HIGH VISCOSITY LNAPL RECOVERABILITY ASSESSMENT

Presented by

Stephen S. Boynton, LSP

Subsurface Environmental Solutions, LLC

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Sponsors

WES Grant Professional Practice Review Committee and LSP Association

SES thanks the WES Grant Review Committee and LSPA Board for encouraging, reviewing and approving this High Viscosity LNAPL Recoverability Assessment

WES Grant Professional Practice Review Committee members:

- Andy Irwin, LSP
- Lauren Konetzny, LSP
- Roger Thibault, LSP

LSP Association
assess. advise. restore.

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Palms Environmental

Subsurface Environmental Solutions, LLC gratefully acknowledges Palms Environmental, LLC Woburn, MA. Palms graciously loaned SES interface probes and a peristaltic pump for this research project.

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Trident Environmental

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Subsurface Environmental Solutions, LLC recognizes Trident Environmental Group for generous assistance with transportation and disposal of LNAPL used during this assessment.

Saybolt, LP

Subsurface Environmental Solutions, LLC acknowledges Saybolt LP in Deer Park, TX for providing discounted viscosity testing, and for providing details and photographs of laboratory viscosity testing apparatus. Special thanks to Michael Calais, Laboratory Manager.

Jacob Butterworth, LSP

Jacob Butterworth, Vice President with Sage Environmental generously supplied SES with the #6 oil used during this research.

SAGE

ENVIRONMENTAL

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David Adilman, PG

David Adilman, Principal Hydrogeologist with Geosyntec assisted SES with most of the research conducted for this assessment.

Geosyntec consultants

davidadilmansculpture.com

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Project Objective

Problem Statement & Objective

Description of the problem or issue to be addressed

In 2014 the MCP was amended to better reflect the actual behavior of Light Non-Aqueous Phase Liquid (LNAPL) in the subsurface. These changes included the requirement to evaluate LNAPL recovery "if and to the extent feasible." **The subsequent 2016 LNAPL Guidance document (Policy #WSC-16-450) clarified that LNAPL recoverability does not correlate with LNAPL thickness, and it identified LNAPL Transmissivity (T_n) as a key element of the recoverability evaluation.**

LNAPL Transmissivity testing has proven to be a valuable approach for evaluating LNAPL recoverability at LNAPL release Sites. **However, high viscosity LNAPLs, (eg. # 6 oil and some machine oils) can be challenging as these oils can coat instrumentation used to measure LNAPL thickness during the tests**.

This proposed "High Viscosity LNAPL Recoverability Assessment" is designed to **determine the viscosity above which typical transmissivity testing equipment (oil/water interface probes and peristaltic pumps) cannot be reliably used**. In the case that high viscosity prevents LSPs from performing transmissivity tests, an equation is available for calculating a conservative estimate for transmissivity.

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Scope of Work Summary

- This study is designed to evaluate the viscosity above which:
  - LNAPL thickness cannot be measured due to LNAPL coating the tip of oil/water interface probes.
  - LNAPL cannot be pumped with a peristaltic pump (commonly used for LNAPL transmissivity manual skimming tests)
- Evaluate a commonly used field test method to determine if reasonably reliable viscosity estimates can be made on site.
- Review how to calculate Transmissivity when field testing is not possible

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What is Viscosity?

What is Viscosity?

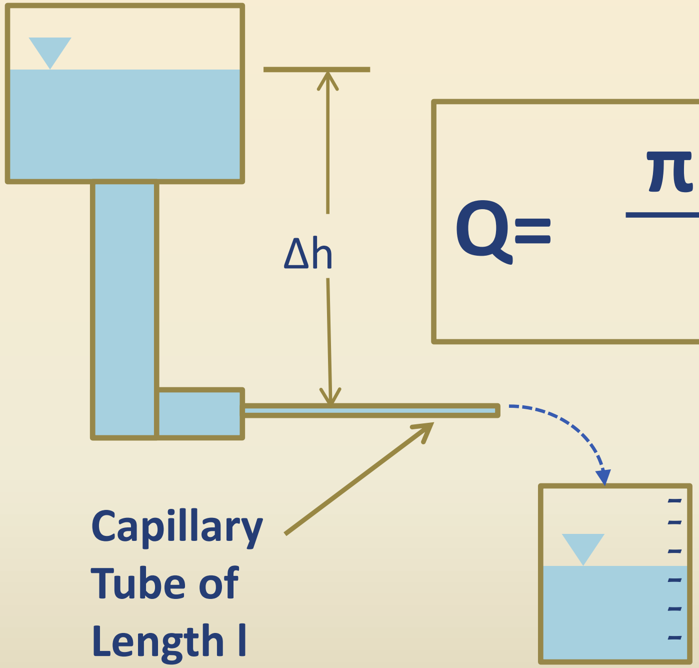
This question is often best answered by example. Imagine a Styrofoam cup with a hole in the bottom. If I then pour honey into the cup I will find that the cup drains very slowly. That is because honey's viscosity is large compared to other liquids' viscosities. If I fill the same cup with water, for example, the cup will drain much more quickly.

Viscosity is a measure of a fluid's resistance to flow. It describes the internal friction of a moving fluid. A fluid with high viscosity resists motion because its molecular makeup gives it a lot of internal friction. A fluid with low viscosity flows easily because its molecular makeup results in very little friction when it is in motion.

Princeton.edu

Two Types of Viscosity

Dynamic or Absolute Viscosity, η
Hagen–Poiseuille Equation



$$Q = \frac{\pi \, \Delta P \, r^4}{8 \eta \, l}$$

- **Q** = Flow rate
- **l** = Capillary tube length
- **η** = Dynamic viscosity
- **r** = Capillary tube radius
- **ΔP** = Change in pressure between along the capillary tube

Kinematic Viscosity, ν
Stokes Law

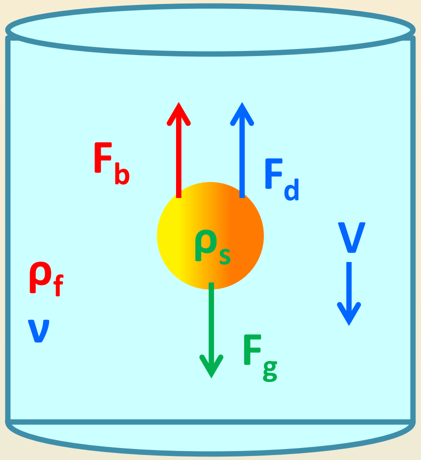
$$F_b = (4/3)\, \pi \, r^3 \rho_f \, g$$

$$+$$

$$F_d = 6 \, \pi \, r \, \nu \, V$$

$$=$$

$$F_g = (4/3)\, \pi \, r^3 \rho_s \, g$$



$$V = \frac{2}{9} \, \frac{(\rho_s - \rho_f)}{\nu} \, g r^2$$

- **V** = Velocity of sphere
- ρ_s = Density of sphere
- P_f = Density of fluid
- **ν** = Kinematic viscosity
- **g** = Acceleration of gravity
- **r** = Radius of sphere

η (eta) = dynamic viscosity, centipoise (cP)
ν (nu) = kinematic viscosity, centistokes (cSt)
ρ (ro) = fluid density, g/cm3

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Dynamic vs. Kinematic Viscosity

Jean Poiseuille
1797-1869

....it's not so bad!!

$$\eta = \nu \cdot \rho$$

η = dymamic viscosity, cP
ν = kinematic viscosity, cSt
ρ = fluid density, g/cm3

George Stokes
1819-1903

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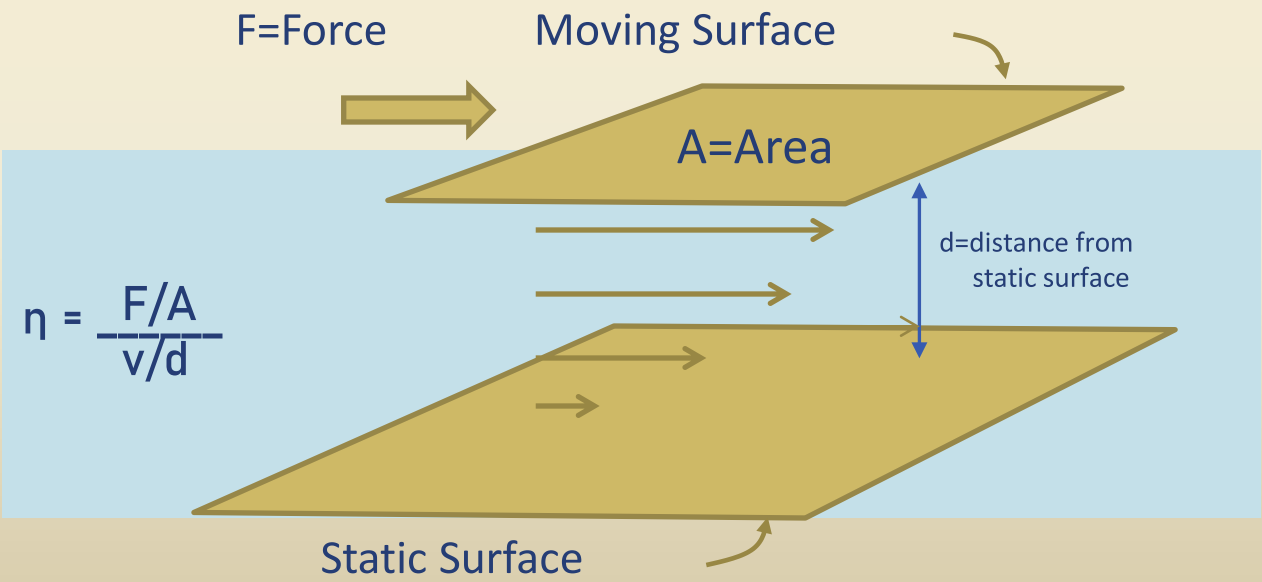
Takeaways

Big Picture Takeaway:

- $\eta = \nu \cdot \rho$
- LNAPL density, ρ, falls in narrow range (0.7 to 1.0)
- Therefore a centistoke and a centipoise aren't all that different!

Things not covered here:

- Newtonian vs. Non-Newtonian Fluids
- Reynold's number
- Shear stress/velocity approach
- Laminar vs. turbulent flow
- Thixotropy



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How is Viscosity Measured?

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Kinematic Viscosity by Capillary Viscometer

Designation: D 445 – 04

An American National Standard
British Standard 2000: Part 71:1990

INTERNATIONAL

Designation: 71/1/97

Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)[1]

This standard is issued under the fixed designation D 445; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope*

1.1 This test method specifies a procedure for the determination of the kinematic viscosity, ν, of liquid petroleum products, both transparent and opaque, by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity, η, can be obtained by multiplying the kinematic viscosity, ν, by the density, ρ, of the liquid.

Note 1—For the measurement of the kinematic viscosity and viscosity of bitumens, see also Test Methods D 2170 and D 2171.

1.2 The result obtained from this test method is dependent upon the behavior of the sample and is intended for application

2. Referenced Documents

2.1 *ASTM Standards:* [2]

D 446 Specifications and Operating Instructions for Glass Capillary Kinematic Viscometers

D 1193 Specification for Reagent Water

D 1217 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer

D 1480 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer

D 1481 Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer

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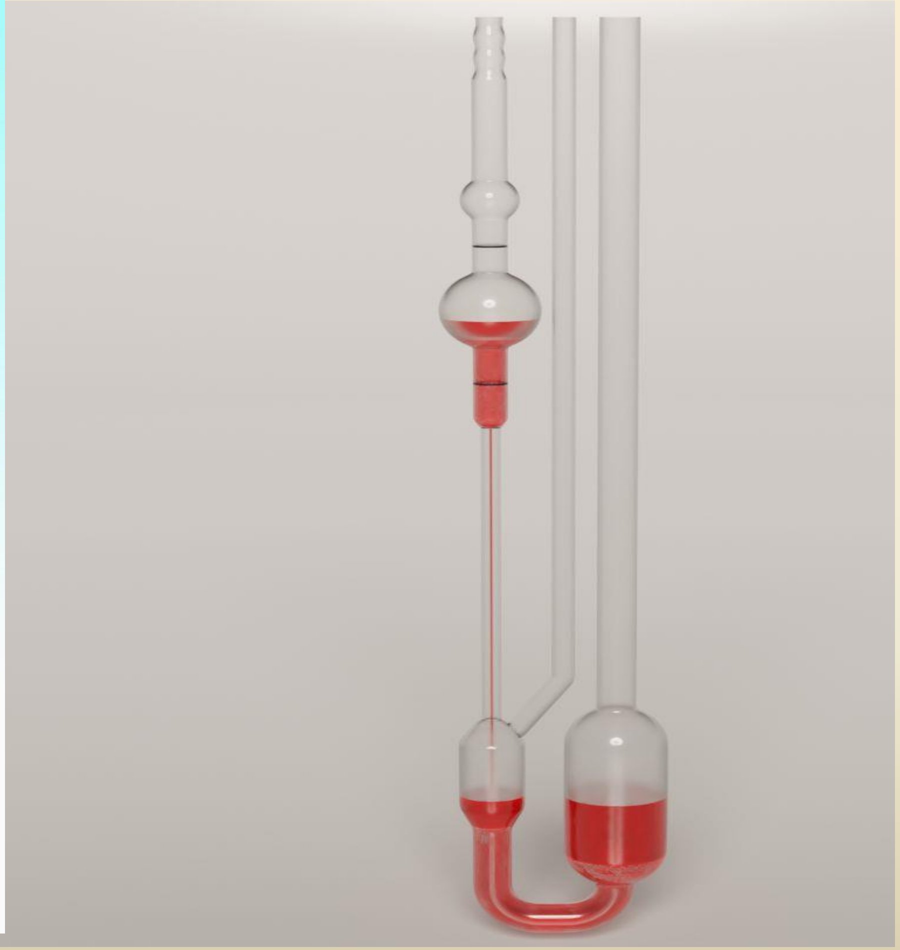
Kinematic Viscosity by Capillary Viscometer



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See how the test is run!!! https://www.youtube.com/watch?v=2I8NMnLW96g

Saybolt, LP Apparatus

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Saybolt
A CORE LABORATORIES COMPANY

Saybolt, LP Apparatus

Zeitfuchs Cross Arm

One factor for any temperature

Left Tube: charge line at top right

Right tube: timer start at lower line and timer stop at upper line.

Seconds x tube factor = Centistokes

Other Ways of Measuring Viscosity

Digital Rotary Viscometer

Marsh Funnel

1914-1915 Vintage Historical Saybolt Standard Universal Viscosimeter - Antique

Saybolt Viscometer

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Cup Viscosity Tests

What is #6 Oil

- **No. 6 fuel oil** is a dense, viscous oil produced by blending heavy residual oils with a lighter oil (often No. 2 fuel oil) to meet specifications for viscosity and pour point. **-Alaska Dept. of Environmental Conservation**

- **Residual fuel oil:** A general classification for the heavier oils, known as No. 5 and No. 6 fuel oils, that remain after the distillate fuel oils and lighter hydrocarbons are distilled away in refinery operations. No. 6 fuel oil includes Bunker C fuel oil and is used for the production of electric power, space heating, vessel bunkering, and various industrial purposes. **-U.S. Energy Information Administration**

- **Bunkering** is the supplying of fuel for use by ships (such fuel is referred to as **bunker**), including the logistics of loading and distributing the fuel among available shipboard tanks. The term bunkering originated in the days of steamships, when coal was stored in bunkers. Nowadays, the term bunker is generally applied to the petroleum products stored in tanks, and bunkering to the practice and business of refueling ships. **-Wikipedia**

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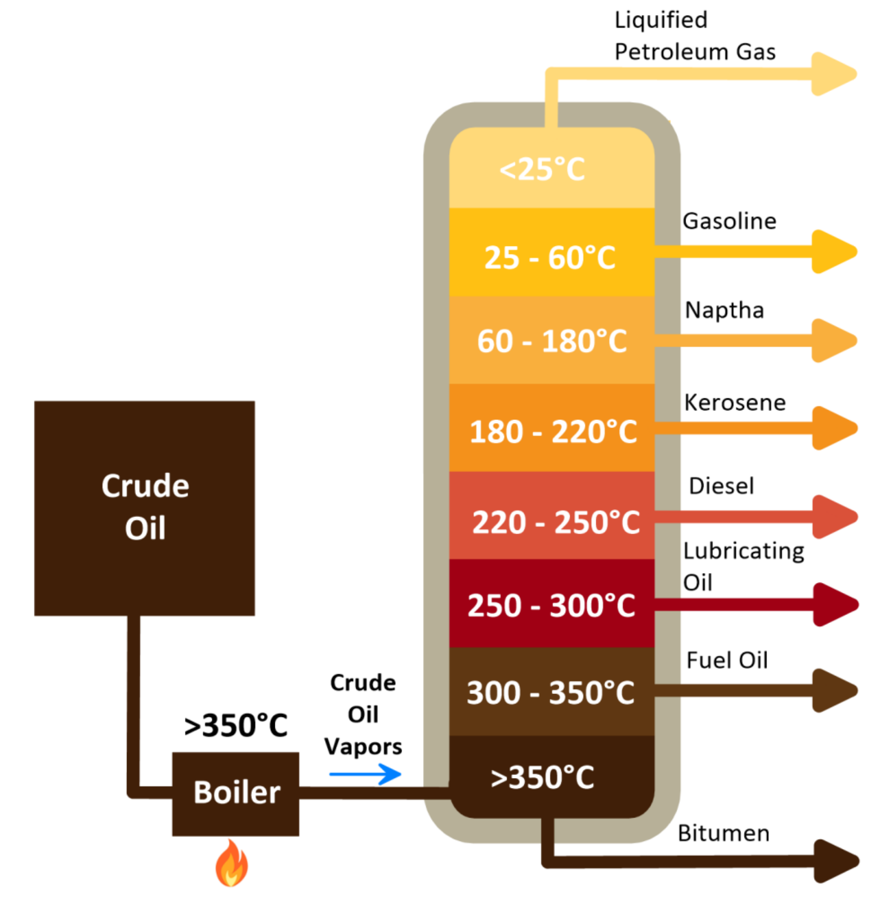
Fractional Distillation



Density (g/cc)	Viscosity (cSt) @ 70F	Carbon Range	Uses
n/a	n/a	C1-C4	LP Gases/ Propane
0.71 to 0.77	0.4 to 1	C5-10	Vehicle Fuel
0.75 to 0.79	0.97	C6-C12	Chemical Production
0.78–0.81	Around 1	C10-C16	Jet Fuel Paraffin
0.82 to 0.85	2.5–3.2	C15-C18	Diesel Engines & Home Heating Oil
0.8 - 0.97	1000?	C20-C50	Cars and Machinery
>0.9	>5000?	C50-C70	Fuel for Ships and Factories
1.01-1.05	Very High	>C70	Asphalt

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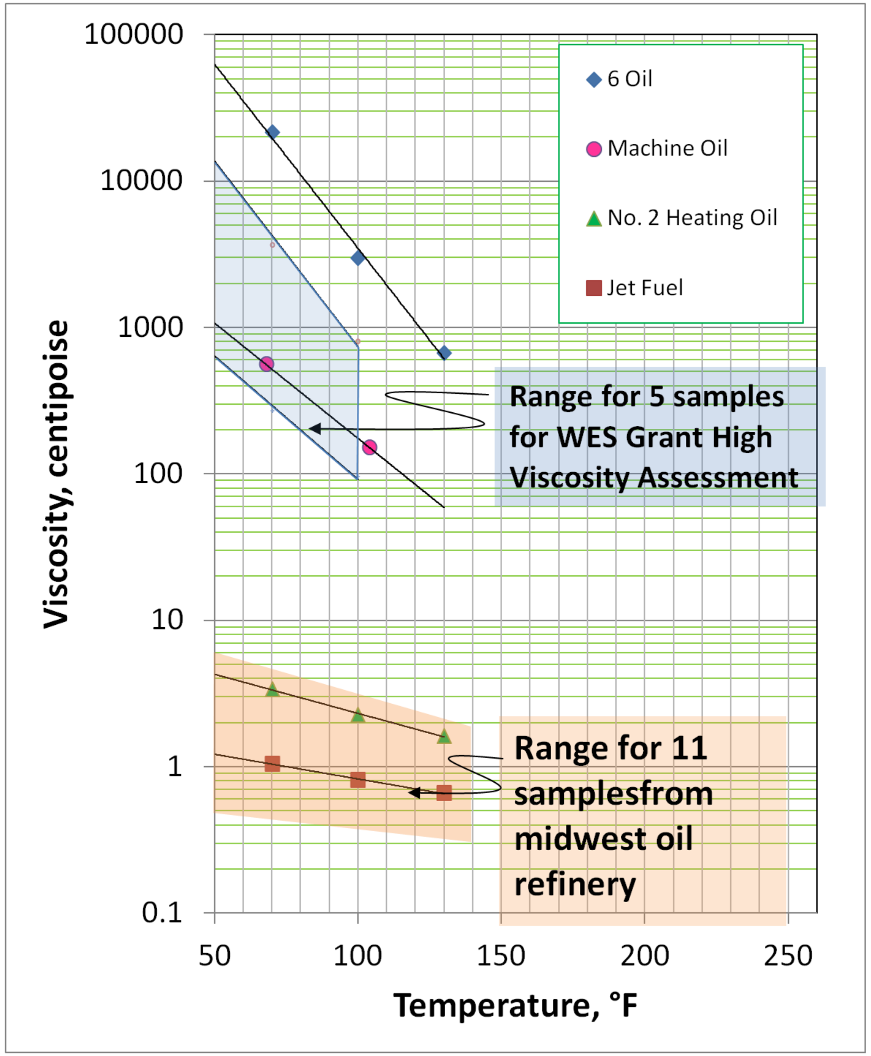
Viscosity for Various Petroleum Products



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Test Samples

- Prepared mixtures of diesel fuel purchased from a local gas station with #6 oil provided by Sage Environmental.

- Initially prepared samples at 20%, 40%, 60% and 80% #6 oil.

- Later added samples at 85%, 90%, and 95% - #6 oil.

Petroleum Used for this Study

Field Viscosity Evaluation

- Determine if an inexpensive and simple field test can be used reliably to estimate LNAPL viscosity

- Perform viscosity tests on mixtures of diesel/#6 oil and compare to laboratory test data and/or published data

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Zahn Cup Immersion Viscosity Cup, Dip Type Stainless Steel Viscometers for Test The Viscosity of Newtonian or Approximate Newtonian Liquid (NO.5)

Brand: Magsoar

18 ratings | 4 answered questions

$19.60

prime

FREE Returns

Size: **NO.5**

NO.1	NO.2	NO.3	NO.4	**NO.5**
$19.80	$19.88 ($26.51 / 100 g)	$19.60	$19.60 ($26.13 / 100 g)	**$19.60**
prime	prime	prime	prime	prime

- 【Precise & Credible】 The Stainless Steel Cup is made by precise mold, and the orifice is drilled using precise high-speed CNC. It's calibrated against National Institute of Standards and Technology (NIST). Therefore, you will get accurate and believable measurements with this Zahn Cup.

VISCOSITY CUP EVALUATION

Applications and Equations

Type	Aperture (mm/inch)	Viscosity Range (cSt)	Efflux Time (sec)	K	C	Formula V=k(t-c)	Application
#1	1.93/0.08	5-60	35-80	1.1	29	V=1.1(t-29)	very thin liquid
#2	2.69/0.11	20-250	20-80	3.5	14	V=3.5(t-14)	thin oil, mixed paint, varnish
#3	3.86/0.15	100-800	20-80	11.7	7.5	V=11.7(t-7.5)	medium viscosity oil, mixed paint, latx paint
#4	4.39/0.17	200-1200	20-80	14.8	5	V=14.8(t-5)	viscous liquid and mixture
#5	5.41/0.21	400-1800	20-80	23	0	V=23t	very viscous liquid and mixture

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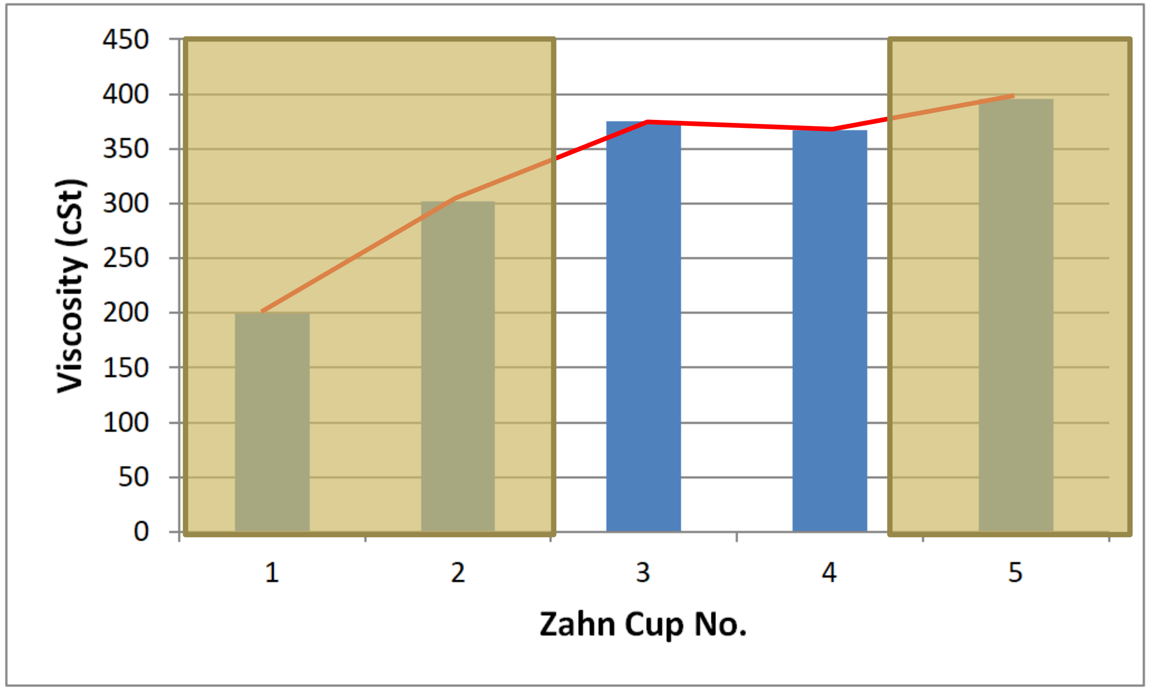
Results for Sample D
(20% Diesel/80% #6 Oil)

Cup No.	Average Drain Time (seconds)	Calculated Viscosity (cSt)
1	210	199
2	100.3	302
3	39.61	376
4	29.78	367
5	17.19	395



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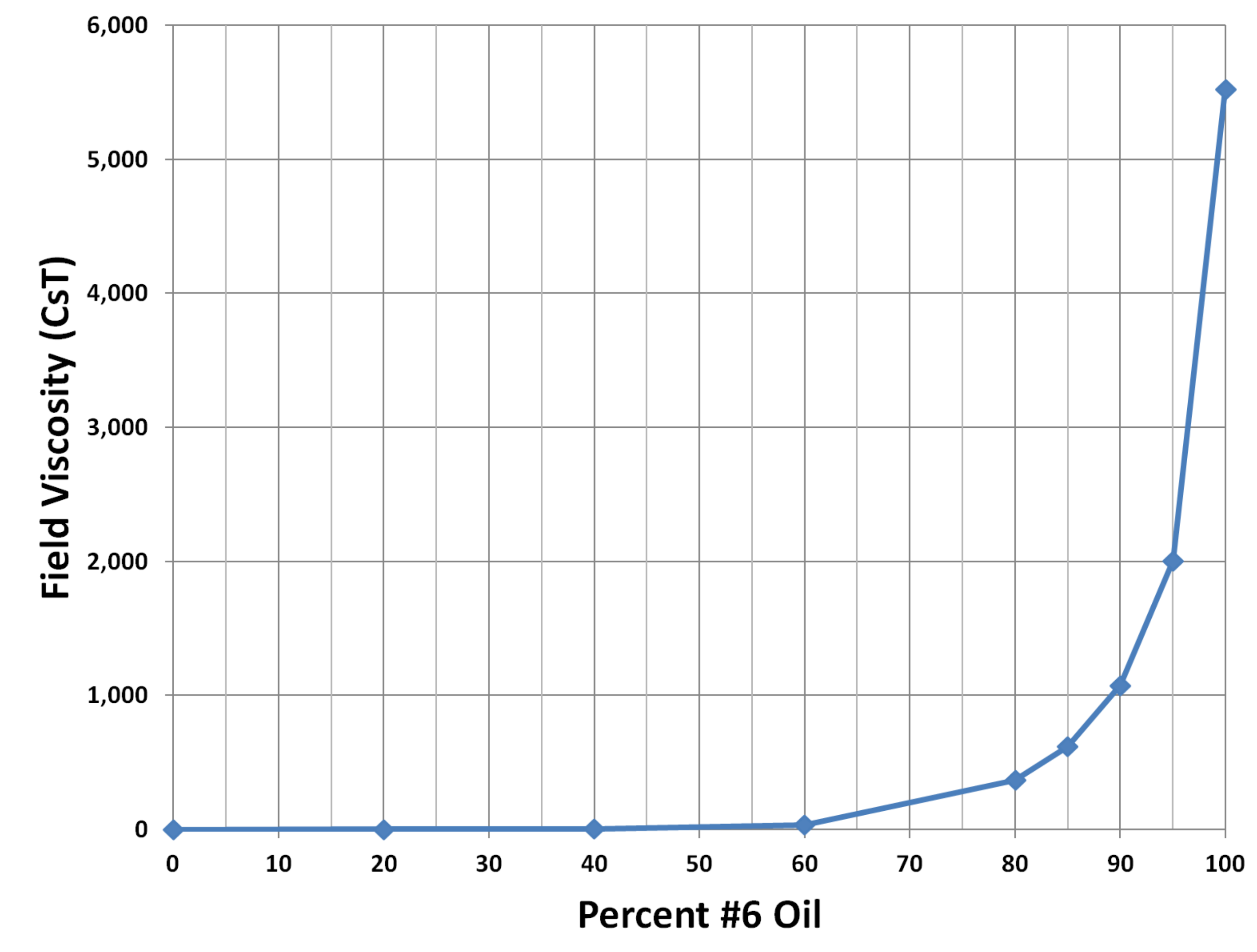
Field Viscosity Results

Percent #6 Oil	Viscosity (cSt)
0	0.09
20	1
40	5
60	34
80	370
85	619
90	1075
95	2006
100	5520



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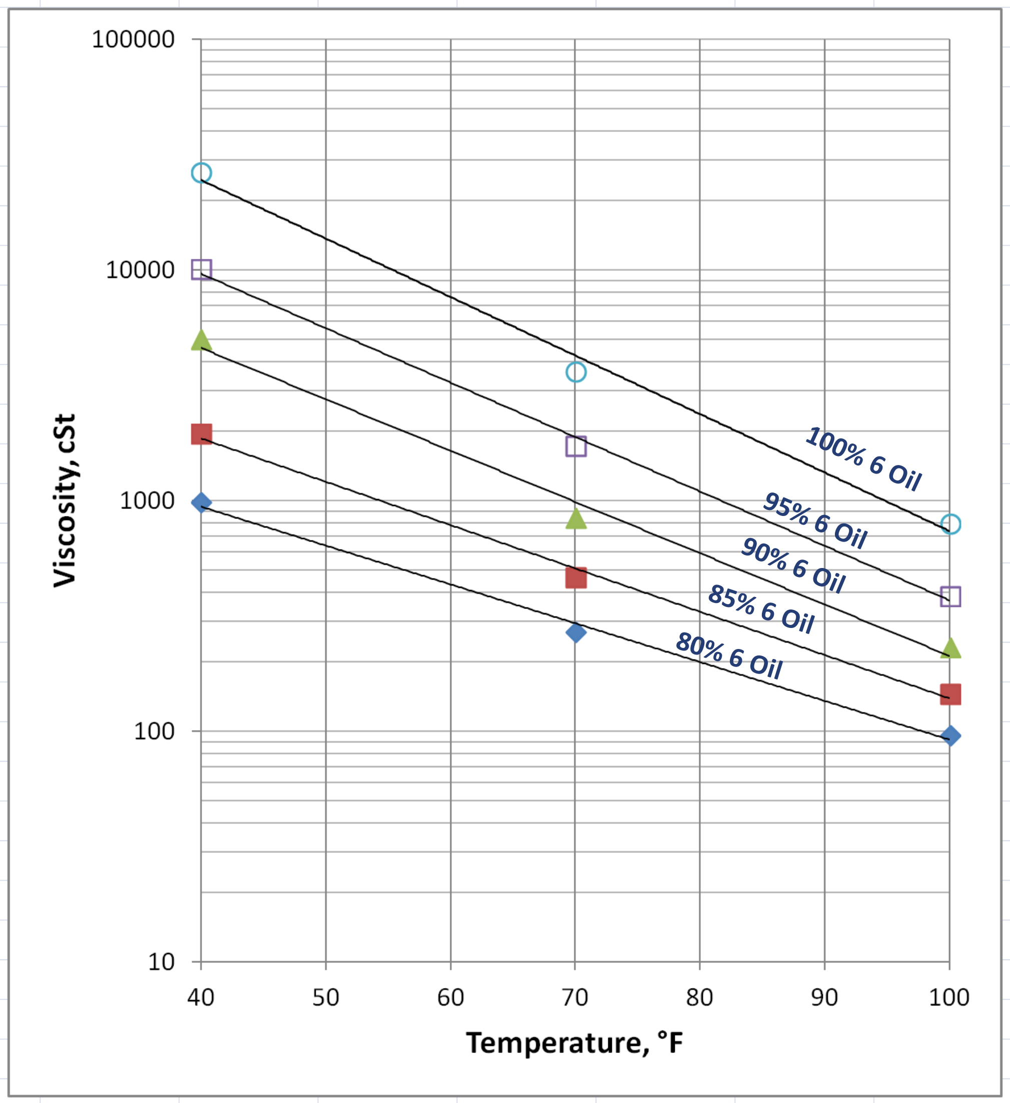
Laboratory Results



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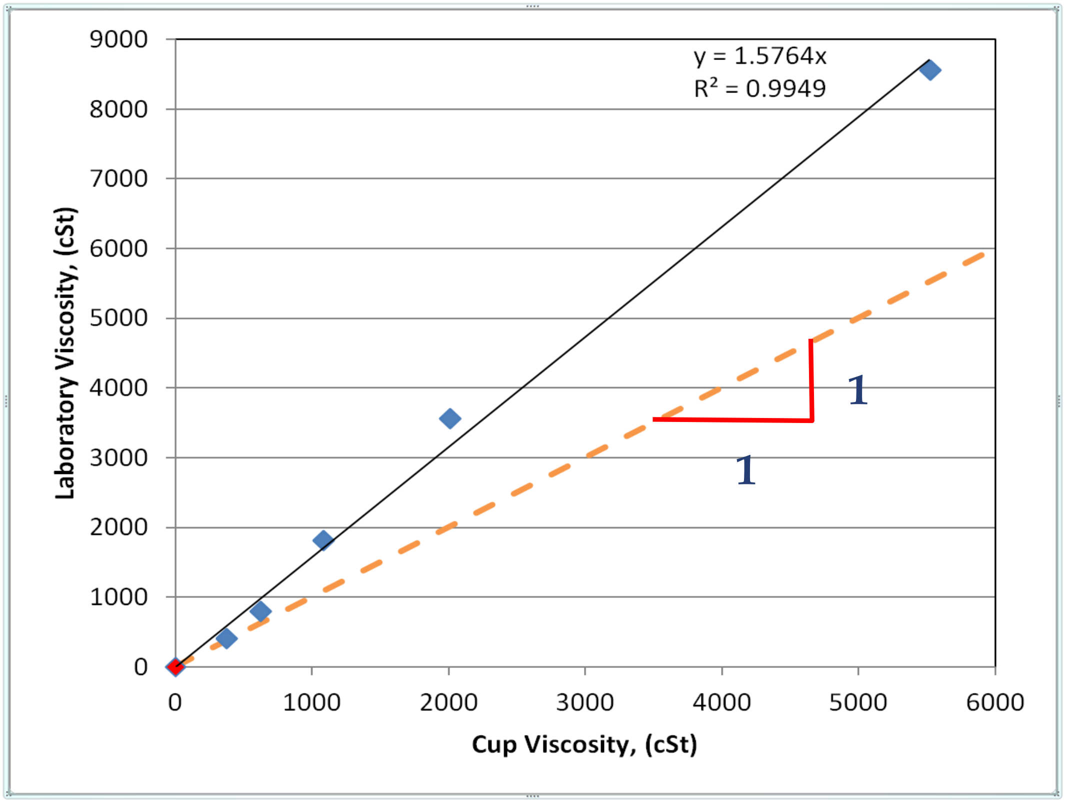
Field vs. Laboratory



Sample I.D	Percent #6 Oil	Zahn Cup No.	Average Drain Time (secs)	Average Temp. During Test	Calculated Cup Viscosity (cSt)	Lab Viscosity at Field Temp	Lab/ Cup Ratio
A	0	1	29.08	58.2	0.09	2.5	
B	20	1	29.93	59.7	1	n.m	
C	40	1	33.3	59.35	5	n.m	
D	60	1	54.15	60.1	34	n.m	
E	80	3	39.61	60.3	370	410	1.1
F	85	5	26.91	58.2	619	805	1.3
G	90	5	46.76	57.3	1075	1820	1.7
H	95	5	87.23	57.3	2006	3573	1.8
I	100	5	240	58	5520	8559	1.6

Notes:

1. Lab viscosity for Sample A (100% diesel) estimated from literature values
2. Highlighted samples outside valid range for cups
3. n.m = not measured
4. Laboratory samples tested by Saybolt, LP

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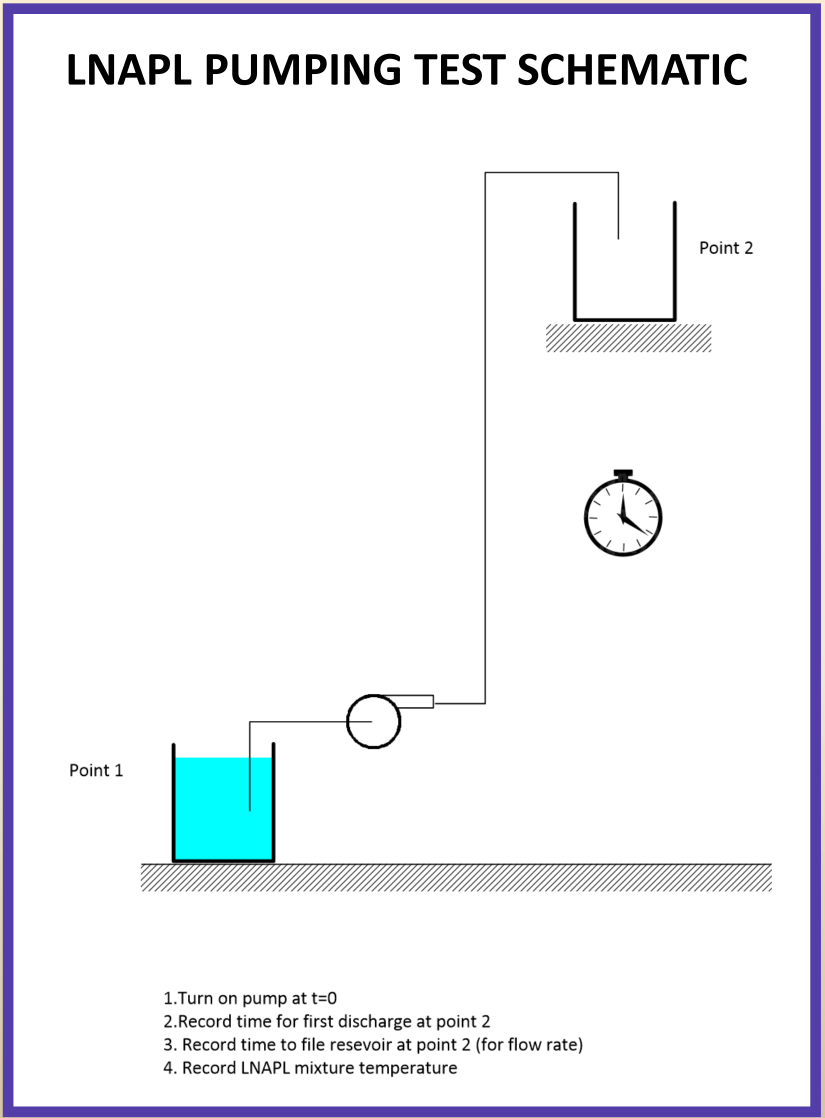
Conclusions

- Zahn viscosity cups provide a reasonable approximation of LNAPL viscosity for in the range of 5 to 1,800 cSt.
- Field cup viscosity measurements could be a valuable line of evidence for assessing sites with comingled LNAPL.
- Cup viscosity results for this study underestimated lab viscosity, particulary for the highest viscosity samples.

Peristaltic Pump Evaluation

Experimental Setup

- Goal to identify viscosity above which it is impractical to “skim” product
- Test setup created to lift LNAPL from a 4” thick layer to a height of 10’.
- Measure time from turning on pump to first discharge.
- Record temperature for future viscosity correction.
- Added a second pump event through a “wetted” tube, (i.e. repump through the same tube after the first run).



Pumping Assessment

Pousielle's Law

- **Poiseuille's law** is a physical law that calculates the pressure drop in an incompressible and Newtonian fluid in laminar flow flowing through a long cylindrical pipe of constant cross section:

$$\Delta p = \frac{8\mu L Q}{\pi R^4}$$

Δp = pressure difference between the two ends

μ = dynamic viscosity

L = length of pipe

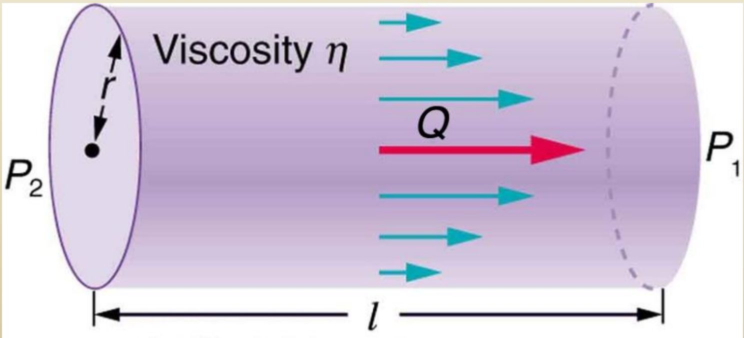
Q = volumetric flow rate

π = pi

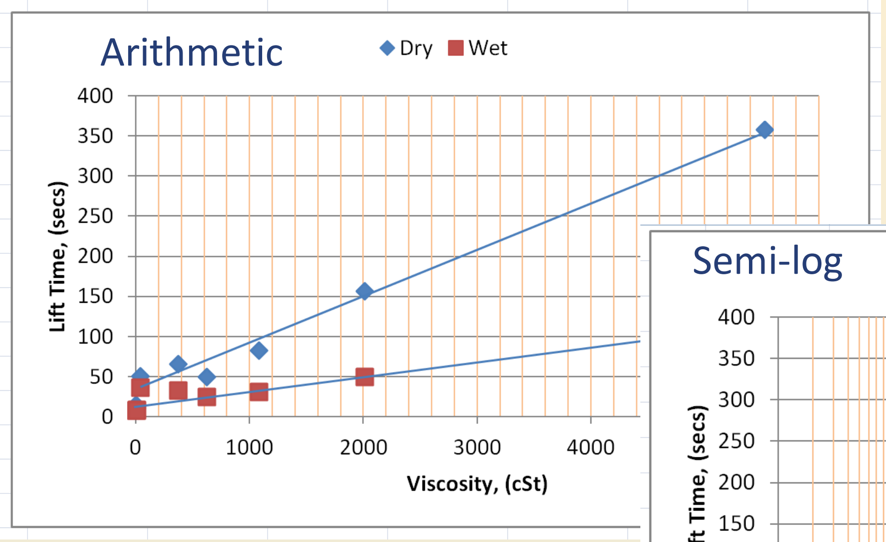
R = pipe radius

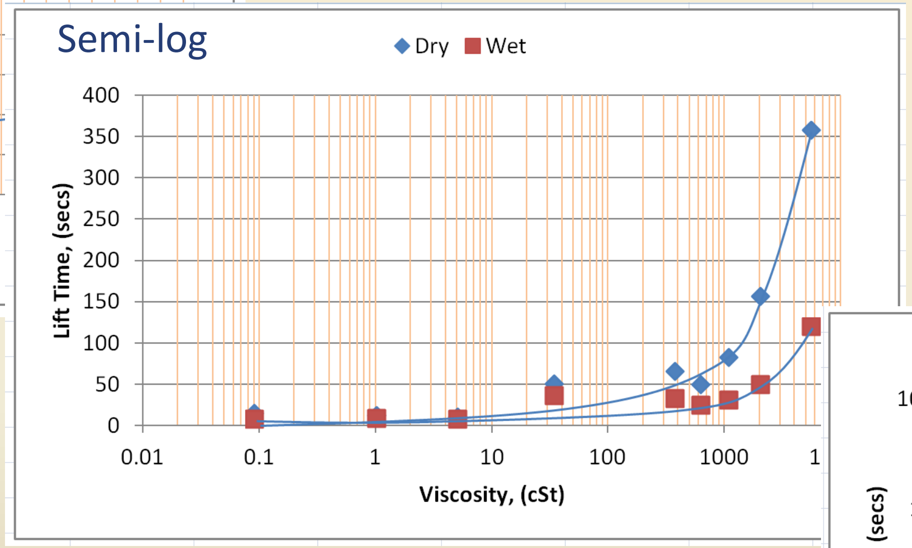
Rearranging the terms we see that flow rate, Q is inversely proporational to viscosity

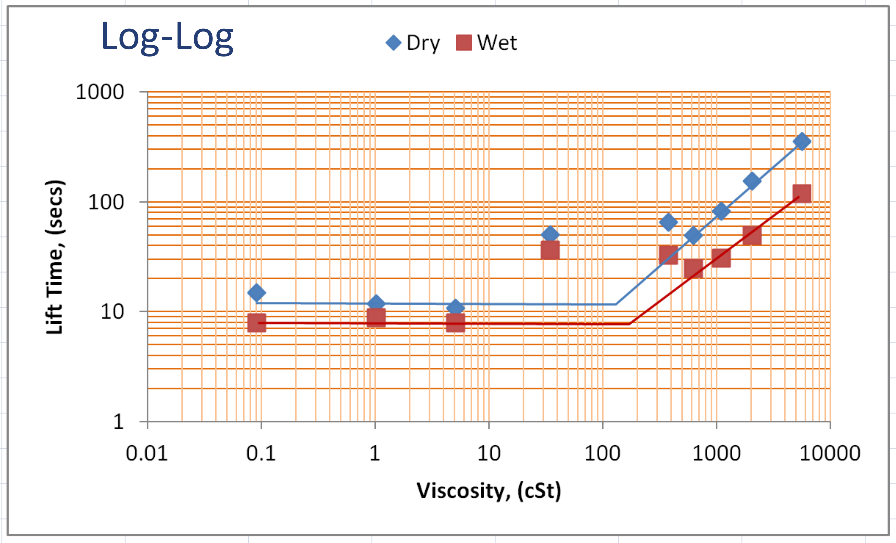
$$Q, = \frac{\pi R^4}{8\ \mu L \Delta p}$$



Time to Lift LNAPL 10-feet







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Conclusions

- Peristaltic pump was able to lift LNAPL 10 feet regardless of viscosity
- Lift time significantly greater with “dry” tubing
- “Lift Time” at low viscosity unaffected by minor viscosity changes
- “Lift Time” increased rapidly at viscosities above above 100 cSt
- Consider pre-wetting tubing with formation LNAPL if needed
- Peristaltic pump does not seem to be a significant limiting factor for performing T_n tests for viscosity values up to 5000 cSt at lifts of 10 feet

Air/LNAPL Interface

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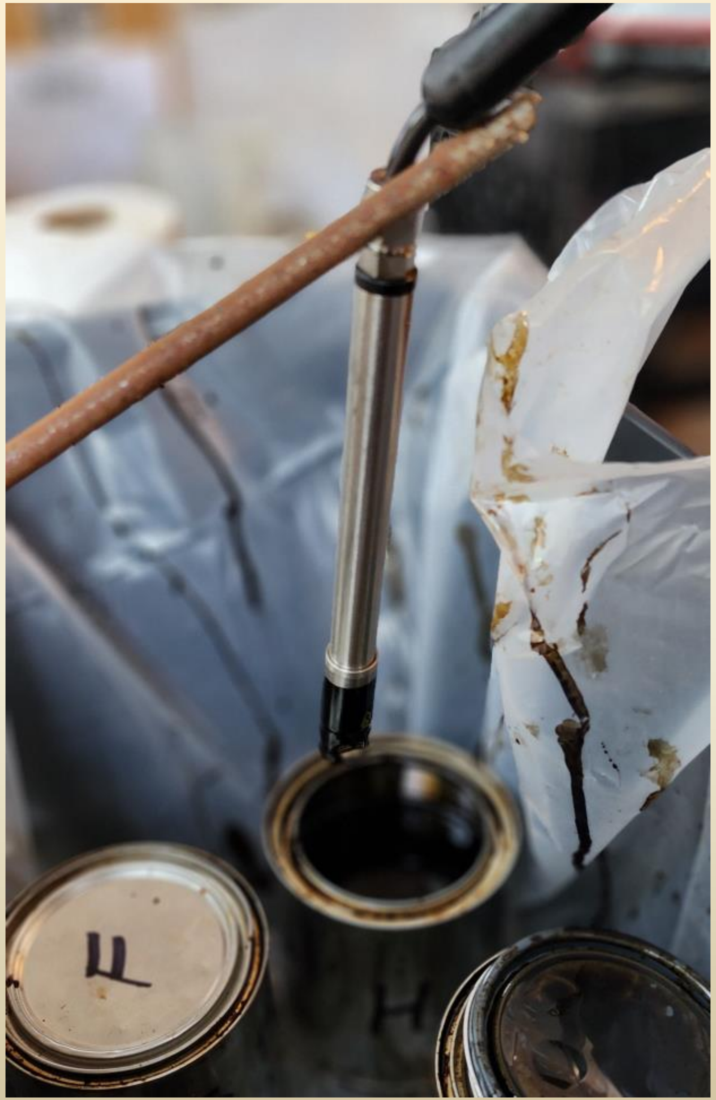
Setup and Procedure

- Objective is to quantify probe coating from passing through the air/LNAPL interface
- Used Solinst and Heron interface probe provided by Palm's Environmental
- Dipped the probes 1-inch into each sample and recorded the time for LNAPL beep to stop



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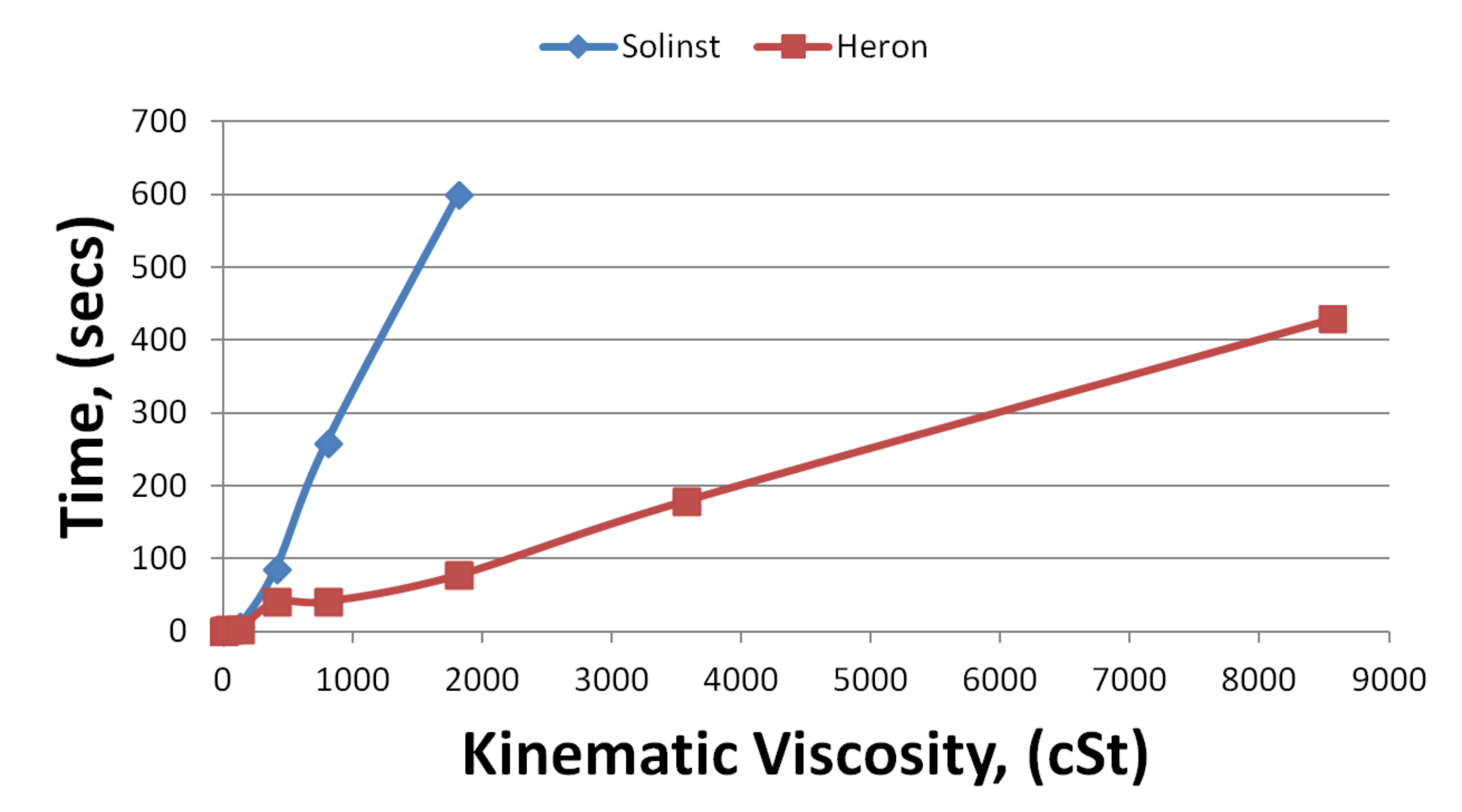
Test Results



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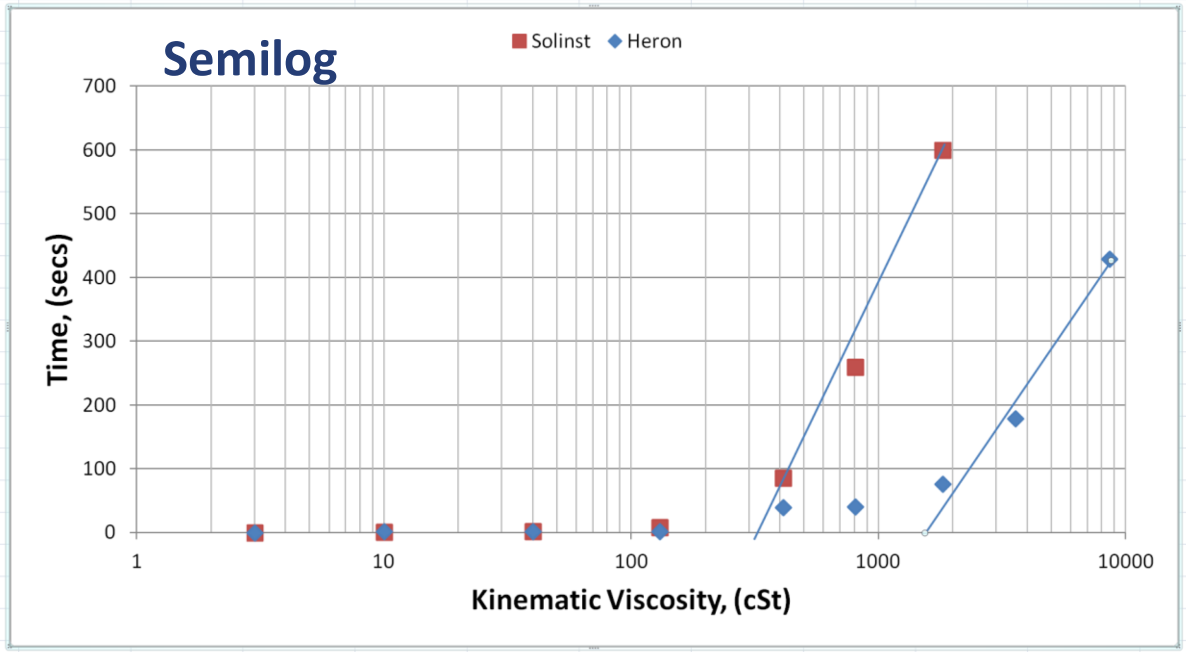
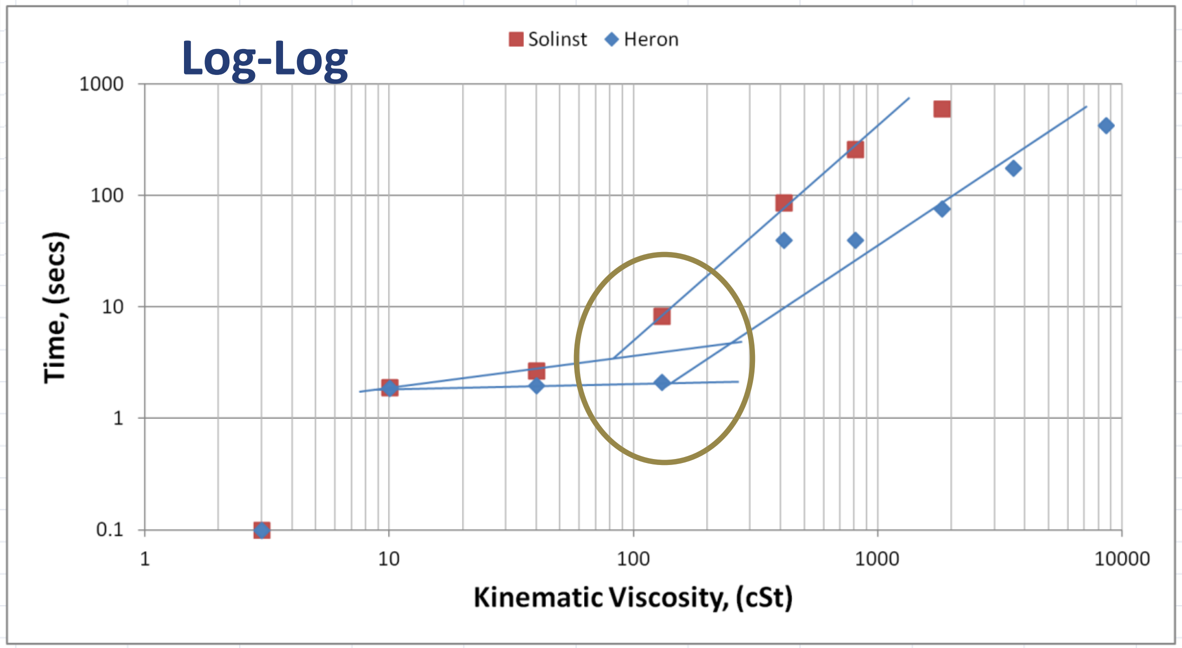
Semilog and Log-Log





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Conclusions

- Probe coating did not have a significant impact at viscosity values below 100 cSt
- Probe coating time increased significantly at viscosity values beginning between 100 and 200 cSt
- Relatively significant coating differences between the Solinst and Heron Probes at high viscosity
- Probe differences could be design related or wear related

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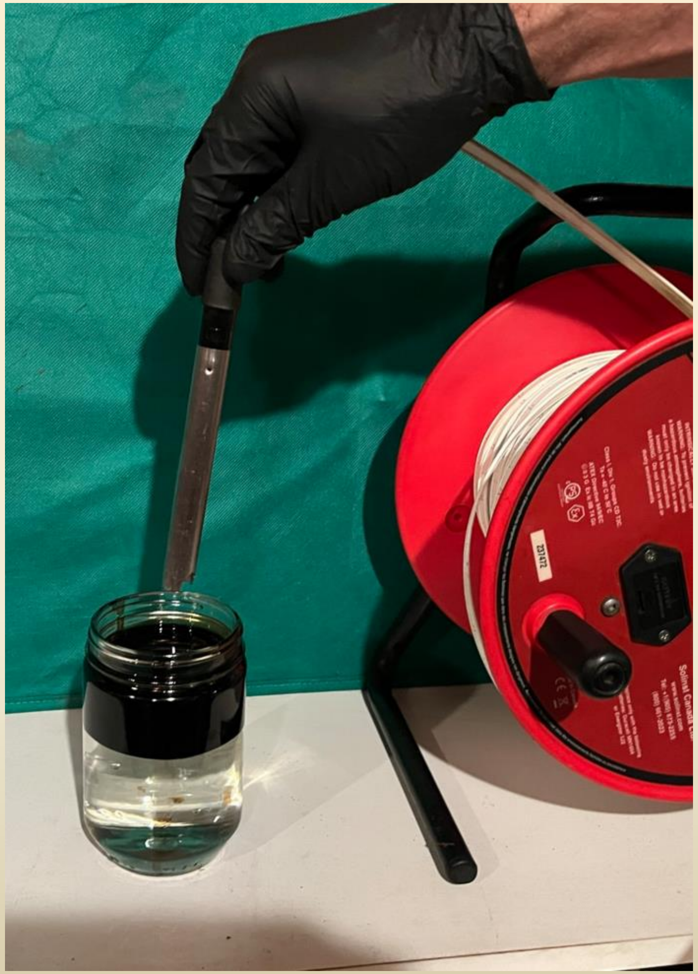
LNAPL/Water Interface Tests

Objective



- Insert probe through a layer of LNAPL into the water layer and measure thetime to obtain water signal or beep at the LNAPL/water interface
- Determine if there is an apparent viscosity above which it is impractical to measure the LNAPL/water interface

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LNAPL/Water Interface Video

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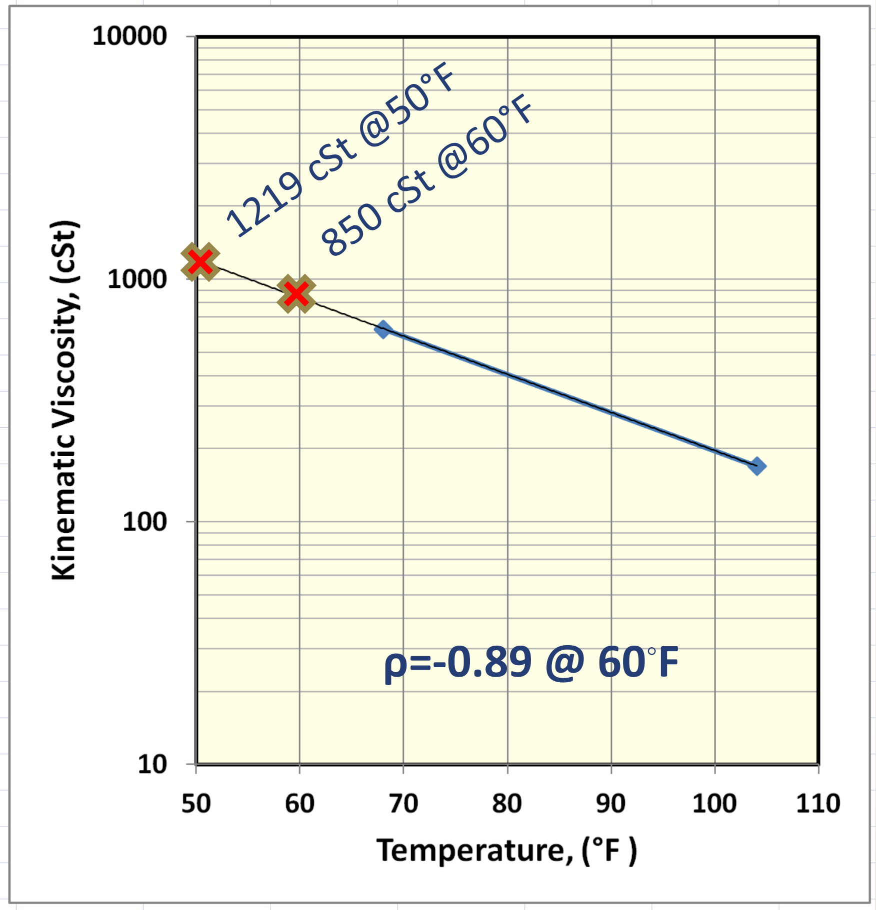
MCP Case Study

Soil Sample EPH Data

EPH Carbon Fractions	Depth BGS (feet)	
	15-16	16-18
C_9-C_{18} aliphatics	100	83
C_{19}-C_{36} aliphatics	6580	6980
C_{11}-C_{22} aromatics	312	375



Data courtesy of RANSOM

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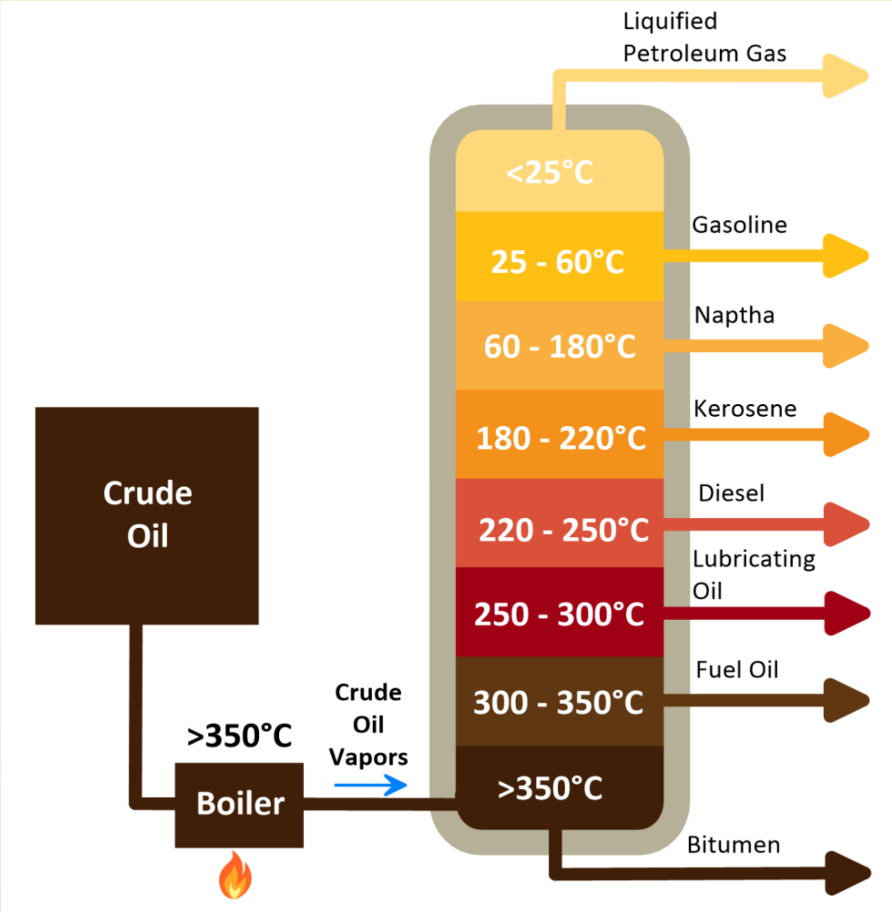
Fractional Distillation



Density	Viscosity (cSt) @ 70F	Carbon Range	Uses
n/a	n/a	C1-C4	LP Gases/ Propane
0.71 to 0.77	0.4 to 1	C5-10	Vehicle Fuel
0.75 to 0.79	0.97	C6-C12	Chemical Production
0.78–0.81	Around 1	C10-C16	Jet Fuel Paraffin
0.82 to 0.85	2.5–3.2	C15-C18	Diesel Engines & Home Heating Oil
0.8 - 0.97	1000?	C20-C50	Cars and Machinery
>0.9	>5000?	C50-C70	Fuel for Ships and Factories
1.01-1.05	Very High	>C70	Ashphalt

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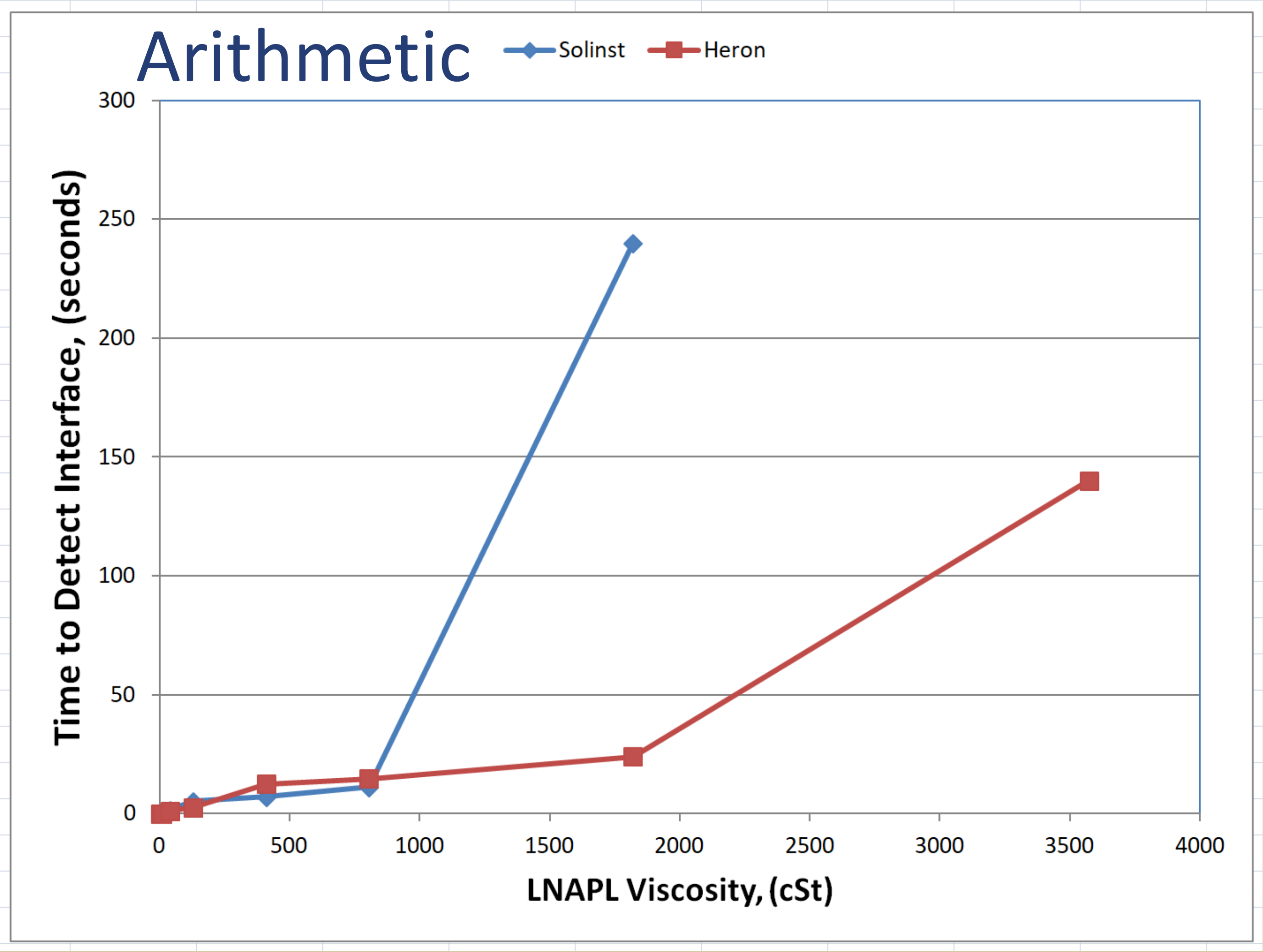
LNAPL-Water Interface Test Results



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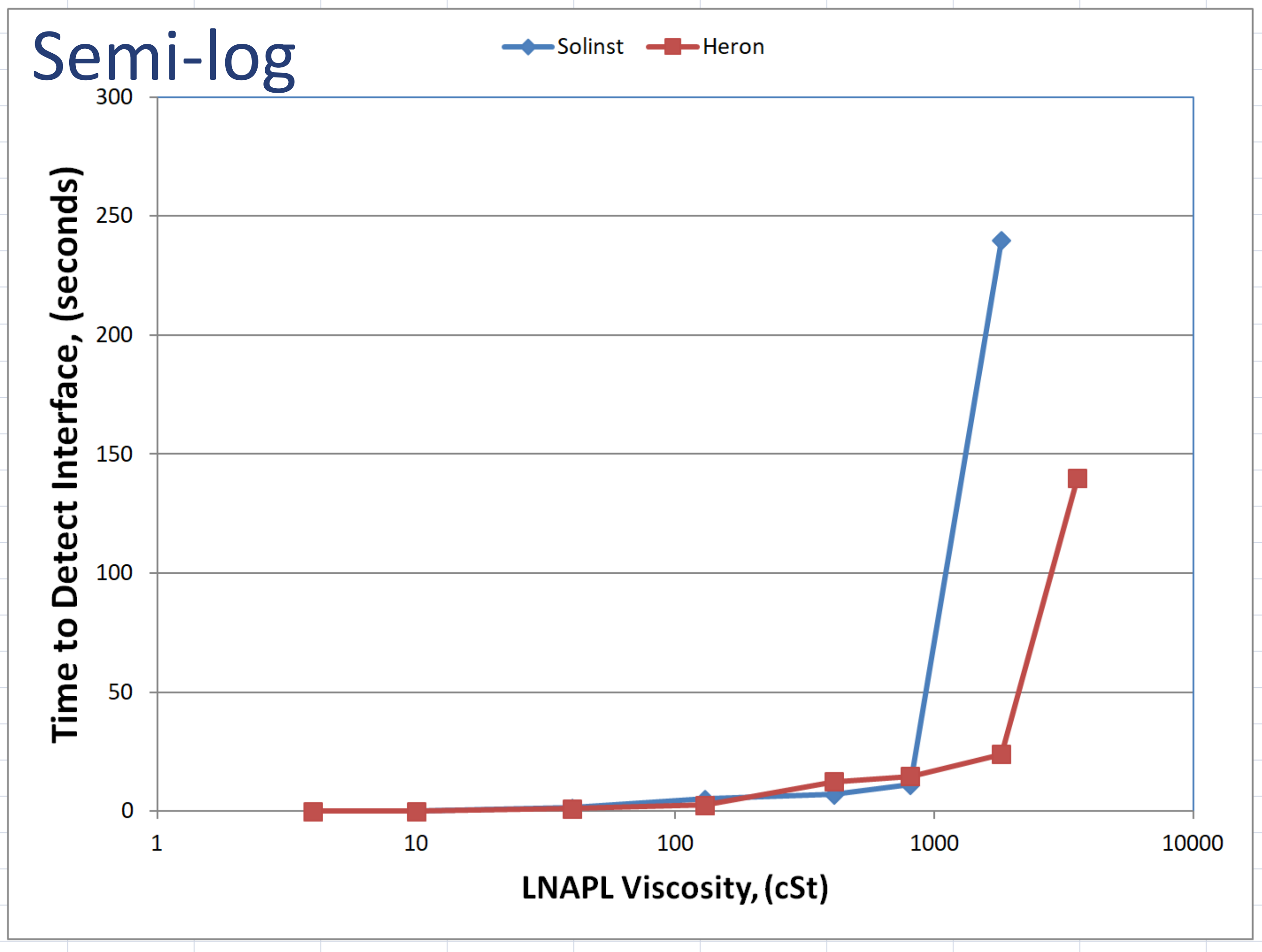
LNAPL-Water Interface Test Results



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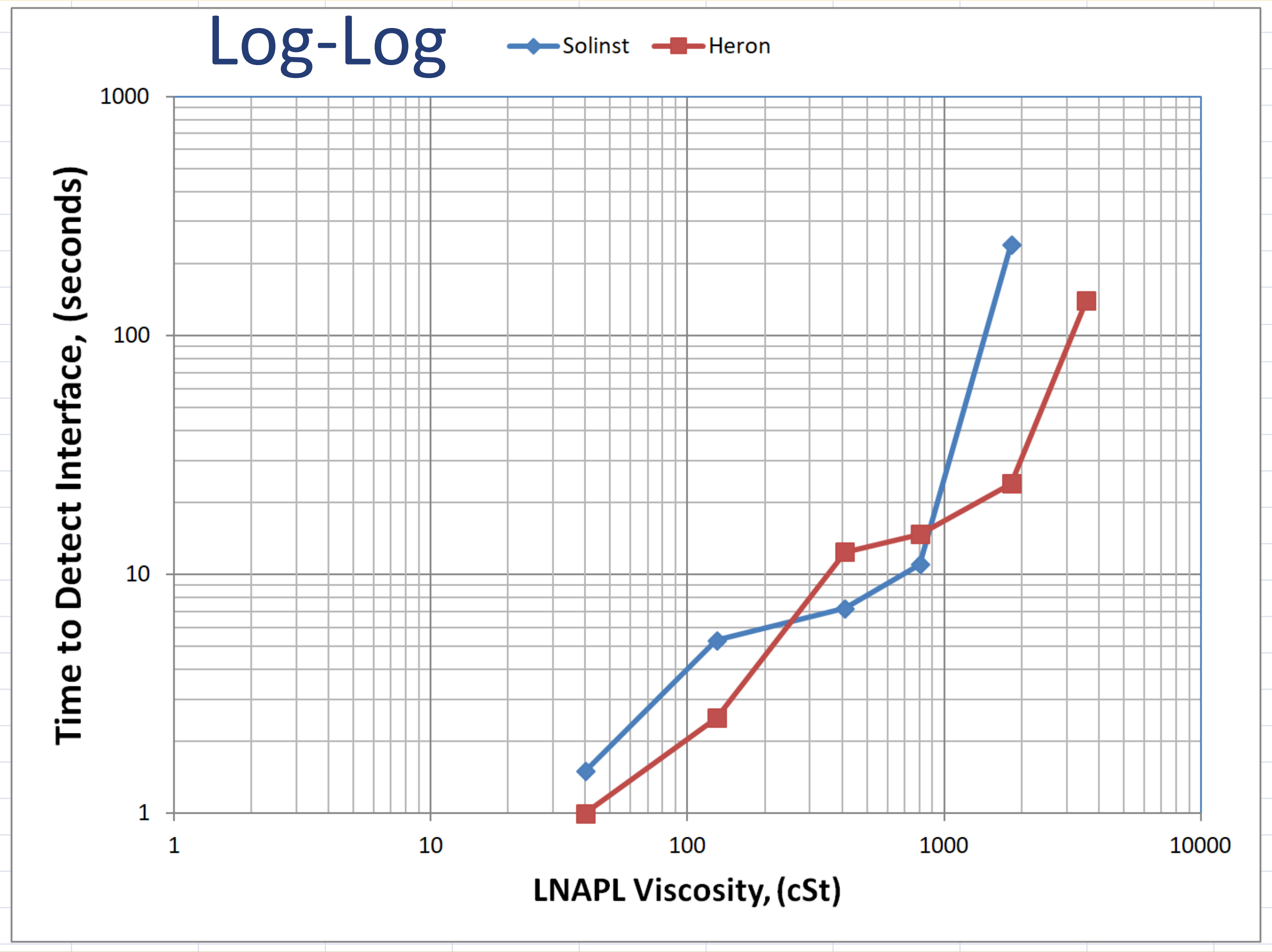
LNAPL-Water Interface Test Results



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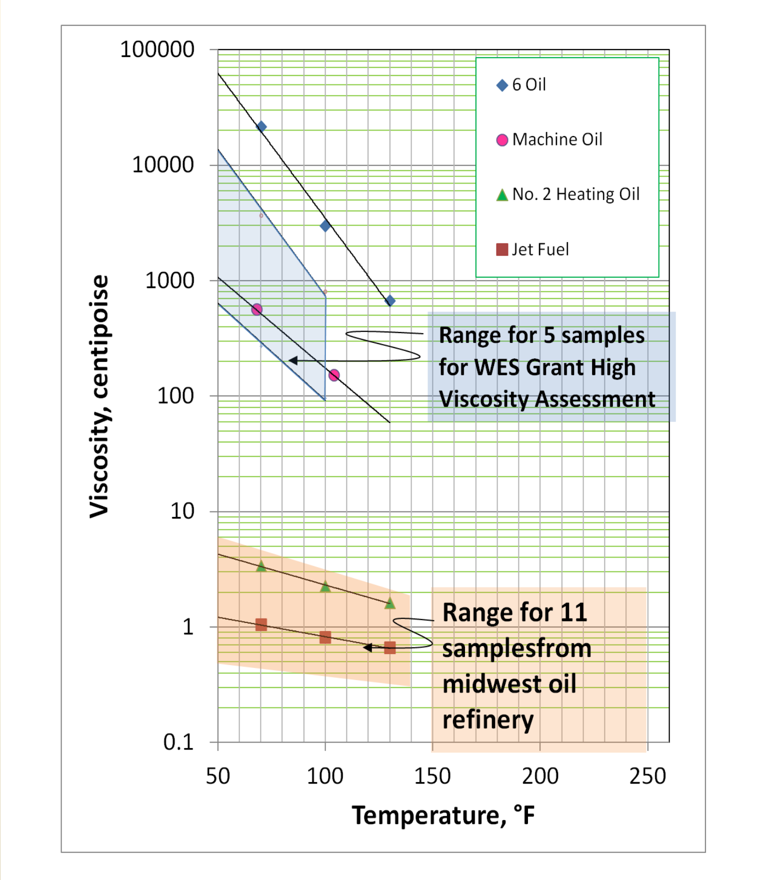
Conclusion

- LNAPL/water interface tests are difficult due to the tendancy of LNAPL to be trapped in the tip of the probe.
- Significant agitation required to move LNAPL from the probe tip
- Amount of agitation used in this study much more than could be accomplished in the field
- Agitation time picks up after 100 cSt and becomes unworkable above 1,000 cst

Recommendation & Justification



- Based on data from this study and the case study presented, SES recommends no field T_n tests at viscosity above 100 cSt (at 50°F)
  - Majority of light LNAPLs (jet fuel, gasoline, diesel) will have viscosities well below 100 cSt
  - Heavy LNAPLs (6 oil, lube oil) will have viscosities well above 100 cSt
  - Case study found oil/water interface probe unworkable at around 1000 cSt
  - LNAPL/Water tests showed increase in agitation time needed above 100 cSt, and significant increase above 1,000 cSt

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Calculating Transmissivity

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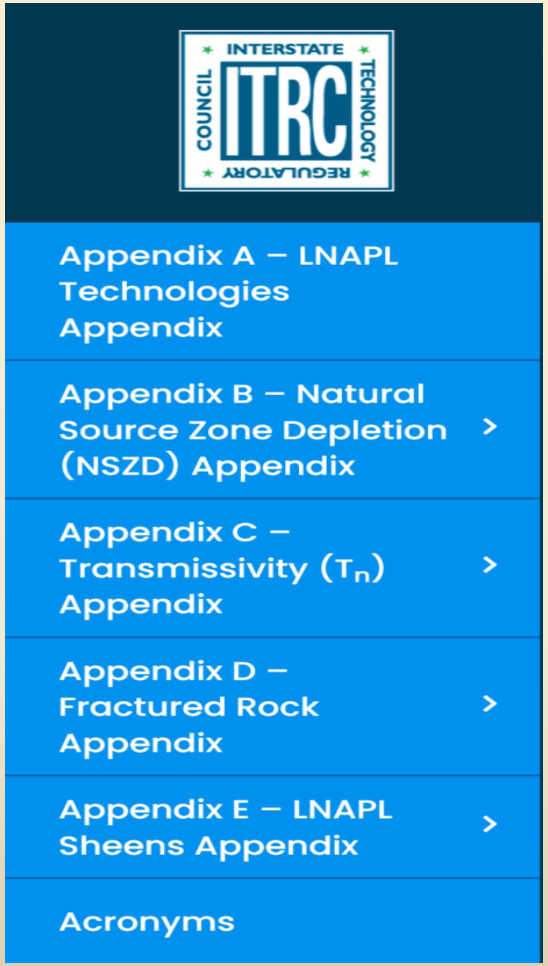
What To Do if T_n Tests Are Not Feasible



- "LNAPL Update 3" (ITRC) provides a path
- https://lnapl-3.itrcweb.org/
- Appendix C – Transmissivity Appendix in particular
- https://lnapl-3.itrcweb.org/appendix-c-transmissivity-tn-appendix/#1

$$T_n = K_w \cdot k_{rn} \cdot \frac{\rho_n \mu_w}{\rho_w \mu_n} \cdot b_n$$

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Breaking Down the T_n Equation

K_w = Groundwater hydraulic conductivity, (feet/day)

k_{rn} = LNAPL relative permeability, (dimensionless)

μ_w= Groundwater density, (grams/milliliter)

ρ_w = Groundwater viscosity, (centipoise)

ρ_n = LNAPL density, (grams/milliliter)

μ_n = NAPL viscosity, (centipoise)

b_n = The thickness of LNAPL accumulation in a well (unconfined) or the mobile LNAPL interval (confined), (feet)

The groundwater density and viscosity are assumed to be 1 gram/liter and 1 centipoise, respectively, at 20 degrees Celsius.

$$T_n = K_w \cdot k_{rn} \cdot \frac{\rho_n \mu_w}{\rho_w \mu_n} \cdot b_n$$

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All You Need Is…

So Great! All you need is…..

- LNAPL Viscosity (measure in the field or laboratory)
- LNAPL Density (measured or assumed)
- Hydraulic conductivity (perform a field K_w test…do not guess)
- Relative Oil Permeability, and (ugh….ummmm….guess!)
- LNAPL Thickness (measure, but it changes all the time)

$$T_n = K_w \cdot k_{rn} \cdot \frac{\rho_n \mu_w}{\rho_w \mu_n} \cdot b_n$$

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Here's What ITRC Says About k_{rn}

- The simplest direct calculation of LNAPL transmissivity is based on an assumption that LNAPL fills all soil pores ***i.e.* k_{rn} *= 1.0 (Conservative)***

- LNAPL transmissivity can also be calculated with an additional correction for the fact that LNAPL does not fill all soil pores at an environmental site (relative permeability is less than one). Multiphase flow calculations include a relative permeability term, which ranges from 0 to 1, to account for this decrease in soil permeability. ***(Not particularly helpful!)***

- While a relative permeability term is useful to decrease the degree of conservativism in the Darcy's Law calculation, there are no simple methods to estimate relative permeability without conducting field LNAPL transmissivity tests or collecting soil samples for lab analysis of petrophysical properties. ***(Expensive and problematic!)***

- In light of this limitation, an analysis of LNAPL transmissivity data that were collected by API from member companies and compiled in a database. Ninety percent of the relative permeability values were below 0.28; 80 percent were below 0.09. ***(hmmmm….seems like 0.3 could be used)***

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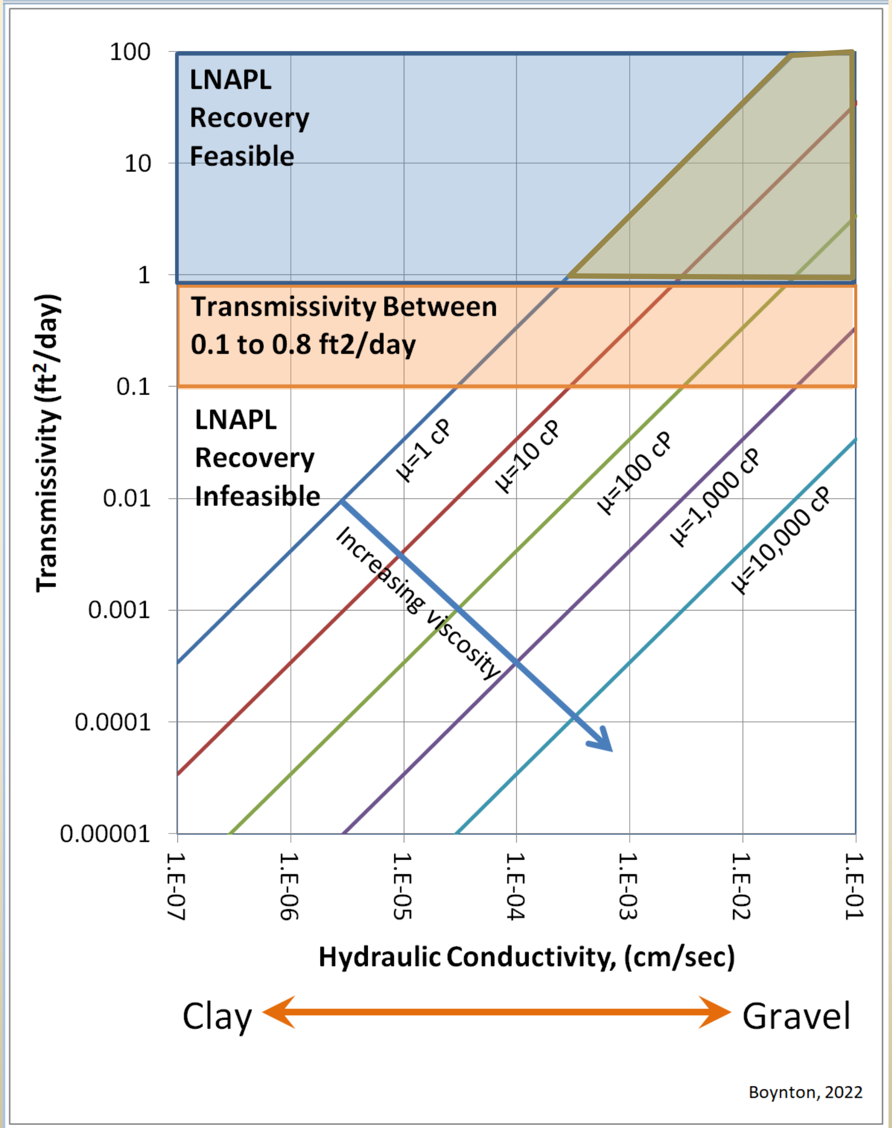
So Let's Do a Hypothetical Calculation!

$$T_n = K_w \cdot k_{rn} \cdot \frac{\rho_n \mu_w}{\rho_w \mu_n} \cdot b_n$$

K_w = Variable
k_{rn} = 0.3
μ_w = 1.0 cP
ρ_w = 1.0 g/cc
ρ_n = 0.8 g/cc
μ_n = Variable
b_n = 5.0



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Thoughts on Hydraulic Conductivity

- Low-flow data can be used to calculate K_w .
- Install a well in a clean down-gradient area near the LNAPL release for K_w tests, dissolved phase data, and LNAPL sentinel well.
- Calculations should be done by experienced professional.
- Do not estimate K_w from literature.
- Somebody should do a course on calculating hydraulic conductivity from low-flow data! There is a lot of data out there that can be used!

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Thank you for attending

Question and Answer Time!

Email: sboynton@subenviro.com
Phone: 781-608-6119
Instagram: @subsurface_env