PORE-SCALE OBSERVATIONS OF THE EFFECT OF SURFACE TREATED NANOPARTICLES ON DRAINAGE PROCESSES

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ABSTRACT
In this study we observe, using pore scale X-ray micro-CT imaging and advanced petrophysical analysis, how surface treated silica nanoparticles improve sweep efficiency of n-octane in drainage corefloods. Specifically, upon injection of n-octane into a brine saturated core, preferential flow paths are observed and attributed to both viscous instability and rock heterogeneity; when the displaced phase contains a modest volume of nanoparticles, the same preferential flow paths are suppressed resulting in higher overall octane sweep efficiency. Grain analysis on microCT images of the core confirms that the flow paths are governed by pore scale heterogeneity. We argue nanoparticle stabilized non-wetting droplets are formed during the displacement, and work to block pores in high permeability regions and divert flow to low permeability regions thus improving overall volumetric sweep efficiency.

INTRODUCTION
Immiscible displacements of a wetting fluid by a less viscous non-wetting fluid within a porous medium often results in the injected fluid moving in preferential flow paths and with poor sweep efficiency. These preferential paths, or fingers, occur because of viscous instability, and are exacerbated by any natural heterogeneity in the medium. This problem is ubiquitous through many subsurface displacement processes.

For example, in gas EOR, poor sweep efficiency and early breakthrough of injected gas results in sub-optimal incremental oil production and unnecessary gas cycling. In geologic carbon sequestration, CO_2 storage volumes and security are not maximized when CO_2 takes preferential flow paths within saline aquifers. Other examples include water injection in oil-wet reservoirs and leakoff of energized fracture fluids into natural fractures.

To this end, many solutions have been offered to remediate this problem. Theoretically, the simplest physical way is by viscosifying the invading fluid through the addition of additives – this is done often in the oil patch by adding polymer to water floods. However there are no effective viscosifiers for gases and other non-aqueous phase liquids. Instead, additives added to the invading aqueous phase can cause the invading fluid to foam or emulsify when in contact with non-aqueous phase. Thus increasing the invading fluid's effective viscosity by increasing the fluid-fluid interface area in the porous media and adds resistance to the flow.

Most of the additives suggested have been surfactants, but recently it has been shown that, when suitable, surface-treated nanoparticles are added to the brine, the resultant CO_2/brine mixture can foam. It has been conclusively determined that foaming occurs when two fluids are co-injected through a porous medium (Aroonsri, 2013; Espinosa, 2010). This occurs for a range of fluid mixture qualities, temperatures, pressures and nanoparticle concentrations. However, foaming during co-injection only occurs above a threshold velocity, which may be difficult to achieve in a reservoir far from the injection site.

An alternatively proposed mechanism to co-injection for foam generation has been drainage displacements, in which a non-wetting phase such as CO_2 or oil displaces brine initially resident in the core. When nanoparticle laden brine is used in such experiments, the displacement pattern has been shown to change from preferential to more piston-like where the CO_2 invades a much larger percentage of the core (Aminzadeh, 2013). This same effect is also seen with low-pressure CO_2 analogs like n-octane (DiCarlo, 2011).

While data such as increased pressure drop, later breakthrough time, and regions of intermediate fluid density in mm-resolution CT images during displacements with nanoparticles suggest in-situ foam/emulsion generation, studies to date have not conclusively proven this increased efficiency is due to generation of foam or emulsion. Thus while these results are very encouraging on the use of nanoparticles ameliorating the low-viscosity effects of CO_2 and other non-wetting phases, the exact physics of how the nanoparticles affect the flow is still in question.

In this work, we report pore-scale evidence of the effect of nanoparticles on drainage displacements. We use n-octane to displace brine with and without nanoparticles in a Boise sandstone core. Spatial distributions of residual brine are measured using micro-CT at the end of each experiment. The 15 μm resolution of the scanning is fine enough to determine the filling of individual pores (regions not seen with larger scale scanning), and we determine how the spatial pore size distribution affects the pore filling with and without nanoparticles. This gives us key insights on the effect of nanoparticles on the displacement physics and how this can increase the core-scale sweep efficiency of injecting a non-wetting phase.

MATERIALS AND METHODS

One cylindrical Boise sandstone core (15.2 cm length, 2.5 cm diameter) was the porous media of choice for the experiments performed because of its availability, low clay content and moderate heterogeneity. The porosity and permeability were 30% and 3.8 D, respectively. The core was confined in a custom epoxy coreholder and fitted with flow fittings. X-ray microCT imaging on the middle section of the epoxy confined core performed using Heliscan microCT (Thermo Fisher Scientific) and the imaging settings were energy 120kV, target current 90µA, and image resolution 15.7µm/voxel.

n-Octane was chosen as an experimentally convenient non-wetting phase. The wetting phase was either a synthetic brine of 0.3M NaI solution in deionized water (the control case) or a 0.3M NaI in deionized water dispersion containing 5 wt% of silica nanoparticles (the nanoparticle case). NaI was added as a dopant to the wetting phase to increase the X-ray attenuation contrast with the non-wetting phase consisting of pure n-Octane. The nanoparticles, EOR-5XS from Nissan Chemical USA, consisted of a silica core 5-30 nm in diameter with a proprietary surface coating to prevent aggregation. These nanoparticles stabilize CO_2-in-brine foams at a range of conditions (Aroonsri, 2013; Worthen, 2013).

For the control experiment, the core was first vacuumed and saturated with the control brine. Next, with the core oriented horizontally, n-octane was injected to displace the aqueous phase at a flow rate of 0.60 cm^3/min (2.4 PV/hour) for 4+ PV to achieve residual water saturation. Throughout the drainage process, pressure drop was measured and recorded from the core inlet to the core outlet. Water cut was also recorded using a fraction collector. Micro-CT image of the same middle section of the core was acquired in the saturated state prior to drainage and after the end of drainage step.

3D micro-CT images of the sample were taken in the following states:

Step	Core state
1.	Dry
2.	Saturated with control brine
3.	Residual control brine after drainage with octane
4.	Core was cleaned and dried to reset to the original dry state
5.	Saturated with brine containing nanoparticle dispersion
6.	Residual aqueous phase after drainage with octane

3D microCT images were first registered to bring all five images in a perfect geometric alignment using VoxelPerfect algorithm [Latham et al. 2008]. This allowed for voxel by voxel subtraction of the reference dry image from other images in step 2-4 and the resulting difference shows the 3D distribution of NaI containing brine. The difference images were used to quantify porosity from the fully saturated images and residual saturation at the end of drainage by segmenting the difference image as by a “total connected porosity” segmentation technique [Ghous et. al., 2007]. From these images, we are able to determine how the presence of nanoparticles affects the pore scale spatial distributions of residual water following drainage processes. 3D visualization, grains segmentation and grain size distribution analysis was performed using PerGeos.

RESULTS

Figure 1a shows the overall pressure drop history as a function of injected n-octane pore volume for both the control (blue) and nanoparticle (red) experiments. For both curves, the pressure drop increases initially because of multi-phase flow in the core, followed by a decrease in pressure with increased n-octane saturation. The pressure drop recorded during the nanoparticle experiment was up to 2.5 times greater than the control case, with the largest difference occurring at the breakthrough of injected n-octane at the core exit.

Figure 1b shows the core-average brine saturation history as a function of injected n-octane pore volume for both the control (blue) and nanoparticle (red) experiments. n-octane arrival at the core exit is indicated on the curve by the deviation from the unit slope. The core-average saturation asymptotically approaches the residual brine saturation value. In the control experiment, n-octane shows early breakthrough, around 0.48PV and reaches a core-average residual brine saturation of 41%. In the nanoparticles case, n-octane breakthrough is delayed to 0.56PV and residual brine saturation is decreased to 31%.

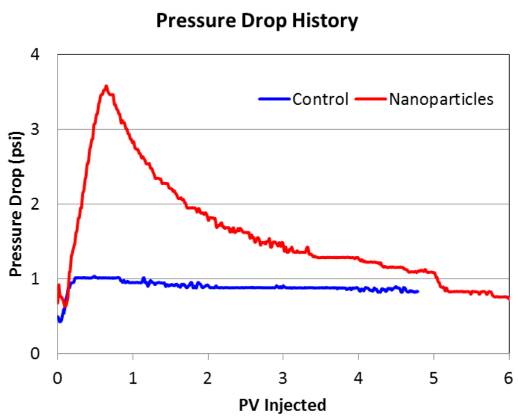

Figure 1a: Pressure drop versus PV of octane injected. Flow switched from brine to octane at PV=0

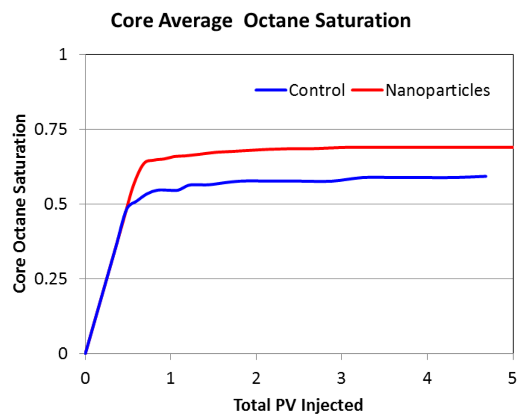

Figure 1b: Core averaged octane saturation versus PV of octane injected.

Figure 2a shows the core with the region scanned. Figure 2b shows a 45mm tall section of the core imaged with microCT at 4 different states. The 3D images in dry, saturated, and drained states are registered, and only a longitudinal cross section is shown here. From the dry image we can see the pores in darker color and grains in various lighter shades as a function of mineral density, chemical composition and mixture of phases (e.g. edge of pore and mineral) finer than the voxel resolution. Figure 2b shows the images after drainage of control brine. n-octane swept regions can be seen in darker shades and unswept or partially swept regions can be seen in lighter colors as they still retain NaI doped brine. In comparison, the after drainage image in nanoparticle dispersed brine case shows more n-octane swept region.

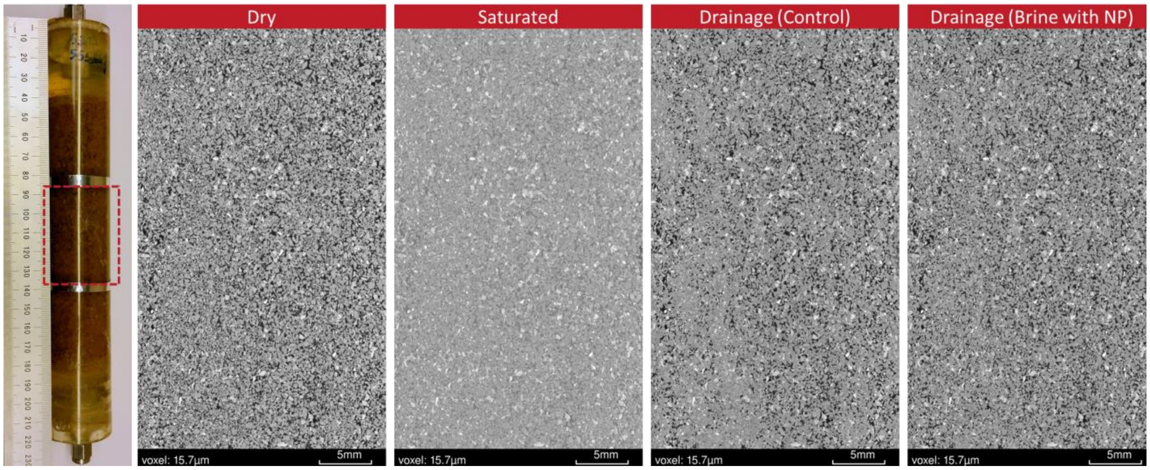

Figure 2a (left): Core with region scanned. Figure 2b (right): Micro-CT images of core at different core flooding states

To quantify the amount of brine present at the end of two drainage processes, the dry image was subtracted from the drained images. Figure 3a shows the resulting difference image, wherein any unchanged voxels compared to the dry image, such as solid grains, get subtracted; while the changes in the pores get highlighted. Hence the coloration in these images ranges from 0% brine saturation at a voxel (black) to a 100% brine filled voxel (white) with grayscale represented weighted sub-voxel saturation. Figure 4 shows the same data in 3D, showing distribution of residual saturation follows along the tight laminations. Overall saturation calculated from micro-CT images was lower than the experimental observation. This could be due to the imaging and analysis was performed only on the middle 1/3rd region away form end zone, while the weight measurement in experimental results would account for the brine saturation in the entire core holder.

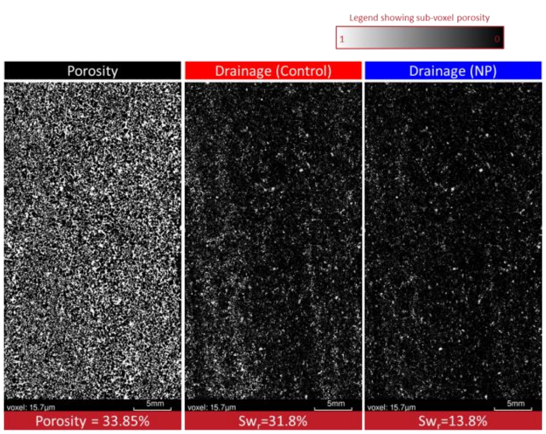

Figure 3: Longitudinal cross section from 3D microCT images showing difference images (a) porosity, (b) residual saturation in control and (c) residual saturation in NP.

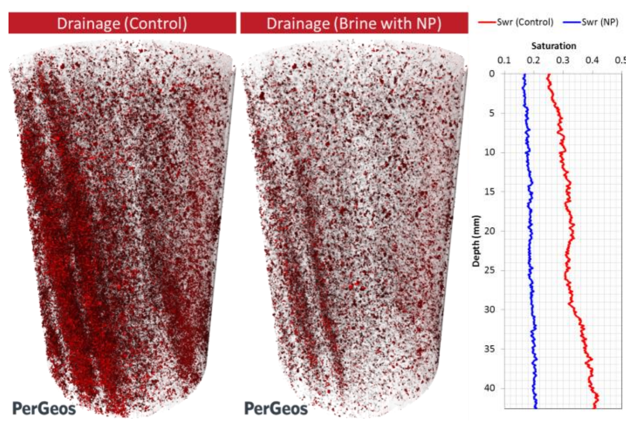

Figure 4: 3D view of pores filled with brine after drainage. The brine is shown in red in this figure.

The distribution of residual brine as seen in Figures 3 and 4 suggests that the displacement front of n-octane is not uniform, but rather bypasses regions of pore space. In particular, brine saturations persist in channels on the left side of the image oriented in the direction of flow. This results in a larger saturation of residual water in the left portion of the figure. Within the left side, there are streaks of high and low residual water saturation, potentially indicative of heterogeneity and layering of different grain types. Compared to the control experiment, the overall residual water saturation is lower and distributed more uniformly, indicating much less bypassing of wetting phase during drainage. Figure 3 and 4 suggests that the presence of nanoparticles increases overall octane saturation by increasing the number of octane filled pores.

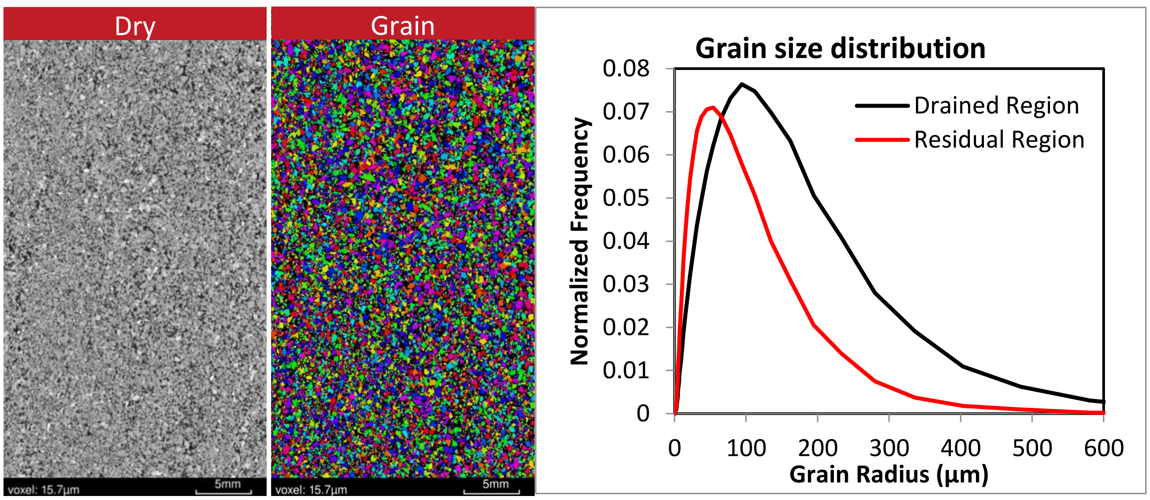

Figure 5: Cross section from 3D grains segmented image showing lamination with finer grains dominating region where residual saturation was observed after the drainage in the control case without nanoparticles and coarser grains dominating drained region.

Saturation profiles along the height of the core were calculated by average saturation in each horizontal cross section from 3D cylindrical image and the residual water saturation profiles confirm the above qualitative observations. The control experiment (red) shows a positive saturation gradient, with an inlet residual water saturation of 25% and outlet saturation of 41%, as expected from a displacement dominated by preferential flow. In contrast, the nanoparticle experiment (blue) saturation profile is lower and relatively constant, indicative of a uniform displacement. Therefore, for the core subsection under microCT inspection, the improvements in n-octane conformance control in the presence of nanoparticle dispersion results in a lower core-average residual water saturation of 19% compared to the control case of 33%.

These pore scale micro-CT results can be compared to earlier experiments performed with a macro mm resolution, modified medical CT scanner. It was shown in DiCarlo et al (2011) that an n-octane displacement front in the presence of nanoparticles is more spatially uniform with a later breakthrough when compared to a control displacement without nanoparticles. The main limitation of the earlier experiments, however, was the inability to correlate core scale fluid displacements with pore scale properties due to the relatively coarse resolution of the CT scanner.

DISCUSSION

The results of the drainage experiments with and without nanoparticles can be summarized as follows:

1. Higher pressure drop and better sweep efficiency was observed during injection of n-octane into a nanoparticle dispersion saturated core, compared to the control case.
2. Following n-octane injection, micro-CT imaging shows less preferential flow, higher core volume swept by n-octane, and lower residual brine saturation when nanoparticles are present.
3. At the resolution of 15.7μm/voxel, it is difficult to comment of the presence of an intermediate emulsion phase. Further investigation at higher resolution will be performed as next part of this study.
4. Grain size distribution calculated from 3D image were split into two parts, the drained region and region showing residual saturation in the control case. This was achieved by using the results of control case as mask. The region showing residual saturation in the control case has smaller grains, and thus smaller pores and lower permeability, on average than the drained region.

Results 1 and 2 are consistent with previous observations described by DiCarlo et al. and Aminzadeh et al. Results 3 and 4 are novel findings that substantiate and provide deeper understanding of Results 1 and 2.

In particular, the micro CT images presented here show, as one wold expect, the pore scale heterogeneity controls the preferential flow paths in control case, where no nanoparticles are present. More importantly, Figure 4 is positive confirmation that nanoparticles divert flow of non-wetting fluid from an area of large grain and pores into a region of smaller pores and lower permeability previously inaccessible. These observations provide insight to the potential mechanisms by which nanoparticle affect flow patterns during drainage displacements.

A simple working hypothesis involves the physics of pore filling. When a non-wetting phase invades a pore saturated with wetting fluid, it progresses until the fluid-fluid interface attains a critical curvature at the smallest radius. Any additional advancement of the invading non-wetting fluid disrupts the configurational stability of the two-phase interface, and an instantaneous decrease in local capillary pressure during this process creates disconnected droplets of non-wetting fluid advancing to the next pore (Roof, 1970). This is known as Roof snap-off. Normally, as each new invading fluid droplet is created, they coalesce and saturate the pore before invading the adjacent pore. In the presence of nanoparticles, however, the subsequent non-wetting droplets are armored by the surrounding nanoparticles during Roof snap-off events, which prevent coalescence and leave separated droplets in the pore (Binks and Horozov, 2006).

One question is whether enough droplets form to make an actual emulsion with lamellae spanning the pores. Previous experiments imaged at the mm scale by DiCarlo et al (2011) and Aminzadeh et al (2013) showed regions of intermediate density when nanoparticles are present; this can either be an artifact of the relatively poor visual resolution, or suggest the in-situ formation of a separate intermediate saturation phase (i.e. an emulsion).

In actuality, Result 3 does not preclude emulsions. Any emulsion lamellae, consisting of a film of nanoparticle dispersion with a thickness of 10s of nm, would be too small to be seen even at this enhanced resolution (~15μm/voxel). If lamellae are present but not visible, an emulsion phase would appear as octane. To confirm the presence of emulsion, in future study, we will perform similar experiments at ~1μm/voxel with higher concentration of NaI. At this resolution, we will not be able to observe films directly (sub-voxel sized features); however grayscale change within the pore would suggest the presence of an intermediate phase.

However, what has been clearly demonstrated is the efficacy of nanoparticles to address preferential flow due to viscous instability in heterogeneous rocks. As found in result 4, the spatial variation in grain sizes correlates to the preferential flow paths observed in the control experiment. Those same flow paths were inhibited during the nanoparticle experiment, resulting in higher contact area between octane and brine. This provides positive confirmation that the mechanism by which nanoparticles improve immiscible displacements during drainage processes is a function of pore scale heterogeneity. Again, whether the exact mechanism is from pore blocking by individual droplets or the viscosification of n-octane through in-situ emulsion generation, this has yet to be determined.

It should be noted that how a small difference in grain size lead to a large improvement in flow pattern (See Figure-5). Differences in grain sizes and level of heterogeneity occur naturally in geologic media and often vary across many orders of magnitude, which begs the question as to what extent can nanoparticles effectively improve subsurface displacement processes? Future work will be conducted with unconventional rocks or rocks with larger permeability contrast (e.g., with a fracture).

CONCLUSION

A pair of drainage experiments in a sandstone core were performed to measure the sweep efficiency of n-octane following injection. 3D micro-CT scanning is used for a comprehensive petrophysical analysis of the core to correlate pore scale properties with core scale flow patterns.

When surface treated silica nanoparticles are present in the resident brine, we observe a higher pressure drop, later breakthrough, and lower residual brine saturation. Through micro-CT scanning, we visualize improved n-octane volumetric sweep efficiency. An analysis of core grain sizes indicates that the n-octane flow path was dictated by grain size. In the absence of nanoparticles, n-octane flows in a region of large grains and bypasses regions of smaller pores. With nanoparticles, n-octane sweep was enhanced to reach more areas previously bypassed characterized by small grains and pores. This is attributed to the in-situ generation of octane-in-brine droplets during pore scale Roof-snap off events, which work to block pores, increase local pressure, and divert flow to low permeability regions.

The observations noted in this paper have significant implications on a variety of subsurface displacement processes, including EOR, CO_2 sequestration, and water injection in oil wet reservoirs. With a deeper petrophysical understanding of this phenomenon of nanoparticle enhanced volumetric sweep efficiency, we can greatly improve oil production from gas EOR, CO_2 storage capacity for geologic sequestration, and other similar subsurface fluid displacement processes.

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