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Stabilization of Interfacially-Active-Nanohybrids/Polymer Suspensions and Transport through Porous Media

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Abstract

Novel amphiphobic nanoparticles based on functionalized carbon nanotubes (CNT) have shown promising applications for enhanced oil recovery, by lowering the water/oil interfacial tension upon adsorption or chemical reaction catalyzed by these nanoparticles. Challenges for this novel approach include a) stabilizing aqueous suspensions of the nanoparticles in the presence of brine, b) propagating these suspensions through a porous media, c) conducting reactions at the interface.

It is well-known that it is difficult to suspend CNT in liquids since they are amphiphobic. Thus, surfactants or polymers are needed to create stable suspensions. Here, several polymers have been tested to disperse CNT in water. Even though some of them produced very stable nanohybrid suspensions in deionized water, when brine was present in the medium, in most cases the suspension destabilized and the nanohybrids settled out.

We were successful in stabilizing nanohybrids suspensions in brine, by using polyvinyl-pyrrolidone (PVP). However, in propagation experiments of these suspensions through a porous media (crushed Berea sandstone, 75-250 μm particle size, $k = 4.2 \text{ D}$, $\Phi = 35\%$), it was observed that the PVP strongly interacted with the sand in the presence of elevated brine (10% solution), leading to low particle recoveries ($< 10\%$). Conversely, with PVP in deionized water, the particle recovery was higher than 90%. After trying to get a good particle recovery of brine nanohybrid suspensions, we discovered an effective binary polymer combination that produced very stable nanohybrid suspensions that propagated through the Berea sand, with a particle recovery of 80%. This polymer combination consisted of a sequential addition of PVP and a proprietary high salinity-resistant polymer, which reduces the rock/polymer interaction.

We envision these engineered nanoparticles having a great impact in the characterization of the reservoir and enhancement of oil recovery.

Introduction

Contributions and studies of the particle propagation phenomena provide fundamental step in developing the application of nanotechnology in enhanced oil recovery. Several factors play crucial roles in the interaction of particle-rock, making the success of the dispersion propagation viable in reservoir-like conditions (e.g. high ionic concentration, tight rock formations, stability of the particle dispersions in the aqueous phase).

Reducing the aggregation or flocculation of particles is the most important step to improve the propagation through porous media. Addition of polymer has shown the best results to disperse nanohybrids in the aqueous phase by increasing the electrostatic repulsion of the particle surface charges when a high entropy polymer like polyacrylamide (Villamizar 2010) is used or by the adsorption on the nanoparticle of a linear polymer like polyvinyl-pyrrolidone is used (O'Connell 2001). Both of these additives reduce the particle attraction between the dispersed particles and onto the rock and therefore decreasing adsorption loss.

Experiments

Materials. The nano-particles used in this study include oxidized and non-oxidized multi-walled carbon nanotubes (MWNT) on alumina core (Al_2O_3) and purified multi-walled carbon nanotubes. Multi-walled carbon nanotubes are grown on an alumina core to produce MWNT- Al_2O_3 by treating the alumina with carbon monoxide at specific

reaction conditions where parameters for the production of the nanohybrids, like the nanotubes length and the surface functionalities, can be changed accordingly as desired; this procedure gives a total carbon content for this nanohybrids of about 30%, and good enough free area on the Al_2O_3 surface in order to provide the hydrophilic characteristics to the nanohybrids. However, the nanohybrid still shows high hydrophobicity, for which an oxidation process in which the MWNT- Al_2O_3 is treated with nitric acid at about 90C for 3 hours; this will provide carboxylic groups that act as hydrophilic sites in the carbon nanotubes. As a matter of fact, an oxidized nanohybrid has shown better behavior on stabilization of emulsions by providing higher fractions of emulsions and smaller droplet sizes. The unique combination of a strong hydrophilic component, like the alumina, and a strong hydrophobic, like the carbon nano-particles, provides the specific characteristics for these nanohybrids to be applied for EOR due to their high interfacial activity that will lead them the oil/water interface.

Purified multi-walled nanotubes are produced from a treatment made on MWNT- Al_2O_3 where fluorhydric acid is used to dissolve the alumina core, and then the carbon nanotubes are dried. These nano-particles present high amphiphobic characteristics which will make them easily deliverable to the oil/water interface at very low energy costs; both oil/water and water/oil emulsions have been formed using these particles. The nanohybrids described above were tried to be dispersed in aqueous phase using different polymers or surfactants and at different conditions of salinity.

Polymers used included Polyacrylamide partially hydrolyzed (PAM, trade name Flopan 934 PWG) from SNF Inc, Polyvinyl-pyrrolidone of molecular weights 10,000 (PVP10), 40,000 (PVP40), 360,000 (PVP360) and 1.3 million Daltons (PVP1.3MM), all from Sigma Aldrich, and a proprietary polymer (DOW) were used as received. Sodium Chloride (NaCl) and Calcium Chloride (CaCl_2) from Sigma Aldrich, were used as received to create the API brine.

Blocks of Berea sandstone of 250md from Berea Sandstone Petroleum Cores were used to create the porous media for the propagation studies. For the packed columns, the sand was crushed using a ceramic mortar and sieved using a standard set of sieves with grain size of 1000 μm , 710 μm , 500 μm , 250 μm and 75 μm . All of the sizes below 1 mm were used for different experiments, and the size range between 250 μm and 75 μm was selected as the primary because of the low permeability and porosity.

The setup for the packed columns uses low pressure glass columns Chromaflex, purchased from Kimble/Kontes Company, and a peristaltic pump for the injection of the different fluids delivered. Pressure drop across the columns was measured using in line digital and analog pressure gauges. The effluents are collected using a timed sample collector. And the analysis of concentrations is performed using a turbidity meter.

Procedures. A description of the experiments performed to create the nano-particle dispersions and to create the propagation in the porous media is presented in this section.

Nano-particle dispersions are created by adding the nanohybrids and polymer to the aqueous phase and dispersing them using a high energy horn sonicator for a period of time that is good enough to break the nanohybrids and create particle sizes that are fairly distributed.

Oxidized MWNT- Al_2O_3 . Dispersion stability was evaluated using PVP and PAM in DI Water using polymer concentrations of 500ppm and nanohybrid concentrations of 50ppm. Dispersions of 2000ppm nanohybrid concentrations were prepared by adding 500ppm of the polymer to the nanohybrids and sonicating the mixture for 1 hour and 30 minutes in order to achieve homogenous dispersions. Then, the stock solution is diluted to different concentrations of nanohybrids and polymer is added in order to maintain the concentration at 500ppm, finally vortex is used to homogenize the final mixture.

MWNT- Al_2O_3 . Using the same procedure as the oxidized nanohybrids, stock solutions of 2000ppm nanohybrids in 500ppm polymer (PVP or PAM) were prepared in DI Water or API Brine accordingly; then dilutions were made to different concentrations as required while keeping the polymer concentration at 500ppm. When the polymers PVP and DOW were used at the same time to create stable dispersions, the process vary as the concentration of nanohybrids is 100ppm and total polymer concentration is 1000ppm (PVP to DOW ratio may vary). Polymer addition is sequential as the PVP is added first to the nanohybrids and the dispersion is sonicated for 2 hours, followed by the addition of DOW and sonication for another 30 minutes. Then the dispersion is treated using centrifugation at 2000rpm for 1 hour; the supernatant obtained from the centrifugation is used for the propagation studies.

Purified MWNT. Dispersions of these CNT are prepared following the same procedure as with MWNT- Al_2O_3 when PVP and DOW are used at the same time to create the stable dispersions.

The glass columns are packed with the crushed Berea sand using a dry packing technique and enforcing a tight packing that eliminates any void space, giving a consistent procedure for every column test run. The setup is such that one-dimensional vertical flow in the upward direction is used in order to avoid gravity effects that will cause the liquids injected to accelerate inside the pores. Injection rate is low enough to avoid the formation of preferential paths.

The sand packed columns are characterized by measuring the porosity and permeability, which will change

accordingly with the crushed sand grain size used. Injection of water is performed until no air bubbles are detected in the effluents in order to measure the porosity (Φ), which will be equal to the ratio between the difference of the volume of water injected and the volume collected at the effluent plus the water trapped in the lines (this is the pore volume or PV), and the total volume that is packed with sand. The columns used are 1 inch in diameter and can be up to 6 inches long.

$$V_{total\ 1inch} = \pi \left(\frac{2.54cm}{2} \right)^2 \times 2.54cm = 12.87cm^3 \quad \dots\dots\dots(1)$$

$$\phi = \frac{Pore - Volume}{Total - volume} \times 100\% \quad \dots\dots\dots(2)$$

Permeability (k) is calculated from the relationship between the pressure drop and the flow rate, using Darcy's law (injection rate is low enough to satisfy laminar conditions). Once the column has been saturated with water, the pressure drop is measured when injection is undergoing different rates.

$$k[mD] = \frac{q \left[\frac{cm^3}{s} \right] L[cm] \mu[cP]}{\Delta p[atm] A[cm^2]} \times 1000 \quad \dots\dots\dots(3)$$

Where q is the flow rate, L is the length of the packing, μ is the viscosity of the injected fluid, Δp is the pressure drop across the column, and A is the area transversal to the direction of flow. A plot of flow rate versus pressure drop was prepared for all the grain sizes used to pack the columns.

Using the slopes of the lines in **Fig. 2**, the permeability was calculated using equation 3. **Table 1** presents the porosity and permeability calculated for all the grain sizes of Berea sand used. Although the easily reproducibility and repeatability of the propagation studies in the sand packed columns is the main reason why they were used in this work, it was decided only to use the smallest grain size because it has the lowest permeability and it will represent up to some extent, the most accurate picture of a rock matrix.

Table 1. Sand Packed Properties.

Material	Berea Sand	Berea Sand	Berea Sand	Berea Sand
Size Range [μm]	75-250	250-500	500-710	710-1,000
Porosity [%]	35%	44%	51%	53%
Permeability [mD]	4,200	8,100	15,000	24,300

Propagation in Porous Media Studies. Columns were packed for 1inch in length and using the Berea sand of grain size 75-250 μm , unless stated otherwise. Once the glass columns are packed with sand, the next step is to saturate the columns with the aqueous phase; a regular procedure is to inject until no bubbles are detected in the effluents. This procedure works perfect with DI Water, however, it was found that in the case of high salinity brines, like the API brine used in this work, it is required to not only saturate the pores with the brine but also to achieve homogenous concentration of ions throughout the entire columns; for this, an injection of 10PV of brine will achieve ion concentration equal between the effluent and the injection.

Nanohybrids dispersions are injected for 5PV consecutively, followed by 5PV of the aqueous phase (DI Water or API Brine). For some cases, an injection of polymer pre or post-flush after the dispersions injection was performed in order to treat the sand and analyze the effect of the polymer on the propagation. Effluents were collected every 1PV and immediately analyzed using turbidity meter in order to measure the concentration of nanohybrids, in order to ensure the homogeneity of the sample, the effluent was well mixed using vortex.

Plots of particle recovery and concentration ratio were prepared in order to analyze the delay of the nanohybrids breakthrough and to compare the effectiveness of the dispersion and propagation between different systems.

Results and Discussion

This section will illustrate all the results obtained from the stability analysis of the dispersions, which is related to how well the nanohybrids are incorporated to the aqueous phase; and the results from the propagation through porous media studies where the effectiveness of the transport is analyzed.

Oxidized and Non-oxidized Multi-Walled Carbon Nanotubes on Al_2O_3 . There is not an important number of available results in bibliographic references where successful stable dispersions in a brine with such a high concentration like the API brine used here (8 wt%NaCl, 2 wt%CaCl₂), neither propagation studies. Most of the references present results in brine that has an ion concentration too low to be comparable with a real ion concentration of the brine found in oil reservoirs. In this section, the results will focus on the use of the polymers presented in the DI Water section and the results obtained, and on the efforts made with new dispersants.

Dispersion and Propagation with PAM and PVP. Initially, dispersions were prepared using PAM as it exhibited excellent propagation for both Oxidized MWNT- Al_2O_3 and MWNT- Al_2O_3 , although the uncertainty was high because it is well known that PAM is not a salt tolerant polymer as viscosity can be reduced by 1 or 2 orders of magnitude by the simple introduction of 2 wt%NaCl, however, since the results in DI water indicated that viscosity was not related to the dispersion stability, then those polymers were used.

Dispersion stability studies indicated that PAM was not able to disperse successfully neither of the two nanohybrids, regarding of the concentration of polymer and/or nanohybrids used. As a matter of fact it was found that with the introduction of just 1 wt% total salt concentration, the stability of the dispersions was lost to agglomeration of particles immediately after sonication.

Stable dispersions of oxidized MWNT- Al_2O_3 were only achieved when PVP10 was added to the solution, although the stability of the dispersion could be compromised over a faster period of time compared to those dispersions analyzed in the DI water section, as agglomeration was observed 3 to 4 days after sonication while before, DI Water dispersions are known to be stable for weeks.

When the dispersion of oxidized MWNT- Al_2O_3 was injected into the 1 inch long column packed with 4,200 mD crushed Berea sand, there was no particle recovery measured in the effluents after the regular 5PV of dispersion were injected followed by the 5PV of API brine flush, but a pressure increase was observed as the particles were arriving at the sand face; pressure drop across the column went from just 1psi when the column was being saturated with brine, to about 8 to 10 psi as the dispersion was being injected, even after the injection fluid was switched to brine, pressure drop was constant at 10 psi. At the end of the experiment, the column was dismantled, and the packed sand was examined. **Fig. 3** presents the pictures taken from the column after the dispersion of oxidized MWNT- Al_2O_3 with PVP10 was injected. Initial observation of the column presents the appearance of zones with high concentration of carbon nanohybrids at the bottom of the column where injection is performed for the upward vertical flow, besides a clear normal color for the rest of the sand in the column is observed.

Further inspection of the column reveals that nanohybrids have created a layer at the sand face which explains the increase of pressure drop and the non-existent particle recovery for the propagation of this dispersion. Since it is known that the stability of the dispersion will dictate the outcome of the propagation through the porous media, and the stability of the oxidized MWNT- Al_2O_3 dispersion with PVP10 it is known to be the not quite effective, there are two main reasons for the catastrophic adsorption at the sand face of the column. First, the particles coated with PVP10 are big enough that the steric effects are reduced and the distance between particles is reduced such that particles are close enough to be attracted by their high hydrophobic forces, which will induce agglomeration, as it is observed in the low stability of the dispersion, and their size impedes them from being able to move through the pore throats even as injection pressure is increasing. Second, adsorption of PVP to sandstone is increased dramatically by the presence of ions. Therefore, the phenomena observed, occurs due to a combined effect of filtration and agglomeration where the first one triggers the latter.

Dispersions of MWNT- Al_2O_3 nanohybrids with PVP1.3MM, PVP360 and PVP40 in API Brine achieved high stability, comparable to the stability observed for the dispersions prepared in DI Water. These dispersions presented a shelf life of weeks and are capable to survive centrifugation of up to 500G's for 1 hour with less than 20% loss of particles. Propagation through porous media was studied for these three dispersions using a 4,200 mD, 1inch column; **Fig. 4** shows the results for these columns. The ions present in the API brine, used as the aqueous phase for these dispersions, play the most important role in the outcome of the propagation as the stable dispersions made with PVP360 and PVP40 produced a particle recovery of just 10.4% and 6% respectively. Regarding the normalized concentration plots, the same behavior is still observed where the concentration increases constantly until a peak in the concentration is accomplished, then a dramatic decreased is observed as the brine flush breaks through. The propagation of the dispersions prepared with PVP1.3MM shows a much more important shockwave of concentration in the effluents as shown in the normalized concentration plot of Fig. 4, where a concentration of up to 3 times larger than for the other 2 polymers, is observed in the 6th pore volume. After the propagation studies were performed, the columns were examined for possible agglomeration and filtration present at the sand face as it was observed for the propagation of oxidized MWNT- Al_2O_3 in Fig 3.

In **Fig. 5**, the pictures for the column used for the propagation of the dispersion created using PVP1.3MM with MWNT- Al_2O_3 are presented. Adsorption of the polymer coated nanohybrids to the sand is confirmed due to the coloration change of the sand packed in the column from the regular light gray to a much darker color, a clear

indication that the carbon nanohybrids are being retained. Also the adsorption-filtration phenomena observed at the sand face for the oxidized nanohybrids are also observed here. The long chain of the PVP1.3MM is capable of providing the steric effects necessary to create a stable dispersion and overcome Van der Waals forces, but the particles are still big enough to be filtrated once they reach the porous media, and the known adsorption of PVP enhances the trapping of the nanohybrids in the rock. In **Fig. 6**, the pictures from the column test for the dispersion of MWNT- Al_2O_3 with PVP360 are presented. The filtration and agglomeration observed at the sand face is much more important, confirmed by the very dark thick layer observed in the column close to the injection point. The fact that the nanohybrids observed at the sand face are more important and that the coloring of the column is less homogeneous compared with the PVP1.3MM scenario, indicates that the particles are bigger in size when the dispersant is the PVP360 which leads to the important agglomeration at the sand face compared to that observed in **Fig. 5**. The pictures for the column test of MWNT- Al_2O_3 with PVP40 in API brine that are presented in **Fig. 7**, indicate that the filtration-agglomeration effect is directly related to the size of the polymer chain. Here again, a layer of nanohybrids is observed at the sand face, and it does not extend beyond that 2 or 3mm into the packed sand; besides, the coloring and aspect of the column behind the layer of nanohybrids at the sand face is very similar to the clean sand for both PVP360 and PVP40, compared to the very uniform black coloring through the entire column for PVP1.3MM. A larger PVP chain is capable to create a much better steric barrier to support the electrostatic attraction created from the ions of the brine, leading to less nanohybrids agglomerated under the same single particle, therefore, a smaller particle size, reducing the filtration effect; since, less nanohybrids are close together join by the same chains of polymer, then, when the PVP is subject to be adsorbed to the sand stone, less amount of nanohybrids are being adsorbed to the rock, leading to a higher particle recovery. Those nanohybrids recovered with the PVP360 and PVP40 may be able to propagate through to the column due to the increase of pressure drop which creates preferential paths for transport, where the adsorption sites are being promptly covered reducing the possibility for adsorption to the upcoming nanohybrids that are being injected.

Dispersion and Propagation With Binary Dispersant. Previously it was explained that although stable dispersions were achieved at any concentration with PVP, their transport in porous media was very poor. In order to achieve proper transport in porous media, the excessive adsorption of PVP onto sandstone was needed to be reduced guaranteeing that the dispersion would keep its stability as it moved through the porous media. For this purpose, a new polymer was introduced in order to coat the PVP molecules that were sustaining the nanohybrids in the dispersion; this polymer is a proprietary polymer, a high salinity high temperature tolerant, ideal for regular polymer flooding in EOR. In this way, carbon nanohybrids would be suspended in dispersion due to coating provide by PVP, and the new DOW polymer would coat these polymer chains of PVP containing carbon nanohybrids, protecting them from catastrophic adsorption in the porous media; from there, the necessity of sonication of dispersions after addition of PVP and carbon nanohybrids before DOW polymer would be finally added and the dispersions sonicated once more. This process would ensure complete dispersion of the nanohybrids in the aqueous solution before PVP chains would be coated with DOW.

The concentration of MWNT- Al_2O_3 was 100ppm and 1000ppm for total polymer were the ratio of PVP to DOW was 1:3 in order to ensure , good enough coating of PVP by DOW, making 250ppm of PVP and 750ppm of DOW. **Fig. 8** shows the results for the propagation of these dispersions using PVP40 and PVP360 separately along with DOW as a binary dispersant. Propagation of carbon nanohybrids non-oxidized MWNT- Al_2O_3 is finally achieved at proper levels since particle recovery has reached up to 69% when using PVP40. Since the particle recovery using PVP40 is much higher compared to PVP360, it suggest that the coverage provided by DOW polymer depends on the length of polymer chain that is coating, i.e. since the polymer chain of PVP40 is much smaller compared to PVP360, polymer DOW is able to coat more effectively the smaller chain preventing its catastrophic adsorption. However, particle recovery has not achieved the levels observed for DI Water when it was above 80% (Villamizar 2010) compared to 69% obtained here, this indicates that adsorption of nanohybrids into the sandstone is not only driven by adsorption of PVP chains that keep the nanohybrids in dispersion, but also by nanohybrids adsorption itself; this nanohybrids adsorption is produced due to the interaction of the alumina core of the nanohybrids with the silica that mainly composes the Berea sandstone.

Carbon nanohybrids dispersions are very close to neutral pH due to the lack of any component that will affect it greatly, and at neutral pH the charge of silica and alumina is opposite with silica being negatively charged and alumina being positively charged. Further efforts will focus on using purified carbon nanotubes, produced from nanohybrids being removed their alumina core.

Purified Multi-Walled Carbon Nanotubes. Introduction of these nanoparticles was sought in order to reduce to the maximum any adsorption that may occur of the carbon nanoparticles studied when they are being transported through the porous media made of Berea sandstone. All of the studies performed with these nanoparticles were under API brine conditions because of the need to produce results that can be related to real field conditions. Dispersions of purified MWNT with PVP achieved complete stability and remain stable for long periods of time as

observed with the nanohybrids (MWNT- Al_2O_3), therefore, propagation studies were performed expecting that adsorption would be highly reduced due to the alumina core being removed, which is being chargedly attracted to the silica from the Berea sand. Propagation for dispersion of purified MWNT with PVP40 in API brine presented poor results with a particle recovery close to 4%, however, this marks a difference because even though the particle recovery was very low, concentrations on effluents were inside readable levels, indicating that some particles are able to travel through the porous media without being adsorbed into the Berea sand, however, propagation through the porous media of carbon nanoparticles (nanotubes and nanohybrids) is mainly affected by adsorption of polymeric dispersant, if the dispersion being injected is stable.

Dispersion and Propagation With Binary Dispersant. Particle recovery reached 90.7% for purified MWNT dispersed with PVP40 and DOW at a ratio of 1:3 in API brine, a much higher particle recovery compared with MWNT- Al_2O_3 using the same binary dispersant in API brine. This difference in particle recovery is an effect of several phenomena, first, adsorption of polymer chains carrying nanoparticles is reduced due to coating provided by the second polymer, in this case DOW, second, attraction of nanohybrids to sandstone (silica) is eliminated when nanotubes are being used due to absence of alumina core, and finally, particle size has been reduced which eases the coating job of the polymers therefore reducing presence of nanoparticle agglomerates that trigger filtration and adsorption effects, while a nanohybrids (MWNT- Al_2O_3) may reach up to 700nm wide, a nanotube (purified MWNT) has an average length of about 250nm, not only this, but since a single alumina core in a nanohybrids may carry several nanotubes attached, it is easy for those nanotubes to interact among themselves and require a higher energy input to be unbundled in order to create stable dispersions.

Optimization of Binary Dispersant Polymer Ratio. It has been already presented and explained that dispersions made only with PVP as polymeric dispersant, although completely stable, will not propagate properly through porous media due to high adsorption of those PVP polymer chains into sandstone; also, DOW polymer will not produce a stable dispersion with either nanoparticle (purified MWNT or MWNT- Al_2O_3), but its presence is necessary in a binary system in order to prevent adsorption of PVP; if ratio PVP to DOW is big then adsorption effects will increase tampering propagation in porous media, and if it is too low then stability if dispersion could be put in jeopardy creating either big agglomerates of nanotubes or not dispersing them at all. Ratios of PVP to DOW investigated are 1:1, 1:2, 1:3, 1:4, 1:6 and 1:9; **Fig. 9**, presents plots of cumulative recovery and normalized concentration in effluents versus pore volume for all the ratios previously mentioned.

Optimal propagation of purified MWNT with binary dispersant made of PVP40 and DOW occurs when the ratio between the two polymers is 1 part of PVP40 per 3 parts of DOW polymer as cumulative particle recovery reached 91%. Although PVP is required to provide a stable dispersion, which is the primary factor in a successful transport in porous media, these results show that PVP is capable to disperse nanoparticles in an efficient way even at very low concentrations, e.g. at ratio 1:3 PVP40 to DOW, 100ppm of purified MWNT are dispersed by 250ppm of PVP40, even at 1:9 ratio, the same 100ppm of purified MWNT are dispersed by only 100ppm of PVP40. However, when concentration of PVP is very low, PVP40 to DOW ratio is very low, every polymer chain is dispersing a higher amount of carbon nanotubes, then, when a polymer chain of PVP is adsorbed into sandstone, more of those carbon nanotubes are being either dragged to adsorption or dropped out of dispersion.

The lowest cumulative particle recovery was present for PVP40 to DOW ratio of 1:6 at 63.6% rather than the bigger ratio 1:9, indicating that even though when DOW polymer concentration is too high and dispersion stability may be tampered, propagation through porous media is optimized at ratio 1:9 compared to 1:6 because at the former, DOW polymer is able to cover efficiently the PVP polymer chains present and at the latter there are more free PVP polymer chains subject to adsorption that are enriched with carbon nanotubes, however, for both of them, stability of the dispersion is still an issue as PVP concentration is very low.

When PVP40 to DOW ratio decreases to increase concentration of PVP in the dispersion, adsorption effects become more important, affecting the propagation of the nanotubes through porous media because the DOW polymer present is not enough to coat all of the PVP present in order to prevent such adsorption, then, PVP as it is adsorbed into the sandstone, drags the nanotubes that is dispersing and reduces the effectiveness of the particle transport in porous media. Interesting to note that cumulative particle recovery for PVP40 to DOW ratio of 1:1 is about two thirds of that obtained with the optimal 1:3 ratio; in general, particle recovery seems to be more affected by high adsorption of PVP chains poorly or not coated by DOW when nanotubes to PVP ratio is low, than when a low number of PVP chains that are not coated by DOW polymer and are enriched with nanotubes, are subject to adsorption.

Effect of Column Length. Propagation through porous media of dispersions made of purified MWNT with binary dispersant (PVP40 to DOW ratio of 1:3) exhibited high particle recovery, but it is still not 100% and is possible that when the sand packed column is longer, therefore more sand with more adsorption sites available, the ratio of nanotubes to polymer may decrease to the point where stability is completely lost and propagation is severely decreased; previously, column tests were run in a 1-inch sand packed column, then, column test experiments were performed in 2- and 3-inch long columns. For these longer columns, effluents were analyzed at 0.5 PV for 2-inch and 0.33 PV for 3-inch long column, rather than one effluent for every PV for 1-inch long column. **Fig. 10** presents plots for cumulative particle recovery and normalized concentrations in effluents versus

pore volume for the 2- and 3-inch long column along with previous presented results for 1-inch column for comparison purposes.

As expected and previously observed on other studies, particle recovery decreased with column length due to more adsorption sites available and specially, due to a longer time that takes for the dispersion injected to flow through the entire column which leads to equilibrium effects where adsorption sites that may be out of the flow streams can be reached along the injection of the dispersion. Normalized concentration plot in Fig. 10, shows that those longer columns present a much faster dispersion breakthrough as normalized concentration in effluents reach 1.0 about one pore volume faster than the 1-inch long column and that at the back of the dispersion injection pulse, concentrations in the effluents drop faster for the long columns. A faster dispersion breakthrough occurs because by the time 2 pore volumes have been injected into each of the columns, the actual volume for the 3-inch column would be three times of that volume injected into the 1-inch column, therefore, particles that are completely coated by DOW polymer and are not subject to adsorption, can propagate through the entire column much faster; concentration drop at the back of the pulse occurs to the same effect because more volume of water has been injected to those columns. In general, since cumulative particle recovery does not present a high difference between long and short column for this dispersion, longer columns or bigger porous media would not affect in a massive way the propagation of the dispersion.

Effect of Oil Saturation Inside the Porous Media. Since the main application for these nanoparticles is EOR, studies are needed to understand their interaction with oil during transport through porous media; in this work, the objective is to create stable dispersions that are capable to propagate through a sedimentary porous media and reach the oil and water interface, therefore, column tests were design in order to analyze this. Sand packed columns were saturated with API brine and then saturated with Decane in order to create residual oil saturation inside the porous media; after this, a dispersion of purified MWNT with a binary dispersant in API brine, as used and presented before, was injected for 5PV. **Fig. 11**, shows the results for this column test and a comparison with the results previously shown where no oil saturation was created inside the sand packed column. It was expected that due to the amphiphobicity nature of the purified MWNT, they will be delivered to the Oil/Water interface as injection through porous media will reach banks of oil, adsorbing the nanohybrids; but, this interfacial activity depends on the hydrophobic/hydrophilic balance of the particles to be delivered in order to interact strongly at the O/W interface and leave the water phase where they are dispersed. Nanohybrids and nanotubes present a very hydrophobic nature which makes them hard to be added into the water phase to be injected into the reservoir, and their need for a dispersant (polymeric dispersant in this work) in order to create hydrophilicity to interact with water. In Fig. 11 it can be seen that particle recovery was higher when the sand packed column was saturated with oil, not only this happened, but also dispersion breakthrough occurred much faster as the normalized concentration plot shows that for the 2nd pore volume in the oil saturated column, effluents present a normalized concentration of about 0.1 compared to concentration under readable levels for that column with no oil; this indicates that presence of oil enhances the propagation of purified MWNT inside the porous media.

Two different effects are happening, first, nanoparticles are not being trapped at the O/W interface, and second, their transport is being enhanced by the presence of oil. The former effect occurs because of high energy input required to form Pickering emulsions with oil due to reduced hydrophobicity of the nanoparticles caused by the coating of the polymer which is increasing their hydrophilicity in order to make them dispersible in water, therefore, their interaction with oil is reduced or completely eliminated and cannot be deposited or adsorbed at the O/W interface. The latter effect occurs because residual oil is trapped in porous where flow streams are not existent or very weak, and covers adsorption sites where under normal conditions, PVP polymer chains would adsorb dragging the nanotubes; this explains why dispersion breakthrough is observed faster in that column with residual oil saturation.

Conclusions

High ionic strength becomes the main factor affecting the stability of the dispersions and propagation of the nanohybrids and nanotubes, by increasing the effect of Van der Waals forces, and the adsorption of polymer chains into the rock. For example, PAM is not capable of providing stability for the dispersions of MWNT- Al_2O_3 oxidized MWNT- Al_2O_3 under API brine conditions while it has been found to create stable dispersions in DI water; and, PVP, although capable of providing stable dispersions for these two nanohybrids and the purified MWNT, is subject to increased adsorption under API brine conditions, impeding transport in porous media of the rock. Additionally to polymer adsorption, it was found that small adsorption of nanohybrids with alumina (Al_2O_3) core occurs onto sandstone due to their opposite charges at neutral pH.

Successful transport in porous media of nanohybrids (MWNT- Al_2O_3) and nanotubes (purified MWNT) occurs when two polymers that provide different characteristics to the dispersions are used, in this case, PVP provides nanoparticle dispersion stability, while DOW assures propagation in porous media by decreasing or avoiding adsorption of nanoparticles coated with PVP.

More studies are needed in order to understand the state of the nanoparticles coated with polymer inside the dispersion and how this interacts with the rock, additionally, how Pickering emulsions can be formed in flow conditions inside the porous media for better applications of EOR using the nanoparticles presented in this work.

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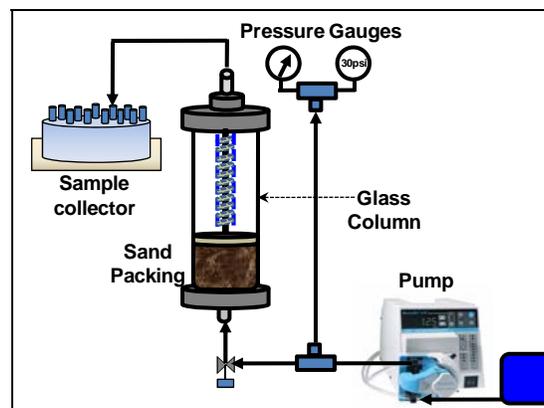


Figure 1. Sand Packed Column Setup.

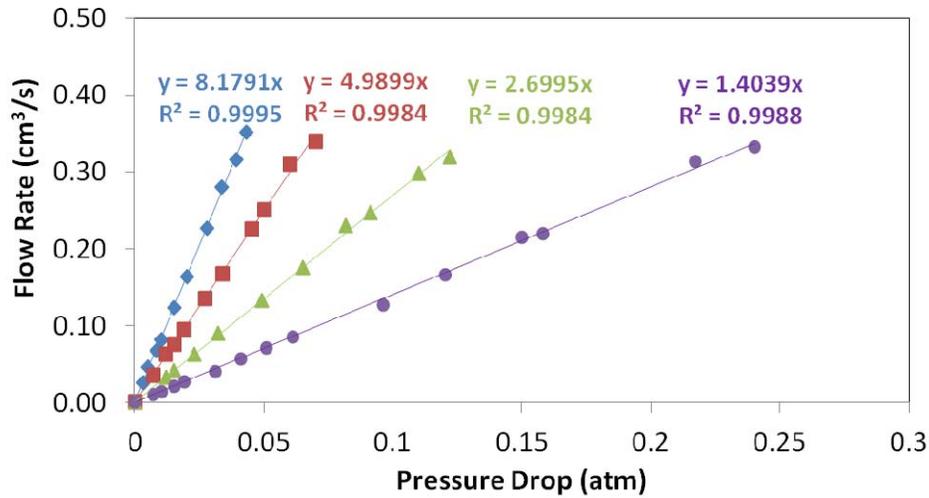


Figure 2. Flow Rate versus Pressure Drop for Packed Column with Different Sand Grain Sizes.



Figure 3. Sand packed column used for propagation study of oxidized MWNT-Al₂O₃. (From left to right: Column, sand face, 3mm from sand face).

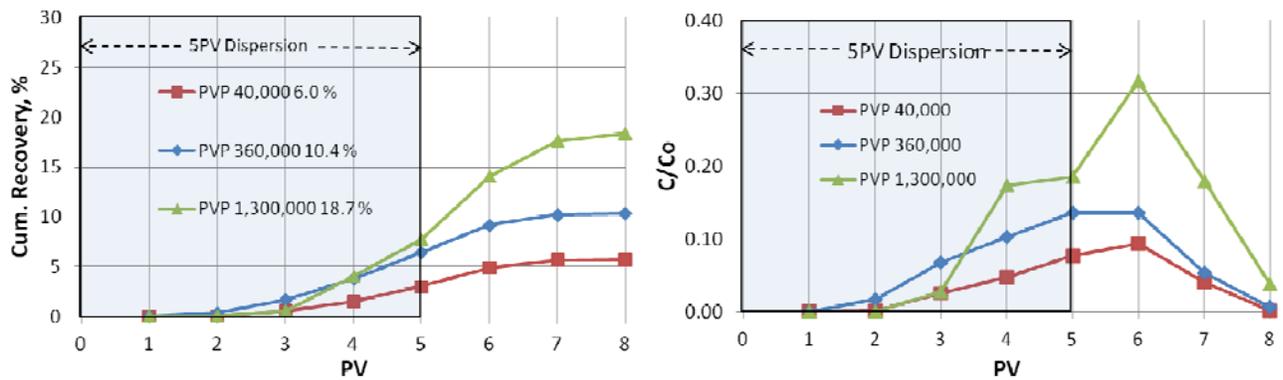


Figure 4. . Effect of polymeric dispersant on propagation of MWNT-Al₂O₃ using PVP of different molecular weights. (Left: Cumulative particle recovery vs. Pore volume. Right: Normalized concentration vs. Pore volume).



Figure 5. . Sand packed column used for propagation study of MWNT-Al₂O₃ with PVP1.3MM in API brine. (From left to right: Column before injection, column after experiment is completed, sand face, 3mm from sand face).

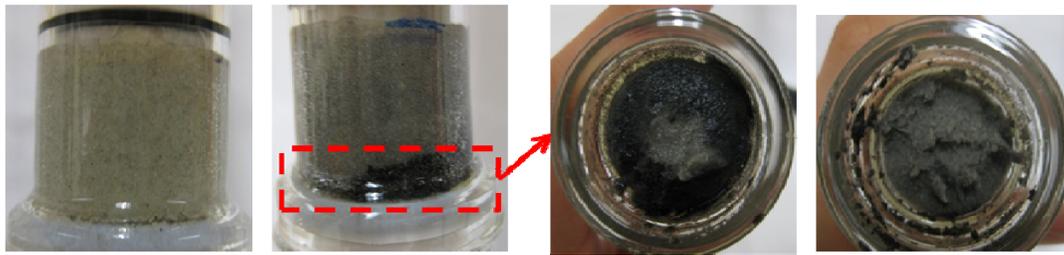


Figure 6. Sand packed column used for propagation study of MWNT-Al₂O₃ with PVP360 in API brine. (From left to right: Column before injection, column after experiment is completed, sand face, 3mm from sand face).



Figure 7. Sand packed column used for propagation study of MWNT-Al₂O₃ with PVP40 in API brine. (From left to right: Column before injection, column after experiment is completed, sand face, 3mm from sand face).

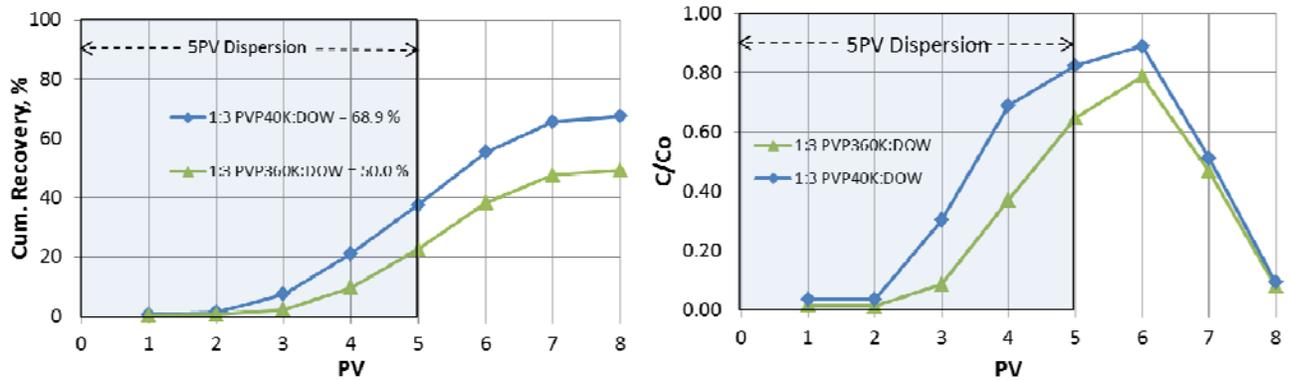


Figure 8. Effect of binary dispersant on propagation of MWNT-Al₂O₃ using PVP of molecular weight 40,000 and 360,000 Daltons. (Left: Cumulative particle recovery vs. Pore volume. Right: Normalized concentration vs. Pore volume).

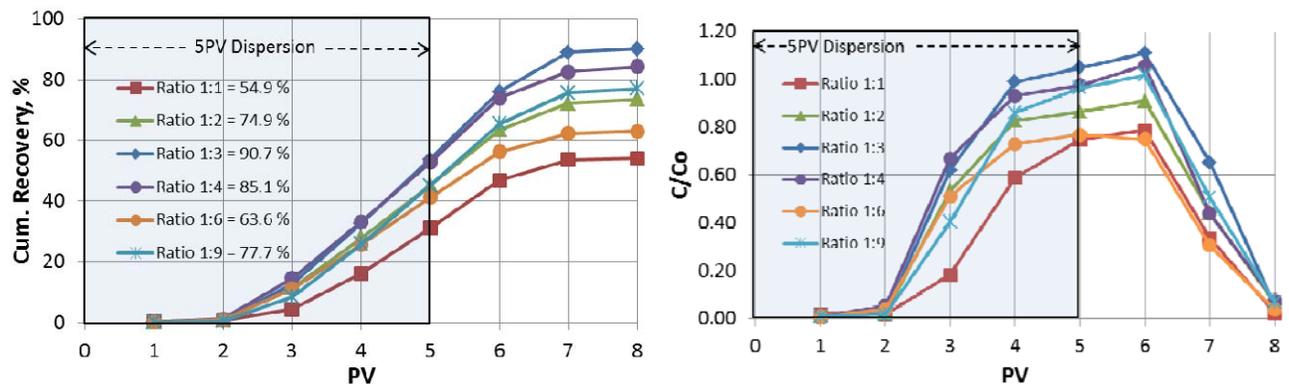


Figure 9. Effect of PVP40:DOW ratio in propagation of purified MWNT in API Brine. (Left: Cumulative particle recovery vs. Pore volume. Right: Normalized concentration vs. Pore volume)

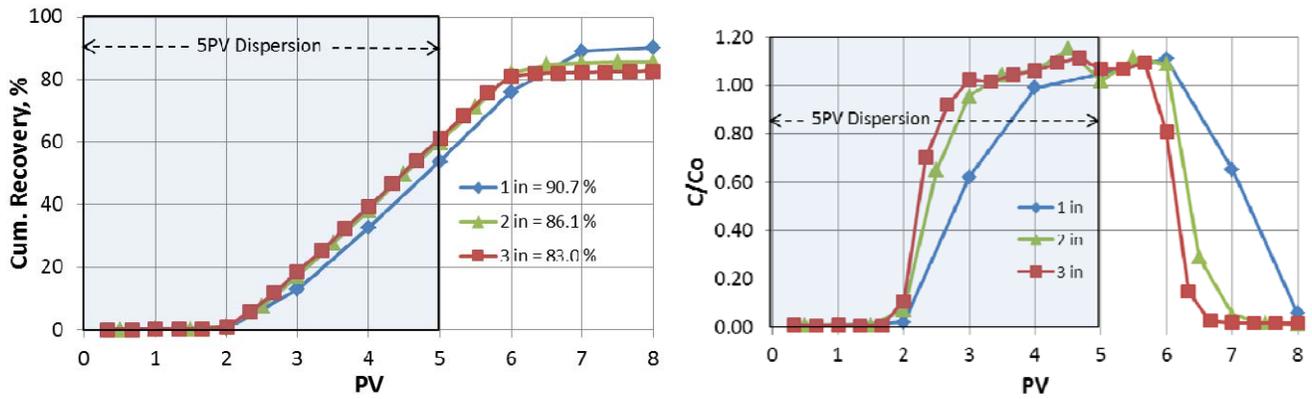


Figure 10. Effect of column length on propagation of purified MWNT with binary dispersant (PVP40 to DOW ratio of 1:3) in API Brine. (Left: Cumulative particle recovery vs. Pore volume. Right: Normalized concentration vs. Pore volume).

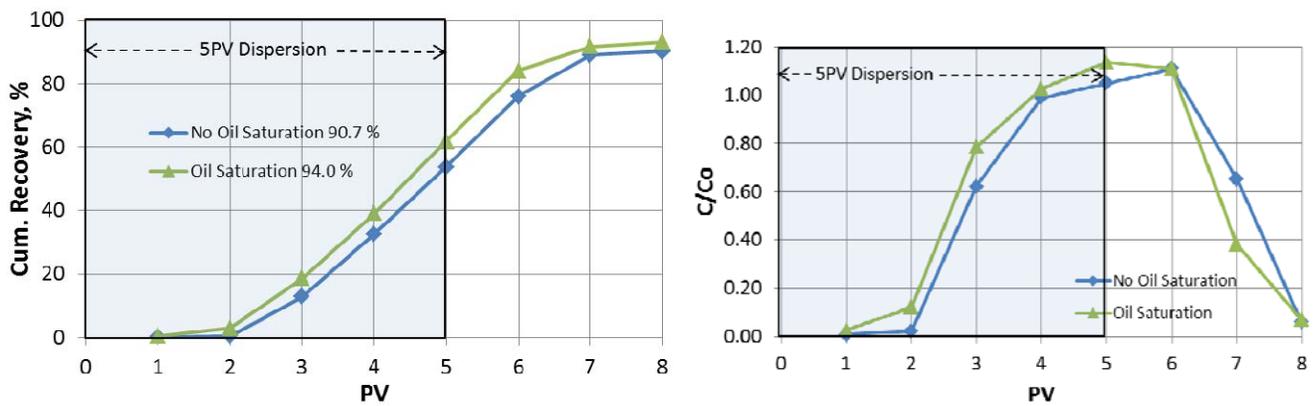


Figure 11. Effect of oil saturation on propagation of purified MWNT with binary dispersant (PVP40 to DOW ratio of 1:3) in API Brine. (Left: Cumulative particle recovery vs. Pore volume. Right: Normalized concentration vs. Pore volume).