Bigger Results With Smaller Particles

By: Katherine Drehr

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Objective

- Improve completion fluids
- Allow completions fluids to penetrate deeper into the formation
- Increase recovery by 20-50% as observed in the laboratory
- More cost effective chemical additives compared to those currently used

Problem: Is there a less harmful but efficient EOR chemical?

Surfactants

Pros	Cons
*Reduce interfacial tension	*Does not break down Asphaltenes
*Water imbibes rock expelling oil	*Can Cause Emulsion

Nano Chemicals

Pros	Cons
*Reduce interfacial tension	*Emulsion that can't easily be broken
*Small particles	*Don't change wettability without added surfactants

Importance

- Low recovery factors of ULR wells
- Refracturing expensive and temporary solution
- Optimization of chemical additives is not a widely applied technique

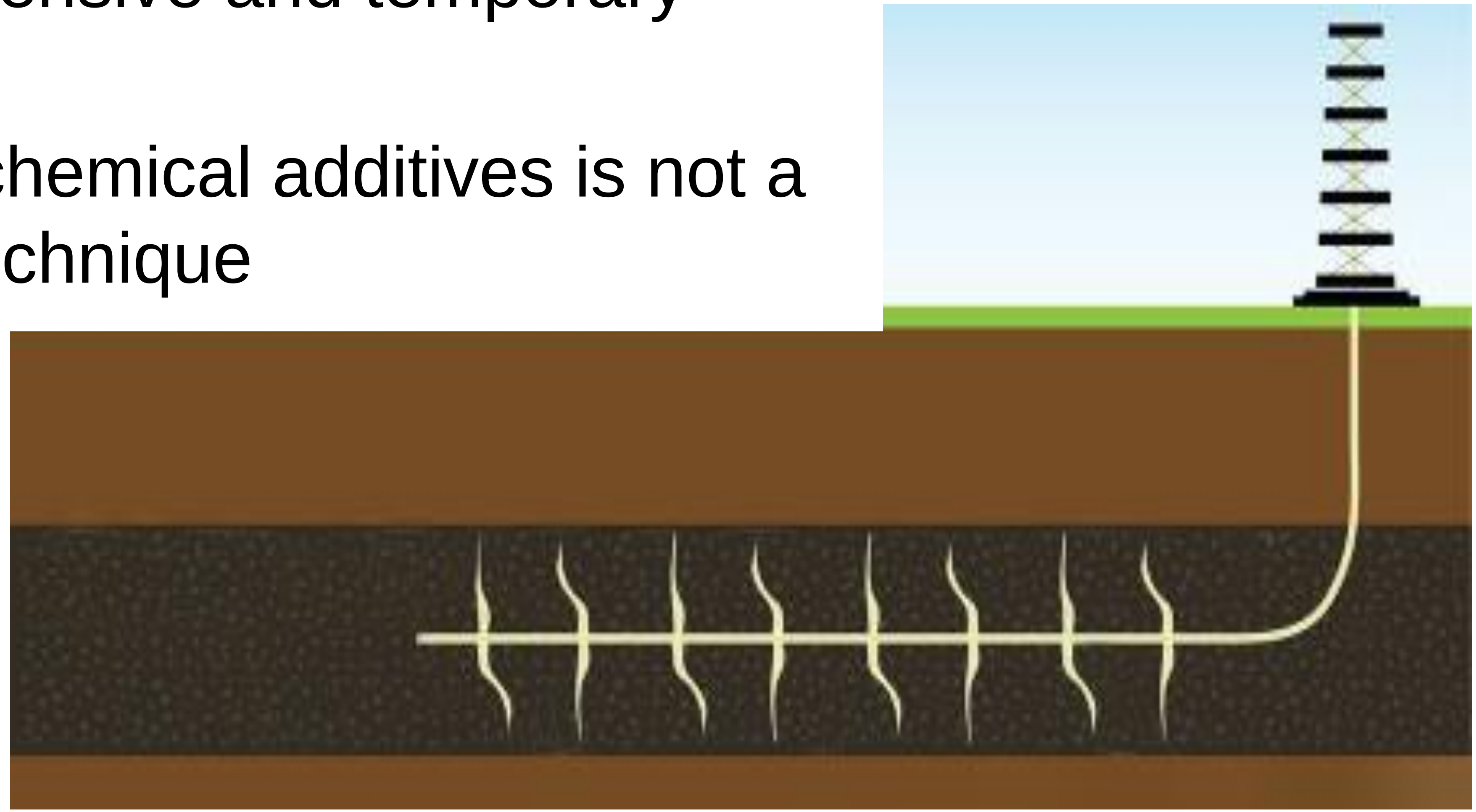


Fig: Drainage profile of horizontal wells.
Ref: J1S Energy-Environmental Responsibility

Possible Solution : Femto (10^{-15}) Chemical

- Tetrahedral Silicate Monomer
- Uses natural properties: Sodium, Silicon, and Oxygen
- Inorganic
- Increased electron potential
  - Alkaline
  - Saturated with excess OH^{-} groups
  - Disrupts weak hydrogen bonding

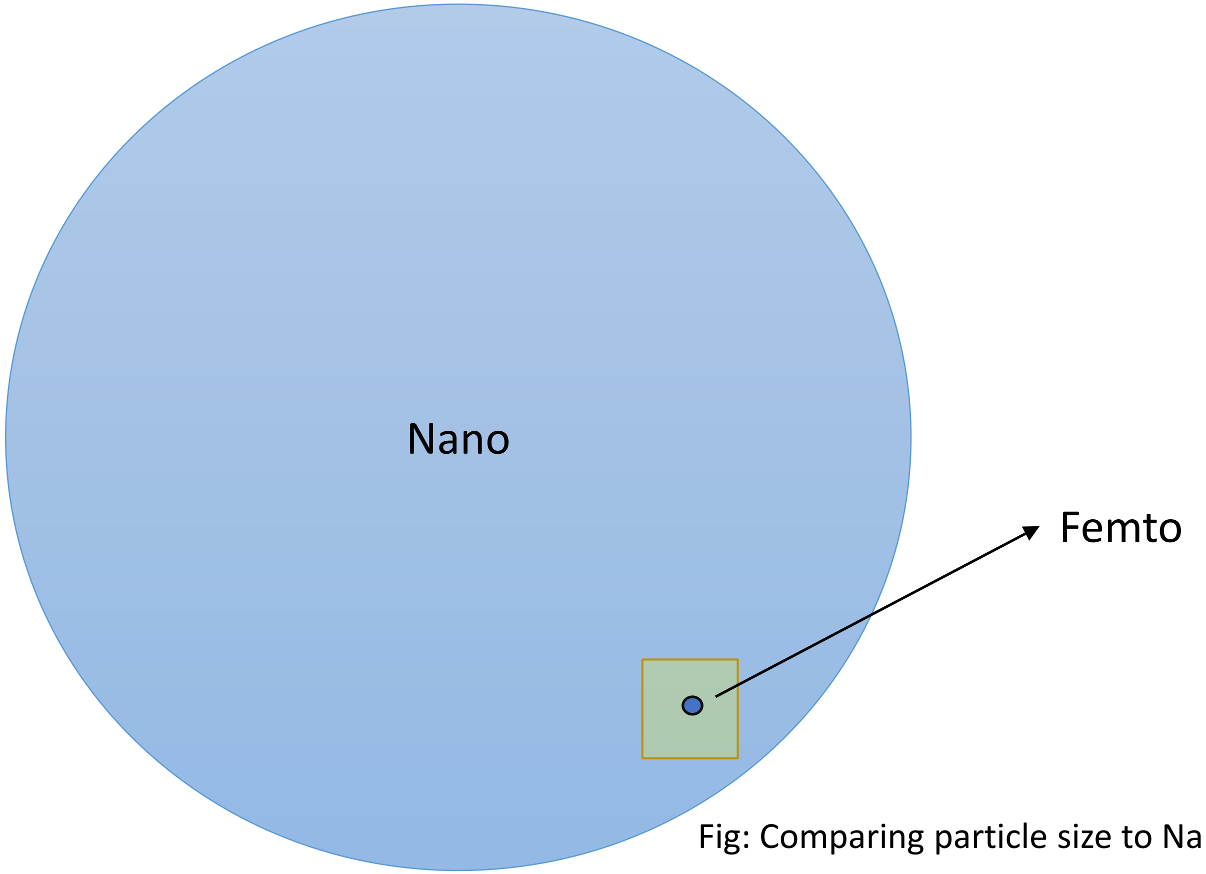
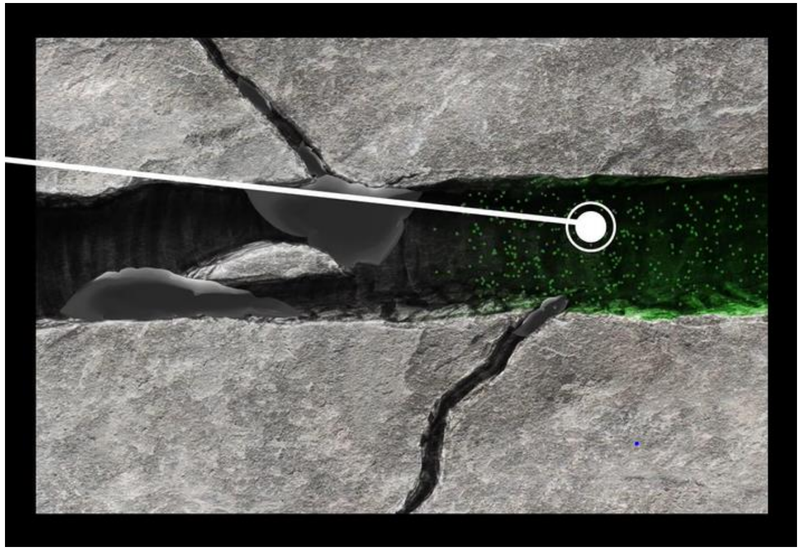
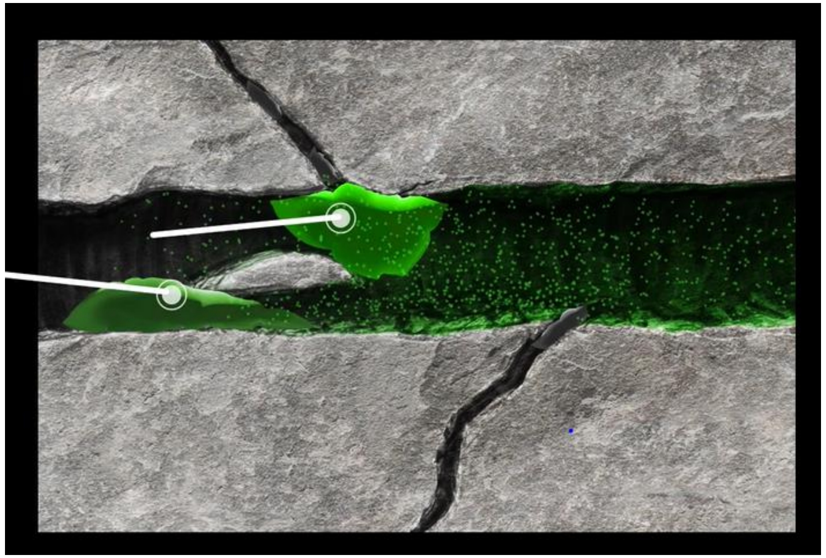


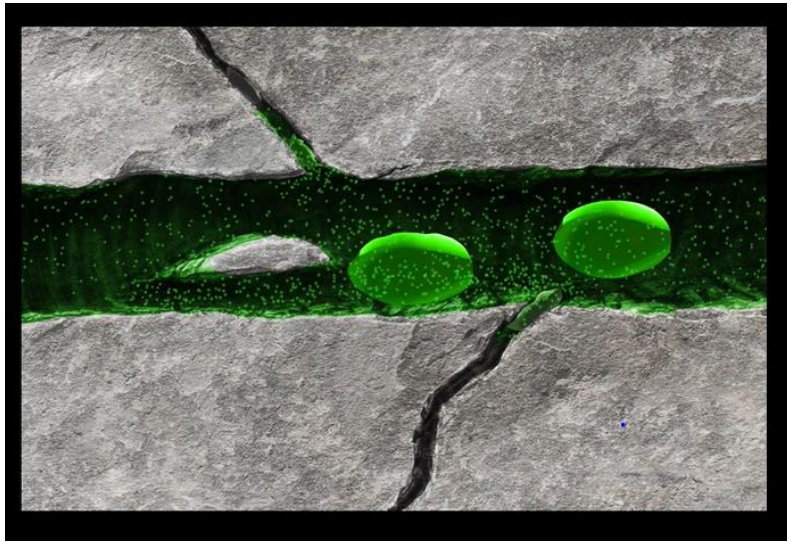
Fig: Comparing particle size to Nano.



- Strong electron exchange as movement due to OH^- groups



- Alters wettability and interfacial tension
- Disrupts weak hydrogen bonding



- Leaves no residue for damage
- Has positive side effects

Added Benefits

- Disperses Paraffin and Asphaltenes
- High PH deters bacterial growth
- H_2S Reduction
- Corrosion inhibition
- Reduce downtime and maintenance cost

Characteristics of Effective Chemical Additives for Completion Fluids

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Wettability

- Main factor to improve IP and EUR
- All shales tested are oil-wet [Barnett, Bakken, Eagle Ford, Wolfcamp]

Main Factors that Effect Wettability

- Interfacial Tension
- Contact Angle

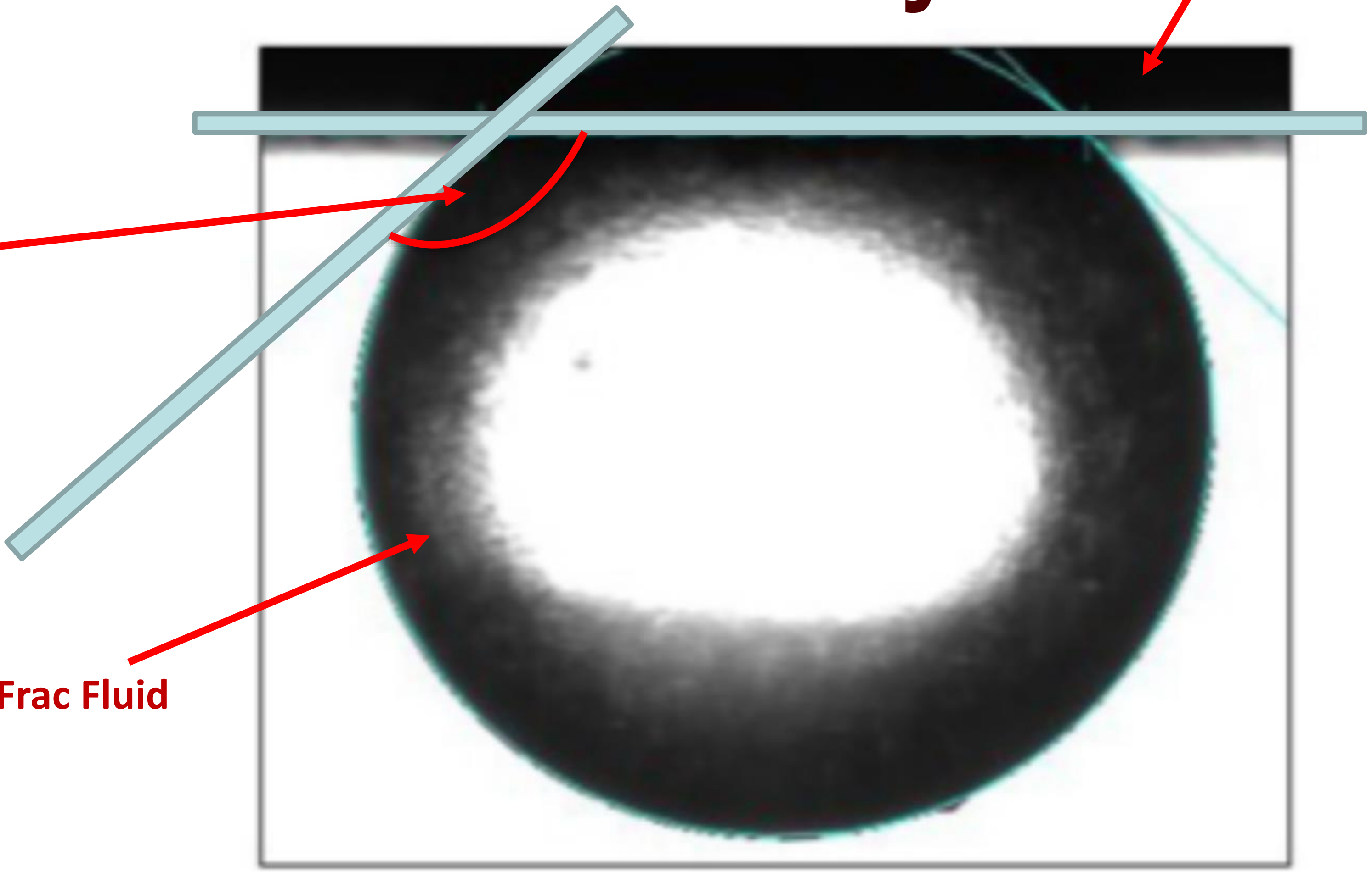
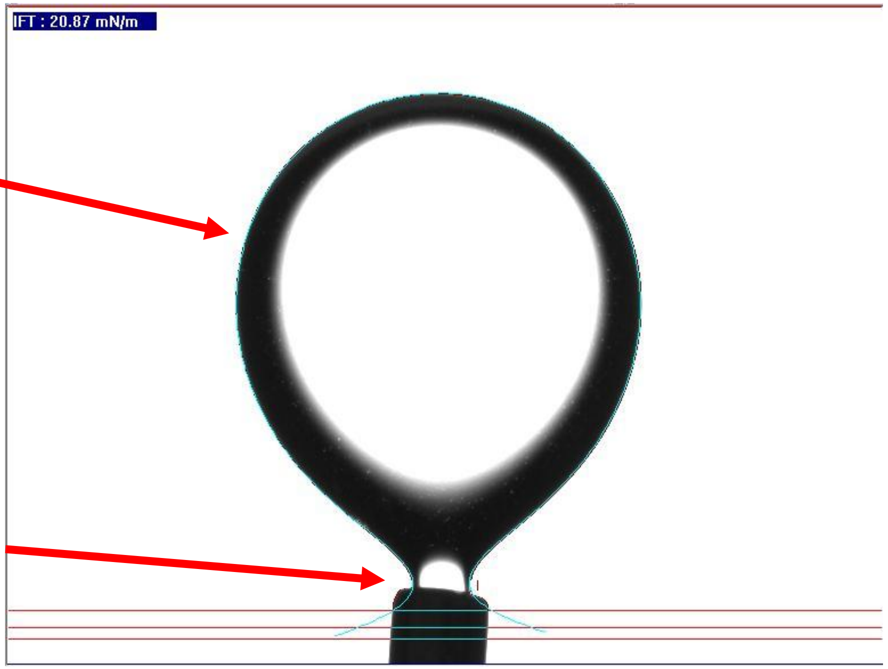
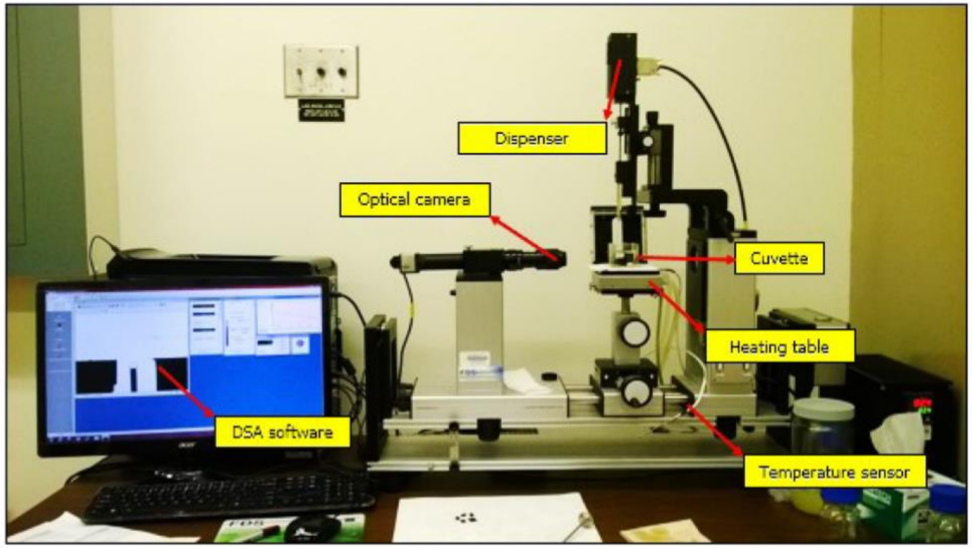


Fig:The contact angle is the angle formed by a line tangent to the droplet meeting the surface.

Testing

- Pendant dropping
- Captive bubble method



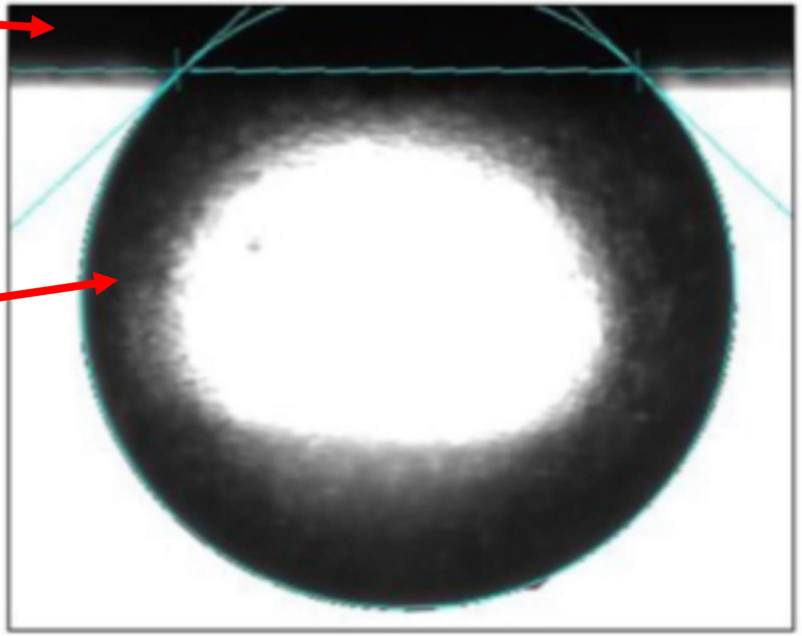


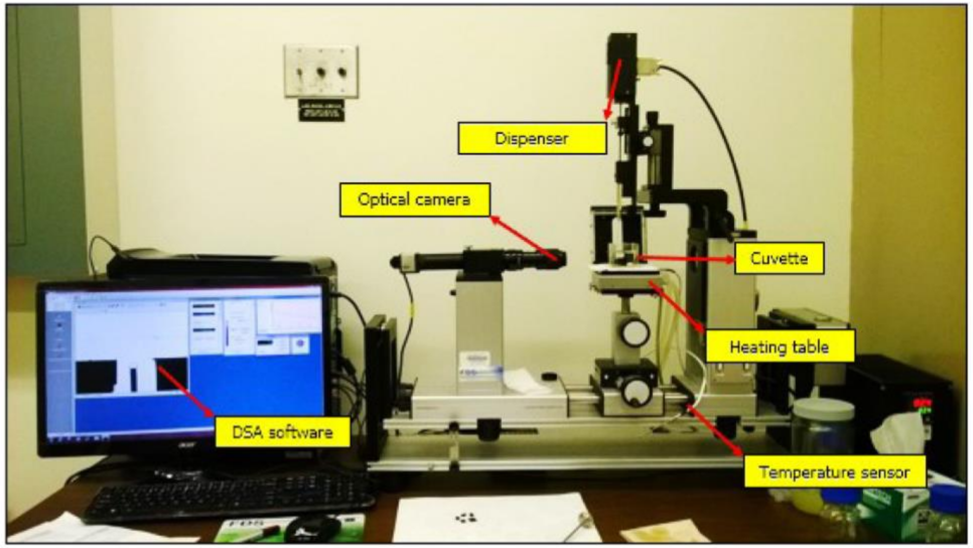
Top: Oil droplet when measuring IFT.
Right: OCA 15 Pro contact angle and IFT measurement system.

Ref:SPE Study of Rock/Fluid Interactions -Valluri, Alvarez. and Schechter

Testing

- Pendant dropping
- Captive bubble method





Top: Oil droplet showing contact angle.
Right: OCA 15 Pro contact angle and IFT measurement system.

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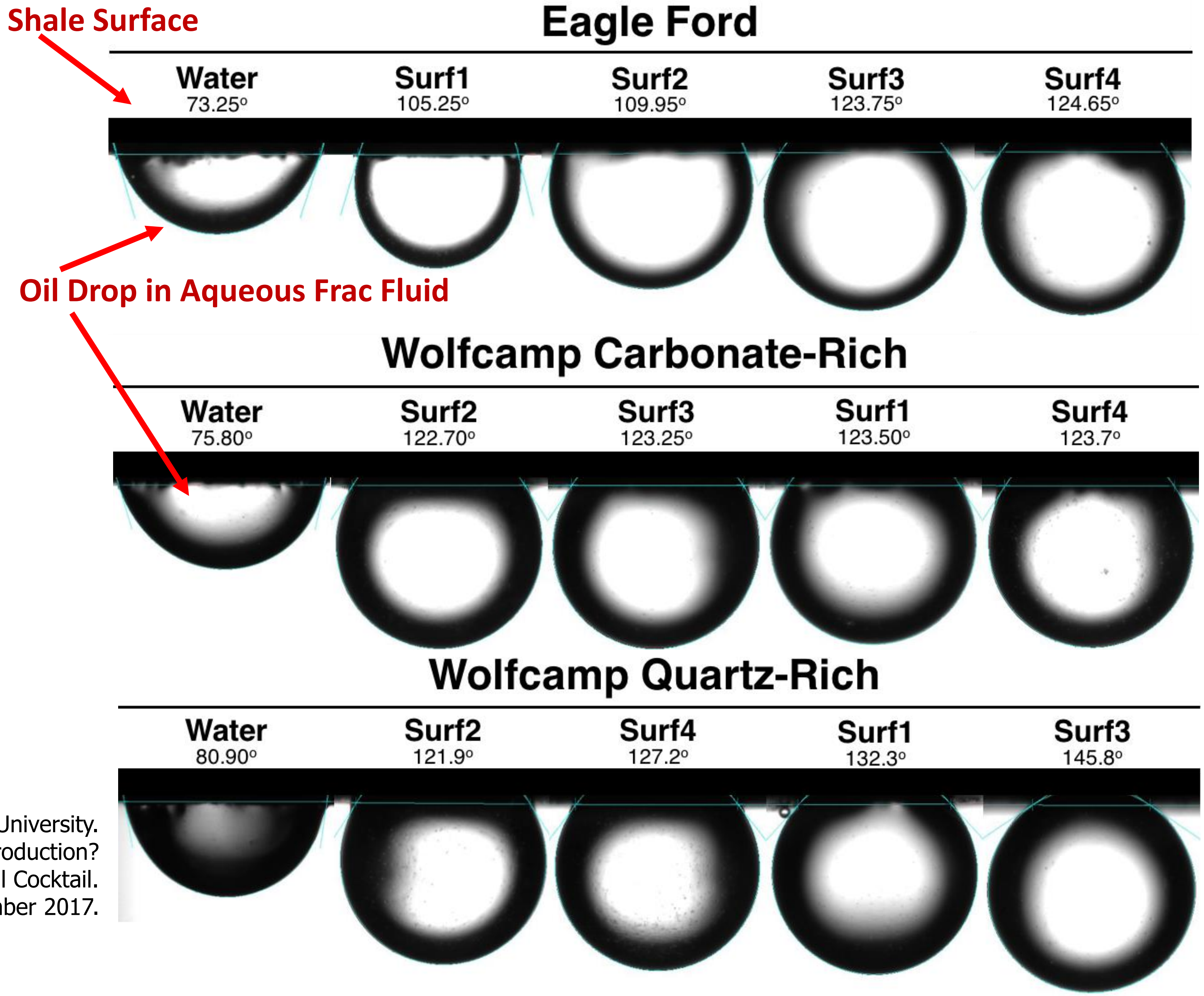
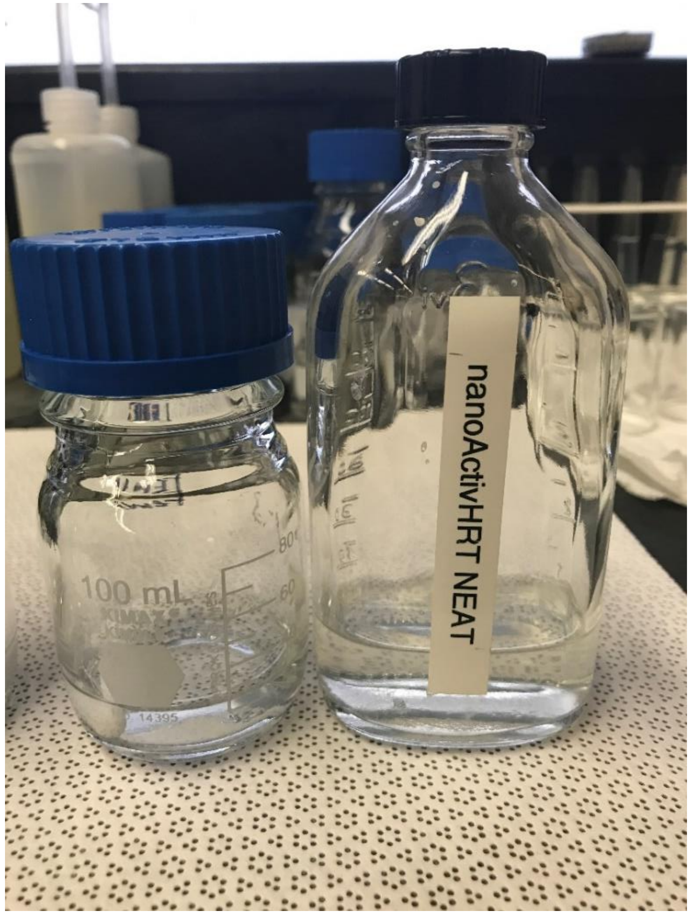
Surfactant Results

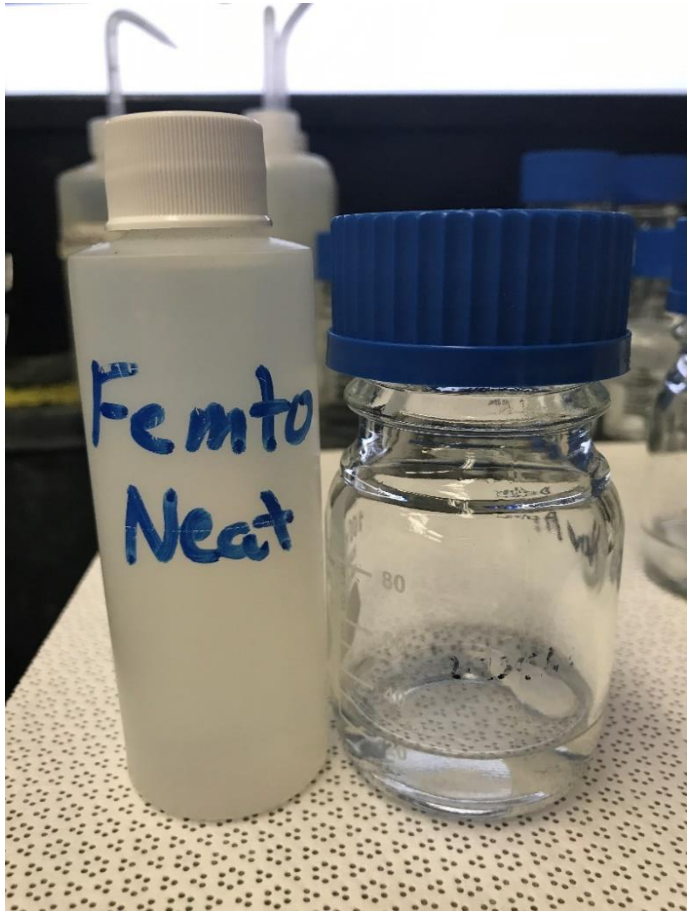


Ref: Texas A&M University. Stressed About Production? Consider a Chemical Cocktail. JPT December 2017.

Nano and Femto Chemicals

- 25% active
  - Diluted to 2 gpt





- 10% active
- Diluted to 2 gpt

Nano and Femto Results

- Eagle Ford Core

	IFT (dynes/cm)	Change	CA (degrees)	Change
Water (Base Case)	27.2		88.6	
Nano	20.2	7.0		
Femto	20.9	6.4		

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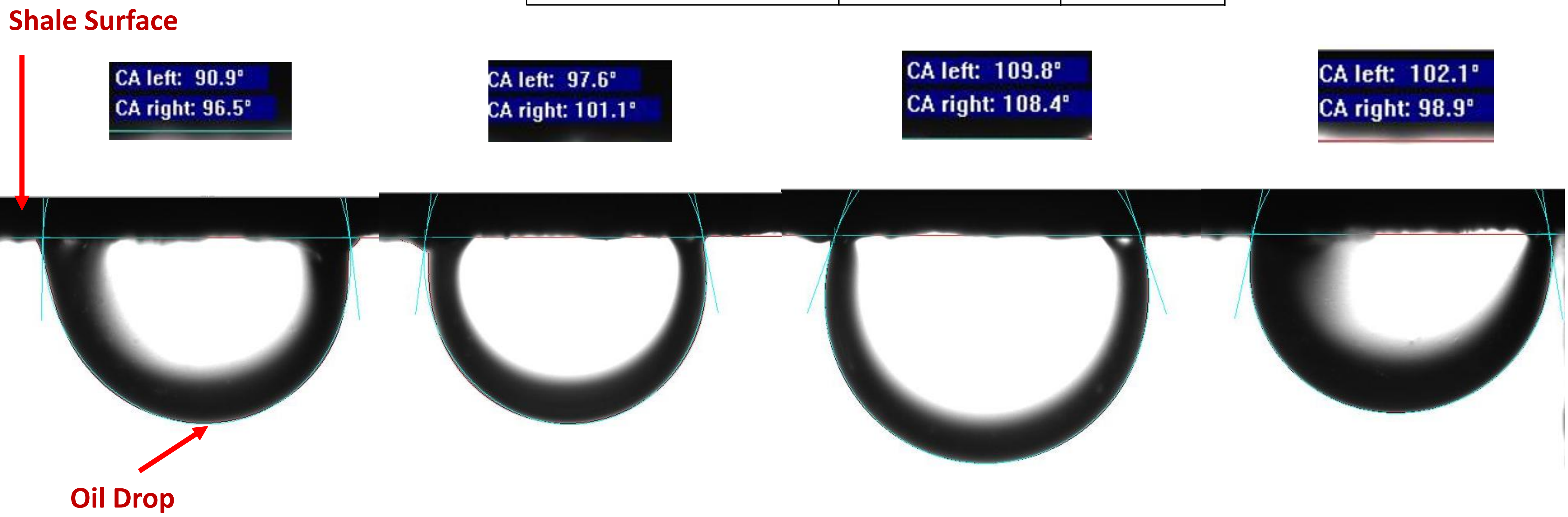
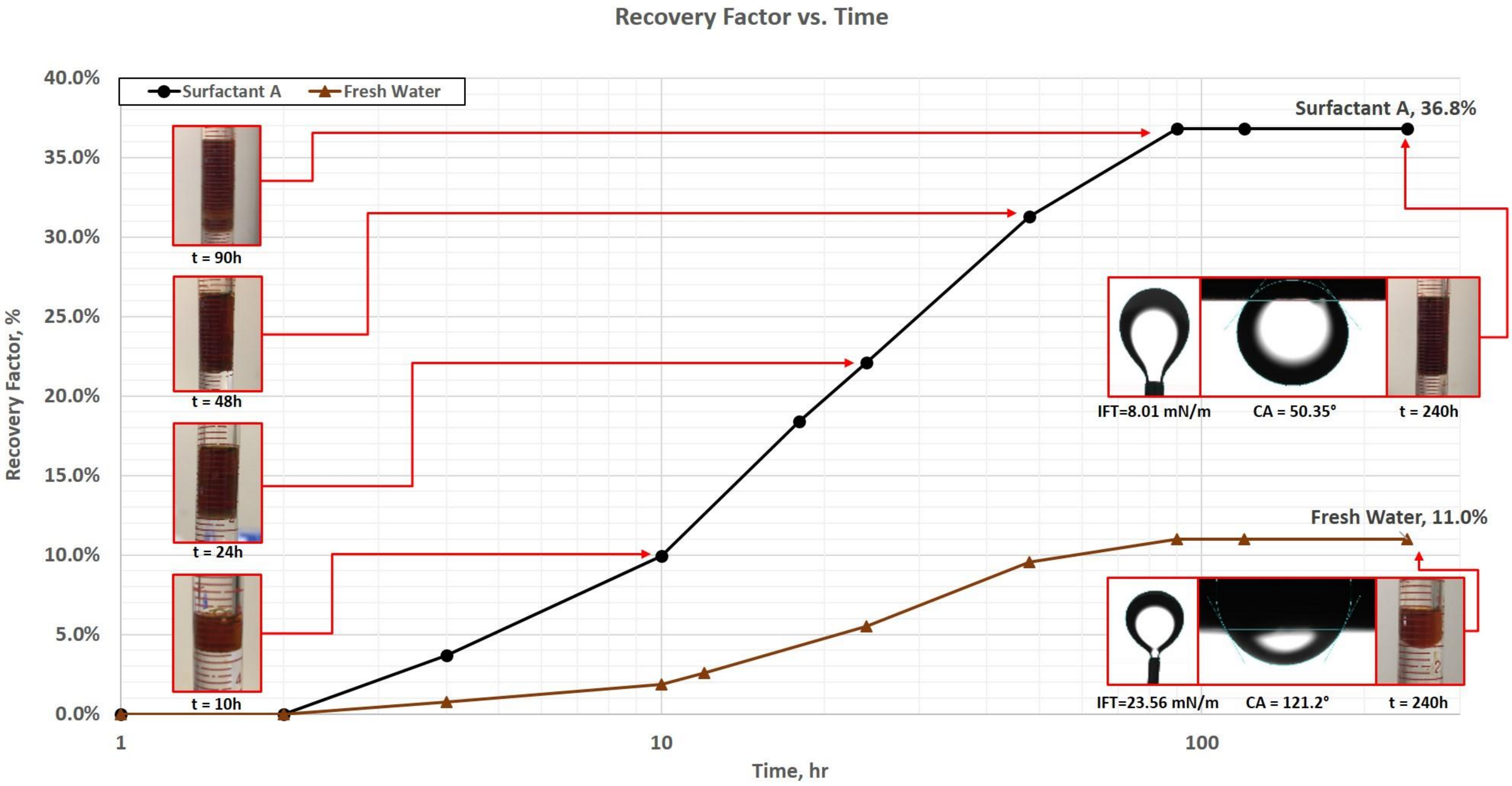
Nano Results

	IFT (dynes/cm)	Change	CA (degrees)	Change
Water (Base Case)	27.2		88.6	
Nano	20.2	7.0	98.7	10.2
Femto	20.9	6.4		

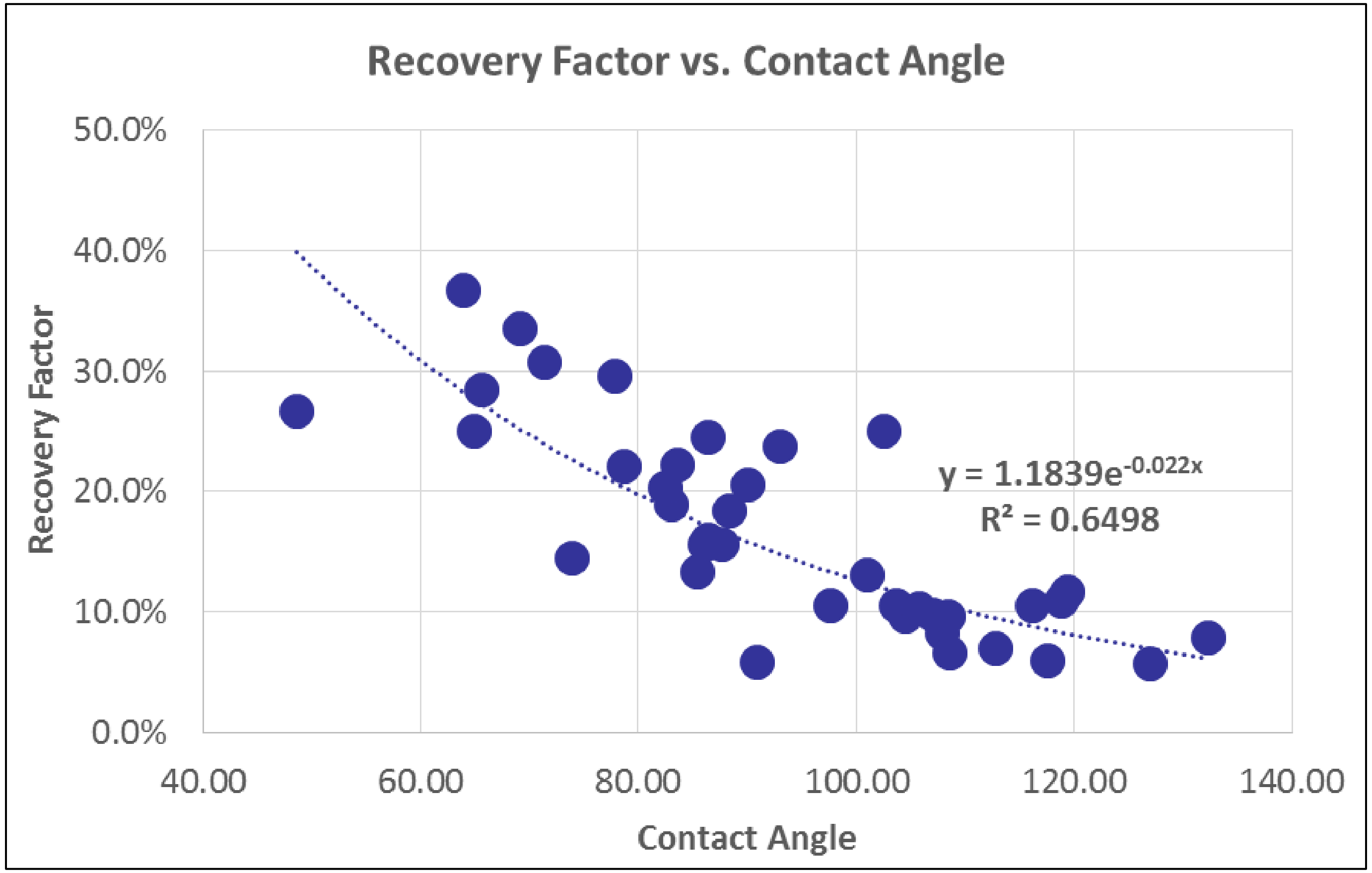


Femto Results



Ref: Research by H. Park and D. Schechter.
SPE HFTC Woodlands, 2018.

Impact of Contact Angle on Oil Recovery



Ref: Research by H. Park and D. Schechter. SPE HFTC Woodlands, 2018.

- **Correlation is based on 38 cases of spontaneous imbibition results. Contact Angle has a strong impact on oil recovery.**
- **Low contact angle (more water-wet surface) results in higher recovery factor.**

Core Lab

- Basic waterflooding testing
  - Basic rock properties of cores
  - Cores saturated with chemical
  - Centrifuged to find S_{wirr}
  - Saturated with oil to find K_o
  - Waterflooded at constant rates

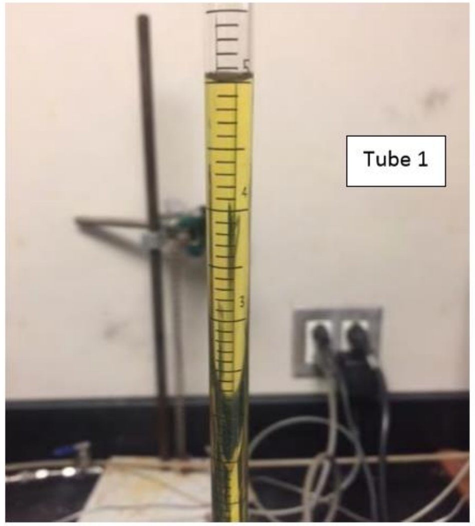
		Nano	Femto
ϕ	(%)	20.1	20.4
Kair	(md)	149	197
Swirr	(%)	19.1	13.4
Ko	(md)	6.94	148
Q	(cc/min)	0.5	4
ΔPi	(psi)	131	20
ΔPf	(psi)	325	27.8

Fig: Core Lab Advanced Core Analysis Study-Mako Chemicals

ADVANCED CORE ANALYSIS STUDY

Mako Chemicals & Services LLC
Berea Sandstone
Waterflood Chemical Tests

Right: Femto showed no emulsion.
Below: Nano with emulsion.
Core Lab Advanced Core Analysis Study- Mako Chemicals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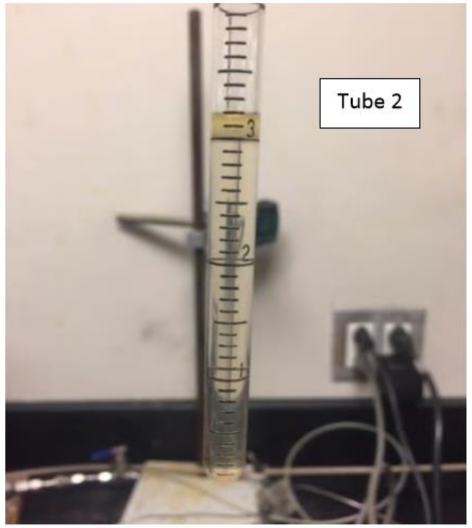
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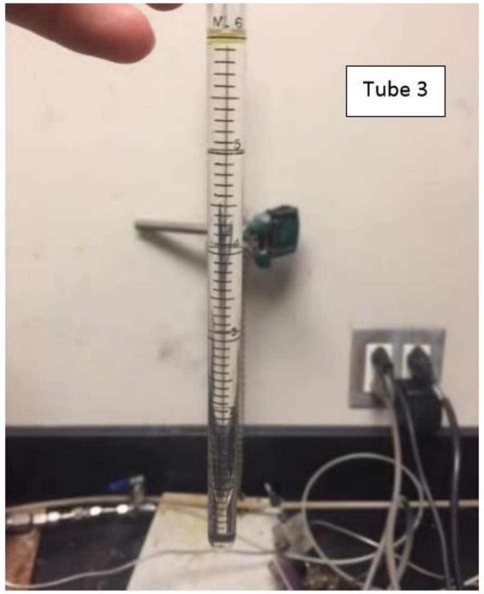
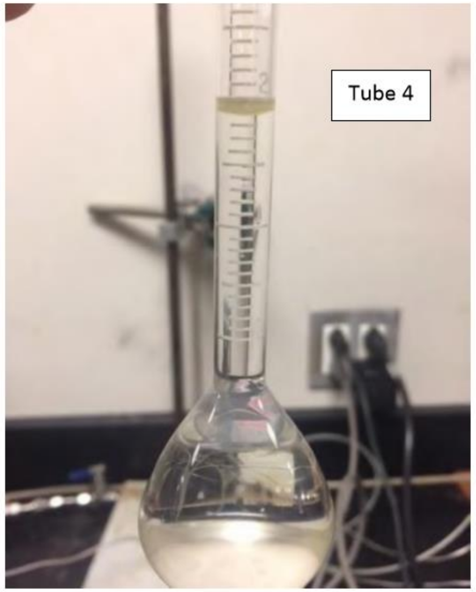

Tube 3


Tube 4


Tube 1

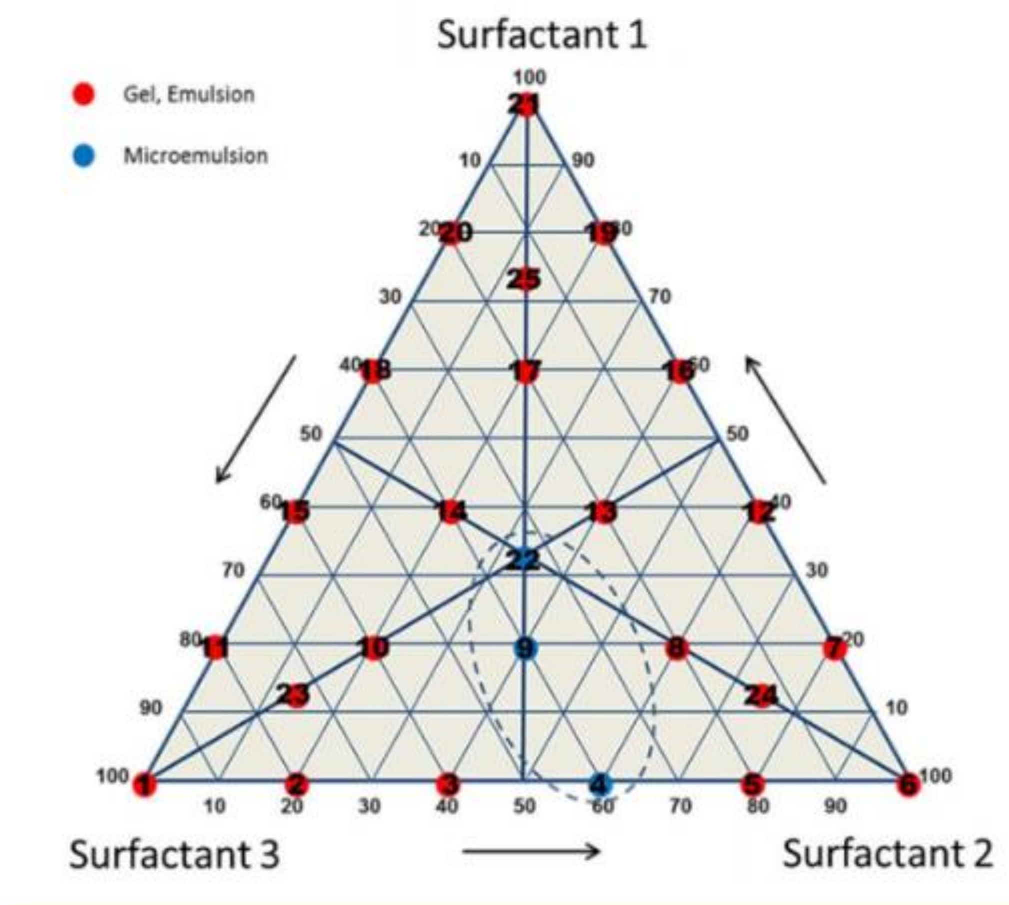

Tube 2

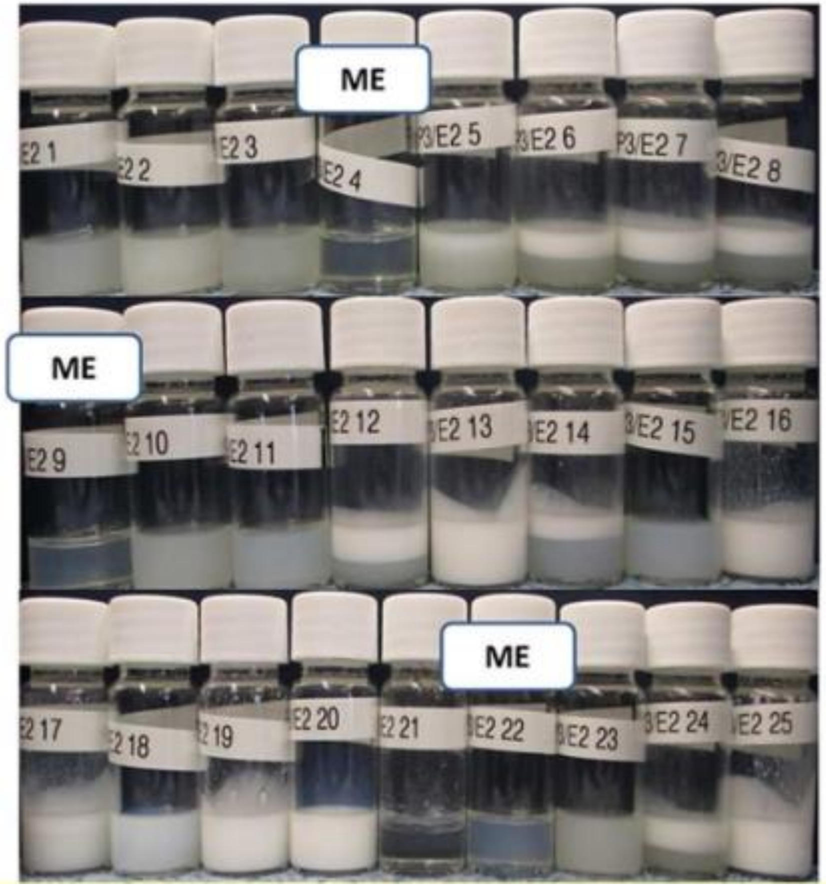

Tube 3


Tube 4


Tube 5

SPE Paper (SPE-173729-MS) - Microemulsions





SPE Paper (SPE-173729-MS) – Microemulsions

"Surfactants, regardless of their mode of state: aqueous or microemulsions, can interact with such phases and disturb the equilibrium thus affecting the dynamic of multiphase flow during oil and gas production."

Move Through Formation

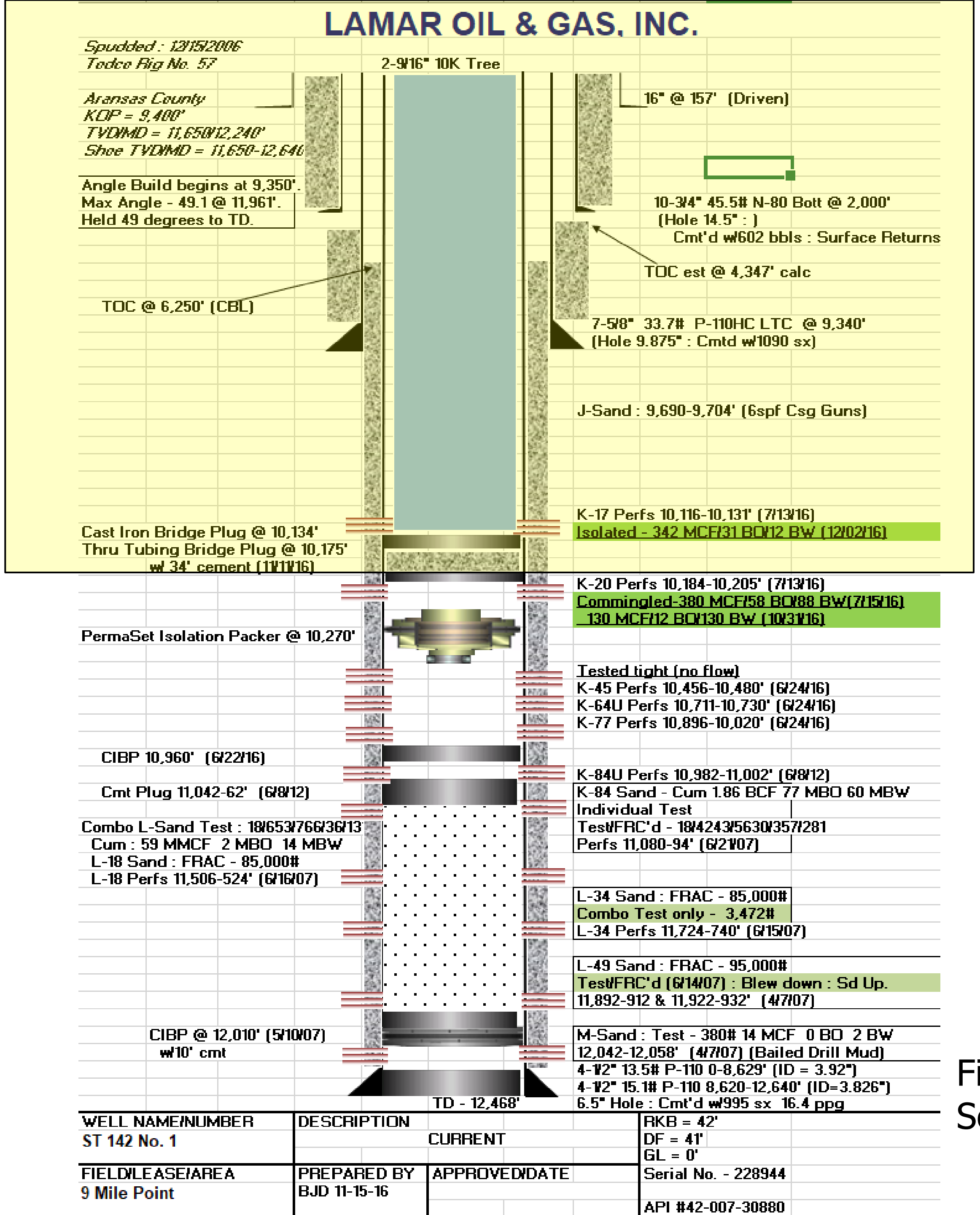
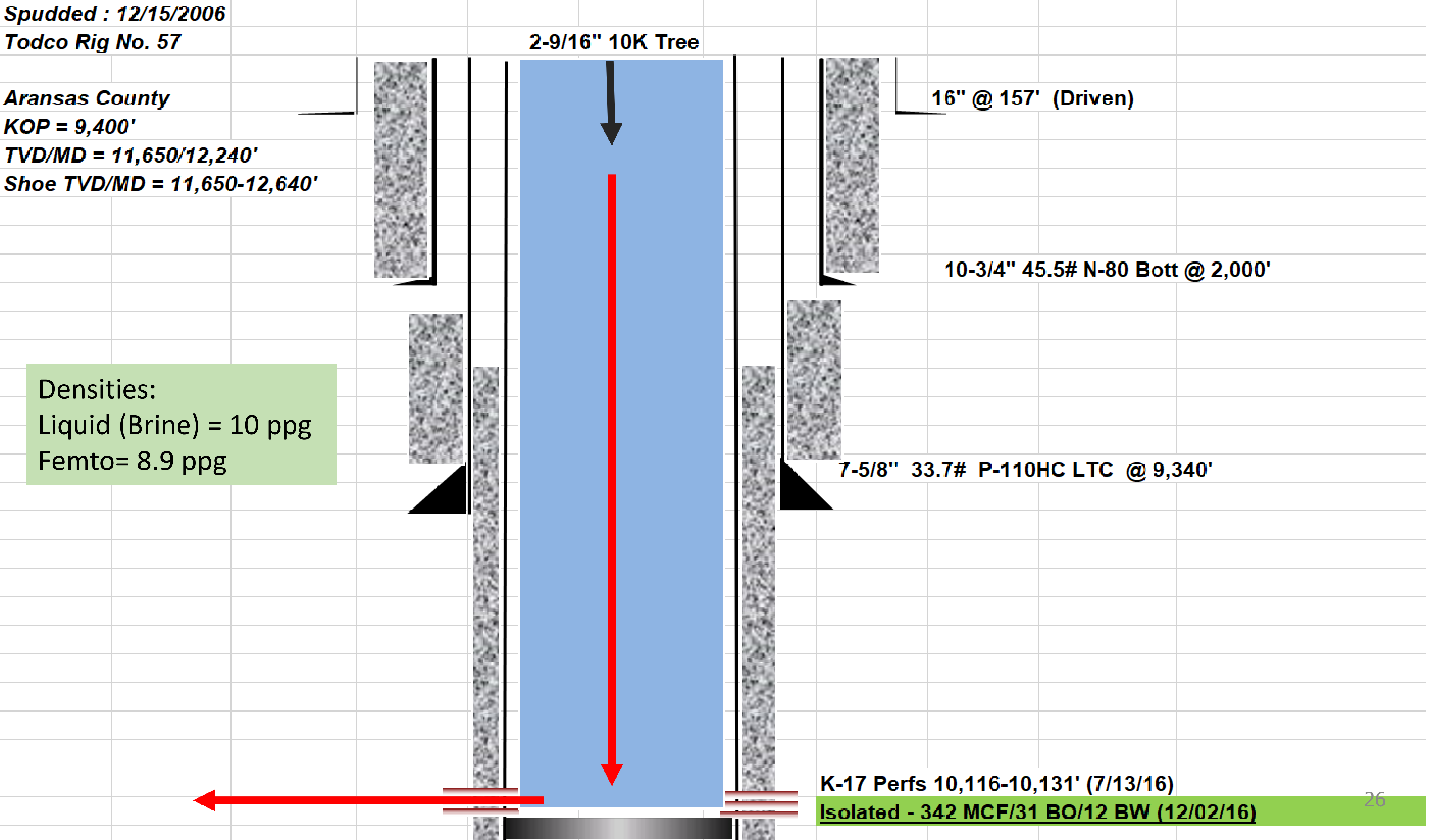
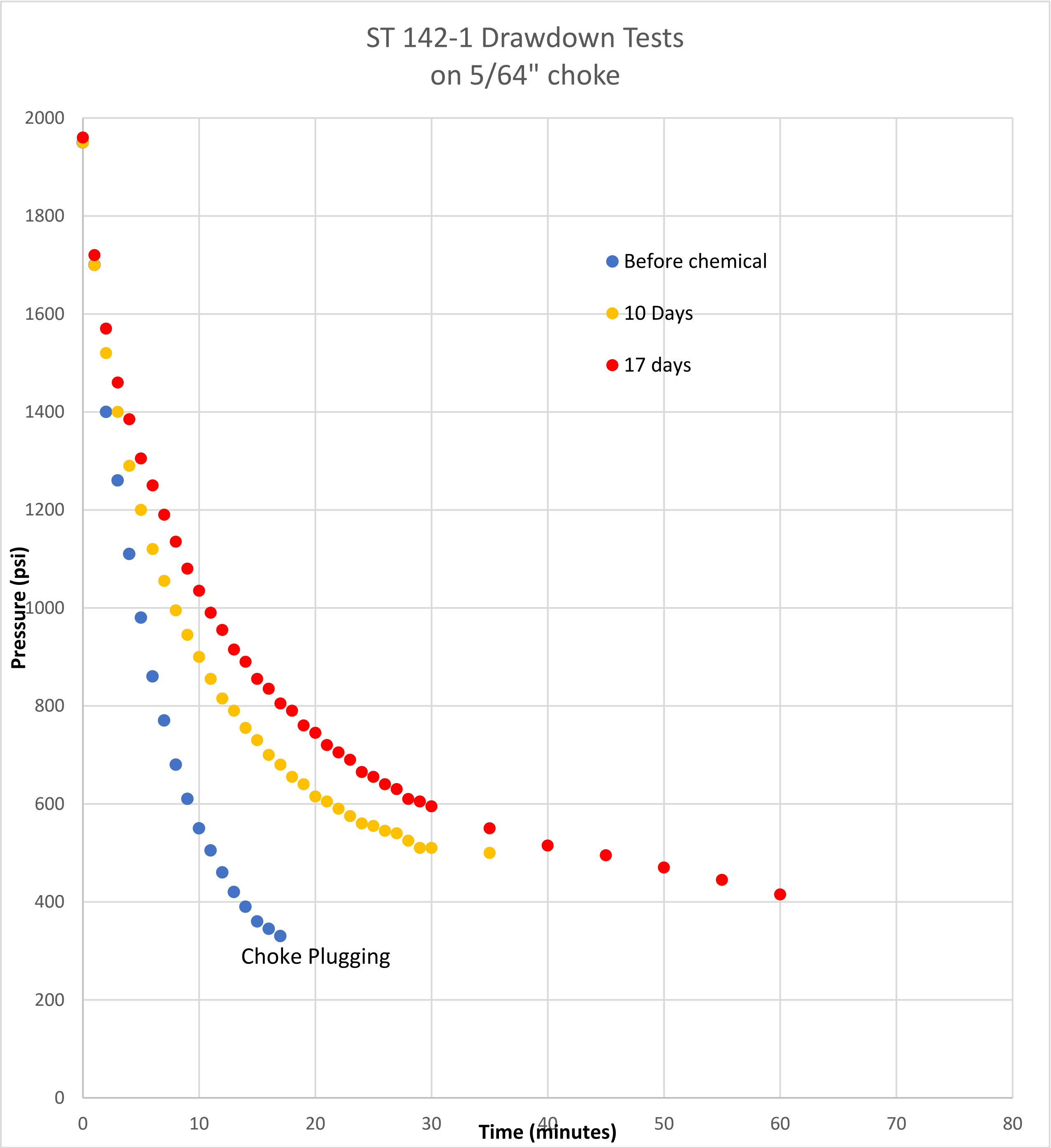


Fig: Wellbore Schematic of ST 142

LAMAR OIL & GAS, INC.





- Skin = 25
- Perm = 0.125 mD
- Porosity = 0.17

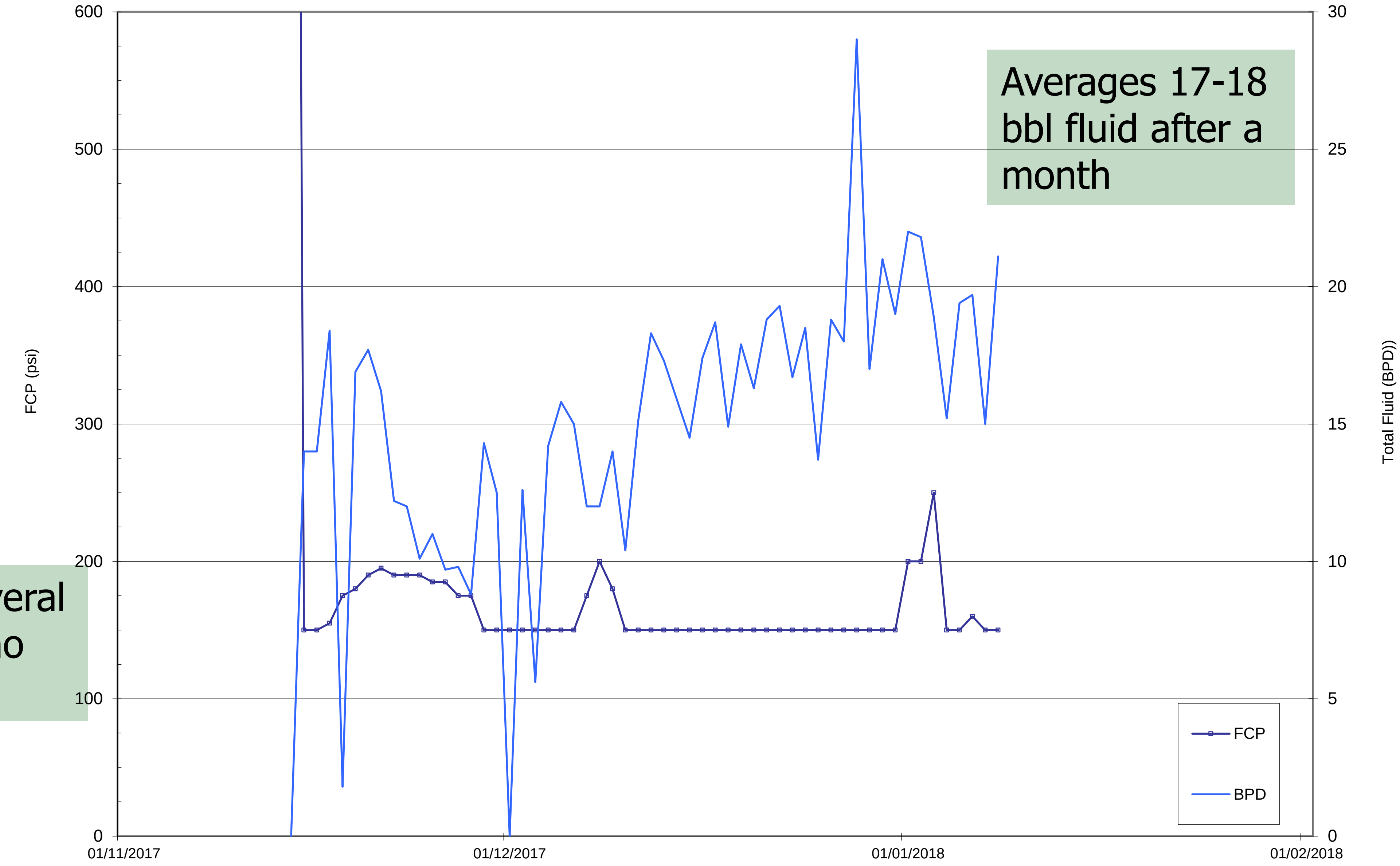
Fig: Pressure improved after chemical was added.

Production History

Lamar ST 142-154 #1

Nine Mile Point (Cons.) Field

Aransas County, Texas



Averages 17-18 bbl fluid after a month

Opened several times and no flow.

Cost

Average Frac Design

- Assuming 40 stages

	(CNF) Surfactant	Nano	Femto
Cost Per Gallon	$17.97	$12.86	$8.52
Gallons Needed Per 8,500 bbl Stage	450	700	879
Cost Per Stage	$8,088	$9,000	$7,490
Total Cost	$323,520	$360,000	$299,600

~~Possible~~ Solution : Femto (10^{-15}) Chemical

- Alters Wettability by reducing CA
- Readily disperse through formation
- Doesn’t create emulsions – less pressure drop
- Added Benefits reducing need for other chemicals
- Cost effective

Bigger Results With Smaller Particles

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SPE Papers

- SPE-173729-MS – Microemulsions as Flowback Aids for Enhanced Oil and Gas Recovery after Fracturing, Myth or Reality.
- SPE-187176-MS – The Impact of Surfactant Imbibition and Adsorption for Improving Oil Recovery in the Wolfcamp and Eagle Ford Reservoirs
- SPE-177057-MS Wettability Alteration and Spontaneous Imbibition in ULR by Surfactant Additives
- SPE-180274-MS Study of the Rock/Fluid Interactions of Sodium and Calcium Brines with Ultra-Tight Rock Surfaces and their Impact on Improving Oil Recovery by Spontaneous Imbibition

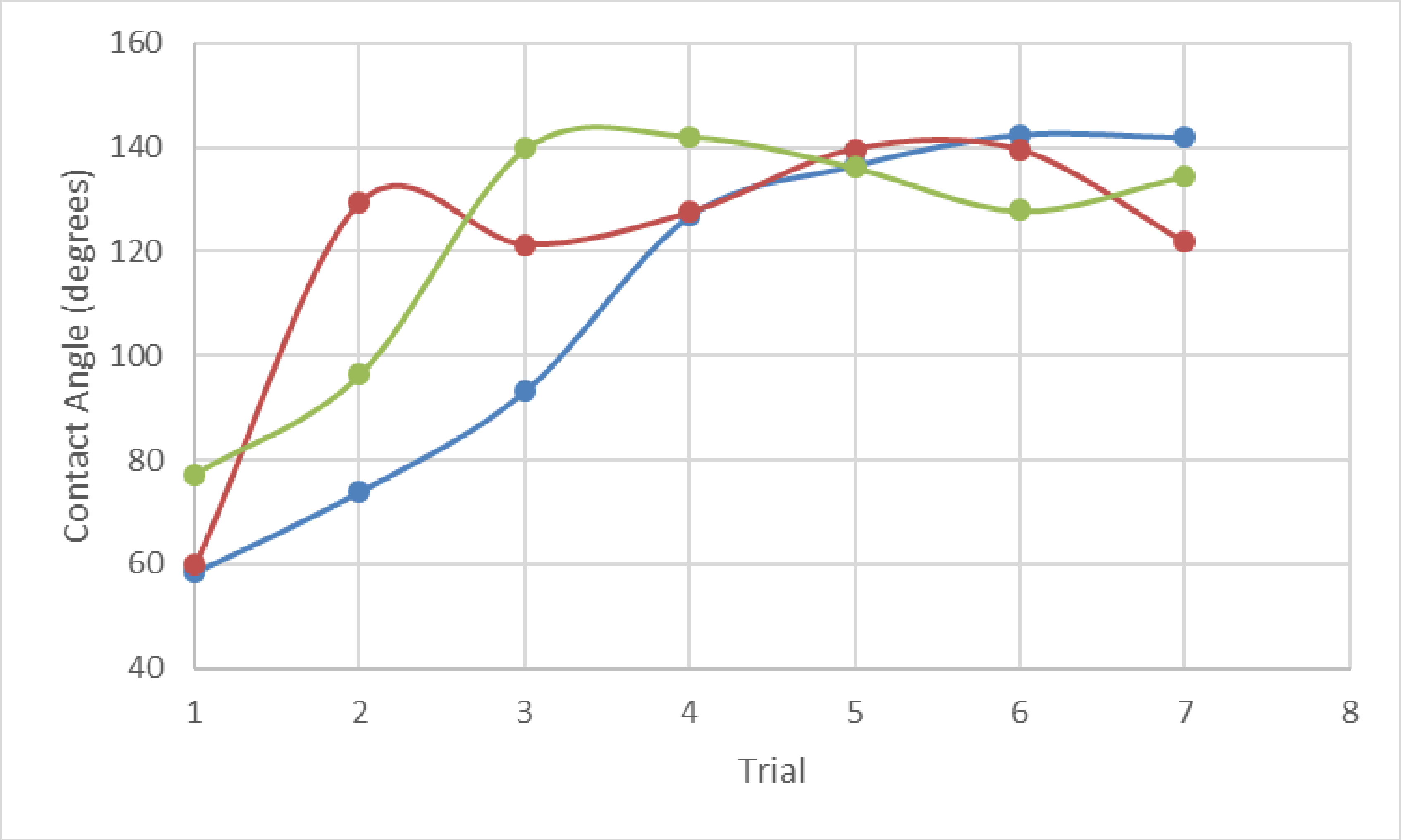
JPT Articles

- Stressed About Production? Consider a Chemical Cocktail. December 2017. Stephen Rassenfoss.
- Innovation Will Drive Shale Survival. Novermber 2017. Vikram Rao.

Back Up Slides

Field Results

Femto CA


160
140
120
100
80
60
40
Contact Angle (degrees)
1
2
3
4
5
6
7
8
Trial

Moody #1

Well Data Sheet and Treatment Design		
Operator	Abaco Operating, LLC	
Well Name	Moody Foundation #1	
Field	Mayes South (F19)	
County	Chambers	
Well Type	Oil	
Lift Method	Gas Lift	
Zone Depth	12922	feet
Thickness	12	feet
Porosity	0.24	
Sw	0.4	
Desired Length (3%)	7.85	feet
Treatment Volume	50.05	gallons
3%	39.72	bbls
5%	23.83	bbls
10%	11.92	bbls
25%	4.77	bbls
Area with 200 ppm	107.92	feet

Flow Characteristics Before Chemical

Producing 10.5 BOPD w/ 0.8 BWPD and 7 MCFPD on gas lift.

Average production 280 BO and 150 MCF per month last 12 months

Well hot oiled recently and swabbed in with TP increasing to 2000 psi after unloading following one swab run.

Treated 12/14/2017 w/ 500 gallons 10% chemical

Flow Characteristics After Chemical Treatment

Turned on after 9 days. Averaged 16 BOPD and 80 MCFPD for first week. Sold over 500 MCFG during first week.

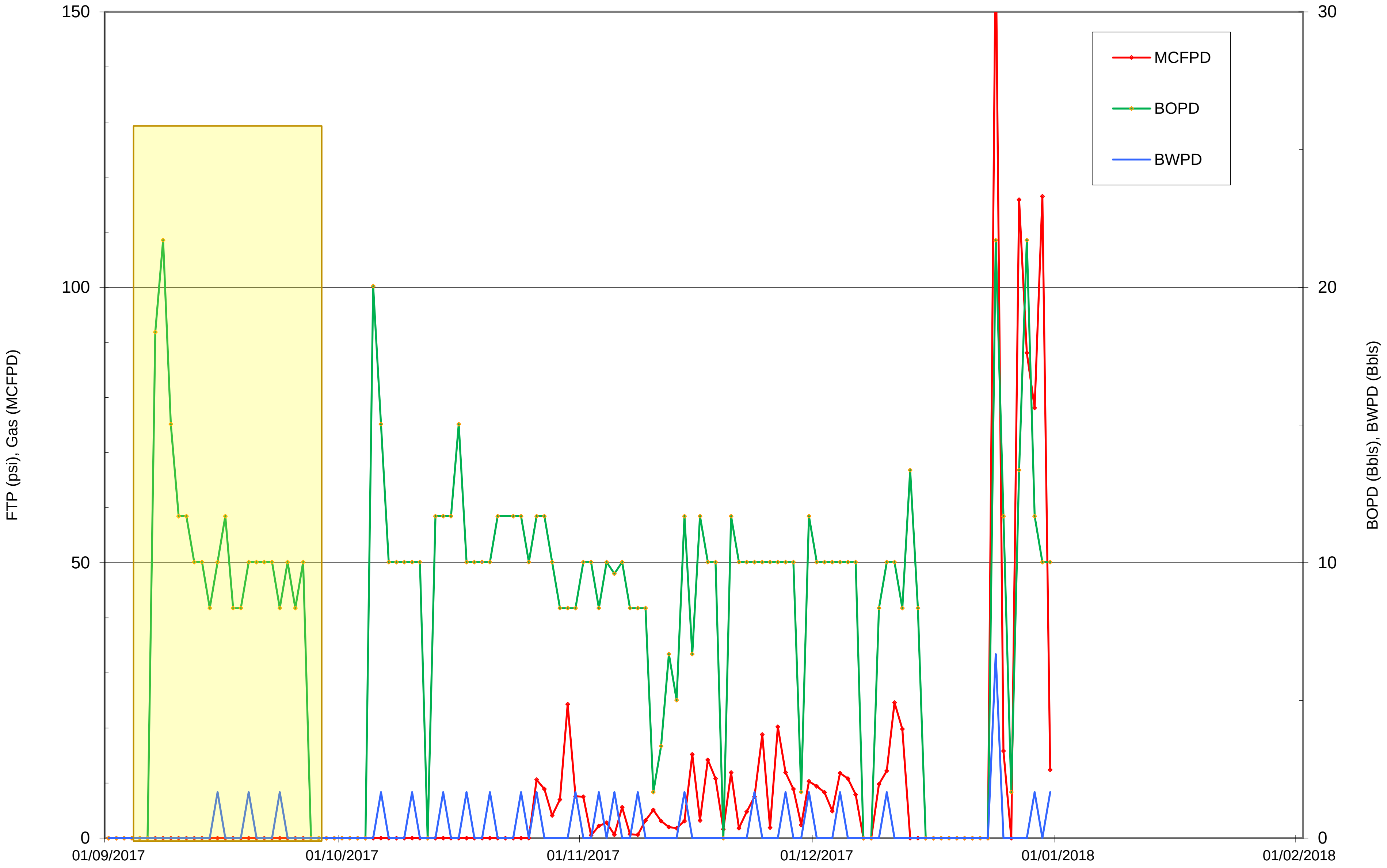
DCP gas sales line froze up and hole in tubing made it difficult to get accurate data after first week.

Production History

Abaco Oerating, LLC

Moody Foundation #1

South Mayes Field



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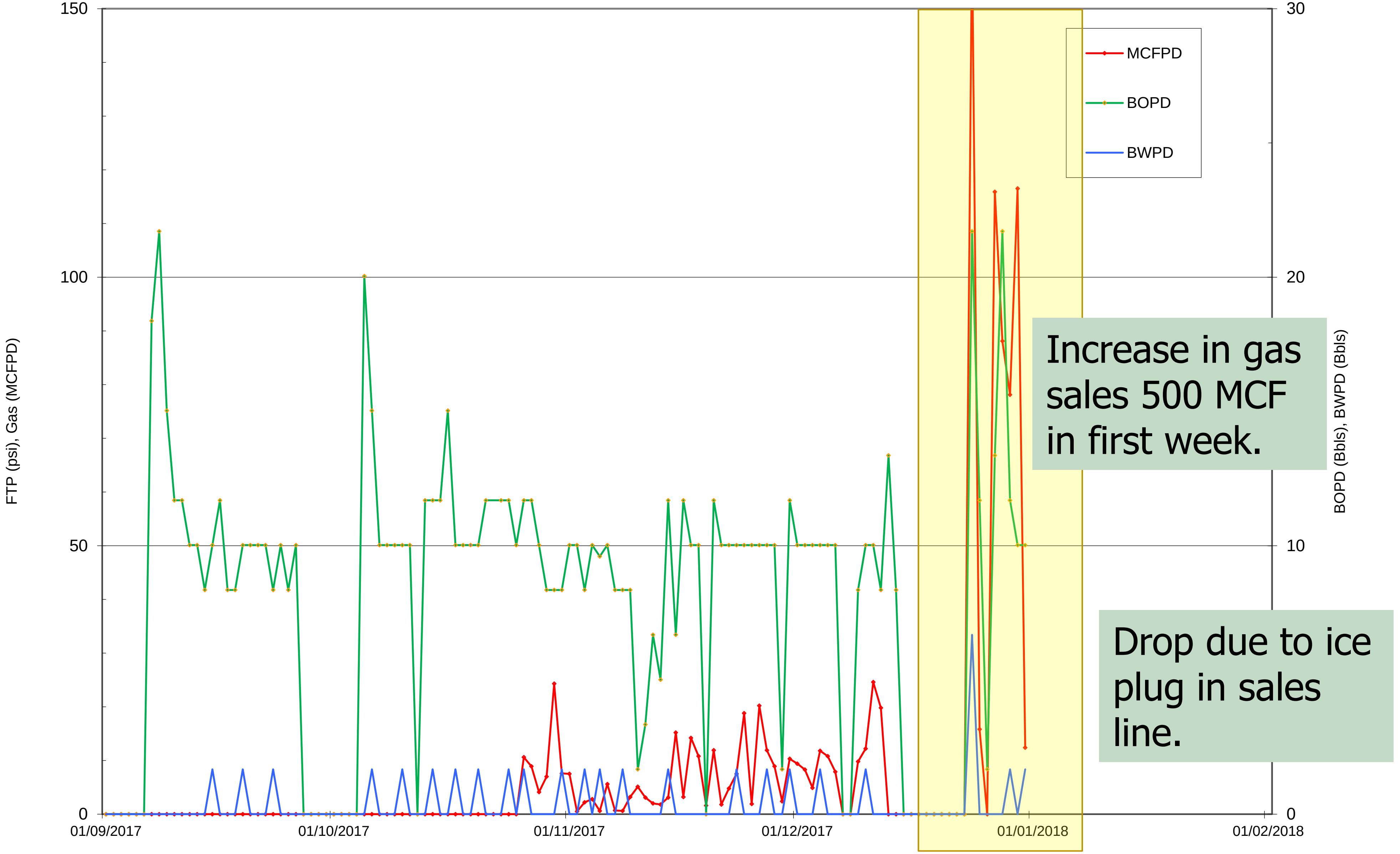

Rodriguez 35-E

Well Data Sheet and Treatment Design			
			Flow Characteristics Before Chemical
Operator	GGG Oil Co.		Wells on pump making ± 5-7 BOPD for entire lease. ± 1-1.5 BOPD and 2-3 BWPD/well
Well Name	Rodriguez SFU #35-E		Were told emulsion at wells and at tank battery.
Field	Mirando Sand		
County	LaSalle		Poor test data prior to pumping chemicals
Well Type	Oil		
Lift Method	Pumping		Well were purchased but after over 2 years forfeited back to GGG Oil Co
Zone Depth	400	feet	No wells have been pulled and pumps checked in over 4 years
Thickness	4	feet	
Porosity	0.27		Treated 11/10/2017 w/ 200 gallons 10% active chemical
Sw	0.5		**Flow Characteristics After Chemical Treatment**
Desired Length (3%)	7.25	feet	
Treatment Volume	20.01	gallons	Owner noticed a considerable increase in production and reduced emulsions
3%	15.88	bbls	
5%	9.53	bbls	Has hole in production tank so not sure of produced volumes or rates after
10%	4.76	bbls	treatments.
25%	1.91	bbls	
			Jim Gould called on 12/18/2017 Oil production up to 13-17 BOPD w/ max 22 BOPD
Area with 200 ppm	99.67	feet	

Benefits Test

Rocker Test

- Pup Joint
- Liquids – femto, xylene, toluene
- Gas – methane, CO_2, H_2S
- Under Pressure
- Corrosion minor
- Reduction in CO_2 and H_2S

Fig: Before (left) and after (right) showing no corrosion took place.

Ref: Dixie Testing.

Surfactant Testing

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Testing

- Captive bubble method
- Pendant dropping
- Spontaneous Imbibition

Fig: Modified Amott cell for imbibition testing.
Ref: SPE Wettability Alteration, Alvarez and Schechter

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Surfactant Results

- Permian Silicous Core

Surfactant	Primary Components	Composition (wt%)	pH	Specific Gravity
Nonionic A	Branched alcohol oxyalkylate	10-30	5.0- 7.0	0.997 - 1.027
Nonionic B	Ethoxylated isodecylalcohol	13-30	7.0 -9.0	1.016 - 1.046
	Quaternary ammonium compound	5-10		
	Quaternary ammonium salt	1-5		
Anionic	Methyl alcohol	40-70	5.8-7.2	0.866 - 0.892
	Proprietary sulfonate	10-30		
Nonionic-anionic	Methyl alcohol	60-90	6.3-7.3	0.823-0.848
	Proprietary ethoxylated	7-13		
	Proprietary sulfonate	5-10		

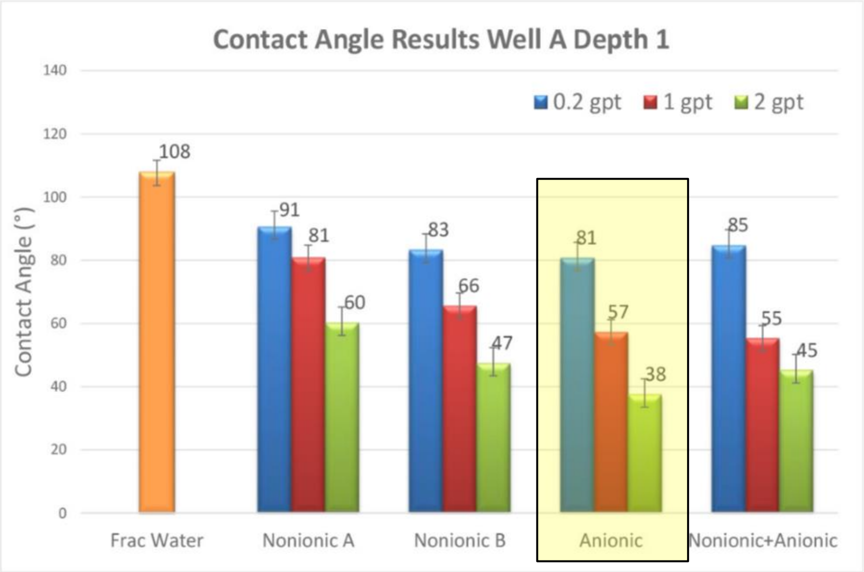
Fig: Surfactants tested.

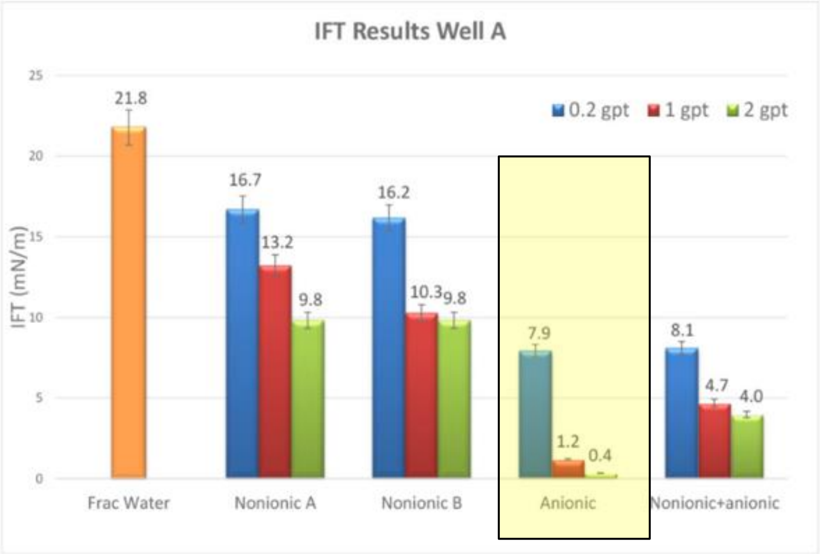
Ref: SPE Wettability Alteration-Alvarez and Schechter

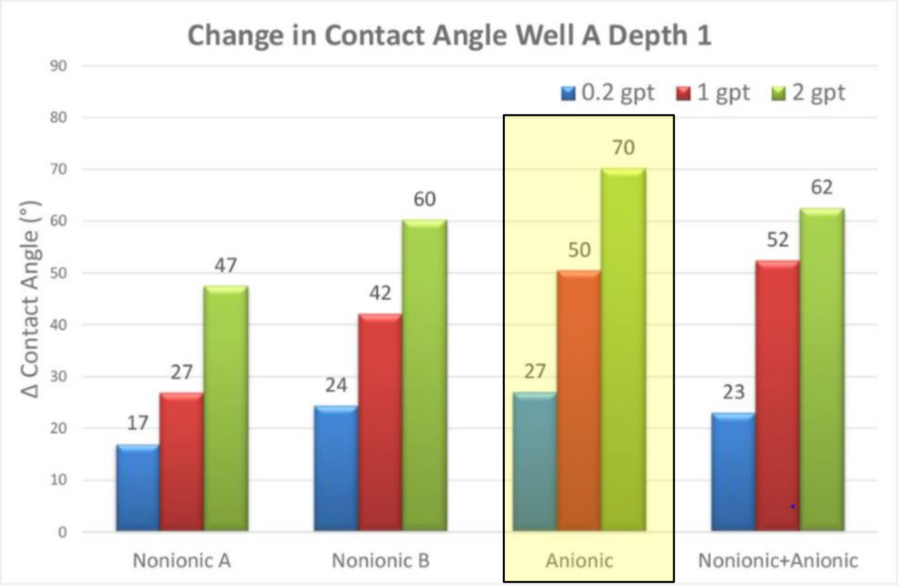
Surfactants CA and IFT

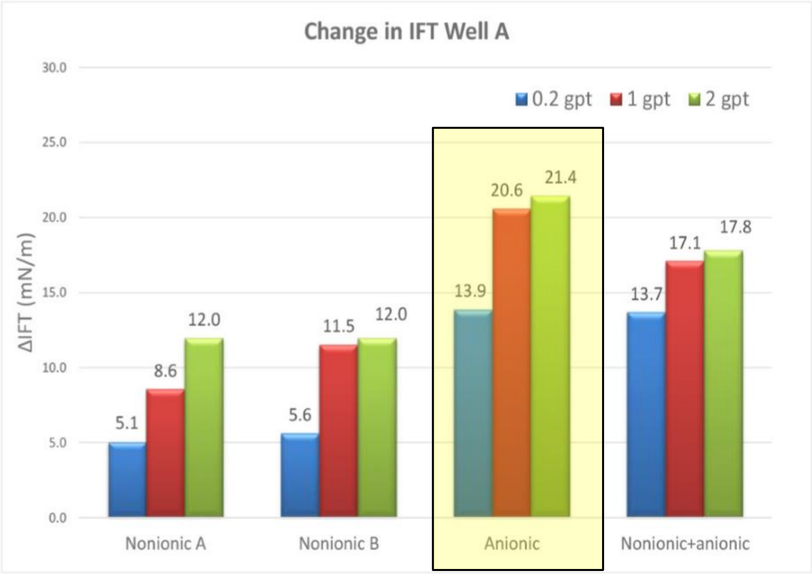
Top: Anionic showed the lowest contact angle.

Bottom: Higher concentration had greater effect.







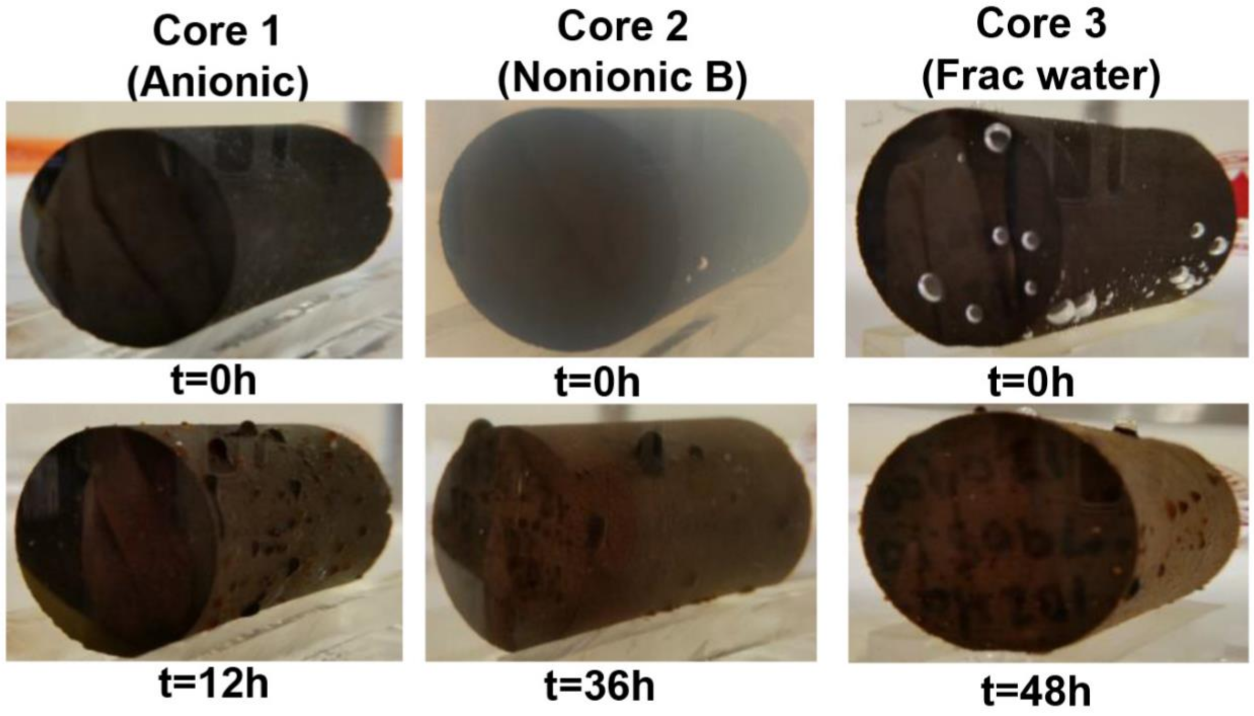


Top: Anionic showed the most reduced IFT.

Bottom: Higher concentration had greater effect.

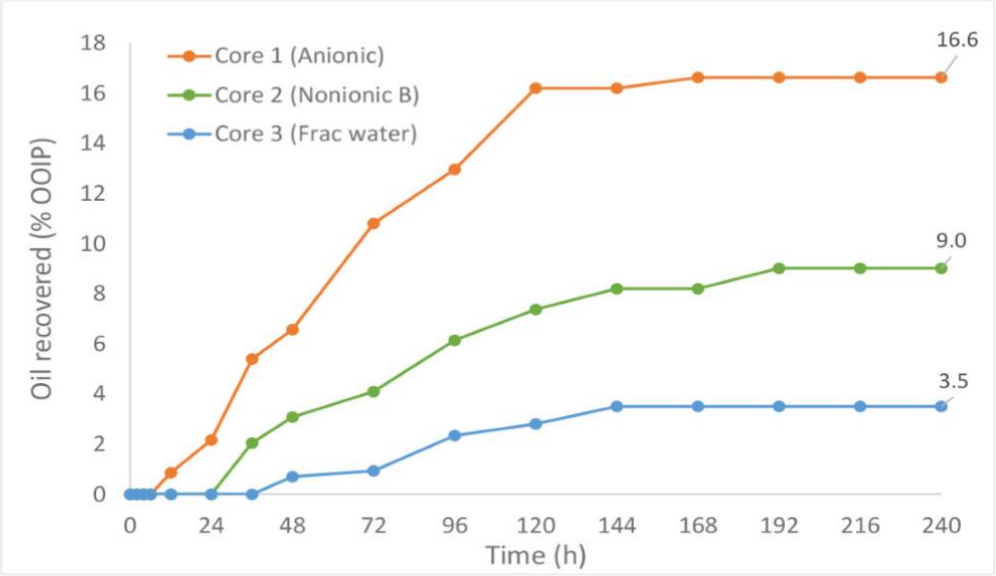
Ref: SPE Wettability Alteration-Alvarez and Schechter

Surfactants Spontaneous Imbibition



Left: Anionic reacted faster to start imbibition.
Below: Anionic resulted in higher oil recovered.

Ref: SPE Wettability Alteration- Alvarez and Schechter



Summery of Surfactants Results

Core	Type of Fluid	Initial Average Core CT (HU)	Final Average Core CT (HU)	Penetration magnitude (HU)	Initial Weight (gr)	Final Weight (gr)	Δ Weight (gr)	Initial CA (°)	Final CA (°)	Oil Recovered (% OOIP)
1	Anionic	2060	2091	31	48.52	48.69	0.17	138.8	57.4	16.6
2	Nonionic B	2390	2416	24	54.27	54.37	0.10	142.4	62.6	9.0
3	Frac Water	2612	2619	7	46.95	46.98	0.02	140.4	110.9	3.5

Resent Surfactants Findings

- Anionic Surfactants best for – Silicates
- Cationic Surfactants best for – Carbonates

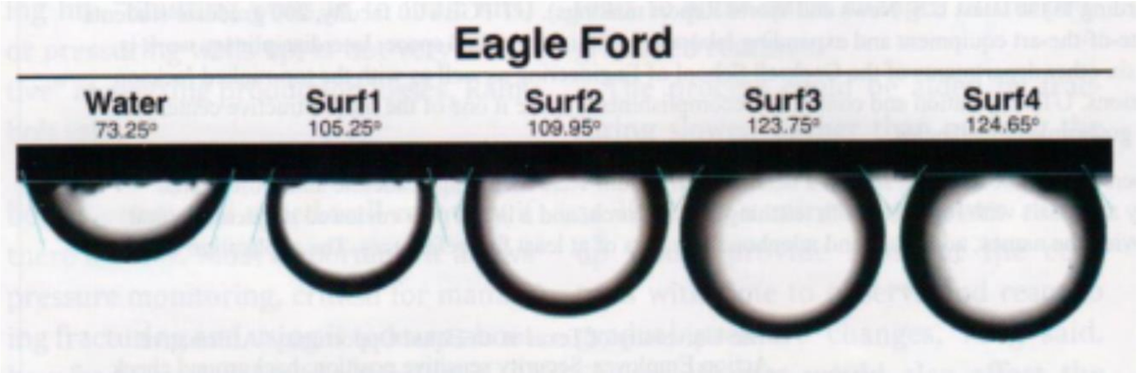


Fig: Showing the cationic surfactants on the Eagle Ford.

- Conclusion: Not one surfactant can be used for all types

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Imbibition

Nano and Femto Results

- Femto 10% active
- Nano 25% active
- 0.2 gpt concentration when comparing to surfactant

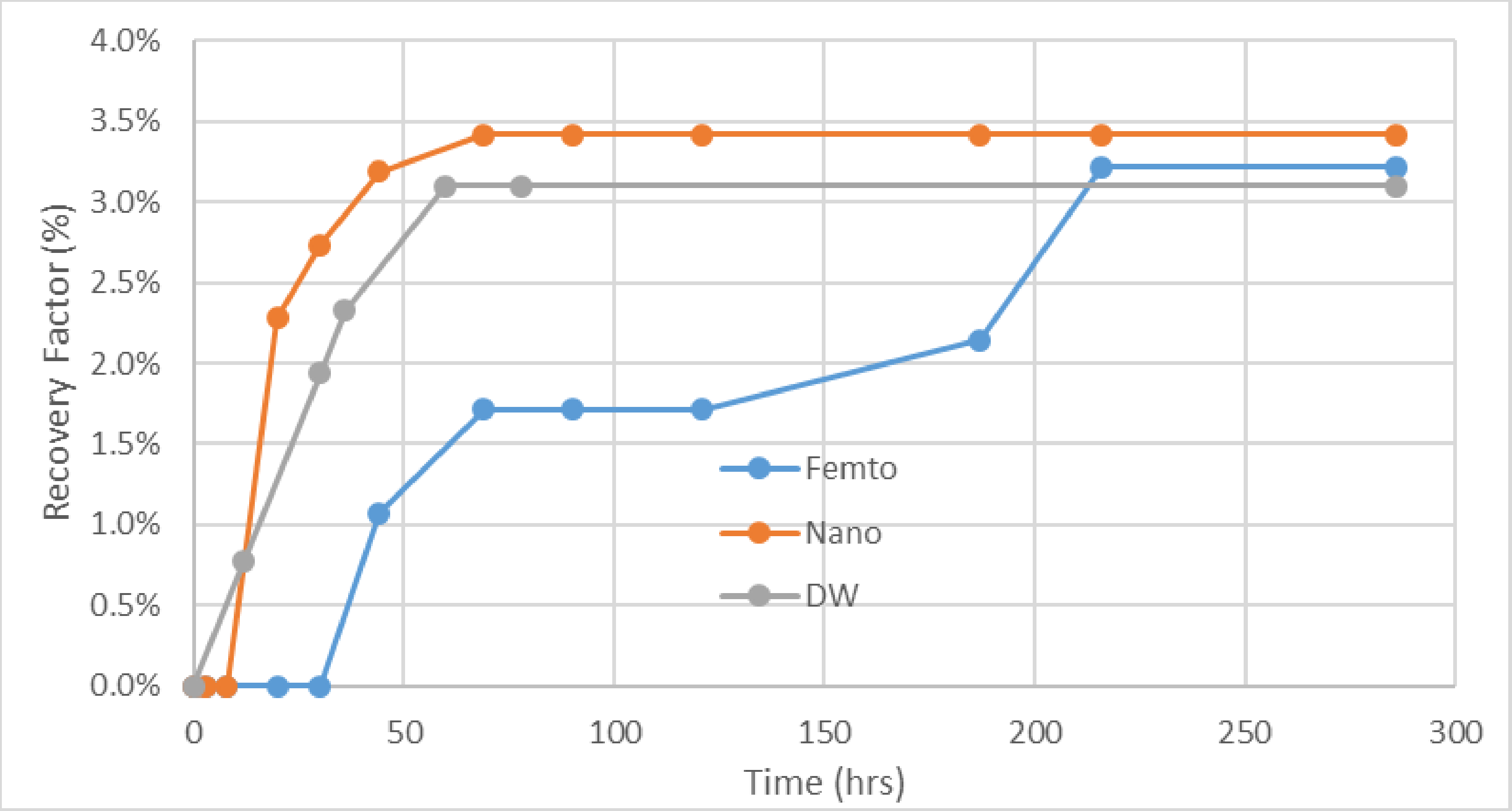

Fig: Nano and Femto showing same recovery in Eagleford, but Femto had smaller active solution.

JPT - Innovation Will Drive Shale Survival

- Enhanced recovery methods to imporve production
- Improve and stabilize conductivity in frac channels through better understanding of surface energies and fracturing techniques specific to unconventional

- Vikram Rao

SPE Paper (SPE-173729-MS) – Microemulsions

"The results of this work was that microemulsions do offer some benefits over individual surfactants, not so much in surface tension modification but very must on non-emulsification of crude oil and water...so often seen as the primary damage mechanism in oil well fracturing."

"A challenge in hydraulic fracturing, especially for tight formations, is associated with remediation of formation damage caused by frac fluid invasion into the porous media of the reservoir and formation of oil/water emulsions."

"Measuring the surface tension of the effluent flowing from the pre-saturated sand column during a surfactant treatment injection acts as an indication of the adsorption effect of surfactant onto the silica."

SPE Paper - Microemulsions

Table 3. Surface tension of surfactants used in this study. All measurements are done at 25 °C

Chemical Identifier	**Surface Tension (mN/m)**	
	DI water	**5% KCl**
SFBA-1	35.0	30.2
SFBA-2	29.7	28.6
SFBA-3	35.6	29.0
SFBA-4	27.3	27.6
MESFBA-4	27.2	27.8
MESFBA-5	40.1	38.5
MESFBA-6	34.4	33.5

SPE Paper - Microemulsions

"Surfactants, regardless of their mode of state: aqueous or microemulsions, can interact with such phases and disturb the equilibrium thus affecting the dynamic of multiphase flow during oil and gas production."

"Microemulsions therefore may be considered as a carrier system which can be used to better deliver surfactant deeper into the reservoir during a frac job."