

## Halliburton IOR Testing on Thermo-thickening Associative Polymers

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## Contents

1.	Executive Summary .....	2
2.	Introduction and Background.....	3
3.	Chemical Formulations.....	4
4.	Equipment Set-up and Test Parameters.....	5
5.	Test Procedure.....	7
	5.1 Establish Baseline Permeability.....	7
	5.2 Baseline Test with 3xSSW .....	8
	5.3 Polymer Injection.....	8
	5.4 Displace Polymer with 3xSSW .....	8
	5.5 Rig-down.....	8
6.	Results and Discussions .....	9
	6.1 Baseline Test with 3xSSW .....	9
	6.2 Injection of 1000ppm A10 Polymer.....	11
	6.3 Injection of 2700ppm A10 Polymer.....	13
7.	Conclusions.....	16
8.	Future Work/Plans .....	<b>Error! Bookmark not defined.</b>
9.	References .....	16

## 1. Executive Summary

The main objective with this work was to demonstrate the possibility of in-depth thermo-thickening behaviour in the reservoir using the associative ATBS-based polymer A10 from BASF. NORCE has tested the polymer and it was found to be suitable. The polymer was mixed at 1000 ppm concentration in brine with salinity 3 times synthetic seawater (3xSSW). The injection through sand pack at 20°C for associative ATBS-based polymer was same as for a regular polymer but the polymer showed thermo-thickening behaviour with mobility reduction (RF) > 400 in 1-meter-long sand pack at 80°C.

This experiment was re-run at Halliburton in a similar set-up, with a new batch of A10 polymer premixed by BASF. The results indicated nearly no thermo-thickening at 80°C with 1000ppm concentration, while a QC-test by NORCE revealed strong thermo-thickening. Thereafter, it was decided to increase the polymer concentration to 2700 ppm in 3XSSW and thermo-thickening was observed with RF = 180 at the termination of the experiment.

The main differences between the NORCE and Halliburton set-ups are described below:

- NORCE used stainless steel columns, or sand filled into a rubber sleeve whereas iron Chiksan pup-joint was used to fill sand at Halliburton.
- Some iron was present in the effluent during testing at Halliburton.
- The production of iron is assumed to explain the deviation in results. This is supported by viscosity loss from inlet to outlet capillary tube viscometer at Halliburton and no viscosity loss was observed in the NORCE set-up. The oxygen content was lowered by N2 bubbling and N2 blanket in both labs.

The hypothesis is that the effective polymer concentration is reduced due to polymer degradation, and it will require higher injection concentrations to achieve thermo-thickening. Currently, it is difficult to say about the most realistic set-up for the field conditions.

Nevertheless, it is recommended to include some safety margins either in terms of polymer concentration or associative content with respect to possible degradation when designing thermo-thickening polymers for the field-testing.

## 2. Introduction and Background

Halliburton has contributed to the National IOR Centre, mainly through the execution of large-scale tests, Stavland et al. (2021) and Åsen et al. (2019). The technical committee of the National IOR Centre held a brainstorming workshop on October 27, 2017 at Halliburton facility on Large Scale Test. The purpose of the workshop was to identify areas of interest which may require larger scale testing to support and validate development of the simulation models that are being developed in the Centre or otherwise in the industry.

The discussion covered a vast area within chemicals for IOR methods focusing on the importance of upscaling and investigating the performance of Synthetic Polymers, Biopolymers, Silicate systems and Tracers in a porous media. The discussion also covered the potential benefits of investigating the use of Foamed Polymer and Silicate systems for Fracture Sealing. Several test concepts and test set-ups were suggested and discussed.

Finally, all proposed test concepts were ranked based on their complexity and it was decided to prioritize evaluation of thermal triggered polymers such as associative polymers using a large-scale test set-up with the objective of studying Polymer retention, polymer propagation and thermal-activation mechanisms and comparing results with concluded laboratory experiments at NORCE. The specific Polymer solution selected for this test is A10 from BASF. This polymer is similar to the polymers used by Reichenbach-Klinke et al. (2016) and the experimental results were well matched by Lohne et al. (2019).

Reichenbach-Klinke et al. (2018) reported experimental work with one class of associative polymers. Thermo-associative side chains had been added to the water-soluble polymer backbone as shows in Figure 1. When injecting the polymer through a porous medium at low temperature the polymer shows flow characteristics like a regular polymer and the mobility reduction was in-line the relative polymer viscosity. However, the thermo-thickening polymers are expected to exhibit significantly higher differential pressure when increasing the temperature. The differential pressure would generally decrease due to lower viscosity for regular polymers.

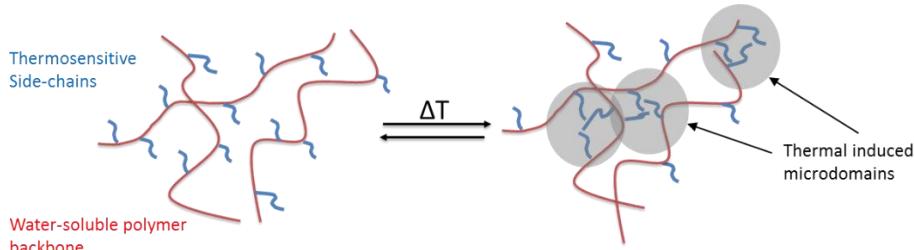


Fig. 1: Structure of Thermo-thickening Associative Polymers

The first experimental testing was carried out using associative polymer A06 from BASF in 2019 but the results were not positive, and the polymer used for the testing did not demonstrate thermo-thickening effect as expected. Therefore, additional testing was carried out with new type of associative polymer which is expected to have improved thermo-thickening characteristics.

The purpose of the experiments is to demonstrate thermo-thickening effect of the associative polymer in porous medium. It is expected that this polymer should demonstrate significantly higher mobility reduction at equilibrium than achieved by viscous flooding.

The test objective includes:

1. Identify appropriate equipment required to perform the test
2. Calibrate instruments such as pressure and temperature sensors, flowmeters, and heating elements
3. Select appropriate sand type
4. Establish baseline permeability and expected differential pressure
5. Rig-up and perform polymer flooding experiment to verify thermo-thickening effect

### 3. Chemical Formulations

A summary of the chemicals required, and chemical formulations are provided in this section.

Table 1: Chemicals Overview

Chemical description	Quantity	Comments
100 Mesh Sand	5 kg	to be packed in sand pack column
A10 Polymer, 1% (Lot: A41074)	20 L	delivered by BASF in ~5 L cans
Synthetic Seawater (SSW)	As required	

Table 2: Formulation for A10 Polymer Dilution

Stock Polymer Conc. (ppm)	Desired Polymer Conc. (ppm)	Volume of Final Desired Conc. (Liter)	Polymer Solution (Liter)	3xSSW Volume (Liter)
10000	1000	50	5	45

\*Add salts to water and total volume should be 1 liter after mixing.

Table 3: Formulation for 3xSSW

Fresh Water (Liter)	NaCl (g)	CaCl <sub>2</sub> ·2H <sub>2</sub> O (g)	SG @20°C	Viscosity @20°C
1	84.0	24.0	1.07	1.20

Properties of 0.1% (1000 ppm) polymer solution in 3xSSW:

- Specific gravity at 20°C: 1.074
- Viscosity at 20°C: approx.: 3.8 – 3.9 cP @ 200 sec<sup>-1</sup>

A summary of the mixing procedure for the 1000 ppm polymer solution is provided below:

1. Prepare 3xSSW (brine) according to the formulation provided in Table 3.
2. Purge with Nitrogen for approx. 4-6 hours to remove any residual oxygen from the system.
3. Add appropriate volume of the 1% polymer solution (i.e., 100 mL/L, refer Table 2) in the brine slowly while agitating with magnetic stirrer.
4. Mix 30 minutes to form a uniform solution. Purge with Nitrogen as polymer is getting mixed.
5. Transfer polymer solution into the dedicated tank. The maximum capacity of the tank is 75 Liter.
6. Transfer Nitrogen into the polymer tank to create a Nitrogen blanket. Maximum pressure should not exceed 0.5-1 bar.
7. Close the valve on polymer tank.

## 4. Equipment Set-up and Test Parameters

A pre-job meeting was held with relevant personnel to ensure that the test objectives are clearly understood. The equipment was rigged-up according to the standard procedure and refer rig-up drawing provided in Fig. 2.

Take note of the following points for the equipment rig-up:

1. Calibrate instruments for the expected pressure, flow rate, temperature ranges etc.
2. Clean 3" chiksan, the end caps and all lines and fitting thoroughly.
3. Fix sintered glass filter-disc at both ends of the chiksan end caps.
4. Mount the chiksan in its vertical position.
5. Measure volume of the chiksan by filling with water.
6. Partially fill chiksan with water first.
7. Slowly start adding sand and water manually. Continue to do this slowly allowing air to escape and ensuring sand is packed properly until the top.
8. Mount the top end cap and secure chiksan on the rack in preparation for the test.
9. Rig-up pumps, flow lines, and all instruments according to rig-up drawing.
10. Measure the volume of the capillary tube and calculate inside diameter.
11. Wrap heating elements and insulation material on the lines to minimize heat loss.
12. Calibrate heat regulator
13. Connect all lines as per rig-up drawing.
14. Barricade the test area to restrict un-authorized personnel access.
15. Perform Low pressure leak test at 20 bar using 3xSSW.
16. Perform High pressure leak test by gradually increasing pressure from 20 to 60-70 bar. Bleed-off pressure and ensure no trapped pressure anywhere in the lines.

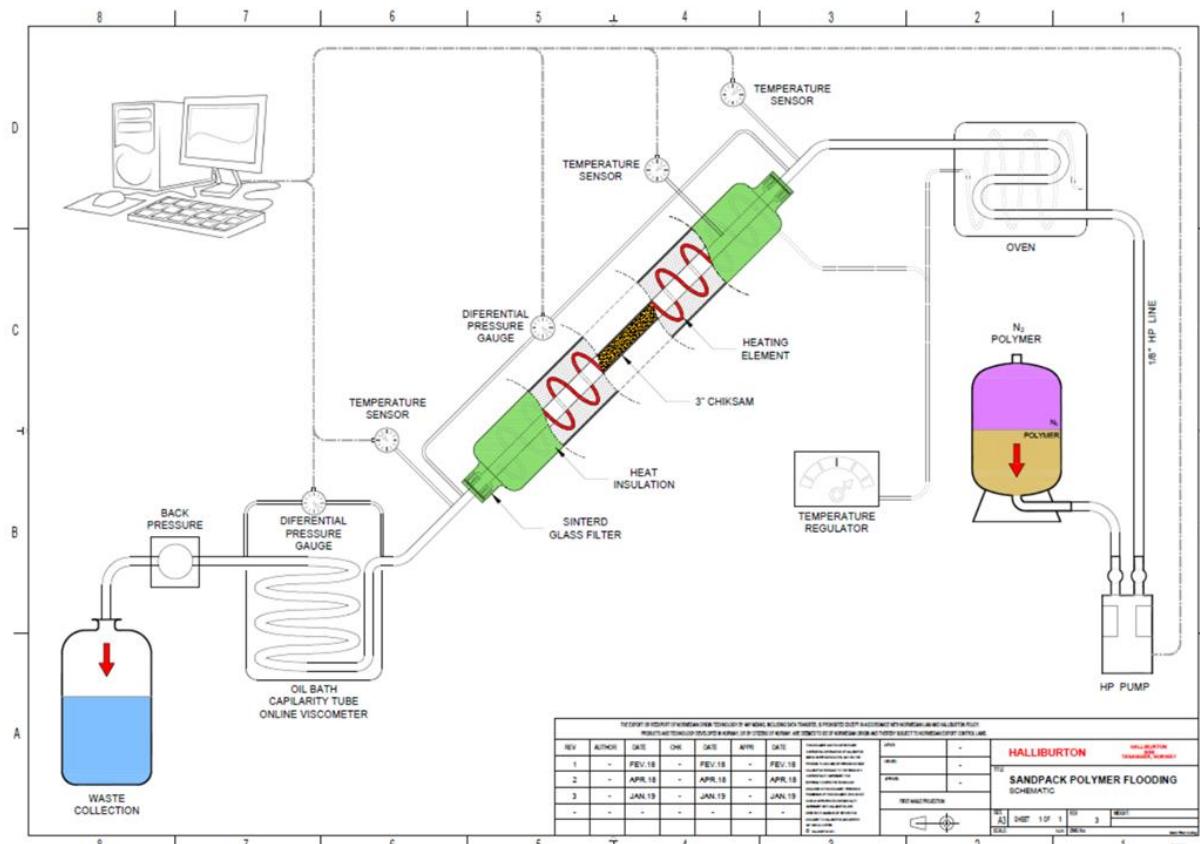


Fig. 2: Schematic of the Equipment Rig-up

Table 4 provides summary of the different input parameters for the polymer testing.

Table 4: Summary of Test Parameters

Parameters	Value
Bulk density, 100 mesh sand	1.635 kg/L
Absolute density, 100 mesh sand	2.656 kg/L
Chiksan length	0.915 m
Chiksan volume	2.92 Liter
Chiksan ID	0.06374 m (2.51 inch)
Amount of Sand packed	4.776 kg
Pore volume (PV)	1.025 Liter
Porosity, measured	35.1 %
Absolute Permeability, theoretical	12.8 mD
*Pump Rate	4.2 mL/min
Test Temperature	80°C
Polymer DP 21051	1000 ppm in 3xSSW
1/8" Capillary tube length	15 m
1/8" Capillary tube ID	1.483 mm
1/8" Capillary tube volume	25.9 mL
Rupture Disc (pressure relief device)	~68 bar (1000 psi)
Differential Pressure Transmitter	0 – 3 bar (capillary tube)
Differential Pressure Transmitter	0 – 6 bar (chiksan sand pack)
Quizix Pump Rate	0 – 45 mL/min

\*Note: Pump rate is defined such that the flow velocity at NORCE is same as velocity at Halliburton.

## 5. Test Procedure

A summary of the test matrix and test procedure is provided in this section.

### 5.1 Establish Baseline Permeability

**Note:** Do not exceed maximum pressure limit of 50 bar at any time. Record data every 1 minute.

1. Perform baseline permeability test at 20°C (room temperature) using 3xSSW.
2. Start injection at 1 mL/min and adjust backpressure to 10 bars. Ensure that the temperature is stable. Continue injection as per schedule in Table 5:

Table 5: Injection Schedule for Baseline Permeability

Establish Baseline Permeability					
Test No. 1	Fluid	Temp (°C)	hrs	Rate (ml/min)	Volume (liters)
1a	3x SSW	20	25.0	1.00	1.50
1b	3x SSW	20	1.5	35.00	3.15
1c	3x SSW	20	1.5	25.00	2.25
1d	3x SSW	20	1.5	10.00	0.90
1e	3x SSW	20	3.0	5.00	0.90
1f	3x SSW	20	25.0	1.00	1.50
<b>Total</b>					<b>10.20</b>

**Note:** The purpose for step 1b is to ensure that all low salinity fluid is displaced.

3. Determine sand pack permeability (refer Table 6). The calculated permeability for the sand was 9.4 Darcy based on the experimental data.

Table 6: Measured values for Differential Pressure across Sand Pack

Sand Pack Calculations for 3xSSW - Baseline Test No. 1				
Pump Rate, mL/min	Velocity, m/s	Shear rate, 1/s	Theoretical dP, mbar	Measured dP, mbar
1	0.0000149	10.2	6.2	5.7
5	0.0000744	50.9	30.9	23.8
10	0.0001488	101.7	61.9	51.2
25	0.0003720	254.3	154.7	147.2
35	0.0005208	356.0	216.6	224.3

4. Verify differential pressure measured using capillary tube (refer Table 7)

Table 7: Measure values for Differential Pressure across Capillary Tube

Capillary Tube Calculations for 3xSSW - Baseline Test No. 1				
Pump Rate, mL/min	Velocity, m/s	Shear rate, 1/s	Theoretical, mbar	Measured, mbar
1	0.0097	52.1	25.3	24.4
5	0.0483	260.4	126.4	123.1
10	0.0965	520.8	252.9	249.7
25	0.2413	1302.0	632.2	698.6
35	0.3378	1822.8	885.1	1053.4
4.2	0.0405	218.7	106.2	104.0
16.8	0.1622	874.9	424.9	451.3

## 5.2 Baseline Test with 3xSSW

Note: Do not exceed maximum pressure limit of 50 bar at any time. Record data every 1 minute.

1. Perform baseline test at 20°C (room temperature) using 3xSSW.
2. Start injection at 4.2 mL/min and adjust backpressure to 10 bars. Ensure that the temperature is stable. Continue injection until stable pressure is observed (approx. 3-4 hours).
3. Increase temperature to 80°C and ensure that the temperature is stable.
4. Continue pumping at this rate for 24-25 hours and ensure stable pressure is observed.

## 5.3 Polymer Injection

Note: Do not exceed maximum pressure limit of 50 bar at any time. Record data every 1 minute.

1. Switch to container filled with 1000 ppm (0.1%) polymer solution and inject at 4.2 mL/min. Maintain temperature at 80°C.
2. Measure viscosity of the injected polymer (or derived using capillary tube at the inlet).
3. Compare injected polymer viscosity with effluent viscosity derived from capillary tube.
4. Continue polymer injection until stable differential pressure or thermo-thickening behavior is demonstrated. It is estimated to inject approx. 40-50 pore volumes.

Note: Do not stop polymer injection at any stage during the testing.

Based on the test results at 80°C, several options might be considered for further testing. A summary possible scenarios is discussed below:

1. Perform rate steps with polymer solution. NORCE has earlier reported strong rate sensitivity, i.e., the mobility reduction increases dramatically by lowering the injection rate.
2. Salt is known to be an important factor for the thermo-thickening. Therefore, it might an option to stepwise lower the brine salinity while keeping the polymer concentration constant. Alternatively, the salt can be fixed, and the polymer concentration can be reduced.

## 5.4 Displace Polymer with 3xSSW

The polymer solution will be displaced with 3xSSW after the polymer flooding experiment.

1. The post-flush with 3xSSW will be initiated at 80°C. Pump brine at 4.2 mL/min until stable pressure is observed.
2. Once stable pressure is observed, lower the temperature to 20°C and continue injection at 4.2 mL/min.
3. Perform rate steps by increasing rate to 5, 25 and 35 mL/min to flush the system. Ensure stable pressure at each rate step before changing the rate.

## 5.5 Rig-down

1. Collect all waste and dispose as per applicable regulations.
2. Rig-down equipment.

## 6. Results and Discussions

The test results for the core flood experiments are described in this section.

The baseline permeability was established based on the actual measured data. The calculated sand pack permeability was 9.4 Darcy. The effluent was also measured for the iron content. The iron measurement was in the range of 2-4 ppm when pumping at 4.2 mL/min. The iron content was reduced to less than 1 ppm when pumping at higher rate.

The measured differential pressure across the sand pack core was in-line with the theoretical values. The actual differential pressure across the capillary tube was higher than the theoretical values at high pump rate. This could be attributed to the fact that the actual measurements were taken on a coiled capillary tube rather than a straight pipe. It should also be noted that the internal diameter (ID) of the capillary tube was calculated from the volume and there might also be some uncertainty with surface roughness. However, this does not affect the test result as the same capillary tube was used for all the experiments.

### 6.1 Baseline Test with 3xSSW

After establishing the baseline permeability, the baseline test was carried out by pumping 3xSSW at 4.2 mL/min. A summary of the test results is provided in Fig. 3-6.

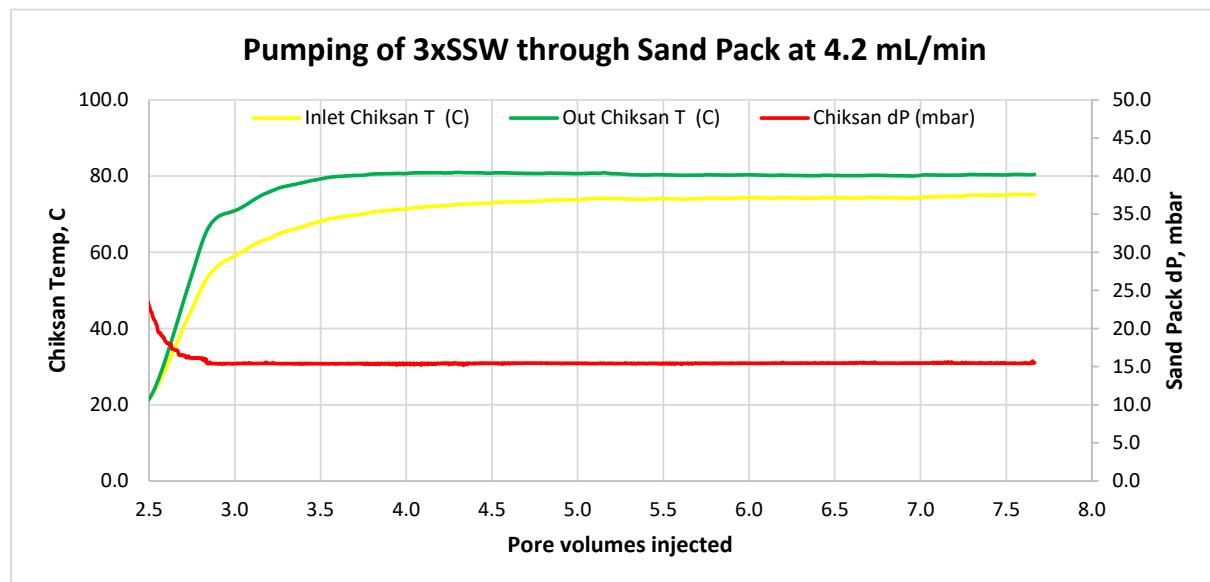


Fig. 3: Pumping of 3xSSW at 80°C – Sand Pack Pressure and Temp

It could be observed from Fig. 3 that the outlet temperature for the sand pack was maintained at 80°C and it was very stable throughout the injection period. The differential pressure across sand pack got stabilized once the temperature reached 80°C and the readings were as expected.

Fig. 4 shows temperature and differential pressure across the capillary tubing. The differential pressure for both inlet and outlet capillary tubing was similar as no change is expected for the brine properties. Fig. 5 and 6 shows mobility reduction for both sand pack and capillary tubing. The mobility reduction is calculated relative to brine injection and therefore it is one (1) for this case.

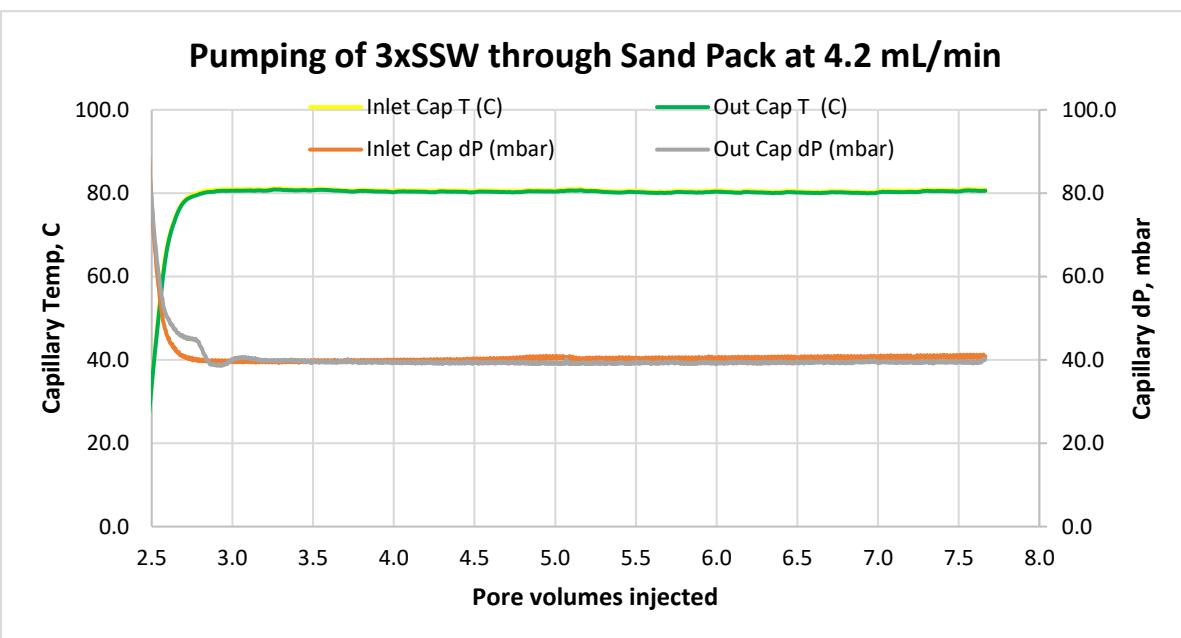


Fig. 4: Pumping of 3xSSW at 80°C – Capillary Tube Pressure and Temp

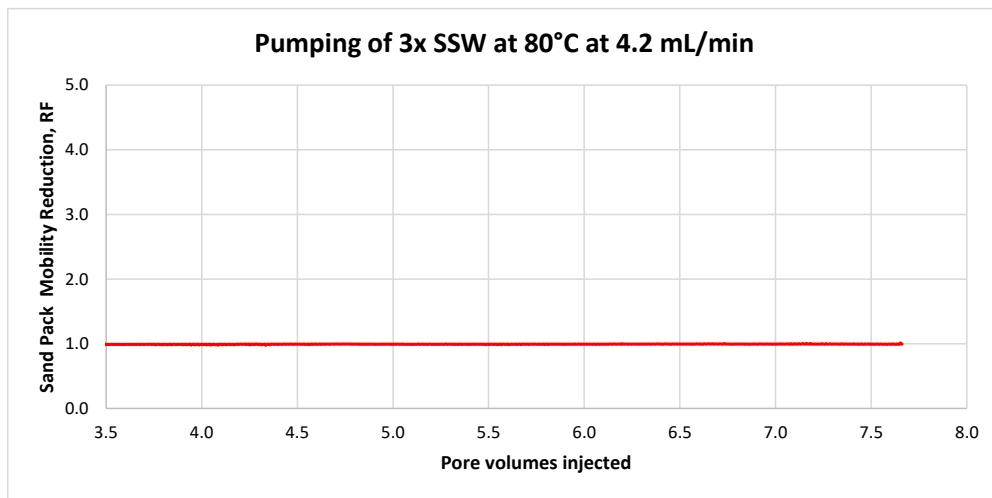


Fig. 5: Pumping of 3xSSW at 80°C – Sand Pack Mobility Reduction

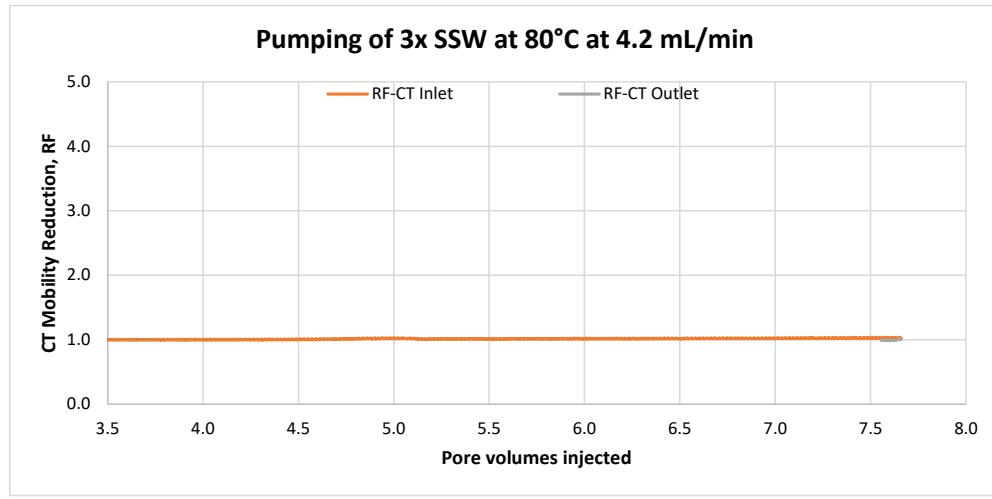


Fig. 6: Pumping of 3xSSW at 80°C – Capillary Tube Mobility Reduction

## 6.2 Injection of 1000ppm A10 Polymer

The injection of 1000ppm A10 polymer was started at 80°C and 4.2 mL/min after baseline injection with 3xSSW. The temperature was stable for both capillary tubing and sand pack. A summary of the test results is provided in Fig. 7-9.

It could be observed from Fig. 7 that the differential pressure across sand pack started to increase gradually as polymer was being injected. This increase in pressure could be attributed to the higher viscosity of the polymer than 3xSSW. A smooth and gradual differential pressure increase was observed across the core as the polymer was propagating and displacing brine. The pressure was stabilized once entire sand pack volume was displaced. However, the pressure response behaviour did not show any thermo-thickening effect even after pumping approximately 11 PV.

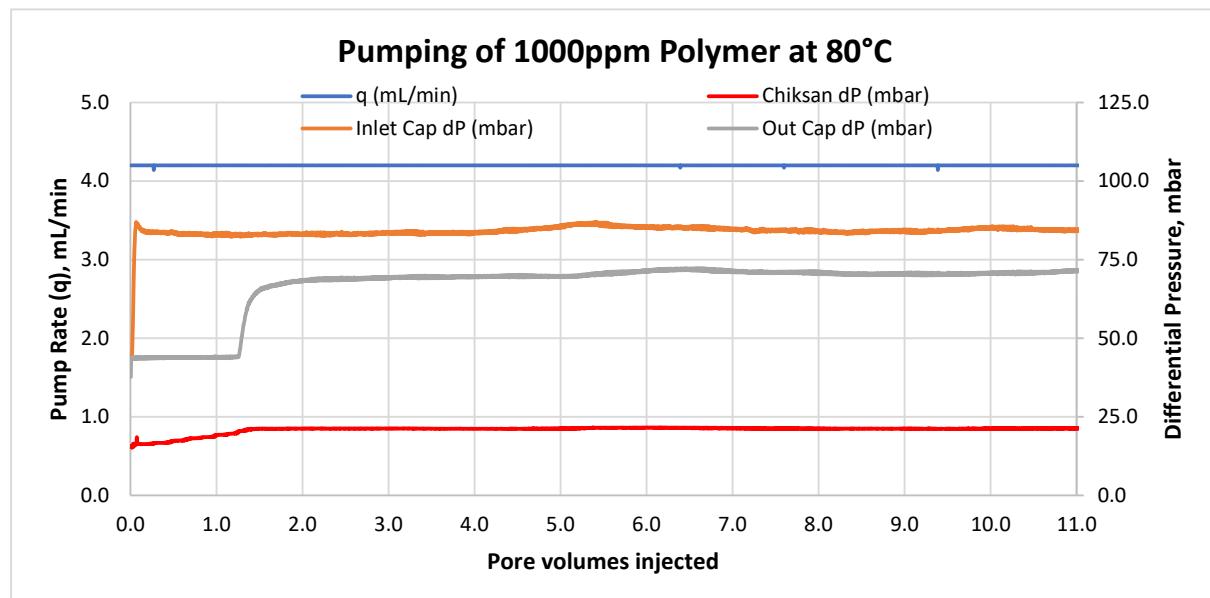


Fig. 7: Injection of 1000ppm A10 Polymer at 80°C

The differential pressure for the outlet capillary tube was low until polymer breakthrough and quickly increased after pumping approx. 1.25 PV. This indicates that the polymer was displacing brine in a piston like manner i.e., very good displacement efficiency. It should also be noted that it took about 1.5 PV before the differential pressure across the core got stabilized.

Fig. 8 shows the mobility reduction for both sand pack and capillary tubing. It is clearly observed that no thermo-thickening effect was observed with 1000ppm polymer concentration at 4.2 mL/min.

➤ RF-SandPack < RF-CT

It could also be observed that mobility reduction for the inlet capillary (RF-CT Inlet) was higher than the outlet capillary (RF-CT Outlet). This might be attributed to the polymer degradation through sand pack or possible adsorption of the polymer on the sand face. The RF-CT Inlet was approx. 15-20% higher than RF-CT Outlet.

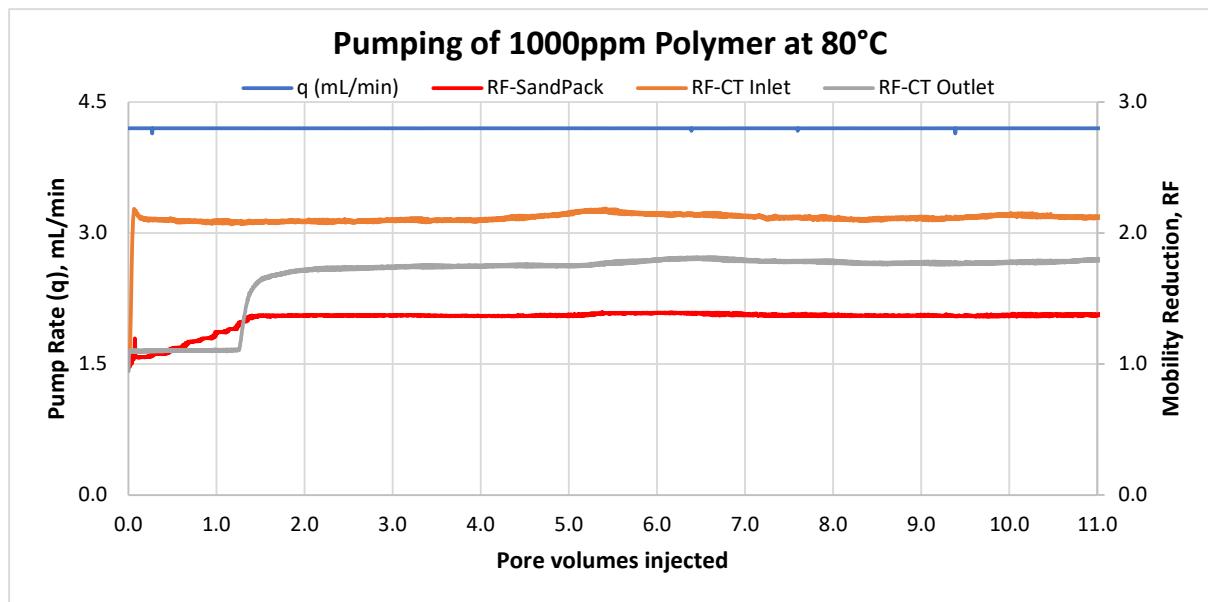


Fig. 8: Injection 1000ppm A10 Polymer at 80°C – Mobility Reduction

After discussion with NORCE, it was decided to increase the pump rate to 16.8 mL/min to see the effect of higher pump rate on the thermo-thickening effect. It could be observed from Fig. 9 that increasing pump rate did not help and the mobility reduction did not change significantly. A much higher mobility reduction is expected because of the thermo-thickening effect. The pump rate was then reduced to 4.2 mL/min and the test was stopped.

Polymer degradation of approx. 10-15% could be observed based on inlet and outlet capillary tube. The polymer degradation seems to be slightly lower at higher pump rate due to shorter residence time in sand pack.

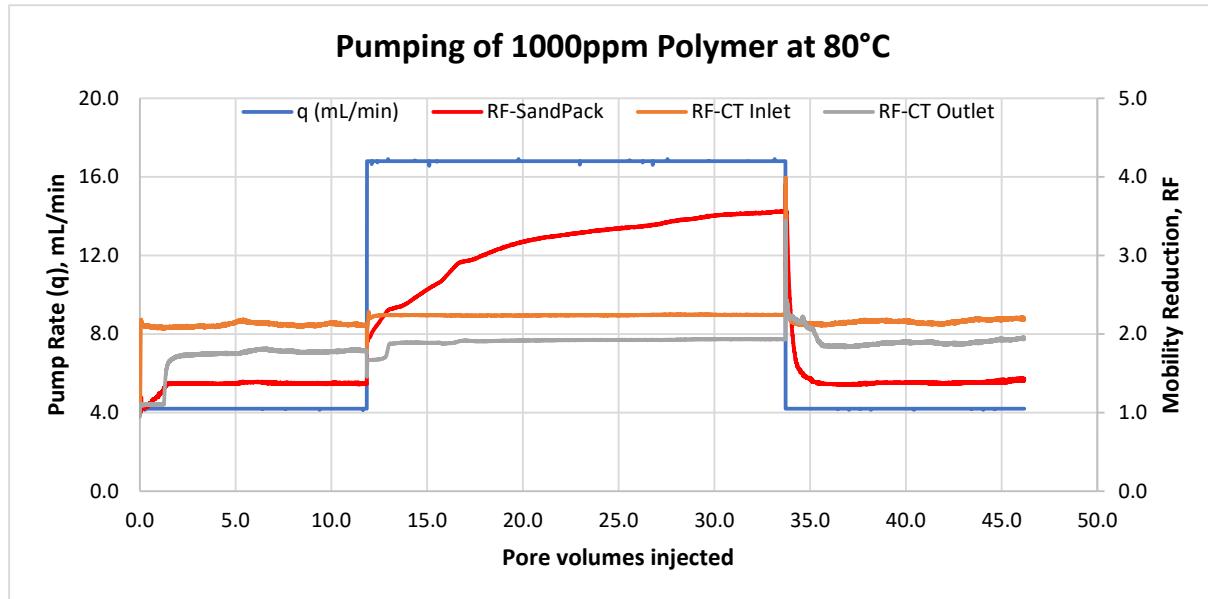


Fig. 9: Injection 1000ppm A10 Polymer at 80°C – Mobility Reduction

The lines were flush with brine (3xSSW), and it was decided to increase polymer concentration to 2700ppm for the next experiment.

### 6.3 Injection of 2700ppm A10 Polymer

The injection of 2700ppm A10 polymer was started at 80°C and 4.2 mL/min. The temperature was stable for both capillary tubing and sand pack. A summary of the test results is provided in Fig. 10-11.

It could be observed from Fig. 10 that the differential pressure across the outlet capillary tube was low until polymer breakthrough and quickly increased after pumping 1.0 PV. This indicates that the polymer displaced the brine from sand pack effectively.

The differential pressure across sand pack started to increase gradually as polymer was being injected. Note that the differential pressure across both capillary tubes was stable and constant. Therefore, the increase in pressure across sand pack could be attributed to the thermo-thickening effect of the polymer. However, the test had to be stopped after pumping approx. 8.0 PV due to increased pressure at the pump which was caused by plugging in the pre-heating coil before inlet capillary tubing.

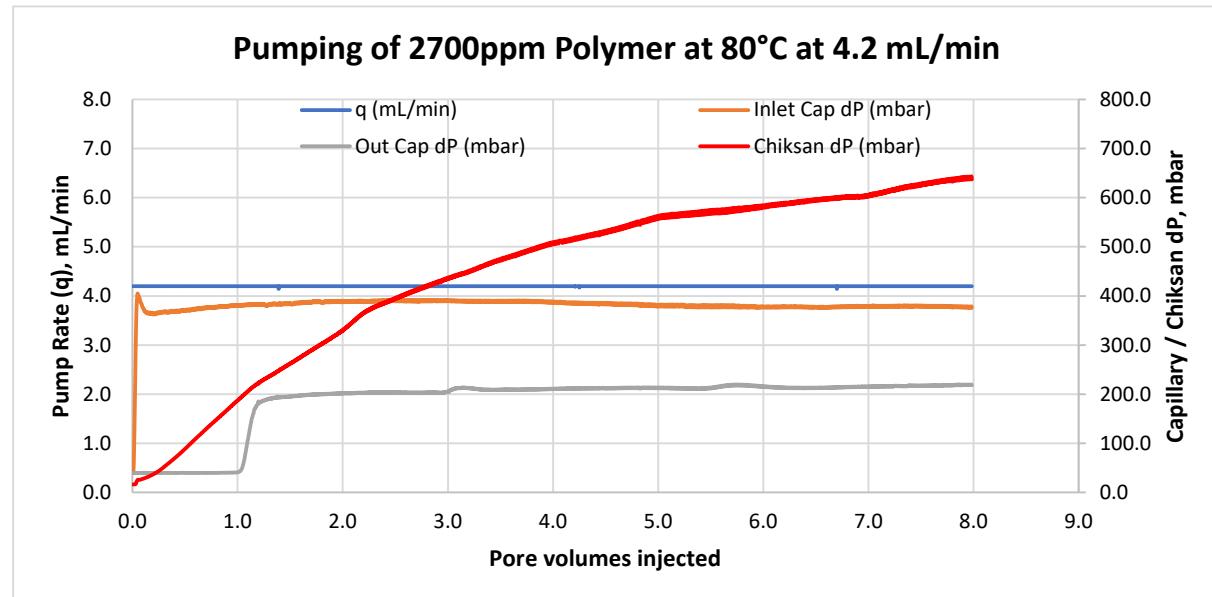


Fig. 10: Injection of 2700ppm A10 Polymer at 80°C

Fig. 11 shows the mobility reduction for both sand pack and capillary tubing. It is clearly observed that the thermo-thickening effect was observed with 2700ppm polymer concentration at 4.2 mL/min.

➤ RF-SandPack >> RF-CT

It could also be noted that the mobility reduction for the inlet capillary (RF-CT Inlet) was higher than the outlet capillary (RF-CT Outlet). This might be attributed to the polymer degradation through sand pack or possible adsorption of the polymer on the sand face. The RF-CT Inlet was approx. 25-30% higher than RF-CT Outlet.

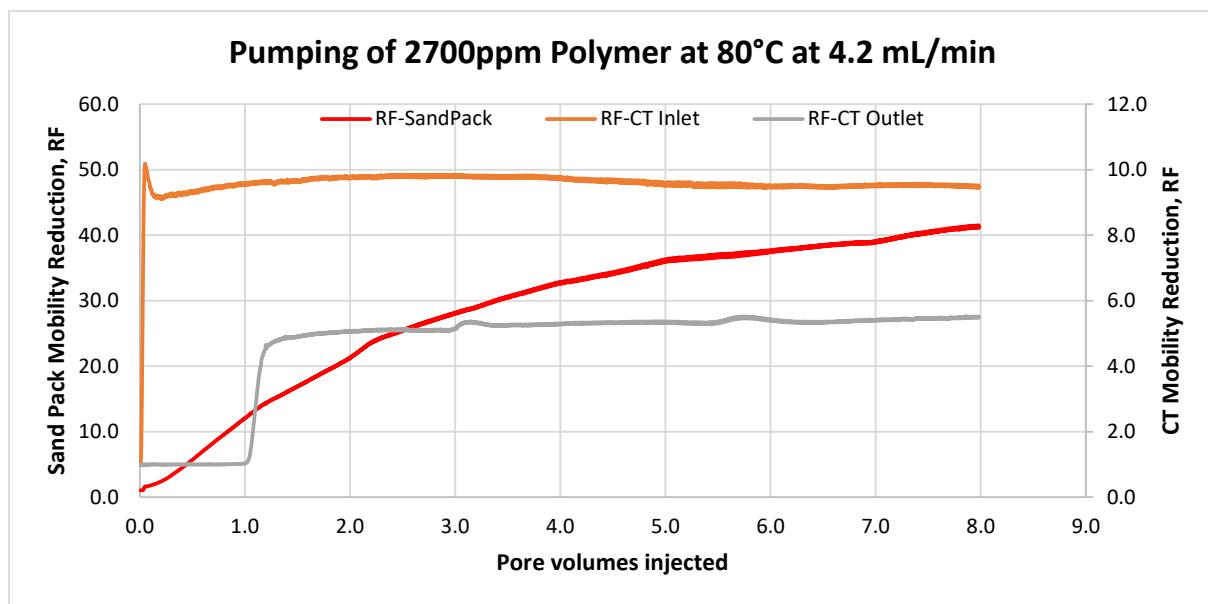


Fig. 11: Injection 2700ppm A10 Polymer at 80°C – Mobility Reduction

The lines were disconnected for flushing due to plugging in the pre-heating coil before inlet capillary tubing. During flushing, some residues were observed from the tubing and the lines were connected again.

The brine was first injected, and temperature was stabilized at 80°C before starting with polymer injection. The injection of 2700ppm A10 polymer was re-started at 4.2 mL/min. A summary of the test results is provided in Fig. 12-13. It could be observed from Fig. 12 that the differential pressure for the capillary tubing was in-line with previous test, but the pressure was slightly higher for the inlet capillary tubing.

The differential pressure across sand pack started to increase gradually as polymer was being injected and started to stabilize after pumping approx. 7.0-8.0 PV. A significant increase in the differential pressure across sand pack could be attributed to the thermo-thickening effect of the polymer. The test was stopped after pumping 18 PV as all polymer solution got injected.

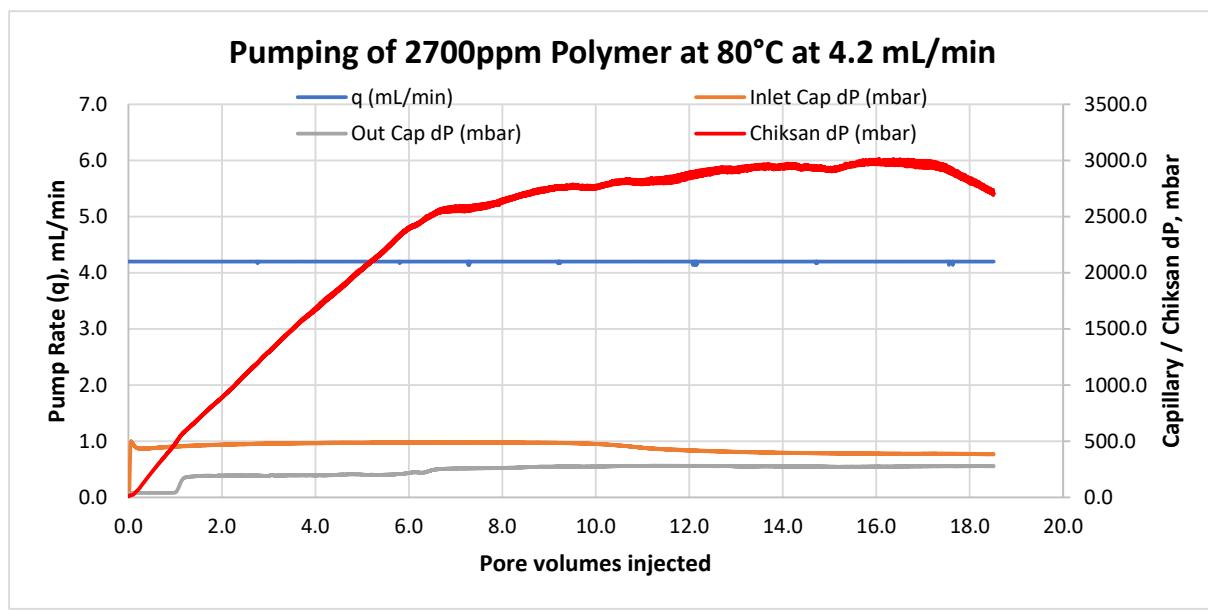


Fig. 12: Injection of 2700ppm A10 Polymer at 80°C

Fig. 13 shows the mobility reduction for both sand pack and capillary tubing. It is clearly observed that the thermo-thickening effect was observed with 2700ppm polymer concentration at 4.2 mL/min.

➤ RF-SandPack >>> RF-CT

It could also be noted that the mobility reduction for the outlet capillary (RF-CT Outlet) increased slightly after pumping 6.0 PV. This could be attributed to the fact that sand pack became saturated with the polymer solution and more polymer is being pumped out of the sand pack. However, the RF-CT Inlet was always higher than RF-CT Outlet and this might be attributed to the polymer degradation through sand pack or possible adsorption of the polymer on the sand face.

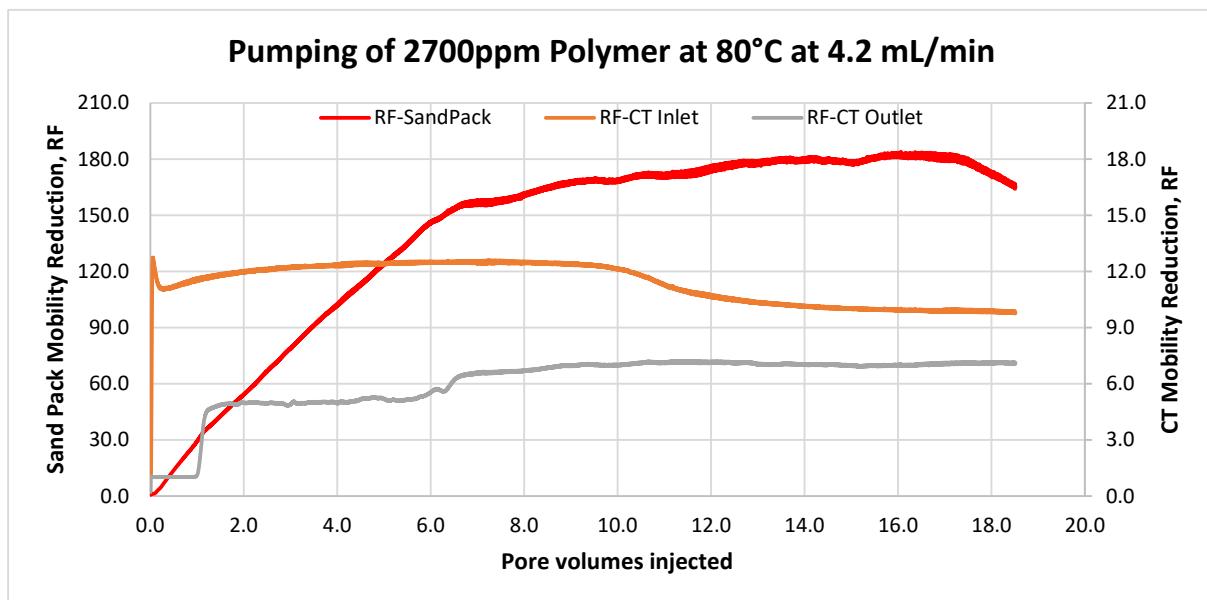


Fig. 13: Injection 2700ppm A10 Polymer at 80°C – Mobility Reduction

## 7. Conclusions

Following conclusions can be drawn based on the test results of the thermo-thickening polymer through sand pack column:

- The A10 polymer showed thermo-thickening behaviour at higher concentration.
  - No thermo-thickening was observed at 1000 ppm.
  - Thermo-thickening behaviour was observed at 2700 ppm. A mobility reduction of ~180 was observed from the testing.
- It was observed that the polymer degrades or adsorbed during pumping through sand-pack which may indicate significantly lower thermo-thickening at lower conc.
- The current set-up may not be suitable for the larger scale test due to chemical degradation through sand-pack.
  - It will be required to consider even higher conc. of the current polymer for the larger scale test set-up.
- Iron measured at the outlet was approximately 4-5 ppm at 4.2 mL/min. It is not known if the presence of iron can affect thermo-thickening behavior of the polymer. It was communicated to BASF and they will investigate the effect of iron on the polymer.

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