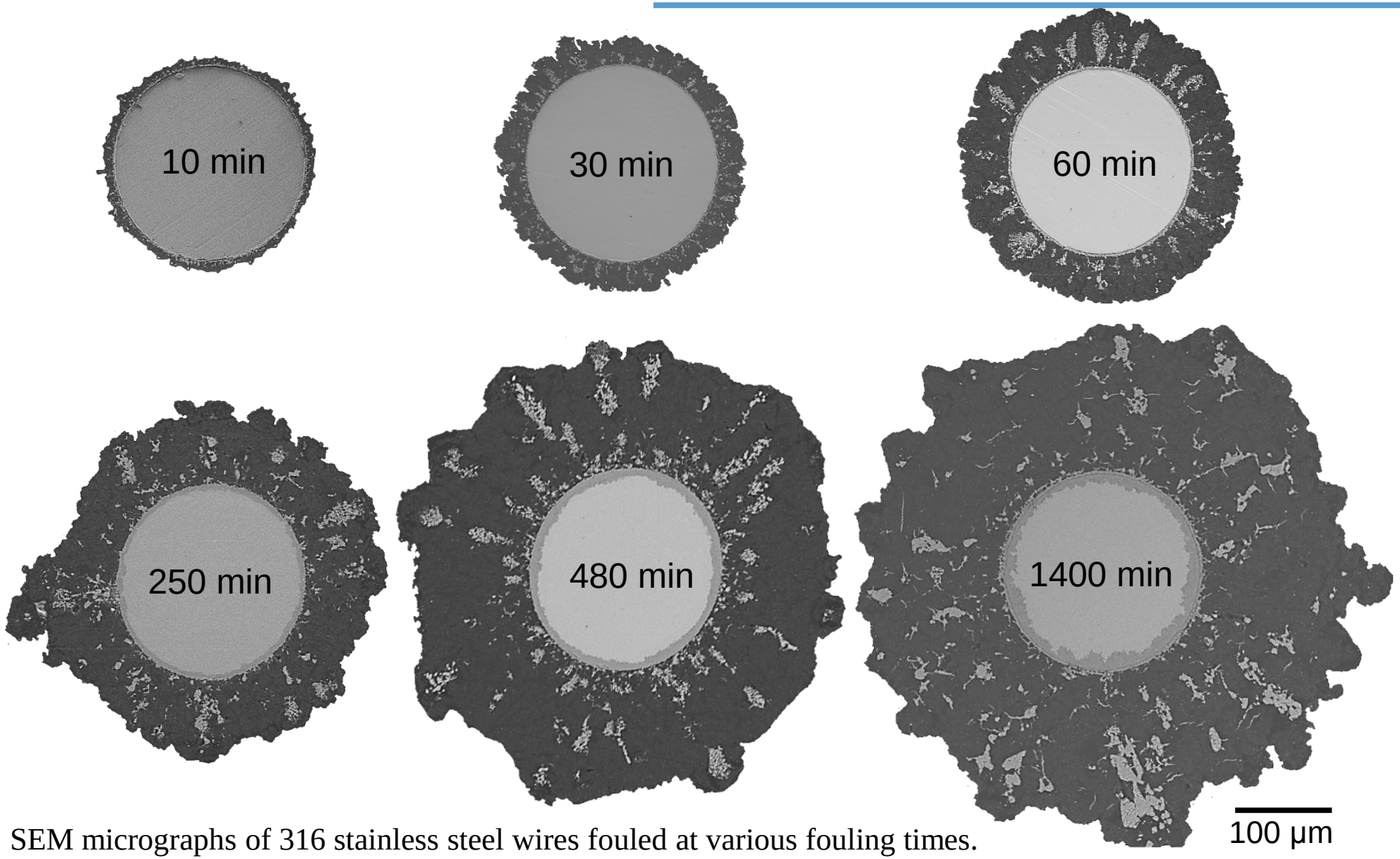








Fouling Formation on Micro Wire

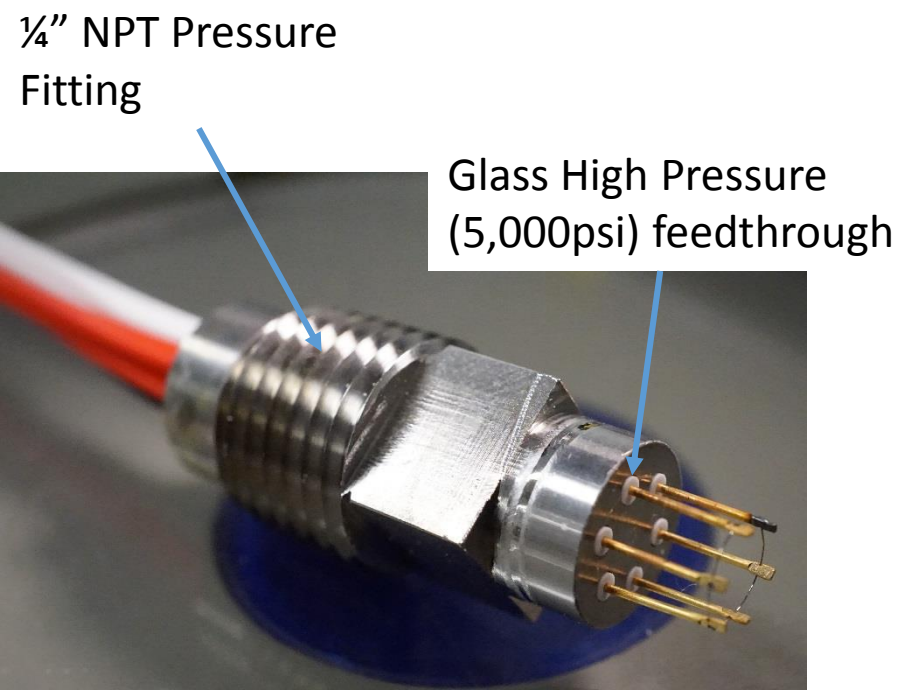


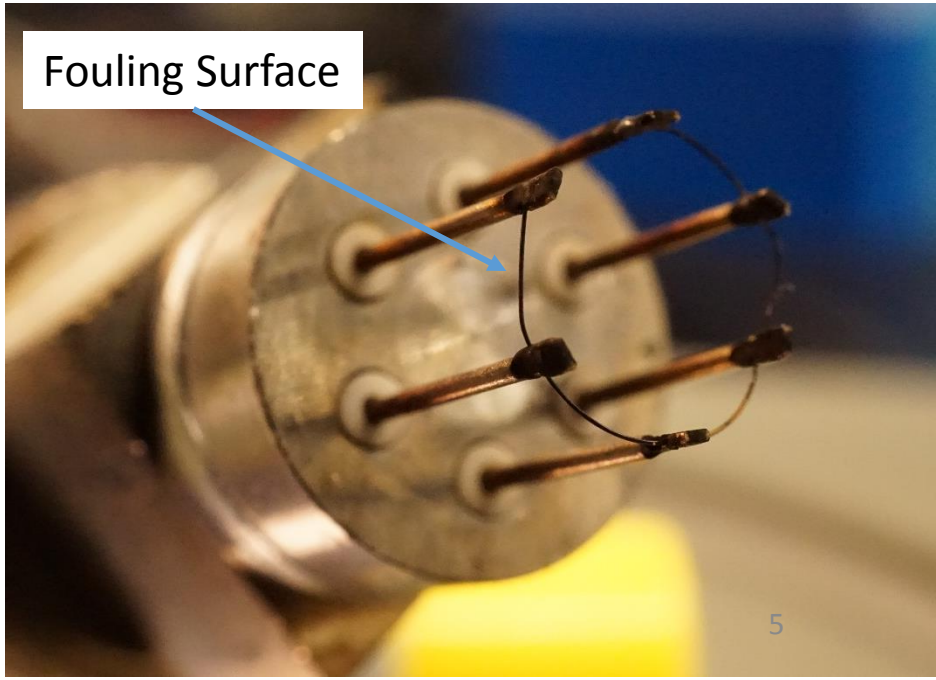
SEM micrographs of 316 stainless steel wires fouled at various fouling times.

Thiophene mitigates high temperature fouling of metal surfaces in oil refining
T Stephenson, M Hazelton, M Kupsta, J Lepore, EJ Andreassen, A Hoff, B Newman, P Eaton, M Gray and D Mitlin
Fuel, 139 (2015) 411-424

New Micro Wire Test Card

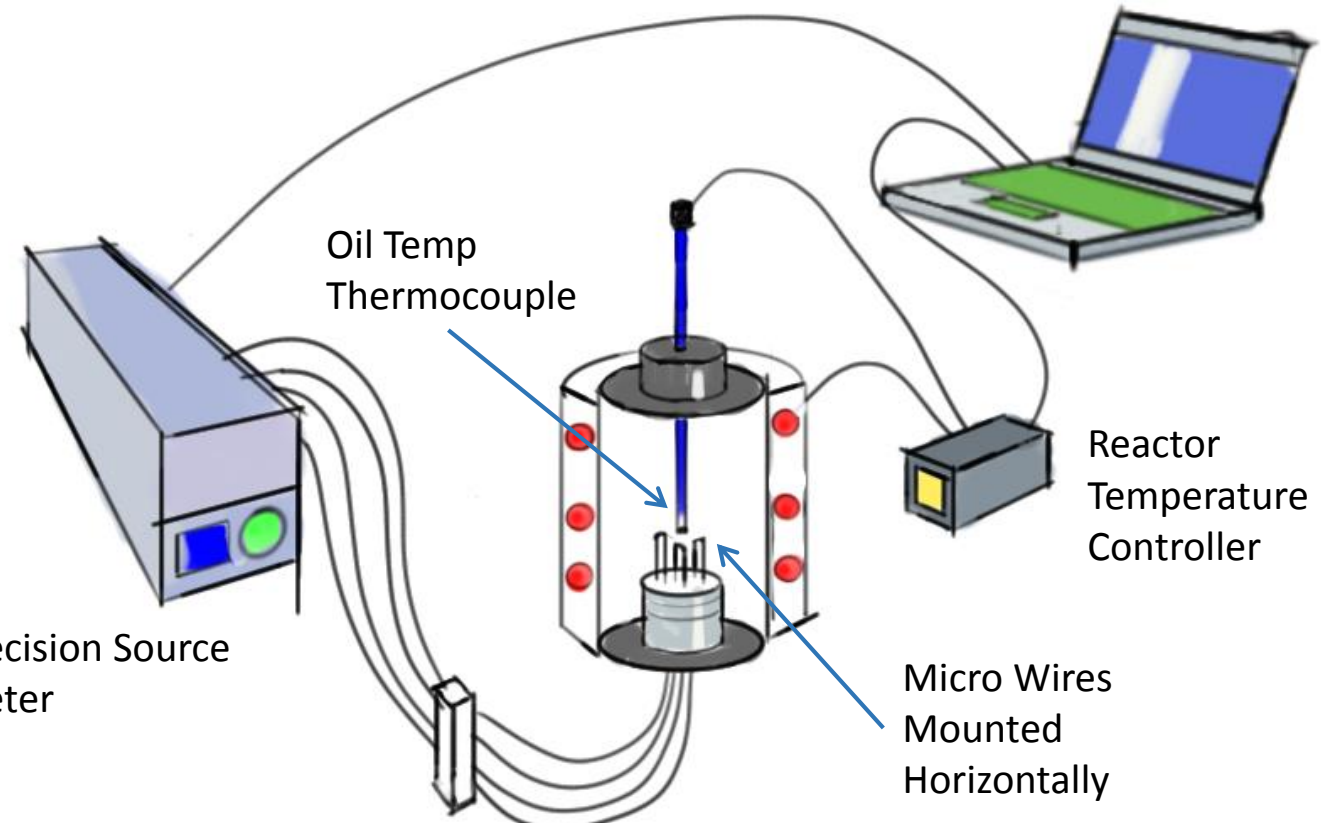
- Fouling occurs on a fine 316 stainless steel wire bonded to the gold coated pins of a high pressure feedthrough
- Five tests with one setup (Temperatures or Fouling Time can be changed)
- Two Teflon insulated wires are bonded to each pin providing four wire connections to the wire sections.
- Sensor is capable of being run at oil temperatures up to 300°C and wire temperatures of 200°C above oil temperature





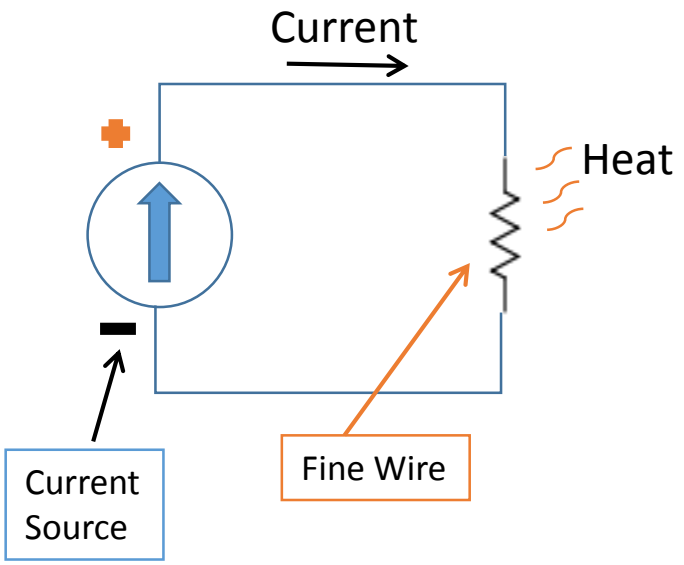
Micro Fouling Test System

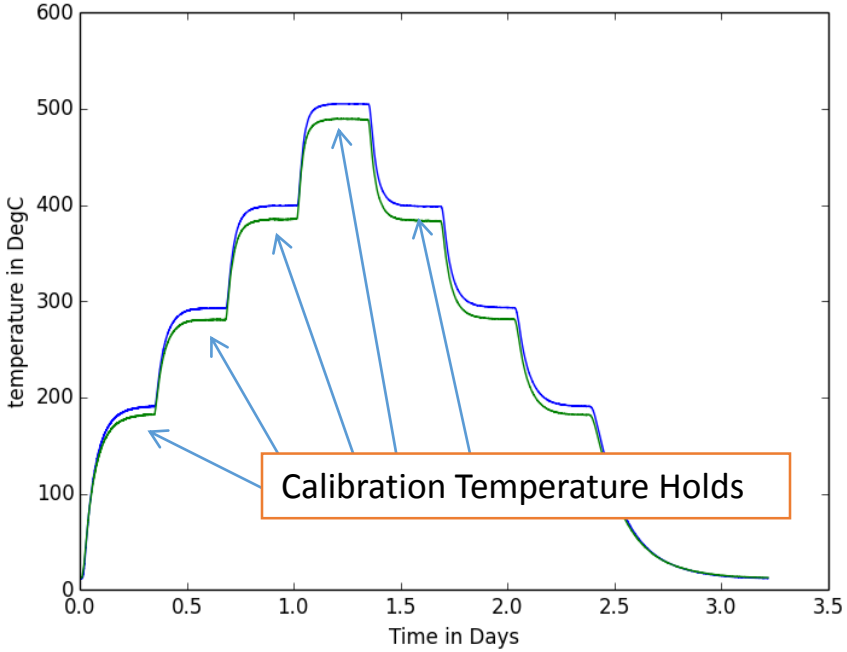
Oil Volume = 12mL
Headspace = 300psi Argon
Oil Test Temperature = 204°C
Wire Test Temperature = 300°C

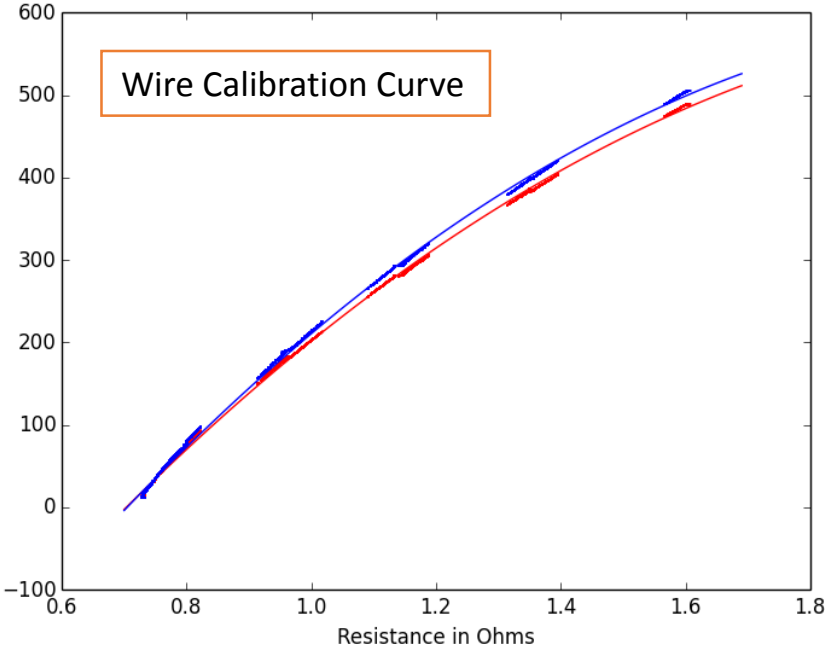


Calibrated Wire Resistance

- Calibrate wire to find resistance vs temperature properties
- Apply required current to reach the desired wire temperature
- Use PID control to maintain a constant wire temperature to simulate fouling condition
- Measure power required to maintain temperature to find fouling rate



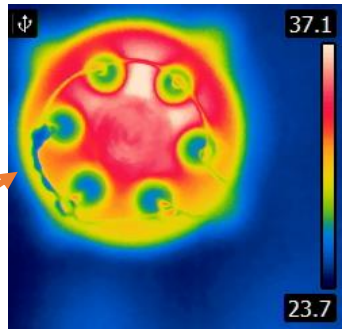


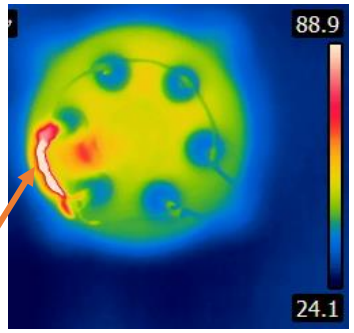


New calibration method

Thermal microscopy calibration of test wire temperature

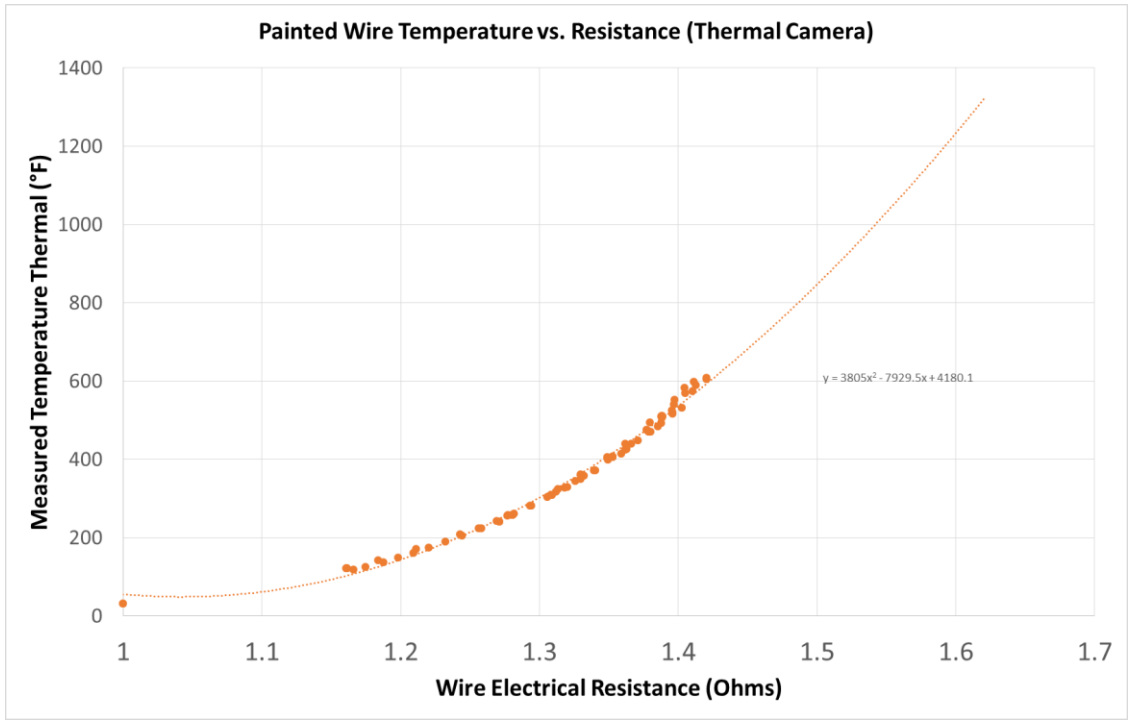
Removes requirement of temperature cycle for each test (can't be done for online fouling probe)





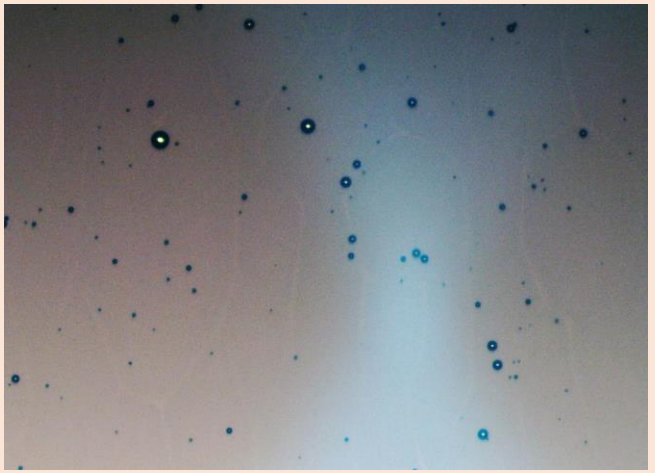
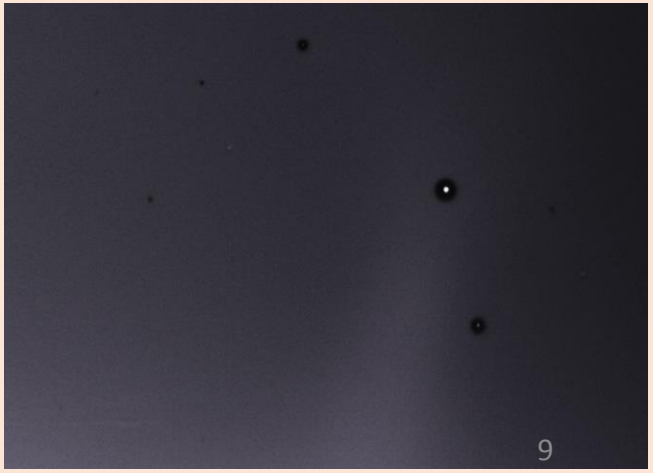
Test wire coated with paint

Coated wire electrically heated



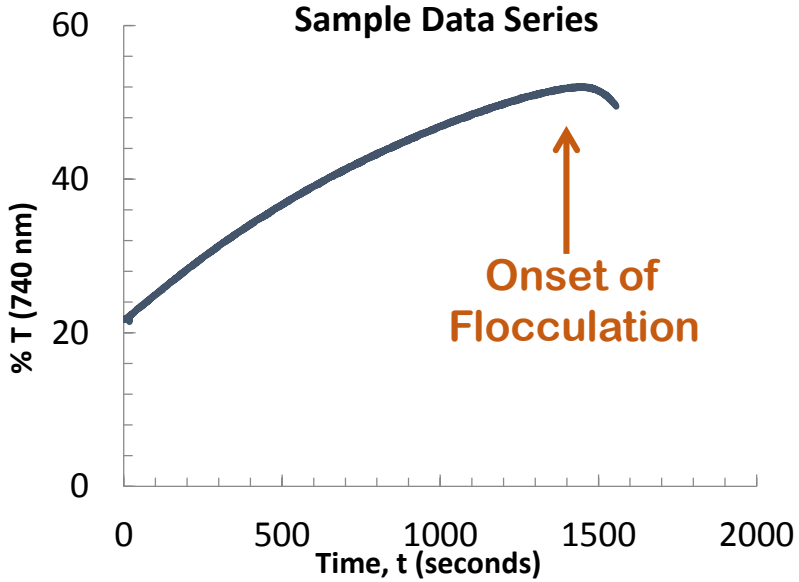
Crude Oil Characterization

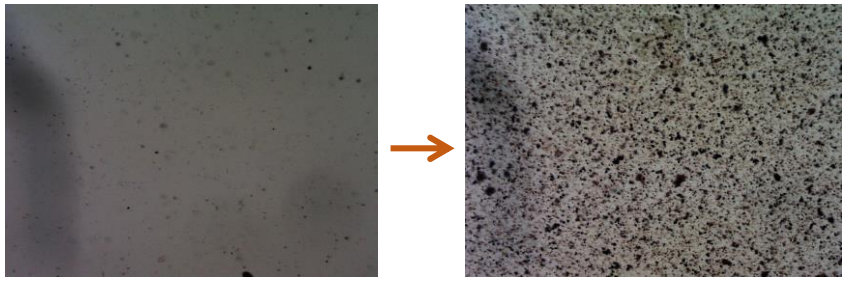
- Asphaltene Stability is Related to Fouling
  - **Microscopy (0.14 mm x 0.8 mm)**
  - AFT
  - SAR-AD

	Light Crude (°API 37.0)	Heavy Crude (°API 16.4)
Neat Crude		
Crude + Nitrobenzene (Dissolves Asphaltenes)		

Crude Oil Characterization

- Asphaltene Stability is Related to Fouling
  - Microscopy
  - **Automated Flocculation Titrimeter (AFT),** ASTM D6703
  - SAR-AD





Heithaus "others"

-P value (10 – 1): Stability of the oil, less than about 2.5 is considered less stable
-Po: solubilzing/peptizing power of oil (higher better at dissolving asphaltenes)
-Pa: solubility/peptizability of asphaltenes (higher means they are more difficult to dissolve)

Heithaus Parameters using Nitrobenzene/Isooctane

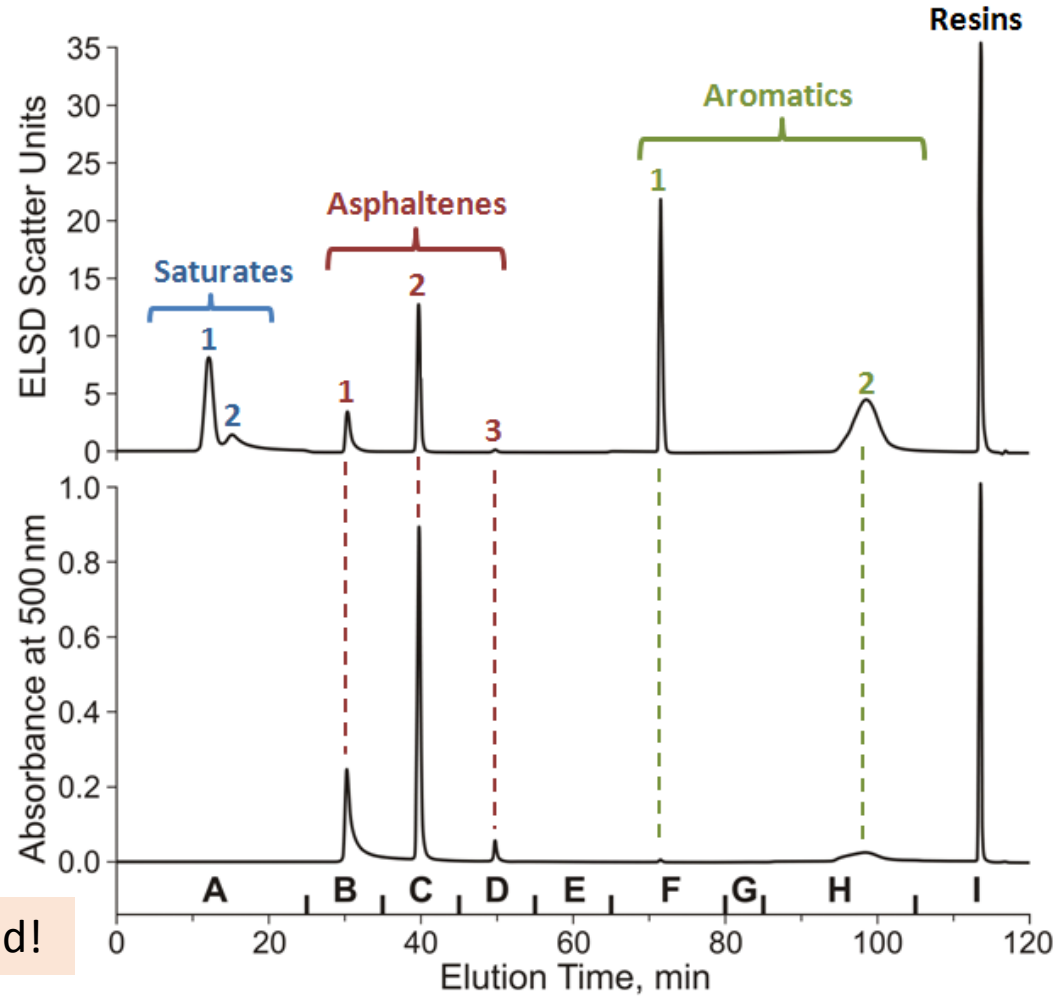
Light Crude (°API 37.0)	Heavy Crude (°API 16.4)
-P value: 1.26 -Po: 0.34 -Pa: 0.79	-P value: 2.5 -Po:0.86 -Pa: 0.66

Crude Oil Characterization

- Asphaltene Stability is Related to Fouling
  - Microscopy
  - AFT
  - **Saturates, Aromatics, Resins-Asphaltene Determinator (SAR-AD™)**

Fully automated HPLC system for SARA separation with AD asphaltene fractionation:

-Repeatable
-4 hrs
-Tunable

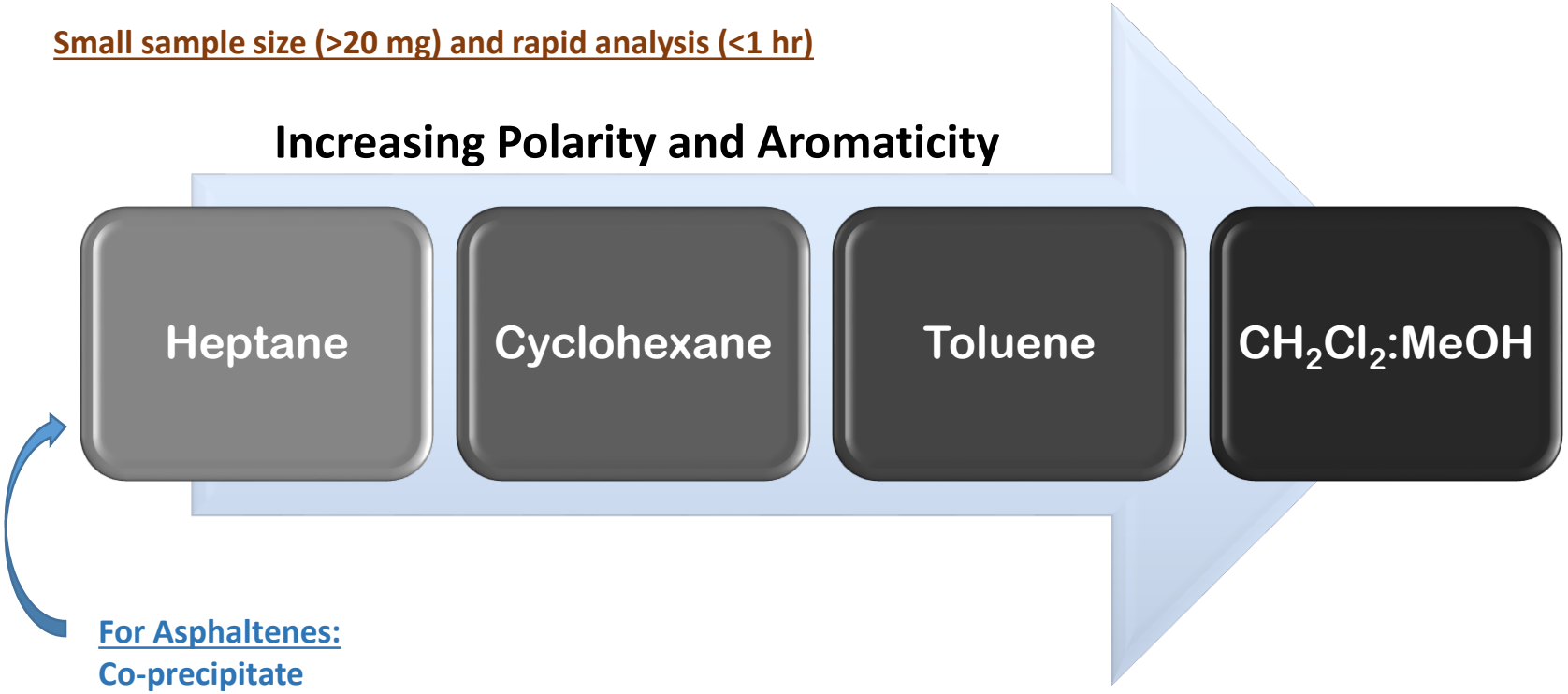


Patented!

Asphaltene Determinator™ (AD)

Automated HPLC System for Fractionating Asphaltenes by Solubility

Small sample size (>20 mg) and rapid analysis (<1 hr)



For Asphaltenes:
Co-precipitate
Trapped material
Resins
Non-colloidal asphaltenes
Bound resins

Detectors:
Optical absorbance
ELSD

John Schabron et. al. Energy Fuels **2010**, 24, 5984–5996

7 Patents Issued

Crude Oil Characterization

- Asphaltene Stability is Related to Fouling
  - Microscopy
  - AFT
  - **Saturates, Aromatics, Resins-Asphaltene Determinator (SAR-AD)**
    - **Distillation of the crude oils to give a distillate and residue**
      - **^{1}H NMR aromaticity converted to ^{13}C NMR aromaticity**
      - **SAR-AD of the residue**

		SAR-AD For Residue									NMR of Distillate		Distilation	
		Maltenes					Asphaltenes							
				Aromatics										
Crude	Detector	Saturates	Nap Sat	1	2	Resins	CyC_6	Toluene	CH_2Cl_2: MeOH	Total ELSD Asphaltenes	C_{ar}	$(1-C_{ar}/100)$	Distillate χ_{mass}	Residue χ_{mass}
Heavy Oil	ELS	19.8	10.3	21.4	22.4	12.7	2.1	10.8	0.5	13.4	14.27	0.86	0.35	0.64
	500 nm			0.4	9.4	19.1	16.8	48.8	5.5					
Light Oil	ELS	52.8	15.2	17.4	10.4	2.9	0.2	1.0	0.1	1.3	13.46	0.87	0.71	0.29
	500 nm			0.8	26.2	22.7	13.4	30.6	6.4					

CII above 0.9 will cause significant fouling

^{1}H NMR SAR-AD

$$CII = \omega_{distillate}\left(1-\frac{C_{ar}}{100}\right)+\omega_{residue}\left(\frac{saturates+asphaltenes}{aromatics+resins}\right)$$

Crude Oil Characterization

- Asphaltene Stability is Related to Fouling
  - Microscopy
  - AFT
  - **Saturates, Aromatics, Resins-Asphaltene Determinator (SAR-AD)**
    - **Colloidal Instability Index (CII)**

^{1}H NMR SAR-AD

$$CII = \omega_{distillate}\left(1 - \frac{C_{ar}}{100}\right) + \omega_{residue}\left(\frac{saturates + asphaltenes}{aromatics + resins}\right)$$

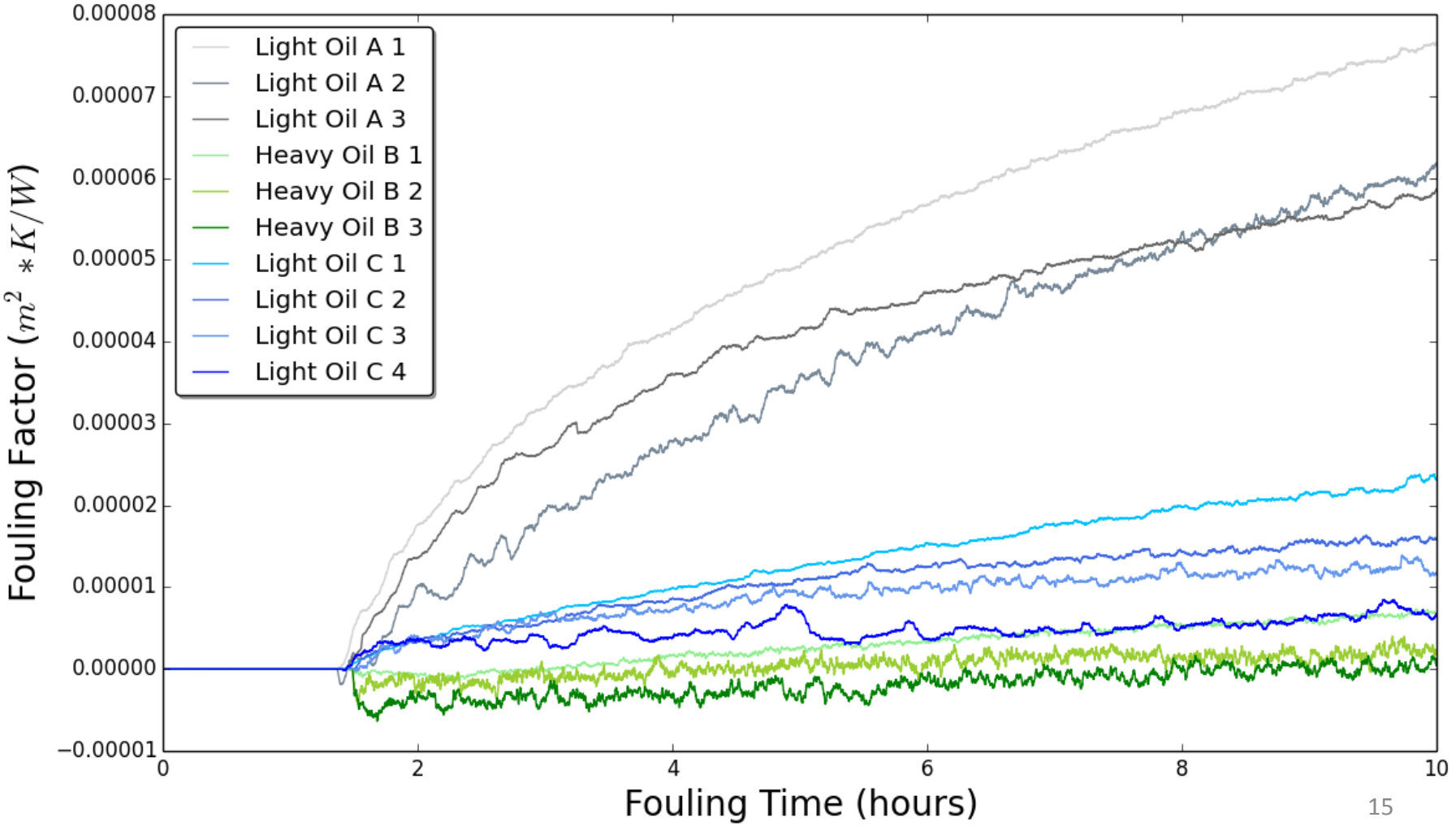
CII above 0.9 will cause significant fouling

Light Crude (°API 37.0)	Heavy Crude (°API 16.4)
CII = 1.26	CII = 0.77

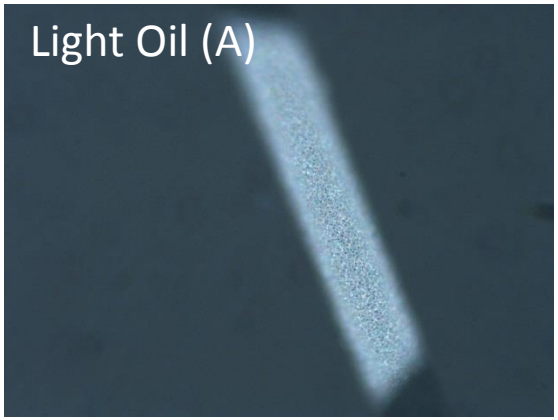
All tests show that the Light Crude with 0.5 wt% asphaltenes should foul to a greater degree than the heavy crude with 11.2 wt% asphaltenes!

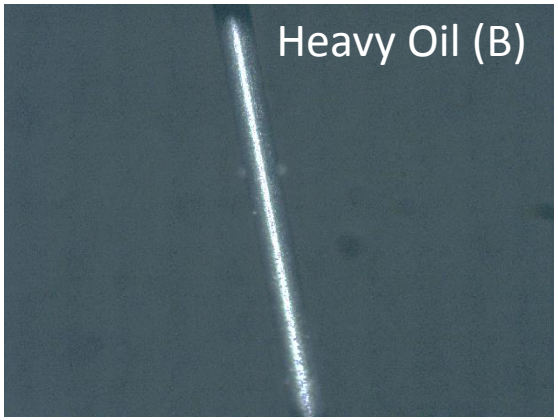
Fouling Rates

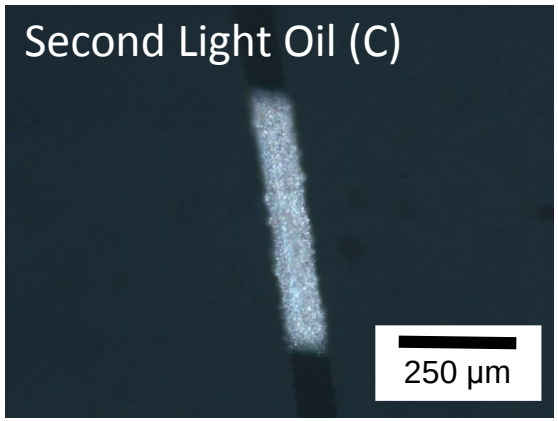
- Very low fouling rate for the stable Heavy Oil
- Successive fouling tests in same oil result in slightly reduced fouling rate

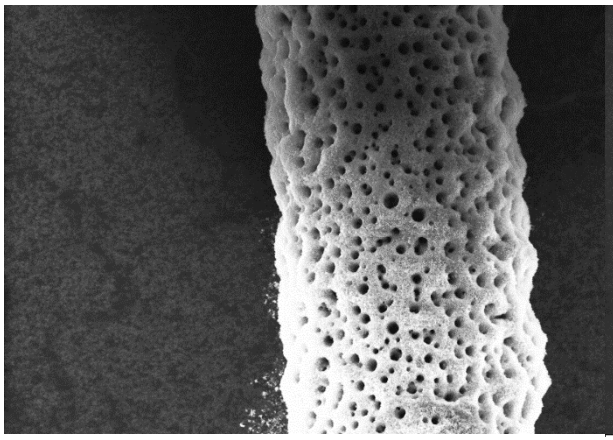


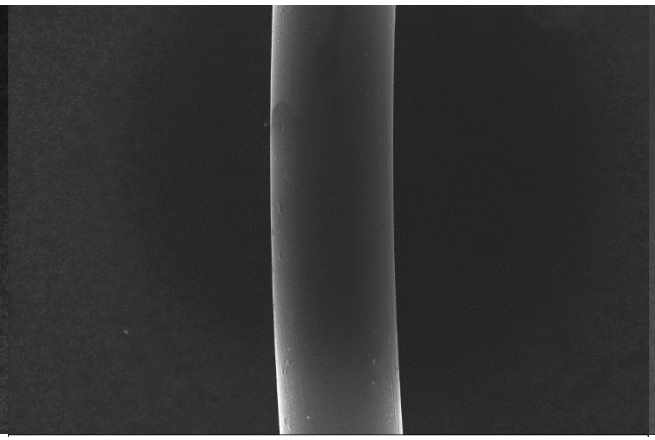
Wire Surface Microscopy

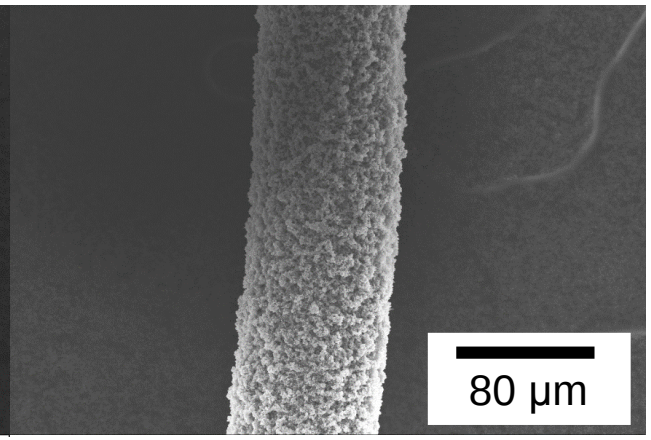


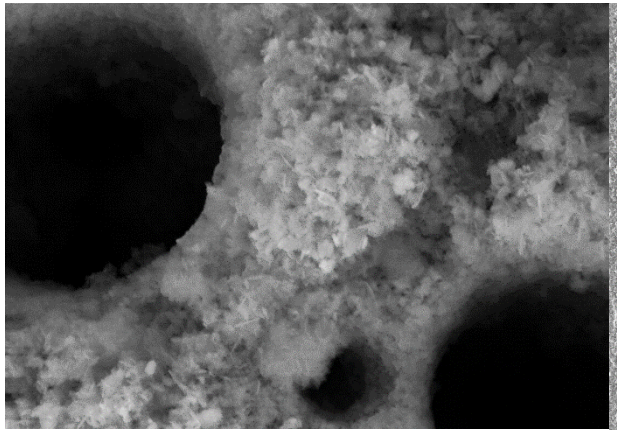


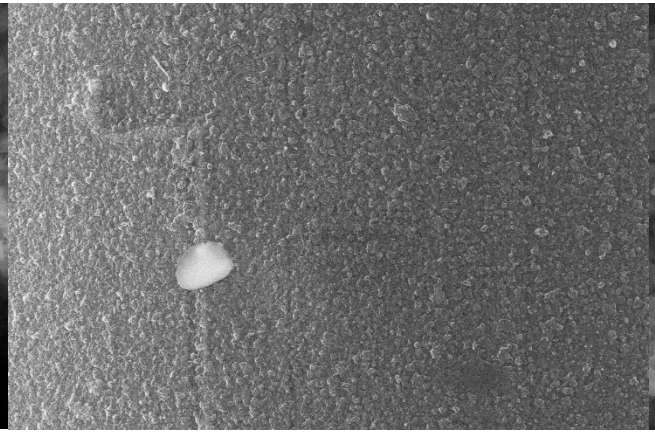


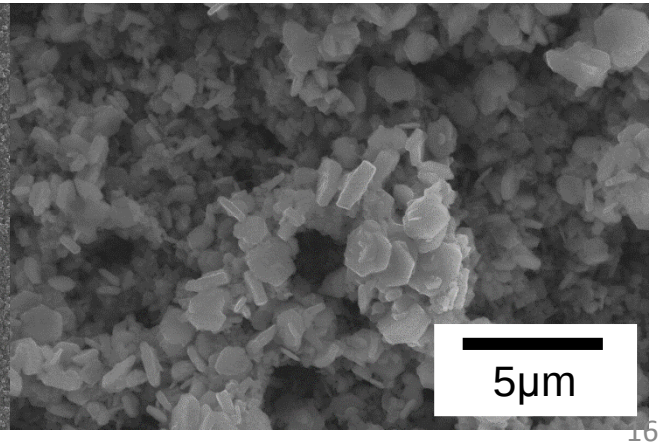






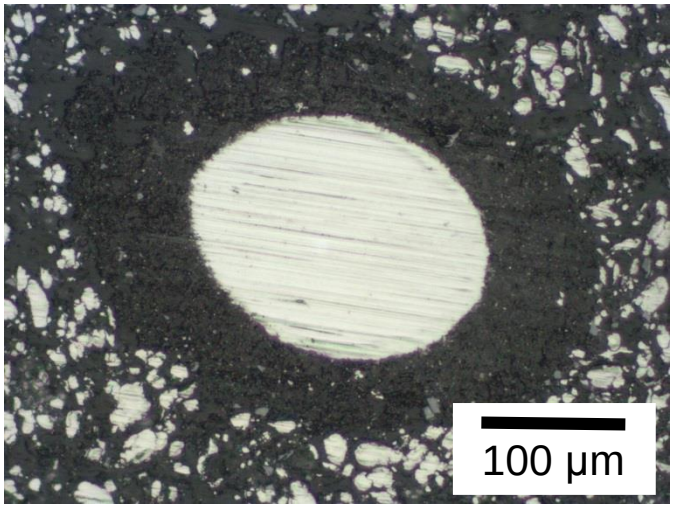




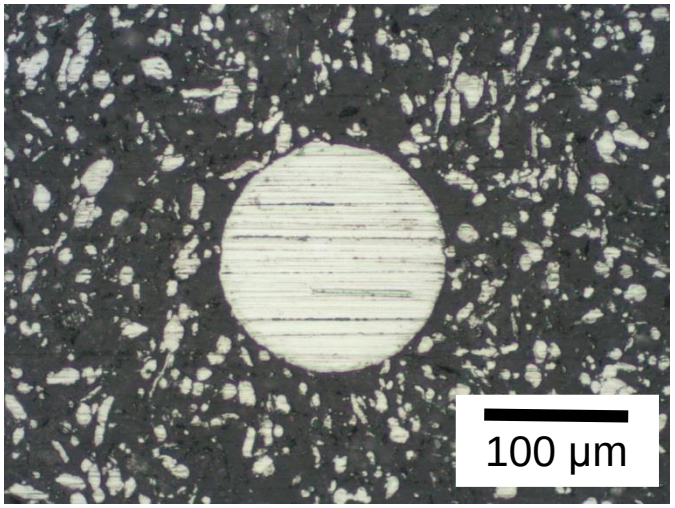


Polished Cross Sections of Tests

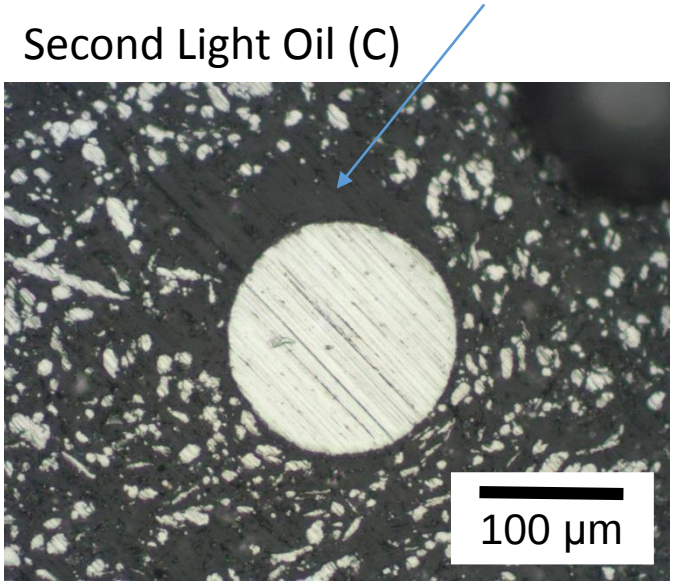
Light Oil (A)



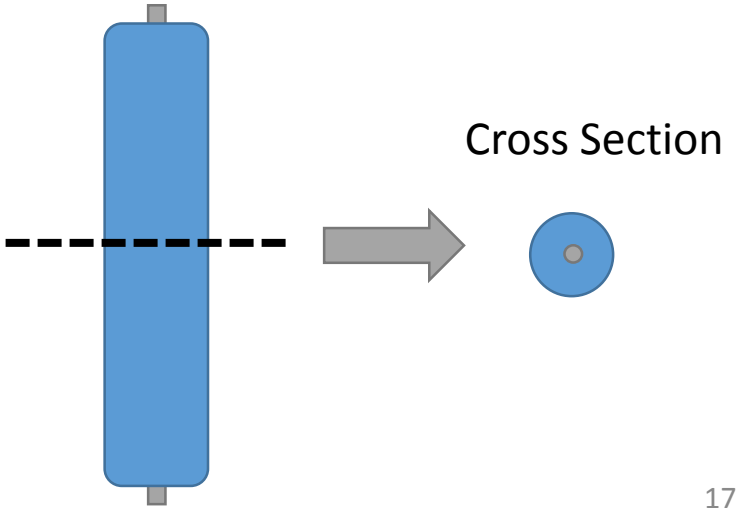
Heavy Oil (B)



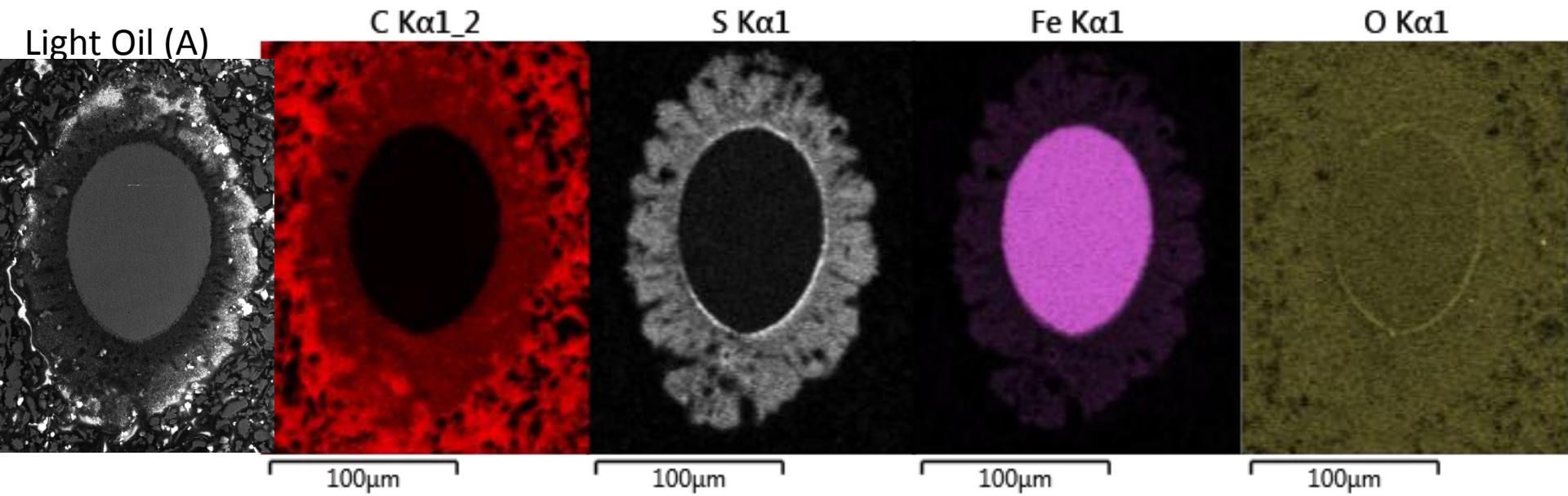
Second Light Oil (C)



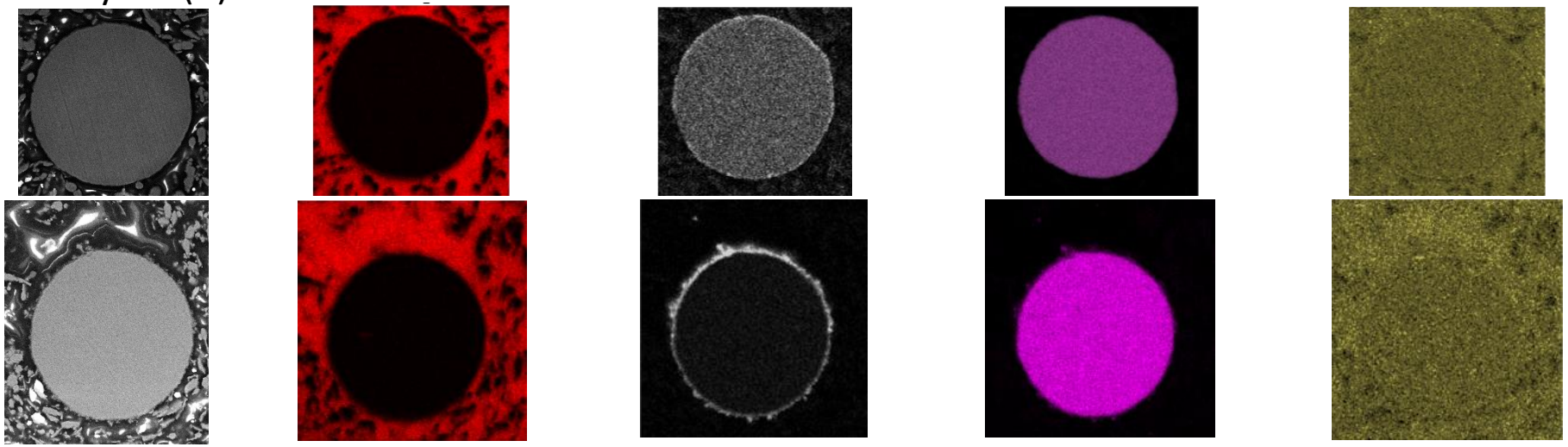
Fouled Wire



Low Magnification Elemental Map



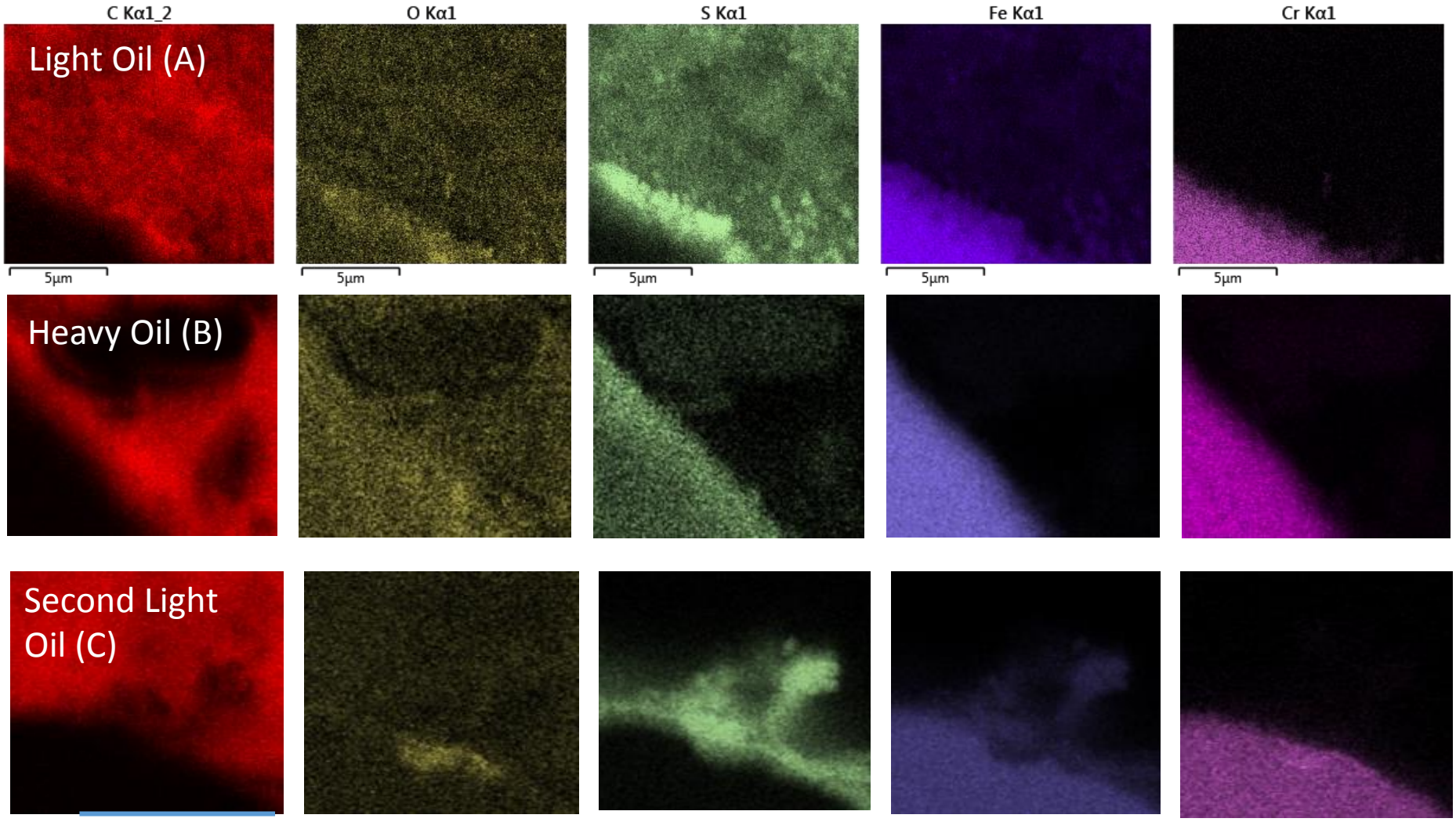
Heavy Oil (B)



Second Light Oil (C)

High Magnification Elemental Map

Heavy oil (B) is 2.56 wt% sulfur
Light oil (C) is 0.90 wt% sulfur



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