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Final Doctoral Dissertation Defense

Petroleum Engineering

Controlled Release of Enzymes from Layer-By-Layer Assembled Polyelectrolyte Multilayered Nanoparticles to Improve Fracturing Clean-Up

Abstract

Hydraulic fracturing treatment, commonly known as fracking, is a stimulation technique in low-permeability reservoirs and tight rock formations. It involves pumping large quantities of fluids (water, sand, polymers, and mixtures of chemical additives) down into the well at extremely high pressure. Due to fluid mechanics (hydraulics), it creates small cracks in the rock formations called fractures, allowing reservoir fluids such as natural gas, petroleum and brine to flow out of tight formations. The hydraulic fluids used during fracking are guar-based polymers. They are the most popular because of their low-cost, high-affinity for water, and ease of handling. Although there are other types of fluids, such as polymer water-in-oil emulsions and aqueous foams, they are all designed to enhance fracture creation by carrying proppant and minimizing formation damage. The guar-based polymers are crosslinked by metal ions, like borate, for the fracture creation and proppant suspension. To minimize formation damage, fracking companies add high concentration breakers comprised of enzymes and oxidizers into the fluids to degrade the polymer gels. Different injection methods utilized in the field are aimed for greater control over high concertation breakers to improve the fracture clean-up process. However, current treatments often underperform expectation due to ineffective fracture cleanup and/or premature degradation.
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Tuesday, May 14th
Starts at 8:00am
298 Slawson Hall

Committee Chair:
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Abstract, cont.

In this study, Layer-by-Layer (LbL) assembled polyelectrolyte multilayered nanoparticles were used as a technique for targeted and controlled release of enzyme breakers. Polyelectrolyte multilayers (PEMs) were assembled by means of alternate electrostatic adsorption of polyanions and polycations using colloidal structure of polyelectrolyte complexes (PECs) as LbL building blocks. High enzyme concentrations were introduced into polyethyleneimine (PEI), a positively charged polyelectrolyte solution, to form an electrostatic PEC with dextran sulfate (DS), a negatively polyelectrolyte solution. Under the right concentrations and pH conditions, PEMs were assembled by alternating deposition of PEI with DS solutions at the colloidal structure of PEI-DS complexes. Stability and reproducibility of PEMs were tested over time. This work demonstrates the significance of PEMs as a technique for the targeted and controlled release of enzymes based on their high loading capacity, high capsulation efficiency, and extreme control over enzyme concentration. Entrapment efficiency ($E\%$) of polyelectrolyte multilayered nanoparticles were evaluated using concentration measurement methods: UV-*vis* spectroscopy, enzyme viscometric assays, and SDS-PAGE. The morphology and size distribution at the nanometer level were determined for both PECs and PEMs using Transmission Electron Microscopy (TEM). Controlled release of enzyme entrapped within PEMs was sustained over longer time periods (> 18 hours) through reduction in viscosity, and elastic modulus of borate-crosslinked hydroxypropyl guar (HPG).

Long-term fracture conductivity tests at 40℃ under closure stresses of 1,000, 2,000, and 4,000 psi revealed high fracture clean-up efficiency for fracturing fluid mixed with enzyme-loaded PEMs nanoparticles. The retained permeability improvement from 25% to 60% indicates the impact of controlled distribution of nanoparticles in the filtercake and along the entire fracture face as opposed to the randomly dispersed unentrapped enzyme. Retained fracture conductivity was found to be 34% for fluid systems containing enzyme-loaded PECs. Additionally, enzyme-loaded PEMs demonstrated enhanced nanoparticle distribution, high loading and entrapment efficiency, and sustained release of the enzyme. This allows for the addition of higher enzyme concentrations without compromising the fluid properties during a treatment, thereby effectively degrading the concentrated residual gel to a greater extent.

Fluid loss properties of polyelectrolyte multilayered nanoparticles were also studied under static conditions using a high-pressure fluid loss cell. A borate-crosslinked HPG mixed with nanoparticles was filtered against core plugs with similar permeabilities. The addition of multilayered nanoparticles into the fracturing fluid was observed to significantly improve the fluidloss prevention effect. The spurt-loss values were also determined to cause lower filtrate volume than those with crosslinked base solutions. The PEI-DS complex bridging effects revealed a denser, colored filtercake indicating a relatively homogenous dispersion and properly sized particles in the filtercake.