

Simulation Study of Macromolecules Inaccessible Pore Volume Mechanism in Heterogeneous Porous Media

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Abstract: *Polymer is one kind of macromolecules that commonly used in petroleum industry to improve oil recovery. Understanding the propagation mechanism of polymer in porous media is critical to a successful polymer-flooding project. However, the transportation of polymer through porous media is complicated especially when inaccessible pore volume (IPV) is considered. With literature review, many factors including fluid properties, rock properties and operations can influence behavior of IPV for polymer flooding. This paper collected the data from literature review and investigated the main factor that contributes to the IPV value analytically. The data analytics result shows that the solid entrapment may be the main reason conducting the IPV. Salinity, porosity and shear rate could be the most influencing factors on IPV value of specified polymer. Based on concept of IPV and the influencing factors, this paper also deployed a correlation model to the current simulator in oil industry.*

Keywords: Polymer, flooding, inaccessible pore volume, IPV

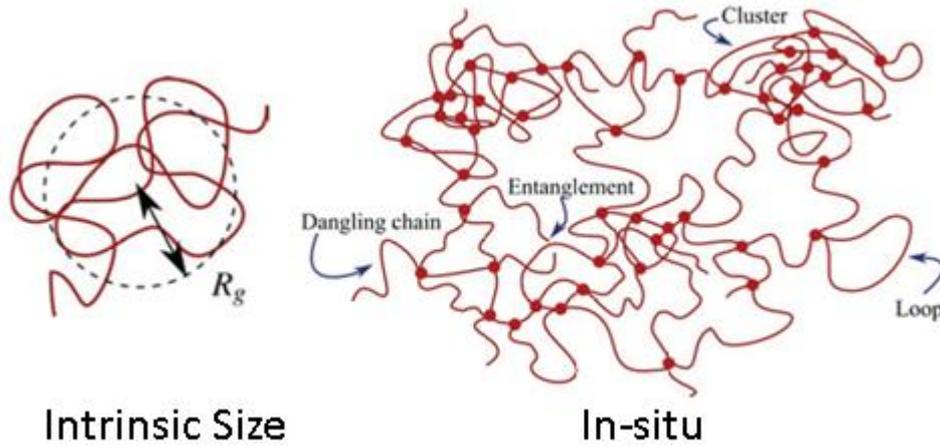
1. Introduction

Polymer flooding has been proven as a cost-effective chemical-EOR method. It can improve sweep efficiency by controlling fluid mobility. However, researchers observed the existence of excluded connected volume when polymer flow through porous media even at very fine mobility ratio ($M < 1$) (Dawson, 1972. Di Marzio, 1970). This fraction of connected pore volume is inaccessible for polymer molecules but accessible for solvent water, which is called inaccessible pore volume (IPV) for polymer. With reported, IPV values are very inconsistent and range from 0 to 48% of pore volume. As a result, optimization of IPV can additionally improve sweep efficiency of polymer flooding, which would result in a more favored polymer flooding efficiency.

The most agreed reason for IPV is summarized in (Dawson, 1972. Liauh, 1979. Shah, 1978), that polymer molecules sizes are larger when compared to solvent molecules and pore sizes. Furthermore, by adsorption on the rock and entrapment by pore throat during polymer flooding, polymer retention can further decrease the pore size. Another reason is that the depletion effect of large molecules builds up a depletion layer at the pore wall and makes the mass centers

of polymer molecules cannot reach the pore wall (Chauveteau, 1981. Sorbie, 1989. Omari, 1989). Third reason is the unfavored entropic effects push polymers away from solid boundaries (Liauh, 1979. Di Marzio, 1965). However, the second and third reasons lose some credibility when polymer can adsorb on the rock surface.

Some researchers criticize these explanations for IPV. Because the polymer molecule diameter (HPAM in 3% NaCl brine) is typically 0.5~0.8 microns (Sorbie 1991) while average pore throat diameter for 470 md Berea sandstone was reported over 6.7 microns (Seright, 2006). Clearly, the pore throat is more than enough for polymer molecule to pass through. However, researchers all agreed the existence of IPV, though mechanism for IPV is under debate. The author supposed that the hydrodynamic radius of polymer spherical coil should be counted as in-situ polymer radius instead of intrinsic radius. Because polymer is a kind of soft matter and its coils can elongate by several hundred times of their initial length under shear. Moreover, the solvent molecules can permeate into polymer colloids, swell the polymer solute and further increase the hydrodynamic radius polymer solution which is shown in figure 1 (M. Doi, 2013).



Intrinsic Size

In-situ

Figure 1: Real In-situ Condition Polymer Illustration vs Static Condition

To prove this point, several researchers reported that the difference between polymer apparent in-situ viscosity and intrinsic viscosity measured by rheometer has strong relationship with IPV behavior (G. Chauveteau, 1984. Ferreira, 2018. Stavland, 2010). The result indicates that the hydrodynamic radius of polymer spherical coil could be much higher than static state molecule radius and cause the polymer unable to penetrate into some part of connected pore volume.

2. Data Analysis

To analysis the sensitivity of each parameter, we collected IPV data from 132 experiments (Ref. 17-32). The relationship between influencing factor and IPV value is plotted in cross plots shown in figure 2.

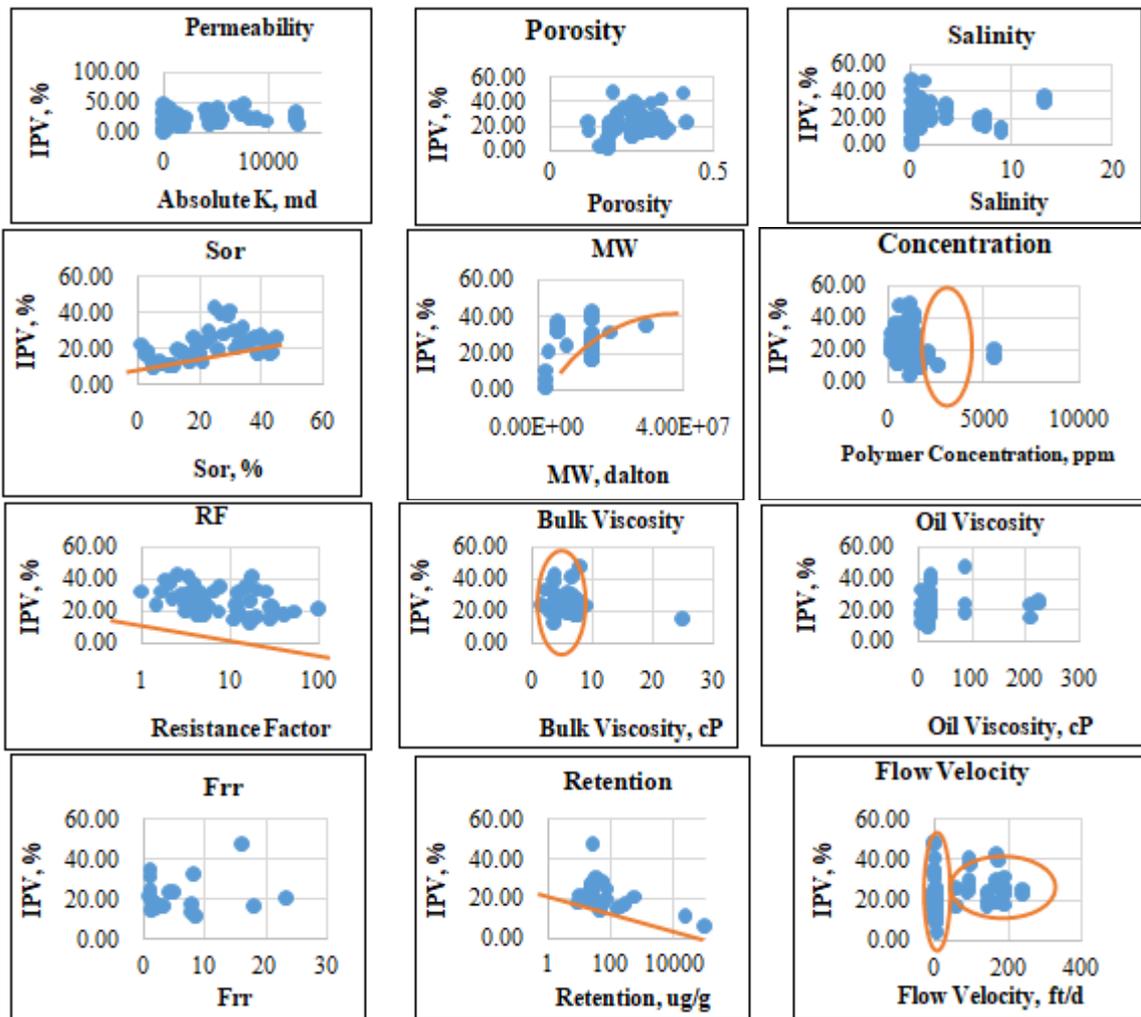


Figure 2: Crossplots for Influencing Factors on Inaccessible Pore Volume

Based on the data set we collected from literature, we can obtain some analytical result listed below:

- 1) Sor can influence IPV value negatively.
- 2) Moleweight of polymer may have a positive effect on IPV value and the relationship is more likely semilog.

- 3) Resistance factor may have a negative effect on IPV.
- 4) The higher retention of polymer, the lower IPV could be.
- 5) Concentration and bulk viscosity of polymer tends to be very low for obvious IPV value.
- 6) Flow velocity (proportional to shear rate) falls at low velocity range and ultra high velocity range (>100 ft/d).

These observations tend to indicate that most of the experiments having a relatively low viscosity of polymer. Velocity range (shear rate range) also provide evidents for this point. Increasing shear rate, polymer especially HPAM can behave a shearthinning (decreasing viscosity at low shear rate range) and then shearthickening (increasing

viscosity at medium shear rate range). The ultra high shear rate may most likely conduct a mechanical degradation for polymer, which can decrease polymer viscosity sharply. The velocity range falls at two separated parts at low velocity and ultra high velocity contributing to our inference.

The reason for this is simple to understand. Since IPV measurement needs polymer breakthrough earlier than solvent, if viscosity of polymer is much higher than solvent (eg. Water), the velocity advance results from IPV cannot overcome retarding by viscosity. The IPV may not be obvious to measure.

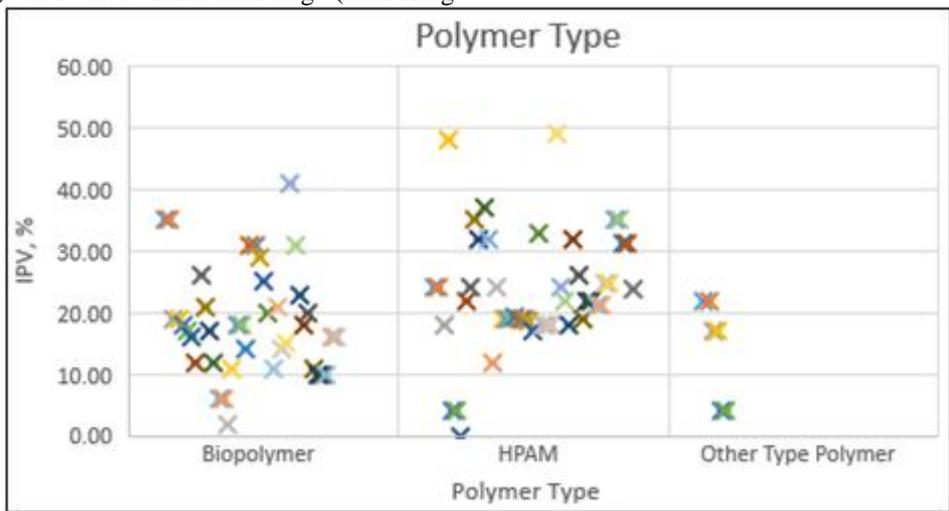


Figure 3: IPV Distribution for Type of Polymer

Polymer type is concluded in Fig 3. The result shows that IPV value is not very sensitive to polymer type because the distribution of each type polymer seem to be all the possible IPV range. The color scale in the plot refers to different cases.

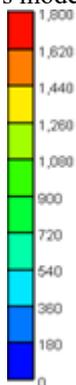
Discussion about Heterogeneous Two-Layer Model:

Polymer flooding in oil industry is commonly used for sweep efficiency improvement. If IPV model in simulator can represent its behavior in experimental result is significant for a successful polymer flooding simulation. However, in current most used simulator for EOR simulation in U.S., CMG, the IPV model cannot fully represent the mechanism. Since concentration is independent with IPV in STARS, two layers will have same concentration of polymer. To illustrate this result, we used a double layer simple CMG STARS model mimicking a core scale polymer flooding process. 1800-ppm polymer solution was injected into two layers model from “INLET”.

Figure 4: Polymer Concentration Distribution, ppm

The figure 4 shows polymer concentration distribution after 60 minutes with injection flow rate 0.1 cc/min. Layer 1 has IPV=0.3, Layer 2 has IPV=0 without crossflow. The polymer front for layer 1 is penetrating deeper than layer 2. The concentration peak along core for both layers can be seen from figure that equal to 1800 ppm. This is not convincible since layer 2 should allow more polymer molecules flow in than layer 1 because of more accessible pores.

In order to better mimic polymer flow regarding of existence of IPV, for pore size larger than critical value that polymer can flow through, distribution of polymer molecules when injected into each layer should be related to each layer’s accessible pores size shown in figure 5.



Molecule distribution

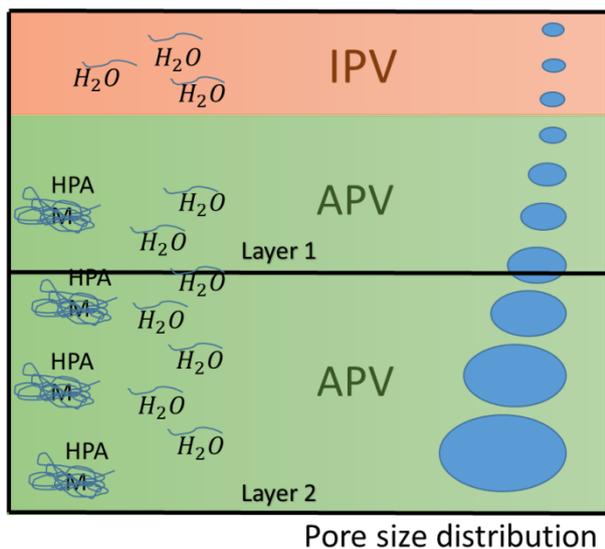


Figure 5: Conceptual Illustration for Molecule Distribution at “INLET” for Two Layers

Figure 5 shows a cross section of the two-layer model. Pink zone is marked as IPV zone. Green zone is marked as APV zone. H₂O molecules with smaller diameters can penetrate to both IPV and APV zones, whereas HPAM molecules with larger diameters can only penetrate to APV zone.

It is very clear that given same concentration in both layers can result in error for polymer flooding efficiency. As a result, we have to correlate concentrations for polymer in porous media flow and build a model based on experimental theories.

Correlation of Concentration:

The concentration in a pore can be a function of pore size and polymer molecular weight. Several researchers investigated experiments for HPAM molecules distribution in APV zones based on ratio of pore radius to polymer molecule radius (Liauh, 1979. M Ali, 2017). Experimental data with same polymer size and different pore size core flooding is fitted using exponential function with 95% confidence bounds shown in figure 6.

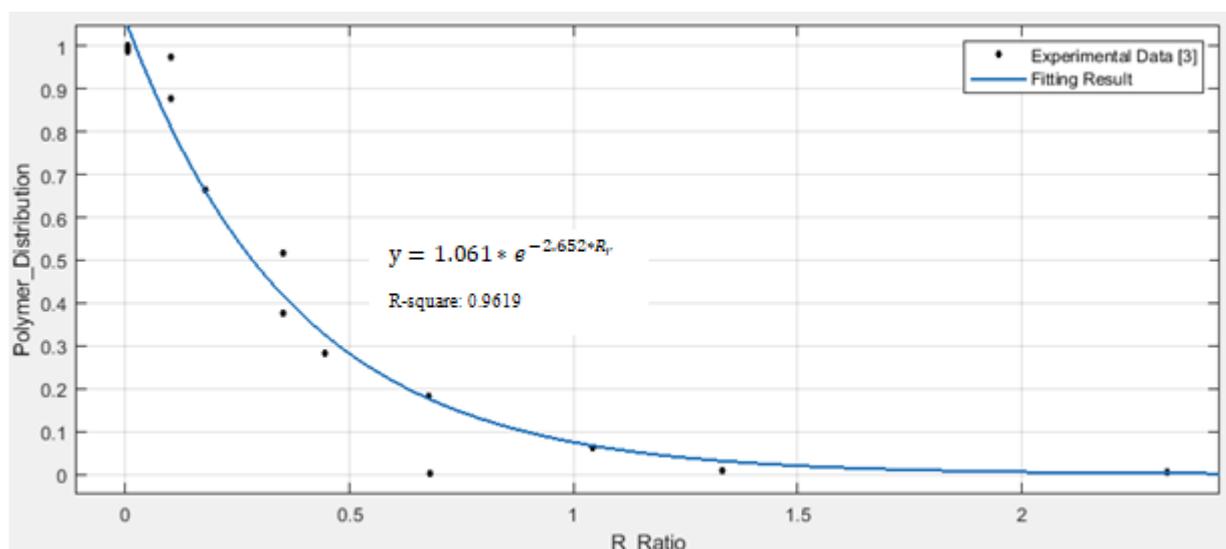


Figure 6: Polymer Molecules Distribution (PMD) vs Radius Ratio ($R_{polymer} : R_{Pore}$) (Marked as R_r)

The fitting result can be expressed in equation 10:

$$PMD = 1.061 * \exp(-2.652 * R_r) \dots \dots (10)$$

Based on the experimental results, more polymer molecules will flow into larger pores and less molecules flow into smaller pores. These experimental results can be illustrated

using figure 8. Based on the same polymer molecule size, the larger the radius ratio R_r is, the less polymer can flow in the pores. For instance, 8% of polymer will flow through pore size with $R_r=1$, 20% of polymer will flow through pore size with $R_r=0.65$ and 50% polymer will flow through pore size with $R_r=0.27$.

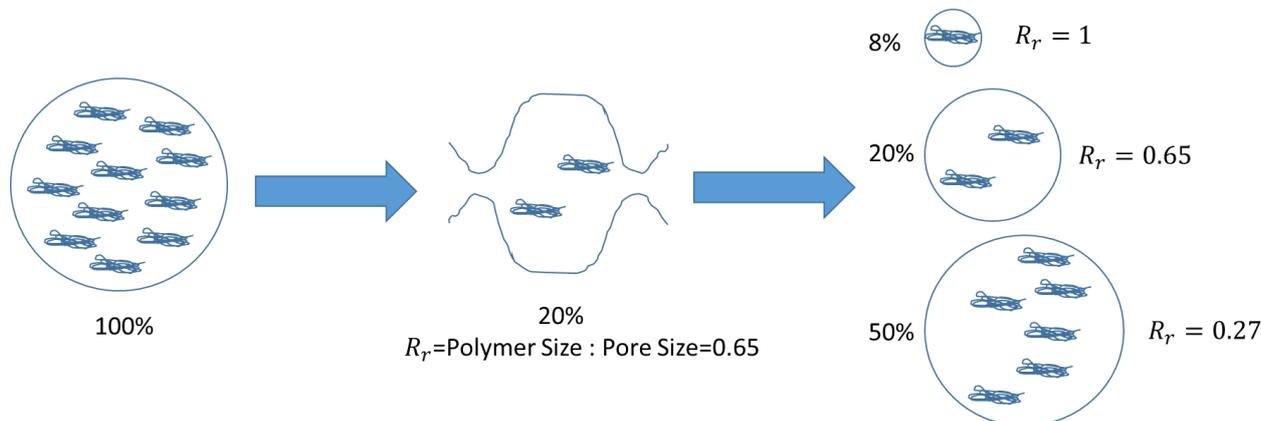


Figure 7: Polymer to Pore Radius Ratio (Rr) Relationship with Polymer Distribution

As a result, with same flow rate, higher IPV will cause smaller APV and in result, a higher velocity is achieved by polymer component to keep material balance. At the same time, considering insensitive to IPV by water molecules, the concentration of polymer component will be lower. With this analysis, all three software cannot correctly reflect the IPV effect on polymer flow.

Based on experiments did by (Liauh, 1979), polymer molecules distribution result is shown in figure 6. Then polymer mole fraction flowing in-to the core can be expressed using equation 11:

$$X_L = \frac{\int_{R_{r,IPV}}^{R_{r,max}} PMD dR_r}{\int_{R_{r,min}}^{R_{r,max}} PMD dR_r} \dots \dots (11)$$

Where, X_L is mole fraction of polymer in the core. $R_{r,min}$ is minimum radius ratio. $R_{r,IPV}$ is critical radius ratio that polymer can propagate through the pore. $R_{r,max}$ is the maximum radius ratio.

Flow rate of polymer injected from inlet:

$$Q_p = Q * C_p \dots \dots (12)$$

Flow rate of polymer flow into APV:

$$Q_{p,APV} = Q_p * X_L \dots \dots (13)$$

Inlet concentration for polymer:

$$C_p = \frac{Q_{p,APV}}{Q} \dots \dots (14)$$

Concentration in IPV is 0 and IPV is calculated assuming that pore radius (R_p) distributes evenly and polymer radius keep constant:

$$IPV = \frac{\int_{R_{r,IPV}}^{R_{r,max}} 1/R_r dR_r}{\int_{R_{r,min}}^{R_{r,max}} 1/R_r dR_r} \dots \dots (15)$$

IPV Sensitivity Analysis with Correlated Model

3. Mathematical Model

A correlation for concentration distribution is set up. The core model used is illustrated in figure 8.

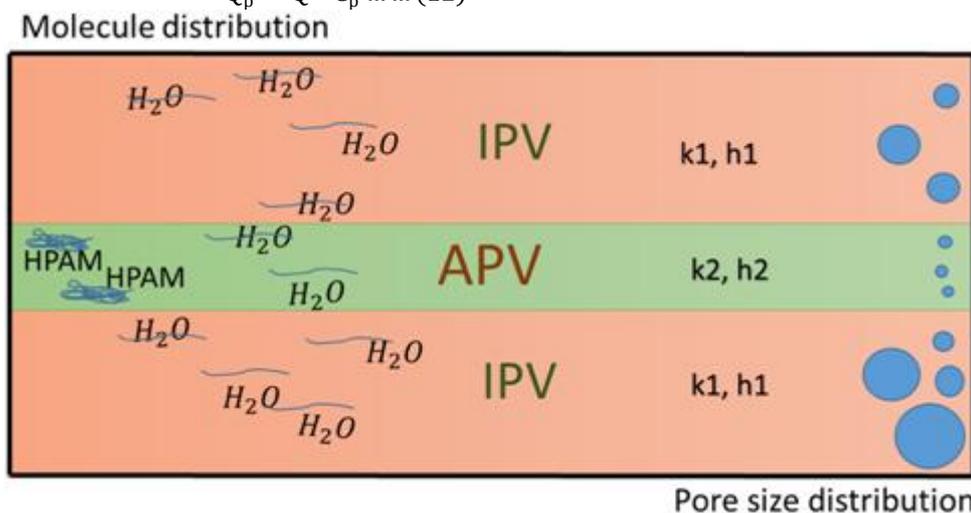


Figure 8: 1D Core Model with Consideration of IPV

Assuming: Only one layer in the core contains IPV, which means some of pore volume is not accessible to polymer, and APV where is freely accessible to polymer; Incompressible fluid flow; Darcy's law equation applied; No movable oil considered; No crossflow. A fractional flow model that is used to conduct sensitivity analysis is shown below.

$$\begin{cases} \nabla(v_w f_w) + \frac{\partial(\phi S_w)}{\partial t} = 0 \\ \nabla(v_p f_p C_p) + \frac{\partial(C_p \phi_p (S_p))}{\partial t} = 0 \dots \dots (9) \\ \nabla(v_w f_w C_t) + \frac{\partial(\phi C_t S_w)}{\partial t} = 0 \end{cases}$$

$$B.C.: \frac{\partial(vf_w C)}{\partial y} = \frac{\partial(vf_w C)}{\partial z} = 0 \text{ for all time } C|_{x=0} = C_{inlet} \quad C|_{t=0, x \neq 0} = 0$$

Where, $f_w = \frac{M_w}{M_w + M_o}$, M is phase mobility. $\phi_p = \phi * (1 - IPV)$, $S_p = S_w * (1 - IPV)$, C_p is polymer concentration, C_t is tracer concentration.

4. Model Description

Table 1: Specification of the Correlated Model for Sensitivity Investigation

Layer Num	Model Length, cm	Cross-section Area, cm ²	Porosity	Permeability, md	Sor
1	4.4	4.5	0.329	100	0.355
Polymer Concentration, ppm	Tracer Concentration, ppm	Polymer MW, Dalton	Layer Thickness, cm	Model Width, cm	Permeability, md
1800	1000	1.8E7	3	1.5	100

Assumptions

In this sensitivity analysis model, minimum radius ratio is assumed as 0.1, and maximum radius ratio is assumed as 2.5 in the sample core. Specification of the model is listed in table 1.

5. Result

Three cases with $R_{r,IPV} = 1.5, 1, 0.5$ respectively were investigated using the correlated model. The corresponding IPV for three cases are 15.87%, 28.47%, 50% which is calculated using equation 15. The results for polymer profile distribution along the core direction after 1 minute and 10 minutes of polymer flooding are shown in figure 9. Injection rate is assumed constant at 0.1 cc/min.

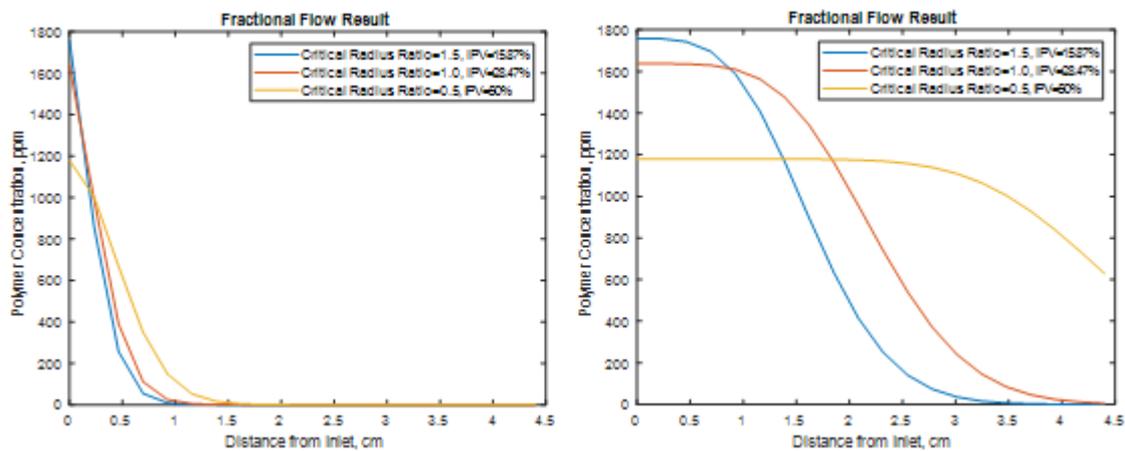


Figure 9: Concentration Profile after 1 min (left) and 10 min (right) of Polymer Flooding

The result indicates that the polymer front moves faster for higher IPV value case than lower IPV value case. At the same time, the concentration for polymer is decreased with decreasing IPV value. It means that the model can treat IPV effectively on both polymer flow velocity and concentration sensitivity.

With experiments (figure 6) using sandpack polymer core flooding, we noticed that for 1800 ppm HPAM, the adsorption could be as high as 1.9 mg/g and max Frr could be 4. This result is implemented in the correlated model. The result of Frr along with changing IPV are shown in figure 10.

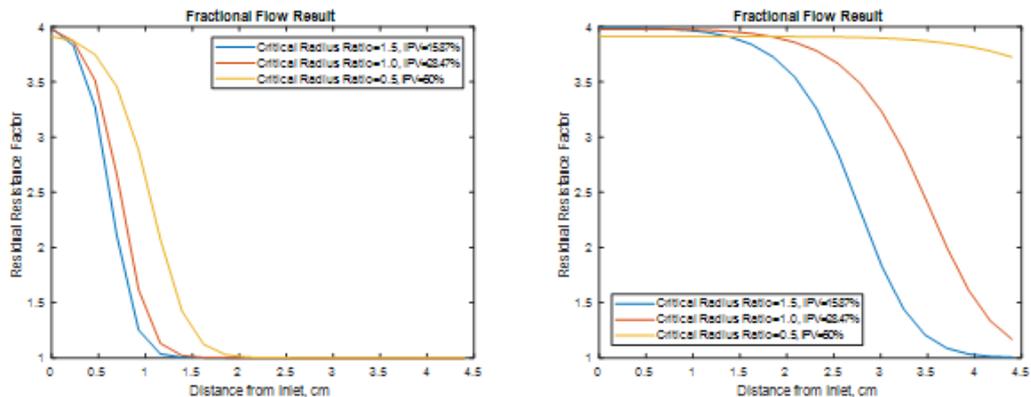


Figure 10: Residual Resistance Factor at 1 min (left) and 10 min (right) of Polymer Flooding

Difference on Max Frr results among three cases are not apparent. This is because the adsorption curve for polymer concentration range from 1200 ppm to 1800 ppm varies very limited shown in figure 6. The influencing front velocity for polymer residual resistance factor is very sensitive to IPV.

Frr can varied a lot when IPV is very high. This can be shown compared with extreme case in figure 11, where three cases with $R_r = 1.5, 0.5$ and 0.1001 respectively are investigated. The IPV for three cases are 15.87%, 50% and 99.97%.

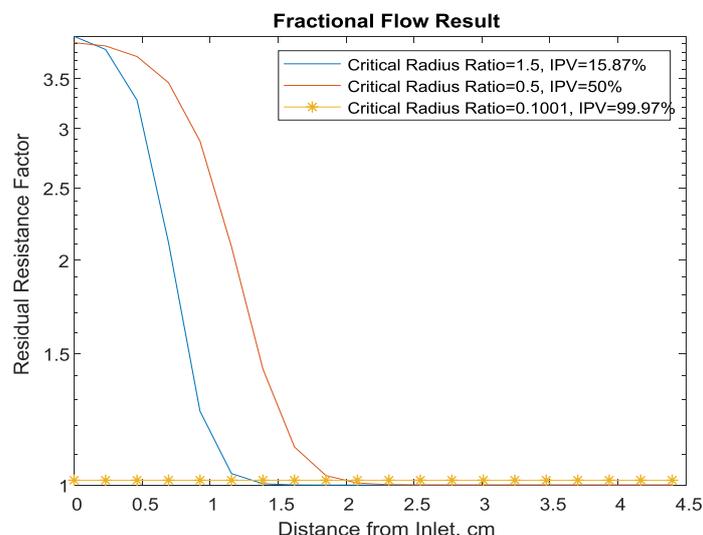


Figure 11: Residual Resistance Factor at 1 min of Polymer Flooding Considering Extreme Case

IPV=99.97% case refers to matrix where polymer can be almost denied from flow in. The star line in figure 11 shows this case Frr distribution, which shows nearly no Frr can be generated in this kind of formation. As a result, for formation with relatively large IPV, very limited damage can be done to this formation by polymer flooding. This result can be very beneficial for conformance control using polymer or gel treatment and the result can match the experimental data better than commercial software result.

6. Conclusion

Inaccessible pore volume has been a key influencing factor for successful conformance control in petroleum industry. With reported, IPV values are very inconsistent and range from 0 to 48% of pore volume. Optimization of IPV can improve sweep efficiency of polymer flooding, which would result in a more favored polymer flooding efficiency. But ignoring the effect of IPV on concentration and retention can result in inaccurate prediction on conformance control efficiency.

Data analysis indicates a relatively positive attributes of Sor, MW, Porosity to IPV, and negative attributes of RF, Frr to IPV. Low viscosity range of IPV indicates the measurements need a close viscosity of polymer to water solvent.

Results of sensitivity analysis indicate that the higher the IPV is, the higher velocity of polymer front and lower concentration of polymer contained in the core. Meanwhile, Frr is sensitive to IPV, and for low permeability zone with ultra-high IPV value, the polymer flooding can barely damage the low permeability zone because Frr in low permeability zone is nearly ignorable.

The correlated model built in this paper can fully describe the polymer concentration change related to inaccessible pore volume and velocity difference based on molecule size

to pore size ratio. Compared with commercial software, this paper's correlated model can better represent polymer distribution and retention in heterogeneous reservoir. Moreover, the correlation can be easily integrated in commercial software.

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