INJECTIVITY AND RETENTION OF NANOCELLULOSE DISPERSIONS IN BEREA SANDSTONE

Reidun Cecilie Aadland(1), Katherine R. Aurand(1), Ole Torsæter(1), Ellinor Bævre Heggset(2) and Kristin Syverud(1,2)

1) Norwegian University of Science and Technology, Trondheim, Norway

2) Paper and Fibre Research Institute, Trondheim, Norway

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Snowmass, Colorado, USA, 21-26 August 2016

ABSTRACT

In this study, the main objective was to examine the interactions between nanocellulose dispersions and Berea sandstone through retention studies using a vertically-oriented particle mobility coreflooding (PMC) procedure. The type of nanocellulose evaluated was cellulose nanocrystals (CNC).

The results showed that CNC in low salinity water (LSW) was able to transport through the core causing moderate rock impairment (permeability reduction between 17 % to 25 %). Furthermore, it was observed an increase in differential pressure as CNC concentration increased. Indicating that retention increases as a function of concentration. A higher pressure was obtained when injecting with a high flow rate (3.0 ml/min) compared to a low rate (0.3 ml/min). CNC at higher salt concentration (3.53%) was not stable and plugged the inlet of the core. More research is required to improve the stability of CNC in brine and thus increase its mobility through the core.

INTRODUCTION

Chemical flooding with polymers is considered one of the most promising enhanced oil recovery (EOR) methods and has been researched for over 40 years. The main objective with polymer flooding is to improve the macroscopic displacement efficiency by increasing the viscosity of the aqueous phase. A higher viscosity of water results in a favorable mobility ratio, which reduces viscous fingering effects and changes the flow pattern in the reservoir.[5,7,8] Polymers will also help to increase microscopic efficiency due to their viscoelastic nature.[5]

When polymer flooding is applied to a reservoir, water-soluble polymers are added to the water prior to injection. Today, two main polymers are used commercially; the biopolymer xanthan gum and the synthetic polymer hydrolyzed polyacrylamide (HPAM).[2] The disadvantages with HPAM are that they are sensitive to high reservoir temperatures and shear degradation. Xanthan gum on the other hand is less sensitive to shear degradation, but the polymer is susceptible to bacterial degradation. In addition, it has a significantly higher cost than HPAM.[7]

This study examines the potential of using a novel additive derived from cellulose for chemical flooding. Cellulose is a renewable, non-toxic and biodegradable biopolymer obtained from wood. A particle character is obtained by utilizing cellulose in the nanoscale (nanocellulose). Particle characteristics at this size attain an advantage in the micron sized pore throats compared to dissolved polymers. The cellulose polymers occurs as bundles, not as single molecules, and they exhibit a high crystallinity. This makes them less vulnerable for degradation. It is therefore assumed that nanocellulose have a higher thermal stability and are less susceptible to bacterial degradation, compared to HPAM and xanthan gum.

Formation damage could be a problem when injecting polymers into a reservoir, as polymer molecules adsorb well at solid interfaces. Retention of particles inside the core creates an extra layer inside the pores and pore throats, which might lead to flow resistance. Furthermore, the adsorption is practically irreversible because it takes a large pore volume of displacing fluid to desorb the polymer.[8] Such a process might not be economically feasible. Hence, the polymeric additive is lost. Another option is to inject polymers with a higher initial concentration to take into account that some will be adsorbed by the rock. This will also cost more money and might not be the best solution. The most promising EOR additives have little to no adsorption. If the polymers exhibit high retention, they need to be modified to alleviate the issue; otherwise they will be excluded from further EOR research. Polymer chemistry, reservoir rock composition, temperature, salinity and polymer composition are the main factors influencing polymer retention.[5] A retention study on xanthan gum in a sandstone core showed that retention increased with increasing polymer concentration, and it also increased somewhat with the flow velocity.[4]

In this study, cellulose nanocrystals were flooded through a dry core plug to evaluate particle mobility. Ionic strength of the dispersion fluid and CNC concentration were varied to see if they displayed a trend with increasing or decreasing retention. The effect of flow rate was also evaluated.

EXPERIMENTAL MATERIALS

Base Fluids

Low salinity water (LSW) and synthetic North Sea water (NSW) were used as base fluids. LSW consisted of 0.1 wt.% sodium chloride (NaCl), while NSW comprised deionized water and seven different salts, resulting in a salinity of 3.53%. The base fluids were used as the aqueous phases into which CNC was dispersed.

Nanocellulose

Cellulose nanocrystals are rod-like particles with sizes in the nanometer range. The CNC used in this study were purchased from the University of Maine. This material was manufactured at the US Forest Service's Cellulose Nano-Materials Pilot Plant at the Forest Products Laboratory in Madison, Wisconsin. The cellulose nanocrystals were produced using 64 % sulphuric acid to hydrolyze the amorphous regions of the cellulose material, resulting in acid resistant crystals.[3] After washing, dialysis and sonication, a dispersion of 12 % CNC was obtained. This suspension was then diluted to 0.5 wt.% and 1.0 wt.% in the LSW and to 1.0 wt.% in the NSW.

Porous Media

The core plugs were extracted from a Berea sandstone block, which is considered to be strongly water-wet. Six core plugs were used in the study and their properties are listed in Table 1.

X-ray diffraction (XRD) analysis was performed for five samples taken from the same block as the core plugs used in this study. The results showed that the rock is composed of three main minerals: quartz (93.7 wt.%), microcline (5 wt.%) and diopside (1.3 wt.%).

Table 1. Properties of Berea sandstone core plugs. Porosity was measured with a helium porosimeter, and permeability was measured with air and corrected by use of the Klinkenberg effect.

Core #	Length [cm]	Diameter [cm]	Pore volume [ml]	Porosity [%]	Permeability [mD]
1	4.5	3.8	9.5	18.1	435
2	4.5	3.8	9.1	17.4	413
3	4.5	3.8	8.5	16.4	307
4	4.5	3.8	8.8	16.8	354
5	4.5	3.8	8.7	16.6	316
6	4.5	3.8	9.2	17.8	307
7	4.5	3.8	8.8	17.0	275
Average	4.5	3.8	9.0	17.2	344

EXPERIMENTAL METHOD

The standard PMC rig set-up was used for this study.[1] A dry core plug was mounted in a vertically-oriented core holder with 20 bar sleeve pressure. The base fluid or nanocellulose fluid was then injected from the bottom of the core. Effluent was collected from the top of the core holder every pore volume (PV) for 5 PV. A pressure gauge measured the pressure drop across the core. The core's final saturation was measured after flooding was complete. The cores were cleaned with methanol using a soxhlet extraction apparatus and dried in an oven at 60°C after flooding. Pre- and post-flooding porosity and permeability measurements were conducted to determine possible rock impairment.

Effluent samples were analyzed for concentration and pH. The concentrations of CNC will be determined quantitatively at a later point. However, CNC solutions become whiter and more opaque with increasing concentration, so it is possible to qualify concentration using visual observation. Therefore, the original injection fluid was placed in a vial and compared to the effluent samples. If the effluent had the same opacity as the original solution, it was concluded that little to no retention had taken place. As the transparency of the effluent increased, more retention was occurring. The retention results from the visual inspection were compared with the differential pressure curves for validation.

An overview of the experimental plan is displayed in Table 2. Concentration of CNC, dispersing fluid, and injection rate were the parameters that were changed for each experiment. The low flow rate was chosen to mimic the typical flow velocity in a reservoir (1 ft/day, which corresponds to 0.24 ml/min with the core's cross-sectional area).

Table 2. The different fluid types that were tested with the corresponding injection rates.

Core #	CNC concentration [wt.%]	Dispersing fluid	Flow rate [ml/min]
1	---	LSW	0.3

2	0.5	LSW	0.3
3	1.0	LSW	0.3
4	0.5	LSW	3.0
5	1.0	LSW	3.0
6	---	NSW	0.3
7	1.0	NSW	0.3

RESULTS AND DISCUSSION

A total of seven PMC experiments were conducted, where two of them were regarded as base cases. The LSW and NSW base cases were pure brines; they did not contain any nanocellulose particles. Therefore, no retention was occurring. The pressure curves from the experiments with nanocellulose particles were compared to the base cases. If the differential pressure was significantly higher than the base case, retention was assumed to occur, causing the pressure increase. On average, the cores were saturated 60 % at the end of the experiment. The pH was measured prior to injection and for the first and fifth pore volume of the effluent samples. It remained constant for all experiments.

LSW as Dispersing Fluid

Both concentrations that were used with LSW were considered stable solutions. The stability of 1.0 wt.% CNC with LSW was also confirmed in the research conducted by Molnes et al.[6] From the experimental results where the low rate was applied, it was observed a higher pressure for the case where 1.0 wt% CNC was used compared to 0.5 wt.% CNC (Figure 1A). The same trend was also observed when the high rate was used (Figure 1B). This indicates that particle retention increases with increasing CNC concentration. The same observation was also found in the retention experiments conducted on xanthan gum by Huh et al.[4]

For the low rate, both fluid systems follows the same trend as the base case, where the low concentration (0.5 wt.% CNC) is almost identical to the pressure curves of pure LSW (Figure 1A). The only difference is a slightly increased pressure at the end (pressure increased from 0.10 bar to 0.12 bar). This could be a result of particles adsorbing onto the rock grains leading to a tighter flow path and hence an increase in pressure. At the very end the pressure dropped to 0.10 bar again, which could mean that these particles were pushed further out or that a new flow path opened in the core.

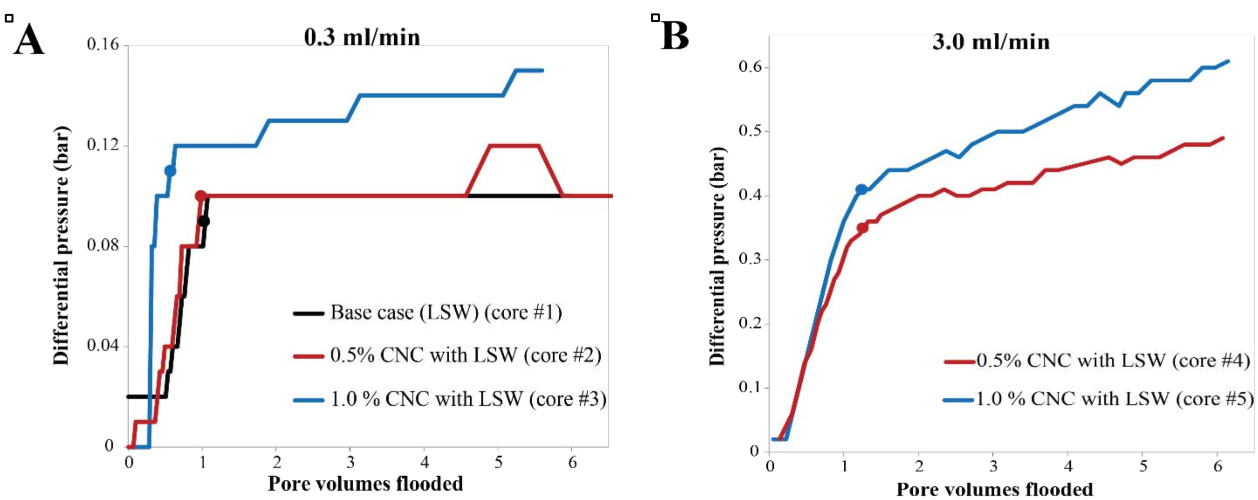

Figure 1. Pressure curves for the low rate (A) and high rate (B) using LSW as dispersing fluid for CNC. The points illustrate the breakthrough times for the water.

A base case was not conducted for the high rate in this particular study. However, Aurand et al.[1] did a PMC study where different rates were tested using NSW as base fluid. In the case where 3 ml/min was used as the rate, the differential pressure reached its maximum at 0.36 bar. It is therefore assumed that the base case for LSW would follow the same trend as NSW. This assumption is based on the fact that NSW and LSW do not contain any particles, and they had the same pressure curve when the low rate was applied. 0.5 wt% CNC and 1.0 wt.% CNC have a higher differential pressure than the base case for the high rate, and particles could be retained within the core.

NSW as Dispersing Fluid

For the solution where NSW was used as dispersing fluid, larger particles were visible with the eye, indicating that the CNC aggregated throughout the duration of the experiment. This caused particle accumulation at the inlet face of the core (Figure 2), inhibiting injection. Differential pressure increased throughout the experiment to a final, maximum pressure of 3.5 bar. This is over 20 times greater than the maximum pressure of the flooding experiments conducted with the low rate. The PMC test cannot be accurately run with particle aggregation, so this test does little more than to show that more work needs to be done on the stabilization in the presence of synthetic saltwater.

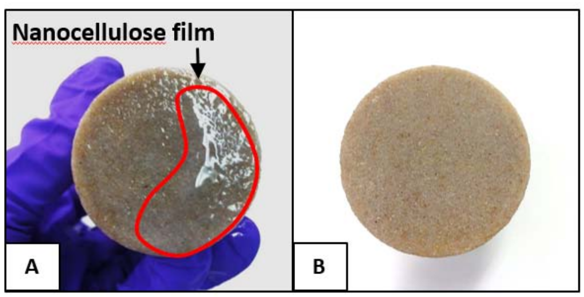

Figure 2. A) Picture of the core inlet for 1.0 wt.% CNC with NSW taken after PMC. A thin film of nanocellulose is observed. B) The other tests did not display this effect, which is illustrated by the core that was flooded with 0.5 wt.% CNC with LSW.

Porosity and Permeability

The permeability was altered during the PMC tests, and lead to a moderate impairment (ranging from 17% to 25%) for the majority of the cores. Core 6 (1 wt.% CNC with NSW) had a significant permeability reduction of 61 %, which could be explained by the nanocellulose film that was created on the inlet of the core. The porosity of the core plugs did not change during the PMC tests.

Effluent Analysis

The effluent analysis confirmed the observations from the pressure curves. From sample 1 PV to 5 PV it is seen that nanocellulose has been transported through the core in the cases where LSW was used as dispersing fluid (Figure 3). However, it is not possible to determine the exact amount of particles by visual analysis only. It is difficult to determine the extent of retention as a function influent concentration and flow rate without a quantitative measurement of the effluent concentrations. The observations from the effluent study therefore just give an indication of which system will perform best for further EOR research.

In the case where NSW was used as dispersing fluid, it is observed that PV 1 to 4 is quite transparent when compared to PV 0 (Figure 3). This indicates that CNC is retained within the core. In the fifth PV it is possible to see that CNC has had a breakthrough in the core because a small amount of CNC is observed in the bottom of the sample.

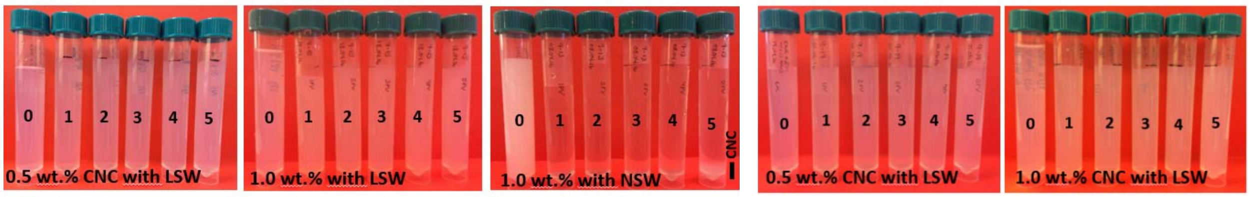

Figure 3. Effluent samples from flooding experiments, where sample 0 is the original fluid prior to injection and sample 1 to 5 illustrates PV 1 to 5, respectively. From left to right: 0.5 wt.% CNC with LSW (0.3 ml/min), 1.0 wt.% CNC with LSW (0.3 ml/min), 1.0 wt.% CNC with NSW (0.3 ml/min), 0.5 wt.% CNC with LSW (3.0 ml/min) and 1.0 wt.% CNC with LSW (3.0 ml/min).

CONCLUSIONS

- The studies show that there is a trend between CNC concentration and retention. Retention is increasing as CNC concentration increases.
- CNC exhibits a greater retention in the core when dispersed in a fluid with high ionic strength (3.53% salinity), which was evident from pressure data, permeability impairment and effluent analysis. This could be a result of an unstable solution. Thus, more research concerning the stability of the nanocellulose dispersions in salt is needed in order to prevent aggregation and plugging of pores.
- A higher flow rate might lead to more particles being retained, but this statement needs to be confirmed by running more parallel experiments together with accurate measurement of effluent concentration.

ACKNOWLEDGEMENTS

The authors would like to thank the Research Council of Norway for their financial support through the grant 244615/E30 in the Petromaks2 programme.

REFERENCES

1. Aurand K., Flatås V. and Aadland R. "Analyzing retention via particle mobility coreflooding". In International Symposium of the Society of Core Analysts, (2016).
2. Chang, H. L. (1978). Polymer flooding technology yesterday, today, and tomorrow. *Journal of Petroleum Technology*, *30*(08), 1-113.
3. Dong, X. M., Revol, J. F. and Gray, D. G. "Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose". Cellulose, (1998) **5(1)**: 19-32.
4. Huh, C., Lange, E. A., & Cannella, W. J. "Polymer retention in porous media". In *SPE/DOE Enhanced Oil Recovery Symposium*, (1990), Society of Petroleum Engineers.

5. Kamal, M.S., Sultan, A.S., Al-Mubaiyedh, U.A., & Hussein, I.A. "Review on polymer flooding: rheology, adsorption, stability, and field applications of various polymer systems". *Polymer Reviews*, (2015) ***55*****(3),** 491-530.
6. Molnes, S.N., Torrijos, I.P., Strand, S., Paso, K.G and Syverud, K. "Sandstone injectivity and salt stability of cellulose nanocrystals (CNC) dispersions—Premises for use of CNC in enhanced oil recovery". Ind. Crops Prod.(2016).
7. Raney, K. H., Ayirala, S., Chin, R. W., & Verbeek, P. "Surface and subsurface requirements for successful implementation of offshore chemical enhanced oil recovery". *SPE Production & Operations*, (2012) ***27(03)***, 294-305.
8. Sheng, J. J., Leonhardt, B., & Azri, N. «Status of polymer-flooding technology". *Journal of Canadian Petroleum Technology*, (2015) ***54*****(02)**, 116-126.