

Paper 2

Static and Dynamic Adsorption of Salt Tolerant Polymers

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Static and Dynamic Adsorption of Salt Tolerant Polymers

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Abstract:

A key parameter for application of polymers for water flood mobility control is the loss of polymer due to adsorption to the rock and more general retention during flow in porous medium. The paper discusses the adsorption and retention properties of sulfonated co-polymers. These polymers have the same backbone structure as partly hydrolyzed polyacrylamide (HPAM), except for modified hydrophobic groups and that the polymer is sulfonated to some extent. The group of polymers has been studied because of unusual salt tolerance compared to other synthetic polymers. There is a need for polymers for high temperature and high salinity reservoirs. This paper studies adsorption and retention of sulfonated polyacrylamide in high salt brine and varying hardness condition. The properties are compared to standard partly hydrolyzed polyacrylamide. Polymer adsorption was measured at static condition using both silica and kaolinite as the solid phase. The dynamic retention was measured in core floods using outcrop Berea cores. The results show a significant lowering of the static adsorption for these sulfonated polyacrylamide polymers respect to HPAM. The adsorption has been studied as a function of sulfonation degree at constant molecular weight and also as function of variation in molecular weight as constant sulfonation degree. Higher sulfonation degree leads to less adsorption, where the adsorption may decrease to 10 per cent of the adsorption level of HPAM. The retention measurements confirm the results from static measurements, and this group of polymers should be considered as alternative to HPAM in more saline brine mobility control EOR processes.

Introduction:

Unstable displacement during water flooding leading to poor sweep efficiency may be improved by adding polymer to the injection water. Both biopolymers and synthetic polymers have been used in classical polymer flooding. The main problem of using biopolymers has been the need of biocides to prevent biodegradation. The synthetic polymers have low tolerance to salinity and have mainly been used in fields with low salinity.

Partially hydrolyzed polyacrylamide (HPAM) is one commonly used synthetic polymer for water flood improvement, but these polymers may be chemically and thermally degraded at high temperatures and salinities. A copolymer of acrylamide and 2-acrylamido-2-methylpropane sulfonate, or sulfonated polyacrylamide (PAMS), has better stability at high temperatures and salinity as studied by Levitt and Pope (2008).

In addition to the increase in viscosity, adsorption of polymers onto the reservoir rock presents a limitation for the use of polymers. Adsorption of polyacrylamide (PAM) has been extensively studied by, (Pefferkorn et al. 1987), (Lee et al. 1991), but the copolymers have been less studied. Hollander and Somasundaran (1983) studied the adsorption of one sulfonated polyacrylamide polymer onto kaolinite at different pHs, ionic strengths and temperatures. Adsorption was nearly independent of pH and temperature in the ranges studied, while increasing the ionic strength led to higher adsorption.

Non-hydrolyzed polyacrylamide adsorption onto kaolinite was studied as a function of electrolyte concentration by (Pefferkorn et al. 1987), (Lee et al. 1991). With PAM the adsorption levels was found to be independent of salinity according to the study by (Lee et al. 1991), while it was found to decrease at very low salinities according to (Pefferkorn et al. 1987). Due to the charges in the polymer backbone in HPAM, the adsorption is found to be increasing with salinity for this polymer also studied by (Pefferkorn et al. 1987).

Adsorption onto silica and silicon carbide (SiC) was studied by (Lecourtier et al. 1990), (Page et al. 1993). Since the surface of silica minerals is negatively charged for pH values over 2, the adsorption was reported to be an order of magnitude lower compared to the other surfaces mentioned. Typical values are 0.1-0.2 mg/g for both SiC and silica as mentioned by (Lecourtier et al. 1990). The adsorption of PAM decreases for temperatures up to 50°C and then remains constant, while HPAM is constant for temperatures up to 50°C, and then decreases for adsorption onto silica.

Dynamic adsorption/retention in a porous medium is a more complex process than static adsorption onto a single type of mineral surface. In addition to adsorption onto the surface of the rock, polymer may be retained in the pore structure by other means, for example in dead-end pores or in pore throats.

Dynamic adsorption has also been studied for HPAM and PAMS with one specific sulfonation degree. Past experiments by Szabo (1975), (Lakatos et al. 1979), Szabo (1979), show that HPAM was retained in the cores more than the PAMS copolymer. By increasing the molecular weight of the polymer, less polymer was retained. This has been explained by inaccessible pore volume; the larger polymers are unable to enter the smaller pores of the rock, Lakatos and Lakatos-Szabo (1980).

So far there has not been a systematic study of adsorption and retention as a function of sulfonation degree and molecular weight of sulfonated copolymers. In this study the focus is on adsorption and retention of sulfonated polyacrylamide polymers with different sulfonation degrees and molecular weight.

Materials and experiments:

Materials:

Polymers: Five different polymers were examined; the characteristics of these polymers are given in Table I. All the polymers were supplied by SNF FLOERGER.

Adsorbents: Two different powdered mineral samples were obtained; kaolinite and silica. The specific surface area of the kaolinite sample was determined using nitrogen adsorption. The silica sample specific surface area was $3.65 \text{ m}^2\text{g}^{-1}$, given by the supplier, while the kaolinite had approximately $10.6 \text{ m}^2\text{g}^{-1}$.

In addition to the powdered minerals, dynamic adsorption was studied by injecting polymer solution into Berea sandstone cores. The cores used were around 10 cm long and 3.7cm in diameter. The permeability was around 500-700 mD, and the porosity around 20%.

Bulk solutions: Two different bulk solutions were used, synthetic sea water (SSW), and 5 wt. % NaCl solution. These two solutions have similar ionic strength, but the seawater also contains divalent cations. To see the effect of different charges and different solvent nature on the adsorbed amount of polymer some other solutions as shown in Table II were chosen.

Measurements:

The polymers were prepared in SSW and 5 wt. % NaCl by using a mechanical stirrer. 1 g of polymer powder was dissolved in 200 g of solvent, yielding a 5000 ppm solution. The initial solution was diluted to appropriate concentrations with a magnetic stirrer.

Concentration measurements: To measure the concentration of polymer after adsorption a starch-triiodide method was used. This method gives a linear response in a range of 0-10 ppm suggested by Scoggins and Miller (1979). The samples had a higher concentration than this, so they needed to be diluted first. Around 30 ml of the diluted sample was used. First of all 5 ml of a buffer solution (pH=3.5) is added. Secondly 1ml of saturated bromine water is added to the sample. After 15 minutes 5 ml of 1 wt. % sodium formate solution is added. At the end after 5 minutes 5 ml of a

solution containing starch and cadmium iodide is added. The iodide is then reduced to iodine by a reaction product of bromine and the polymer. Starch forms a colour complex with iodine and the adsorbance of the sample is measured using a UV-VIS spectrometer.

The adsorbance at peak wavelength, at around 568 nm, is used. It is necessary to have standard curve to measure the polymer concentration. The standard curve is made by using the same method as described above for known concentrations of polymer solution. The standard curve gives a linear relationship between polymer concentration and absorbance of the solution.

For the dynamic adsorption the same method was used to determine polymer concentration. In addition to the polymer, a tracer (LiNO_3) was used. To measure the lithium concentration inductively coupled plasma atomic emission spectrometry (ICP-AES) was used. The varying polymer concentrations were found to affect the measurement, higher polymer concentrations led to a lower measured lithium concentration. This is probably because the changes in viscosity and/or surface properties affect the sample introduction system so that less sample is introduced with polymer present. To solve this, the effluent samples were diluted 100 times with a 1 wt. % HNO_3 solution, and an internal standard (1 ppm Yttrium) was used to correct the signal.

Static Adsorption

As shown in Fig. 1 and Fig. 2, and also mentioned by (Argillier et al. 1996), the solid-liquid ratio influences how much polymer is adsorbed. By increasing the S/L ratio flocculation reduces the surface area available for polymer to be adsorbed. However, if the S/L ratio is too low, it is difficult to measure the adsorption amount accurately because of the small difference in initial and final concentration. An S/L ratio of 0,005 was chosen to get a compromise between accurate measurements and representative values for adsorption.

The samples were prepared by weighing around 0.05 g of kaolinite into a 15 ml sample glass. Then varying amount of SSW or 5 wt. % NaCl and polymer solution was added to get a concentration range between 20-300 ppm. Then the kaolinite/polymer suspensions were agitated with a mechanical tumbler for 24 hours at room temperature, this has been shown to be more than enough time to reach equilibrium as suggested and studied by (Hollander et al. 1981). After this, the solid and liquid were separated by centrifugation. In the next step the concentration of the polymer was determined using the method described earlier.

In the adsorption amount calculations there are several sources of uncertainty, both in sample preparation and concentration measurement. The final uncertainty in adsorbed amount is calculated using propagation of uncertainty. Since the relative difference in initial and equilibrium concentration is smaller for large concentrations the uncertainty is higher for larger concentrations Fig. 3, Fig. 4.

Dynamic Adsorption

For the dynamic adsorption the cores were mounted in a core holder and saturated with the appropriate solution (SSW or 5 wt. % NaCl) by using a vacuum pump. Then 2 pore volumes (PV) of the polymer and tracer solution was injected, followed by 3 pore volumes of the same solution as the core was saturated with. Samples were collected in 4 ml intervals at the other end, and the polymer and tracer concentrations were measured. Adsorbed amounts were calculated by subtracting the total amount produced from the total amount injected.

Results and discussion

As mentioned in the introduction, surface charge is one important factor that can affect adsorption. In this research two different mineral types are studied. Kaolinite, a type of clay with negative overall charge and positive charge at the edges, was studied first and silica, which has only negative surface charges. Adsorption onto silica was found to be too small to reliably quantify with the method used for determining polymer concentration Fig. 3. Since both the surface and polymer is negatively charged they repulse each other, and adsorption is negligible. Similar results are reported by (Lecourtier et al. 1990), (Page et al. 1993).

Changing the solid phase from silica to kaolinite gave higher adsorption. In addition the particles coagulated in some cases. By varying the solid to liquid ratio and plotting the adsorbed amount, the trend is less adsorption with increasing S/L ratio. This is explained by coagulation of the particles reducing the surface available for adsorption. This is seen clearly in Fig. 1 in SSW and Fig. 2 in 5 wt. % NaCl solution. The effect of flocculation is less pronounced in the 5 wt. % NaCl solution than the SSW solution. Based on the flocculation power for monovalent and divalent ions ($\text{Na}^+ = 1$, $\text{K}^+ = 1.8$, $\text{Mg}^{2+} = 27$, and $\text{Ca}^{2+} = 45$), as reported by (Lu et al. 2002), this is to be expected. Some flocculation was also observed in the 5 wt. % NaCl solutions at polymer concentrations higher than 250 ppm.

In Fig. 4 the adsorption isotherm of a polymer with 8 million Dalton (mDa) molecular weight and sulfonation degree of 13 (mole %) is seen. The adsorbed amount is increasing with concentration, and afterwards reaches a plateau. This trend was observed for all the different sulfonated polyacrylamide polymers. The adsorption levels for both sulfonated polyacrylamide polymers and HPAM is reported in Fig. 5. By increasing the amount of sulfonation degree, the adsorbed amount decreases, but all the sulfonated polyacrylamide polymers have less adsorption than HPAM. A study of the adsorption of another PAMS with 3 (mole %) sulfonation degree onto hematite was done by Moudgil and Somasundaran (1983). and the results show a higher adsorption per square meter than the adsorption onto kaolinite in our study.

In Fig. 6 the effect of molecular weight on static adsorption is seen. The adsorption for sulfonated polyacrylamide polymers increase with increasing molecular weight. This is in accordance with theory, since a polymer with a higher molecular weight would form a thicker layer of polymer when adsorbed on a surface (Hlady et al. 1982).

In the dynamic adsorption experiments a slug of 2 PV polymer solution flows through a cylindrical Berea sandstone core, followed by a 3 PV post flush of SSW or 5 wt. % NaCl solutions. The concentration is measured from samples collected at the outlet of the core. Polymers may be retained in the core by other means than adsorption, for example trapping in small pore throats. Additionally there is a constant shearing of the polymers due to flow, which may affect the adsorption process.

The effect of molecular weight on retention was also studied. As shown in Fig. 7, the tracer is produced later than the polymer for the high molecular weight sample, indicating that some of the pore volume is accessible to the tracer, but not to the polymer. This effect is also seen for the sample with the lowest molecular weight, e.g. AN125VLM Fig. 8, but not to the same degree as before. This can explain why the low molecular weight polymer is more retained than the one with high molecular weight Fig. 9. A similar trend also was found by Lakatos and Lakatos-Szabo (1980).

In the core flooding Fig. 10, by increasing the sulfonation degree, fewer polymer molecules are retained in the core; this is the same trend as found in the static adsorption experiments. The retention and adsorption amounts are very low for AN125VLM, AN125, AN125VHM and AN132, and HPAM still has the highest retention.

By increasing the NaCl concentration from 1 wt. % to 5 wt. %, the retention increases Table III. The reason for this is additional coiling up of the polymer molecules, leading to increase the density of the adsorbed layer as also studied by Hollander and Somasundaran (1983). To study the effect of divalent cations two solutions with the same ionic strengths were used; 5 wt. % NaCl and SSW. Results show that the retention in SSW solution is more than retention for 5 wt% NaCl solution, the reason for this is the increased charge screening of Ca^{2+} and Mg^{2+} ions. Another reason is that the divalent cations may be more effective than monovalent ions in acting as a binding ion between the surface and the negative groups in the polymer as studied by (Lu et al. 2002).

For practical use of polymers in a polymer flooding process, adsorption and retention are not only important; several other parameters should be taken into the consideration. As results shown sulfonated polyacrylamide polymers have less adsorption and retention than HPAM.

Another important parameter, which is the main reason for injecting polymer into the water, is for increasing the viscosity of water. As studied by (Dong et al. 2008) HPAM was used in practical polymer flooding in Daqing oil field. HPAM has been studied by several other authors e.g. Zaitoun and Potie (1983), and reported to be limited to reservoirs with salinity below 50000 ppm. Viscosity studies of PAMS and HPAM shows that the PAMS have general higher viscosity than HPAM at high salinity (our unpubl. results).

Conclusions



In this research the adsorption and retention amount for sulfonated polyacrylamide polymers for a range of sulfonation degree and a range of different molecular weight were compared to hydrolyzed polyacrylamide (HPAM), for two different salinities, one was around sea water salinity and the other was 5 wt. % NaCl.

The main conclusions from this research are:

1. The results show that the adsorption and retention for these sulfonated polyacrylamide polymers are reduced with increasing sulfonation degree, however all sulfonated polyacrylamide polymers have considerably lower adsorption and retention than HPAM.
2. The static adsorption results of these sulfonated polyacrylamide polymers, with the same sulfonation degree e.g. 25 mole % and different molecular weights, show that for the sample with the highest molecular weight the adsorption is higher.
3. The retention of these sulfonated polyacrylamide polymers, with the same sulfonation degree e.g. 25 mole % and different molecular weights, show that for the sample with the highest molecular weight the retention is lower.
4. For the same ionic strength, the presence of divalent cations leads to increased adsorption and retention of these polymers.
5. For these sulfonated polyacrylamide polymers, other results have shown only minor reduction in viscosity by increase in sulfonation degree, but there is a substantial decrease in retention and adsorption. The results show that high sulfonation degree may be favourable and should be further investigated for polymer flooding in moderate high salinity reservoirs.

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Table I. Polymers characteristics

Polymer	MW ^a (MDa ^b)	SD ^c (mole %)
AN105	6	5
AN113	8	13
AN125VLM	2	25
AN125	8	25
AN125VHM	12	25
AN132	8	32
HPAM	8	0

^aMolecular weight (given by supplier); ^bMillion Dalton; ^cSulfonation degree

Table II. Synthetic seawater composition – grams of salts in 1 kg solvent

Salt	Amount in g/kg solvent
NaCl	25.0
MgCl ₂ ·6H ₂ O	11.1
Na ₂ SO ₄	4.1
CaCl ₂ ·2H ₂ O	1.7
KCl	0.7
NaHCO ₃	0.2

Table III. The effect of ionic strength on retention, Berea Sandstone, 2 PV followed by 3 PV post flush, at 20°C.

Polymers	Retention ($\mu\text{g/g}$)						
	AN105	AN113	AN125VLM	AN125	AN125VHM	AN132	HPAM
1 wt. % NaCl							52.49
5 wt. % NaCl	93.43	29.48	32.45	7.36	1.29	6.76	108.92
SSW	111.46	58.64	38.96	-----	3.23	16.48	124.20

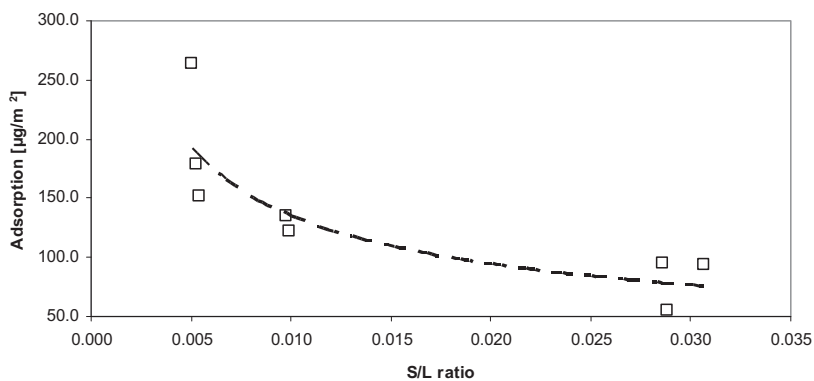


Fig 1: Adsorption of AN125 on kaolinite in SSW, 20°C.

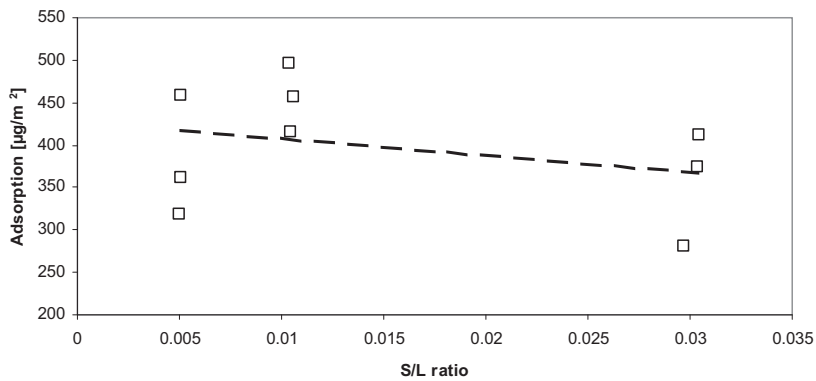


Fig 2: Adsorption of AN113 in 5 wt. % NaCl, 20°C.

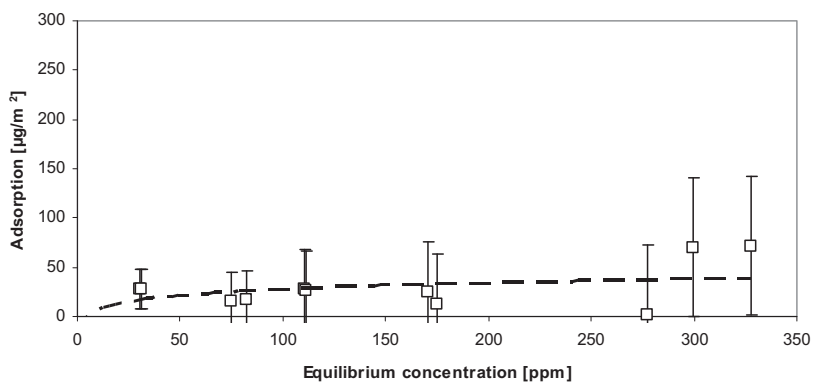


Fig 3: Example of adsorption isotherm on silica for the AN105 polymer, SSW, S/L 0.1, 20°C.

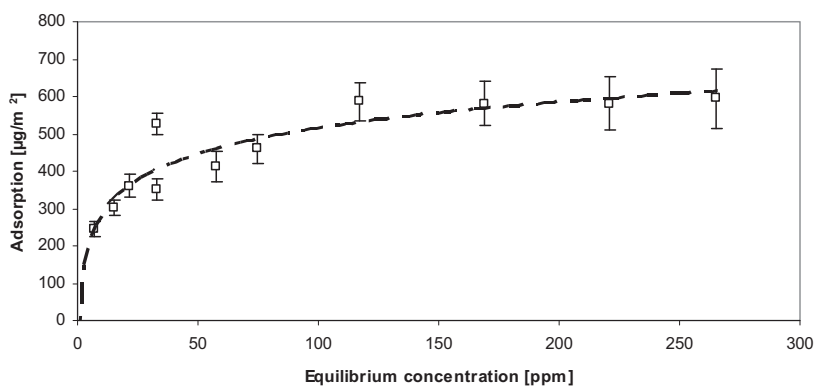


Fig 4: Example of adsorption isotherm on kaolinite for AN113, 5 wt. % NaCl, with uncertainty estimates, S/L 0.005, 20°C.

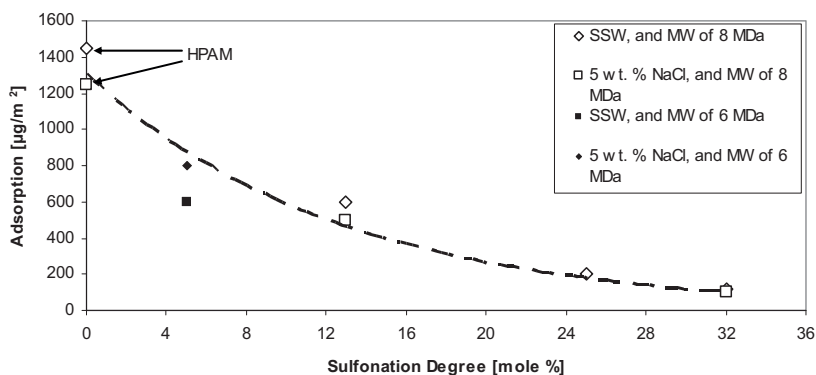


Fig 5: Adsorption of sulfonated polyacrylamide polymers, and HPAM on kaolinite as a function of sulfonation degree, S/L 0.005, 20°C.

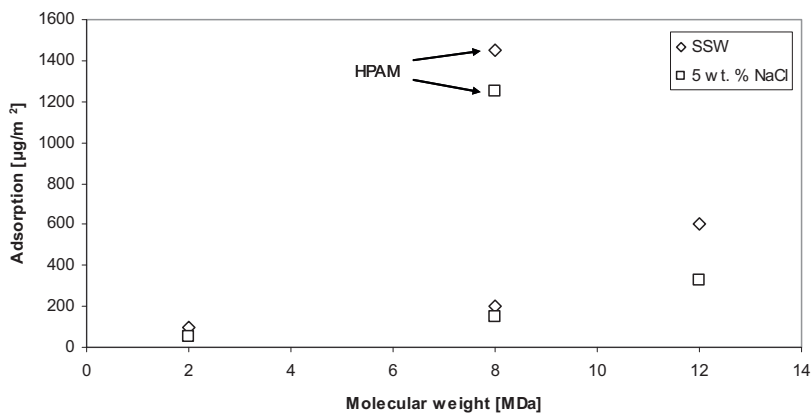


Fig 6: Adsorption of sulfonated polyacrylamide polymers with the same sulfonation degree (25 mole %), and HPAM as a function of molecular weight, S/L 0.005, 20°C.

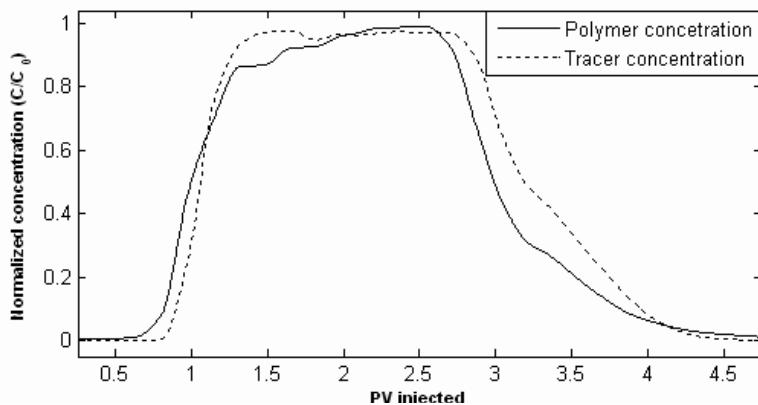


Fig 7: Example of effluent production from injection 2 PV of AN125VHM in SSW, 1000 ppm, retention on Berea at 20°C.

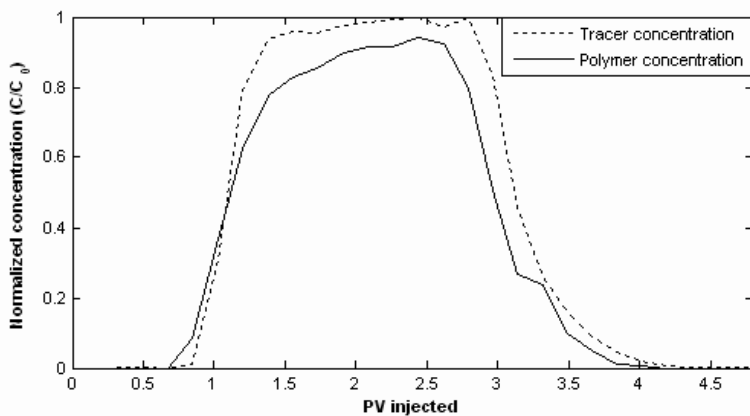


Fig 8: Example of effluent production from injection of 2 PV of AN125VLM in SSW, 1000 ppm, retention on Berea at 20°C

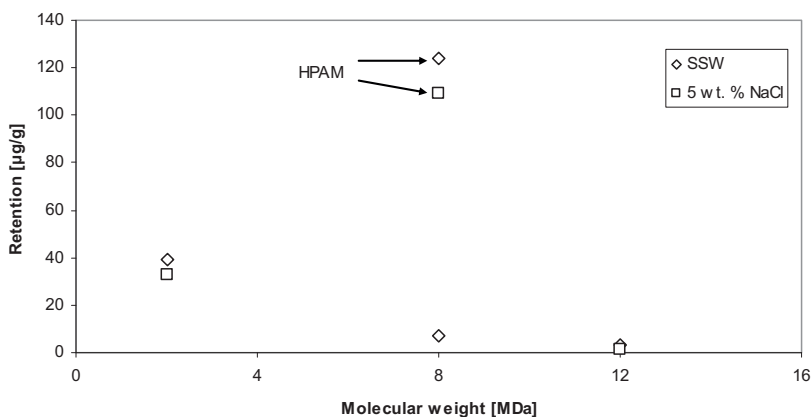


Fig 9: Retention of sulfonated polyacrylamide polymers with the same sulfonation degree (25 mole %), and HPAM as a function of molecular weight, on Berea, 20°C.

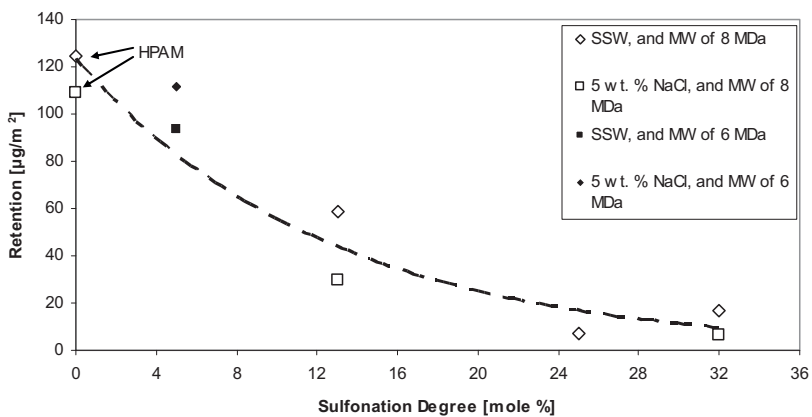


Fig 10: Retention of sulfonated polyacrylamide polymers, and HPAM as a function of sulfonation degree, on Berea, 20°C.

