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## Enhanced Oil Recovery Using Silica Nanoparticles: Sandpack Flooding Experiments in a Low Salinity Environment

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ENHANCED OIL RECOVERY USING SILICA NANOPARTICLES: SANDPACK  
FLOODING EXPERIMENTS IN A LOW SALINITY ENVIRONMENT

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A Thesis  
Presented to  
the Graduate School of  
Clemson University

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In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science  
Hydrogeology

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by  
Brightin Rex Blanton  
December 2019

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## ABSTRACT

Mobilizing and recovering crude oils from geological strata is crucial for the management and development of petroleum reservoirs. Unlike conventional oil production methods, enhanced oil recovery (EOR) processes can increase the recovery of most oil products from the reservoir above the secondary recovery baseline. Recent studies have demonstrated that nanoparticles (NPs) have the potential to improve EOR processes. Therefore, understanding how NPs impact the mechanisms that govern the interaction between the fluids interface, the fluid-solid interface, and the mobility of oil in porous media is critical to alter the properties of nanofluids for specific geofluid conditions and increase EOR efficiency. The objectives of this research are to determine the impacts of NPs on the fluid-fluid interfaces, the fluid-solid interfaces, the mobility of oil in porous media, and oil recovery. This research seeks to evaluate the different production processes in petroleum engineering commonly implemented at the field scale. *Sequencing* is a process that is heavily implemented by the petroleum industry and involves the injection of an aqueous phase (brine) prior to the injection of EOR fluid. *Non-sequencing* involves the immediate injection of chemical-EOR fluid to displace crude oil and is more of a theoretical process which allows for a direct comparison of the immediate impact of chemical-EOR fluid with oil displacement associated with waterflooding and sequenced chemical-EOR injection. In this study, silicon dioxide nanoparticles ( $\text{SiO}_2$  NPs) were employed to improve the efficiency of the chemical-EOR process that utilizes surfactant flooding in an oil wet sandstone aquifer analogue. Although sandstone aquifers are most frequently water wet, the imbibing liquid is crude oil in these experiments, resulting in more conservative oil recovery rates. Quartz silica sand was used to simulate the porous media material. Light (West Texas

Intermediate, or WTI) crude oil was selected as the oil phase, due to its ubiquity as a global standard for crude oil characteristics and price. De-ionized water and one weight percent (1 wt %) NaCl brine, with 2 critical micelle concentrations (CMC) of anionic surfactant (sodium dodecyl sulphate, or SDS) and concentrations of silica nanoparticles including 0, 0.01, and 0.1 wt% were used to create the nanofluids. Experiments were conducted to measure the contact angle between the microscope glass slide and SiO<sub>2</sub> / SDS - based aqueous nanofluid systems. The contact angle between the aqueous nanofluid and the microscope glass slide is a factor used to assess the alteration of the sand wettability, a property critical to the mobilization of crude oil from porous media. Microscope glass slides were used to simulate quartz silica grain surfaces for contact angle measurements. Sandpack flooding column experiments were conducted to test the impacts of the various nanofluids injected into the crude oil saturated sandpack on the cumulative and fractional recovery rates of WTI crude oil. The effective oil displacement by the SiO<sub>2</sub> / SDS – based aqueous nanofluids tested was monitored over time and expressed as a function of the number of pore volumes (PVs) of fluid injected into the system during various processes. Cumulative and fractional oil displacement are plotted as a function of PVs injected during events designed to simulate common practices in the petroleum industry. Primary Oil Recovery is simply the process of oil recovery due to natural gravity drainage or pressure head driving fluid from the subsurface. This process is analogous to the initial oil injection phase, during which the column is saturated with oil to the extent that WTI crude oil is flowing out the effluent tube and into the designated pre-experiment effluent sample tube. Secondary oil recovery, or waterflooding as it is commonly called, involves the re-injection of natural aquifer fluids such as water or brine to displace an additional amount of crude oil. Finally, tertiary or Enhanced Oil Recovery (EOR) involves the injection of heat, gas, or chemicals to further improve

the displacement efficiency of crude oil. This research seeks to evaluate the different impacts of processes commonly implemented at the field scale. The research demonstrated that SiO<sub>2</sub> NPs can be used with surfactants such as SDS in crude oil to change the wettability of petroleum reservoir systems from oil wet to water wet, allowing for a more efficient displacement of crude oil and consequently yielding significantly higher oil recovery rates.

Keywords: Aqueous Nanofluids, Brine, Crude Oil Imbibement, Enhanced Oil Recovery, Surfactant, Waterflooding, Wettability

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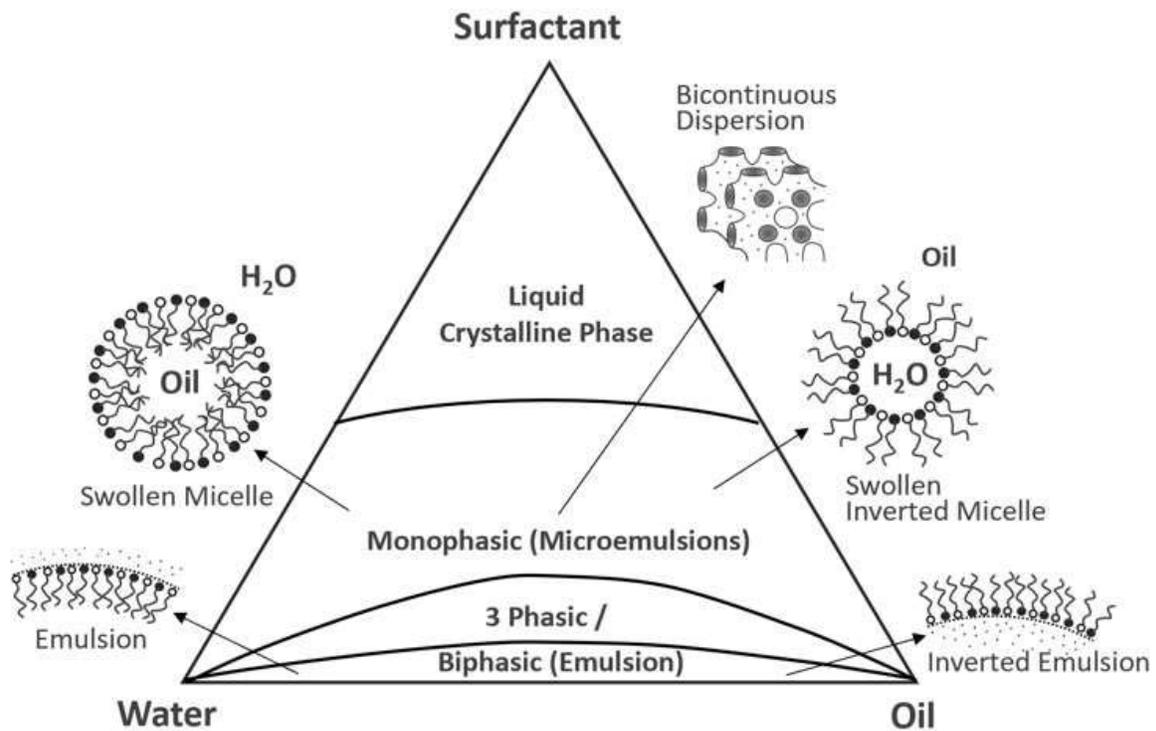
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## INTRODUCTION

### Literature Review

Nanoparticles (NPs) and nanomaterials have been implemented for a variety of scientific and engineering processes, including foam stability simulations and chemical Enhanced Oil Recovery (EOR). Particles added to chemical suspensions consist of nanocellulose (Wei, Li, Jin, Li, & Wang, 2016), aluminum oxide NPs (Joonaki & Ghanaatian, 2014), silicon dioxide NPs (Binks & Rodrigues, 2007), and others. Due to their low cost and identical chemical composition to sand, a common reservoir material, silicon dioxide ( $\text{SiO}_2$ ) NPs are especially prevalent in industrial and academic chemical-EOR applications. Surface Active Agents (more commonly known as surfactants) were implemented for cleaning purposes long before the development of EOR techniques. Today, surfactants are used commonly in detergents, cleaners, and pharmaceutical goods. However, these chemicals have also been shown to increase bulk foam stability and oil displacement efficiency in a laboratory setting (Osei-Bonsu, Grassia, & Shokri, 2017). As shown in the Ternary Phase Diagram below, adapted from the Polymer Properties Database, a low concentration of surfactant in the presence of oil and water will contribute to the formation of a biphasic emulsion in which oil and water mix together to form a fine dispersion of immiscible fluids (Phase Diagram 1; Polymer Properties Database, 2015). This emulsification process enables the chemical-EOR fluid to more effectively flush crude oil from an oilfield, significantly improving the volumetric sweep efficiency during EOR operations.

## SCHEMATIC TERNARY PHASE DIAGRAM OF WATER–OIL–SURFACTANT MIXTURES



Phase Diagram 1 above depicts the different phases formed by mixtures of water, oil, and surfactant, with varying concentrations of each of the three components (Polymer Properties Database, 2015).

Bulk foam stability (foam volume over time) is a physical characteristic that has a significant impact on oil displacement efficiency during foam flooding for EOR operations. Over the course of a chemical injection event, foams with greater stability will consistently lead to a stronger propagating displacement front, thus mobilizing crude oil more effectively than a system in which preferential flow paths or viscous fingering dominate the flow regime (Wang et al., 2013). Surfactants are added as solutions in the chemical-EOR fluid due to their ability to increase the water wettability of porous reservoir material and reduce surface tension between phases (Ravari, Strand, & Austad, 2011), prevent flocculation and aggregation of NPs (Singh & Mohanty, 2015), and to produce stable foams in the presence of NPs for the purpose of forming a mobile crude oil displacement front (Yang et al., 2017).

There is an expansive body of previous work on Enhanced Oil Recovery. A synergistic relationship between positively charged surfactant and negatively charged nanoparticles at a high pH has been demonstrated by mixing silica nanosuspensions with surfactant, then measuring the volume of the foam and time. The governing mechanism of foam stability is the electrostatic attraction between the surfactant and nanoparticles in the mixture, and it is this attraction that causes “foam formation and stability due to the adsorption of surfactant molecules onto particle surfaces” (Binks, Kirkland, & Rodrigues, 2008). A similar experiment was conducted in 2015 by researchers at the University of Texas, except with a different application. The research sought to test the effectiveness of various foams for oil recovery in a Berea sandstone core, and ultimately showed that “surfactant or surfactant–nanoparticle blends can increase the oil recovery over water flood by about 10% of the original oil in place” (Singh & Mohanty, 2015). A major factor contributing toward increased crude oil mobility is wettability alteration of the porous media.

Through nanoparticle and surfactant dispersion experiments conducted for EOR of various crude oils in Boise and Berea sandstone, surface wettability of the porous media has been shown to increase due to lessened surface interactions with the imbibing crude oil. This decrease in crude oil contact on the porous media facilitates a loss of oleophilicity and an increase in hydrophilicity, thus effectively mobilizing more oil from the core (Huibers et al., 2017).

Other experiments involving surfactant flooding within a sandpack have been conducted under various experimental parameters. In 2014, Qian Sun et al. conducted experiments with different concentrations of SDS surfactant and observed that, with silica nanoparticles, an optimal concentration of SDS surfactant promotes foam stability while reducing the effects of viscous fingering. The mechanism responsible for this increased foam stability, reduction in viscous fingering, and subsequent improvement in “plugging performance” is the tendency of silica nanoparticles to migrate to the interfacial film and reinforce the foam boundary (Sun et al., 2014). “Plugging performance,” as it is called in the Sun article, refers to the ability of a chemical to exhibit “plug flow” during an Enhanced Oil Recovery simulation, particularly in a column experiment. “Plug flow” is the ideal scenario for crude oil mobilization because in a plug flow regime the chemical-EOR phase forms a strong interfacial boundary with the imbibed crude oil and displaces the oil from the column, bottom to top, in a manner similar to a piston moving through a cylinder. The effects of preferential flow paths and viscous fingering are mitigated during plug flow, and the residual Original Oil In Place (OOIP) left behind in the porous media is minimized. An investigation of immiscible foam flooding in the presence of various surfactants and electrolytes, but without any added nanoparticles, was recently conducted by Hosseini-Nasab and Zitha. This research indicates that co-injection of gas with the surfactant and cosolvent solution

could mobilize an additional 33% of OOIP compared to experiments involving waterflooding alone (Hosseini-Nasab & Zitha, 2017).

Some common themes uniting much of the literature on chemical-EOR include the improvement of bulk foam stability (foam volume over time), wettability alteration causing an increase in hydrophilicity and a decrease in oleophilicity, reinforcement of the displacement front resulting in lessened effects of preferential flow paths and viscous fingering, and finally a greater percent of Original Oil In Place (OOIP) mobilized over the secondary (waterflooding) recovery baseline volume. Optimal concentrations of surfactant and NPs have been shown to exist for the different chemical-EOR, aqueous dispersion, and waterflooding-preceded-chemical-EOR injection systems.

#### Rationale

This research project seeks to combine many of the useful characteristics of prior research, while also expanding the knowledge base of outcomes associated with the injection of different nanoparticle and surfactant systems. For example, previous experiments have been conducted on low-salinity waterflooding (Hussain et al., 2013). Prior work has also been done on the synergistic impact of silica nanoparticles with a cationic surfactant (Binks, Kirkland, & Rodrigues, 2008), as well as on the impacts of waterflooding and chemical-EOR in a sandpack (Dong, Ma, & Liu, 2009). Experiments involving Berea sandstone cores pre-saturated with crude oil and placed in a jar with a silica nanofluid dispersion have shown the effectiveness of the dispersion in removing 50% or more of the crude oil from the column over the course of one to two weeks (Zhang, Nikolov, & Wasan, 2014). This body of previous work is described in partial

detail above to illustrate the breadth of recent work on EOR, particularly in the presence of NPs and or surfactant.

The experiments and analysis completed over the course of this project test a unique combination of EOR parameters, including oil mobilization from a sandpack, oil mobilization due to waterflooding with a low salinity (1 wt% NaCl) brine, sequenced and non-sequenced injection techniques and their impact on oil displacement efficiency, and the effect of various concentrations of silica NPs on chemical-EOR.

It is the endeavor of this paper and the associated research to accurately construct a microcosm of an oil wet subsurface petroleum reservoir system and associated exploitation techniques. According to the literature (United States Department of Energy), common practice within the petroleum industry is to first extract any oil available through primary oil recovery. Primary oil recovery is a process that simply involves pumping oil directly out of the subsurface (without the fluid or chemical/thermal injection processes associated with secondary and tertiary recovery). Natural gravity drainage due to pressure head is also responsible for primary recovery processes. Unfortunately, the 10-25% of an oil field's Original Oil In Place (OOIP) that is extractable through primary oil recovery is insufficient to keep pace with growing demands. The declining availability of primary oil reserves is highly responsible for the advent of novel oil recovery techniques, including waterflooding (secondary oil recovery), and EOR (tertiary oil recovery). New drilling and extraction processes, such as horizontal drilling and hydraulic fracturing are examples of technologies developed to maximize the oil displacement from a formation. An additional 10-20% of crude oil is mobilized during secondary recovery (waterflooding), regardless of the salinity, pH, and physicochemical properties of the aquifer fluid used for waterflooding (Mid-Con Energy

Partners, LP, 2014). By calculating the percentage of oil extracted from a system over the secondary baseline cumulative recovery volume, the volumetric crude oil displacement can be evaluated and compared for various chemical-EOR systems.

Secondary recovery involves flushing the experiment column with 320 mL of 1 wt% NaCl brine in this research project. 1 wt% brine was selected primarily because the scientific community's understanding of chemical-EOR would significantly benefit from more research involving low salinity flooding of an oil-saturated sandpack, prior to injection of nanofluids or a control solution. Dissolved ions have been shown to alter permeability within a Berea sandstone, "by the lifting, migration and subsequent plugging of pores by fine particles" (Hussain et al., 2013). According to previous work, low salinity brine injections have proven productive in terms of mobilization of trapped crude oil reserves. This is because, "When injecting low salinity (LS) water, it is believed that destabilization of oil layers adhering to mineral surfaces could be a contributing mechanism to enhanced oil recovery (EOR)" (Johannessen & Spildo, 2013). Following waterflooding, an additional 30% or more of OOIP can be mobilized using tertiary recovery, or EOR. EOR consists of thermal, chemical, or gas injection, and implements a pumping well and an injection well for mobilizing trapped and often isolated droplets of heavily-imbibed crude oil.

## Objectives

The objective of the research is to demonstrate that SiO<sub>2</sub> NPs can be used with surfactants such as SDS, with a variety of processes, to change the wettability of systems from oil wet to water wet, allowing for a more efficient displacement of oil and consequently yielding significantly higher recovery of crude oil. By observing the impact of SDS surfactant and various NP concentrations on oil recovery operations above the secondary baseline recovery volume

(simulated by injecting 320 mL of brine into the system), techniques for Enhanced Oil Recovery can be optimized for different subsurface environments and injection scenarios.

The implementation of two different injection schemes, sequencing and non-sequencing, allows for an expansion of the knowledge that is accessible from the dataset. The traditional sequencing technique is largely implemented by the petroleum industry during Enhanced Oil Recovery and hydraulic fracturing operations. Sequencing is quite prevalent and widespread due to the lack of cost associated with extracting and reinjecting whatever brine or aquifer fluid is already present in order to displace an additional volume of oil above the Original Oil In Place (OOIP). This secondary recovery process is not intended to alter the physical or chemical properties of the porous media, but rather to mobilize an additional volume of crude oil in a cost-effective manner. By preceding the  $\text{SiO}_2$  / SDS – based aqueous nanofluid injection with brine injection, the researcher hopes to construct a comparative baseline, which should provide a comparable volume of cumulative oil recovery and a graphical relationship between fractional / cumulative recovery and volume of brine or EOR fluid injected. The data from the first 320 mL of injection in each sequenced injection experiment represent the same process of waterflooding, a common industry practice and an effective way to establish a baseline for oil recovery (Zargartalebi, Barati, & Kharrat, 2014). The average cumulative volume of oil recovery from the waterflooding experiments can be compared with the average cumulative volume of oil recovery from each  $\text{SiO}_2$  / SDS – based aqueous nanofluid system, and a percent change can be calculated to determine the percent increase in oil mobilized above baseline associated with each of the different silica nanofluid systems.

## MATERIALS AND METHODS

### Methodology

To maximize crude oil yield, different processes are implemented involving the type of chemicals injected for EOR and the sequence in which they are injected. Thus, in the petroleum industry, “Sequencing” indicates that Enhanced Oil Recovery is preceded by secondary oil recovery (waterflooding). In experiments designed to simulate *sequenced injection*, waterflooding precedes chemical-EOR (Figure 1). In experiments designed to simulate *non-sequenced injection*, EOR is commenced immediately following crude oil imbibement (Figure 2). Non-sequenced injection is hardly ever practiced at the field scale, due to the lack of cost associated with a preceding waterflooding event. However, this research includes a set of non-sequenced chemical-EOR experiment replicates to compare against the crude oil recovery from waterflooding and traditional sequenced injection. In the case of the brine used for waterflooding, as well as the 2 Critical Micelle Concentration (CMC) Sodium Dodecyl Sulphate (SDS) surfactant-in-brine control solution and the SiO<sub>2</sub> / SDS – based aqueous nanofluids, each fluid is injected in the amount of 320 mL. Volume of fluid injected over the course of an experiment is determined by labeling the sample tubes and timing the removal and replacement of each sample tube from underneath the effluent outlet. Each tube is labeled to indicate what chemical injection process it is associated with and numbered to indicate where in the sequence of sample tubes it falls. The sample tubes are also given a letter/number combination to correspond with which of the four columns was used to run the experiment and how many experiments had been conducted in that column previously, and silica concentration, timing, and chemical constituents involved in each injection event are recorded. 20 mL of effluent (oil/brine, oil/aqueous nanofluid phases) are collected in

each sample tube, so 16 sample tubes are used for each injection event (20 mL of effluent in each of 16 sample tubes equals 320 mL of fluid injected). Therefore, the sequencing experiments involve injection of a total of 640 mL of fluid (320 mL of the 1 wt % brine, followed by 320 mL of the EOR silica nanofluid or control solution), while the non-sequencing experiments involve injection of only 320 mL of fluid: the silica nanofluid or control solution. See Figure 3 below for a table cataloguing the chemicals and techniques involved in each pair of experiment replicates.

# Sequencing

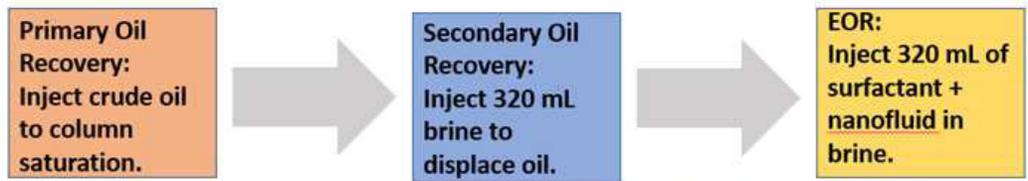


Figure 1 above is a flow chart of the processes involved in sequenced injection, along with photographs of the experiment setup during the different injection events.

# Non-Sequencing

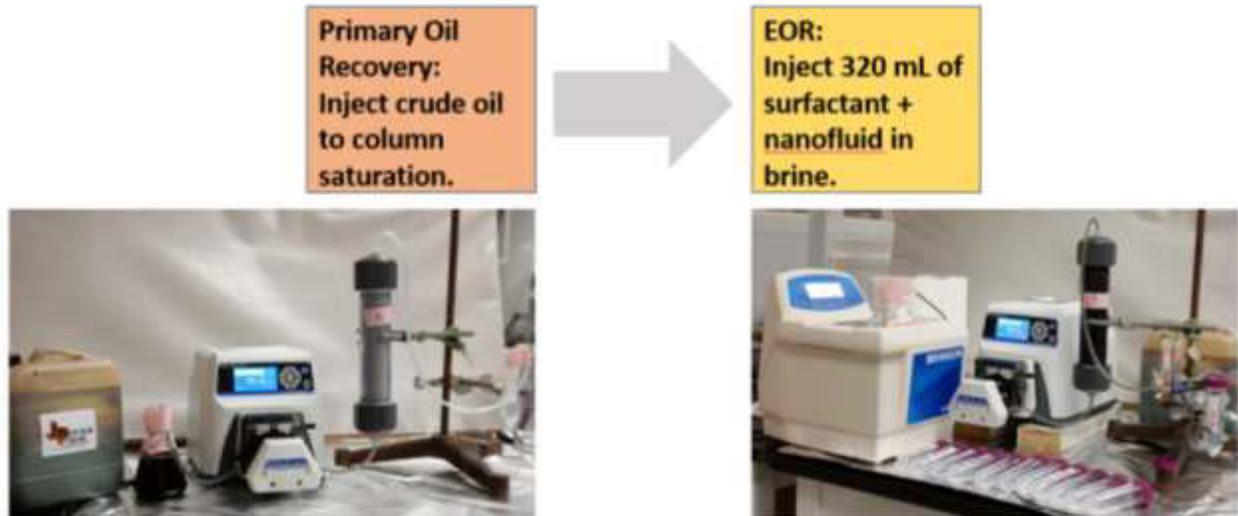


Figure 2 above is a flow chart of the processes involved in non-sequenced injection, along with photographs of the experiment setup during an EOR injection event.

1 wt % NaCl Brine + 2 CMC SDS (all systems)			
Silica NP wt % :	0	0.01	0.1
WTI Sequencing	☑ ☑	☑ ☑	☑ ☑
WTI Non-Sequencing	☑ ☑	☑ ☑	☑ ☑

Figure 3 above is a table consisting of a record of all the experiments conducted as part of this research project. The two processes tested were sequenced and non-sequenced injection to mobilize WTI crude oil in a fine grained sandpack. 1 wt% brine for waterflooding, as well as EOR fluids with 2 CMC SDS surfactant and 0 (the control), 0.01, and 0.1 wt% silica NPs were injected. Duplicate experiments of each injection scheme and NP system were conducted.

The purpose of the non-sequencing injection experiments is to observe the immediate impact of the SiO<sub>2</sub> / SDS – based aqueous nanofluid on the rate of oil displacement from the system. Based on previous research, it is expected that the SDS-in-brine control solution and the aqueous nanofluids will mobilize more crude oil from the fine sandpack than the 1 wt% brine alone. Prior research shows that SDS with NPs has effectively enhanced oil recovery compared to systems with surfactant or NPs alone, suggesting a synergistic relationship between silica NPs and SDS surfactant (Worthen et al., 2014). This research seeks to verify that SDS surfactant does effectively displace larger volumes of crude oil in the presence of increasing concentrations of silica NPs. See Figure 4 below for a flowchart representation of the experimental setup and procedure.

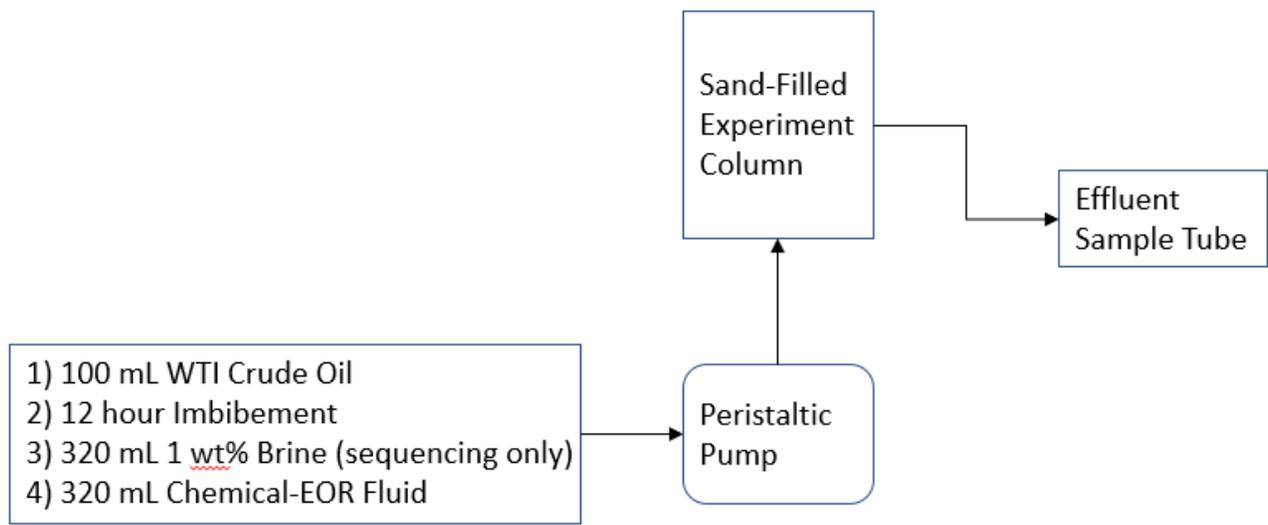


Figure 4 above is a flowchart rendering of the experimental setup and procedure.

The contact angle of the microscope glass slide-SiO<sub>2</sub> / SDS based aqueous nanofluid systems, a factor used to assess the alteration of the sand wettability to water, was estimated qualitatively by taking photographs of a drop of each aqueous solution or nanofluid. Microscope glass slides were used to simulate quartz silica grains for contact angle measurements. As seen in Photographs 1-4 below, the increasing concentrations of silica in suspension increase the contact angle between the nanofluid and the microscope glass slide. Zeta potential and flocculated aggregate size (particle size, or hydrodynamic diameter) were also measured using electrical conductance and Dynamic Light Scattering, respectively. Sandpack flooding column experiments test the impact of various nanofluids injected into an oil-saturated sandpack on the recovery of crude oil. Effective oil displacement by the SiO<sub>2</sub> / SDS – based aqueous nanofluids was monitored over time and expressed as a function of the number of pore volumes (PVs) of aqueous fluid injected.

The pictures below are of droplets of the aqueous solutions or chemicals used during waterflooding and chemical-EOR injection events during this research.

Photo 1 below is a droplet of the 1 wt% brine solution.



Photo 2 below is a droplet of the SDS-in-brine control solution.



Photo 3 below is a droplet of the Low concentration silica NP fluid.



Photo 4 below is a droplet of the High concentration silica NP fluid.



Following is a step-by-step description of procedures implemented during the experimentation and analysis phases:

1) A 25 cm long column (3.7 cm diameter) is filled with 520.5 g of 20/40 US Silica fine grained silica sand. The column is made of a heavy-duty transparent PVC material, with threads on both ends. The threads are wrapped with Teflon tape in order to prevent leakage, and a plastic plug is tightened on each end of the column. A small, threaded hole is drilled in the center of each of the end-plugs. Using a wrench, plastic hose barbs are gently tightened into the two holes, and these hose barbs are connected to the influent and effluent silicone Masterflex platinum-cured pump tubing which connects the crude oil/brine/aqueous nanofluid or control solution beaker to the peristaltic pump, to the experiment column, and finally to the effluent sample tube.

2) Aqueous suspensions are prepared with the following chemicals: 0, 0.01, or 0.1 wt% NPs, and 2 critical micelle concentrations (CMC) of sodium dodecyl sulphate (SDS) anionic surfactant with 1 wt% NaCl brine. To make 1 L of each solution, 10.101 g of NaCl, 4.758 g of SDS surfactant (2 CMC for 1 Liter of solvent), and 0, 0.10001, and 1.001 g of silica NPs are added to 1 Liter of de-ionized water (the three different masses of silica NPs result in 0, 0.01, and 0.1 wt% SiO<sub>2</sub>). After adding the solutes, a magnetic chemical mixer is used to dissolve the SDS and NaCl into solution over a 12-hour period. Next, a point-source sonicator is used to mix the silica NPs into a (relatively) homogeneous suspension. The point-source sonicator settings are as follows: Time-5 min, Power-40 W; Amplitude-45 (Huibers et al., 2017). During the experimental phase, all aqueous NP suspensions are placed in the bath sonicator immediately prior to the 320 mL EOR injection for both sequencing and non-sequencing experiments.

3) Using a peristaltic pump, at least 100 mL of West Texas Intermediate crude oil are injected into the column. One pore volume (PV) is  $297 \text{ cm}^3$  (the volume of the enclosed column) times a porosity of 0.30, or 89.1 mL. According to various computational methods, the PV of the column sandpack system is 78.75 mL (using the product of flow rate [mL/hr] and time taken to fully saturate the column [hr]), PV is 83.3 mL (using difference in mass [g] of the column before and after injection of deionized water), and PV is 87.73 mL (using difference in mass of a beaker before and after injection of de-ionized water from that beaker into the column sandpack).

4) At least 12 hours are required for the crude oil to fully imbibe on the porous media. During this time the experiment column should remain stationary and within a controlled environment.

5) 320 mL of 1 wt% NaCl brine are injected into the experiment column to simulate secondary oil recovery or waterflooding. Since one PV  $\sim$ 80-90 mL, 320 mL is  $\sim$ 3.5-4 PVs. 320 mL of brine and nanofluids are injected for both secondary oil recovery and chemical-EOR to ensure that three PVs is exceeded. All the experiment effluent sample tubes should be labeled prior to conducting any experiments. During experimentation, each effluent sample tube must be removed and replaced with a new sample tube every time 20 mL of brine or chemical-EOR fluid is injected into the column. This greatly facilitates accounting for the volume of fluid injected in the column during analysis.

6) 320 mL of 0, 0.01, or 0.1 wt% silica NP fluid are injected with 2 CMC of SDS surfactant in 1 wt% brine into column to simulate chemical-EOR.

7) The above process is repeated for each NP/surfactant system, omitting step five (secondary oil recovery or waterflooding). This will allow for a comparison between two processes: oil recovery-

over-baseline simulated by experiments in which EOR is preceded by waterflooding (sequenced injection), and oil recovery because of immediate EOR (non-sequenced injection).

8) Fractional and cumulative oil recovery rates are plotted up for the various NP/surfactant systems as a function of the number of pore volumes (PVs) injected. The percent of Original Oil In Place (OOIP) mobilized over the secondary recovery baseline volume, and the control surfactant-brine solutions, for both the sequenced and non-sequenced injection processes is calculated by dividing the difference between cumulative oil recovery for the control/waterflooding injection event and the chemical-EOR cumulative oil recovery by the control/waterflooding cumulative oil recovery. This fraction (or percent, if multiplied by 100) indicates the amount of OOIP displaced over the control system for each experiment replicate, or the average or experiment-specific secondary recovery baseline volume achieved during experimentation (see Table 1).

9) Important physicochemical properties of the nanofluids and control solution are measured, including the contact angle of the solution/suspension on a glass microscope slide substrate, zeta potential, pH, and hydrodynamic diameter (particle size of flocculated aggregates).

10) The data is analyzed to determine which experimental conditions most effectively maximize oil displacement.

#### Materials:

- West Texas Intermediate (light) crude oil
- 20/40 US Silica fine grained silica sand (porosity is 0.30)
- 25 cm cylindrical column (diameter is 3.7 cm, volume is 297 cm<sup>3</sup>) with threaded ends and plugs

- Hose Barbs
- Teflon Tape
- Cole-Parmer peristaltic pump
- Cole-Parmer silicone Masterflex platinum-cured pump tubing
- Silica nanoparticles (NPs)
- Sodium dodecyl sulfate (SDS) surfactant
- De-ionized Water (18.2 ohms)
- Sodium chloride to prepare 1 wt % NaCl brine solution
- Point-source Sonicator
- Bath Sonicator
- Mettler Toledo Benchtop pH Meter
- Brookhaven Instruments Corporation 90 Plus Particle Sizing Software
- Brookhaven Instruments Corporation Phase Analysis Light Scattering Zeta Potential Analyzer

## RESULTS

The results of these experiments indicate different optimal chemical-EOR techniques for sequencing and non-sequencing injection. When considering the most effective methods for presenting the crude oil displacement results, it becomes apparent that there are many aspects to each experiment, as well as points of comparison between the various SDS / aqueous nanofluid systems. Analysis of the results of the non-sequencing experiments is relatively straightforward. Because this process involves only the injection of chemical-EOR fluid, there is no baseline against which to compare the non-sequenced injection results. The cumulative volume and fractional recovery rate are measured over the course of the injection event, and then analyzed after completion of the experiment. It is worthwhile to note the percent change in cumulative oil displacement from system to system for the non-sequenced chemical-EOR experiments, so percent OOIP displaced above the control solutions' average is calculated in Table 1 for all systems. For non-sequenced experiments, the average of all cumulative crude oil volumes displaced during waterflooding in the sequenced experiments (40.33 mL) is used to calculate the percent OOIP over the average observed secondary baseline for each system. All the same calculations are performed for the sequenced experiments, except using the volumes of oil recovered over the control solution and baseline for the respective experiment replicate, instead of the average baseline oil recovery volume. A final tool for assessment of the performance of each SDS / aqueous nanofluid system in terms of crude oil displacement and recovery is the Efficiency Ratio. The Efficiency Ratio is simply the ratio between cumulative oil displacement by a particular system and the volume of fluid injected during that experiment. The purpose of this metric is to unilaterally evaluate and compare the effectiveness of each surfactant solution or

nanofluid. Because sequencing experiments involve a total injection of 640 mL of fluid, 640 is the denominator in these ratios. If instead, only the 320 mL involved in chemical-EOR during a sequencing experiment was used in this calculation, then only the volume of crude oil recovered *after* waterflooding could be used as the numerator. All in all, this changes the specific results insignificantly. Furthermore, the Efficiency Ratio is best interpreted broadly, as a rough indicator of the rate of valuable oil removed from a system to costly chemicals injected into that system.

Sequencing injection experiments demonstrate a complex relationship between silica NP concentration and cumulative oil displacement. In terms of volumetric oil recovery, the outcomes of the sequencing experiments show a wide range of outcomes between the replicates of various SDS / aqueous nanofluid systems. To most effectively compare the data, the fractional and cumulative volumetric results of each experiment are graphed as a function of pore volumes of brine or EOR fluid injected. First, six curves are plotted in the same space, with each curve corresponding to a different experiment and curves labeled with the specific SDS / aqueous nanofluid system injected during chemical-EOR (Figure 5).

Next, the results are averaged for each pair of experimental replicates associated with the same chemical-EOR system. Figure 6 shows the average of each of the two experimental replicates' results for the three silica nanofluid systems as a function of pore volumes of brine and chemical-EOR fluid injected. This averaged, or "normalized," result for the replicates of each of the three nanofluid system experiments shows the same general relationship between silica NP concentration and oil recovery volume for sequenced injection. The 0.01 wt% silica nanofluid performed slightly better than the other two systems during chemical-EOR following waterflooding for sequencing experiments. The low concentration (0.01 wt% NP) suspensions

displaced an average of 49.65 mL of West Texas Intermediate crude oil over the two experiment replicates, mobilizing an average of 15.05 mL of oil, or about 32.79% OOIP, more than the secondary recovery baseline achieved during waterflooding (Table 1). The control solution performed marginally worse than the low silica suspension, displacing an average of 13.55 mL of oil, or around 32.11% OOIP, over the secondary recovery baseline (Table 1). The high (0.1 wt% NP) concentration silica nanofluid mobilized just an average of 8.65 mL of oil, or around 30.69% OOIP, over the secondary recovery baseline (Table 1).

System	Cumulative Oil Displacement (ml)	% OOIP Displaced Over Control Solution	Secondary Baseline Volume (ml)	Volume of Oil Over Secondary Baseline (ml)	% OOIP Displaced Over Secondary Baseline	% OOIP Displaced by EOR over Control	Efficiency Ratio
<b>Sequencing</b>							
SOS + 1 wt% Brine	44.4	20.22	35.7	10.7	51.75		0.269
SOS + 1 wt% Brine	66.9	20.22	50.5	16.4	33.48		0.105
Average	55.65	0	42.1	13.55	52.11		0.087
Standard Deviation	15.91		11.88	4.03			
0.01 wt% Silica NPs	56.1	0.81	38.9	17.2	44.23		0.288
0.01 wt% Silica NPs	73.3	81.72	60.4	12.9	21.36		0.115
Average	84.7	18.26	49.65	25.05	52.78	11.07	0.101
Standard Deviation	12.16		15.20	3.04			
0.1 wt% Silica NPs	34.6	-37.85	25	9.6	38.40		0.094
0.1 wt% Silica NPs	41.2	-25.97	38.5	7.7	22.99		0.094
Average	37.8	-31.90	29.25	8.65	50.69	-38.16	0.099
Standard Deviation	4.67		6.01	1.84			
<b>Non-Sequencing</b>							
			Secondary Baseline Volume (ml)	Volume of Oil Over Average Baseline (see below) (ml)	% OOIP Displaced Over Average Baseline		
SOS + 1 wt% Brine	34.8	-2.95	(Not Applicable)	5.53	-13.72		0.109
SOS + 1 wt% Brine	56.9	2.95		-5.43	-8.51		0.115
Average	35.85	0.00		-4.48	-11.17		0.112
Standard Deviation	1.48			1.48			
0.01 wt% Silica NPs	36.2	1.00		-4.13	-10.25		0.118
0.01 wt% Silica NPs	56	58.21		25.67	38.84		0.175
Average	46.1	18.59		5.77	14.30	28.59	0.144
Standard Deviation	14.00			14.00			
0.1 wt% Silica NPs	78.6	119.22		38.27	94.88		0.246
0.1 wt% Silica NPs	76.4	113.11		36.07	89.42		0.239
Average	77.5	116.18		37.17	92.15	116.18	0.242
Standard Deviation	1.56			1.56			
			Average Baseline (ml):	40.33			

Table 1 above is a spreadsheet compilation containing all the relevant calculations and data associated with this research. Average Baseline is an average of all the cumulative oil volumes displaced by 1 wt% NaCl brine during waterflooding. Efficiency Ratio here is the ratio between the volume of fluid injected into a system and the cumulative volume of oil recovered from that system. For more information regarding the calculations or data, please contact the authors at: [cdarnau@clemsn.edu](mailto:cdarnau@clemsn.edu) or [brightinblanton@gmail.com](mailto:brightinblanton@gmail.com).

The key insight from these sequenced experiments is that, for all three chemical-EOR systems, an additional 30% or more of OOIP is mobilized over the respective average secondary baseline recovery achieved for the pairs of experimental replicates. Notice how the fractional crude oil recovery rate spikes shortly after transitioning from brine injection to chemical-EOR in Figures 7 and 8 below. These sequenced injection results indicate that low (magnitude of 0.01 wt% silica) concentration nanofluids perform similarly to the 2 CMC SDS in brine control solution in terms of cumulative oil displacement. The high (magnitude of 0.1 wt% silica) concentration nanofluids performed distinctly worse in terms of the average volume of oil recovered over baseline, but only around 2% worse in terms of the difference in percent of OOIP removed over average secondary baseline. The surprisingly low effectiveness of 0.1 wt% silica nanofluid to displace crude oil during chemical-EOR in sequencing experiments distinctly contrasts with the relationship observed during the non-sequencing experimental results (see below). There are several possible explanations for this behavior. The most likely explanation for low mobilization of oil over the secondary baseline by the high concentration silica nanofluid is that the preceding waterflooding event introduced enough sodium and chloride ions to greatly increase the rate of flocculation of suspended particles. This flocculation of silica NPs and removal of salt from solution has been shown to possibly enable a positive reinforcement cycle of flocculation of NP aggregates and solutes, removal from suspension and solution, and growth of large hydrodynamic diameter masses of previously well-dispersed material (Worthen et al., 2014).

# Sequencing-Cumulative Oil Displacement (all data)

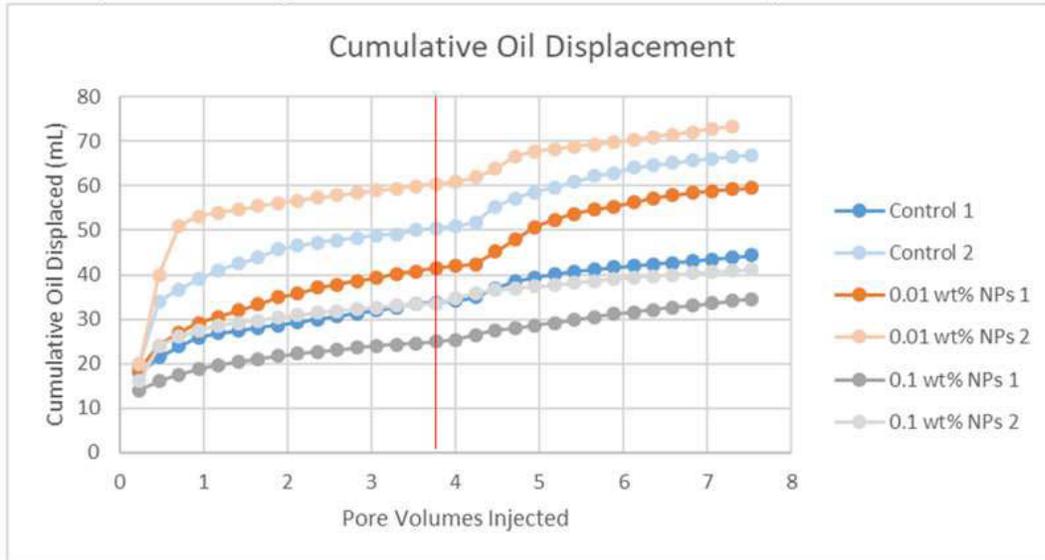


Figure 5 above shows results of all of the experiments conducted, as a function of pore volumes injected, consisting of 320 mL of injection of 1 wt% brine, followed by 320 mL injection of the control solution, low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

# Sequencing-Cumulative Oil Displacement (normalized result)

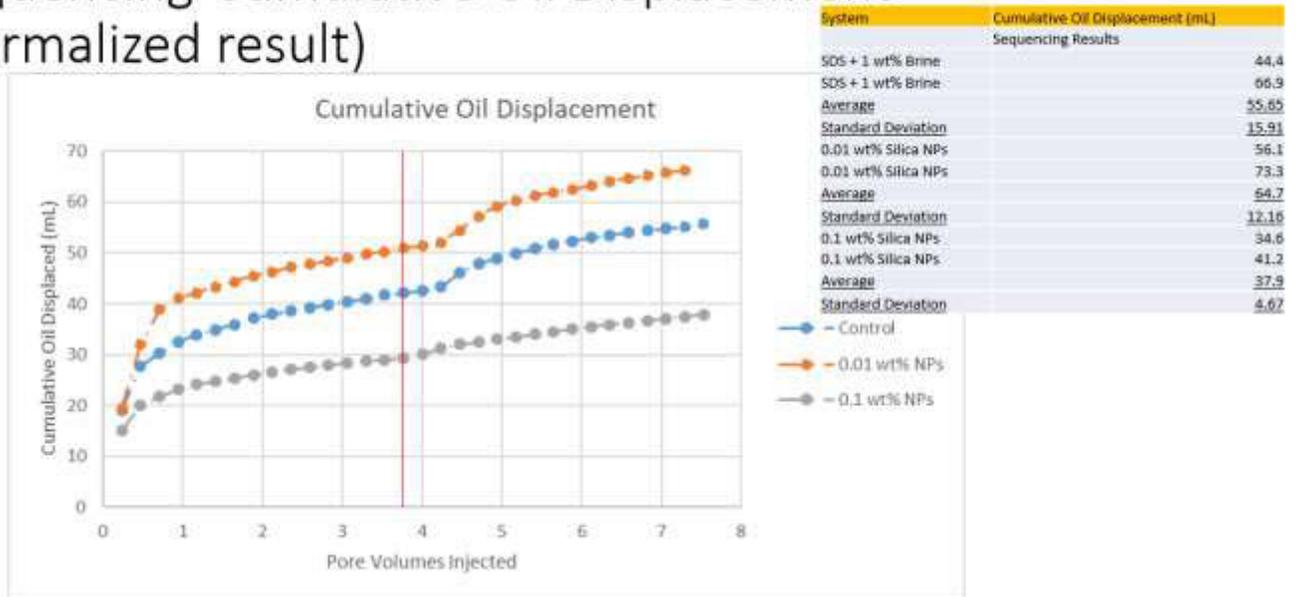


Figure 6 above shows normalized results, as a function of pore volumes injected, of the experiment consisting of 320 mL of injection of 1 wt% brine, followed by 320 mL injection of the control solution, low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

# Sequencing-Fractional Oil Recovery (all data)

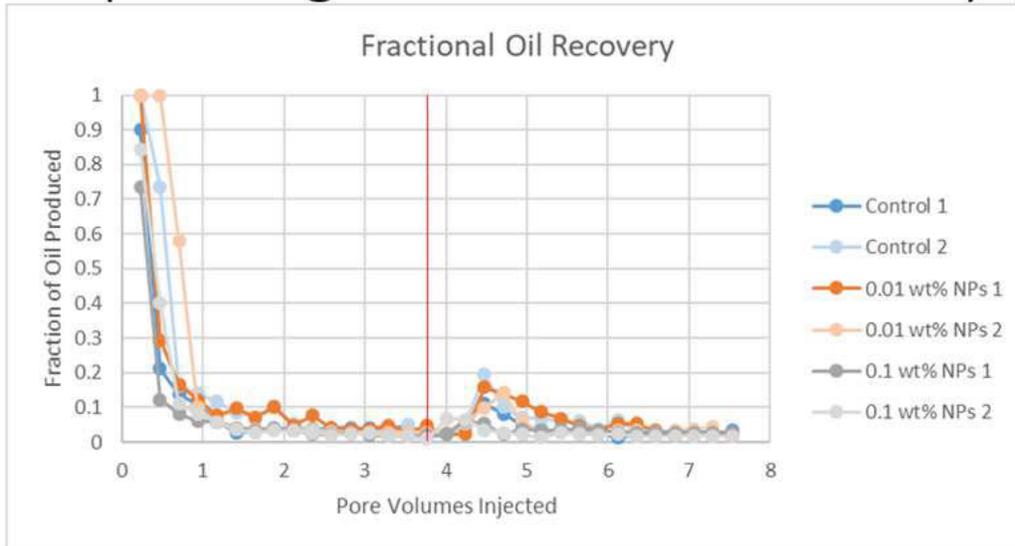


Figure 7 above shows fractional oil recovery results of all of the experiments conducted, as a function of pore volumes injected, consisting of 320 mL of injection of 1 wt% brine, followed by 320 mL injection of the control solution, low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

# Sequencing-Fractional Oil Recovery (normalized result)

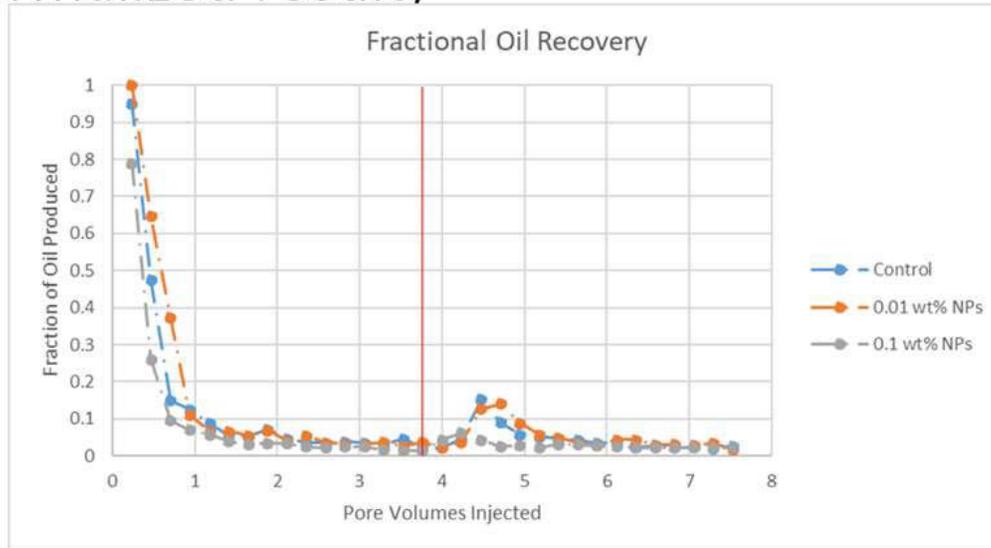


Figure 8 above shows normalized fractional oil recovery results, as a function of pore volumes injected, of the experiment consisting of 320 mL of injection of 1 wt% brine, followed by 320 mL injection of the control solution, low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

Non-sequenced injection showed a direct relationship between silica NP concentration and cumulative oil recovery (Figures 9 and 10). The cumulative volumetric oil displacement results for each non-sequenced injection experiment were very similar for each pair of replicates of SDS brine or nanofluid systems. For example, apart from the non-sequencing experiments involving low concentrations of silica NPs (0.01 wt%), the cumulative oil displaced by the two 0.1 wt% silica nanofluid systems and the two control solutions in each experiment was less than 5 mL different from the volume displaced by the respective experimental replicate for those two NP systems (Figure 9). In other words, the standard deviations between the final cumulative oil displaced by each pair of control and 0.1 wt% silica nanofluids is approximately 1.5 (around 1.48 for the pair of SDS-in-brine control solutions, and around 1.56 for the pair of 0.1 wt% silica nanofluids). The single outlier of the experimental dataset of non-sequencing injection experiments is one of the 0.01 wt% NP suspensions, which displaced only 36.2 mL of oil while the same nanofluid system displaced 56 mL of oil in another experimental replicate. The standard deviation between the pair of 0.01 wt% nanofluid suspensions' cumulative oil displacement volumes is 14. The two experiments involving SDS-in-brine control solution injection displaced 34.8 mL and 36.9 mL of crude oil, and the pair of experiments involving 0.1 wt% silica nanofluid injection displaced 78.6 mL and 76.4 mL of oil (Table 1). Overall, the fractional crude oil recovery rate is directly related to the concentration of silica NPs in these non-sequenced injection experiments (Figures 11 and 12). See Table 1 for a statistical overview of each pair of experimental replicates, including averages, standard deviations, performance over secondary recovery baseline, and performance over control solution.

# Non-Sequencing-Cumulative Oil Displacement (all data)

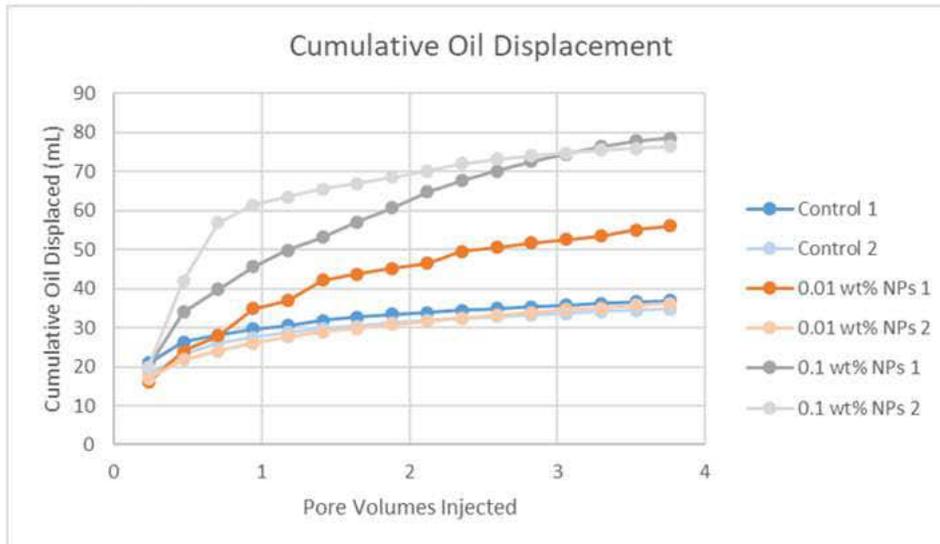
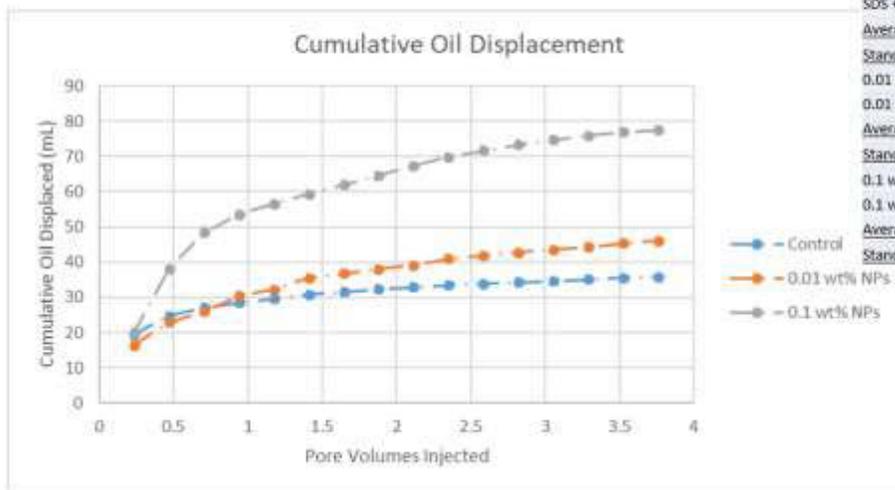


Figure 9 above shows results of all of the experiments conducted, as a function of pore volumes injected, consisting of 320 mL of injection of the 1 wt% brine + 2 CMC SDS surfactant solution, as well as injection of the low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

# Non-Sequencing-Cumulative Oil Displacement (normalized result)



System	Cumulative Oil Displacement (mL)
Non-Sequencing Results	
SDS + 1 wt% Brine	34.8
SDS + 1 wt% Brine	36.9
Average	35.85
Standard Deviation	1.48
0.01 wt% Silica NPs	36.2
0.01 wt% Silica NPs	56
Average	46.1
Standard Deviation	14.0
0.1 wt% Silica NPs	78.6
0.1 wt% Silica NPs	76.4
Average	77.5
Standard Deviation	1.56

Figure 10 above shows normalized results, as a function of pore volumes injected, of the experiment consisting of 320 mL of injection of the 1 wt% brine + 2 CMC SDS surfactant solution, as well as injection of the low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

# Non-Sequencing-Fractional Oil Recovery (all data)

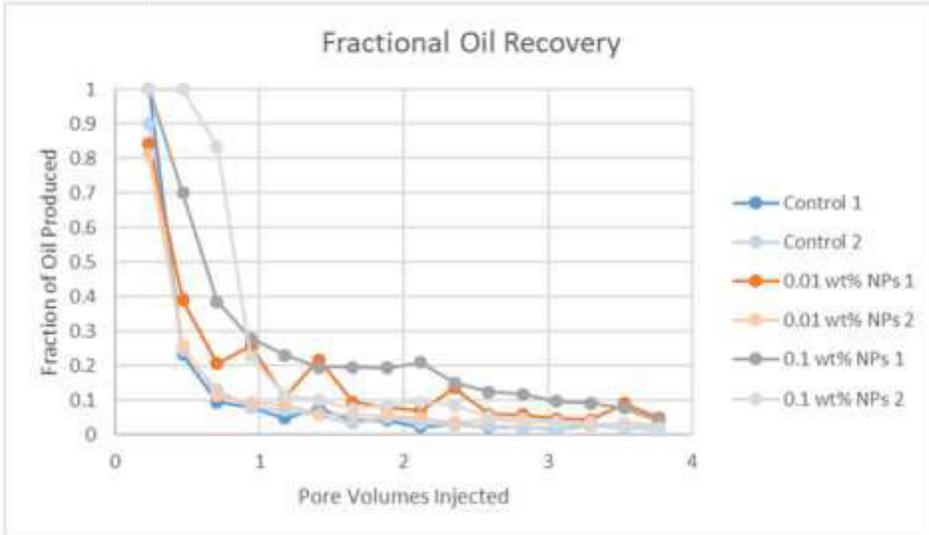


Figure 11 above shows fractional oil recovery results of all of the experiments conducted, as a function of pore volumes injected, consisting of 320 mL of injection of the 1 wt% brine + 2 CMC SDS surfactant solution, as well as injection of the low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

# Non-Sequencing-Fractional Oil Recovery (normalized result)

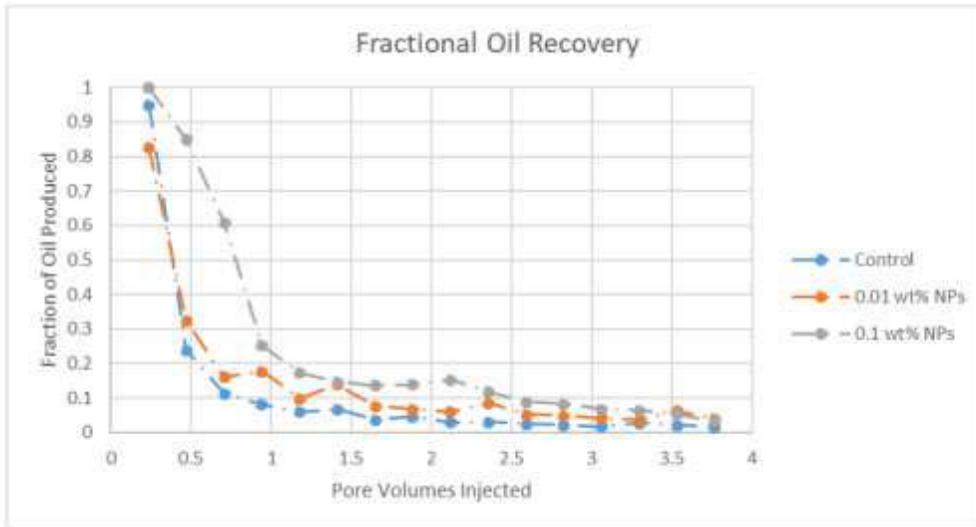


Figure 12 above shows normalized fractional oil recovery results, as a function of pore volumes injected, of the experiment consisting of 320 mL of injection of the 1 wt% brine + 2 CMC SDS surfactant solution, as well as injection of the low (0.01 wt%) concentration NP suspension, and high (0.1 wt%) concentration NP suspension.

When comparing experimental results from various oil recovery simulations generated during similar research projects, or when attempting to use the model presented above to predict the behavior of a natural system, direct comparisons between cumulative and fractional oil recovery outputs may be difficult. This is because it is problematic to interpret laboratory scale results or extrapolate chemical-EOR productivity at the field scale when fractional and cumulative oil recovery rates are presented as a function of volume of fluid injected. While a relatively small volume of fluid will displace a relatively large volume of crude oil in the experiment column, at the field scale the same exact volume of chemical-EOR or waterflooding fluid injected would likely result in an insignificant amount of crude oil mobilized. To correct for this, and to make the experimental results more practically relevant and comparable to other research and systems, all results are plotted as a function of pore volumes injected. The number of PVs injected is determined simply by dividing the volume of fluid injected (mL) by the PV of the sand-filled experiment column system (around 85 mL; see Methods section above). To facilitate comparisons between these results and other experimental data, as well as to ease applications of these results in the field, all cumulative and fractional oil recovery graphs are plotted as a function of the number of PVs of chemical-EOR fluid injected.

## DISCUSSION

The experimental results described above demonstrate a complex relationship between silica NP concentration and crude oil mobility enhancement. As described in the Worthen (2014) paper, the presence of salt in an aqueous silica nanofluid can act as an impediment to crude oil displacement, mobilization, and recovery. In the Worthen research, emulsions (immiscible dispersions of oil and water) were generated to observe the impact of silica NPs on the

coalescence of oil droplets. Instead of conducting flooding experiments in porous media, the Worthen et al. project seeks to identify the chemical mechanisms responsible for facilitating the coalescence of two distinct phases within an insoluble mixture, or emulsion, by observing the behavior of the liquids within a test tube. Ideally, the emulsion will separate into its component phases naturally, due to differences in properties such as polarity and density. However, this is often not the case, especially when dealing with a heavily-imbibed contaminant plume or petroleum reservoir in porous media. In order to access volumes of oil trapped in the subsurface, it is useful to enable the coalescence of droplets of the liquid by introducing new chemicals to the system. Worthen et al. conducted experiments to determine the impact of silica NPs on this coalescence. Because salt is a common dissolved mineral found in the brackish waters of the deep subsurface, the Worthen research group looked at the impact of NaCl on the behavior of their emulsions, comparing the coalescence of phases in emulsions with de-ionized water and synthetic seawater with a variety of oil/water ratios. The team observes that “salt is shown to produce weak NP flocculation, which increases the hydrodynamic forces for NP adsorption relative to electrostatic repulsion and also provides a more effective barrier to droplet coalescence” (Worthen et al., 2014). Essentially, the dissolved salt ions tip the balance away from electrostatic repulsion towards hydrodynamic adsorption of suspended solids, a process which decreases the effectiveness of the NPs and surfactant in flushing the oil droplets from the aqueous phase. NPs and surfactant perform best when they are well mixed and dissolved (respectively) within the aqueous phase, and subsequently “sweep” oil droplets out of the aqueous phase and into another distinct, coalescing oil phase.

Although the emulsions generated by the Worthen research team are mixed in test tubes, rather than in porous media as would be seen in the natural environment, the impact of the salt as a deterrent to oil coalescence is a valuable takeaway considering how common brine and brackish water are around contaminant oil plumes and petroleum reservoirs. Another paper, described in the Rationale section above, argues that low salinity waterflooding, high flow velocity, pH, and temperature may all contribute to a reduction in water permeability due to an activation of fine particle migration. The article states, “Numerous methods of fines immobilization by chemical treatment or nano-particle injections are presently under intensive development” (Hussain et al., 2013). Although the presence, behavior, or characteristics of these fine particles were not considered within the initial scope of this research project, the Hussain article provides an excellent segue to the core flooding experiments described above by positing that NP injection can immobilize fine particles, allowing them to clog flow paths in the porous media through which water would otherwise pass, preserving a low relative water permeability, and increasing oil recovery. The Hussain paper does comment on the ambiguity present across the experimental results of various papers, noting that some researchers have observed fines migration in response to low salinity waterflooding while others have not. The exact impact of fine particles on EOR productivity is undetermined, although the use of saltwater brine for waterflooding may certainly influence fine particle mobility and thus oil recovery.

Previous research projects have sought to quantify the production results of EOR experiments in different ways. Most commonly, oil recovery is presented as a function of pore volumes of waterflooding or chemical-EOR fluid injected. As stated earlier, plotting results as a function of PVs of fluid injected allows for the results of various experimental configurations to be

compared side-by-side. Also, experimental results can be easily scaled up to the field scale when considering the productivity of an oil field in terms of PVs of fluid injected. For cumulative oil recovery results, it is difficult to extrapolate from volumetric oil recovery at the experimental scale to volumetric oil recovery at the field scale because differences in oil properties such as imbibement, density, viscosity, etc., as well as subsurface properties including porosity, permeability, and temperature all contribute to the productivity of an oil field. Still, it is worthwhile to consider the relative cumulative volumetric oil recovery of various chemical-EOR systems and presenting this data as a function of PVs injected facilitates a comparison between the results of the experiments conducted during this research project and those of other experimenters. Fractional oil recovery rates are more apt for comparison between different chemical-EOR systems and research projects, as fractional oil recovery presents a ratio of the volume of crude oil recovered to total volume of liquid recovered. At the laboratory scale, 3 PVs of fluid injected would be around 255 mL (for this research project), and a fractional oil recovery of 0.2 would imply 4 mL of oil and 16 mL of the aqueous phase recovered in a particular 20 mL effluent sample tube. At the scale of an oil field, 3 PVs of fluid injected could be hundreds of thousands to millions of liters, while a fractional oil recovery rate of 0.2 could mean 4,000 liters of crude oil and 16,000 liters of the aqueous phase recovered over the course of an injection event. Of course, the numbers given for the oil field example above are completely arbitrary, but the fact remains that the fractional oil recovery rates presented as a function of PVs of injected fluid are readily scaled up to predict the behavior of natural systems based on laboratory observations.

## CONCLUSIONS

The results of these experiments indicate that a low concentration of silica NPs does enhance the oil recovery process with 2 CMC of SDS surfactant in 1 wt% NaCl brine during sequenced injection experiments. An increased fractional recovery rate and cumulative volume of oil was produced from a column sandpack because of the 0.01 wt% silica NP fluid injection. For experiments in which EOR is preceded by waterflooding (sequenced injection), the 0.01 wt% silica nanofluid chemical-EOR process produced the optimal (greatest crude oil over baseline) result. When compared to the secondary baseline recovery and the control solution, the 0.01 wt% silica NP suspension increased the volume of oil displaced the most. However, for experiments in which non-sequencing injection procedures were implemented, there was a direct relationship between the wt% concentration of silica NPs in the chemical-EOR nanofluids and cumulative oil displacement. These non-sequencing results can be compared independently with one another to provide insight on the immediate impact of various concentrations of silica nanofluids on the subsurface environment. Based on these non-sequenced results alone, it appears that average volume of oil displaced is most for the 0.1 wt% silica nanofluid, oil displacement is intermediate for the 0.01 wt% silica nanofluid, and the 2 CMC SDS in 1 wt% NaCl brine control solution performed the worst. There are a few possible explanations for why the highest concentration of SiO<sub>2</sub> NPs performed so well in non-sequenced injection experiments but was surpassed by the 0.01 wt% silica nanofluid in terms of productivity in sequenced injection experiments. The Worthen et al. (2014) article provides a logical explanation for this, describing the mechanisms through which saline water initiates flocculation and aggregation of particles (Worthen et al., 2014). The Hussain article (2013) implies greater complexity in the relationship between salt

concentration and crude oil mobility, by describing the impacts of physical and chemical properties on the displacement of fine sediment particles. Fine sediment particles have been shown to alter the water permeability of the subsurface by clogging flow paths through which water would otherwise pass. Regardless of the mechanisms responsible for the poor performance of 0.1 wt% silica nanofluid in sequencing injection, at the scale of an oil field the high concentration  $\text{SiO}_2$  aqueous NP suspension is neither practical nor efficient for the sequenced injection regime that is predominantly employed by the petroleum industry. Due to the very low cost of extracting and re-injecting brine for waterflooding, sequenced injection appears to be a surefire technique for minimizing cost and maximizing crude oil displacement for petroleum engineering applications. Furthermore, under a sequenced injection scenario the low concentration silica nanofluid is optimal for oil mobilization, due to the caveats associated with the injection of brine during waterflooding described by Worthen et al. and Hussain et al. in their research on the behavior of emulsions and porous media (respectively) in a saline environment. Injecting a lower concentration silica nanofluid reduces the (already low) cost of adding additional NPs to the chemical-EOR fluid. When considering the costs and benefits of implementing these injection strategies at the scale of an oil field, the additional expense of increasing the order of magnitude of NP concentration is likely significantly greater than the expense associated with a preemptive waterflooding event.

Future applications of this research involve testing oils with different properties such as viscosity and density, including Nigerian heavy Antan, Brentheimer, and Lloydminster. The combination of WTI crude oil and 20/40 silica sand with various chemical-EOR systems produced the specific set of results described earlier in this paper, but it is very likely that these

experiments, if repeated, would result in slightly different fractional and cumulative crude oil displacement. As seen in Table 1, every pair of experimental replicates was responsible for slightly different levels of cumulative oil displacement. Heterogeneities within the column sandpack, including preferential flow paths, macropore flow, varying degrees of compression and compaction, and different degrees of crude oil imbibement may all contribute to variability between the results of experiments subjected to seemingly identical conditions. Heterogeneities within the porous media are especially responsible for the behavior of different systems, as even though 520.5 g of sand are added to each column, the orientation, packing, and permeability/hydraulic conductivity characteristics of each sandpack system are as unique as the three-dimensional geometry of the volume of sand grains within. For this reason, nanofluids with higher and lower NP concentrations could also be studied for applications with different physical and chemical properties of the reservoir, various crude oil characteristics, and other types of porous media. A broader range of experimental concentrations of silica NPs would likely provide a more robust data set for analysis. Other silica NP concentrations may prove optimal for chemical-EOR of types of crude oil and porous media not considered within the scope of this research project. Testing different surfactants and different types of NPs, such as aluminum oxide, nanocellulose and quantum dots, in the chemical-EOR fluid may also provide relevant results. Silica NPs were used in this paper due their low cost and widespread availability. Based on the results of the experiments described above, as well as the many other similar projects across the scientific community, there are limitless variations and opportunities for applying chemical-EOR to increase the productivity of oil fields within the constraints of the natural environment.

## APPENDIX

Solution/Suspension	pH						
<b>Batch 1</b>		System	Average pH	pH Standard Deviation	System	Cumulative pH Average	Cumulative pH Standard Deviation
Control	6.99				Brine	7.00	0.01
Control	6.17				Control	5.97	1.34
Control	6.16	Control	6.44	0.48	0.01 wt% NP	4.13	0.23
0.01 wt% NP	4.01				0.1 wt% NP	4.33	0.33
0.01 wt% NP	4.01						
0.01 wt% NP	4.01	0.01 wt% NP	4.01	0			
0.1 wt% NP	4.36						
0.1 wt% NP	4.44						
0.1 wt% NP	4.52	0.1 wt% NP	4.44	0.08			
<b>Batch 2</b>							
Control	6.99						
Control	6.19						
Control	6.18	Control	6.45	0.46			
0.01 wt% NP	4.01						
0.01 wt% NP	4.01						
0.01 wt% NP	4.01	0.01 wt% NP	4.01	0			
0.1 wt% NP	4.01						
0.1 wt% NP	4.01						
0.1 wt% NP	4.01	0.1 wt% NP	4.01	0			

Table 2 above contains pH measurements, with cumulative averages and standard deviations for each system, collected using a Mettler-Toledo Benchtop pH Meter.

Solution/Suspension	pH			
<b>Batch 3</b>		<b>System</b>	<b>Average pH</b>	<b>pH Standard Deviation</b>
1 wt% Brine	6.99			
1 wt% Brine	6.99			
1 wt% Brine	6.99	<b>1 wt% Brine</b>	6.99	0
Control	3.85			
Control	4.03			
Control	4.13	<b>Control</b>	4.00	0.14
0.01 wt% NP	4.46			
0.01 wt% NP	4.48			
0.01 wt% NP	4.49	<b>0.01 wt% NP</b>	4.48	0.02
0.1 wt% NP	4			
0.1 wt% NP	4.06			
0.1 wt% NP	4.29	<b>0.1 wt% NP</b>	4.12	0.15
<b>Batch 4</b>				
1 wt% Brine	7			
1 wt% Brine	7			
1 wt% Brine	7	<b>1 wt% Brine</b>	7	0
Control	6.99			
Control	6.99			
Control	6.99	<b>Control</b>	6.99	0
0.01 wt% NP	4.01			
0.01 wt% NP	4.01			
0.01 wt% NP	4.01	<b>0.01 wt% NP</b>	4.01	0
0.1 wt% NP	4.74			
0.1 wt% NP	4.74			
0.1 wt% NP	4.75	<b>0.1 wt% NP</b>	4.74	0.01

Table 3 above contains pH measurements collected using a Mettler-Toledo Benchtop pH Meter.

System	Average Hydrodynamic Diameter (nm)
<b>Brine</b>	<b>Not Applicable (no suspended solids).</b>
<b>Control</b>	<b>Not Applicable (no suspended solids).</b>
HighNano1 Average	254.8
HighNano2 Average	239.3
HighNano3.1 Average	196.50
HighNano3 Average	197.3
<b>High Nano Standard Deviation</b>	<b>29.64</b>
<b>High Nano Cumulative Average</b>	<b>221.98</b>
LowNano1 Average	293.5
LowNano2 Average	230.7
LowNano3.1 Average	220.2
LowNano3 Average	239.3
<b>Low Nano Standard Deviation</b>	<b>32.66</b>
<b>Low Nano Cumulative Average</b>	<b>245.93</b>
System	Zeta Potential Average (mV)
Brine1 Average	-0.15
Brine2 Average	-0.01
<b>Brine Standard Deviation</b>	<b>0.10</b>
<b>Brine Cumulative Average</b>	<b>-0.08</b>
Control1 Average	-4.18
Control2 Average	-0.15
Control3 Average	-2.45
<b>Control Standard Deviation</b>	<b>2.02</b>
<b>Control Cumulative Average</b>	<b>-2.26</b>
HighNano1 Average	1.15
HighNano2 Average	-0.25
HighNano3 Average	0.24
<b>High Nano Standard Deviation</b>	<b>0.71</b>
<b>High Nano Cumulative Average</b>	<b>0.38</b>
LowNano1 Average	-0.69
LowNano2 Average	2.91
LowNano3 Average	-0.58
<b>Low Nano Standard Deviation</b>	<b>2.05</b>
<b>Low Nano Cumulative Average</b>	<b>0.55</b>

Table 4 above contains average Hydrodynamic Diameters (nm) for each batch of chemicals, as well as a cumulative average Hydrodynamic Diameter for each system tested. Also, the table contains average Zeta Potentials (mV) for each batch of chemicals and a cumulative average Zeta Potential for each system tested. The data corresponds to outputs from the Brookhaven Instruments Corporation 90 Plus Particle Sizing Software and the Brookhaven Instruments Corporation Phase Analysis Light Scattering Zeta Potential Analyzer associated with each of the solutions and suspensions implemented during waterflooding or chemical-EOR during this research.

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