Transport Properties of Nanoparticles in Sandstones

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Abstract

Challenges and technology gaps within the area of enhanced oil recovery (EOR) which need to be addressed in the coming research programs have been identified in the OG21 strategy document[1] on "Exploration and Increased Recovery": Especially, there is a need for more cost-efficient EOR chemicals and to assure environmental acceptable chemicals and methods to avoid unwanted discharge to sea. There is therefore a clear need for increased competence on new technologies in the field of EOR. There has recently been an increasing interest in applying nanotechnology to EOR but still many topics are uncovered. Nanotechnology, which has mainly been developed in mechanical engineering, medicine and biological sciences, is expected to have a large potential for EOR applications. There is a wide range of applications of this technology, which is relevant for EOR, from employing general concepts and principles from nanotechnology, to advanced reservoir monitoring using nano-sensors and nano-analysis and to more specific technologies to overcome shortcomings in traditional EOR methods. The latter includes tailoring chemical molecules for more efficient EOR, and smart and more efficient delivery of the EOR agent. Development of efficient drug delivery in the human body is an example where such technology may be applied to improve efficiency in chemical flooding.

The current work is part of the HyGreGel project, which addresses the need to develop more efficient water diversion techniques for in-depth placement of gelling chemicals. Blockage of paths that have excessive water flow can increase oil recovery and reduce unwanted water circulation in heterogeneous reservoirs. The main objective of HyGreGel is to develop a hybrid gel system based on conventional polymers and nanoparticles with functional groups as crosslinkers. The functional groups will initially be deactivated. By slow activation in the reservoir, it will be possible to place the gel constituents deep into the reservoir before gelling prohibits further flow.

The present work addresses core-flooding experiments in low and high permeability sandstone cores where polymer and nanoparticles were injected separately or in mixture. The results indicate that polymer adsorption, polymer retention and IPV were generally reduced by the presence of nanoparticles. Adsorption, total retention and IPV were significantly higher in Berea compared to Bentheimer, for both polymer and nanoparticles. The adsorbed or otherwise retained polymer during injection was not released during following water floods, while the retained nanoparticles were partly released during following water floods. Nanoparticles had negligible effect on rock permeability (and thus differential pressure across the core), while polymer significantly reduced rock permeability (and increased differential pressure).

Keywords

Water diversion; nanoparticles; polymer; transport mechanisms; adsorption; retention; inaccessible pore volume; residual resistance factor

1. Introduction

High water cut becomes an increasing problem late in the field production period often due to heterogeneities or high permeable reservoir zones (*i.e.,* thief zones) when the field is produced by water flooding. Deep placements of gels which will result in blocking the flow channels of water and divert the water into other reservoir areas has a potential of reducing the water production significantly and improve the water flood in unswept areas. Placement of gels is, however, a challenging task since a high viscous gel cannot be transported deep into the formation. The oil industry has applied various chemical and mechanical methods for water control during more than three decades[2-4]. The methods are often characterized as near-wellbore or in-depth reservoir treatments. Correct diagnostics of the excess water problems based on extensive reservoir engineering and completion engineering studies is essential for selecting suitable technologies for successful treatments[5].

The primary challenge in using gels for blockage is correct in-depth placement of the high viscous gel for a given reservoir situation, and in many cases the delay in gelation time may not be appropriate for the actual reservoir situation. In addition, some of the crosslinking agents (*i.e.,* chromium) in most polymer gel systems may not be environmental acceptable.

Nanotechnology is taking advantage of synthesizing materials on a molecular scale level. With their very small size (below 100 nm), nanosized particles possess a very high surface specific area that gives them enhanced surface properties compared to bulk, like high reactivity. Such reactivity may be controlled in a proper way in order to prepare gel networks of particles with the surrounding. The development of nanotechnology has revolutionized engineering and sciences in several areas, especially within electronics, mechanical engineering, medicine and biological science. Recently, there has been a lot of interest and discussions on how nanotechnology may be applied within EOR[6-8]. There is an expectation that nanotechnology is going to find a large range of applications within petroleum technology in general, and in EOR specifically. Research projects on nanotechnology have been initiated within the area of EOR[9-11]. These include studies of nanoparticles, which offer different ways of controlling oil recovery processes related for instance to wettability, mobility control or for improved efficiency of EOR chemicals or more efficient transport of chemicals into the formation. The transport properties of particles in porous media on a nanoscale level have become important for these applications[12].

The objective of the present work is to investigate transport of polymers and functionalised nanoparticles in porous media by characterizing their stability, retention and other physical properties. Several nanoparticle and polymer flooding experiments were carried out with Bentheimer and Berea sandstones.

2. Aqueous dispersions of nanoparticles and polymer: transport and retention

Lotsch et al. have summarized the definitions and measurement methods of retention, adsorption and inaccessible pore volume (IPV)[13]. Changes in composition of the injected solution (*e.g.,* polymer, nanoparticles, salt concentration) affect the responses measured by various sensors. *Figure 1* shows a few idealized cases of such responses. An ideal piston-like plug flow would look like a step function. However, the real world effect from dispersion reforms the step function into a curve.

Inaccessible pore volume and retention can shift the curve in *Figure 1*. The portion of the porous media that cannot be accessed by the particle under study (*e.g.,* the polymer) is referred to as Inaccessible Pore Volume (IPV). The reduced accessible pore volume results in a faster transport of the particles across the porous medium and therefore shifts the response curve to the left. On the other hand, some of the particles under study are adsorbed on the surface of the rock (adsorption) or are stuck and filtered in small pore throats (mechanical entrapment). These are effects that delay particle flow through porous media, which are collectively referred to as retention. As a result, the response curve is shifted to the right.

One should only expect the effect of dispersion on responses for step changes in the salt concentration. However, polymer and nanoparticle responses can experience any combination of effects from dispersion, IPV, retention, and flooding history.

In order to determine inaccessible pore volume of *e.g.* polymer, one can compare the production profiles of polymer and a tracer as a function of pore volumes injected. Figure *2* illustrates such a comparison. The

relative response of polymer is the ratio of measured effluent concentration to the injected concentration. The tracer should ideally have no IPV, *i.e.,* the area below the tracer response should be equal to one. Changing the concentration in salt tracer will yield a close enough response. The area between the two responses determines the IPV.

Provided that the adsorption of polymer is irreversible and no mechanically entrapped polymer is released during water injection, the IPV will result in a response curve with an area under the curve of less than 1. Thus, IPV for polymer will be a positive value. However, if the system experiences desorption of the mechanically entrapped component, the area under the curve may become larger than the tracer area, resulting in a negative IPV indicating release of retained component.

Total retention of a component in the rock depends on adsorption and mechanical entrapment. A multi-slug experiment can be used to quantify adsorption. Assuming that adsorption for the component under study were irreversible, all the adsorption happened in the first slug, *i.e.,* no more adsorption took place during the second slug, and the magnitude of mechanical entrapment in both slugs were equal, one can compare the relative responses from the two slugs to find adsorption for the component. This is illustrated in Figure *3*.

3. Coreflood experiments for studying transport phenomena
3.1. Materials
Nanoparticle and polymer solutions were prepared with synthetic sea water (SSW) as the solvent. Table 1 shows the recipe for SSW used in this work. In order to make a nanoparticle solution, FunzioNano particles[14] were dissolved in SSW with a magnetic stirrer and then exposed to ultra-sonic bath a better dissolution. Finally, the solution was filtered through a 0.45 µm membrane filter. Partially hydrolysed polyacrylamide (HPAM) was employed as the polymer. HPAM powder was dissolved in SSW with a propeller at 500 rpm followed by magnetic stirring. The polymer solution was then filtered through a 500 mD Berea core. In this set of experiments, two types of sandstone were used: Berea and Bentheimer. Berea has a significantly lower permeability and more clay materials than Bentheimer.

3.2. Experimental setup
A schematic of the experimental setup is shown in *Figure 4*. At the beginning of the setup there were reservoirs containing either SSW, nanoparticle solution, polymer solution or mixtures of the latter two. The solutions were then pumped by a Pharmacia P-500 pump, and injected into the core from the bottom of the vertical core holder. The core itself was wrapped in nickel foil and inserted into a Viton rubber sleeve, around which a net overburden pressure of 50 bar was exerted. This ensures that no side flow occurs around the core.

Several online measurement systems were placed downstream of the core. Conductivity of the effluent was measured by a Radiometer CDM 83 Conductivity Meter, determining the resistance of the fluid between two small rodded platinum electrodes integrated in a flow channel in a small housing made of polyoxymethylene. Since conductivity is substantially affected by temperature, these readings were temperature corrected. Viscosity of the effluent was measured by a spiral viscometer of 1/16" outer diameter. In order to avoid temperature effects, the viscometer was submerged in a water bath with a constant temperature. A refractive index detector (Shodex RI SE-51) and UV detector (KNAUER Azura MWD 2.1L) were employed interchangeably, in order to determine nanoparticle concentration. Several pressure transducers were implemented along the system. A back pressure of 3 – 6 bar was applied. At the far end of the experimental setup, the effluents were collected and weighed.

3.3. Coreflood experiments
First, a new core (of diameter and length approximately 3.8 cm and 20 cm, respectively) was mounted in the core holder. After leakage testing of the system, the core was flooded with isopropanol until full saturation. Next several PVs of SSW were flooded through the core in order to displace the isopropanol and ensure stable flow conditions. After that, porosity and permeability measurements were conducted.

Each experiment started with injection of a slug with only nanoparticles, only polymer or a mixture of nanoparticles and polymer (Stage 1). After some time, the measurements stabilised. In Stage 2, the injected

fluid was switched to pure brine (with lower salt concentration in the experiments only involving polymer) and the injection continued until the measurements became stable. In Stage 3, a second slug with additives was injected, followed by a second slug with only brine (Stage 4). In other words, stages 3 and 4 were a repetition of stage 1 and 2. Both stages ran until measurements became steady state. The experiment ended with a final water permeability measurement. During the experiment, process parameters and detector/sensor readings were continuously logged.

Figure 5 shows normalized responses of nanoparticles and polymer based on RID, UVD and viscometer measurements. The figure also shows normalized conductivity responses and differential pressure measured across the core. Event lines indicate the starting point of each stage and after one pore volume injected.

For the experiments involving nanoparticles, the conductivity responses were determined in separate runs from the main core floods. This was because changes in salt concentration affected both UV absorption at low wavelengths and especially the refractive index of the fluid. The conductivity responses were measured with the same injection rates with slugs of SSW and 80% SSW into the cores.

4. Results and discussion

Table 2 lists the six combinations of experiments conducted for this work. Detailed results from the first five experiments are amplified in a SPE publication[15]. Here, the focus will be on Experiment 6 and the overall results from all experiments.

Figure 5 shows concentration responses from Experiment 6, with Berea as the sandstone and a mixture of nanoparticles and polymer in SSW as the active solution. The profiles include normalized responses of nanoparticles (RI and UV detector) and polymer (viscometer), normalized conductivity responses and the differential pressure measured across the core. Event lines indicate the starting point of each stage and after one pore volume injected, indicating the four stages of the experiment.

In order to generate concentration responses for nanoparticles and polymers, a calibration model has to be in place mapping measured data from the UV detector and the viscometer to concentrations of nanoparticles and polymer. Figure 6 illustrates calibration models for UV absorption and pressure drop in the viscometer tube. As seen in the figure, the pressure drop over viscometer tube is almost only affected by polymer concentration, giving a second order model in polymer concentration. This model was therefore used to find the concentration of produced polymer. On the other hand, UV absorption data resulted in a model with first and second order terms with respect to both nanoparticles and polymer, as well as a cross term (*i.e.,* the product of concentrations). UV absorption measurement was used to generate nanoparticle responses. The calibration model for RI generated a plot similar to that of UV. RI measurements were used to confirm UV absorption measurements.

Figure 7 shows polymer adsorption in presence and absence of nanoparticles and in Bentheimer and Berea. At first glance, the plot shows that polymer adsorption in Berea is significantly higher than that of Bentheimer. Moreover, in both of the rock systems, addition of nanoparticles reduces polymer adsorption.

Figure 8 shows IPV for polymer quantified at stages 2 and 4. It can be expected that IPV is a constant quantity for a given polymer/rock system and the difference in the IPV determined at the two stages indicate the uncertainty in the quantification. Generally, IPVs are higher in Berea than in Bentheimer. Furthermore, addition of nanoparticles reduces the IPV in Berea but has no significant effect on IPV for polymer in Bentheimer sandstone.

Figure 9 shows nanoparticle IPV for stages 2 and 4. For each injected solution, IPVs are lower in Berea than in Bentheimer. Furthermore, addition of polymer generally increases IPV for each stage. As explained before, the physical meaning for negative IPVs in this figure is partial desorption/release of nanoparticles.

Figure 10 illustrates the residual resistance factor (RRF) for all six experiments. RRF is the ratio of initial and final absolute rock permeabilities (*i.e.,* before and after flooding). The figure shows that flooding nanoparticles alone will keep the RRF close to one, meaning that it does not significantly affect absolute permeability and hence differential pressure. However, in all the experiments with polymer, RRFs are well below one, indicating a reduced absolute permeability and increased differential pressure across the core.

Figure 11 illustrates total retention of nanoparticles and mechanical retention of polymer (*i.e.* retention above adsorption) across all six experiments. Total retention (*i.e.,* the aggregated effect of adsorption and mechanical entrapment) was calculated by mass balances for each stage of the experiment. Looking at

experiments with only one component (either nanoparticles or polymer) it is observed that total retention in Berea is higher than that of Bentheimer for every single stage. For experiments with both components, nanoparticles show a higher retention in Berea than Bentheimer, while polymer exhibits the opposite behavior. In any given experiment retained polymer is not released during subsequent water floods whereas retained nanoparticles are partially released. The errorbars for nanoparticle retention in Experiment 6 for (Berea with nanoparticles and polymer) indicate the difference in the mass balance calculations done using the UVD and RID measurements for determination of nanoparticle concentrations.

5. Conclusions

Through a typical methodology for studying polymer transport in porous media, transport properties of nanoparticles and polymers in two types of sandstones was investigated.

The results indicated that polymer adsorption, polymer retention and IPV were generally reduced by the presence of nanoparticles. Adsorption, total retention and IPV were significantly higher in Berea compared to Bentheimer, for both polymer and nanoparticles. The adsorbed or otherwise retained polymer during injection was not released during following water floods, while the retained nanoparticles were partly released during following water floods.

Nanoparticles had negligible effect on rock permeability (and thus differential pressure across the core), while polymer significantly reduced rock permeability (and increased differential pressure).

Acknowledgements

Nomenclature

EOR, enhanced oil recovery
HPAM, partially hydrolysed polyacrylamide
IPV, inaccessible pore volume
MDa, million Daltons (unified atomic mass unit)
mD, milli Darcy
nm, nanometres
PV, pore volume
RI, refractive index
RID, refractive index detector
RRF, residual resistance factor
SSW, synthetic seawater
UV, ultraviolet
UVD, ultraviolet detector

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Table 1—Synthetic Sea Water (SSW) recipe

Salt	Mass (g)
NaCl	23.612
$CaCl_2 \cdot 2H_2O$	1.911
$MgCl_2 \cdot 6H_2O$	9.149
KCl	0.746
Na_2SO_4	3.407

Table 2—Experiments: Rock and fluid combinations

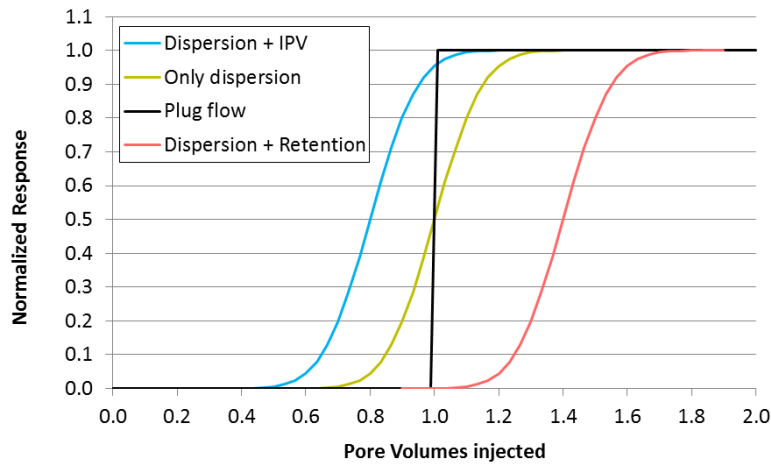| Exp. no.	Rock	Injected additive
1	Bentheimer	NP
2	Bentheimer	pol
3	Bentheimer	NP + pol
4	Berea	NP
5	Berea	pol
6	Berea	NP + pol

Figure 1—Effect of dispersion, inaccessible pore volume (IPV) and retention on relative responses
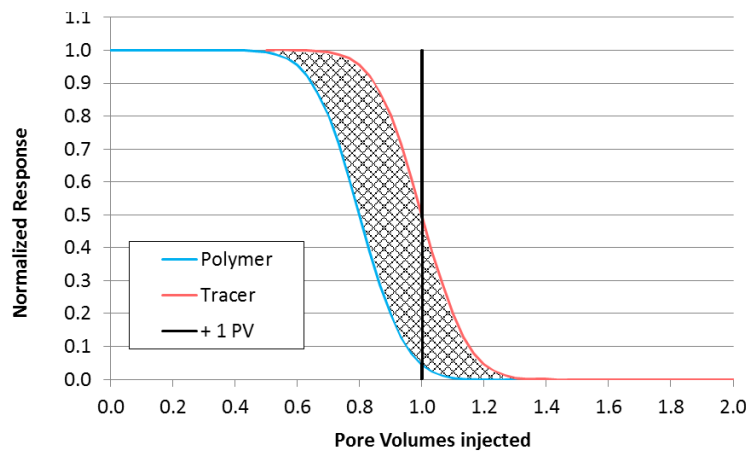

Figure 2—Typical responses after changing the injected solution from a polymer solution to a solution containing only a tracer ion at a different concentration. The difference in areas defines the inaccessible pore volume.
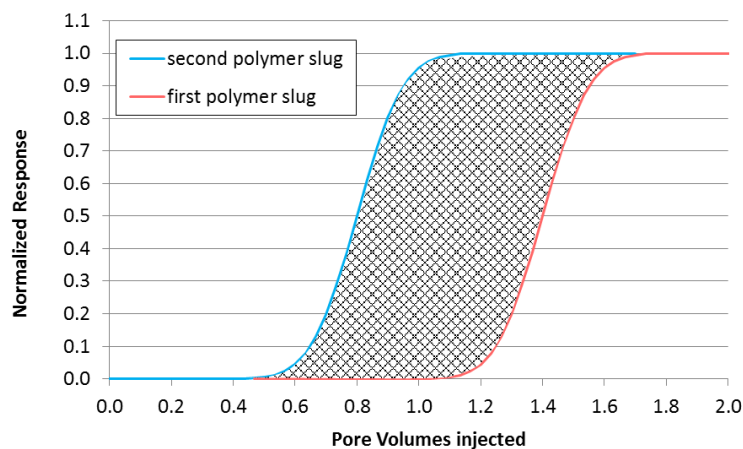

Figure 3—Typical difference between responses of the first and second polymer slugs. The difference in areas defines adsorption at stage 1.
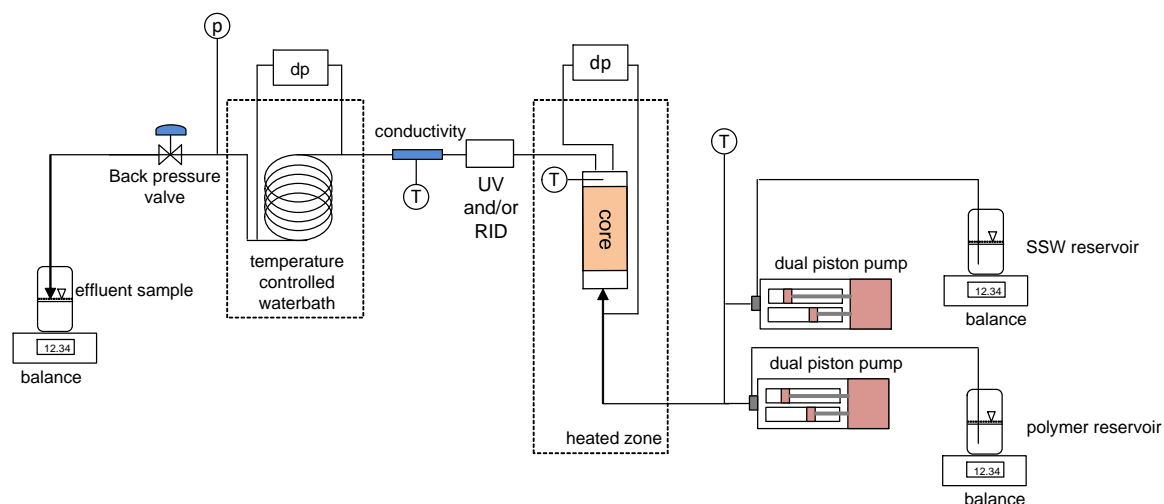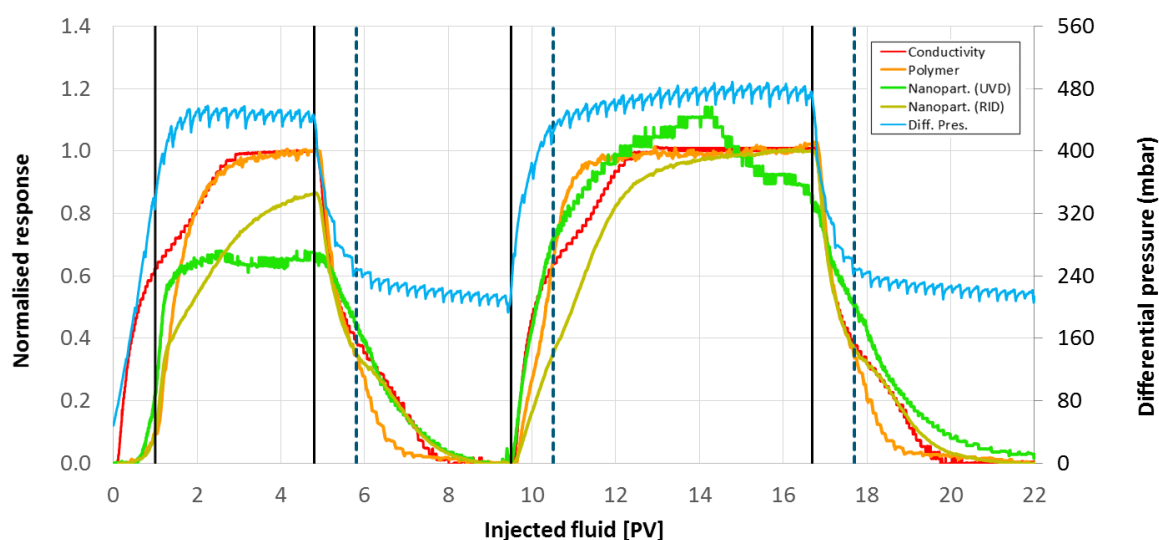
Figure 4—Schematic of coreflood set-up

Figure 5—Normalized responses of nanoparticles and polymer based on RID, UVD and viscosity measurements, normalized conductivity responses and the differential pressure measured across the core.
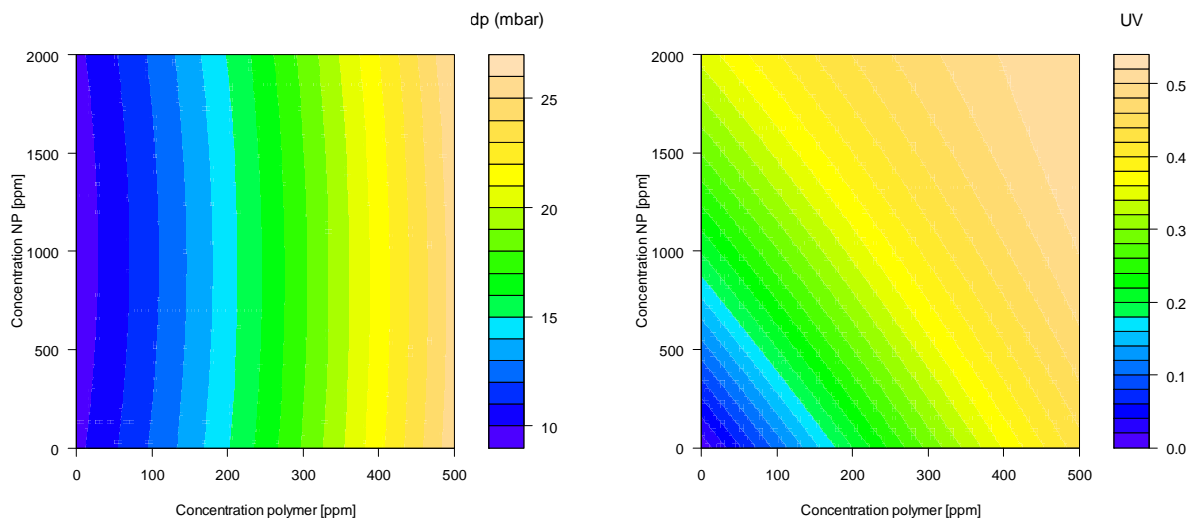
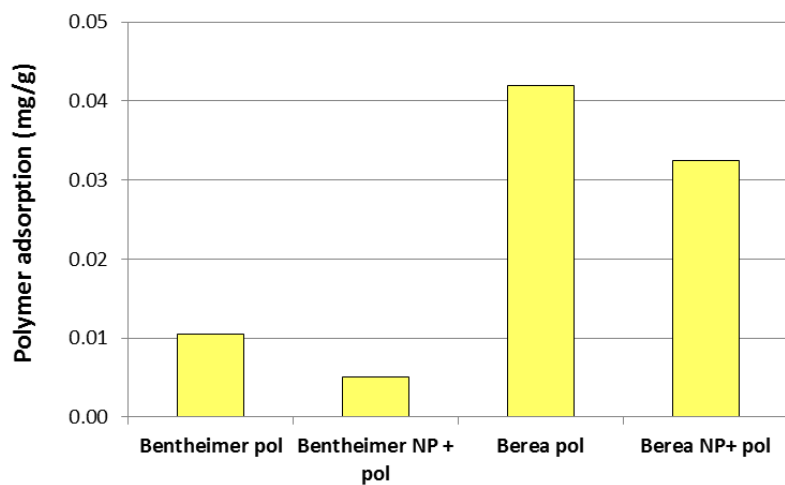Figure 6—Calibration models for pressure drop in viscometer and UV absorption in UV detector

Figure 7—Polymer adsorption in presence and absence of nanoparticles in Bentheimer or Berea
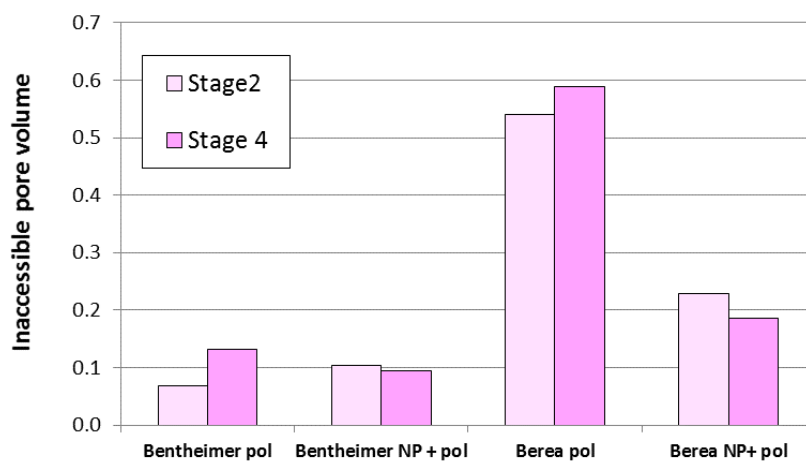

Figure 8—Inaccessible pore volume for polymer for stages 2 and 4 of experiments
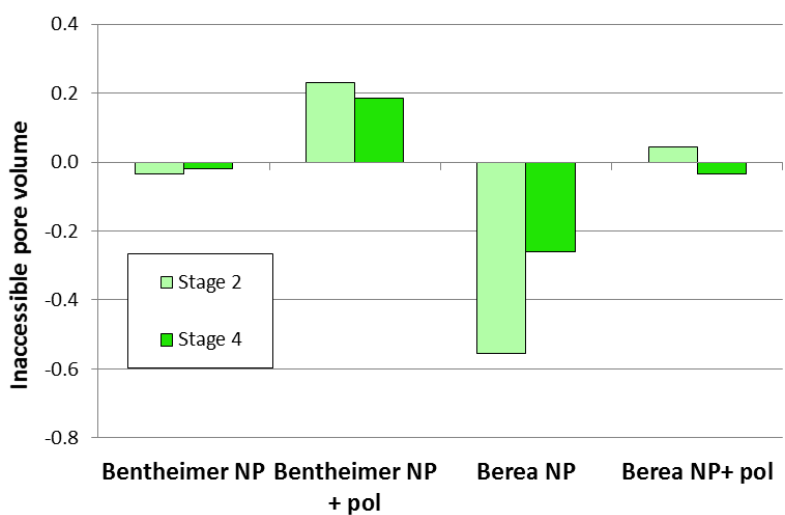

Figure 9—Inaccessible pore volume for nanoparticles for stages 2 and 4 of experiments
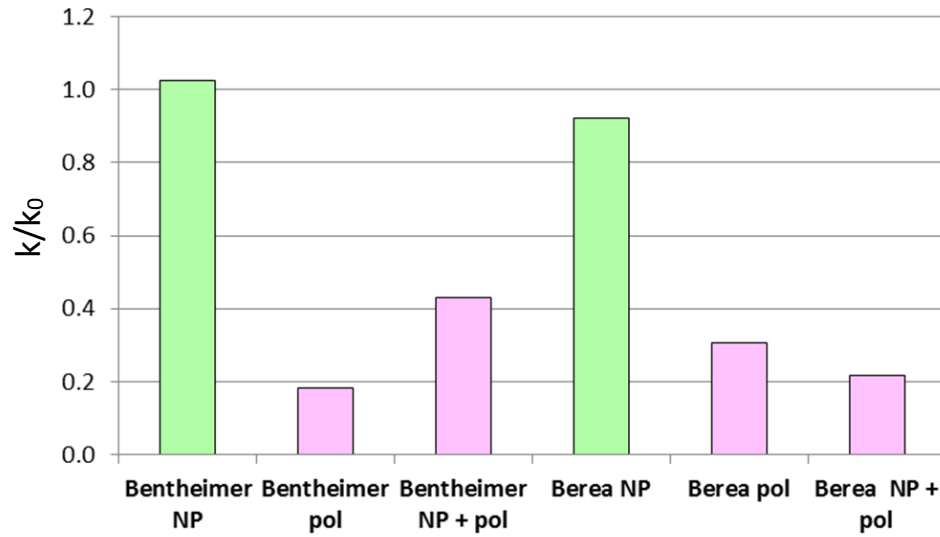
Figure 10—Residual Resistance Factor (K/K_0) for all experiments where K_0 is the initial permeability (before flood) and K is the final permeability (after flood)
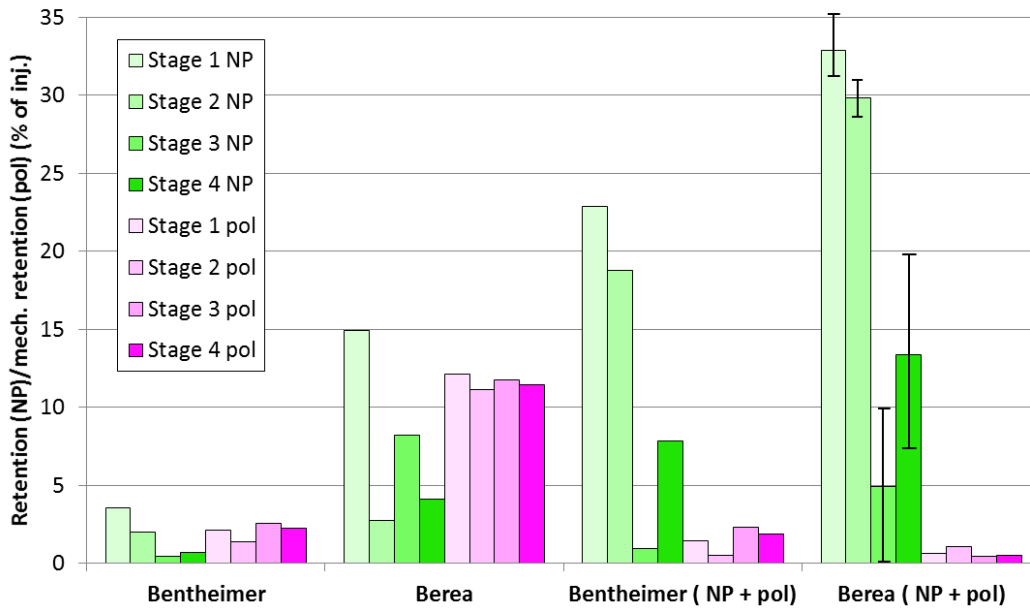

Figure 11 — Total retention of nanoparticles and mechanical retention of polymer determined at each stage for all experiments