PHYSICAL PROPERTIES OF ASSOCIATIVE POLYMER SOLUTIONS

A THESIS SUBMITTED TO THE DEPARTMENT OF ENERGY RESOURCES ENGINEERING OF STANFORD UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as partial fulfillment of the degree of Master of Science in Petroleum Engineering.

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Abstract

Approximately half of oil production nowadays is a result of waterflood and a major concern of this process is mobility control of the injected phase. With the unfavorable mobility ratio, chanelling through permeable zones and the fingering effect can occur that leads to an early water breakthrough and inefficient flooding. By adding polymer to the injection water and, consequently, increasing the water viscosity, the displacement becomes more stable and a greater flood efficiency can be achieved. A large number of polymer field applications were carried out in recent years with varying degrees of success.

During this period, new kinds of polymers have been developed to improve displacement properties. Associative water-soluble polymer is a new type of polymer that is recently introduced to oil field application. The main attractions of these polymers are their significant viscosity enhancement ability compared with the conventional polymers and their potential salinity-tolerance that would be more practical in the real application.

This research investigates the physical properties of associative polymer solutions using laboratory work. The experiments were conducted in a sand-packed column to measure 2 main properties: permeability reduction and inaccessible pore volume.

Permeability reduction is the ratio of water permeability upon the polymer solution permeability. For each polymer, permeability reduction is observed and it increases with increasing molecular weight and concentration. In the case of conventional polymer, permeability reduction is more sensitive to the polymer concentration especially at high concentration.

Inaccessible pore volume is observed in each kind of polymer development. The effluent concentration profiles of the polymer and the salt used as the tracer from the experiment indicate that the IPVs for both associative and conventional polymers are approximately 30%. The superposition method is used to construct the model to interpret the experimental data more accurately.

The effect of adding salinity into the polymer solutions is also observed. Increasing salinity leads to reduced viscosity of the solutions in both associative and conventional polymers. The permeability reduction and the inaccessible pore volume of the polymer are also decreased.

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Contents

Α	bstra	ıct		v
A	cknov	wledgr	nent	vii
Ta	able (of Con	tents	viii
Li	st of	Table	s	x
\mathbf{Li}	st of	Figur	es	xi
1	Intr	oduct	ion	1
	1.1	Litera	ture Review	2
		1.1.1	Polymer Flooding	2
		1.1.2	Polymer Flooding Process	3
		1.1.3	EOR Polymer	5
		1.1.4	Rheological Behavior of Polymer Solutions	8
	1.2	Assoc	iative Polymer Flooding in Micromodel	10
2	Exp	oerime	ntal Method	14
	2.1	Polym	ner Solution Preparation	14
	2.2	Viscos	sity Measurement of the Polymer Solutions	14
	2.3	Interfa	acial Tension Measurement	19
		2.3.1	Water and Decane	22
		2.3.2	Polymer solutions and Decane	23
		2.3.3	Polymer solutions and Crude Oil	23
	2.4	Core 1	Properties	24

	2.5 Experimental Set-up	26
3	Permeability Reduction	28
4	Inaccessible Pore Volume	31
5	Conclusion and Recommendations	43
	5.1 Conclusion \ldots	43
	5.2 Recommendations	44

List of Tables

2.1	Technical data of polymer solutions.	15
2.2	Power law coefficient and power law exponent of each polymer from the	
	experiment	18
2.3	Measured interfacial tension between water and decane. \ldots	23
2.4	Measured interfacial tension between polymer solutions and decane. $\ . \ . \ .$	23
2.5	Measured interfacial tension between polymer solutions and crude oil. $\ . \ .$	24
2.6	Core properties	26
4.1	IPV results from the experiment	35
4.2	${\cal N}_{pe}$ from the least norm minimization of the experimental and predicted data.	40
4.3	The range of IPV from the model estimation	40
4.4	The range of IPV from the model estimation as a function of salt concentration.	41

List of Figures

1.1	Effect of mobility ratio on the areal sweep efficiency. (Littmann, 1988)	2
1.2	Fractional flow curves for displacement of oil by water and polymer solution	
	(Littmann, 1988)	4
1.3	Mobility ratio for the displacement of oil by water and polymer solution	
	(Littmann, 1988)	4
1.4	Polymer flooding process (Lindley, 2001)	5
1.5	Chemical structure of HPAM (Littmann, 1988)	6
1.6	Chemical structure of Xanthan (Littmann, 1988)	7
1.7	Three-dimensional network structure of associative polymer in aqueous solu-	
	tion (Caram et al., 2006)	8
1.8	Relationship between shear rate and viscosity of polymer solution (Lake, 1989).	9
1.9	Scanning electron microscope image of micromodel pore space (Aktas et al.,	
	2008)	11
1.10	Micromodel images of 1250 ppm associative polymer flood (Buchgraber, 2008).	12
1.11	Micromodel images of 1250 ppm conventional polymer flood (Buchgraber,	
	2008)	13
2.1	DV-II-Pro+ Brookfield © viscometer and spindle (Buchgraber, 2008)	16
2.2	Relationship between the viscosity and the shear rate of SuperPusher B192.	16
2.3	Relationship between the viscosity and the shear rate of SuperPusher D118.	17
2.4	Relationship between the viscosity and the shear rate of SuperPusher S255.	17
2.5	Relationship between the viscosity and the shear rate of FLOPAAM 3630s.	19
2.6	The effect of salinity on the viscosity in associative polymer	20
2.7	The effect of salinity on the viscosity in conventional polymer	20
2.8	The University of Texas spinning drop interfacial tensiometer (UTSDIT).	21

2.9	Sands and core holder used in the experiment.	25
2.10	Cumulative probability curve of sand grain diameter	25
2.11	LDC/Milton Roy Constametric IIIG metering pump	27
3.1	Permeability reduction for different polymer solutions.	30
3.2	The effect of salinity on permeability reduction	30
4.1	UV Spectrophotometer.	32
4.2	Scanning Result from UV Spectrophotomete.r	33
4.3	Effluent profiles from the experiment.	34
4.4	Schematic of superposition method.	37
4.5	The experimental data and the superposition model fitting of SuperPusher	
	B192	38
4.6	The experimental data and the superposition model fitting of SuperPusher	
	S255	39
4.7	The experimental data and the superposition model fitting of SuperPusher	
	D118	39
4.8	The experimental data and the superposition model fitting of FLOPAAM	
	3630s	40
4.9	The experimental data and the superposition model fitting of SuperPusher	
	D118 (2 % NaCl added)	42
4.10	The experimental data and the superposition model fitting of SuperPusher	
	D118 (10 % NaCl added)	42

Section 1

Introduction

In general, the production period of the petroleum reservoir is divided into various stages. The primary stage is oil and gas production from the energy contained in the reservoir itself. The secondary stage of production is usually when the reservoir pressure is maintained by injecting water or gas into the producing formation. After secondary recovery, approximately 30 - 35% of the oil originally in place has been produced, while almost 70% of the oil is left underground. In recent decades, several techniques have been developed in order to produce this unrecoverable potential and these techniques are grouped into enhanced oil recovery (EOR) methods.

EOR is oil recovery by the injection of materials not normally present in the reservoir (Lake, 1989). Polymer flooding is considered to be one of the EOR techniques. It was introduced to oil field application with the purpose of achieving mobility control in waterflood. It is widely known that approximately half of oil production nowadays occurs by waterflood and the main concern in waterflood process is mobility ratio, the ratio of water mobility to oil mobility. In the favorable case, mobility ratio is less than 1, sweep efficiency from waterflood is much greater than the case that is unfavorable. During unstable floods, early water breakthrough generally occurs. The purpose of adding polymer into the water is to reduce the mobility ratio by increasing water viscosity and also reducing the formation permeability.

The objective of this research is to investigate the physical properties of associative polymer solutions and to contrast these properties with conventional polymers. Associative polymers were introduced in oil field applications to eliminate some limitations of the existing conventional polymers. The viscosity increase occurs from the association of the hydrophobic molecules that forms a 3-dimensional network structure when it dissolves in water. The main attractions of these polymers are their significant viscosity enhancement ability compared with the conventional polymers and their ability to maintain viscosity under saline brine conditions.

Laboratory work is performed in order to determine the physical properties of the associative polymer solutions when they flow through porous media, such as the presence of permeability reduction and plugging of the formation. Understanding these properties is tremendously beneficial in explaining the mechanisms of polymer flooding, designing an EOR process, and understanding the applicability of associative polymers.

1.1 Literature Review

1.1.1 Polymer Flooding

Polymer flooding results from adding a polymer to the injected water in a waterflood to decrease its mobility (Lake, 1989). By adding a polymer to the water, the viscosity of that polymer solution increases which leads to significant decrease in the mobility ratio of the waterflood.

The mobility ratio is the ratio of the displacing fluid mobility to the displaced fluid mobility. It is the primary factor that affects the areal sweep efficiency of a given well spacing and pattern of waterflood. It is defined for water floods as:

$$M = \frac{k_{rw}\mu_o}{k_{ro}\mu_w} \tag{1.1}$$



Figure 1.1: Effect of mobility ratio on the areal sweep efficiency. (Littmann, 1988)

1.1. LITERATURE REVIEW

Figure 1.1 clearly illustrates the enhancement in recovery related to the decreasing mobility ratio. The areal sweep efficiency is greater whenever the mobility ratio is low. Furthermore, by reducing the mobility ratio, the breakthrough time of the water increases, and the oil can be recovered at a lower water cut, with lower lifting costs.

In the displacement process of flooding, the mobility ratio is not a constant value. It varies with the saturation of the flowing phase. Assuming that the oil and the water are flowing simultaneously through a porous medium, the fractional flow of crude oil, f_o , and water, f_w , is;

$$f_o = \frac{1}{1 + \frac{\mu_o k_{rw}}{\mu_w k_{ro}}} \tag{1.2}$$

$$f_w = \frac{1}{1 + \frac{\mu_w k_{ro}}{\mu_o k_{rw}}} \tag{1.3}$$

Figure 1.2 depicts the fractional flow curves for the displacement of oil with a viscosity of 15 mPas by water of 1 mPas and a polymer solution of 15 mPas (Littmann, 1988). The saturation at the front of the polymer flood, S_{pf} , and the water flood, S_{wf} , as well as the saturation at the breakthrough, S_{btp} and S_{btw} , are also presented by constructing the tangent line to the fractional flow originate from the irreducible water saturation (Pope, 1980). In the polymer flood case, note that the saturations at both the flood front and at the breakthrough are significantly greater than those in the waterflood case. This increasing in flood front saturation indicates a greater performance of the polymer flood as compared to the water flood.

The mobility ratios corresponding to Figure 1.2 are observed in Figure 1.3. Obviously, the mobility ratios in the water flood case are greater than those in the polymer flood case at the same saturation.

1.1.2 Polymer Flooding Process

Figure 1.4 demonstrates a typical polymer flood schematic (Lake, 1989). The polymer flood process usually starts with a pre-flush of low-salinity brine, followed by the flushed oil bank and the polymer solution. Fresh water or a lower concentration of polymer solution is usually used as a buffer to protect the polymer solution from backside contamination. These precautions are taken because of the significant sensitivity of conventional polymers



Figure 1.2: Fractional flow curves for displacement of oil by water and polymer solution (Littmann, 1988)



Figure 1.3: Mobility ratio for the displacement of oil by water and polymer solution (Littmann, 1988)

1.1. LITERATURE REVIEW

to brine salinity and chemistry. The final step is injecting the chasing or driving water to push the polymer solution into the reservoir.



Figure 1.4: Polymer flooding process (Lindley, 2001)

1.1.3 EOR Polymer

The two most general polymer types used in the EOR process are a synthetic material, polyacrylamide, in its partially hydrolysed form (HPAM) and the biopolymer, xanthan (Sorbie, 1991). These kinds of polymers are extensively used in several industries as the thickening agents or as the parts of the manufacturing process.

Polyacrylamide

The polyacrylamide used in polymer flood application is in its hydrolysed form (HPAM). HPAM is a straight-chain polymer that has the acrylamide molecule as the monomer as shown in Figure 5. This partial hydrolysis can occur in some of these monomers. Typical degrees of hydrolysis are 25% - 35% that are chosen to optimize the specific properties of the polymer solutions. If the degree of hydrolysis is too small, the polymer will not be water soluble. If it is too large, its properties are overly sensitive to salinity and hardness (Shupe, 1981)

The typical molecular weight of HPAM used in polymer flood is within the range of $2 - 20 \times 10^6$ g/mole. The viscosity-increasing feature is derived the repulsion between polymer molecules and between the segments of the same molecule. This repulsion causes the molecule to lengthen and snag on other molecule. This increase in viscosity causes the lower mobility of the polymer solution.



Figure 1.5: Chemical structure of HPAM (Littmann, 1988)

HPAM is very sensitive to the brine salinity and hardness. The viscosity enhancement property is significantly reduced when it dissolves in high salinity or hardness brine. This characteristic represents the disadvantage of using this kind of polymer in the oil and gas reservoir, which generally exhibits some degree of salinity.

Xanthans

Xanthan, a polysaccharide, is produced by bacteria during the fermentation of glucose. In order to protect the bacteria from dehydration, they produce the polymer. The result of this process is the fact that this polymer is very sensitive to bacterial attack on surface and after it is injected into the reservoir. The main advantage of this polymer is that it is less sensitive to brine salinity and hardness in comparison to HPAM.

The molecular weight of Xanthan is typically around 2×10^6 g/mole.

Because of these limitations in the existing polymers for polymer flood, a new kind of polymer with improved properties is required in order to apply polymer flooding to unconventional reservoir conditions such as viscous oil.



Figure 1.6: Chemical structure of Xanthan (Littmann, 1988)

Associative Polymers

The associative water-soluble polymer is a relatively new class of polymers, which has recently been introduced to oil field applications. Essentially, these polymers consist of a hydrophilic long-chain backbone, with a small number of hydrophobic groups localized either randomly along the chain or at the chain ends (Lara-Ceniceros et al., 2007). When these polymers are dissolved in water, hydrophobic groups aggregate to minimize their water exposure. In aqueous solutions at a basic pH, hydrophobic groups form intramolecular and intermolecular associations that give rise to a three-dimensional network (Caram et al., 2006). This behavior significantly increases the viscosity of the polymer solution. The three-dimensional network structure of associative polymers is illustrated in Figure 1.7.

Another important fact is that the functional groups on this polymer is less sensitive to brine salinity compared to a conventional polymer solution, as compared to polyacrylamide, whose viscosity dramatically decreases with increasing salinity.



Figure 1.7: Three-dimensional network structure of associative polymer in aqueous solution (Caram et al., 2006)

1.1.4 Rheological Behavior of Polymer Solutions

Viscosity

The viscosity of a fluid may initially be defined as its resistance to shear (Sorbie, 1991). When a fluid is placed between two parallel surfaces moving in the same direction with different velocity, the velocity gradient in the vertical direction of the fluid is found to be linear for many fluid types. This velocity gradient is called the shear rate and is defined as,

$$\dot{\gamma} = \frac{dV}{dr} \tag{1.4}$$

The shear stress that causes the movement of the two surfaces is given by,

$$\tau = \frac{F(\text{force})}{A(\text{area})} \tag{1.5}$$

The viscosity (μ) is then defined as the ratio of the shear stress to the shear rate. The relationship between these parameters is described as,

$$\tau = -\mu \frac{dV}{dr} = \mu \dot{\gamma} \tag{1.6}$$

1.1. LITERATURE REVIEW

Equation 1.6 is known as a material function (Bird et al., 1987) and the fluids that exhibit this behavior are known as the non-Newtonian fluid.

The fundamental unit of viscosity measurement is the poise. A material requiring a shear stress of one dyne per square centimetre to produce a shear rate of one reciprocal second has a viscosity of 1 poise, or 100 centipoises. The types of fluids can be classified into 2 groups using this characteristic, the one that has constant viscosity over the range of shear rate or the Newtonian fluid and the one whose viscosity does not remain constant at different rates of deformation or the non-Newtonian fluid. Many experiments have demonstrated that the viscosity of the polymer solution varies with the shear rate, and the polymer solution is classified as the non-Newtonian fluid.

Viscosity

Figure 1.8 shows the plot between the polymer solution viscosity and the shear rate at fixed salinity (Lake, 1989). At low shear rates, the solution acts like a Newtonian fluid whose viscosity does not change with the changing shear rate. At greater shear rates, however, the viscosity of the solution decreases with the increasing shear rate and the solution shows non-Newtonian behavior.



Figure 1.8: Relationship between shear rate and viscosity of polymer solution (Lake, 1989).

Considering flows from the wellbore through the formation as the radial flows, the flow rates at the injections and production wells are relatively high and decline with increasing distance from the well (Shalaby et al., 1991). Far from the well, the polymer solution propagates at very low shear rate; therefore, it is possible to achieve favorable mobility ratios in the waterflood applications.

The relationship between the polymer solution viscosity and the shear rate is described by a power-law model (Lake, 1989).

$$\mu = K_{pl}(\dot{\gamma})^{n_{pl}-1} \tag{1.7}$$

where K_{pl} and n_{pl} are the power-law coefficient and exponent, respectively and n_{pl} is less than 1 in the case of non-Newtonian fluid. K_{pl} and n_{pl} depend on the molecular weight of the polymer and the polymer concentration.

Experiments are conducted, in this research, to determine the physical properties of the associative polymer solutions not only under standard conditions, but also under flowing conditions through porous media.

1.2 Associative Polymer Flooding in Micromodel

The pore-level immiscible displacement of the conventional and associative polymer solutions with crude oil was observed via micromodel flooding in the experiments done by Aktas et al. (2008). The micromodel contains an etched pattern that represents the pore space of homogenous Berea sandstone and this flow pattern can be observed with a microscope as shown in Figure 1.9. In the experiment, the micromodel was first saturated with brine and then crude oil with medium viscosity of 200 cp was injected to establish the initial condition. The displacements were done with 3 displacing fluids, reservoir brine, conventional polymer solution, and associative polymer solution. The polymer solutions used were at the same concentration of 0.5 wt%. The experimental results indicated that, at the low concentration, the associative polymer solution significantly improves the waterflooding recovery of viscous oil with more stable displacement and better sweep efficiency compared with the conventional polymer flooding at the same concentration.

In later micromodel experiment by Buchgraber (2008), studied the fingering behavior, the sweep efficiency, and frontal stability of associative polymer displacement with different concentration were compared with the results of the conventional polymer case. From the



Figure 1.9: Scanning electron microscope image of micromodel pore space (Aktas et al., 2008).

experiment, the increasing concentration of the polymer solutions led to increasing sweep efficiency and frontal stability of the flooding in both polymer solutions. The experiment also demonstrated that there was an upper limit for the polymer solution concentration. With higher concentration, pore plugging could be observed and led to reduced recovery.

The finger analysis from this study presented that the number of fingers decreased with increasing concentration during polymer flooding. The conventional polymer flood fingers were reported to be smaller and closer to each other while the associative polymer flood fingers seemed to be thicker and merge together at the later stage of the flood which indicated more stable displacement.

Figures 1.10 and 1.11 are the micromodel images that presents the flood front and finger behavior in associative and conventional polymers, respectively.

The study was extended further to observe the fingering behavior of the combination flooding of conventional brine flood and associative polymer. The associative polymer solution was injected after the breakthrough of the brine to the opposite side of the micromodel. By injecting associative polymer solution, the developed fingers from the brine flooding could be thickened and the flood front could be smoothened. Such studies have shown that associative polymer is a promising tool for improving waterflooding recovery especially in medium to high viscosity oil.



Figure 1.10: Micromodel images of 1250 ppm associative polymer flood (Buchgraber, 2008).



Figure 1.11: Micromodel images of 1250 ppm conventional polymer flood (Buchgraber, 2008).

Section 2

Experimental Method

2.1 Polymer Solution Preparation

The polymer solutions used in each experiment were prepared from both associative and conventional polymers. Three types of associative polymers used were SuperPusher S255, SuperPusher D118, and SuperPusher B192 and one type of conventional polymer was FLOPAAM3630S. All samples were obtained from SNF FLOEGER s.a.s. company.

The principal property that differentiated these polymers was the molecular weight that varied from low to ultra-high. Each molecular weight leads to different characteristics of these polymer solutions when they flow in the porous media.

Table 2.1 represents some of the technical properties of the polymer solutions (Gil, 2008). For each experiment, the polymer powder was carefully mixed with deionised water using a mechanical stirrer at low shear rate until it was completely dissolved.

2.2 Viscosity Measurement of the Polymer Solutions

The most important property of a polymer is its ability to increase the solution's viscosity. As mentioned earlier, the polymer solution exhibits non-Newtonian behavior. Its viscosity is a function of the shear rate. The viscosity of these polymer solutions was measured using a DV-II-Pro+ Brookfield © viscometer as shown in Figure 9. In each measurement, the shear rate was changed, and the effect of this change on the viscosity was measured. Because the viscosity is sensitive to temperature, all of the measurements were done at constant room temperature conditions.

	FP3630	D118	S255	B192
Molecular weight	Ultra-high	Very high	Medium	Low
Ionic character	Anionic	Anionic	Anionic	Anionic
Charge density	Medium	Medium	Medium	Medium
approximate bulk density	$0.67 \text{ kg}/m^3$	$0.8 \text{ kg}/m^3$	$0.8 \text{ kg}/m^3$	$0.8 \text{ kg}/m^3$
	@ 5.0 g/l	@ 5.0 g/l	@ 5.0 g/l	@ 5.0 g/l
	1800 cp	$1700 \mathrm{~cp}$	$2000 \mathrm{~cp}$	2200 cp
Viscosity Mossurements	@ 2.5 g/l	@ 2.5 g/l	@ 2.5 g/l	@ 2.5 g/l
viscosity measurements	700 cp	$650 \mathrm{~cp}$	$550 \mathrm{~cp}$	$650 \mathrm{~cp}$
	@ 1.0 g/l	@ 1.0 g/l	@ 1.0 g/l	@ 1.0 g/l
	260 cp	270 cp	190 cp	140 cp
Dissolution time	90 min	90 min	120 min	120 min

Table 2.1: Technical data of polymer solutions.

The principal function of the DV-II-Pro+ Brookfield © viscometer is to drive a spindle which is immersed in the tested fluid, through a calibrated spring. The viscosity of the fluid is measured and calculated from the spring deflection. The measurement range is 1.5 - 30,000 cp.

Figures 2.2, 2.3, 2.4, and 2.5 present the relationship between the viscosity and the shear rate for each type of polymer solution with different concentrations.

Based on these measurements, it is observed that, at a constant shear rate, the viscosity of the polymer solution is greater for larger polymer concentrations. Furthermore, the polymer solution viscosity decreases with an increasing shear rate. This behavior is favorable in polymer flooding implementations because the polymer solution propagates through the reservoir at a very low shear rate and solution viscosity increases which leads to higher sweep efficiency.

The power law model is applicable to describe the relationship between the viscosity and the shear rate. Table 2.2 presents the power law coefficient, K_{pl} and the polymer exponent, n_{pl} of each polymer with different concentration. This correlation is used later in the permeability reduction measurement.

The effect of salinity on the solution viscosity was also observed by adding 2 wt% and 10 wt% NaCl to the polymer solution. Figure 2.6 and 2.7 presents the relationship between shear rate and viscosity of the associative polymer (SuperPusher S255) and conventional polymer (FLOPAAM 3630s) respectively. From the experiment, adding salinity to the



Figure 2.1: DV-II-Pro+ Brookfield © viscometer and spindle (Buchgraber, 2008)



Figure 2.2: Relationship between the viscosity and the shear rate of SuperPusher B192.



Figure 2.3: Relationship between the viscosity and the shear rate of SuperPusher D118.



Figure 2.4: Relationship between the viscosity and the shear rate of SuperPusher S255.

Table 2.2: Power law coefficient and power law exponent of each polymer from the experiment.

		n	K
	500 ppm	0.548	81.753
SuperDusher \$255	1000 ppm	0.4471	216.68
Superi usher 5255	1500 ppm	0.3973	461.38
	2000 ppm	0.4033	956.88
		n	K
	500 ppm	0.5073	147.25
SuperPusher B102	1000 ppm	0.5091	314.83
Superrustier D192	1500 ppm	0.5083	532.03
	2000 ppm	0.4631	962.5
		n	K
	500 ppm	n 0.3399	K 517.09
SuperPusher D118	500 ppm 1000 ppm	n 0.3399 0.2765	K 517.09 1100
SuperPusher D118	500 ppm 1000 ppm 1500 ppm	n 0.3399 0.2765 0.2444	K 517.09 1100 1661
SuperPusher D118	500 ppm 1000 ppm 1500 ppm 2000 ppm	n 0.3399 0.2765 0.2444 0.2413	K 517.09 1100 1661 2372
SuperPusher D118	500 ppm 1000 ppm 1500 ppm 2000 ppm	n 0.3399 0.2765 0.2444 0.2413 n	K 517.09 1100 1661 2372 K
SuperPusher D118	500 ppm 1000 ppm 1500 ppm 2000 ppm 500 ppm	n 0.3399 0.2765 0.2444 0.2413 n 0.4232	K 517.09 1100 1661 2372 K 227.38
SuperPusher D118	500 ppm 1000 ppm 1500 ppm 2000 ppm 500 ppm 1000 ppm	n 0.3399 0.2765 0.2444 0.2413 n 0.4232 0.2622	K 517.09 1100 1661 2372 K 227.38 739.19
SuperPusher D118 FLOPAAM 3630s	500 ppm 1000 ppm 1500 ppm 2000 ppm 500 ppm 1000 ppm 1500 ppm	n 0.3399 0.2765 0.2444 0.2413 n 0.4232 0.2622 0.2622 0.2130	K 517.09 1100 1661 2372 K 227.38 739.19 1096.3



Figure 2.5: Relationship between the viscosity and the shear rate of FLOPAAM 3630s.

polymer solution reduces the viscosity of that solution for both polymers. The effect of salinity on the conventional polymer solution however seems to be more severe. The viscosity reductions are approximately 85% in 2 wt% NaCl added solution and 87% in 10 wt% NaCl added solution. For associative polymer, the percentage of viscosity reduction are 75% and 80% in the case of adding 2 wt% NaCl and 10 wt% NaCl, respectively.

2.3 Interfacial Tension Measurement

The interfacial tension is the differential attraction force that occurs at the interface of 2 immiscible fluids due to the interaction of different type molecules in each fluid. Measurements were made of the interfacial tension between the polymer solutions and the oil and also a comparison made with that of the water-oil system.

The interfacial tension is measured using the University of Texas spinning drop interfacial tensiometer (UTSDIT) as shown in Figure 2.8 which is designed for measuring ultralow interfacial tension (<0.01 dyn/cm).

A small drop of fluid is placed in a liquid of higher density contained in a horizontal glass tube that is rotated along its axis with constant angular velocity. Centrifugal force



Figure 2.6: The effect of salinity on the viscosity in associative polymer.



Figure 2.7: The effect of salinity on the viscosity in conventional polymer.

2.3. INTERFACIAL TENSION MEASUREMENT



Figure 2.8: The University of Texas spinning drop interfacial tensiometer (UTSDIT).

causes the drop to elongate along the axis of rotation. The deformation occurs until the centrifugal forces are balanced by the interfacial tension (Princen et al., 1967).

Using Vonnegut's equation (Vonnegut, 1942), the interfacial tension can be calculated from the diameter, the density difference, and the angular velocity. When the drop's length exceeds four times of the drop's radius, it is considered to be a cylindrical shape, where the contributions of the two semi-spherical caps at the two ends can be neglected.

The total Gibbs energy of the drop is the summation of rotational energy and interfacial Gibbs energy (Lyklema, 2000). At the stationary state, the length and the radius of the cylinder adjust themselves until the minimum internal energy is reached.

The moment of inertia of the cylinder is given by;

$$I = \int_0^a 2\pi r dr \ l \ \Delta \rho r^2 \tag{2.1}$$

where r is the radial distance from the axis, l and a are the length and the radius of the cylinder, respectively, and $\Delta \rho$ is the density difference between two fluids. The integration yields

$$I = \frac{1}{2} V \ \Delta \rho a^2 \tag{2.2}$$

where the volume of the cylinder, V, is constant and equals to $\pi a^2 l$.

The rotational energy is

$$U(rot) = \frac{1}{2}I\omega^2 = \frac{1}{4}V \ \Delta\rho\omega^2 a^2$$
(2.3)

The interfacial Gibbs energy of the cylinder is

$$U(int) = 2\pi a l \gamma = \frac{2V}{a} \gamma \tag{2.4}$$

The minimum total energy is acquired by setting the derivative of the total energy with respect to the radius a to be zero.

$$\frac{d}{da}\left[\frac{1}{4}V\ \Delta\rho\omega^2 a^2 + \frac{2V}{a}\gamma\right] = 0 \tag{2.5}$$

where V is a constant. The result is

$$\gamma = \frac{\omega^2 \Delta \rho a^3}{4} \tag{2.6}$$

The interfacial tension is calculated from the radius of the cylindrical drop, the density difference between two fluids, and the angular velocity of the tensiometer.

The measurements were performed in 4 fluid systems as follows:

- water and decane
- surfactant solution and decane
- polymer solutions and decane
- polymer solutions and crude oil

The polymer solutions are the denser fluid in the interfacial tension measurement using spinning drop tensiometer.

2.3.1 Water and Decane

The interfacial tension between water and decane was measured in the first step to be used as the calibration for the following measurements. Theoretically, the interfacial tension of water and decane at 20 deg C is 52.33 mN/m (Zeppieri et al., 1967). The non-ionic surfactant, Triton X-100, was then added into the water to observe the effect of the surfactant to the water-decane interfacial tension.

2.3. INTERFACIAL TENSION MEASUREMENT

Fluids	IFT (mN/m)
Water + Decane	57.4
Surfactant Solution + Decane	9.5

Table 2.3: Measured interfacial tension between water and decane.

Fluids	IFT (mN/m)	SD
Associative Polymer		
S255	22.7	2.7
B192	21.1	1.8
D118	24.6	1.8
Conventional Polymer		
3630S	29.5	1.3

Table 2.4: Measured interfacial tension between polymer solutions and decane.

The measured interfacial tensions are shown in Table 2.3. This value is in agreement with the literature value indicating that the tensiometer achieves a sufficient angular velocity to measure large IFT. The experiment also showed that the interfacial tension of water and decane can be significantly reduced when the surfactant were added to the system.

2.3.2 Polymer solutions and Decane

The interfacial tensions between each type of polymer solutions and decane are shown in Table 2.4. The average interfacial tension for the associative polymers is approximately 23 mN/m while the interfacial tension of the conventional polymer is 29.5 mN/m. The polymer solutions do reduce IFT somewhat, but not as dramatically as the surfactant.

2.3.3 Polymer solutions and Crude Oil

The interfacial tensions of polymers solutions and crude oil are shown in table 2.5. The crude oil is the same as that employed by Buchgraber (2008) in his micromodel experiments.

In the case of polymer solutions with crude oil, the interfacial tension is much lower in comparison to the case of polymer solutions with decane. The average value for the associative polymers is approximately 11 mN/m while the interfacial tension of the conventional polymer is 16.1 mN/m.

Fluids	IFT (mN/m)	SD
Associative Polymer		
S255	11.2	0.2
B192	8.5	0.2
D118	12.1	0.1
Conventional Polymer		
3630S	16.1	0.3

Table 2.5: Measured interfacial tension between polymer solutions and crude oil.

The interfacial activity of polymers is due to the fact that polymers have both hydrophilic and hydrophobic parts distributed along their backbones. At the interface between polymer solutions and oil, polymer molecules adjust themselves until the non-polar or hydrophobic groups are located in the oil phase and the hydrophilic groups are located in the aqueous phase. This behavior causes the contact area between oil and water to reduce and therefore reduces the interfacial tension (Shalaby et al., 1991).

Adding polymers into water in the water-oil system causes a similar effect on IFT as adding the low molecular weight surfactants, at low concentration. In general, the abilities of polymers to decrease interfacial tension are much less than those of the low molecular weight surfactants. Significant oil mobilization through reduction of IFT does not appear to be an EOR mechanism for associative polymers. However, due to their large molecular structures and the effect of hydrophobic chains, the polymer solutions can significantly increase viscosity of the water and this characteristic is very important in EOR process.

2.4 Core Properties

The porous medium used in the experiment was a sand-packed column in core holder. The core holder was 14.7 cm long and 4.91 cm^2 in cross section as shown in Figure 2.9. The sand particle size distribution was measured by sieve analysis.

The measured cumulative distribution curve of sand grain diameter is shown in Figure 2.10. The mean grain diameter of the sand used in the experiment was 0.347 mm. The pore volume of the sand-packed core was calculated from the difference between the core holder's volume and the packed sand volume assuming that the sand density was 2.65 g/cc. The porosity was the ratio of the pore volume to the bulk volume of the core holder.

2.4. CORE PROPERTIES



Figure 2.9: Sands and core holder used in the experiment.



Figure 2.10: Cumulative probability curve of sand grain diameter.

Core dimension	$14.7 \text{ cm x } 4.91 \text{ cm}^2$
Avg grain diameter	$0.347 \mathrm{~mm}$
Pore volume	18.98 cc
Porosity	26.3%
Permeability to water	12.6 Darcy

Table 2.6: Core properties.

The core was first flooded with deionised water until the flow was stable. The pressure drop across the core was then measured at a different flow rates. Assuming linear, incompressible, and one-dimensional flow, Darcy's equation was used to calculate the absolute permeability of the core. The properties of sand-packed core are as shown in Table 2.6.

2.5 Experimental Set-up

The experiments were conducted by flooding the sand-packed core with the distilled water and different kinds of polymer solutions. The LDC/Milton Roy Constametric IIIG metering pump (Figure 2.11) was used to inject water and polymer solutions into the core holder with constant flow rate. The pump was first calibrated to obtain the accurate value of flow rate. Two pressure gauges were inserted in the flow line at the inlet and outlet of the core holder to measure the pressure drop along the core. First, the core was flooded with distilled water until the pressure drop along the core was constant which indicated that the flow reached the stable state and the core was fully saturated with water. All experiments were conducted under these similar initial conditions. A new sand-packed was used for each test and the porosity and permeability relative to water of the core were measured at the beginning of the experiment. The injected pore volume was calculated from the flow rate, core dimension, and porosity in each experiment.

2.5. EXPERIMENTAL SET-UP



Figure 2.11: LDC/Milton Roy Constametric IIIG metering pump.

Section 3

Permeability Reduction

When any polymer solution flows through porous media, there may be significant interactions between the transported polymer molecules and the porous medium (Sorbie, 1991). One of these interactions is the polymer absorption on the solid surface. This absorption causes the flow path to be smaller which may ultimately be fully plugged. Several experiments (Jennings et al., 1971; Hirasaki and Pope, 1974; Chauveteau and Kohler, 1974) were done with a conventional polymer to observe this plugging behavior, which reportedly led to the reduction of porous media permeability.

These experiments studied the permeability reduction accompanying associative polymer solution injection. Each polymer solution was used one at a time to observe its unique characteristics. The experimental steps of this experiment are listed below;

- Saturate the core with deionised water in order to measure absolute permeability (k_w) using Darcy's equation.
- Flood the core with the polymer solution at a constant Darcy velocity of 1 meter/day.
- Measure the pressure drop along the core holder.
- Calculate the shear rate of the solution as it propagates in the core and obtain the corresponding solution viscosity.

The shear rate is estimated by assuming the non-Newtonian fluid flows through circular capillary using the following equation (Christopher and Middleman, 1965).

$$\dot{\gamma}_w = \left(\frac{1+n}{n}\right) \frac{u}{\sqrt{8k\phi}} \tag{3.1}$$

where n is the power law exponent, u is the flow velocity, k is the permeability, and ϕ is the porosity of the core.

- Use Darcy's equation to calculate the absolute permeability based on specific polymer (k_p) .
- Repeat the procedure with different concentrations. The concentrations of polymer used in this experiment are 500, 1000, 1500, and 2000 ppm.

The permeability reduction factor is the ratio of permeability of water to that of a single phase polymer solution flowing under the same conditions.

$$R_k = \frac{k_w}{k_p} \tag{3.2}$$

 R_k is sensitive to the polymer type, the molecular weight, the degree of hydrolysis, the shear rate, and the permeable media pore structure (Lake, 1989).

Permeability reduction is observed for all experiments as illustrated in Figure 3.1. For every polymer used in this experiment, the R_k increases with increasing polymer concentration. The R_k and polymer concentrations have approximately linear relationship in the case of associative polymers. For the conventional polymer however, increasing concentration has significant impact on permeability reduction especially at the high concentration (more than 1500 ppm). It is also observed that, at the same concentration, permeability reduction increases with increasing polymer molecular weight.

The polymer absorption is a function of concentration as shown by the Langmuir-type isotherm (Lake, 1989),

$$C_{4s} = \frac{a_4 C_4}{1 + b_4 C_4} \tag{3.3}$$

where C_4 and C_{4s} are the concentration in the aqueous and of the rock surface respectively. This relationship shows that the absorption of polymer at the rock surfaces increases with higher solution concentration. The greater absorption is the main factor that causes the permeability to be smaller than the polymer flood case.

The effect of salinity on the permeability reduction was observed by adding 2 wt% NaCl and 10 wt% NaCl to the polymer solution. Due to its lower viscosity, the permeability reduction decreases with increasing salinity in both conventional and associative polymer cases as shown in Figure 3.2



Figure 3.1: Permeability reduction for different polymer solutions.



Figure 3.2: The effect of salinity on permeability reduction.

Section 4

Inaccessible Pore Volume

When there is no polymer absorption, many studies report that polymer molecules are transported through the porous media faster than those of inert tracer species (Sorbie, 1991). This characteristic, referred to as "inaccessible pore volume" (IPV) was first observed and reported by Dawson and Lantz (1972). It was concluded that some high molecular weight polymer molecules might not be able to access all of the connected pore volume with a smaller pore throat. Nevertheless, the amount of inaccessible pore volume for each type of polymer can be determined from the experiment.

In order to minimize the polymer absorption while measuring IPV, experimental floods were conducted for each type of polymer in three steps;

- Saturate the core with the 2000 ppm polymer solution until it reaches equilibrium.
- Inject 1PV of bank solution, which is the 500 ppm polymer solution mixed with 1 wt% NaCl into the core.
- Resume the injection of the 2000 ppm polymer solution.

During the experiment, the effluent from the core outlet was collected. These samples were separated into two parts to measure the polymer and salt concentrations.

The polymer concentrations were measured using a UV spectrophotometer (Figure 4.1). The UV/vis spectrophotometer is widely used to determine the concentration of organic compounds that absorb light in the UV or visible regions of the electromagnetic spectrum. It measures the intensity of light passing through a sample (I), and compares it to the intensity

of light before it passes through the sample (I_o) . The ratio $\frac{I}{I_o}$ is called the transmittance. The absorbance, A, is calculated from;

$$A = \log(\frac{I}{I_o}) \tag{4.1}$$

The UV/vis spectrophotometer was used in this experiment to measure the polymer concentration of the collected samples. In each measurement, 1.5 ml liquid sample was put into the UV transparent cell and attached to the cell holder. The UV light was split into two beams before it reached the sample. One beam was used as the reference; the other beam passed through the sample. The 2 detectors measured the reference and the sample beams at the same time and the absorbance was calculated from the ratio of light intensity of these 2 beams (Skoog et al., 2007).

First, the standard polymer solution was scanned by the machine to obtain the wavelength that gave maximum UV absorbance. This wavelength was then used to measure the UV absorbance for all of the samples. The polymer concentration was calculated relative to the standard solution concentration.



Figure 4.1: UV Spectrophotometer.

Figure 4.2 presents the scanning result from the UV spectrophotometer. The wavelength used was between 250 - 400 nm. The maximum absorbance for all kinds of polymer occurs approximately at the same wavelength of 257 nm.

The salt concentrations were measured by titration with silver nitrate $(AgNO_3)$. This is a soluble silver salt that reacts readily with all halide ions, F^- , Cl^- , Br^- , and I^- . For



Figure 4.2: Scanning Result from UV Spectrophotomete.r

example, the silver cation (Ag^+) reacts with chloride (Cl^-) and forms an insoluble silver chloride (AgCl) precipitate, that can be observed using the appropriate indicator.

$$Ag^+ + Cl^- = AgCl(s) \tag{4.2}$$

Finally, the inaccessible pore volume of associative polymer solutions is acquired by calculating the difference in break-through time between the polymer and the salt. Figure 4.3 shows the effluent profiles from some of the experiments. The salt and polymer concentration profile clearly separate. It is shown that the two miscible flood fronts flow through the porous media with different velocities. The velocity of polymer that propagates in the core is greater than that of the water. The interstitial velocity of the fluid is calculated from the following equation;

$$V = \frac{q}{A\phi} \tag{4.3}$$

where q is the flow rate, A is the cross-sectional area opened to flow, and ϕ is the porosity of the porous media. In the case of polymer flood, the effective porosity occupied by polymer is less than the effective porosity of the water; therefore the polymer flows faster. This difference in the porosity available to the two liquids is the inaccessible pore volume (Dawson and Lantz, 1972).



Figure 4.3: Effluent profiles from the experiment.

The experiment was completed for 4 polymers, 3 associative and 1 conventional. The inaccessible pore volume (IPV) is measured from the difference in breakthrough time of the polymer and the salt which is considered to be the tracer added to the water and is shown in Table 4.1.

The IPVs from the experiment are on the high side. For the associative polymer the amount of IPV increases with increasing molecular weight. The greater molecular weight means the larger molecule size compared with the pore throat leads to greater IPV. For the conventional polymer, the measured IPV is slightly less than those from the associative polymers.

The limitation of this experiment is that there is only one type of the conventional polymer available for the experiment and the molecular weight of this polymer is different

Polymer	MW	%IPV
Associative Polymer		
SuperPusher B192	Low	21.2
SuperPusher S255	Medium	24.9
SuperPusher D118	High	34.1
Conventional Polymer		
FLOPAAM 3630s	Ultra-high	35.2

Table 4.1: IPV results from the experiment.

from the molecular weight of the associative polymers. It is impractical to compare the properties between the associative polymer and the conventional polymer with different molecular weight. It is clear, though, that the associative polymers display considerable IPV and only moderate to light permeability reduction.

An alternative method was also considered for interpretation. Consider the miscible displacement with 1 dimensional flow in the homogeneous medium (Lake, 1989), the continuity equation for the concentration is described as,

$$\frac{\partial C_D}{\partial t_D} + \frac{\partial C_D}{\partial x_D} - \frac{1}{N_{pe}} \frac{\partial^2 C_D}{\partial x_D^2} = 0$$
(4.4)

that is solved with the following boundary and initial conditions on $C_D(x_D, t_D)$:

$$C_D(x_D, 0) = 0$$
$$C_D(x_D \to \infty, t_D) = 0$$
$$C_D(x_D \to -\infty, t_D) = 1$$

 C_D is the dimensionless concentration and it is defined as,

$$C_D = \frac{C - C_I}{C_J - C_I} \tag{4.5}$$

where C_I and C_J are the initial and injection concentrations, respectively.

The Peclet number is the ratio of convection and dispersion effect and is described as,

$$N_{pe} = \frac{uL}{\phi D} \tag{4.6}$$

where u is the Darcy velocity, L is the length of the medium, ϕ is the porosity, and D is the dispersion coefficient.

The partial differential equation is then solved and the concentration of polymer is calculated from the following equation (Lake, 1989).

$$C = C_I + \frac{C_J - C_I}{2} \left[1 - erf(\frac{x_D - t_D}{2\sqrt{\frac{t_D}{N_{re}}}})\right]$$
(4.7)

For this experiment, 2 sets of floods were conducted. The first flood was the initial fluid which was 2000 ppm polymer with 500 ppm polymer and then followed by the second flood which was the replacement of 500 ppm polymer with the initial fluid of 2000 ppm. In this case, the super position concept is used, Figure 4.4, to obtain the full concentration history.

Figure 4.4 (a) presents the slug condition of the experiment. The super position method states that the total flood can be treated as the sum of the individual floods as shown in Figure 4.4 (b) and (c).

The solution for first flood as in Figure 4.4(b) is

$$C = C_I + \frac{C_J - C_I}{2} \left[1 - erf(\frac{x_D - t_D}{2\sqrt{\frac{t_D}{N_{pe}}}})\right]$$
(4.8)

and the solution for the imposed flood as in Figure 4.4 (c) is

$$C = C_J + \frac{C_I - C_J}{2} \left[1 - erf(\frac{x_D - (t_D - t_{Ds})}{2\sqrt{\frac{(t_D - t_{Ds})}{N_{pe}}}})\right]$$
(4.9)

Therefore, the solution for the super position is as follow,

$$C = C_I + \frac{C_I - C_J}{2} erf(\frac{x_D - t_D}{2\sqrt{\frac{t_D}{N_{pe}}}}) + \frac{C_J - C_I}{2} erf(\frac{x_D - (t_D - t_{Ds})}{2\sqrt{\frac{(t_D - t_{Ds})}{N_{pe}}}})$$
(4.10)

Using the superposition method, the effluent profile model of salt and polymer is constructed.

The only unknown in the superposition is the Peclet number, N_{pe} . The method of least norm solution is used to determine the most optimum N_{pe} that fits with the experimental data. The norm function is the measurement of the difference between 2 sets of data.

$$||e|| = \sqrt{(C_{m1} - C_{D1})^2 + (C_{m2} - C_{D2})^2 + (C_{m3} - C_{D3})^2 + \dots + (C_{mn} - C_{Dn})^2}$$
(4.11)



Figure 4.4: Schematic of superposition method.

where C_m is the measured concentration fraction and C_D is the concentration fraction obtained from the superposition model. The optimum N_{pe} is presented in table 4.2. With these N_{pe} , the superposition model that fit the experimental data is constructed as shown in Figure 4.5, 4.6, 4.7, and 4.8.



Figure 4.5: The experimental data and the superposition model fitting of SuperPusher B192.

The N_{pe} is a function of porosity and dispersion coefficient. In the case of salt effluent profile, the only unknown is the dispersion coefficient and it can be calculated from the obtained N_{pe} . From the previous studies, the polymer dispersion is consistently greater that of the chloride tracer by approximately a factor of 2(Sorbie, 1991). A 10 % uncertainty is applied to this polymer dispersion coefficient estimation to obtain the range of the core porosity relative to polymer solution. The inaccessible pore volume is then calculated as

$$IPV = 1 - \frac{\phi_{polymer}}{\phi_{water}} \tag{4.12}$$

with the results shown in Table 4.3

The IPVs obtained from the superposition model are lower than the ones that are estimated from the difference in breakthrough time of the 2 profiles. However, the molecular



Figure 4.6: The experimental data and the superposition model fitting of SuperPusher S255.



Figure 4.7: The experimental data and the superposition model fitting of SuperPusher D118.



Figure 4.8: The experimental data and the superposition model fitting of FLOPAAM 3630s.

Table 4.2: N_{pe} from the least norm minimization of the experimental and predicted data.

	N_{pe} : Salt	N_{pe} : Polymer	$\ e\ $
SuperPusher B192	86.3	44.5	0.4
SuperPusher S255	72.2	42.2	0.5
SuperPusher D118	150.4	86.3	0.3
FLOPAAM 3630s	98.6	88.8	0.2

Table 4.3: The range of IPV from the model estimation.

	MW	IPV from the model	Uncertainty
SuperPusher B192	Low	3.1~%	$\pm 3~\%$
SuperPusher S255	Medium	16.2~%	$\pm 4.2 \%$
SuperPusher D118	High	12.7~%	$\pm 4.4\%$
FLOPAAM 3630s	Ultra-high	31.0~%	$\pm 0.3~\%$

	% IPV	Uncertainty
No Salt	12.7~%	$\pm 4.4\%$
2 % NaCl	12.8 %	$\pm 4.4\%$
10 % NaCl	6.8~%	$\pm 4.7\%$

Table 4.4: The range of IPV from the model estimation as a function of salt concentration.

weight seems to be the main factor that affects the amount of IPV in each kind of polymer. SuperPusher B192 which has lowest molecular weight exhibits 3 ± 3 % of IPV while the higher molecular weight polymers have more IPV. The conventional polymer, FLOPAAM 3630s, has highest IPV from both approaches.

It is still inconclusive that the conventional polymer tends to have more amount of inaccessible pore volume since the conventional polymer used in this experiment has greater molecular weight than other associative polymers. This greater molecular weight may lead to greater inaccessible pore volume when flooding with the same concentration.

The effect of salinity on the inaccessible pore volume was also observed. Salt (NaCl) at 2 wt% and 10 wt% was added to the SuperPusher D118 polymer solution, which is the highest molecular weight associative polymer used in this experiment and the IPV was calculated using the previous method. The experimental result shows that the %IPV decreases with increasing salinity. Adding salinity reduces the viscosity and permeability of the solutions as proved in Chapter 2 and 3. It also reduces the absorption on the surface of the porous media and leads to reduction in the inaccessible pore volume as shown in Table 4.4 and Figure 4.9 and 4.10.



Figure 4.9: The experimental data and the superposition model fitting of SuperPusher D118 (2 % NaCl added).



Figure 4.10: The experimental data and the superposition model fitting of SuperPusher D118 (10 % NaCl added).

Section 5

Conclusion and Recommendations

5.1 Conclusion

Associative water-soluble polymer is a relatively new class of polymers, that has recently been introduced for enhanced oil recovery process. The viscosity-increasing feature of this polymer originates from the intramolecular and intermolecular associations of the hydrophobic groups in the polymer molecules. This association is stronger with increasing salinity which makes the associative polymer more favorable in the real application, in comparison to conventional hydrolyzed polyacrylamide.

Like other polymers, the experiment shows that the associative polymer solution exhibits non-Newtonian fluid behavior. Its viscosity increases with decreasing shear rate. The relationship between the viscosity and the shear rate can be described by the power law model. The experiments were conducted in the laboratory to determine the physical properties of the associative polymer when it propagates through the porous media.

The polymer solutions used in each experiment were prepared from both associative and conventional polymers from the same manufacturer, SNF FLOEGER. The three types of associative polymers used were SuperPusher S255, SuperPusher D118, and SuperPusher B192 and one type of conventional polymer that was FLOPAAM3630S. The principal property that differentiated these polymers was the molecular weight that varied from low to ultra-high. The porous media used in the experiment is a sand-packed column contained in the core holder. The average grain diameter is 0.35 mm and the porosity of the core is approximately 26.3%. The permeability reduction (R_k) is the ratio between water permeability to the polymer permeability. Flow of polymer solution through the porous medium caused polymer retention on the grain surface and occasionally plugging that leads to the reduction in permeability. The measurement was performed by flooding the core with water and polymer until it reached steady state. The pressure drop along the core holder was measured in each experiment and the absolute permeabilities based on water and polymer flow were calculated using Darcy's equation. For each polymer, permeability reduction is observed. The R_k increases with the increasing molecular weights and concentrations. In the case of conventional polymer, the permeability reduction is more sensitive to the change in polymer concentration especially at the high concentration. Adding salinity into the solution causes the permeability reduction to decrease in both associative and conventional polymers.

In case of high molecular weight polymer, the molecular size may be larger than some pore throats and leaves that pore space inaccessible to polymer. The amount of this inaccessible pore volume is observed from the separation between the polymer and the tracer profile of the effluents. Because of less effective porosity, the polymer propagates through the porous media faster than the water. The IPVs were measured from the experiment for each polymer by using the salt as the tracer. The separation in concentration profiles of the polymer and the salt from the experiment indicate that the IPV's in both associative and conventional polymers are on the high side which is approximately 30%. The superposition method is used to construct the model that fits the experimental data. The experiment shows that the molecular weight, and consequently molecular size, is the main factor that affects the amount of IPVs in each kind of polymer solutions.

5.2 Recommendations

- Associative and conventional polymers with equivalent molecular weight are recommended to be used in the experiment in order to have a proper comparison between the physical properties of the 2 classes of polymer.
- A sensitivity analysis should be performed to observe the uncertainty of the experimental results.
- The future experiments could be the observation of other polymer solution properties, such as the absorption characteristics, the polymer stability, and the polymer

5.2. RECOMMENDATIONS

dispersion in porous media, and also the study of the lithology effect on the polymer solution flow properties.

• Additionally, the numerical simulation could be conducted to have the better understanding in the solution properties of polymer when it flows through porous media.

Nomenclature

- ϕ = Porosity (%)
- k = Permeability (d)
- M = Mobility ratio
- k_{rw} = Water relative permeability
- k_{ro} = Oil relative permeability
- μ = Viscosity (cp)
- f_w = Water fraction flow
- $f_o =$ Oil fraction flow
- $\dot{\gamma}$ = Shear rate (1/s)
- τ = Shear stress (N/m²
- R_k = Permeability reduction
- k_w = Water permeability
- k_p = Polymer solution permeability
- v = Interstitial velocity (cm/s)
- u = Superficial velocity (cm/s)
- $q = \text{Flow rate (cm^3/s)}$
- $A = \operatorname{Area} (\operatorname{cm}^2)$
- L = Length (cm)
- $D = \text{Dispersion coefficient } (s/cm^2)$
- C = Polymer concentration (ppm)
- I = Light intensity (cd)

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