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Microvisual investigation of polymer retention on the homogeneous pore network of a micromodel

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ABSTRACT

A new experimental technique is reported for visualization of polymer retention on the solid surfaces of porous media. Etched silicon micromodels with well-characterized pore networks were used during single-phase flow to examine the retention of 0.2 wt% partially hydrolyzed polyacrylamide (HPAM) solution. Image analysis included an image subtraction and an RGB-based global thresholding technique for quantification of polymer retention/adsorption. Results are reported as the percentage of porosity occupied by immobile polymer.

Three factors were investigated including the salinity of displacing water, the change of wettability of the micromodel surface, and mechanical degradation of polymer. With respect to salinity in displacing water, the experiment confirmed that 5 wt% NaCl results in less polymer retention (6.3 ± 0.3%) than without NaCl (7.5 ± 0.3%). The increase in Na^+ concentration was sufficient to induce contraction of the size of the flexible HPAM molecules and, therefore, decrease the thickness of polymer adsorption on the grain. Two methods were used to alter the initially strongly water-wet surface of the micromodel. Wettability was changed by the deposition of crude oil and CTAB (cetyl trimethylammonium bromide) in aqueous solution. The micromodels treated using crude oil and CTAB showed polymer retention of 15.0 ± 0.3%% and 5.0 ± 0.3%%, respectively. Oil-wet micromodels aged by crude oil showed larger polymer retention than the polymer retention on water-wet micromodels (7.5 ± 0.3%). Otherwise, the polymer retention on the CTAB treated micromodel was lower than the polymer retention on the water-wet micromodel. Finally, polymer solution flowed through a 7 μm filter was tested. Average polymer retention was 4.3 ± 0.3% and this is 3.2 ± 0.3% point lower than the value of unfiltered polymer solution. Further investigation of microgels within pore networks provided a chance to demonstrate that a size and structural flexibility of microgel leading to a transition from mobile to immobile conditions.

1. Introduction

Mobility control is one of the most important factors in enhanced oil recovery (EOR) process design. As mobility-control agents for the aqueous phase, partially hydrolyzed polyacrylamide (HPAM) has been used extensively in surfactant-polymer and alkali-surfactant-polymer EOR processes (Chang et al., 2006). With increasing use of polymers, improved polymer products have been rapidly manufactured with consequent needs to characterize the behavior of EOR polymers ex-situ and in-situ. It is widely recognized that as polymer solution flows through a porous medium, a portion of the polymer is retained. In other words, both an additional resistance to flow and a loss of polymeric additive from the aqueous phase are driven by the retention of polymer layers on rock surfaces. Permeability reduction during polymer flooding with a large quantity of polymer solution has been reported (Treiber and Yang, 1986). Hence, analysis of polymer retention is of fundamental importance to EOR operations that involve the flow of polymer solutions through porous media (Cohen and Christ, 1986). Most laboratory design studies of a polymer flood involve the measurement of the effective viscosity of polymer solutions in representative field cores.

Even though active research is underway to quantify accurately polymer molecules adsorbed at solid interfaces, such as the rock surfaces found in petroleum reservoirs, there is little information in the literature about qualitative and quantitative visualization of polymer adsorption. In other words, it is necessary to perform visual studies in order to improve our understanding of polymer retention as an important mechanism in loss of mobility control. This experimental study illustrates the successful application of silicon-wafer micromodels with interpretation using image processing techniques. Thus, this study establishes methodology for the direct visualization of polymer retention that can be applied to more complicated pore networks.

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Nomenclature

M	molecular weight, g/mol
A	cross sectional area, cm^2
Δp	pressure drop
μ_w	viscosity of water, cP
q	volumetric flow rate, cm^3/s
L	length, cm
k	absolute permeability, Darcy
cP	centipoise
s	second
np_{w_p}	the number of white pixels from polymer retention image and
np_{w_b}	the number of white pixels from the base image

2. Polymers for enhanced oil recovery (EOR)

There are several important characteristics that must be tested before injecting polymer solution into a formation. These include low cost, good filtration properties, suitable viscosity, surfactant compatibility, salinity and calcium tolerance, thermal stability, mechanical stability, good injectivity, good transport in reservoir rocks, and low retention on rock surfaces. Among the characteristics, this study focused on the transport and retention of polymers. Polymers in this study are polyacrylamides. They are water-soluble polymers and produced for many different purposes. Water-soluble polymers are produced by the hydration (hydrolysis) of the chain of monomer acrylamide. During the hydrolysis, some of the amide ($CONH_2$) groups react and cause anionic carboxyl groups (COO^-) to be scattered along the backbone chain. The properties of polyacrylamide in water solution are strongly related to the degree of hydrolysis determined by the amount of carboxyl group (COO^-) in the molecule chain. The negatively charged carboxyl groups on the backbone chain cause anionic repulsion between polymer molecules and segments on the same molecules. The repulsion is the main reason for the elongation of polymer molecules; hence, the mobility reduction (viscosity increase) takes place. Specifically, the HPAM macromolecule has a structural flexibility that makes it very sensitive to the ionic environment.

Cations, especially divalent cations, have screening effects on the electrostatic repulsions between charged monomers, that decrease the excluded volume and, as such, the macromolecular size. In other words, greater viscosity is obtained when the polymer molecule is uncoiled in a low salinity environment occupying the largest possible volume. In practice, the salt sensitivity of HPAM has drawn attention for EOR processes because the reservoir is an ion-rich environment. In terms of the rheological behavior of polymer solutions, HPAM shows viscoelastic behavior even when fairly dilute due to its flexible coil molecular structure. On the other hand, the more rigid rod-type xanthan structure yields a purely pseudoplastic and inelastic solution at lower concentrations. Such structural differences give rise to different aspects of polymer retention of xanthan and HPAM, as discussed in relation to Experiment IV.

2.1. Polymer degradation

Polymer degradation mechanisms include mechanical degradation, chemical degradation, and biological degradation. Mechanical degradation occurs when the polymer solution is exposed to large shear rates. Such conditions arise, during the mixing of polymer solution, flow through chokes, injection through perforations or the near well bore area where flow velocity is very high. Seright (1983) showed a polyacrylamide that is very sensitive to shear degradation. In that study, the viscosity–shear rate curve of a given polyacrylamide solution is shown before and after different levels of shearing through a consolidated sandstone core. After fairly modest levels of shearing for the polyacrylamide solution (above 30 feet/day), the viscosity is considerably reduced. After extreme shearing at a very large flow rate through the sandstone core, the viscosity is only slightly above that of the brine. Later, Zechner et al. (2013) also investigated shear-thinning behavior of polyacrylamide solutions flowing through fractures to explain measured injectivity.

2.2. Salinity/hardness

As Sorbie (1991) pointed out, the relative viscosity of HPAM is a function of both salinity (Na^+, $C1^-$, etc.) and hardness (Ca^{2+}, Mg^{2+}, etc.). The repulsion among the backbone charges is screened by the local double layer formed by the small electrolyte species. At greater salt concentrations, the screening effect is more marked, and consequently the viscosity is lower. The effect of divalent ions, such as Ca^{2+} and Mg^{2+}, is even more significant than that of monovalent species, such as Na^+ and K^+. The divalent ions bind even more tightly to the polyelectrolyte because of their greater charge density and polarizability. Sorbie also reported the study of Sandvik and Maerker (1977) showing Ca^{2+} has a much greater effect on the reduction of intrinsic viscosity of HPAM than Na^+.

2.3. Polymer retention

Dominant polymer retention mechanisms were explained by Huh et al. (1990). Polymer retention occurs predominantly via two mechanisms including the adsorption of polymer molecules on the surfaces of large pores, and mechanical entrapment in small pores. The first mechanism for mechanical entrapment is “straining” (Huh et al., 1990). Mechanical entrapment can be described by the accumulation of polymer molecules in the pore channel whose radius is comparable to or smaller than an average size of polymer molecule. Even though the fact that the size of the pore channel is smaller than that of polymer molecule, a flexibility of the polymer molecule allows the solvent to force the polymer molecules into the smaller channel. The polymer chain is then trapped via adsorption at opposite walls of the pore. Consequently, the number of trapped polymer chain increases as the solvent flows through the channel and brings more polymer into the channel.

Secondly, Maerker (1973) has proposed hydrodynamic retention that is associated with a “sticky” surface. As the solvent brings more polymer molecules into a small pore, a large chemical potential gradient is generated. Due to large chemical potential, the channel releases some trapped polymer molecules without continuously flowing solvent. On the other hand, the “sticky” surface with large adsorption energy prevents the chemical potential gradient from causing outward release of polymer when the flow of solvent stops. Alternative to these mechanisms, DeGennes (1979) describes that as flow continues, a macromolecule remains statistically adsorbed because the desorbing “trains” of polymer are always replaced by adsorbing “loops”. Consequently, all retention mechanisms are interrelated and contribute to the trapping of polymer in small pores and being adsorbed on the surface of grains.

Earlier studies indicated how significantly the retention mechanisms contribute to the polymer retention in different pore structures. Polymer retention in very permeable porous media should be due mainly to adsorption and the level of polymer retention is not significantly high. For instance, the xanthan retention levels obtained (Sorbie et al., 1987) in permeable Clashach sandstone cores