# **POLYMER PROPERTIES DETERMINATION FOR DESIGNING CHEMICAL FLOODING**

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#### *ABSTRACT*

*Waterflooding became the standard practice in many reservoirs formation in petroleum industries, the strengths and weaknesses of the methods were quite well established. In particular, the inefficiency of the waterflood oil displacement mechanism as a result of either an unfavorable mobility ratio or heterogeneity was largely identified. Therefore, chemicals injections as the improvement displacement processes had been proposed to support petroleum industries to recover the production of oil. Chemical injection normally consists of alkaline, surfactant, and polymer (ASP). They could be injected as standalone fluid or mixture of fluids; it depends upon the injection fluid design appropriate for particular field. Polymer solution could be prepared for mixtures of injection fluid and or as chase fluid injection which is injected behind surfactant or ASP. The main function of polymer solution primarily is to viscosity the injection water as a mobility control. This work is proposed to determine the important polymer properties which are suitable for mobility control in such EOR plan in the particular field. This field is sandstone reservoir with oil gravity*  of 23 to 26<sup>o</sup>API and viscosity of 3cp at 90°C. Two kinds of polymers have been chosen such as: *HPAM-1 and HPAM-2 and subject to be tested for the properties characteristic. Intensive works have been done to evaluate the bulk polymer properties at laboratory scale which include rheology, filtration, thermal stability, retention/adsorption, and injectivity or permeability reduction tests. The results indicated that HPAM-1 polymer is suitable for injection fluid design for Zone-B while HPAM-2 for Zone-A.*

*Key Words: polyacrylamide (PAM), partially hydrolyzed polyacrylamide (HPAM), mobility control*

## **I. INTRODUCTION**

After implementing water injection, even though under the most favorable conditions, some 30 to 50% of the oil remains trapped in the pores of rock within the regions that have been efficiently swept by a waterflood. The oil is basically trapped by mechanism of capillary forces along the reservoir pores.

Chemical injections basically have been proved as the enhanced oil recovery processes at laboratory scale. This technology includes alkaline, surfactant, and polymer flooding. They can be injected into oil reservoir as an individual chemical or mixture of chemicals. The design of chemical injection will

depend on the field screening result. They could be categorized as alkaline, surfactant, polymer flood for individual chemical injection; and AS (alkalinesurfactant mixture), SP (surfactant-polymer mixture), and ASP (alkaline-surfactant-polymer mixture) injections as chemicals mixtures injection.

Surfactant injection mainly contributes in the microscopic displacement where the separated trapped oil is displaced into the form of oil bank. To improve displacement sweep efficiency in macroscopic term is not only reducing the interfacial tension between displaced and displacing phases necessary but also improving the mobility ratio. In

order to improve the mobility ratio, a viscous chase fluid should be added behind the surfactant solution. Polymer is normally used to improve the mobility ratio in tertiary displacement process in oil reservoir rocks.

# **II. MOBILITY CONTROL**

Addition of a polymer to water reduces its mobility in porous medium can be done in two ways: i. by increasing the viscosity of the injection water, and ii. by altering the effective permeability of the rock. Fractional theory of Buckly Leverate sweep efficiency indicates that by increasing the polymer viscosity as displacing fluid and reducing the permeability to water phase therefore the mobility ratio (M) will be reduced below unity. There is little point in considering polymer in this situation during water flood, and it is only when  $M \geq 5$  that polymer would be seriously considered.

Poor sweep of waterflood arises principally from unfavorable mobility ratio and heterogeneity occurring in the reservoir. Those problems normally result in early water breakthrough and poor sweep efficiency. Improving the mobility below unity is the case to increase sweep efficiency, and typically M of around 0.1 to 0.3 commonly improves vertical sweep efficiency in heterogeneous reservoirs.<sup>3</sup>

A polymer solution moves in a more uniform manner, while flow still tends to be greatest in high permeability zones and along the shortest path between the injection and production wells. It is generally accepted that polymer solution do not significantly affect final, endpoint, residual oil saturation except surfactant solution is added in the injection and therefore the capillary number could increase several order of magnitude.<sup>1</sup>

# **III. POLYMER CHARACTERISTICS**

Polymer solutions commonly show pseudo plastic, non-Newtonian behavior in capillary flow. The viscosity tends to reduce as shear rate increases. The flowing polymer is subjected to a range of shear rate as it passes through successive pores and pore throats. The average shear rate will depend upon the pore size distribution and the tortuosity of the medium, as well as the gross parameters such as Darcy velocity, permeability, and porosity. Increasing shear rate near well bore at high injection rate

should take into account that the polymer is still in the range of viscoelastic form and therefore it could be reversible and return into original viscosity after passing through the well bore at high rate.

There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variations in shear rate. The most common types of non Newtonian fluids include pseudoplastic, dilatants, and plastic.

Pseudoplastic is a type of fluid that displays a decreasing viscosity with an increasing shear rate. Probably the most common of non Newtonian fluids are pseudoplastic, and called shear thinning. On the other hand dilatant fluid increases the viscosity with an increase in shear rate. Dilatancy is also referred to as shear thickening flow behavior. Furthermore, plastic is the type of fluids that behave as a solid under static condition. A certain amount of stress must be applied to the fluid before any flow is induced; this stress is called the "yield stress".

# **IV. POLYMER TYPES**

At present two main types of polymer are used in enhanced oil recovery, bio-polymer such as *Xanthan*, and synthetic polymers such as *Polyacrylamides*.

*Xanthans* is a polysaccharide, a bio-polymer. It is produced by microbial action of Xanthomonas Campestris on a substrate of carbohydrate media, with a protein supplement and an inorganic source nitrogen. The biopolymer is an extracellular slime which forms on the surface of the cells. Xanthan gum is well known to have excellent performance in high salinity brine, relatively insensitive to temperature and pH. This is because in the simple model, Xanthan has been considered to be a rigid rood. The strong pseudoplastic behavior is also expected for long rod like molecules. A wide range of molecular weight (MW) has been reported for Xanthan varying from about 2 to 50 x  $10<sup>6</sup>$ . The molecular weight is very important as the parameter for EOR project as well as the molecular weight distribution (MWD).

On the other hand Polyacrylamide (PAM) or Partially hydrolyzed polyacrylamide (HPAM) is obtained by hydrolyzing polyacrylamide with sodium of potassium hydroxide. The degree of hydrolysis ranges from 0% to 35% for the polymers currently used in EOR. Indeed, to this day over 90% of field applications have used HPAM.3

HPAM is a synthetic straight-chain polymer of acrylamide monomers, some of which have been hydrolyzed. The degree of hydrolyzed may be important in certain physical properties such as polymer adsorption, shear stability and thermal stability. However, even though commercial polymers are supplied with a state degree of hydrolysis, it is well known that at elevated temperatures the hydrolysis of amide will continue.

The HPAM molecule is a flexible chain structure sometimes known as a random coil in polymer chemistry. Therefore this type of polymer may be more sensitive to salt or hardness than those of Xanthan. Using current technology for manufacturing polyacrylamide, very high molecular weight species can be produced. Polyacrylamide used in EOR applications may typically have weight averaged molecular weights in the range 2 to  $10 \times 10^6$ .

Although the majority of polymers used in EOR projects are dry powder polymers, there are field specific conditions that may dictate the use of emulsion polymers. Chemical injections conducted from offshore platform for example, are a case where emulsion polymer can be more appropriate. Some companies offers emulsion polymers in either 30% or 50% active system.

## **V. RESERVOIRS CANDIDATE**

Based on industrial standard a candidate reservoir for chemical injection, especially for chemical flooding, has been determined in very detail by Taber.<sup>4</sup> on the EOR's screening criteria, see Table 1.

Based on the criteria on Table 1 the candidate fields should fulfill those criteria for chemical flooding. The oil is produced from Talang Akar Formation which consists of sandy conglomeratic, coarse sand, and interbedded shale-clay-fine sand. Ultimate recovery for this field is still very low approximately 28.36% and water cut at this time is around 96%.

Reservoir permeability, rock composition, oil viscosity, and water chemistry are important factors to select the optimum molecular weight polymer for particular field. Sampling of core, formation waters and oil have been done for this reservoir. Oil characteristic is identified by gravity of around 23 to 26°API and viscosity of 3cp at 90°C. Moreover the core and formation water had been analyzed and the results are presented in Table 2 and Table 3 respectively.

## **VI. POLYMER SELECTION**

For initial test as candidate chemical for injection, polymer should have a property as shown in Table 4,

Table 1 Summary of Screening Criteria for Chemical Injection <sup>1</sup>										
<b>Oil Properties</b>			<b>Resevoir Characteristics</b>							
					Oil		Net	Average		
	<b>EOR</b>	Gravity	Viscosity	Composition	Saturation	Formation	<b>Thickness</b>	Permeability	Depth	Temperature
No	Method	(oAPI)	(cp)		$(\%PV)$	Type	ft	md	(f <sup>t</sup> )	(OF)
-	Micellar/	$20$ $\sim$ 35	$\mathcal{F}$ < 35 $\sqrt{13}$	Light,	$53 \times$ $>35$ $\sim$	Sandstone	NC	>10 450	$< 9,000 \rightarrow 3250$	$>200 \times 80$
	Polymer			intermediate.		prefered				
	ASP, and			some organic						
	Alakaline			acids for						
	Flooding			alkaline floods						
2	Polymer	>15	< 150, > 10	NC	$80 \times$ $.50$ $\sim$	Sandstone	NC	$10\epsilon$ $800$ b	< 9,000	$>200$ 140
	Flooding					prefered				





the detail of the physico-chemistry property of the polymer selection criteria. Nine (9) items listed in Table 4 should be fulfilled before selected for further intensive laboratory tests.4 Two kinds of HPAM are chosen for this project such as HPAM-1 and HPAM-2 that fulfill Table 4 criteria. Both polymers are heat tolerance and salt resistance polymer. HPAM-1 is an ionic polyacrylamide having Mw around  $25 \times 10^6$ , while HPAM-2 is an anionic polyacrylamide with very high MW.

After polymer passes through the screening criteria in Table 4, to optimize the polymer properties for designing chemical flooding such as: polymer, surfactant-polymer, SP (surfactant-polymer mixture), and ASP (alkaline-surfactant-polymer mixture) injections, it is necessary to do an intensive laboratory works to determine the important parameters for selecting an appropriate polymer for chemical flooding. This papers will discuss intensively bulk polymer properties at laboratory scale which include rheology, filtration, thermal stability, retention/ adsorption, and injectivity or permeability reduction tests. Figure 1 shows the workflow of the polymer selection.

All laboratory tests must be performed under un-aerobic condition, unless oxygen scavenged necessary to be added in the solution during lab test. It needs to be confirmed that the field produced water has dissolved oxygen below 2 ppb. If dissolved oxygen is present in the makeup water, gas stripping is usually the most practical and least risky way to remove it. Use of chemical oxygen scavengers and anti-oxidant packages is usually expensive and risky. Dissolved iron is often not of concern if dissolved oxygen is not present.

## **A. Polymer Solution Preparation**

With dry powder polymer, the brine is stirred using a magnetic stirrer at a high enough intensity to make a strong vortex. The powder is introduced slowly into the side of the vortex to avoid formation of fisheyes and microgel which can be formed if the powder is not wetted evenly. The solution is stirred then slowly for approximately 90 minutes to ensure

**Table 3 Water Analysis of the Formation Waters**

<b>ZONES</b>	A	В
<b>CATION</b>	mg/1	mg/1
Sodium, Na <sup>+</sup> (calc.)	2,507.0	1,446.00
Calcium, Ca <sup>++</sup>	16.92	24.50
Magnesium, $Mg^{++}$	37.20	29.80
Barium, Ba <sup>++</sup>	0.73	0.448
Iron, $Fe^{++}$ (total)	0.00	0.00
<b>ANION</b>	mg/l	mg/l
Cloride, Cl	9,720.0	8,600.00
Sulfate, $SO_4^-$	0.00	0.00
Carbonate, CO <sub>3</sub>	96.00	319.20
Bicarbonate, HCO <sub>3</sub>	2,427.80	1,969.08

<b>Chemical Properties of Polymer</b>					
No.	<b>Item</b>	Unit	<b>Criteria</b>		
1	Appearance/Type of polyacrylamide		Solid Granule or Solution		
2	Molecular weight		18-25 million		
3	Solubility	hr	≤2.0		
4	Viscosity at 1000 mg/l and produced water	mPa.s	$\geq 7$		
5	<b>Residual Monomer Content</b>	wt%	≤0.05		
6	<b>Hydrolysis Degree</b>	mol%	≤15		
$\overline{7}$	Water-insoluble	wt%	≤0.1		
8	Solid Content	%	≥89		
9	Particle Size of Powder	$\leq 0.15$ mm	%	$\leq 5$	
		$\geq 1.00$ mm	%	$\leq$ 5	

**Table 4 Chemical Properties of Polymer**



**Table 5** Thermal Stability of 500 ppm Polymer after 3 Months Ageing at 90°C





complete dissolution. The time for polymer mixing varies and depends on the type of polymers; some polymers need 2 days for the mixing.

Basically the stock polymer solution is made up as a mother solution with a concentration of 5000 ppm by weight for both HPAM-1 and HPAM-2 using formation waters. These solutions, then, are poured into dark (brown) bottles and saved in a dark place as well. These stock solutions are diluted with the formation waters to get target solutions for analysis such as: 500, 1000, and 1500 ppm each use for the day.

## **B. Rheology Test**

Polymer rheology normally measures relationships between viscosity and shear rate. Polymer solution generally indicates shear thinning. The viscosity of polymer solution is related to the size and extension of the polymer molecule in that particular solution; large polymer species are generally associated with higher solution viscosities.

Viscosity polymer can be made using a low shear viscometer such as a Brookfield LVT with UL adaptor. Three polymer solutions i.e. 500, 1000, 1500 ppm each for HPAM-1 are mixed with formation water of Zone-A and Zone-B reservoirs, while HPAM-2 with formation water of Zone-A and Zone-B reservoirs as well. The measurement results are presented in Figure 2 to Figure 13 for three different temperatures i.e.  $25$ ,  $70$ , and  $90^{\circ}$ C. From these figures decisions can be drawn that Zone-A reservoir is appropriate to use 500 ppm of HPAM-2 with viscosity of about 3.4 cp at 132 sec-1 shear rate at reservoir temperature of 90°C, while Zone-B reservoir will use 500 ppm of HPAM-1 with viscosity of 4.12 cp at  $132 \text{ sec}^{-1}$  shear rate and reservoir temperature.

The selection of the polymers and its concentrations are based on the measured viscosity,

**Table 7 Permeability Reduction Evaluation**

Core	Permeability			
	(mD)		<b>PRF (%)</b>	
	$K_{w\text{-initial}}$	585.69	100.00	
Zone-A	Kp	154.56	73.61	
	$K_{w\text{-final}}$	322.31	44.97	
	$K_{w\text{-initial}}$	84.08	100.00	
Zone-B	Kp	24.17	71.25	
	$K_{w\text{-final}}$	54.86	34.75	

the viscosity must be at least similar or above the viscosity of displaced oil to create more favorable displacement efficiency.

# **C. Filtration Ratio**

To ensure whether a polymer solution is free from aggregates or solid due to precipitation, coagulation, and degradation it may be screened on sand faces during injection and plugging formulation. Filtration tests were done only for the selected solution such as 500ppm HPAM-1 and HPAM-2. To reduce uncertainty, firstly the formation waters of Zone-A and Zone-B must be screened. About 500cc of the solution are pumped through a 5 micron filter membrane with a different pressure of 2 bars. The flow rate is measured vs. time, and it should remain nearly constant during the test indicating it is free of aggregates.

Filtration Ration (FR) is defined as the time for 300th ml minus the time for the 200th ml divided by the time for the 200<sup>th</sup> ml minus the time for the  $100<sup>th</sup>$  ml and the equation is formulated as follow:

$$
FR = \frac{t_{300ml} - t_{200ml}}{T_{200ml} - t_{100ml}}
$$
 ...... (1)

The results of filtration test of those two polymer solutions are presented in Figure 14. Using the above equation of filtration ratio, both of 500ppm HPAM-1 and HPAM-2 solutions yield FR of about the same numbers of 1.035 proving that those solutions are free from aggregates. The value of FR for passing the selection criteria is about 1.2. FR below 1.2 is the range of a good category polymer for EOR project.

## **D. Thermal Stability**

Basically the resident time for a chemical stay in the reservoir is approximately between 6 months to 2 years, depending on the distance between injector and producer wells, and reservoir permeability. Because of the time span and temperature any polymers may experience degradation, break the chemical bond (thermal decomposition), and change their properties. In addition, the level of the salinity and pH of the reservoir brine also affect the polymer stability. In order to evaluate the capability of a chemical to withstand in high pressure and temperature environment, it is necessary to test the chemical properties stability under reservoir conditions. However, to minimize the time consuming, normally thermal stability is performed at elevated temperature as long as 3 until 6 months.

Thermal stability of polymer solution should be done under unaerobic condition; Figure 15 shows the diagram of thermal stability test ampoule at unaerobic condition. A special procedure allows vacuum degassing down to 10-20 parts per billion of oxygen. Prior polymer solutions should be deoxygenating with nitrogen flow for 20 minutes, and then load the sample solution into the ampoule bottles in glove box, quickly seal the glass ampoule mouth and store in the oven at reservoir temperature such as: 90°C.

The result of thermal stability test is presented in Table 5. Thermal stability is expressed as percent of the viscosity retained after a chosen period of high temperature exposure. Viscosity may be measured at reservoir temperature after and before ageing in the reservoir condition. Table 5 indicates that the viscosity reduction of the selected polymer is only 2.18 and 2.94%. These numbers identify that those two polymers are appropriate for EOR proposal each for Zone-A and Zone-B. Passing grade for the thermal stability is normally 20% of viscosity reduction after thermal test.



**Rheology of 500ppm HPAM-1 in Zone-A FW**



**Figure 3 Rheology of 1000ppm HPAM-1 in Zone-A FW**



**Figure 4 Rheology of 1500ppm HPAM-1 in Zone-A FW**



**Rheology of 500ppm HPAM-2 in Zone-A FW**



**Figure 8 Rheology of 500ppm HPAM-1 in Zone-B FW**



**Figure 6 Rheology of 1000ppm HPAM-2 in Zone-A FW**



**Figure 9 Rheology of 1000ppm HPAM-1 in Zone-B FW**





**Figure 10 Rheology of 1500ppm HPAM-1 in Zone-B FW**

#### **E. Retention**

This work is actually to determine the amount of polymer lost during flow in porous media or reservoir rock. Four methods are normally suggested to measure the magnitude of polymer lost on to rock surfaces; they are large slug method, multiple slug retention method, recirculation method, and static method. The first three methods are also called dynamic methods.

Retention of polymer on to surfaces of rock is mainly influenced by rock wettability. In addition, the type and size of polymer molecules, polymer concentration, and rock characteristics may also contribute into the adsorption rate. Therefore, preserved native core is suggested for adsorption experiment. In case only available unpreserved core, a clean and dry core should be restored to field condition to obtaining representative results.

Polymer adsorption is normally assumed irreversible with polymer concentration and reversible with salinity concentration. A Langmuirtype isotherm model is used to describe the polymer adsorption onto the rock surface.2 Polymer molecules adsorb onto the rock surface as a monolayer with the thickness equal to the diameter of the polymer molecule. Once the monolayer saturation level is reached, no more adsorption will occur. The adsorption of polymer on the surface of rock normally can be written as  $\mu$ g/g. Frequently, in flow through porous media, retention is quoted in mass of polymer per unit volume of rock  $(\Gamma_m)$ . The most common field unit for this is lb/acre-foot (lb/AF) and written down as follow:



- $\Gamma_{\rm m}$  = x 2.7194  $\rho_{\rm R}$  lb/AF ...... (2)
- Γm : polymer adsorption per unit volume of rock lb/AF
- $x :$  polymer adsorption  $\mu$ g/g
- $\rho_{\rm p}$  : bulk rock density g/cm<sup>3</sup>

In this experiment the static method is proposed due to easier and more practical. Static adsorption tests can provide a preliminary screening of polymers. The tests are fairly simple and inexpensive compared to procedures involving flow in cores. The result of the static adsorption tests of both HPAM on reservoir rocks are presented in Table 6. Adsorption polymers on to rock are about 240 and 250 µgr/gr rock. These numbers are considered high, therefore a dynamic adsorption is suggested to be performed to get a more realistic number.

The dynamic retention includes not only adsorption but also determine other polymer lost processes due to<sup>3</sup>:

- Polymer adsorption
- Mechanical entrapment
- Hydrodynamic retention

#### **F. Injectivity Test**

Injectivity test actually measures the capability of polymer solution to flow through the reservoir rock at approximately constant rate during the injection period. The term of injectivity is sometime used at the same meaning with permeability reduction, permeability reduction factor (PRF), resistance factor (RF), and residual resistance factor (RRF). All of those terms relate with permeability reduction measurement during polymer injection.



**Rheology of 1000ppm HPAM-2 in Zone-B FW**

Even though the high polymer viscosity could improve the mobility ratio in some extent it may create permeability impairment. Some of the adsorption polymer on to rock surfaces is irreversible; therefore it could reduce permeability permanently. The ratio between the mobility of water to that of polymer solution is defined as resistance factor, while the ratio of the water before and after polymer flooding is called residual resistance factor.

In this experiment, the permeability reduction factor is the only parameter measured to observe the polymer injectivity. Three kinds of permeability have been computed, i.e during initial waterflood, injected polymer, and chase water injection. Table 7 shows the results of PRF indicating that those two polymer solutions significantly change the permeability in between 71 and 74% reduction during polymer flooding, and then retains the permeability impartment of 35 to 45% as the permanent permeability reduction. These phenomena are normally occurrence during polymer flooding, the magnitude of permeability reduction depends on the type and size of polymer molecules, polymer concentration, and rock characteristics i.e. permeability, porosity, and rock minerals composition.

### **VI. CONCLUSIONS**

Polymer as mobility control in any EOR project should fulfill the selection criteria and passing the screening tests which include rheology, filtration, thermal stability, retention/adsorption, and injectivity or permeability reduction tests. The assessment of polymer HPAM-1 and HPAM-2 candidates for Zone-A and Zone-B are done and some of conclusions can be withdrawn as follows:

- 1. Zone-A reservoir is appropriate to use 500ppm of HPAM-2 with viscosity of about 3.4 cp at reservoir temperature of 90°C, while Zone-B reservoir will use 500ppm of HPAM-1 with viscosity of 4.12 cp at reservoir temperature.
- 2. Filtration ratio both of 500ppm HPAM-1 and HPAM-2 solutions yield FR of about the same numbers of 1.035 is the range of good category polymers for EOR project.
- 3. Thermal stability expressed as viscosity reduction reveals that the viscosity reduction of both polymers are only 2.18 and 2.94%. These numbers identify that those two polymers are appropriate for EOR proposal.



**Figure 13 Rheology of 1500ppm HPAM-2 in Zone-B FW**



**Figure 14 Filtration Tests Result**



4. Adsorption of polymers on to rock are about 240 and 250 µgr/gr rock. These numbers are considered high, therefore a dynamic adsorption is suggested to be performed to get a more realistic number.

- 5. PRF indicates that those two polymer solution significantly change the permeability in between 71 and 74% reduction during polymer flooding, and then retain the permeability impartment of 35 to 45% as the permanent permeability reduction. These phenomena are normally occurrence during polymer flooding.
- 6. In general HPAM-1 and HPAM-2 fulfill the criteria for injection fluid at Zone-B and Zone-A reservoirs respectively.

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