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Abstract

Understanding polymer transport through porous media is key to successful field implementations, including well conformance control and EOR processes. Polymer retention is typically assessed indirectly through its effect on pressure drops and effluent concentrations. Microfluidic techniques represent convenient tools to observe and quantify polymer retention in porous media. In this paper, we demonstrate how a soft-lithography microfluidics protocol can be used to gain insights into polymer transport mechanisms through rocks.

The design of the microfluidic chips honors typical pore-size distributions of oil-bearing conventional reservoir rocks, with pore-throats ranging from 2 to 10 μm . The fabrication technology enables the design transfer on a silicon wafer substrate using photolithography. The etched wafer holding the negative pattern of the pore-network served as a mold for building the microfluidics chip body out of polydimethylsiloxane (PDMS). The oxygen plasma bonding of the PDMS to a thin glass slide resulted in a sealed microfluidic chip, conceptually referred to as “Reservoir-on-a-Chip”. We conduct single-phase polymer flooding experiments on the designed chips to understand how polymer-rock interactions impact polymer transport behavior in rocks. These experiments allow for polymer transport visualization at the molecule-scale owing to the use of polymer tagging and single-molecule tracking techniques.

This study presents, for the first time, a direct visualization of polymer retention mechanisms in porous media. We identified three mechanisms leading to polymer retention: adsorption, mechanical entrapment, and hydrodynamic retention. Polymer adsorption on the chip surfaces resulted in flow conductivity reduction in specific pathways and complete blockage in others, inducing alterations in the flowpaths. This mechanism occurred almost instantaneously during the first minutes of flow then, dramatically diminished as adsorption was satisfied. In addition to static adsorption, flow-induced adsorption (entrapment) was also distinguished from the binding of flowing polymer molecules to the already adsorbed polymer layer. Evidence of polymer desorption was observed, which consents with the presumed

reversibility character of polymer retention mechanisms. The narrowest channels along with the reduced area due to adsorption, created favorable conditions for polymer entrapment. Both mechanical and hydrodynamic trapped polymers were successfully imaged. These phenomena led to polymer clogging of the porous network, which is one of the major concerns for operational aspects of polymer flooding processes.

Better understanding and quantification of polymer retention in porous media can help to make better decisions related to field-scale implementations of polymer-based processes in the subsurface. In this study, we used a soft-lithography fabrication technique and single-molecule imaging, to show, for the first time, polymer transport insights at the molecule- and pore-scales. This approach opens a new avenue to improve our understanding of the first principals of polymer retention while flowing through porous media.

Introduction

Over the last four decades, significant efforts in the literature have been devoted to study and quantify polymer retention in reservoir rocks, motivated by its impact on the design of optimum EOR schemes (Al-Hajri et al. 2018). Various experimental studies showed that polymer retention is influenced by many factors including polymer type, molecular weight, degree of hydrolysis and concentration, rock pore-throat size distribution and permeability, wettability, and the reservoir's salinity and temperature (Lakatos, Lakatos-Szabó, and Tóth 1981; Rashidi et al. 2009; Sheng 2011; Broseta et al. 1995; Zhang and Seright 2013; Huang and Sorbie 1993; Miklos T. Szabo 1972; Smith 1970).

Sorbie (Sorbie 1991) proposed three different mechanisms that contribute to the overall retention of polymer during flow into porous rock, namely polymer adsorption, hydrodynamic retention, and mechanical entrapment. Polymer adsorption, driven by fluid/rock surface forces, may occur at static and dynamic conditions, while hydrodynamic retention and mechanical entrapment occur at dynamic conditions during flow. The contribution of each constituent, static and dynamic, to the total retention, can be inferred experimentally by measuring polymer adsorption on crushed rock, and polymer loss during coreflooding. However, conclusive measurements of each separate entrapment mechanism at dynamic conditions are currently unavailable. Consequently, it is challenging to develop an accurate model to capture polymer retention from all mechanisms, given that each mechanism is driven by different parameters and forces (L. W. Lake 1989; Sorbie 1991). The current heuristic approach in petroleum engineering literature that suggests using pseudo-adsorption to capture total polymer retention is unreliable (L. W. Lake 1989). The objective of this work is to provide a close look at understanding the separate retention mechanisms using microfluidics and imaging technologies, which would help to develop more accurate models.

The interaction between the rock surface and the polymer molecules in the aqueous phase is referred to as adsorption, which is a well-studied, yet complex and not fully understood phenomenon. This interaction causes polymer molecules to bind and attach to the rock grain surface mainly by physical adsorption, driven by van der Waal's and hydrogen bonding rather than by chemisorption (Cohen and Christ 1986; Hirasaki and Pope 1974; Klein and Kulicke 1980). Depending on the polymer/rock interactive properties, adsorption could be the primary mechanism for polymer retention, contributing as high as 60% of the total retention (Necmettin Mungan 1969). However, in other situations, the relative contribution of adsorption could be much lower (below 20%) compared to the contributions of the other entrapment mechanisms. For instance, polymer adsorption increases with decreasing molecular weight (i.e., lower adsorption with higher molecular weight); nonetheless, lab and field observations show that the overall polymer retention increases with increasing molecular weight.

The Langmuir isotherm is commonly used to model polymer adsorption in field-scale EOR applications. The model is influenced by multiple factors, among which polymer type and concentration, and water salinity are the most prominent (Sorbie 1991).

The hydrodynamic entrapment is defined by the proportion of polymers trapped in stagnant zones, no-flow area, or secondary flow zones at the pore-scale level, where the pore throats act as a filter for the polymer. This mechanism is a function of flow rate and tortuosity, which is not well understood and difficult to quantify (Chauveteau and Kohler 1974). This mechanism is believed to have a minimal effect at the field scale (Chen et al. 2016; Zhang and Seright 2015b).

On the other hand, retention by mechanical entrapment occurs when larger polymer molecules become lodged within narrow flow channels. Mechanical retention is a function of the ratio between the effective hydrodynamic radius of the polymer and the rock pore-throat radius, which is more pronounced in low permeability reservoir rocks (M. T. Szabo 1975; Gogarty 1967; Dominguez and Willhite 1977; Smith 1970). Oversized polymers may damage the formation, and therefore the proper polymer molecular size should be carefully selected (Sorbie 1991).

Polymer retention may accumulate near-wellbore leading to continuous deteriorating of well injectivity that may jeopardize the success of the project. The retained polymer introduces both an additional unexpected resistance to flow and loss of the polymeric material from the injected solution. On the other hand, the resistance factor induced by polymer retention may improve the polymer flood sweep efficiency and, eventually, the oil recovery factor. Polymer retention often reduces the effective permeability of the aqueous phase, especially in water-wet formation, thus retarding water breakthrough, without significant alteration of the oleic phase permeability. This mechanism helps to further reduce the water/oil mobility ratio beyond the expected reduction from viscosity enhancement (Barreau et al. 1997; Zaitoun and Kohler 1988; Barrufet and Ali 1994). Therefore, a successful field implementation requires, among other parameters, careful selection of the optimum polymer type that balances the pros and cons of polymer retentions (Sorbie and Seright 1992; Seright, Seheult, and Talashek 2009; Lotfollahi et al. 2015; Santos, Torrealba, and Hoteit 2020; Torrealba and Hoteit 2019; Dwarakanath et al. 2016).

Controversies regarding the relation between polymer retention and flow resistance were flagged since early experimental studies in the literature. Some experimentalists (Jennings RR, Rogers JH, and West TJ 1971; Smith 1970) claim little or no interrelation between polymer retention and flow resistance. For instance, in calcareous formation, the flow in macro-sized heterogeneity bodies such as thief layers and fractures may not be impacted by permeability perturbation from polymer adsorption on the rock surface (Townsend and Becker 1977).

However, others (N. Mungan, Smith, and Thompson 1966; Necmettin Mungan 1969) observed a strong dependency between the two phenomena and attributed the increase in flow resistance that could not be achieved solely by the viscoelastic properties of the solution, to polymer retention. This mechanism is known as the residual resistance factor, which represents a measure of irreversible permeability reduction relative to pre-polymer waterflood (L. Lake et al. 2014; Huh, Lange, and Cannella 1990).

The characteristic of reversibility or irreversibility of polymer retention and permeability reduction is not well understood. Some studies suggested that the irreversibility of polymer retention occurs when adsorption and mechanical entrapments are predominant (D'Angelo, Chertcoff, and Rosen 2003), while reversibility may occur when hydrodynamic entrapment is predominant (Al-Hajri et al. 2019).

Other studies in the literature, based on coreflood experiments and field observations (Townsend and Becker 1977) experienced partial or total reversibility of polymer retention in dolomite-anhydrite formation after the injection of sufficient chase water. For instance, results showed that after 1.2 PV of injected water, more than 11% of the permeability was recovered. Other experimental results showed that even after 100 PV of injected chase water, permeability in the core was not restored entirely, which indicates partial reversibility (Seright 2016, 2017). Hoteit et al. (2016) confirmed this behavior and emphasized that the typical models, adopted in reservoir simulators, that assume irreversibility are unrealistic, and typically overestimate the recovery factor from chase water, which could mislead the design of the polymer-flood slug size.

Polymer retention is typically assessed indirectly from the pressure drop and effluent concentration profiles. Since the early eighties, Klein and Kulicke (1980) were among the first researchers to provide direct observation about polymer deposition (adsorption and other retention mechanisms) in porous media

utilizing Scanning Electron Microscopy, combined with energy dispersive X-Ray analysis. With the emerging science of microfluidics, numerous publications have addressed a different aspect of single-phase and two-phase polymer flood experiments in porous media such as sweep efficiency, flow divergence, recovery factor, and others (Gogoi and Gogoi 2019; Wang et al. 2015; M Buchgraber et al. 2011; Markus Buchgraber 2013; Lacey et al. 2017; Meybodi, Kharrat, and Wang 2011; Ghahremani et al. 2018). With this technology, a polymer is observed by the behavior of its hosting aqueous phase, which is seen as a homogenous phase. To our knowledge, the transport behavior of the polymer molecules within the hosting phase has not been reported previously.

In this paper, we used a soft-lithography fabrication technique, wide-field microscopy and single molecule tracking, to provide polymer transport insights at the pore-scale and to present dynamic visualization of the three main mechanisms of polymer retention in porous media. We show, for the first time, the behavior of individual polymer molecules, including adsorption, clustering, and transport within the aqueous phase while flowing within a microfluidic model mimicking a porous medium. This new approach opens a new avenue to improve our understanding of the first principals of polymer retention while flowing through porous media.

The paper is organized as follows: we first introduce the microfluidics design and fabrication workflow. Then briefly describe the characteristics of the polymer solution, and the experimental setup and methods used for the flow experiments and for image processing. The results are then discussed, where we emphasize the direct observations of three main mechanisms of polymer retention in porous media. The last part of the paper focuses on the reversible character of these mechanisms. We conclude the paper by summarizing the findings.

Micromodel design and fabrication

Microfluidic chips serve as a two-dimensional proxy to avoid the complexity of the three-dimensional porous network in rocks, which facilitate isolating and visualizing the mechanisms of interest that occur at pore-scale.

We designed the configuration of the 2D pore-structure micromodel to mimic a key feature related to the heterogeneous nature of rock pore throats. The design of the microfluidic chips consists of multiple identical flowing units, where each unit consists of parallel pore-throats (flow channels) with aperture ranging from 2 to 10 μm . These dimensions are within the range of pore-size distribution of oil-bearing conventional reservoir rocks (Browne, Shih, and Datta 2019; Gundogar et al. 2016). The microfluidic chip consists of five interconnected rows, with forty units each (see Figure 1). The array of flow units is designed to achieve several objectives: ensure repeatability of observations in different units, minimize the influence of boundary conditions, and prevent complete chip plugging. Besides, we incorporate two identical networks to serve as inlet and outlet for the fluids in the device.

The dimensions of the microfluidics device, conceptually referred to as “Reservoir-on-a-Chip”, is 1cm x 2cm, while a single flow unit is 150 μm in width and 72 μm in height. A flow unit structure is symmetric and consists of 5 channels with apertures 10, 5, 2, 5, 10 μm , respectively, as also appears in Figure 1 which shows a top view of the designed microdevice.

Figure 1: Schematics of the microfluidic device structure (left), including the pattern of the flow units (middle), and the channels within a flow unit (right).

We fabricated the microfluidic device at the KAUST nanofabrication labs out of polydimethylsiloxane (PDMS) using soft-lithography. However, our fabrication protocol did not follow a traditional procedure. We used an etched silicon wafer as a mold for the PDMS mixture to create superior quality in the smallest features. The fabrication techniques enabled us to transfer the design first to a chrome mask using laser lithography and then to a silicon wafer substrate through photolithography. The deep reactive ion etching is used to imprint the negative pattern of the pore-network, creating approximately 6 μm deep channels in the silicon wafer. The etched wafer served as a mold for the soft-photolithography technique, in which the microfluidics chip body was constructed out of PDMS, using a mixture of 10:1 ratio of the polymeric base to the currying agent. The channels for fluid flow were created by bonding the PDMS part with a glass slide, using oxygen plasma. Even though PDMS is a hydrophobic material, the plasma treatment modifies the chemistry of the PDMS surface that renders the surface to be more hydrophilic.

Polymer solution

We used a fluorescently-labeled polymer, Poly(fluorescein isothiocyanate allylamine hydrochloride), from Sigma Aldrich in our experiments. The polymer is cationic with 56000 Dalton molecular weight. The labeled polymer was excited at 488 nm and emission was detected through 540 $\pm$ 40 nm bandpass filter. Detailed specifications of the wide-field microscopy, are described in the following section. The polymer powder was dissolved in distilled water to obtain a polymer solution with a concentration of 10 $\mu\text{g}/\text{ml}$.

The experimental hydrodynamic size of polymer molecules in solution was determined using dynamic light scattering method. The measurements were done by using Zetasizer Nano-ZS instrument by Malvern Panalytical with 5s correlation time to minimize photo-induced agglomeration. The results showed bimodal distribution of the hydrodynamic diameter, centered at about 60 nm (individual polymer molecules with almost 100% relative abundance) and 4000 nm (polymer agglomerates, with minimal abundance), see in Figure 2. The results of the hydrodynamic size of polymers and the low abundance of polymer agglomerates compared to the polymer molecule are consistent with the direct observation of the polymer solution imaged during flow experiments by the epifluorescence microscopy setup, see the sections below.

Figure 2: Dynamic light scattering histogram illustrating the volume (left) and number (right) vs hydrodynamic diameter distribution of polymer molecules (60nm) and agglomerates (4000nm).

Experimental setup

The single-molecule fluorescence imaging experiments were conducted on a custom-built epifluorescence

microscopy setup. The setup consists of an inverted microscope (IX71, Olympus, Tokyo, Japan), illuminated with a CW 60 mW 488-nm laser (MLD, Cobolt). The 488-nm lasers passed through a FF01-488/6-25 excitation filter (Semrock, Lake Forest, IL, USA). The laser was introduced into the microscope through two $5 \times$ beam expanders (Thorlab, NJ, USA) and then through a focusing lens ($f=300$ mm). The laser lines were reflected to an Olympus UPLANFL N 20x NA0.5 objective lens by a FF506-Di03 25 $\times$ 36 dichroic mirror (Semrock). By means of an acousto-optical tunable filter (AOTF; AA Optoelectronics), the output of the excitation laser was synchronized to an iXon Ultra EMCCD camera (Andor Technology, Belfast, Ireland) to illuminate the sample only during image acquisition and thus to minimize photo-bleaching. After illuminating the sample and before being introduced into the camera, the fluorescence from single molecules was collected by the same objective lens and then passed through a FF01-540/50-25 emission filter (Semrock).

Methods

The flow experiments aimed to visualize polymer retention mechanisms occurring at dynamic conditions. In this respect, the data was acquired using a custom-built epifluorescence microscopy setup, which granted molecule-scale visual observation of polymer solution. The flow behavior of polymer molecules within the hosting aqueous solution and their interaction with the microfluidics device were captured.

The ports of the microfluidic chip were plumbed with blunt needle tips connected through polyethylene tubing at the inlet of the fluid holding vial open to the atmosphere, and at the outlet to a Harvard syringe pump. The microfluidics chip was initially saturated with the polymer solution by creating negative pressure in the system using a 10 μ l/min preset flow rate. After saturation, the pump was shut off, and fluids were flowing into the system as a result of tubing dilation, which created microscopic flow rates.

We conducted single-phase polymer flooding experiments on the designed chips to study the polymer transport behavior. These experiments allowed us to visualize the transport mechanisms at the molecular scale owing to the use of polymer tagging and single molecule imaging techniques.

The fluorescence images were recorded for 35 ms sampling time with a pixel size of 500 nm. The image acquisition was done using the Andor iQ imaging software. Typically, 1000 frames (512 x 512 pixels) were acquired in each stack of frames. The entire field of view obtained with the chosen objective was 256 x 256 μ m. However, the actual field of observation where the fluorescent polymer solution composition and flow behavior was captured, was around 180 x 130 μ m, fitting one flow unit of the microchip.

We processed the raw images using a well-known image analysis software, Fiji-ImageJ (<https://fiji.sc/>). For better visualization, the acquired greyscale images were converted to RGB scale. With this technique, the RGB scale emphasizes different fluorescence intensity levels, where blue represents low intensity or no polymeric material, and green and red correspond to moderate and high-intensity levels, respectively. This color scale indicates the presence of polymer molecules, in green, or polymer agglomerations, in red. In Figure 3 is shown that the flow direction of the polymer solution is from left to right. It remained unchanged throughout the entire duration of the experiments, which was approximately six hours.

Figure 3: Time-lapse fluorescence images, at 28 frames/second, showing polymer molecules as green dots flowing in the micro-channels (2-10 μm) with polymer clustering (red spots). The flow behavior of two polymer aggregates in the lower 10 μm -channel is tracked by the white arrows.

Results and Discussion

During the flow experiments, we were able to dynamically capture the manifestation of the presumed mechanisms that underlie polymer retention in porous media. In flow, three mechanisms are thought to act: adsorption, mechanical entrapment and hydrodynamic retention, which are illustrated in the well-known schematic diagram after (Sorbie 1991), in Figure 4.

Figure 4: Schematic diagram of polymer retention mechanisms in porous media after (Sorbie 1991).

Based on their character, polymer retention mechanisms can be divided into two categories: static and dynamic. A significant part of the adsorbed polymers represent the static component of polymer retention

and is a fundamental fluid-rock interaction, where molecules are adsorbed onto the rock surface. Since they come into existence during flow conditions, the mechanical and hydrodynamic retentions correspond to the dynamic component. The illustration in Figure 4 portrays adsorption as molecules attached to the grain surface, the mechanical entrapment as polymer molecules being lodged into the narrow pore-throats, and the hydrodynamic retention as polymer molecules caught in stagnant flow zones.

Polymer adsorption

The extended duration of the flow experiments allowed us to observe two time-dependent adsorptions, at early and late times, based on their contrasting characteristics.

The adsorbed polymer molecules were visible under the microscope only for a limited period as a result of photobleaching. The phenomenon can be caused by different reasons: local change in pH which represents the loss of fluorescence signal due to the formation of non-fluorescent protonation state of the fluorophore, and self-quenching which represents the loss of fluorescence signal due to short-range inter-fluorophore interactions. Fluorescence signal loss is known to be a disadvantage of fluorescence microscopy, and in our experiments, it was manifested mainly for the adsorbed polymer molecules, that is, the immobile ones, while the flowing molecules were less affected.

The temporal color maps for two flow units in Figure 5 were obtained using ImageJ, which show the state of the adsorbed polymer after one hour of polymer flow in the micromodel. Other flow units show similar behavior. The early-time adsorption of the polymer layers on the microfluidics walls is showed in orange in Figure 5, whereas the areas available for fluid flow is shown in grey. The trapped polymeric material in the middle channels (shown in orange) is due to both static and dynamic components. However, in this case, clear distinction between the polymers entrapped by adsorption and by mechanical entrapment can not be made.

Figure 5: Temporal color maps showing, the adsorption of polymer molecules occurred during the early time of flow experiment, in orange, and the area available for fluid flow, in grey, in two different flow units within the microfluidic device, which confirms a consistent behavior.

The polymer molecules bound to the microchip surface by physical adsorption, mainly by van der Waal's and hydrogen bonding. The adsorption mechanism happens almost instantaneously when the polymer molecules get in contact with the PDMS. Thus, the polymers occupy surface adsorption sites and form an adsorbed layer covering the PDMS internal walls. The polymer adsorbed layer does not appear to have a uniform thickness. In Figure 5 (left), for example, by comparing the polymer adsorbed layer in both 10 μm -channels, we observe a significant cross-area reduction on the entire length of the lower channel, while on the identical upper channel, it is more localized, leading to a flow obstruction towards the end of the channel. As regarded in Figure 5, the early-time adsorption is characterized by high adsorption rates. In contrast, late-time adsorption exhibits low adsorption rates, as an outcome of adsorption mechanisms

already being satisfied. The main driving force of adsorption, namely the difference in polymeric material concentration between the surface and the solution, reasons the drop in adsorption rates. On this basis, after early time polymer trapping, the state of the flow structures should remain relatively unchanged until the end of the experiments.

Mechanical entrapment

The mechanical entrapment, known as a dynamic component of polymer retention, occurs when larger polymer molecules get trapped in narrow flow channels during flow. This polymer/pore-size incompatibility may lead to partial or total pore clogging by the polymeric material. It should be noted that polymer molecule clustering and entanglements in the solution can significantly increase the apparent size of the polymer, leading to unexpected mechanical entrapments.

The polymer solution flow through the microfluidics device enabled us to record the mechanical entrapment of polymers in the flowing channels, in several flow units. The pore-clogging phenomena, captured in one of the flow units, is displayed through the trailing particle pathways of the polymers in Figure 6. The captions from a. to f. represent the cumulative streamlines of polymer molecules for subsequent substacks of 250 frames and emphasizing the cumulative pathways polymer molecules traveled during 8.75s in each one. The flow of polymeric material is illustrated in green and red, reflecting moderate and high fluorescence intensity, respectively.

Figure 6: Sequence of cumulative trailing particles pathways showing polymer flow in the top 10 μm-channel by continuous green and red streamline, in a. – d., polymer pore-clogging in the top-10 μm channel by discontinued streamlines, in e., and no flow of polymer solution in f., at 28 frames/second.

Polymer mechanical entrapment and the resulting clogging is observed in the upper 10 μm-channel and was captured at 28.7s (Figure 6). A closer look at the streamlines within the channel from the first four captions (a.-d.) shifts our attention to an abnormal deviation of flow direction caused by strangulation. The reduction of the area available for flow is due to a large amount of polymeric material, represented

by the blue zone, which got retained and lost its fluorescence. The mechanical entrapment captured at 28.7s, occurred in the restriction, as it was too small relative to the size of the flowing polymer agglomerate. The polymer pore-clogging is highlighted by a disruption in the flowpath in e. and by the complete disappearance of the flowpaths in f.

The flux of polymer transport was quantified using the Multi ROI Profiler functionality in ImageJ. Figure 7 shows the relative mean pixel intensity as a function of time of a cross-sectional area located downstream of the clogged zone within the top 10 μm -channel. As shown in Figure 7, there are two stages of the polymer dynamic behavior in the microchannel. In the first stage, the relatively high values of pixel intensity indicate a nearly constant flux of polymeric material. Furthermore, the fluctuating behavior in the fluorescent signal is related to the non-uniform distribution of the polymer aggregates. The red dashed line marks the start of stage two at 28.7s (marked with a white arrow in Figure 6) with diminishing intensity, which indicates a clogging behavior of the channel by the polymer accumulation. The steep decline indicates no flow of polymer solution through the investigated cross-section, as a result of the complete clogging of the channel.

Figure 7: Relative mean pixel intensity of a cross-sectional area downstream of the restriction that indicates polymeric material flow by the intensity fluctuating behavior in the first stage, the clogging phenomenon marked by the red dashed line at 28.7s, and no polymer flow by the descending trend in fluorescence intensity in the second stage.

Beyond mechanical entrapment, the trailing particle pathways from Figure 6 emphasize the effects of polymer retention on the flow streamlines. The blue color of the middle three channels implies a lack of streamlines and therefore, a complete blockage for the polymeric material on those channels. The discontinued flowpaths in the lower 10 μm -channel suggest tortoise flowing polymers between the entrapped ones. Based on the observations, polymer retention in porous media may cause flow conductance reduction, flow divergence, and diminished number of available conduits for flow.

Besides the decrease in flow conductance, another critical effect of polymer retention in porous media is porosity reduction. The fraction of pore-volume available for flow depends on the amount of polymer trapped by adsorption or by dynamic stresses. By blocking certain channels, the pore-volume available for polymer solution to flow, also called effective pore-volume, decreases. The relation between polymer retention and effective pore-volume has been addressed in various studies (Zhao et al. 2017; Chauveteau and Kohler 1974). This clogged pore-volume should not be confused with the inaccessible pore-volume

(IPV). The clogged pore-volume is the effect of pore blockage due to retained polymers. On the other hand, IPV refers to the pore-volume that is too small to allow polymer molecules to flow through but is accessible to water and oil. In field applications, IPV could be as high as 20%.

Hydrodynamic retention

The second mechanism that occurs at flow conditions is hydrodynamic entrapment. It is the least studied and the least understood from all polymer retention mechanisms. Literature reports that entrapment of polymer due to hydrodynamic drag forces may happen in dead-end pores or stagnant-flow zone (Sorbie 1991). It is a flow-dependent mechanism, where polymer entrapment could be reversible. Polymer release could be driven by flow-velocity fluctuations or by molecular diffusion resulting from the contrast in concentration between the polymers in the stagnant areas and the ones in the flowing channels.

We were able to visualize this mechanism in our experiments. Figure 8 shows time-lapse fluorescence images of what appears to be hydrodynamic retention captured during the flow experiments. The captions a. to c. display how a polymer molecule is drifted towards a non-flowing channel for polymers and remains trapped in that area, for around 10s. Apparently, in this $2\mu\text{m}$ -channel, the flow is restricted only for polymer molecules (the blue color in the scale represents no polymeric material). The flow of the aqueous solution through the channel creates hydrodynamic forces that transports and holds the polymer molecules at the entrance of the channel. Later, due to changes in the flow conditions, the polymer molecule discharges into the flux and flows towards other flow conduits, as shown in d.. The last two captions, e. and f., emphasize no polymer agglomerate entrapped in the same area.

Figure 8: Time-lapse fluorescence images showing a polymer agglomerate dragged and entrapped by the flow of the aqueous solution in the highlighted zone in a.; the entrapment continues in the area by hydrodynamic drag forces in b. and c.; and afterwards discharges and flow towards the lower $5\mu\text{m}$ -channel in frame d.. The last two snapshots, e. and f. show no entrapment in that area.

Figure 9 shows the relative mean pixel intensity versus time of the highlighted white area in the captions from Figure 8. The peaks in intensity correspond to polymer agglomerates trapped by the hydrodynamic force in the investigated zone. The peaks in the plot suggest that four polymer agglomerates were entrapped during the time of observation, where the first two agglomerates get released after a couple of seconds. The fourth peak correlates with the hydrodynamic entrapment presented in Figure 8. A comparison with Figure 7 highlights the distinct behavior of the hydrodynamic retention from other retention mechanisms. The fluorescence signal does not resemble the fluctuating behavior, particular for an almost constant flow flux of polymeric solution.

Figure 9: Relative mean pixel intensity of the trapping area (highlighted in white in Figure 8) shows four intensity peaks corresponding to four entrapped polymer agglomerates while the constant low intensity trends imply the release of the polymers from the investigated area.

The direct observations of the phenomenon, achieved through single-molecule imaging, show that hydrodynamic entrapment of polymers could be temporary. Therefore, hydrodynamic retention does not seem to cause a permanent alteration of the pore-structure and permeability reduction. The postulation comes in agreement with experimental results from core floods which reported almost stable residual resistance factors after brine post-flush (Zhang and Seright 2015a; Marker 1973; Dominguez and Willhite 1977). Nonetheless, this mechanism, when combined with other entrapment mechanisms, may lead to polymer accumulation and potentially clogging as shown previously.

Reversibility of polymer retention

Many researchers have thoroughly studied the polymer-rock interactions and proposed theoretical models for various retention mechanisms. In spite of this, the reversibility aspect of polymer retention in porous media is not well understood in the literature. Some of the mechanisms are believed to be reversible while others are expected to be irreversible. This section presents direct visualization of polymer detachment, which supports the presumption of the reversibility of polymer retention mechanisms.

Figure 10 captures a reversible entrapment of polymer that creates partial clogging of the flow channel for a short time, followed by the release of the polymer accumulation and re-opening of the channels. Snapshots a.-c. (first row) illustrate the binding of a polymer agglomerate to the adsorbed polymer layer occurred at an earlier time. The bind is the result of hydrodynamic forces becoming large enough to push macromolecules over the osmotic barrier of the 'static' adsorbed layer. This phenomenon has been reported in the literature by (Chauveteau, Denys, and Zaitoun 2002) as a proposed mechanism for polymer adsorption under high flow rate using coreflood experiments with cationic polyacrylamide. The increased thickness of the adsorbed macromolecules creates partial clogging of the bottom flow channel, thus reduces the flow conductance in the conduit. The second row in Figure 10 (d.-f.) captures polymer detachment owed to increased hydrodynamic forces generated by a big polymer molecule from the flow flux. The g.-i. snapshots (third row) show the reestablishment of polymer solution flow through the entire cross-section as a result of polymer detachment. The release of the agglomerate leads to channel unclogging and flow conductance restoration.

Figure 10: Time-lapse fluorescence images at 28 frames/second showing, in the highlighted area, the attachment of polymer agglomerates in a.-c. (first row), the release of polymer accumulations caused by another flowing agglomerate in d.-f. (second row), and flow restoration in g.-i. (third row).

Figure 11 depicts the relative mean pixel intensity versus time of the area corresponding to the polymer accumulation, as shown in Figure 10. Figure 11 supports the desorption mechanisms of the polymer molecule from the static adsorbed layer, captured in the snapshots. Two flow stages can be differentiated on the plot, also delimited by the red dotted line. The first stage, with the high-intensity values, indicates the presence of the adsorbed polymer agglomerate, corresponding to the first row of snapshots in Figure 10. The decline in intensity is owed to fluorescence loss as the agglomerate binds, it becomes immobile. This behavior is typical for static molecules and is discussed in more details in the adsorption section. The sharp drop in intensity, marked by the red line, corresponds to the desorption of polymer agglomerate. The time of the event in this plot matches with the detachment of the polymer behavior observed in Figure 10f. In the second stage of the plot, the fluorescent signal is characteristic of a nearly constant supply of fluorescence material by the flow flux. The increase to values higher than 0.6 is reasoned by the flow of a big polymer agglomerate that has higher fluorescence intensity. The trend shows that polymer desorption provoked channel unclogging and the polymer flow pathways in that area are restored.

Figure 11: Relative mean pixel intensity of the highlighted area from Figure 10 indicates the polymer agglomerate attached by high-intensity values, in the first flow stage (left side of the dashed-line), the desorption by abrupt drop to lower values, marked by the red dashed line, and polymer solution flow by fluctuating behavior, in the second flow stage.

Conclusions

Motivated by the field implementation of polymer flood for EOR and other applications, this work presents, for the first time, a direct visualization of polymer retention mechanisms in porous media. We observed three mechanisms leading to polymer retention: adsorption, mechanical entrapment, and hydrodynamic retention. The key contributions are summarized as follows:

- We presented, for the first time, a new procedure for direct visualization of polymer transport occurring at the molecule-scale of polymers and the pore-scale of rocks.
- We introduced a fabrication workflow for a custom-designed microfluidics device, which honors the pore-size distribution of oil-bearing conventional reservoir rocks, with pore-throats ranging from 2 to 10 μm .
- The polymer solution flow experiments conducted on the microdevice combined with advanced single-molecule fluorescence microscopy provided polymer transport insights at the pore-scale.
- Three predominant mechanisms have been identified to contribute to polymer retention in porous media: adsorption, hydrodynamic retention and mechanical entrapment.
- The early stages of the experiment were characterized by high polymer retention rates, with polymer molecules binding almost instantaneous to the microfluidics device walls. The retained polymers reduced the available area for flow, creating conditions that enhanced polymer entrapment.
- Direct visualization of polymer molecules while clogging the pore-throats was presented, for the first time. The complete blockage of the channel resulted from the mechanical entrapment of polymer agglomeration. Polymer retention in porous media caused flow conductance reduction, flow divergence and diminished number of available conduits for flow.
- We dynamically captured polymer retention by hydrodynamic drag forces followed by a reversible process. The observations emphasize that hydrodynamic entrapment of polymers could be temporary and flow-rate sensitive, without causing a significant alteration in flow conductance.
- Visual observation of a polymer aggregate detachment causing partial pore clogging, was also shown. The reversibility of this dynamic component is consistent with the observed reversible

character of polymer retention mechanisms, discussed in the literature.

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