

NANOPARTICLES TRANSPORT THROUGH POROUS MEDIA FOR ENHANCED OIL RECOVERY

A Thesis

Presented to

the Faculty of the Department of Chemical and Biomolecular Engineering

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In Partial Fulfillment

of the Requirement for the Degree

Master of Science

in Chemical Engineering

by

Devesh K. Agrawal

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ABSTRACT

Application of nanoparticles is envisaged for enhanced oil recovery applications because of their unique transport and surface wettability properties along with their relatively small sizes compared to the size of pores in porous rocks of an oil reservoir. In the current work stable, dilute dispersion (20 ppm by weight) of the spherical shaped, negatively charged functionalized carbon nanoparticles of different sizes (5 nm, 50 nm) and spherical shaped, neutrally charged polymer grafted silica nanoparticles (35 nm) were injected through the sandstones and carbonates cores (with permeabilities ranging from 2 mD to 400 mD). The pressure profiles and breakthrough curves were obtained and the fluorescence microscopy on the rock surface was performed. The early breakthrough occurred in most cases and retention of nanoparticles in the porous media was found to be dependent upon the pore – nanoparticle relative sizes and temperature.

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Chapter 1 Introduction

1.1 Motivation

Energy is not a commodity but a necessity for development. The global demand for energy is increasing rapidly and is further anticipated to rise over the next few decades (Figure 1) because of the expected rise in consumption by about 40 % in the next two decades. Although the production of energy from alternative energy sources like nuclear and renewable is expected to increase in the future, their role is just going to supplement but not to replace the use of fossil fuels for at least next two decades. Therefore, keeping up with the increasing global demand of energy is a huge challenge and can only be met by either finding the new hydrocarbon reserves or by improving the recovery efficiency from the known reservoirs.

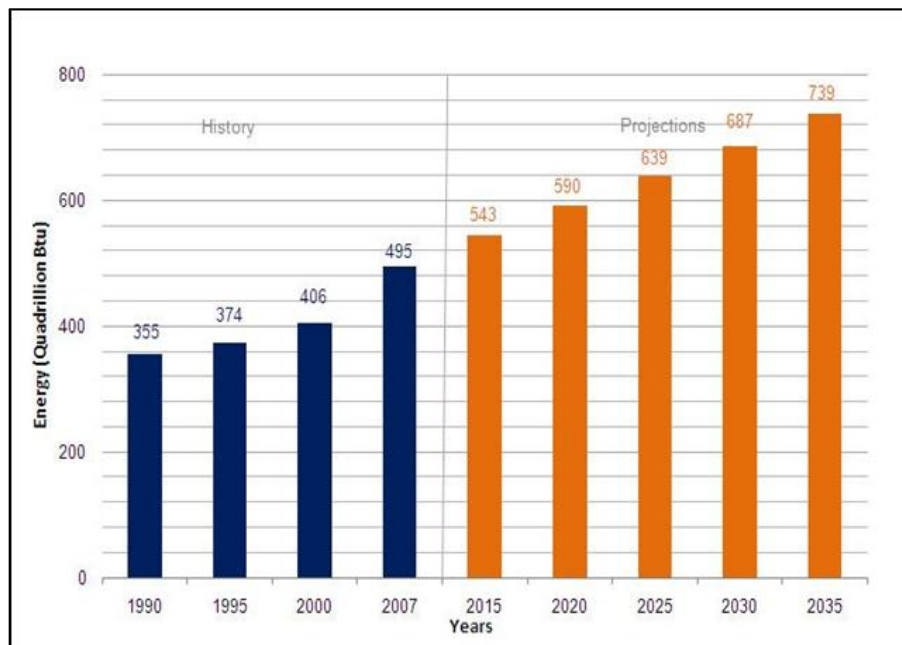


Figure 1. World marketed energy consumption, 1990 – 2035.¹

The scientific community is trying to explore all the possible ways to determine new reserves and develop economical techniques for recovering more oil from existing reservoirs. Unfortunately, the rate of new oil reserves discoveries is declining and many of the already producing oilfields are in the advanced stage of production.² The newer oil reserves are found deeper in more challenging geographical environments which require advanced oil exploration and production techniques. Thus, improving efficiency of the existing reservoirs by developing new techniques is required and any efforts in this direction are highly appreciated and greatly acknowledged considering the fact that overall two third of the world total oil in place cannot be recovered by traditional oil recovery methods. As shown in the Figure 2, the volume of oil discovered and not recovered is much larger than oil produced so far. This clearly explains the importance and necessity of developing new recovery techniques for extracting more oil economically and delay the abandonment of the reservoirs.

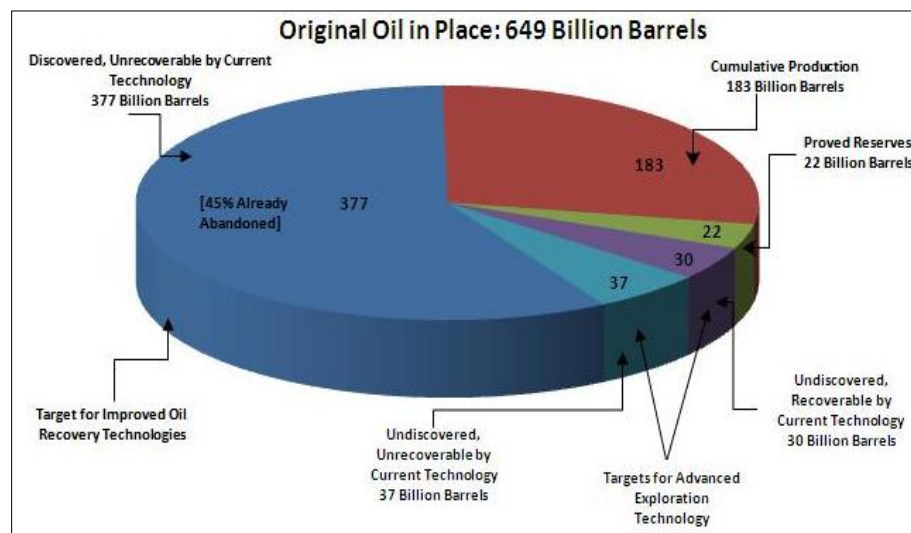


Figure 2. Potential world reserves.

The current enhanced oil recovery (EOR) techniques give some hope but are limited by one reason or another. The breakthrough in the current EOR technologies is needed. Nanotechnology can provide the solution to the challenges offered in enhanced oil recovery. Being at nanoscale, the nanoparticles can flow through the micro sized pores without any mechanical entrapment. The very tiny sizes of nanoparticles make them potential candidates for oil recovery from low permeability reservoirs. If the suitable functional groups are coated on the surface, they are expected to perform the desired functions like viscosity improvement of the water flood or wettability change of the rock or both.

Application of nanotechnology is not new to the oil and gas industry as industry has been making use of nanoparticles in drilling mud over more than fifty years but the application of nanoparticles based technology into more sophisticated applications like EOR, sensing or imaging are recently under early stages of development. The mobility control of the injected nanoparticles is very important for these applications. Also, inside the porous media relative sizes of nanoparticle as compared with pores' size and their interactions with rock's surface are expected to influence their movement in porous media. Therefore, studying the transport behavior of these particles into porous media is essential.

The purpose of this study is to understand the role of pore - nanoparticle surface interactions and their relative sizes on the transport behavior of functionalized carbon nanoparticles (5 nm, 50 nm), polymer grafted silica nanoparticles (35 nm) through the porous media (Berea sandstones (BSS) and Indiana limestone (ILS) cores). Hence, in the current work influence of the

nanoparticle - pore surface interactions, pore - nanoparticle relative sizes on breakthrough curves for nanoparticles transport through porous media is studied. The one dimensional convection diffusion (1D-CD) model is used to simulate the experimental breakthrough curves. The dispersion coefficient and the pore velocity are obtained from the model parameters.

1.2 Oil Recovery Methods

The crude oil recovery from oil reservoirs can be categorized in the three stages: primary, secondary and tertiary or enhanced oil recovery. During the primary recovery, oil flows freely from the reservoir to the production well and the flow is primarily because of the pressure inside the reservoir. The length of this phase is the shortest in the production life of a reservoir. The oil recovery during the primary stage is typically 5-15%. During the next phase, which is called “secondary oil recovery”, the energy is supplied to the reservoir by injecting the water or gas to be able to sweep the oil towards the production wells. The water flooding is the most common secondary oil recovery method and is injected for pressure maintenance (above bubble point) or oil displacement towards production wells. The oil is displaced slowly (~30 cm/day) through the microscopic pores (1-100 μ m), pore throats and channels in the porous medium and due to poor sweep efficiency, many of the areas in the reservoir does not come in contact with water at all and are missed at the macroscopic scale (1-10 m).³ The secondary recovery methods can produce up to 20-40 % of the original oil in place (OOIP). The enhanced oil or tertiary oil recovery methods target the residual oil in the reservoir after primary and secondary oil recovery.

1.3 Enhanced Oil Recovery

The enhanced oil recovery deals with the two important factors which are responsible for the large quantity of unrecovered oil in the reservoir. First, the interfacial tension between the reservoir fluids and the reservoir rocks; and second the viscosity difference between the reservoir oil and the water flood which cause viscous fingering and hence early breakthrough of the water.

The EOR can be broadly categorized as thermal, gas, chemical.⁴ The oil recovery through the microorganisms is also under developmental phase.⁵ In the thermal recovery, target is to increase the temperature of the reservoir and hence reduce the viscosity of heavy, viscous oil and improve its mobility through the porous medium. In gas injection, gases like nitrogen, natural gas or carbon dioxides are injected to displace the oil, or a gas which dissolves in the oil is injected to reduce the viscosity of oil. In chemical injection, the detergent like-surfactants are injected to reduce the interfacial tension (γ) or polymer solution in water or brine is injected to increase the viscosity of water to improve the sweep efficiency. In the microbial injection, the microorganisms are injected into the reservoirs to produce biosurfactants, biopolymers or other chemical on the pore's surface, or to selectively plugging the high-permeability channels in the reservoir. The selection of these methods entirely depends upon the characteristics of the reservoir, the availability of resources around and most importantly the economics of the project.

Although, EOR presents certain advantages over the new reserves, such as the exact location, size of the oil reserve is already known and old production

facilities can be used with some addition of new equipments⁶ but field scale success is still not guaranteed because of the high cost involved or inefficient oil recovery. The chemical EOR processes are limited by the high cost of the injected fluids, and entrapments of the injected material in the reservoir which results in the loss of mobility control and absolute permeability reduction and hence low oil recovery.⁷ The drawbacks like pore entrapment, log-jamming, inaccessible pore volume and mechanical wear and tear limits the wide scale use of polymers, copolymers and associative polymers as EOR material.^{8,9,10,11} The use of traditionally used polymers like partially hydrolyzed polyacrylamide (HPAM) and polysaccharides and other copolymers is limited because of plugging¹², shear breakage¹³, bacterial degradation, thermal in-stability, susceptibility to salinity, sensitivity to multivalent ions and absorption on the oil wetted parts. So the cost effective injectants which are stable and effective at reservoir conditions are greatly needed for enhanced oil recovery application and nanotechnology has the potential to revolutionize the field of enhanced oil recovery because of the unique properties found at the nano-scale compare to micro and macro.^{3,7,14,15}

Chapter 2 Overview

2.1 Nanotechnology for enhanced oil recovery (EOR)

Various reviews have highlighted the potential of nanotechnology for EOR applications.^{15,16,17} Tippee et. al. points out that the nanotechnology may someday boost the average recovery efficiency by 10 %.¹⁸ According to Jenn-Tai Liang, KU Professor, nano-based injection fluids could "lead to tens of billions of dollars in savings and improved oil recovery".¹⁹ The unique properties at nano scale are due to the surface effect i.e. the change of the nanoparticle's properties due to huge increase in the number of surface atoms with the decrease in the size of particles. For example: as the size of spherical particle decreases from the micro to nano, the surface to volume ratio increases by 1000 times. These surface atoms on the nanoparticles are not surrounded by atoms therefore their behavior differs from the atoms in the bulk. Due to these unsaturated dangling bonds, they tend to be coalescent with other particles and become stabilized which leads to rapid increase in the specific surface area, surface energy and surface coalescence energy and hence high chemical activity and absorption ability.⁷

2.2 Advantages of nanotechnology for EOR

- The pores, pores throat and channels in the porous media are of the order of micron size and the nanoparticles are of nanometer scale which means it can easily pass through the porous medium without getting trapped geometrically and hence less injectant is required.⁷

- The addition of the nanoparticles can tune up the viscosity of the injected fluid to the optimum level. Shah and Rusheet et. al. reported that the viscosity of CO₂ combined with 1% CuO nanoparticles and a small amount of dispersant is over 140 times greater than the conventional CO₂.²⁰
- Due to very high surface area to volume ratio, the nanoparticle based modifiers are expected to produce nano-fluids with extremely superior desired properties with the addition of smaller nano-particle concentrations.¹⁵ The desired properties at low concentrations of nanoparticles will bring down the cost of the application of the process.
- The wettability of the porous medium can be changed by the addition of the nanoparticles. Binshan et al. reported in three different papers that lipophobic and hydrophilic polysilicon nanoparticles (LHPN) changes the wettability of the reservoir rocks through its adsorption on the porous walls. The oil-wet reservoir can be changed into water-wet reservoir by the adsorption of the LHPN on the porous rocks and hence the relative permeability of the oil phase increase and hence oil production increases.^{21,22,23} Figure 3 explains the change in wettability by the adsorption of the LHPN. The contact angle for the water drops on the furbished surface of rock slice changes after adsorption of LHPN from $> 90^\circ$ to $<90^\circ$ which essentially indicates that the surface is changed to water wet by the adsorption of the LHPN.

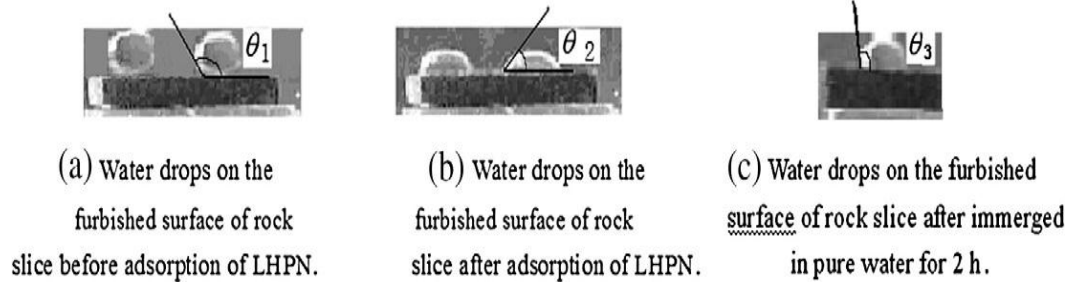


Figure 3. Wettability change of sandstone after absorbing.²¹

2.3 Relevant Forces at Nanoscale in EOR

The laws which govern nano-scale materials are drastically different than laws governing the macro and micro scale behavior because of the vast differences in surface area to volume ratio and the proximity of nano to atomic scale.²⁴ The three forces capillary (forces due to curvature of fluid interfaces), viscous (forces due to viscosity mismatch between fluids) and gravity (forces due to density differences, buoyancy effect) are considered traditionally for oil recovery but at nano-scale coulombic interaction forces (intermolecular forces such as van der Waals forces), disjoining forces (steric and double layer forces) and Marangoni forces (forces due to gradient in property such as concentration and interfacial tension) are also important.³

2.4 Retention Mechanisms

The retention in the porous media can occur in different ways such as pore entrapment, log-jamming, inaccessible pore volume and adsorption. The term retention represents total amount of nanoparticles in the porous media.

2.4.1 Pore Entrapment or Mechanical Entrapment

The blocking of narrow pore throats by larger particles, is known as mechanical entrapment or straining.⁸ The evidence for mechanical entrapment is that the particle concentration in the effluent does not reach the injected concentration.²⁵ or that it would do so only after injecting a large volume of particles or polymer.¹⁰ This retention mechanism is more common for poly-disperse solution.

2.4.2 Log-jamming

The log-jamming explains about the phenomena of blocking of the pores by the particles smaller than the pore's size. This phenomenon can be explained by the mass difference between the particle and the solvent. Due to the smaller size of pore throats and constant differential pressure, the flow velocity is increased in pore throats compared to pore bodies. At the entrance of pore throat, water molecules will accelerate faster than the heavier particles which results in an accumulation of particles at the pore throat entrance. The pore throat radius will thus slowly be reduced and eventually blocked. As described by Bolandtaba et. al, the main factors governing the log-jamming effect are particle concentration and effective hydrodynamic size, pore size distribution and flow rate.²⁶

2.4.3 Inaccessible Pore Volume

Inaccessible pore volume (IPV) quantifies the volume of the reservoir pores which will not be swept by the polymer flood because they are smaller than the polymer molecules. The IPV represents the total pore volume that does not come in contact with the polymer flood. The explanation for the IPV is the wall

exclusion effect.²⁷ The viscosity of the polymer solution layer near the wall is lower than that in the pore center which causes an apparent fluid slip resulting in polymer solution accumulating in the center of the pore along a narrow channel rather than invading the whole volume of the pore. The IPV depends upon molecular weight or molecular size of the polymer; permeability, porosity and pore size distribution of the medium. The IPV will increase if the ratio of permeability to porosity (characteristic pore size of the medium) decreases and the polymer molecular weight increases.

2.4.4 Adsorption

The adhesion of nanoparticles on the rock surface is defined as adsorption. The adsorption on the rock depends upon the NPs-NPs interactions and the NPs-Pore surface interactions. The forces like electrostatic forces of attraction/repulsion, van der Waals forces of attraction (between nanoparticles and pore wall, similar to the colloidal particles^{28,29,30}), disjoining and Marangoni can play significant roles on the adsorption of nanoparticles on pore walls. In addition, Brownian motion plays a significant role at this length scale (Stoke-Einstein equation, $D=kT/6\pi\mu r_p$) which influences adsorption and transport of the nanoparticles.

2.4.5 Permeability Reduction

The permeability reduction is represented by a number called resistance factor, R_F , which essentially is an indication of the mobility reduction power of the polymer. Mathematically, it can be represented as³¹

$$R_F = \frac{\lambda_1}{\lambda_1'} = \lambda_1 \mu_{app} = \left(\frac{k_1}{\mu_1}\right) \cdot \left(\frac{\mu_1'}{k_1'}\right) \text{-----} (1)$$

where k_1 and k_1' are the porous medium's permeability to brine and to polymer solution respectively and μ_1 and μ_1' are the brine and polymer solution viscosity respectively. The resistance factor for constant flow experiments can be obtained by taking the inverse ratio of pressure drops and for constant pressure experiments by taking the ratio of the flow rates of brine and the polymer phases respectively.

The permeability reduction factor, R_k , quantifies the permeability reduction effect due to polymer flood alone, is given by

$$R_k = \frac{k_1}{k_1'} = \frac{\mu_1}{\mu_1'} R_F \text{ ----- (2)}$$

The residual resistance factor, R_{RF} , is a measure of the permanence of the permeability reduction effect caused due to polymer flood. It is defined as the ratio of the mobility of a brine solution in the porous medium before and after the polymer flood

$$R_{RF} = \frac{\lambda_1}{\lambda_{1a}} \text{ ----- (3)}$$

2.5 Nanoparticles solution in Porous Medium

The nanoparticles transport into the porous medium is not thoroughly studied. Traditionally, the work done in this area is mostly by environmental engineers^{32,33} because of the environmental health concerns and the most work considers the aggregates of nanoparticles rather than the individual nanoparticle, so the mechanism and theories applicable to colloidal particles can be applied.³⁴ However, these mechanism and theories might not be true for studying the

transport of well dispersed individual nanoparticles. Also, for environmental impact studies, the permeability of the soil samples used is much higher than the reservoir rocks. Therefore, the results obtained for these studies cannot be applied directly to porous rocks.

Recently, various researchers have been trying to investigate the transport of nanoparticles into porous media and have injected the nanoparticles in deionized water into packs of sand, glass microsphere or even into the high permeability solid reservoir rocks at various temperatures. In most of the studies various researchers have reported aggregation of nanoparticles resulting into face plugging, pore plugging resulting into poor recovery efficiency of these nanoparticles. The primary objective of all of these exercises is to target one or the other reservoir applications like nano-sensor for reservoir imaging, viscosity or interfacial properties modifier for enhanced oil recovery. The real interest is to study the transport behavior of nanoparticle into the tight reservoir rocks (low permeability carbonates or sandstones, shale or gas hydrates) as these reservoirs are the potential for future oil recoveries. Therefore, in this study we are particularly interested in the transport of nanoparticles dispersed in artificial sea water through the low permeability rocks at various temperatures.

Chapter 3 Material description, experimental setup and core flooding experiments

3.1 Material description

3.1.1 Nanoparticles

The carbon based nanoparticles of 5 nm and 50 nm sizes (CNPs) were prepared using citrate chemistry³⁵, and the PolyOligo-EthyleneOxide-MethylAcrylate (POEOMA) grafted on silica nanoparticles³⁶ (35 nm) were synthesized using living radical polymerization.

CNPs are synthesized using the citrate chemistry. The carboxylic acid is attached on the surface which has negative charges. These particles are spherical, fluorescent and have negative surface charge on it. The nanoparticles dispersed in the deionized water are shown in the Figure 4.

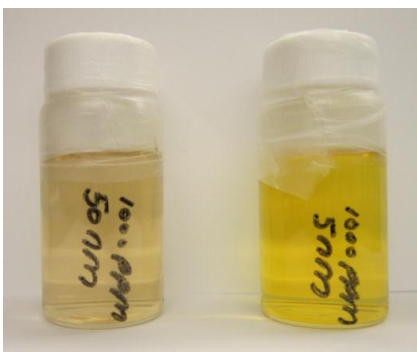


Figure 4. 1000 ppm of the 5 nm and 50 nm CNPs dispersed in deionized water.

The Si-POEOMA nanoparticles are also spherically shaped neutrally charged and are 35 nm in size. The 15 nm is the size of the core and the 20 nm is the size of the polymer brushes grown on its surface³⁶. The weight average

molecular weight of the polymer chain is 80K Da and chain density on the surface is $\sim 1 \text{ chain/nm}^2$ ³⁶.

3.1.1.1 Measurement of particle sizes

The particles size is determined in deionized water by the cornel laboratory using transmission electron microscopy (TEM). The carbon nanoparticle sizes were found 5 and 50 nm.

The Si-POEOMA size in 1 wt. % brine was measured on the DLS and was found to be 35 nm. The 5 nm carbon nanoparticle size could not be measured on DLS as the signal intensity and particles count was low and noise in the signal was too high at low concentrations and at high concentration, the nano-particles were not well dispersed in the solution.

3.1.1.2 Measurement of surface charges on the nanoparticle

The 20000 ppm concentrated dispersion of 5 nm carbon nanoparticles and 1000 ppm concentrated dispersion of 50 nm CNPs in deionized water are prepared separately and the zeta potential is measured on the particle sizer nano from Malvern. The high concentrations are used for sufficient particle count and signal intensity for the measurements. The zeta potential for 5 nm particles in deionized water is -25 mV and for 50 nm particles in -35 mV.

3.1.1.3 Fluorescence on rock surface

The CNPs are coated on the Berea sandstone and Indiana limestone carbonate rock surface (Figure 5) and fluorescence microscope (Figure 6) is used for fluorescence measurment on the rock surface.

The excitation wavelength is 360 nm and the emission wavelength is 460 nm. The filter used is DAPI - EX 377/50 EM 447/60 (blue). The following steps for the CNPs coating on rock surface are followed.

Step 1. 1000 ppm of the 5 nm CNPs solution in the DI water is prepared.

Step 2. 2-3 mD ILS and 100-200 mD Berea core (1.5" dia.) was cut into thin disk shaped slices of ~ 2 mm thickness perpendicular to the axis.

Step 3. Thin slices were washed in DI water and IPA and subsequently dried in vacuum oven for 6 hrs at 100 °C.

Step 4. Now, 20 drops of the CNPs solution were put drop wise on the center of the rock samples.

Step 5. All these samples were placed in a paper boats and put in the vacuum oven at 35°C overnight.

Step 6. The slices were observed on the fluorescence microscope.



Figure 5. Slice of the Berea (left) and Indiana limestone (right) cut from the cylindrical core.

The fluorescence microscopy is performed on the surface of the neat sandstone rock (Figure 7), neat carbonate rock (Figure 9), 5 nm CNPs on sandstone rocks (Figure 8) and 5 nm CNPs on carbonate rocks (Figure 10). The fluorescent images for these neat rock samples clearly shows that the rock

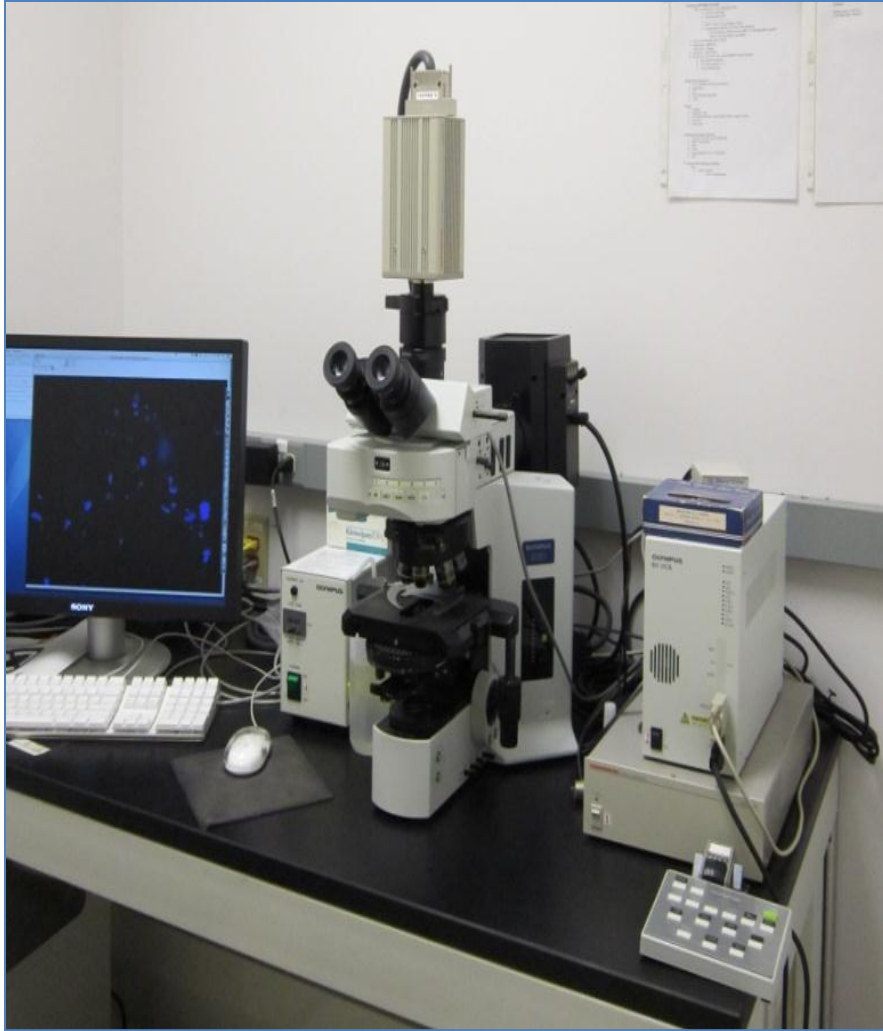


Figure 6. Fluorescence microscope setup in BioMedical Engineering Research Core Laboratory (BMERCL).

surfaces are not fluorescent but the CNPs coated rock surfaces are clearly fluorescent. The UV fluorescence image from the sandstone and the carbonate rock surfaces for the 5 nm carbon nanoparticles exhibit different distribution of the fluorescence on the rock surfaces. The fluorescence for the case of sandstones looks uniformly spreaded on the rock surface which might be due to the repulsion forces between negative charges on CNPs and the distributed

negative charges on the sandstone surface. The fluorescence on the carbonate surface is more concentrated at some places which might be due to the attractive force between negative charges on the CNPs and the positive charges on the carbonates. The different surface interactions results into different fluorescence distribution and intensity from the rock surface.

The experiment is different than the actual situation inside the porous media as the nanoparticle solution is most likely wetting the upper surface and the nanoparticles are not as confined as they are inside the porous media because of geometrical confinement. In the porous media, the nanoparticles are confined in the microscopic length scale so chances of nanoparticles interactions with the pore surface in the more confined pore space are greater and hence its influence on the transport behaviour of the nanoparticles can be significant.

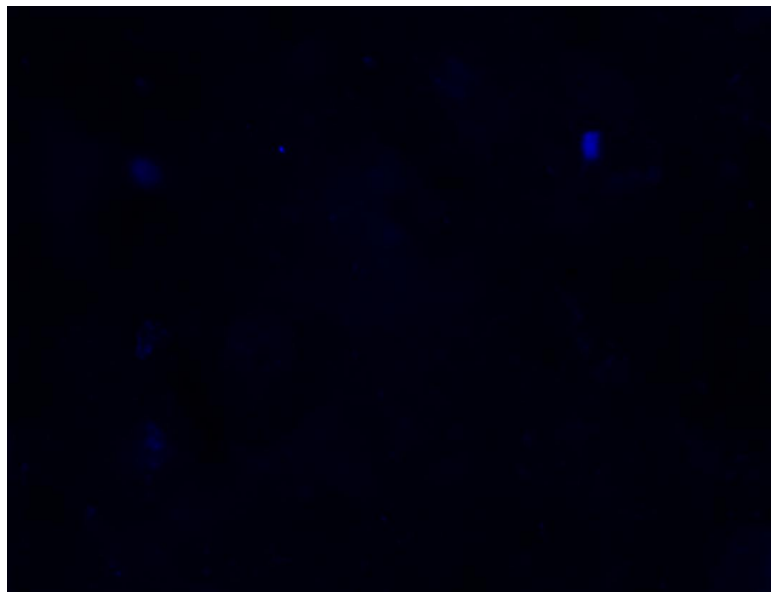


Figure 7. Fluorescence image for the neat Berea core slice (without CNPs) at 10X zoom. (Simple 2D capture, 1344 Pixels × 1024 Pixels, Microns/pixel: 0.64 × 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

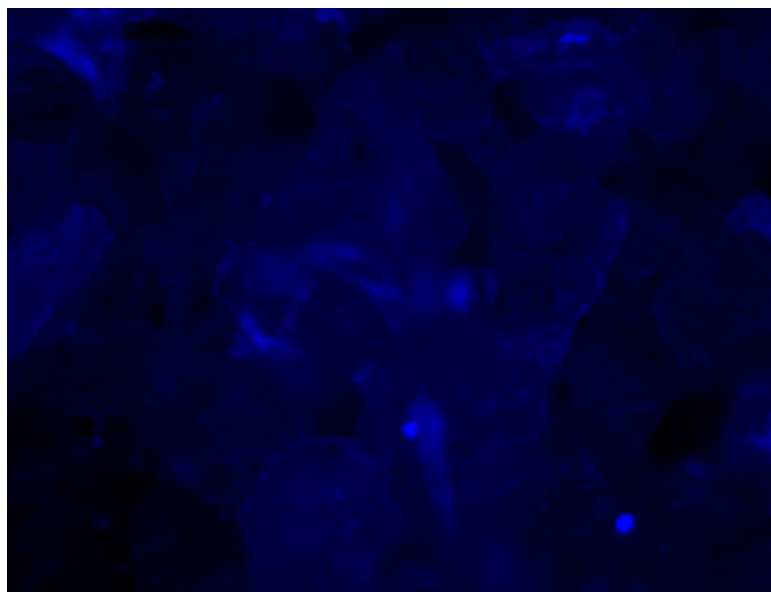


Figure 8. Fluorescence image for Berea sandstone core slice (with 5 nm CNPs) at 10X zoom (Simple 2D capture, 1344 Pixels $\times$ 1024 Pixels, Microns/pixel: 0.64 $\times$ 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

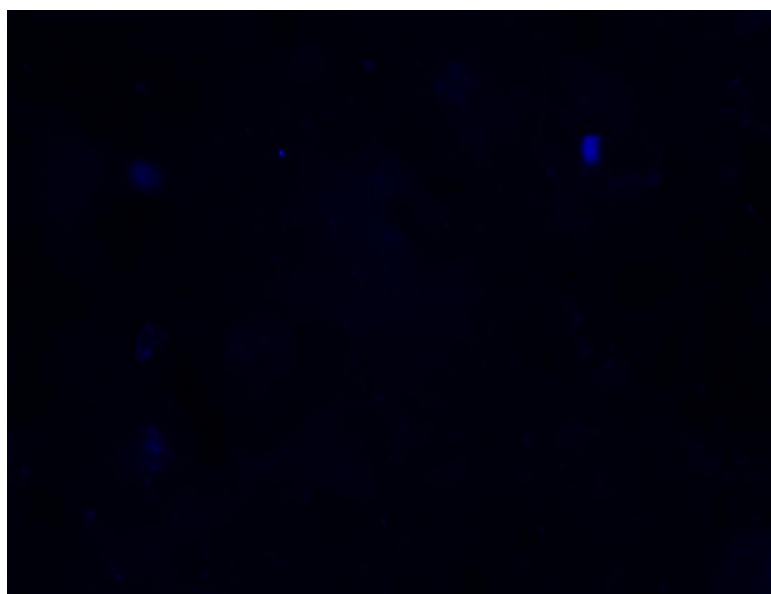


Figure 9. Fluorescence image for the neat ILS slice (without CNPs) at 10X zoom (Simple 2D capture, 1344 Pixels $\times$ 1024 Pixels, Microns/pixel: 0.64 $\times$ 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

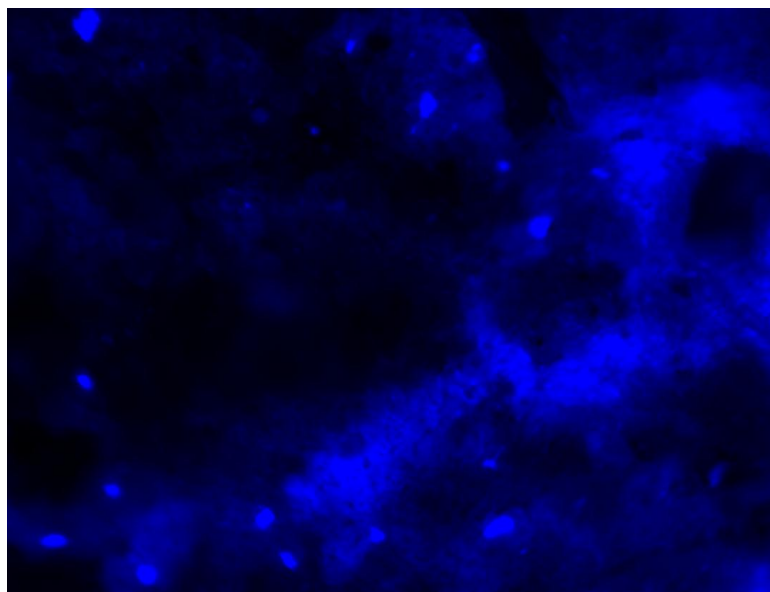


Figure 10. Fluorescence image for the ILS core slice (with 5nm CNPs) at 10X zoom (Simple 2D capture, 1344 Pixels × 1024 Pixels, Microns/pixel. 0.64 × 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

3.1.1.4 Stability of CNPs in artificial sea water

The stability of nanoparticles in sea water is crucial as the presence of many monovalent and divalent surrounding ions make them more prone to aggregation and chemical degradation. In the literature, various researcher have reported huge retention of nanoparticles in the porous media due to aggregation which results in either face plugging, pore or pore throat blocking leading to the nanoparticles transport only up to few inches in the rock. The confirmation of the stability is essential.

3.1.1.4.1 Stability of 5 nm Carbon nanoparticles

The diluted concentration (20 ppm) of the carbon nanoparticles in artificial sea water is prepared by 24 hours of stirring using magnetic stir bar. The diluted dispersion is vacuum filtered through the 0.2 micrometer hydrophilic PTFE filter

(from VWR) to remove the presence of any foreign particles, aggregated CNPs and the filtrate is observed on UV-Visible spectrophotometer (Figure 11 and 12). The UV-Vis absorption spectra for unfiltered and filtered dispersion of CNPs are measured and found to be almost same.

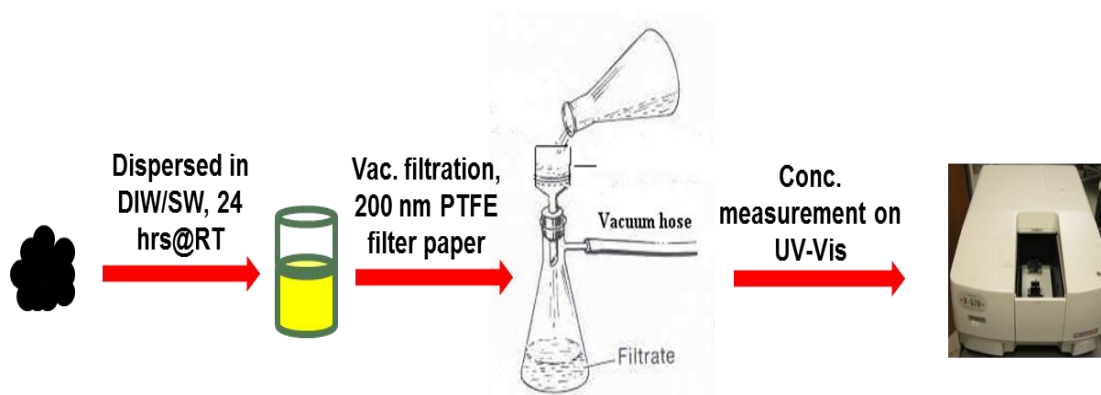


Figure 11. Preparation of the nanoparticle solution.

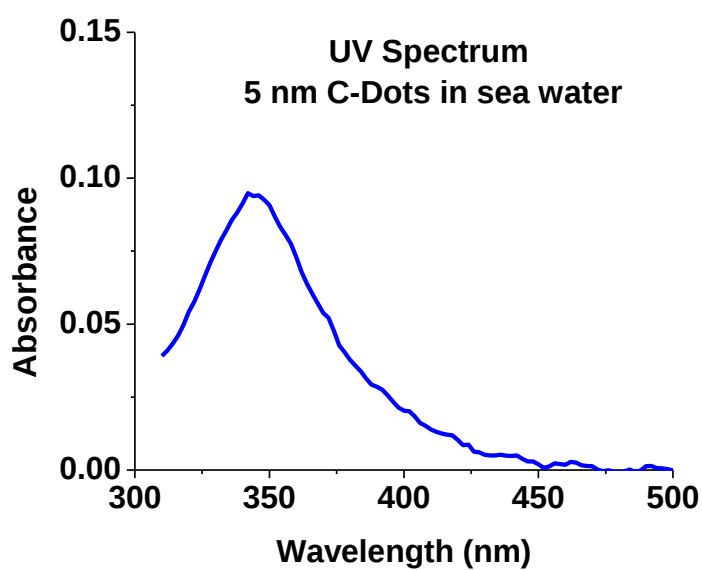


Figure 12. UV-Vis absorbance peak for the 5 nm C-Dots in sea water.

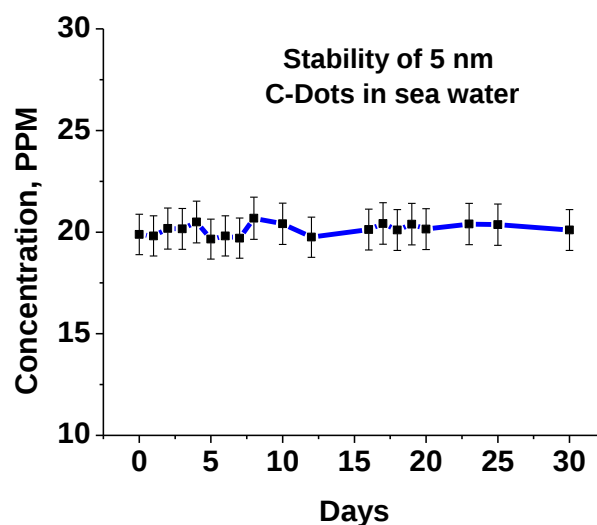


Figure 13. Concentration of 5 nm CNPs in artificial sea water over thirty days.

The 20 ppm nanoparticle dispersion concentration is measured on UV-Vis over the period of a month. The concentration was found to be around 20 ± 0.5 ppm which is within the range of instrument error (Figure 13). It confirms the stability of these particles in the sea water.

3.1.1.4.2 Stability of 50 nm carbon nanoparticles

The 50 nm CNPs are dissolved in artificial sea water and stirred for 24 hours on the stir plate using magnetic stir bar to make the 20 ppm diluted dispersion. The diluted dispersion concentration was measured on UV-Vis for the period of one month. It is observed that the absorbance peak at 282 nm (after 24 hours) is shifted to 252 nm (Figure 14) after five days of stirring and no further change in the peak position is observed over the period of 30 days. The concentration over a period of the 30 days (Figure 15) was found almost same within the range of instrumental error.

The shifting of the peak towards the lower wavelength during the first five day period is due to the dispersion of the initially aggregated nanoparticles and once they are fully dispersed, no change in the peak position is observed. So, the dispersion time is very important for preparing the stable dispersion.

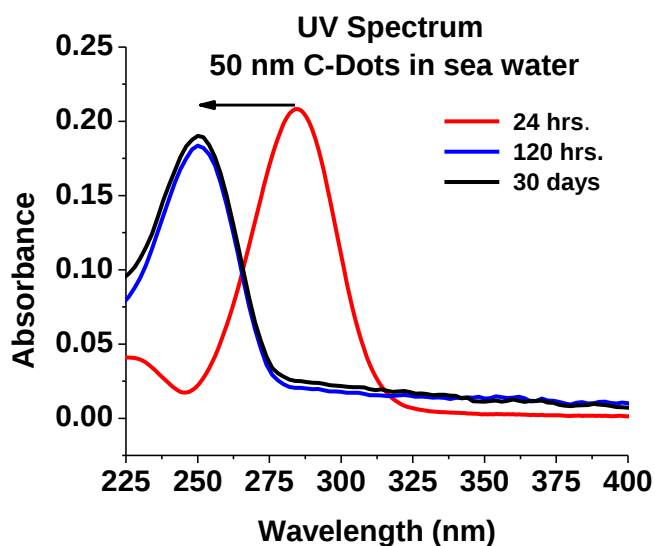


Figure 14. UV-Vis absorbance peak for the 50 nm CNPs in the artificial sea water after 24 hrs. (in red), after 120 hrs. (in blue) and after 30 days (in black).

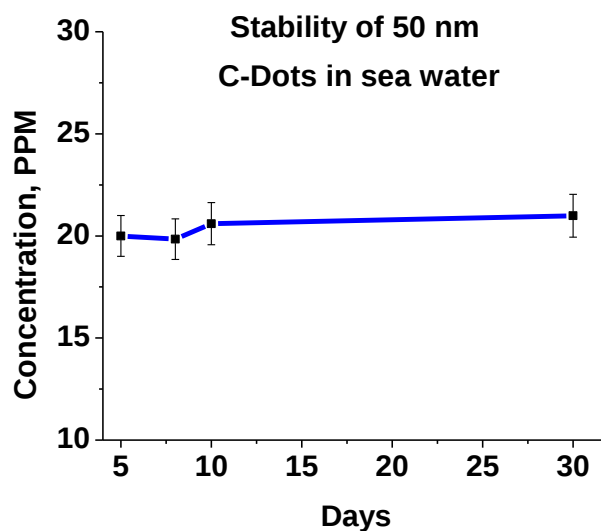


Figure 15. Concentration of 50 nm CNPs in artificial sea water over thirty days.

3.1.2 Artificial sea water

The artificial sea water (ASW) is prepared in the laboratory using the salt composition mentioned by Kester et. al. (1967) as shown in Table 1.³⁷

Table 1. Composition of artificial sea water.

A. Gravimetric Salts		
Salt	Molecular Wt.	G/Kg of Solution
NaCl	58.44	23.926
Na ₂ SO ₄	142.04	4.008
KCl	74.56	0.677
NaHCO ₃	84	0.196
KBr	119.01	0.098
H ₃ BO ₃	61.83	0.026
NaF	41.99	0.003

B. Volumetric Salts				
Salt	Molecular Wt.	Moles/kg of solution	Conc.	Density (23°C), g/ml
MgCl ₂ ·6H ₂ O	203.33	0.05327	1	1.071
CaCl ₂ ·2H ₂ O	147.03	0.01033	1	1.085
SrCl ₂ ·6H ₂ O	266.64	0.00009	0.1	1.013

3.1.3 Porous media

Porous media are very complex structures of porous bodies, pore-throats and are characterized by permeability and porosity. Since almost all the oil reservoirs are either sandstone or carbonate rocks, these porous media are used for transport studies (Figure 17). Both carbonate and sandstone rocks are sedimentary rocks. Sandstones are predominantly composed of silica minerals

which are negatively charged at neutral pH.³⁸ The carbonates are positively charged because they are rich in calcium and magnesium ions.

The Berea sandstones are made of well-sorted and well-rounded sand grains that are predominantly composed of quartz and are cemented by dolomite and clays. The Indiana limestone is composed of grainstones which are cemented by calcite and made of fragments and oolites which are often bigger than 1 mm in diameter. The chemical composition of the Berea and Indiana limestone cores are shown in Table 2 and Table 3.

The Berea and Carbonate cores of dimension 6 × 1.5 inches (length × diameter) and various permeabilities are purchased from the Cleveland Quarries and Kocurek Industries.

Table 2. Composition of the Berea sandstone core.

Silica	SiO ₂	93.13%
Alumina	Al ₂ O ₃	3.86%
Ferric Oxide	Fe ₂ O ₃	.11%
Ferrous Oxide	FeO	.54%
Magnesium Oxide	MgO	.25%
Calcium Oxide	CaO	.10%

Table 3. Composition of the Indiana limestone core.

Chemical Name	Indiana Lime Stone
Carbonate of Lime	97.07
Carbonate of Magnesia	1.2
Silica	0.8
Alumina	0.68
Iron Oxide	0.12
Water and Loss	0.13



Berea Sandstone Core



Yellow Lime Stone Carbonate Core

Figure 16. Berea sandstone and Yellow limestone carbonate core.

3.2 Core flooding set up

The core flooding set up was built in the lab for flow studies of the nanoparticles solution. It is used extensively for mimicking the reservoir conditions at lab scale and carry out experiments on porous medium. The set up consists of tri-axial core holder for placing the cylindrical rock piece, floating piston accumulator for storing nanoparticle solution and crude oil, automatic sample collector for collecting the eluting samples, pressure transducers for recording the inlet and outlet pressures and oven for carrying out experiments at high temperatures. The line diagram and the pictures of the set up are shown in Figures 17 and 18. The oven is used for carrying out the core flooding experiments at high temperatures (Figure 19).

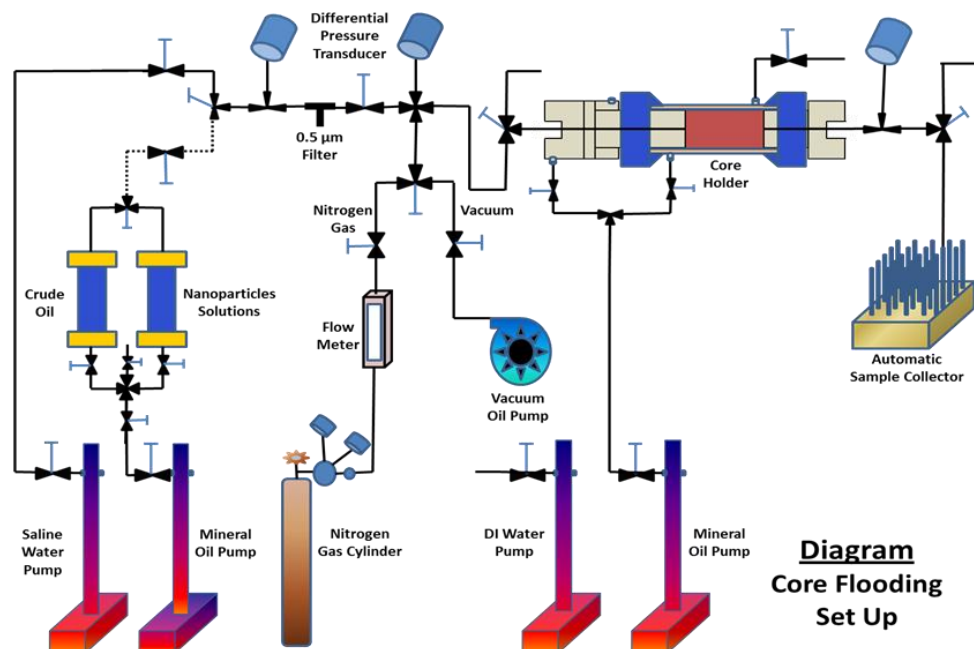


Figure 17. Line diagram for the core flooding setup.

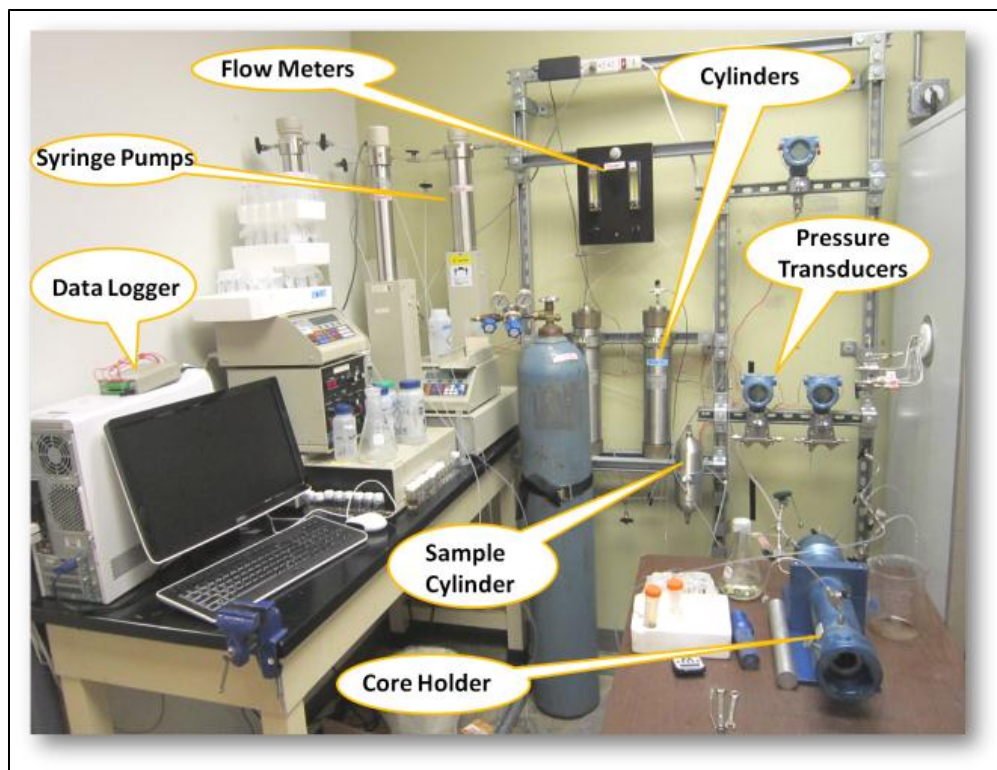


Figure 18. Core flooding set up in the laboratory.



Figure 19. Core holder inside the oven for high temperature core flood experiments.

3.3 Core flooding experiments

The core flooding experiments are conducted in the laboratory on the newly built core flooding set up. The step input of the nanoparticles solution is injected into the brine artificial sea water saturated cores and the differential pressure across the core is recorded and effluent samples are collected for concentrations measurements. The concentration is calculated from the

calibration plot for concentration from the UV-Vis absorbance peak intensity. The retention in the porous media is quantified as percent of the total amount of nanoparticles injected into the core that remained inside the porous media after brine flushing.

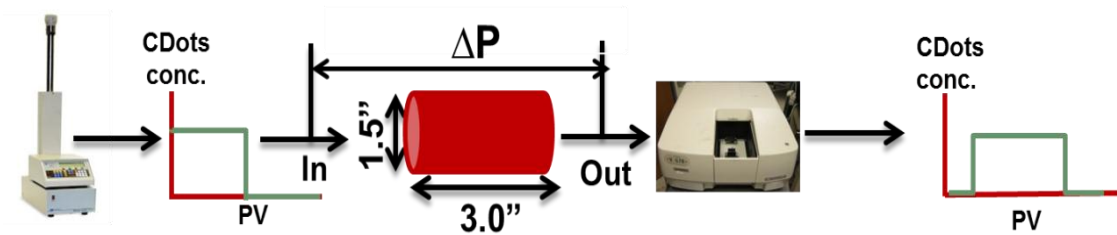


Figure 20. Pictorial description of the core flooding procedure.

In the preliminary experiments 5 nm sized carbon nanoparticles (5CNP) in deionized water (DIW) through low permeability (LP) Yellow limestone (YLS) (5CNP-YLS-LP-DIW, particle size particle type-core type-permeability range-dispersion medium); 5 nm sized carbon nanoparticles (5CNP) in deionized water (DIW) through medium permeability (HP) Indiana limestone (ILS) (5CNP-ILS-HP-DIW); 35 nm sized polymer functionalized silica nanoparticles (POLYNP) through medium permeability (HP) Berea sand stone (BSS) (POLYNP-BSS-HP) are injected into 1 wt. % NaCl saturated cores at room temperatures. In the more advanced experiments, (5CNP-ILS-LP1 to 50CNP-BSS-LP), the 5 nm and 50 nm CNPs are dispersed in artificial sea water and are injected into the sea water saturated cores of permeabilities ranging from 2 mD - 250 mD at various temperatures. The core flooding results are summarized below.

3.3.1 20 ppm of 5 nm CNPs in deionized water injected in 1 wt. % NaCl saturated core

The core flooding experiments are performed on the Berea Sand Stone and Carbonate cores. The cores were put in the core holder and the radial pressure of ~1000 PSI and axial pressure of ~500 PSI were applied by SOLTROL. The core was evacuated by vacuum pump and was saturated with the nitrogen. The pressure vs. flow rate (60 mL/min-480 mL/min) data was obtained and permeability of the core for nitrogen was calculated. Now, the core was again evacuated and saturated with 1 wt.% brine. The pore volume of the core was calculated. The pressure as a function of flow rate (0.2 mL/min-1.4 mL/min) was recorded and the permeability to the 1 wt. % brine was calculated. The core flooding run was conducted for fluorescent carbon nanoparticles (CNPs) (Size: 5 nm) (CNP-YLS-LP-DIW, 5CNP-ILS-HP-DIW, POLYNP-BSS-HP) and for PolyOligo-EthyleneOxide-MethylAcrylate (POEOMA) polymer chains on silica particles (Size: 35 nm). The pressure at the inlet and outlet of the core is recorded in the data logger and the automatic sample collector is connected at the outlet to collect the samples.

3.3.1.1 5CNP-YLS-LP-DIW - The 20 ppm fluorescent nanoparticles (CNPs) through the Yellow Lime Stone Core

The square pulse input of CNPs (shown in black rectangle) at 0.2 mL/min is injected after one PV of 1 wt. % brine injection and was continued up to little more than ~7 PV. The pressure profile increases until breakthrough and become steady until 6 PV. At 6 PV, the steep in pressure is due to change in flow rate

from 0.2 mL/min to 1.2 mL/min. The flow rate is reduced to 0.2 mL/min and the pressure reduces. The post flushing is started and the new steady state which is higher than the original steady state pressure for 1 wt. % brine is achieved because of the removal of most of the CNPs during post flushing.

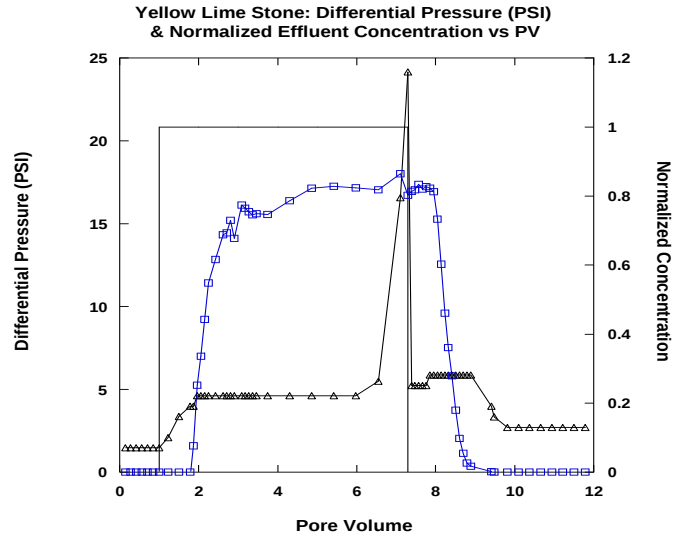


Figure 21. Differential Pressure (triangles) and Normalized Concentration (rectangles) vs. Pore Volume for 5CNP-YLS-LP-DIW.

The pressure and concentration profiles are shown in Figure 22. The concentration profile shows the early breakthrough of the CNPs through the core and the concentration never reached to the injected concentration. The system reached the steady state and fraction of the CNPs got entrapped in the porous media is 21%.

3.3.1.2 5CNP-ILS-HP-DIW - The 20 ppm fluorescent nanoparticles (CNPs) through the Indiana Lime Stone Core

The square pulse input of CNPs (shown in black rectangle) at 2.0 mL/min was given after one PV of 1 wt.CNPs % brine injection and was continued up to ~7 pore volume. The pressure and concentration profile (Figure 22) in this case

exhibits the same features as in the last plot. The pressure increases when flow shifts from the 1 wt.% brine to CNPs and the early breakthrough is observed. The concentration did not reach to the initial concentration and the pressure did not reach to the steady state during the injection of CNPs. After post flushing, the new steady state which is at slightly higher pressure than initial steady state pressure (for 1 wt.% brine) was achieved and ~ 7.5% of the CNPs retained in the porous media.

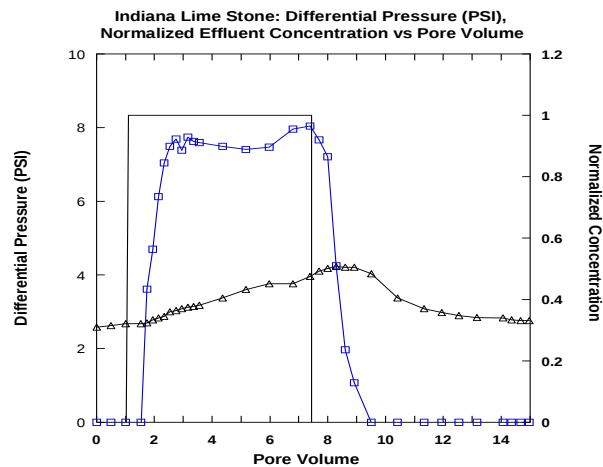


Figure 22. Differential Pressure (triangles) and Normalized Concentration (rectangles) vs. Pore Volume for 244.8 mD Indiana Lime Stone Core.

The high retention in the porous media can be explained from the fact that the pore surface has distributed positive charge and CNPs being the negative in charge are getting adsorbed. The reason for the concentration not reaching to initial concentration is that the all the surface charges are not saturated and the concentration is so dilute that it might require thousands of pore volume of

nanoparticle solution for completely saturating all the pores before saturating all the pores.

The lower retention for the high permeability ILS as compared to the YLS can be attributed mainly to the higher permeability and bigger pore size so that only a small fraction of the nanoparticles are getting in contact with the surface and majority is passing through the bulk of the flow .

The summary for the core flooding experiments 5CNP-YLS-LP-DIW, 5CNP-ILS-HP-DIW and POLYNP-BSS-HP are presented in the Table 4 below.

Table 4. Summary of Experiments # 5CNP-YLS-LP-DIW, 5CNP-ILS-HP-DIW and POLYNP-BSS-HP.

		5CNP-YLS-LP-DIW	CNP-ILS-HP-DIW
CNPs, Particle Size: 5 nm	Concentration	20 ppm	20 ppm
	Solvent	Water	Water
	Filtration	Twice through 0.2 μ m Cellulose Filter	Twice through 0.2 μ m Cellulose Filter, 0.5 μ m online
	Plugging	No	No
	Flow Rate (ml/min)	0.2	2.0
Core Dimension	Diameter and Length, inches	1.5 and 6	1.5 and 6
	Orientation	Horizontal	Horizontal

Permeability, mD	Nitrogen	52.2	287.9
	1 wt. % Brine	53.6	244.8
Pore Volume, cm³		42.6	39.6
Porosity, %		25.2	23.2
Stress, psi	Radial	800	800
	Axial	470	450
Differential Pressure at Steady State, psi	1 wt. % Brine	1.4	2.6
	20 ppm CNPs	Steady State Reached (5.4 PSI, 5.5 PV Injected)	Steady State Reached (4.2 PSI, 5.2 PV Injected)

3.3.1.3 POLYNP-BSS-HP. Core flooding with the 0.5 wt.% Si-PolyOligo-EthyleneOxide-MethylAcrylate (POEOMA) in 1wt. % brine in the 1 wt. % brine saturated 380 mD Berea sand stone core

The 0.5 wt. % Si-POEOMA polymer brushes grown on the silica nanoparticles and dissolved in the 1 wt. % Brine were injected through the Berea sandstone rocks of 1.5 inch diameter and 9 inches of length. The porosity and brine permeability are calculated as 22.8 % and 380 mD respectively. The pressure drop for the 5 mL/min, 10 mL/min flow rates is reached to steady state after the injection of 2 PV to 5.6 PSI, 11.5 PSI respectively. The flow rate was step shift from 5mL/min to 10 mL/min at 3.86 PV.

The concentration reached to initial concentration after the injection of ~6 PV. The neutral charge on the Si-POEOMA and high permeability of the core might be the reason for concentration to reach the initial concentration after the

injection of ~6 PV. Surprisingly, the concentration at some point is even more than the injected concentration. It might be because of the delayed arrival of some of the particles adsorbed on the pores. The effluent concentration didn't reach to zero which indicates that the post flushing is required for few more pore volume. The net retention of the particles in the porous medium was calculated and found to be 10.0 % (Figure 22).

The breakthrough occurs around almost after a pore volume and the concentration front is more plug flow like. No face plugging or pore plugging was observed and these particles were used for the oil displacements. The enhanced oil recovery was found 7.9 % for 1 wt. % of the Si-POEOMA nanoparticles solution.³⁶

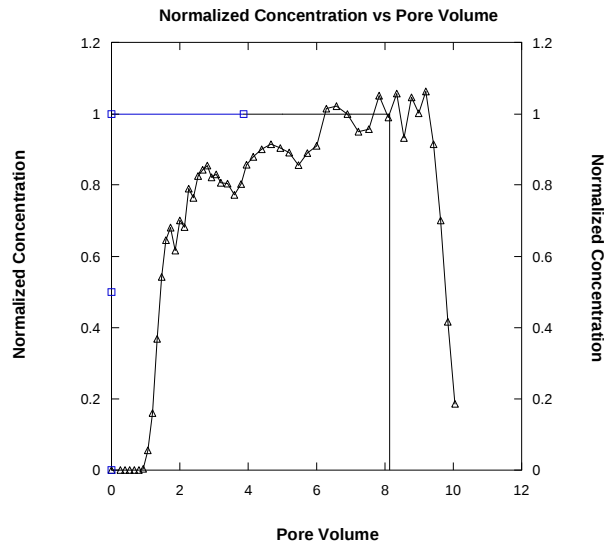


Figure 23. Normalized Concentration (triangles) vs. Pore Volume for 380 mD Berea Sand Stone Core at 0.5 wt.% POEOMA in 1wt.% Brine.

3.3.1 20 ppm of 5 and 50 nm CNPs in artificial sea water (ASW) is injected into ASW saturated core

The core flooding experiments are performed on the Berea Sand Stone and Carbonate cores. The cores were put in the core holder and the radial pressure of ~950 PSI and axial pressure of ~450 PSI were applied by SOLTROL. The low and high permeability cores were evacuated for 48 hours, 12 hours respectively by vacuum pump. The core was saturated by the ASW and pore volume was measured. The pressure vs. flow rate (0.50-1 mL/min) data was obtained and permeability of the core for ASW was calculated. Now, the core was conditioned in the ASW for 12 hours and 5 – 10 PV of the ASW is injected before injecting the nanoparticle solution. The core flooding run was conducted for fluorescent carbon nanoparticles (CNPs) (size: 5 nm, experiment # 5CNP-ILS-LP1, 5CNP-ILS-LP2, 5CNP-BSS-LP, 5CNP-BSS-LP-ASWSTABILITY) and for CNPs (size: 50 nm, experiment # 50CNP-ILS-LP, 50CNPA-BSS-LP, 50CNPA-ILS-HP, 50CNP-BSS-HP, 50CNP-ILS-HP, 50CNP-BSS-LP). The pressure at the inlet and outlet of the core is recorded in the data logger and the automatic sample collector is connected at the outlet to collect the samples. The total of nine core flooding experiments (Table 5) are conducted for low to high permeability Berea sandstones and Indiana limestone cores with 20 ppm dispersion of 5, 50 nm of carbon nanoparticle concentration for various temperatures. The concentration breakthrough curves for all the core flood experiments are prepared.

Table 5. Core flooding experiments with CNPs in artificial sea water.

Exp. #	5CNP -ILS- LP1	5CNP -ILS- LP2	50CN P-ILS- LP	50CNP A-BSS- LP	5CNP -BSS- LP	50CNP A-ILS- HP	50CN P- BSS- HP	50CN P-ILS- HP	50CN P- BSS- LP
Core Types	ILS	ILS	ILS	BS	BS	ILS	BS	ILS	BS
Nanoparti cle Size (nm)	5	5	50	50	5	50	50	50	50
ASW Permeabili ty (mD)	2	36	2	21	16	144	228	173	18

3.3.2.1 5CNP-BSS-LP-ASWSTABILITY. The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (48.6 mD) Berea Sand Stone Core

The Berea sandstones contain clay is prone to swelling and migration resulting in the abrupt reduction in the permeability³⁹. Now, for the experiments with Berea sand stones, before injecting the nanoparticles, the stability of the porous media is checked against injection of ASW into ASW saturated low permeability Berea core for swelling and potential migration of the clay. The fifty pore volume of the ASW is injected and differential pressure is recorded across the core. The pressure profile is found stable after around eight pore volume and is constant for ~ 50 PV of ASW injection which indicates that porous medium and its permeability is not changing (Figure 24). Now, around twenty pore volume of the 20 ppm – 5nm – CNPs in ASW are injected into the porous medium. There is no sticking of the particles and the recovery of the particles is around 100 % and the permeability before and after is same.

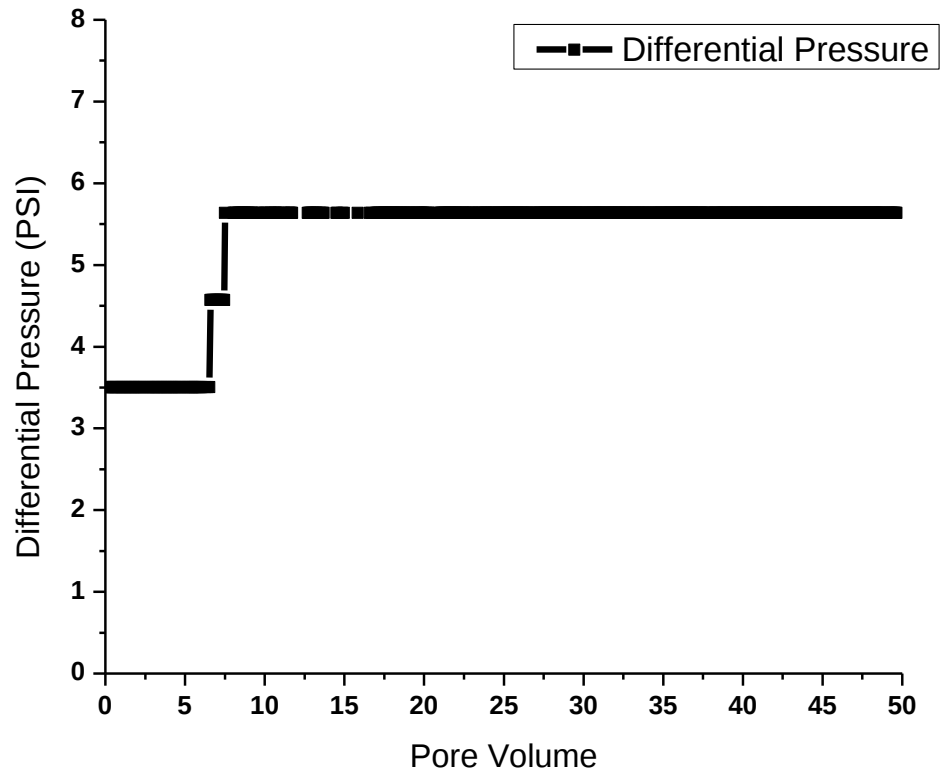


Figure 24. Differential Pressure vs. Pore Volume for 5 nm CNPs in SSW injected through the Berea sand stone core.

3.3.2.2 5CNP-ILS-LP1. The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (1.97 mD) Indiana Lime Stone Cores at 24 °C, 50 °C and 95 °C

A solution containing 20 ppm of 5 nm CNPs successfully transport through the low permeability ILS with almost no retention at 50 °C and 95 °C but at room temperature there is retention of ~ 11 % (Figure 25). The breakthrough (point when nanoparticles are first collected in the eluting concentration) at all the

temperature occurs before one pore volume and the concentration at for room temperature never reached to the inlet concentration.

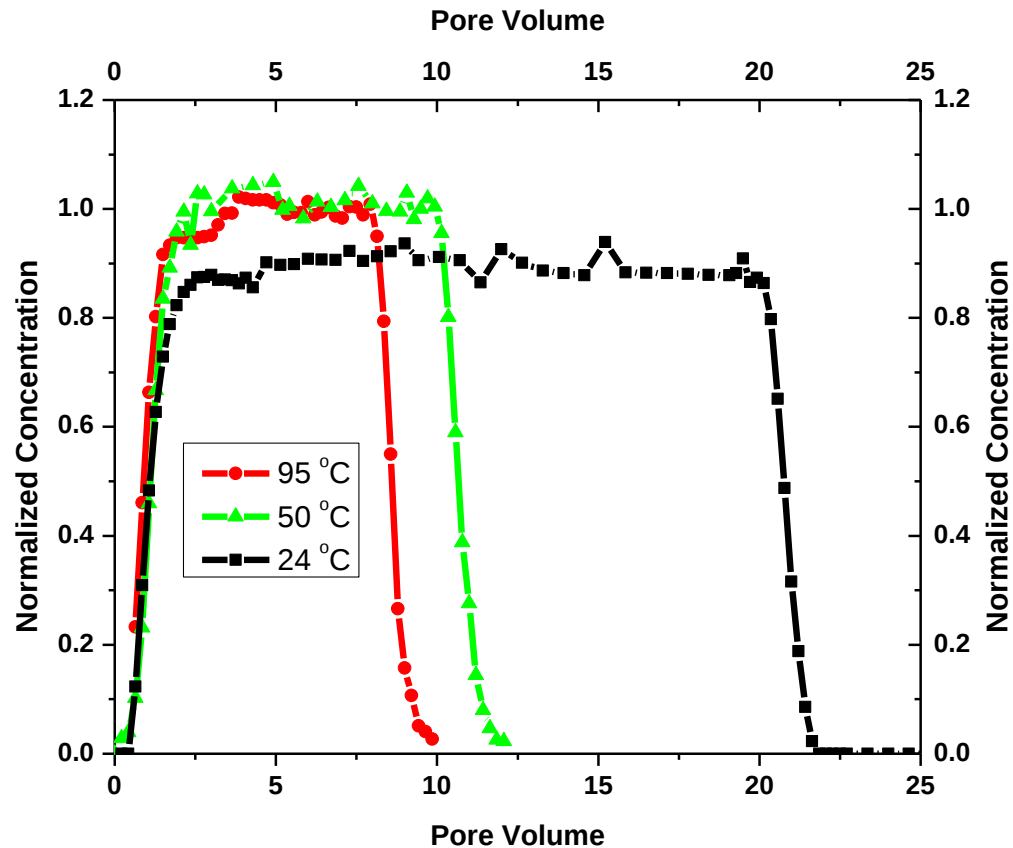


Figure 25. Core Flooding Experiments # 5CNP-ILS-LP1: The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (1.97 mD) Indiana Lime Stone Cores at 24 °C, 50 °C and 95 °C.

3.3.2.3 5CNP-ILS-LP2. The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the 36.09 mD Indiana Lime Stone Cores

A solution containing 20 ppm of 5 nm CNPs as in experiment # 5CNP-ILS-LP1 is injected through the low permeability ILS. As the permeability of the core is increased, the pore size gets bigger and the 20 ppm of 5 nm CNPs successfully transport with almost no retention at all the temperatures. The

breakthrough at all the temperature is before one pore volume and the concentration quickly reaches to the inlet concentration (Figure 26).

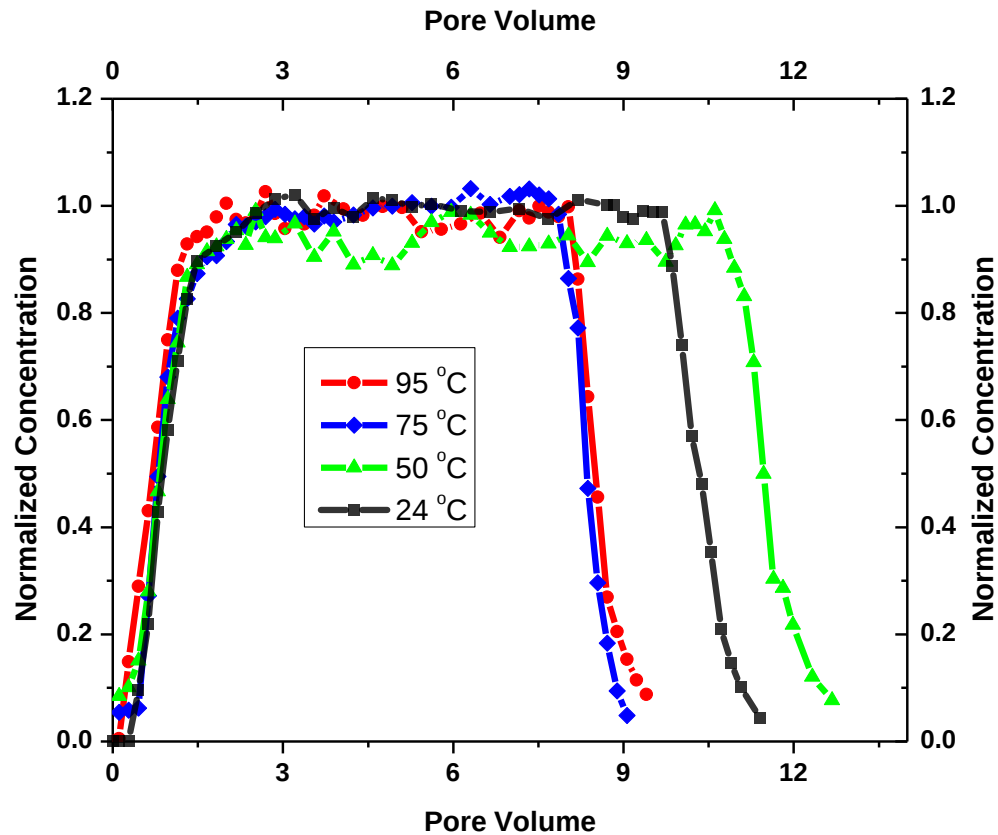


Figure 26. 5CNP-ILS-LP2: The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the 36.09 mD Indiana Lime Stone Cores.

3.3.2.4 5CNP-BSS-LP. The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (16.30 mD) Berea sandstone cores

A solution containing 5 nm CNPs successfully transport through the low permeability Berea sandstone core without any retention at all the temperatures.

No sticking is found and the breakthrough occurs before one pore volume (Figure 27).

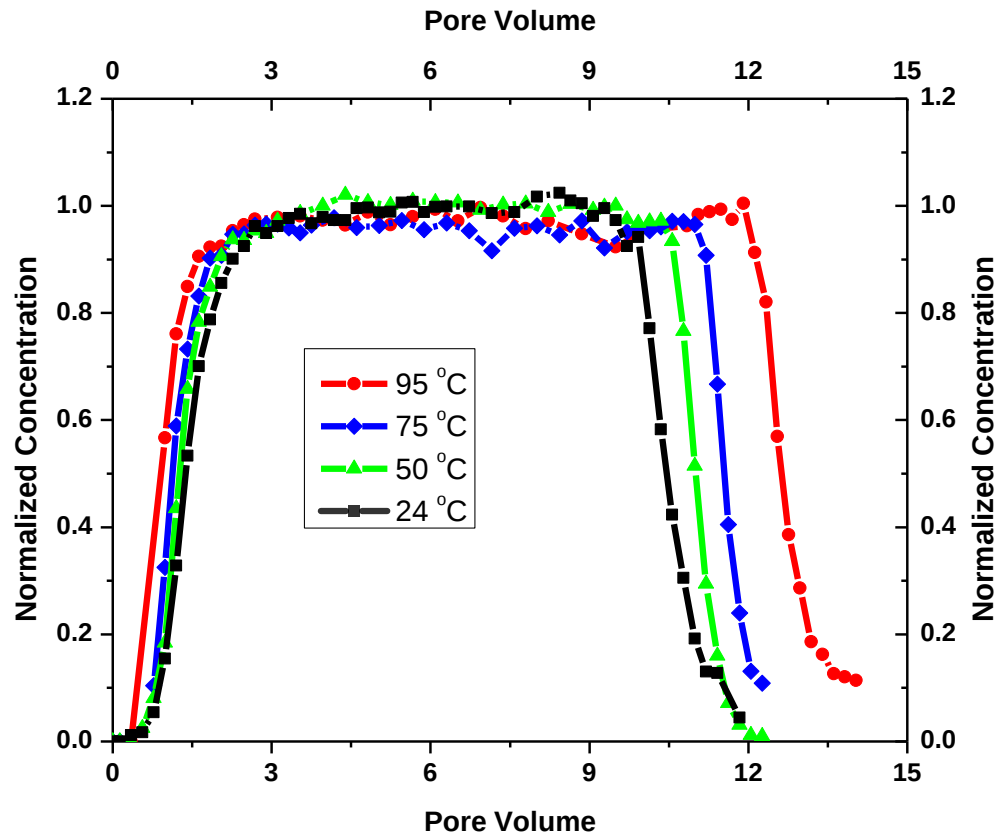


Figure 27. 5CNP-BSS-LP. The 20 ppm of 5 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (16.30 mD) Berea sandstone cores.

3.3.2.5 50CNP-BSS-HP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the 228.34 mD Berea sandstone cores

The 50 nm CNPs do not stick to the rock surface and breakthrough occurs at less than a pore volume. The concentration quickly reaches to the injected concentration (Figure 28).

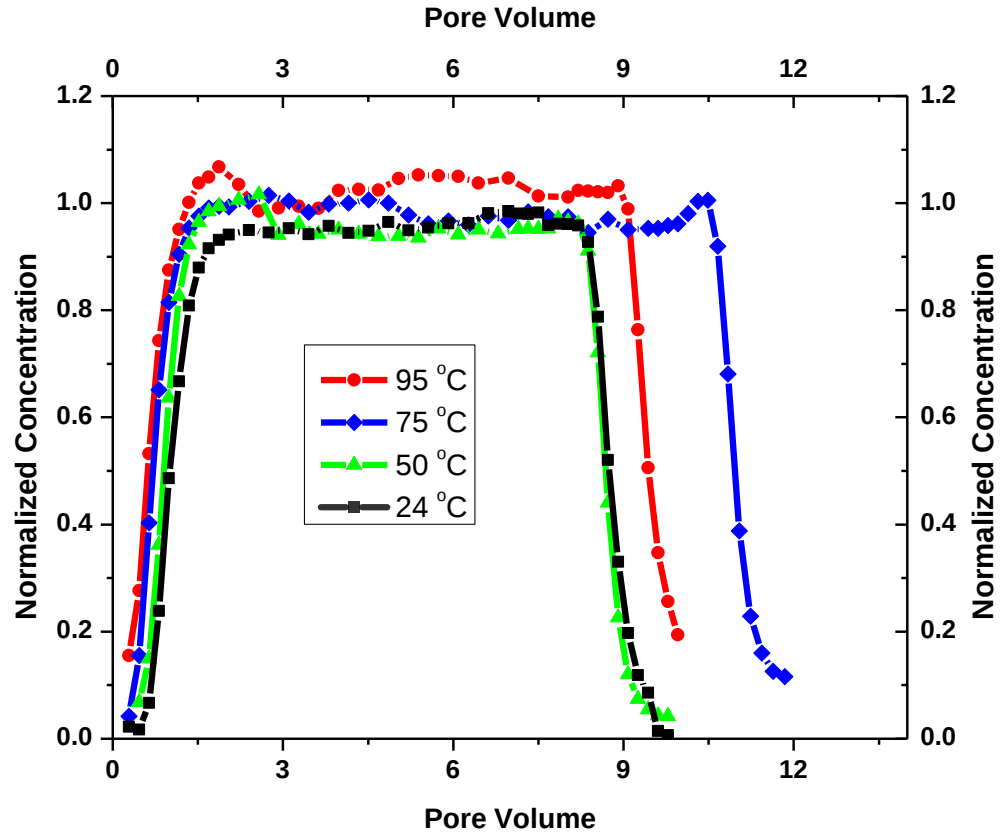


Figure 28. 50CNP-BSS-HP: The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the 228.34 mD Berea sandstone cores.

3.3.2.6 50CNP-ILS-HP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the 173.46 Indiana Lime Stone Cores

The 50 nm CNPs do not stick to the rock surface and breakthrough occurs at less than a pore volume. The concentration quickly reaches to the injected concentration (Figure 29).

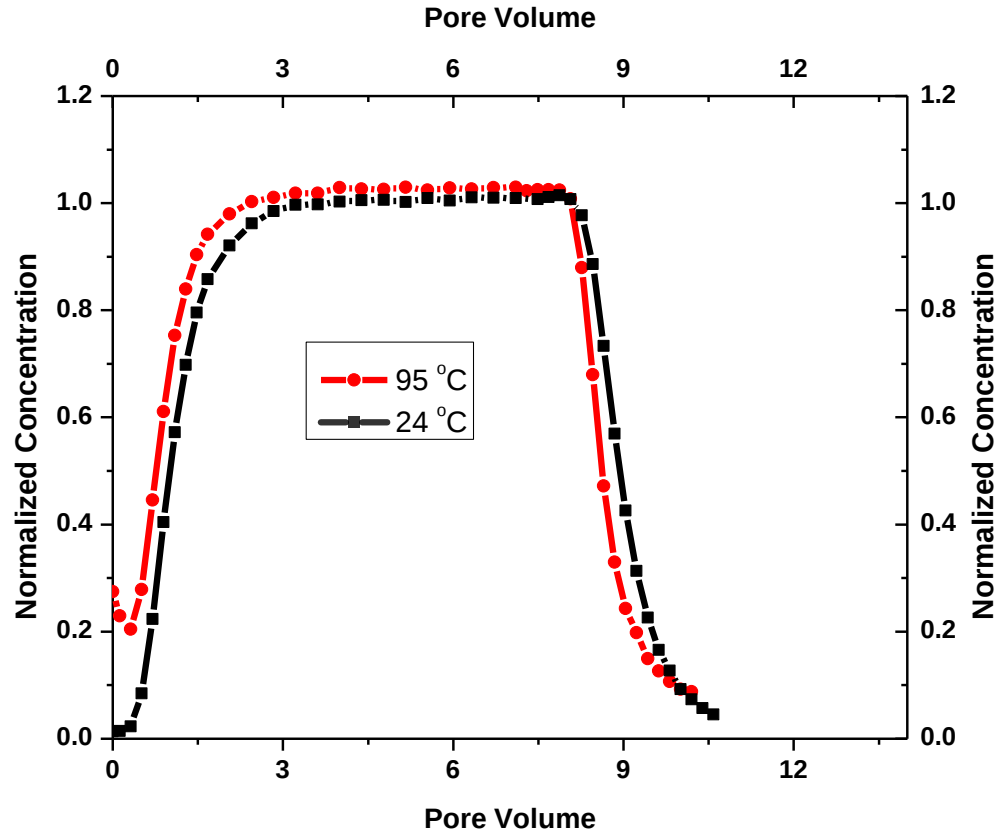


Figure 29. 50CNP-ILS-HP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the 173.46 Indiana Limestone Cores.

3.3.2.7 50CNP-BSS-LP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (17.55 mD) Berea sand stone cores

The 50 nm CNPs do not stick to the rock surface at 95 °C but at 24 °C and 50 °C temperature some of the particles were blocked into smaller pores. The breakthrough occurs at less than a pore volume (Figure 30)

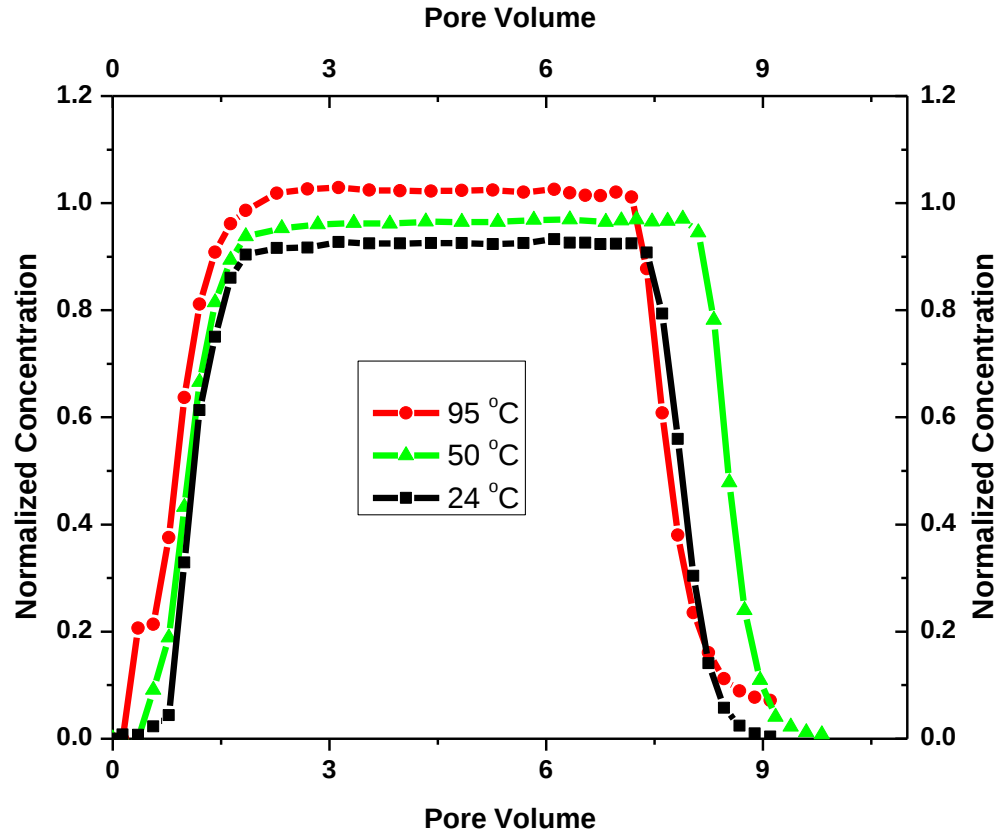


Figure 30. 50CNP-BSS-LP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (17.55 mD) Berea sandstone cores.

3.3.2.8 50CNP-ILS-LP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (1.97 mD) Indiana Lime Stone Cores at 50 °C

The 50 nm CNPs in ASW was found to be sticking in the porous media at 50 °C temperature. The concentration didn't reach to the inlet concentration and the early breakthrough is observed (Figure 31).

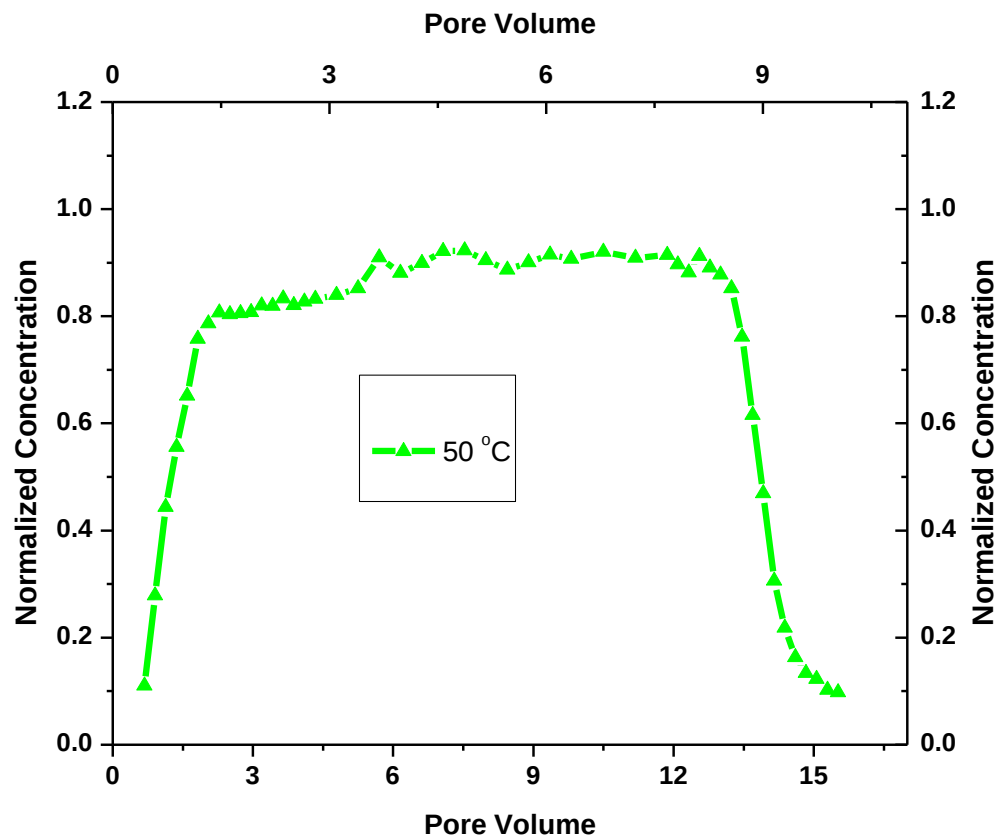


Figure 31. 50CNP-ILS-LP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (1.97 mD) Indiana Limestone Cores at 50 °C.

Table 7. Percentage retention for the various core flood run at different temperatures.

Tem p (°C)	5CNP- ILS-LP1	5CNP- ILS-LP2	50CNP- ILS-LP	5CNP- BSS-LP	50CNP- BSS-HP	50CNP- ILS-HP	50CNP- BSS-LP
95	0	0		0	0	0	0
75		1		4	0	0	
50	0	2	11	1	2		4
24	11	0		1	3	2	9

Table 6. Permeability of the cores for ASW measured before nanoparticles injection and after flushing nanoparticles solution by ASW.

Run #	5CNP-ILS-LP1	5CNP-ILS-LP2	50CN P-ILS-LP	5CNP-BSS-LP	50CNP-BSS-HP	50CNP-ILS-HP	50CNP-BSS-LP
Permeability (mD, before C-Dots)	2.0	36.1	2.0	16.3	228.3	173.5	17.6
Permeability (mD, after C-Dots)	1.8	33.0	1.5	14.1	209.2	160.0	16.1

3.3.2.9 50CNPA-BSS-LP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the low permeability (21.07 mD) Berea sandstone cores

The 50 nm CNPs is found to be sticking with the Berea at all temperatures. The breakthrough occurs at less than one pore volume and the concentration doesn't reach to the injected concentration.

3.3.2.10 50CNPA-ILS-HP. The 20 ppm of 50 nm fluorescent carbon nanoparticles (CNPs) through the 143.68 mD Indiana Limestone Cores

The 50 nm CNPs are sticking on the porous media at all the temperatures. The concentration does not reach to the injected concentration and breakthrough occurs at less than a pore volume.

The retention of the 50 nm nanoparticles is huge for 50CNPA-BSS-LP and 50CNPA-ILS-HP which is due to the unstable dispersion of the CNPs solution (24 hrs) used for these experiments.

Table 6. Percentage retention at different temperatures for experiments 50CNPA-BSS-LP and 50CNPA-ILS-HP.

Temp (°C)	50CNPA-BSS-LP. % Ret.	50CNPA-ILS-HP. % Ret.
95	33	44
75	44	60
50	51	37
24	48	27

Table 7. Permeability of the core for ASW before nanoparticle injection and after flushing the core with ASW.

Run	50CNPA-BSS-LP	50CNPA-ILS-HP
Permeability (mD, before C-Dots)	21.1	143.7
Permeability (mD, after C-Dots)	15.7	56.1

Table 8. Summary of the core flooding experiments.

Exp. #	5CNP-ILS-LP1	5CNP-ILS-LP2	50CNP-ILS-LP	50CNP A-BSS-LP	5CNP-BSS-LP	50CNP A-ILS-HP	50CNP-BSS-HP	50CNP-ILS-HP	50CNP-BSS-LP
Core Types	ILS	ILS	ILS	BS	BS	ILS	BS	ILS	BS
Nanoparticles Size (nm)	5	5	50	50	5	50	50	50	50

Permeability (mD, before CNPs)	2.0	36.1	2.0	21.1	16.3	143.7	228.0	173.5	17.6
Permeability (mD, after CNPs)	1.8	33.0	1.5	15.7	14.1	56.1	209.2	160.0	16.1
Porosity (%)	16.3	21.3	15.3	18.0	17.0	20.0	22.4	18.4	17.9
Pore Volume (cm³)	14.03	17.43	13.14	15.04	14.10	16.36	17.06	15.48	14.05
Length (cm)	7.53	7.40	7.53	7.40	7.41	7.42	7.21	7.61	7.3
Diameter (cm)	3.81	3.74	3.810	3.77	3.77	3.74	3.66	3.74	3.7
Inlet Dead Volume (cm³)	7.03	7.03	7.03	7.03	7.03	7.03	7.03	7.03	7.03
Outlet Dead Volume (cm³)	5.05	3.06	5.05	5.05	3.06	3.06	3.06	3.06	3.06
Flow Rate (cm³/min)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Dead Time (in PV I/L + O/L)	0.86	0.58	0.92	0.80	0.72	0.62	0.59	0.65	0.72

3.4 Modeling

The one dimensional advection-dispersion partial differential equation is widely used for transport of the non-reactive particles through the soil samples⁴⁰. Recently, Jie Yu et. al. (for carbon NPs through dolomite, Berea packed column)⁴¹ and F. He et. al. (for cellulos-coated iron oxide NP through packed column)⁴² reported using the one dimensional convection diffusion with a 1st

order reaction term (analytical solution is possible)⁴³ to model the breakthrough curves obtained for nanoparticle transport through porous media.

The 1D convection diffusion (with or without first order reactive term) is used to model the breakthrough curves. The dispersion coefficient and the pore velocity are obtained from the model. The model equation is given by

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} - GC, \quad (4)$$

where D is dispersion coefficient, U is pore velocity, G is 1st order removal rate constant, C is concentration of the particles, x is length and t is the time.

The initial conditions and boundary conditions for the equation are as follows

$$C(x, t) = 0, 0 \leq x \leq L, t = 0 \quad (4A)$$

$$C(x, t) = C_0, x = 0, t > 0, \quad (4B)$$

$$\frac{\partial C(x, t)}{\partial x} = 0, x = L, t > 0 \quad (4C)$$

The analytical solution to the above model equation is possible and is used to simulate the experimental breakthrough curves⁴³. The 1st order removal rate constant (G) when there is no retention in porous media can be taken zero. The dispersion coefficient and the pore velocity are determined from the model fit on the OriginPro8.5.

Chapter 4 Results and Discussions

4.1 Effect of pore – nanoparticle relative sizes

4.1.1 Effect of pore – nanoparticle relative sizes on % retention

The pore – nanoparticle relative size will have direct impact on the retention in the porous media. The bigger the pore sizes are, the more likely they are to be entrapped in the smaller pores and pore-throats in addition to sticking on the pore surface. In the experiment # 5CNP-BSS-LP, the 5 nm particles pass through the 16.3 mD Berea core without any retention at room temperature. On the other hand, in the experiment # 50CNP-BSS-LP, ~ 9 % retention is calculated for the injection of 50 nm CNPs through the 17.6 mD Berea sandstones. Similarly, for the carbonates, at 50 °C, the 5 nm carbon nanoparticles passes through the core without any sticking (5CNP-ILS-LP1) but there is sticking of ~ 11 % for the 50 nm CNPs (50CNP-ILS-LP) through the similar permeability Indiana limestone core (Figure 32). On the other hand, when the solution containing 20 PPM of 50 nm CNPs is injected into relatively higher permeability Berea (Exp. # 50CNP-BSS-HP) and Indiana limestones (Exp. #50CNP-ILS-HP), no sticking or blocking of the carbon nanoparticles was found.

The explanation for no sticking at higher permeability is that as the permeability increases, the pores and pore throats size in the rock also increases which increases the pore – particle size ratio (relative size) and hence the majority of the nanoparticles pass through the pores' volume and little percentage of the nanoparticles actually comes into influence of the charged pore surfaces. In addition, the probability of blockages into the relatively bigger

pore throats is lower as compared to the low permeability core. The cumulative effect of the reduced surface interactions (lower sticking) and increased pore – particle ratio (lower blocking) leads to no retention in the porous media.

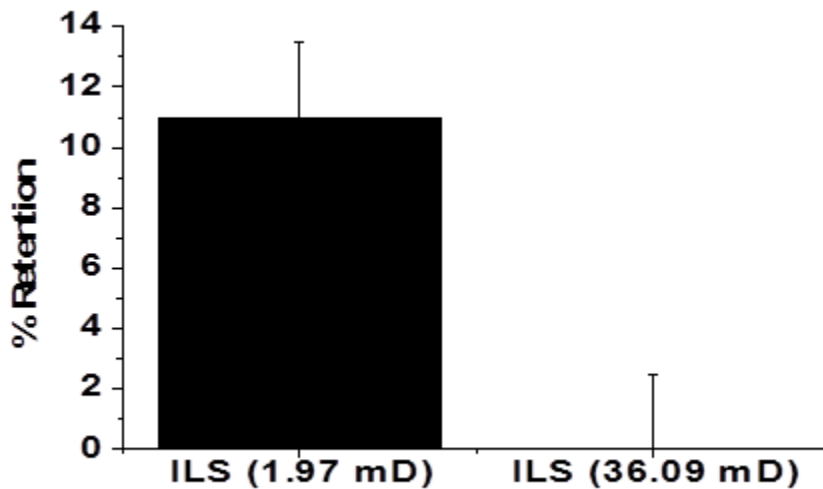


Figure 32. % retention of 5 nm CNPs through different permeability Indian limestone cores.

4.1.2 Effect of pore – nanoparticle relative sizes on breakthrough curves

The breakthrough curves for the higher permeability cores are found to be shifting to the left for ILS and Berea sandstones at all the temperatures as shown in the Figure 33 and Figure 34 which indicates earlier breakthrough of the nanoparticles through higher permeability cores as compared with low permeability cores. The same explanation as was given for zero % retention in higher permeability cores in section 4.1.1 applies here. The nanoparticles for higher permeability pass through the pores' volume and only a small percentage of the nanoparticles actually come into influence of the charged pore surfaces. In

addition to this, the tortuosity for higher permeability (hence higher porosity) cores is lower than the lower permeability (hence lower porosity) cores which means that nanoparticles in the higher permeability cores travel through the less tortuous channels that contain larger pores. The combined effect of the reduced surface interactions and the tortuosity results in the earlier breakthrough.

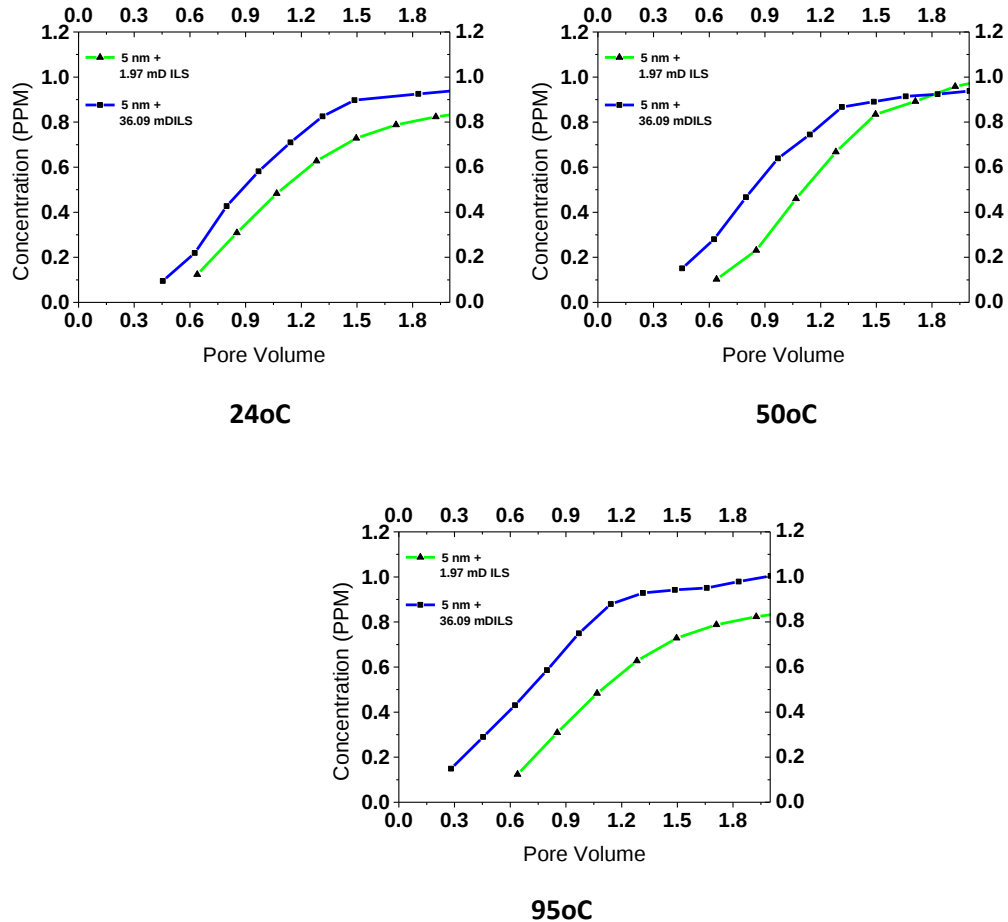


Figure 33. Breakthrough curves for 5 nm CNPs through ILS. At all the temperatures, CNPs breakthrough time is earlier for higher permeability cores.

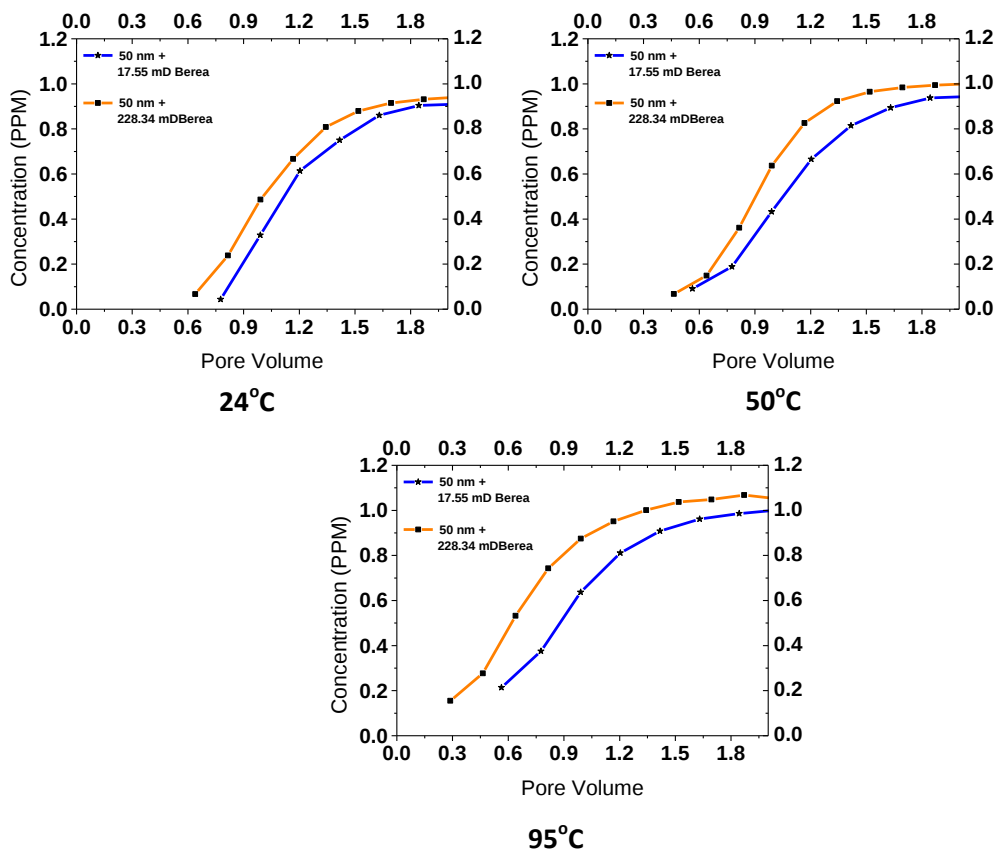


Figure 34. Breakthrough curves for 50 nm CNPs through BSS. At all the temperatures, CNPs breakthrough time is earlier for higher permeability cores.

Interestingly, the breakthrough of the polymer grafted silica nanoparticles (Si-POEOMA) occurs little after one pore volume and the concentration front is also like plug flow. The eluting concentration reaches to injected concentration after six pore volume of the injection (Experiment # POLYNP-BSS-HP). The particle size is 35 nm and the delay in breakthrough as compare to the 5 nm, 50 nm CNPs cannot be explained on the basis of the size alone. The possible explanation can be given on the basis of the structural difference between CNPs

and the Si-POEOMA. The CNPs structure consists of a thin functionalized layer on spherical core whereas longer polymer brushes (20 nm) are grown on the 15 nm spherical silica core. Structurally, the Si-POEOMA nanoparticles would therefore experience more drag forces that slow their transport, which results into delay in breakthrough time.

4.2 Effect of pore – nanoparticle surface charge

The negatively charged nanoparticles are more likely to stick more inside the ILS cores than inside the Berea cores due to forces of electrostatic attractions. In the experiment # 5CNP-ILS-LP1, the 5 nm CNPs at room temperature is stick to the Indiana limestone pore surface while there is no sticking to the 16.3 mD Berea sandstone core (5CNP-BSS-LP). At higher permeability no retention is found for BSS and ILS, which might be because of the pore – particles size effect discussed in the section 4.1.1. The comparison of the retention is shown in Figure 35.

To verify the amount of retention inside Indiana limestone (1.97 mD) and Berea sandstone core (16.30 mD), three discs were cut along the length (at inlet, outlet and in the middle) and was observed under fluorescence microscope. The fluorescence data as shown in Figure 36 and Figure 37 are in agreement with amount of retention obtained from material balance. The bright fluorescence on the Indiana limestone rock surface is observed everywhere while little fluorescence is observed from the Berea sandstones, confirming higher sticking for the ILS and lower or minimal sticking for the Berea.

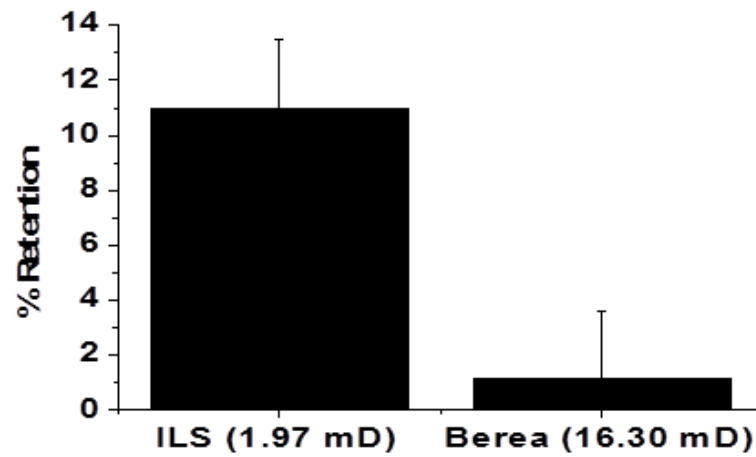


Figure 35. Percentage retention for the injection of 5 nm CNPs through the low permeability ILS and Berea cores.

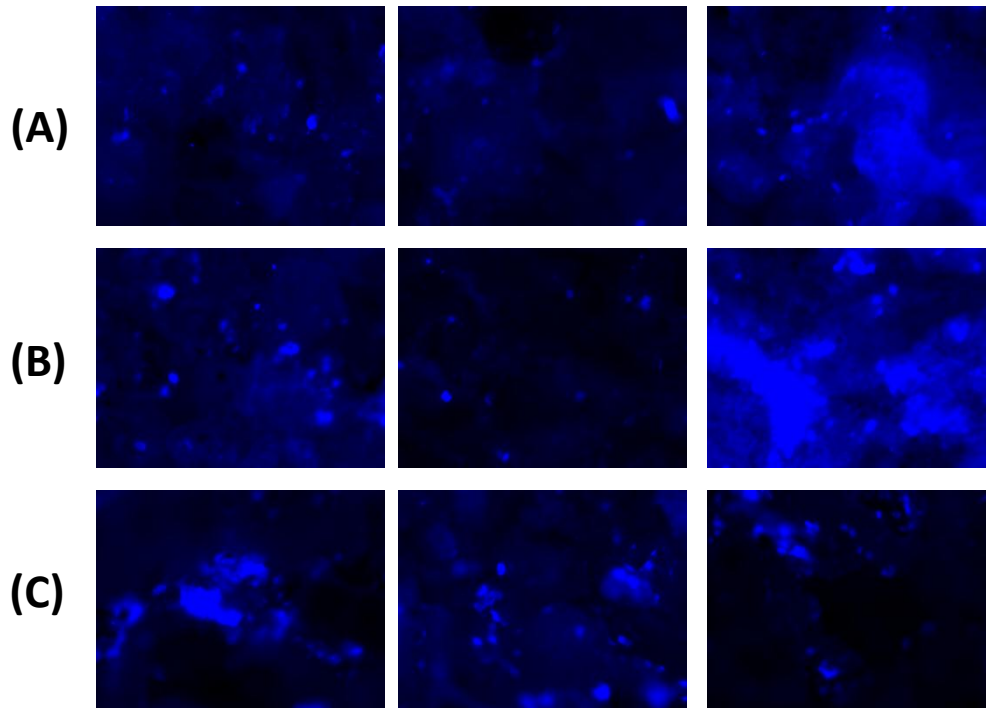


Figure 36. 5CNP-ILS-LP1 for ILS (1.97 mD) (A)-Front face (top row), (B)-Middle face (middle row) and (C)-Rear face (bottom row) (Simple 2D capture, 1344 Pixels × 1024 Pixels, Microns/pixel: 0.64 × 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

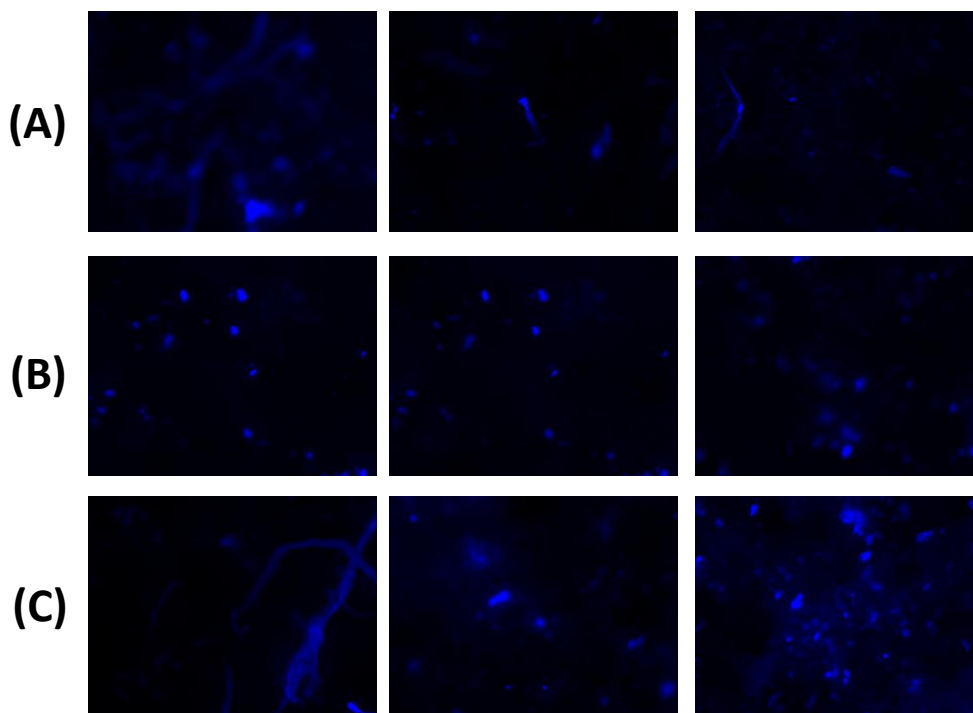


Figure 37. 5CNP-BSS-LP for Berea (16.3 mD): (A)-Front face (top row), (B)-Middle face (middle row) and (C)-Rear face (bottom row) (Simple 2D capture, 1344 Pixels $\times$ 1024 Pixels, Microns/pixel: 0.64 $\times$ 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

4.3 Effect of temperature

4.3.1 Effect of temperature on percentage retention

In the core flood experiment # 5CNP-ILS-LP1, the 5 nm CNPs passes through the ILS cores with almost no sticking at all the temperatures except at room temperature. There is $\sim 11\%$ sticking at room temperature. The permeability also drops from the 1.97 mD to 1.75 mD. Similarly, in the core flood experiment # 50CNP-BSS-LP, the bigger size (50 nm) nanoparticles passes through the low permeability Indiana limestone cores with no sticking at higher

temperatures but there is ~ 8 % sticking at the at room temperature. The lower size CNPs (5 nm) passes through the Berea core (experiment # 5CNP-BSS-LP) at all the temperatures without any sticking.

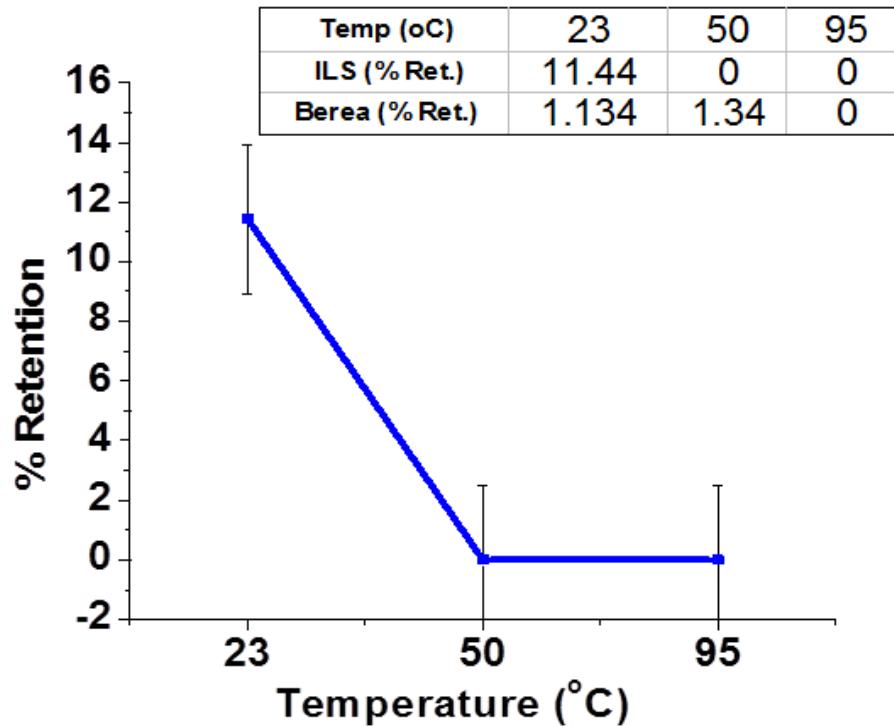


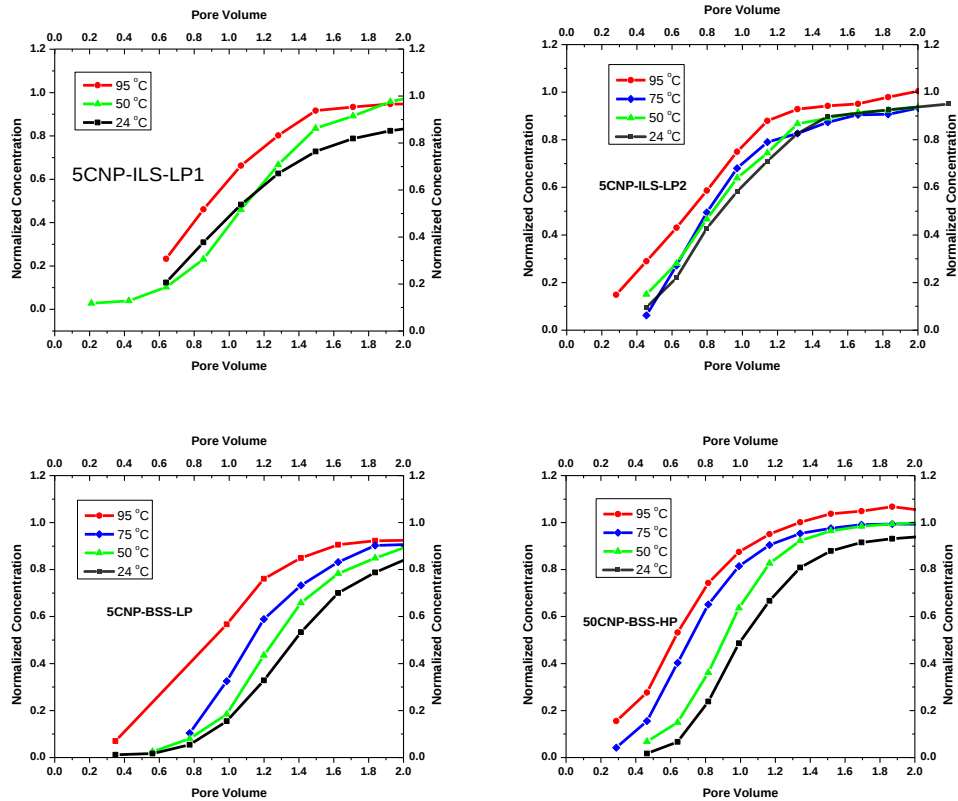
Figure 38. Percentage retention of 5 nm CNPs with temperature. Also, percentage retention at different temperatures for Berea shown in the table.

The low retention for all the core floods at high temperature can be explained as, at high temperatures the diffusion coefficient of the particles is higher and particles can diffuse through the electrical double layer and adsorb on the pore surface but at the same time reverse adsorption i.e. desorption is also higher and there is no net retention in the porous media. This adsorption desorption coefficient is also dependent upon the surface charges on the pores. The like charges would have the lower adsorption coefficient as compare to

unlike charges but higher desorption coefficient. The temperature dependent adsorption desorption kinetics is responsible for this temperature dependency of percent retention in the porous media.

4.3.2 Effect of temperature on breakthrough curves

The early breakthrough was observed in all the cases of 5 nm, 50 nm particles injection in the Berea sandstones and Indiana limestones (Figure 39).



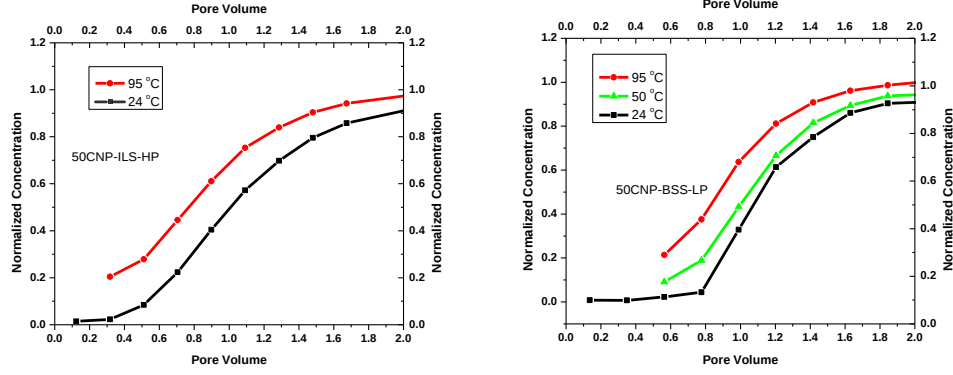


Figure 39. Breakthrough curves for the various core flooding runs. Nanoparticle concentration is eluting before one pore volume in all the cases.

The explanation for the early breakthrough is the dispersion of the nanoparticles inside the porous media, which smears the concentration front resulting in the early breakthrough. The dispersion in porous media is a cumulative effect of convection, molecular diffusion and tortuosity of the porous media. All the breakthrough curves at higher temperatures are shifting to the left (Figure 39) which indicates that breakthrough time at higher temperature is earlier than at lower temperatures. The shift in the breakthrough curves to the left when there is no sticking can be explained by higher molecular diffusion at higher temperatures (equation 7). The increase in the molecular diffusion is not linear but exponential function with the temperature. The molecular diffusion coefficient can be calculated by Stokes Stoke-Einstein equation which is

$$D = \frac{kT}{6\pi\mu r_p}, \quad \dots\dots\dots (5)$$

where, k is Boltzmann constant, T is temperature, μ is medium viscosity and r_p is the particle size. The viscosity of the medium is dependent upon the temperature and the dependency is given by Arrhenius as

$$\mu(T) = \mu_o \exp\left(\frac{E}{RT}\right), \quad \dots\dots\dots (6)$$

The diffusion coefficient from the above equations can be written as

$$\ln D = \ln \frac{kT}{6\pi\mu_o r_p} - \frac{E}{RT}, \quad \dots\dots\dots (7)$$

$$D_o = \frac{kT}{6\pi\mu_o r_p}, \quad \dots\dots\dots (8)$$

where T is temperature, μ_o is viscosity at 0 K temperature, E is the activation energy, R is the universal gas constant and D_o is the molecular diffusion coefficient at 0 K. The natural logarithm of the molecular diffusion coefficient is plotted as an inverse function of temperature. The molecular diffusion is contributing for the shift in the breakthrough curves towards left but the molecular diffusion alone might not be sufficient for the disproportionate shift in breakthrough curves towards left at 95 °C so another strong temperature dependent mechanism is required to explain the physics of the system.

4.4 Effect of the salt ions on % retention

In the core flooding experiments with nanoparticles in deionized water (Experiment # 5CNP-YLS-LP-DIW, 5CNP-ILS-HP-DIW), the retention is higher as compare to the nanoparticles in artificial sea water (5CNP-ILS-LP1 to 50CNP-BSS-LP). The possible explanation could be the relatively more screening of the negatively charged CNPs by the positively charged monovalent and divalent ions in the artificial sea water.

4.5 Effect of the dispersion time on % retention

The dispersion of 50 nm CNPs in artificial sea water is not well dispersed after 24 hours of stirring. The stable dispersion is formed after 120 hrs when the nanoparticles get segregated in the artificial sea water and no aggregation is found after one month of tracking the concentration. The 24 hrs. dispersion is injected into the experiment # 4 and experiment # 6. The huge amount of retention is found in both the cases for all the temperatures. The permeability also drops significantly from 21.07 mD, 143.67 mD to 15.73, 56.10 mD for experiment # 4 and 6 respectively. The huge retention is also confirmed from the fluorescence images. The fluorescence images have carbon nanoparticles sticking everywhere on the rock surface (Figure 40 and 41).

Table 9. Summary of the core flooding experiments.

Exp #	5CNP-ILS-LP1	5CNP-ILS-LP2	50CNP-ILS-LP	50CNP-A-BSS-LP	5CNP-BSS-LP	50CNP-A-ILS-HP	50CNP-BSS-HP	50CNP-ILS-HP	5CNP-BSS-LP-ASWS STABILITY	50CNP-BSS-LP
Core Types	ILS	ILS	ILS	BS	BS	ILS	BS	ILS	BS	BS
Nanoparticle Size (nm)	5	5	50	50	5	50	50	50	5	50
ASW Permeability (mD)	1.97	36.1	1.97	21.1	16.3	143.7	228.3	173.5	48.6	17.6

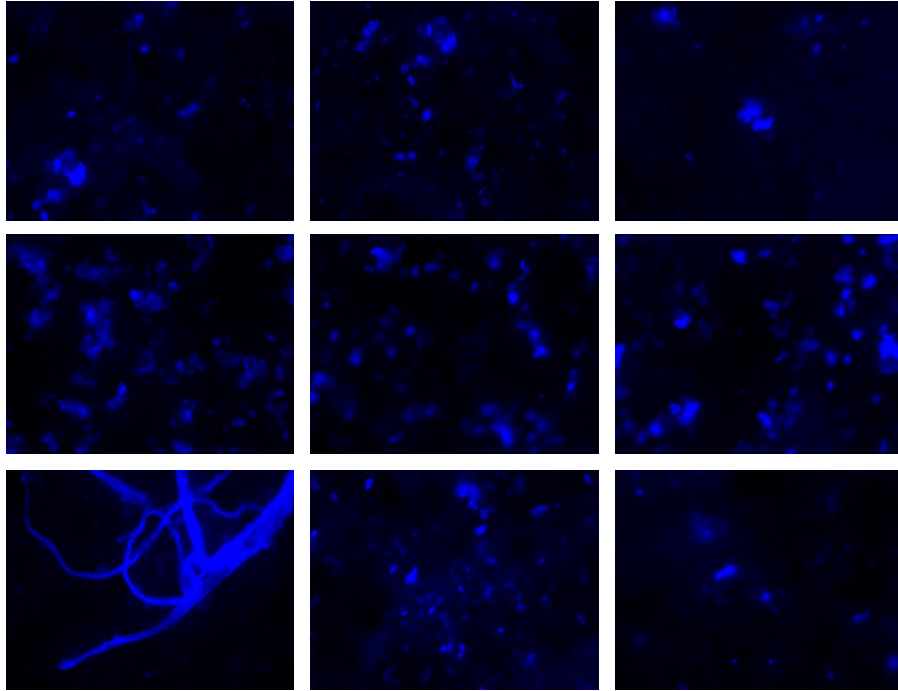


Figure 40: 50CNPA-BSS-LP for BS (21.07 mD): Front face (top row), Middle face (middle row) and Rear face (bottom row) (Simple 2D capture, 1344 Pixels $\times$ 1024 Pixels, Microns/pixel: 0.64 $\times$ 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

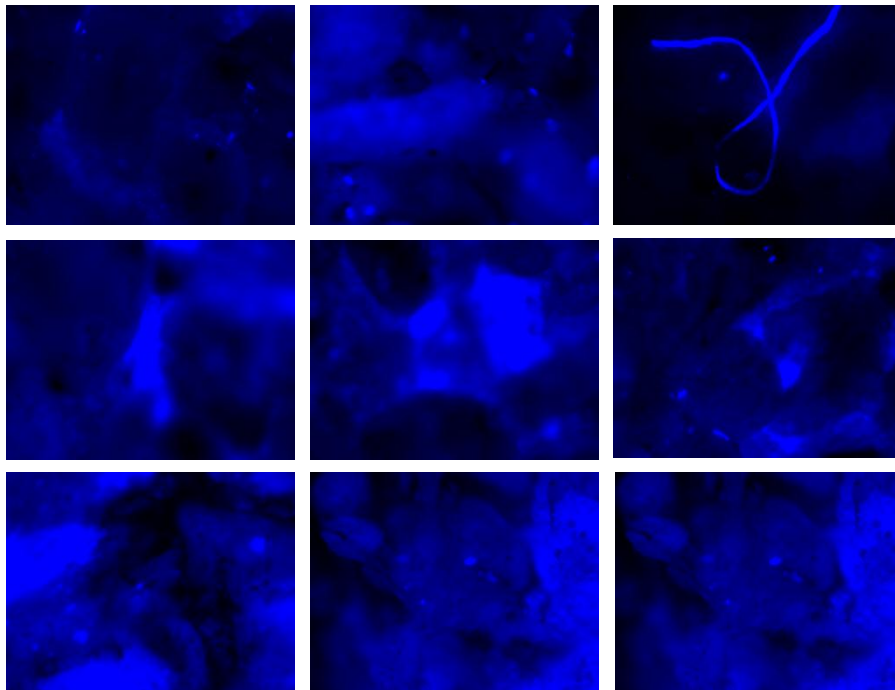


Figure 41: 50CNPA-ILS-MP for ILS (143.67 mD) Front face (top row), Middle face (middle row) and Rear face (bottom row) (Simple 2D capture, 1344 Pixels $\times$ 1024 Pixels, Microns/pixel: 0.64 $\times$ 0.64 micrometer, Objective lens: 10X Air, Exposure: 1000 ms at 460 nm).

Table 10. Percentage retention in the cores at various temperatures for the CNPs in ASW through the Berea sand stone and limestone cores (5CNP-ILS-LP1 to 50CNP-BSS-LP). The retention in case of aggregation of nanoparticles is indicated in bold numbers.

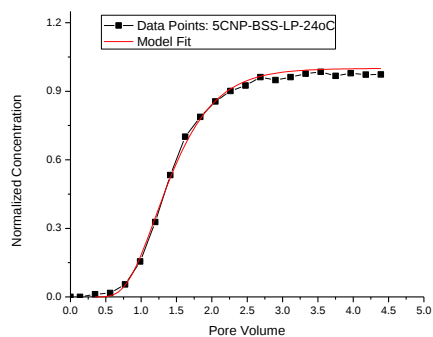
Temp (oC)	5CNP-ILS-LP1	5CNP-ILS-LP2	50CN P-ILS-LP	50CN PA-BSS-LP	5CNP-BSS-LP	50CN PA-ILS-HP	50CN P-BSS-HP	50CN P-ILS-HP	50CN P-BSS-LP
95	0	0		33	0	44	0	0	0
75		1		43	4	60	0	0	
50	0	2	11	50	1	37	2		4
24	11.4	0		48	1	27	3	2	9

Table 11. Permeability of the Berea sandstone and carbonate cores before and after the nanoparticle injection.

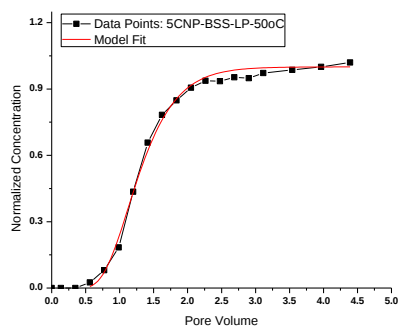
Exp #	5CNP-ILS-LP1	5CNP-ILS-LP2	50CNP-ILS-LP	50CNP A-BSS-LP	5CNP-BSS-LP	50CNP A-ILS-HP	50CNP-BSS-HP	50CNP-ILS-HP	50CNP-BSS-LP
Permeability (mD, before C-Dots)	2.0	36	2.0	21.1	16.3	143	228	173	17.5
Permeability (mD, after C-Dots)	1.8	33	1.5	15.7	14.1	56.1	209	160	16.1

4.6 Estimation of parameters (D, U) using 1D convection diffusion model (1D-CD)

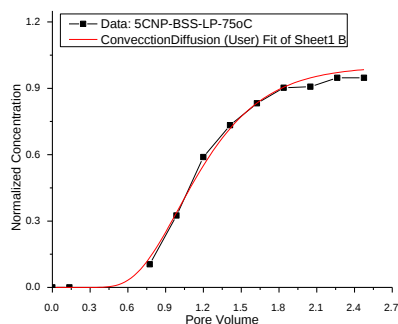
The 1D convection diffusion model (equation 4) without any reaction term was used to simulate the experimental data and it was found that the 1D-CD model captures the experimental data points well (Figure 42 and Figure 43).



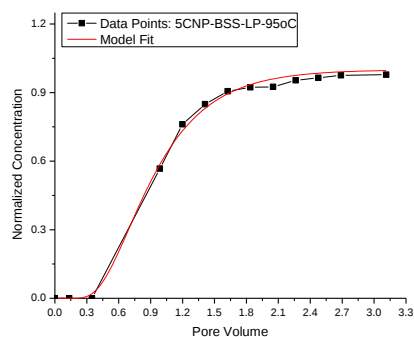
5CNP-BSS-LP-24°C



5CNP-BSS-LP-50°C

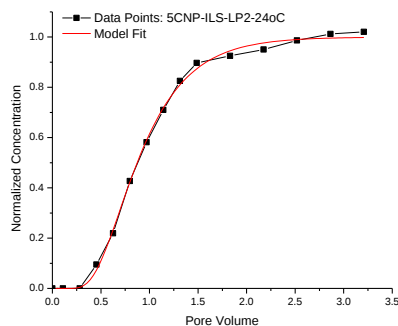


5CNP-BSS-LP-75°C

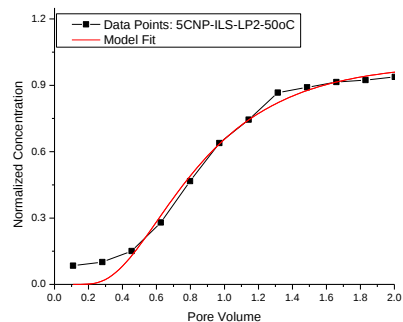


5CNP-BSS-LP-95°C

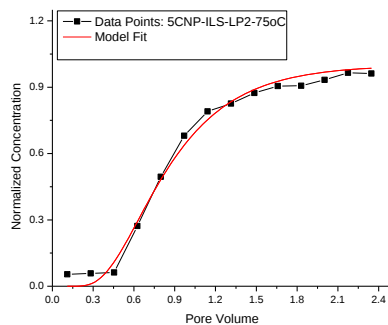
Figure 42. 1D-CD model fitting for the breakthrough curves of 5CNP-BSS-LP at various temperatures.



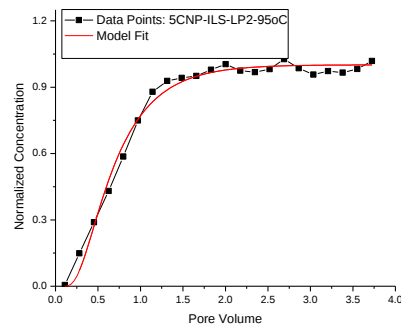
5CNP-ILS-LP2-24°C



5CNP-ILS-LP2-50°C



5CNP-ILS-LP2-75°C



5CNP-ILS-LP2-95°C

Figure 43. 1D-CD model fitting for the breakthrough curves of 5CNP-ILS-LP2 at various temperatures.

The fitting parameters (dispersion coefficient, cm^2/min and pore velocity, cm/min) are estimated from the model fitting and are summarized in Table 14.

Table 12. Dispersion coefficient (cm^2/min), pore velocity (cm/min) estimation from the 1D convection diffusion model.

Temp., ($^{\circ}\text{C}$)		24	50	75	95
5CNP-ILS-LP1	D		0.22 ± 0.03		0.43 ± 0.05
	U		0.43 ± 0.01		0.49 ± 0.01
5CNP-ILS-LP2	D	0.36 ± 0.03	0.47 ± 0.04	0.42 ± 0.05	0.78 ± 0.11
	U	0.38 ± 0.00	0.38 ± 0.01	0.40 ± 0.01	0.42 ± 0.03
5CNP-BSS-LP	D	0.14 ± 0.01	0.14 ± 0.01	0.17 ± 0.02	0.52 ± 0.09
	U	0.27 ± 0.00	0.29 ± 0.00	0.32 ± 0.01	0.35 ± 0.02
50CNP-BSS-HP	D	0.17 ± 0.02	0.15 ± 0.01	0.34 ± 0.02	0.44 ± 0.04
	U	0.37 ± 0.01	0.43 ± 0.01	0.51 ± 0.00	0.57 ± 0.01
50CNP-ILS-HP	D	0.34 ± 0.01			0.61 ± 0.05
	U	0.32 ± 0.00			0.39 ± 0.01
50CNP-BSS-LP	D		0.19 ± 0.02		0.30 ± 0.02
	U		0.35 ± 0.01		0.42 ± 0.01

The pore velocity as obtained from the table 14 clearly indicates increasing trends with temperature in all the cases. The pore velocity dependence can be explained on the basis of temperature dependent adsorption desorption kinetics. The dispersion coefficient (D) as a function of the temperature is plotted in the

Figure 44. It is observed that the dispersion coefficient at higher temperature (95 °C) is higher than at lower temperatures (50 °C and 24 °C). This temperature dependency of the dispersion coefficient leads to earlier breakthrough as was observed from the breakthrough curves.

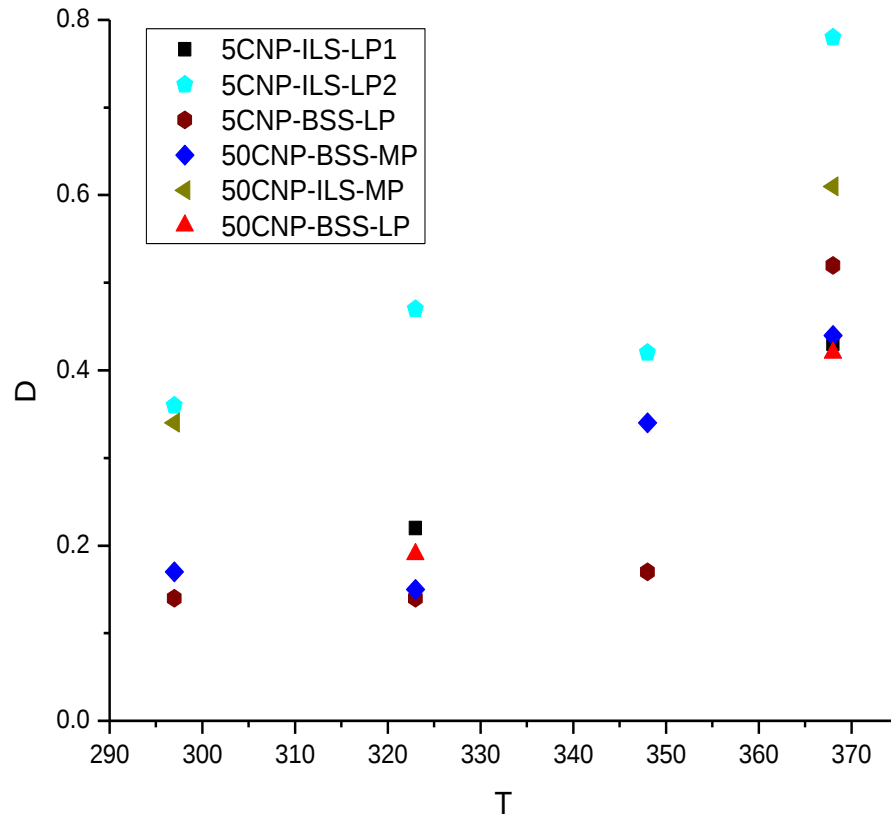
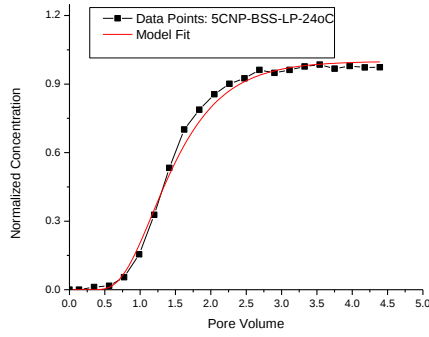


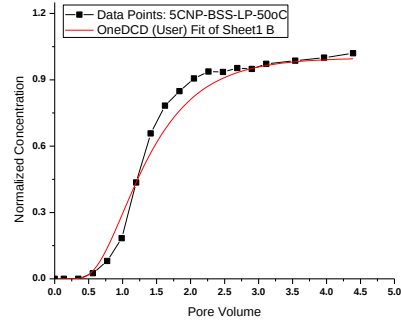
Figure 44: Dispersion coefficient as a function of the temperature (values given in Table 12 are plotted).

Now, we used one parameter 1D convection diffusion model (D varies and U fixed) and keep the other parameter pore velocity (U) fixed (Figure 46) by taking the average of the pore velocities at different temperatures obtained from the two

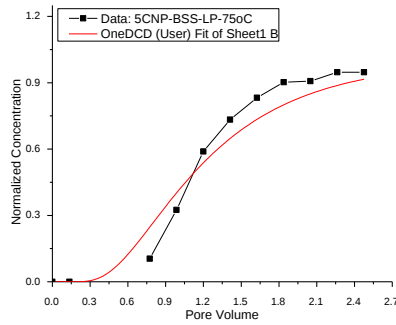
parameter model (0.3075 cm/min for 5CNP-BSS-LP and 0.395 cm/min for 5CNP-ILS-LP2). We found that one parameter model with pore velocity same for all the temperatures for a particular porous media does not fit the breakthrough curves.



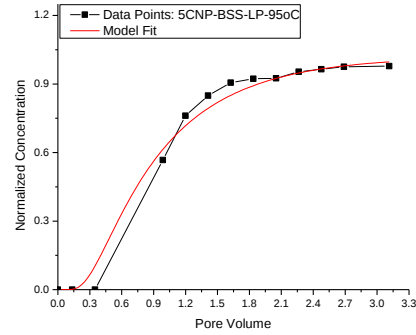
5CNP-BSS-LP-24°C



5CNP-BSS-LP-50°C

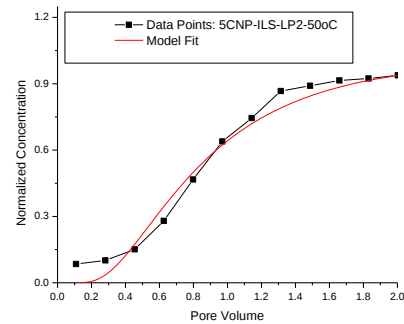
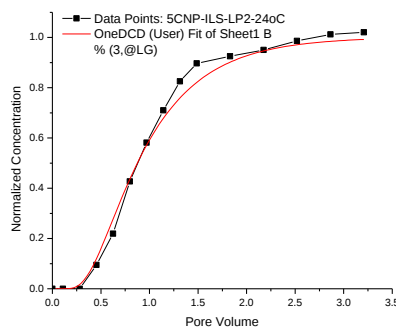


5CNP-BSS-LP-75°C

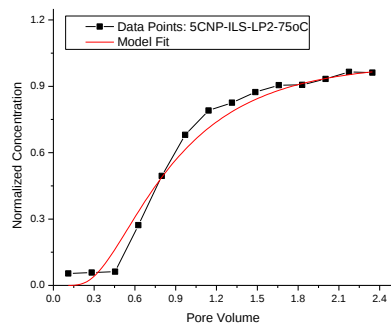


5CNP-BSS-LP-95°C

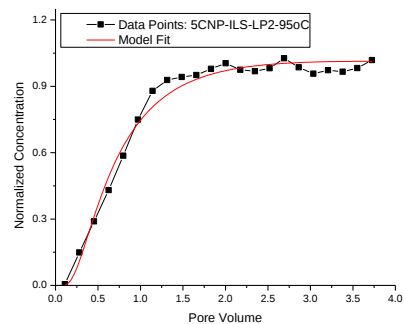
Figure 45. 1D-CD model fitting for the breakthrough curves of 5CNP-BSS-LP at various temperatures.



5CNP-ILS-LP2-24°C



5CNP-ILS-LP2-50°C



5CNP-ILS-LP2-75°C

5CNP-ILS-LP2-95°C

Figure 46. 1D-CD model fitting for the breakthrough curves of 5CNP-ILS-LP2 at various temperatures.

Chapter 5 Summary and Conclusions

- **No face plugging or pore plugging**

The CNPs and Si-POEOMA in this study are found to be transporting thorough the porous media without causing any face plugging or major pore blocking. One of the requirements for the enhanced oil recovery application is that the nanoparticles should not cause face plugging or pore blocking and the sticking on the rock surface should be minimal.

- **No filtering of the nanoparticles in the cores**

The sticking of the nanoparticles (like in experiment 5CNP-ILS-LP1, 50CNP-BSS-LP at RT) are found everywhere on the core surfaces and there is no filtering out of the nanoparticles (concentration gradient) which indicates that the particles are uniformly transported everywhere coming in contact with most of the rock's surface. This kind of behavior could be useful in the wettability alteration of low permeability carbonates reservoirs kind of application in wettability alteration for enhanced oil recovery.

- **Sticking is temperature dependent**

The CNPs successfully transport through low permeability Indiana limestones and Berea sandstones cores without any sticking at higher temperatures. Some sticking is observed at the room temperature for the 5 nm through the 1.97 mD ILS and 50 nm through the 17.55 mD Berea sand stones.

- **Dispersion time (mixing) is important**

The dispersion time is very important. The smaller carbon particles (5 nm)

disperse well in 24 hrs and no change in peak position or peak height is observed within a period of a month. The bigger particles take longer time (120 hrs) to disperse as compared to the smaller particles. The retention of CNPs when dispersed for 24 hours and injected into the Berea sandstone core or Indiana limestone core is huge but when the same nanoparticles are dispersed for 120 hrs, the retention in the porous media is less.

- **Surface chemistry of the particles plays an important role**

The surface chemistry of the particles plays an important role in the particles transport. The neutrally charged Si-POEOMA particles breakthrough occurs almost at one pore volume while early breakthrough occurs for the negatively charged 5 nm, 50 nm particles.

- **Breakthrough time is dependent upon the pore - particle size**

The breakthrough of the 5 nm and 50 nm carbon nanoparticles occurs earlier than a pore volume. The 5 nm carbon particles breakthrough the core earlier than the 50 nm carbon particles. Similarly, breakthrough from the high permeability core occurs earlier than the low permeability core.

- **Dispersion results in early breakthrough**

The dispersion is playing an important role in the nanoparticle transport which results into early breakthrough of the particles. The pore scale adsorption-desorption mechanism is responsible for the retention in the porous media.

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