# NANOPARTICLE DISPERSIONS AND DISJOINING PRESSURE PROVIDE A NEW MECHANISM FOR PARAFFIN REMOVAL, IMPROVED CRUDE OIL RECOVERY, AND SWD INJECTIVITY IMPROVEMENT

David L. Holcomb, PhD, and Golda Pilecki
FracTech Services, LLC

## INTRODUCTION

A new surface energy mechanism, based on recent joint industry-university research using nanoparticle dispersions (NPD) is now available to the oil and gas industry, and is being laboratory and field tested for improving stimulation fluid recovery, remediating wellbore damage issues such as paraffin, waterblock and deep induced imbibition, as well as for enhancing the recovery of oil, gas and water following their application by a variety of intervention methods. Also being readied for implementation, is the use of NPDs to provide increased hydrocarbon production and injection efficiency from waterflooding and other improved hydrocarbon recovery operations. Increasing injectivity into saltwater disposal wells (SWD) has been accomplished in beta test field trials. Graphic experimental demonstrations of these mechanisms will be shown and discussed, with emphasis on their current and potential field treatment applications, and with comparisons to another successfully utilized additive technology.

Nanoparticle dispersions (or colloidal particle dispersions in the classic surface chemical sense) provide a unique enabling mechanism to improve the efficiency of fluids and additives in the performance of their intended actions during a number of reservoir intervention applications.
Nanofluids are stable colloidal dispersions or micellar dispersions that accelerate recovery of hydrocarbon from oil and gas reservoirs, developed by the authors in conjunction with the Illinois Institute of Technology. This paper will focus on the colloidal dispersion of solid particles. The nanoparticles in NPD utilize a relatively new application for the mechanism of disjoining pressure (Fig. 1) by self-assembling into a wedge film (Fig. 2) once the nanoparticles encounter a discontinuous phase. This wedge film acts to separate formation fluids (oil, paraffin, water, and/or gas) from the formation's surface, thereby recovering more fluids than previously possible with conventional additives or fluids.

Typical fluid recovery issues for well interventions, well stimulation, and wellbore remediation include problems involving induced imbibition, capillary pressure, contact angle, surface and interfacial tension, and mixed wettability. Traditional solutions for dealing with these issues include surfactants, solvents, microemulsion additives, aqueous $CO_2$ and $N_2$ foams, alcohols, $CO_2$ and $N_2$ or mixtures thereof.
Innovative aqueous dispersed; 4 - 20 nanometer amorphous silicon dioxide nanoparticle fluids have been developed and tested which uniquely demonstrate disjoining pressure functioning with respect to wetting agent and nanoparticles dispersed in various type aqueous phases.
Research laboratory and actual field treatment beta testing has demonstrated that higher fluid recoveries and injection rates can be achieved, by enabling conventional intervention fluids to function more efficiently.
Well stimulation, and in particular near -wellbore remediation, formation damage removal, and mitigation, as well as water disposal and well efficiency improvement are the first successful applications for disjoining pressure energized, nanoparticle dispersion technology. Brownian motion activated NPD's are illustrated and photographed from fundamental experiments conducted over a two year development period.
Treatment applications for NPDs to date include the following:

- Remediation and /or mitigation of fines stabilized, acid /oil sludge, paraffin, asphaltene, water-block, and formation damage.
- Stimulation Treatments such as slick-water, and linear gels
- Salt Water Disposal Wells
- Heavy oil, bitumen, and tar sand extraction

Example beta test field results in almost 80 wells over the past year include successful results using the remediation and stimulation applications summarized in the previous bullets.

## Typical Problems Associated with Reservoir/ Wellbore Treatment Effectiveness

- Induced Imbibition
  - Depending on the wetting properties of the fluids there are essentially two different types of displacement in two-phase flow in porous media. In this thesis we are considering drainage displacements where a non-wetting invading fluid displaces a wetting fluid. The opposite case, imbibition, occurs when a wetting fluid displaces a non-wetting fluid. The mechanisms of the displacements in drainage and imbibition are quite different and the two cases should not be confused. Typically, slow drainage is characterized by piston-like motion inside the pores where the invading non-wetting fluid only enters a pore if the capillary pressure is equal to or greater than the threshold pressure of the pore. The threshold pressure corresponds to the capillary pressure in the narrowest part of the pore. However, in imbibition at low injection rate the invading fluid will enter the narrowest pores before any other is entered.

- Contact Angle
  - The contact angle is the angle at which a liquid/vapor interface meets the solid surface. The contact angle is specific for any given system and is determined by the interactions across the three interfaces. Most often the concept is illustrated with a small liquid droplet resting on a flat horizontal solid surface. The shape of the droplet is determined by the Young Relation. The contact angle plays the role of a boundary condition. Contact angle is measured using a contact angle goniometer. The contact angle is not limited to a liquid/vapor interface; it is equally applicable to the interface of two liquids or two vapors.

- Surface Tension
  - The cohesive forces between liquid molecules are responsible for the phenomenon known as surface tension. The molecules at the surface don't have other like molecules on all sides and consequently they cohere more strongly to those directly associated with them on the surface. This forms a surface "film" which makes it more difficult to move an object through the surface when it is completely submersed.
  - Surface tension is typically measured in dynes/cm, the force in dynes required to break a film of length 1 cm. Equivalently, it can be stated as surface energy in ergs per square centimeter. Water at 20°C has a surface tension of 72.8 dynes/cm compared to 22.3 for ethyl alcohol and 465 for mercury.

- Interfacial Tension
  - Interfacial tension arises due to the attractive forces between the molecules in different fluids. Generally, the interfacial tension of a given liquid surface is measured by finding the force across any line on the surface divided by the length of the line segment. Thus, the interfacial tension becomes a force per unit length which is equal to the energy per surface area.

- Capillary Pressure
  - For two-phase flow in porous media the interfacial tension of curved pore-interfaces gives rise to a capillary pressure between the two liquids. At pore level, the curvature of the interface is often assumed to be equal to the pore size, denoted by $a$. Thus, the capillary pressure between the fluids in a pore of size $a$ is approximately given by 2 (IFT)/a.

- Reservoir Wettability
  - The wettability of a liquid is defined as the contact angle between a droplet of the liquid in thermal equilibrium on a horizontal surface. The wetting angle, $\theta$, is given by the angle between the interface of the droplet and the horizontal surface.

- Zeta Potential
    - Zeta potential is the electrical potential across the interface of liquids or solids. Particles interact according to the zeta potential not the surface charge. In colloidal suspensions the particles are stable at above +30mV or lower then -30mV, meaning that the particles have the most potential to stay suspended in a solution at these measurements.

## EXPERIMENTAL EVALUATION

A number of laboratory experiments and techniques were developed to illustrate the effect of disjoining pressure for removing oil, paraffin and other heavy hydrocarbons from surfaces and porous media as a result of nanoparticle dispersions acting at the three phase contact point between the aqueous phase containing NPDs, the solid substrate on or in which hydrocarbons are contained and the hydrocarbon itself.

### Demonstration 1: Oil recovery from between microscope slides

#### Set up

San Andres Crude oil (API gravity 33, 17.76% asphaltenes and 53% paraffins) from West Texas was coated onto a standard microscope slide and aged for 30 min at 100 degrees C. and covered with a second slide to create paraffinic/asphaltenic crude blocked. Two of these double slide cells were prepared identically and then placed into glass beakers. Tests were conducted at ambient condition. No fluid movement was used during the duration of the tests. Comparative tests were run with one cell covered with a solution containing 17 volume percent of a commercially available microemulsion additive in 2 % KCl water. The other cell was covered with a 17 volume percent of a new NPD series additive.

#### Results

The subsequent time lapse illustrates the NPD removing the oil from between the slides and then effectively stripping the paraffinic oil coating from the glass surfaces. The microemulsion additive shows little to no oil removal, and does not clean the silicate glass surface. NPD removal of oil is around 50-70% while the microemulsion removes between 0-5% of the oil from between the two glass slides.

The test was ran as described and results photographed and shown over a one hour period as described in Figs. 3–5:
Fig. 3 description: The two slides of oil initial after the treatment fluid of 1:5 NPD-2000 (left) and 1:5 microemulsion (right) has been added to the beakers.

Fig. 4 description: The two slides of oil 20 min after the treatment fluid of 1:5 NPD-2000 (left) and 1:5 microemulsion (right) has been added to the beakers. The NPD-2000 nano fluid has started to remove the oil from in-between the slides. The microemulsion has not removed any oil at this point Fig 5 description: The two slides of oil 1 hour after the treatment fluid of 1:5 NPD-2000 (left) and 1:5 microemulsion (right) has been added to the beakers. The NPD-2000 nano fluid has removed oil from between the slides and moved the slides. The microemulsion has not removed any oil at this point.

### Demonstration 2: Acid/Oil/ Iron Sulfide Sludge break-up and removal by 17% NPD Solution

#### Set up

Oil sludge was made with the combination of 15% HCl , iron, and San Andres Crude oil (API gravity 33, 17.76% asphaltenes and 53% paraffins) from West Texas. A 10 cc test tube was cleaned and dried. The sides and bottom of the test tube were coated with the sludge and aged for 24 hours in a well ventilated area. After 24 hours, 5 cc of a mixture of 1:5 NPD in water and a green paraffin solvent was added to the test tube at ambient conditions.

Results

Sludge was broken up and removed from the sides and bottom of the test tube. The removal of the sludge from the glass test tube takes place over a time span of 4-6 hours (Fig. 7). The solution of NPD and solvent removed the sludge from the sides and bottom of the test tube in droplets. The sludge was broken down to pourable acid and oil solutions.

## CASE HISTORY EXAMPLE #1

- Near -welbore1 Paraffin Remediation
- 2000 Gal total Treatment
- 60% =17% NPD in Fresh water + 40% Paraffin Solvent

- Chaves Co. NM
- Sprayberry Formation
- Treatment type – Paraffin remediation
- Results: High amounts of paraffin flowed back when well placed on pump for several days. Initial Production after job increased from 6 BOPD -12 BOPD
- Treatment benefits lasted 90 days w/ NPD vs. 30 days w/ Hot Oil

CASE HISTORY EXAMPLE # 2:

- Paraffin Remediation using 20% NPD mixed in produced water
- 150 gal NPD concentrate
- Scurry Co. TX
- Pumped using hot oil truck
- Treatment type – Paraffin remediation
- Results:
  - Doubled oil production (90 BFPD to 140 BFPD (50% oil cut))
  - Increased gas production slightly
  - Treatment lasted longer and worked better than non-NPD treatments

CASE HISTORY EXAMPLE # 3:

Treat two SWD wells in the Nacotoch Formation, in the red River Parrish, Louisiana with the following schedule in one Stage at 5 BPM down casing and tubing simultaneously

| | |
|---|---|
| 2,000 | Gallons of Load Water |
| 2,000 | Gallons of Acidize 10.1% - 15% HCl Acid |
| 215 | Gallons of Sweep Paraffin Solvent |
| 660 | Gallons of Pad 15% NPD Mixture #1 |
| 1,000 | Gallons of Diverter 2% KCl Water #1 |
| 2,000 | Gallons of Acidize 10.1% - 15% HCl Acid |
| 215 | Gallons of Sweep Paraffin solvent |
| 660 | Gallons of Pad 15% NPD Mixture #1 |
| 1,000 | Gallons of Diverter 2% KCl Water #2 |
| 2,000 | Gallons of Acidize 10.1% - 15% HCl Acid |
| 215 | Gallons of Sweep Paraffin solvent |

660 Gallons of Pad 15% NPD Mixture #1
500 Gallons of Flush 2% KCl Water #3

RESULTS

Two NPD Treatments were run on two salt water disposal (SWD) wells. One used ball sealers and one used rock salt in between stages. Results immediately after treatment and over the next six months showed both wells went from 500 bpd to 1500 bpd injection volume. At $1/bbl. disposal cost, they paid for themselves in 30 days. Previous treatment procedure involved pumping paraffin solvent /acid jobs periodically, with only about a 200-300 bbl/day increase in injectivity. This was a successful controlled experiment in that the only variable changed was the addition of NPD.

CONCLUSIONS

The use of aqueous nanoparticle dispersions( NPDs) with 4 -20 nm silicon dioxide particles has been demonstrated in both experimental laboratory evaluations and field trials to provide improvements in wellbore remediation of paraffin, production improvement and increased injectivity over conventional treatments . To date over 50 successful beta test applications similar to those documented in this presentation have been pumped and documented. Additional work is being done to develop improved NPD formulations that will better enable these type applications as well as hydraulic fracturing, acidizing, production chemicals, waterflooding, tar sands, heavy oil, hydraulic fracturing and improved oil recovery applications.

REFERENCES:

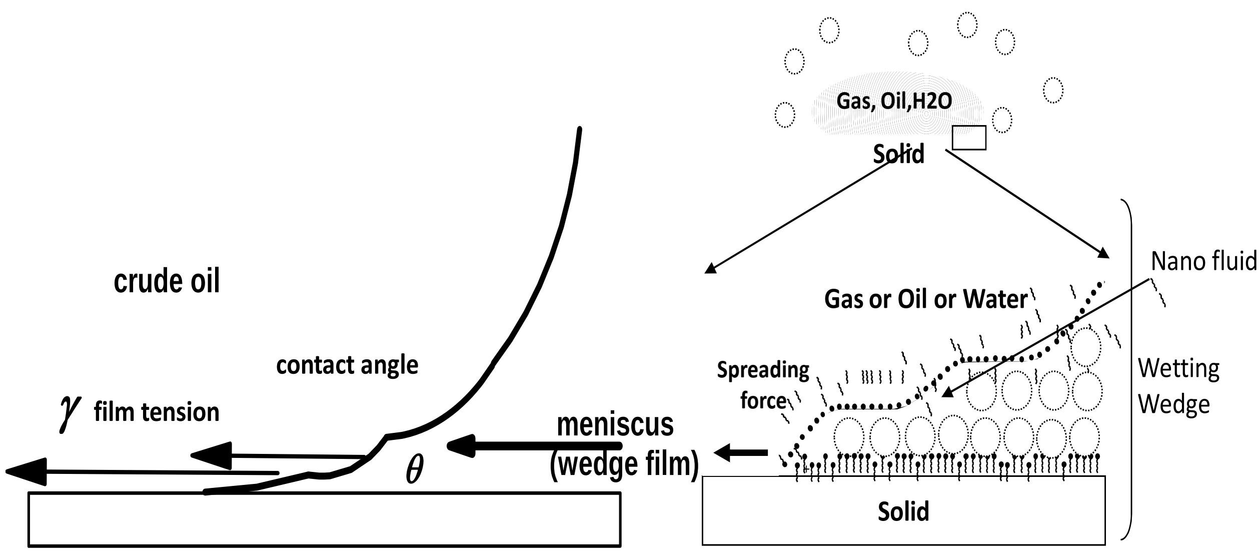
*1.Pressure profile on the wedge walls for 0.5 º contact angle at the vortex as a function of radial distance, D. Boda, K. Y. Chan, D. Henderson, D. T. Wasan, and A. D. Nikolov, Langmuir, 15, 4311-4313, 1999*

2."Spreading of Nanofluids on Solid" D.T. Wasan and A.D. Nikolov, *Nature*, 423: 156-159 (2003).

3."A Simple Calculation of Structural and Depletion Forces for Fluids/Suspensions Confined in a Film" A. Trokhymchuk, D. Henderson, A. Nikolov, and D.T. Wasan, *Langmuir*, 17:4940-4947 (2001).

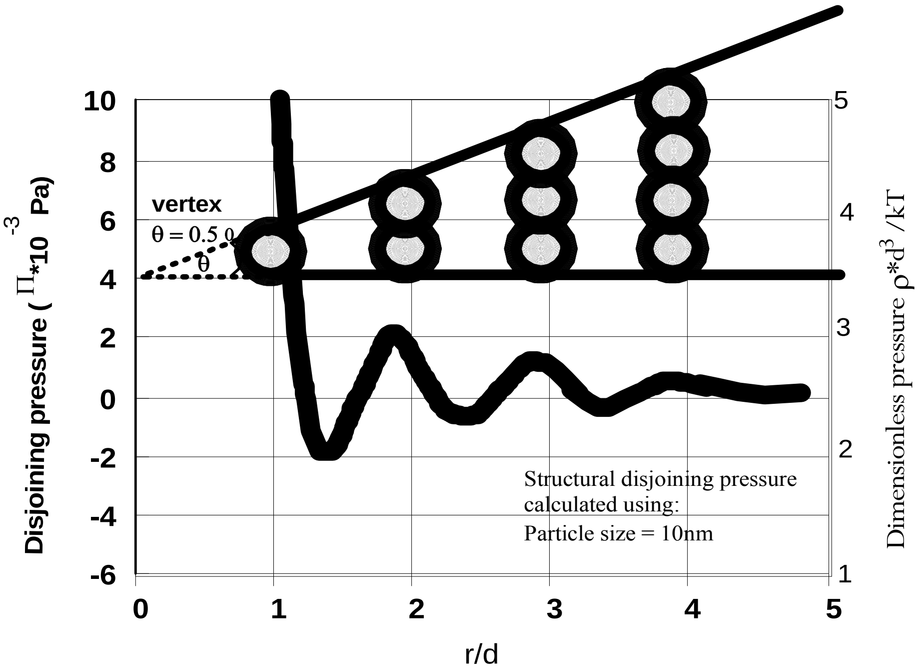
4."Spreading of Nanofluids Driven by the Structural Disjoining Pressure Gradient" A. Chengara, A.D. Nikolov, D.T. Wasan, A. Trokhymchuk, and D. Henderson, *Journal of Colloid and Interface Science*, 280:192-201 (2004).


Summary of Nano-Fluid spreading to Form a wetting wedge which creates a spreading force that removes oil, gas and/or water from solid surfaces relative to three phase contact angle and the surface tension of an adsorbed film of oil, gas and/or water.



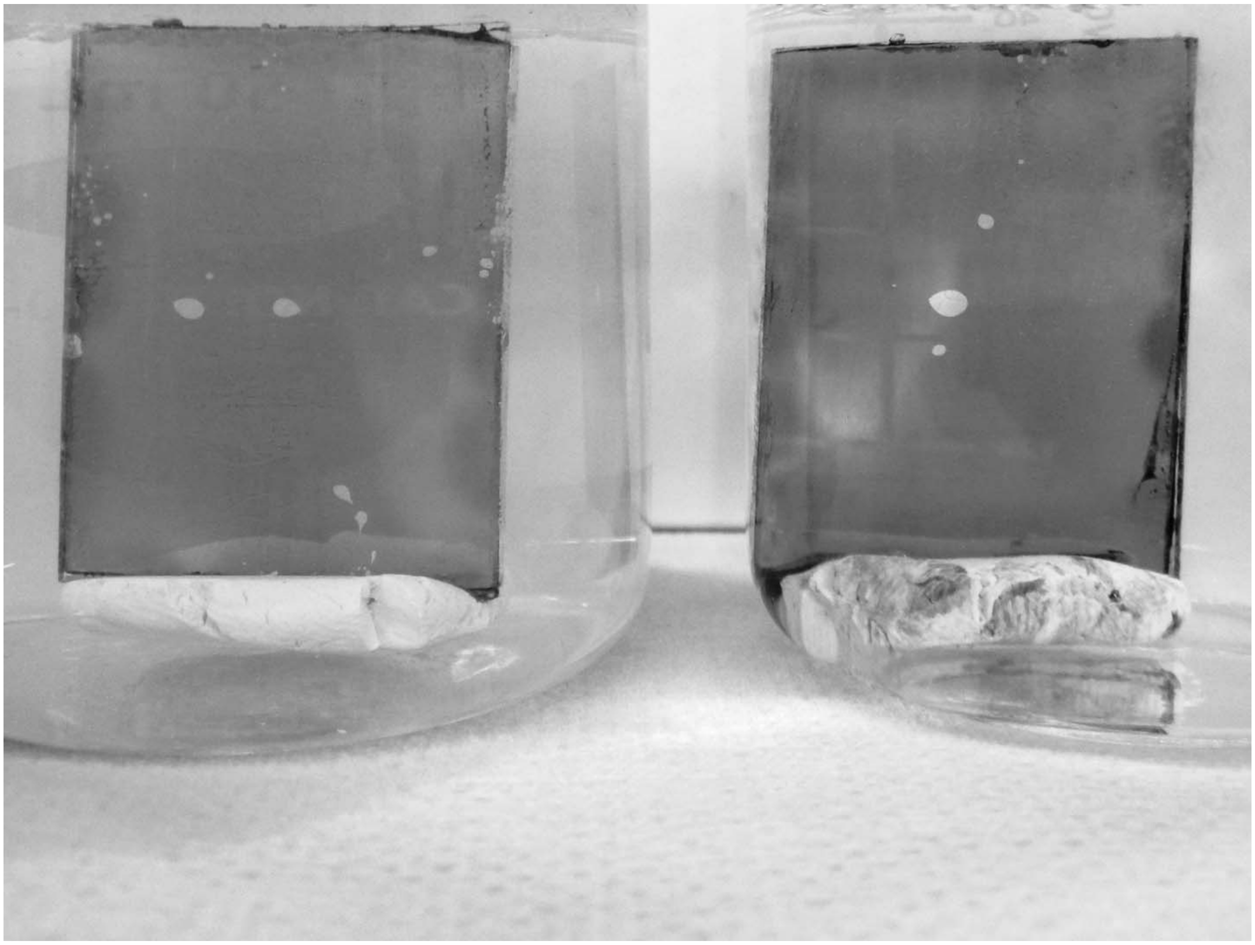

Gas Oil and/or Water Removal Mechanism in the Presence Of Nano-Fluid
(Colloidal Particle Dispersion)

Figure 1



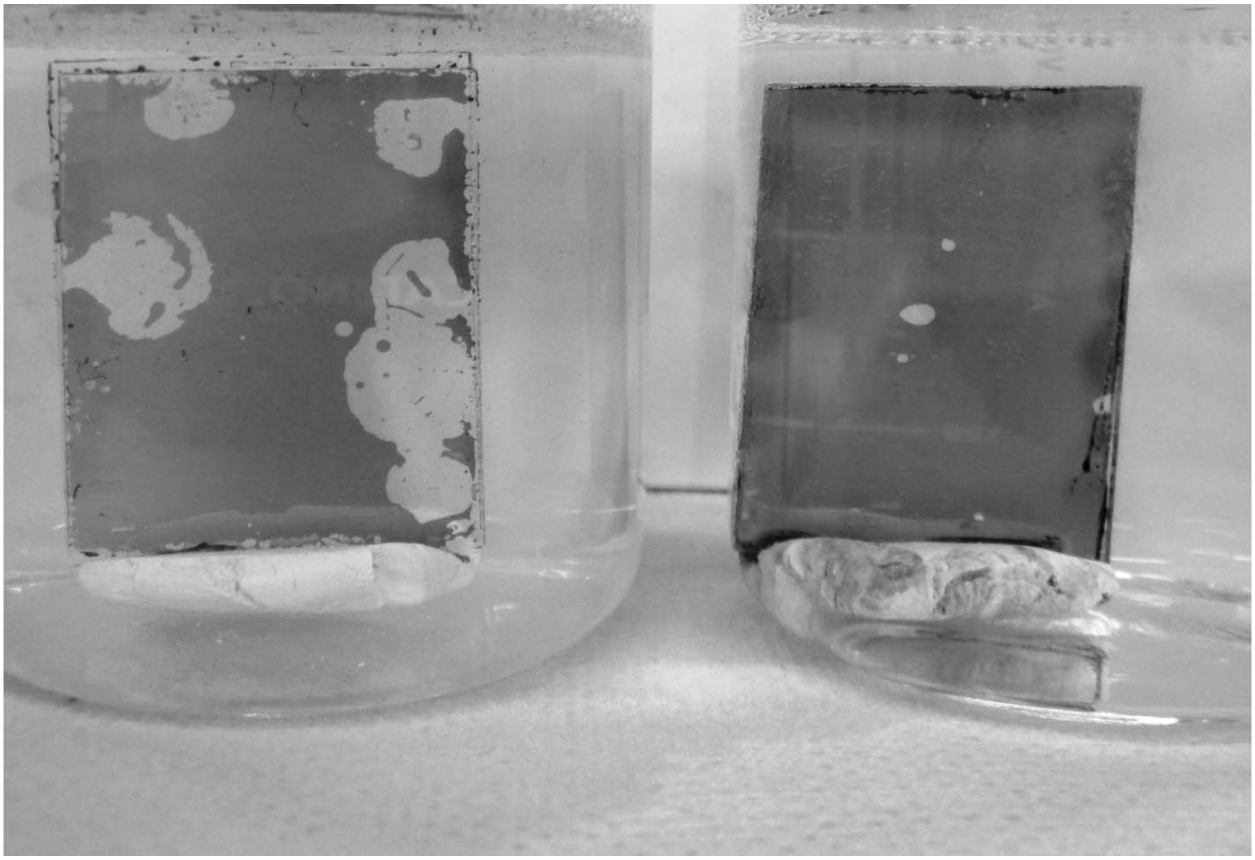

**"Pressure profile on the wedge walls for 0.5 º contact angle at the vortex as a function of radial distance"**

Figure 2 - Particle distance scaled by diameter, r/d; pressure near the vortex is approximately 50,000 Pascals which is dependent on the effective particle volume fraction and particle size. d= particle diameter; r= particle to center (radial) distance.



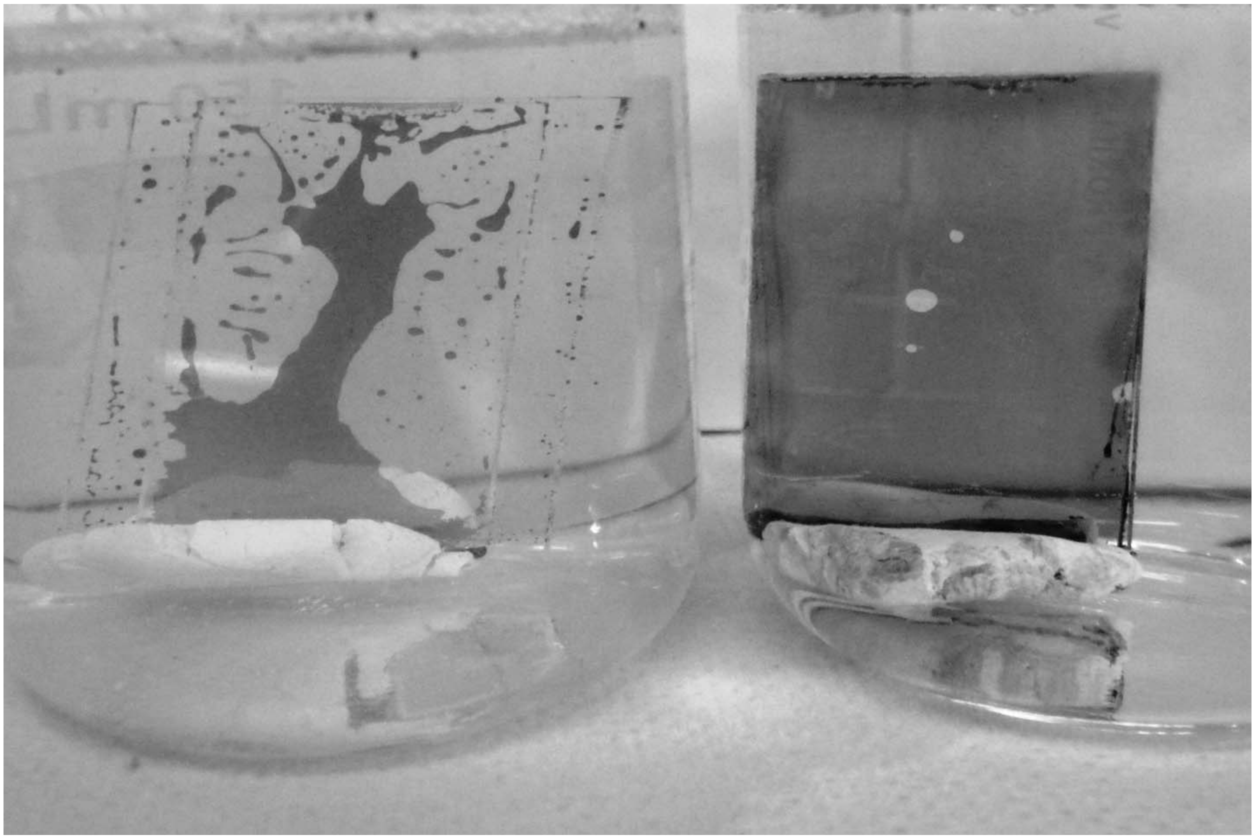
Dual slides in17% NPD Solution VS. Dual Sildes in 17% Microemulsion Solution

Figure 3- Demonstration 1: Oil recovery from between microscope slides



Crude recovery after 20 minutes in 17% NPD      VS   Crude Recovery after 20 minutes in 17% Nicroemulsion

Figure 4



Crude Recovery after 1 hour in 17% NPD VS Crude Recovery after 1 hour in 17% Microemulsion

Figure 5

Demonstration 2: Acid/Oil/ Iron Sulfide Sludge break-up and removal by 20% NPD Solution