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Development of stable polymeric structures for harsh oil-reservoir conditions

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Understanding the structure-function relationship in polymeric materials enables the development of stable products to optimize hydrocarbon recovery under harsh conditions.

To enhance the production rate of hydrocarbons (i.e., our primary energy source), we must optimize our exploitation of oil reservoirs. This is generally achieved by adding external agents (e.g., solvents, thermal energy, and chemicals) to enhance oil mobility into the reservoir. However, the range of commercial technologies that enable the optimization of this process under harsh conditions is currently limited. For this reason, a great deal of research and development is focused on discovering functional chemicals that are suitable for such conditions (e.g., the high temperature, high salinity, and high divalent-cation concentration found in a carbonate reservoir). For instance, a number of polymers and gels have been developed to improve the displacement of trapped oil and to modify the flow patterns in oil reservoirs, respectively.

The development of commercial polymers for improved oil recovery has primarily focused on the conditions found in sandstone reservoirs (i.e., low temperature, low salinity, and low divalent-cation concentration). Under harsher conditions (e.g., those of a carbonate reservoir), the solution is usually to incorporate a water-treatment process, thus increasing the overall cost. However, for a carbonate reservoir—in which divalent cations are naturally present—efforts have focused on developing chemicals that can be directly applied without the need for additives or prior treatment. This approach is based on integrating an understanding of the application with laboratory experience.

Using this approach, we have established new procedures for developing chemical processes that can increase the extraction of hydrocarbons from harsh oil-reservoir conditions. Our procedures take into account the requirement for chemical processes that can be scaled up, and enable the proper evaluation of structure-function relationships during chemical-product development.

Acrylamide (AAm)-based polymers and gels are commonly used for optimizing the production rate of hydrocarbons. However, their performance is reduced as a result of the surrounding reservoir environment. For instance, amide groups can be hydrolyzed due to extreme conditions in the reservoir, causing the gel volume to shrink (syneresis) and decreasing its efficacy. To overcome this issue, we have incorporated different functional groups—i.e., vinylpyrrolidone (VP) and sodium 2-acrylamido-2-methylpropane sulfonate (AMPSNa)—on the AAm backbone. The incorporation of VP and AMPSNa monomers can

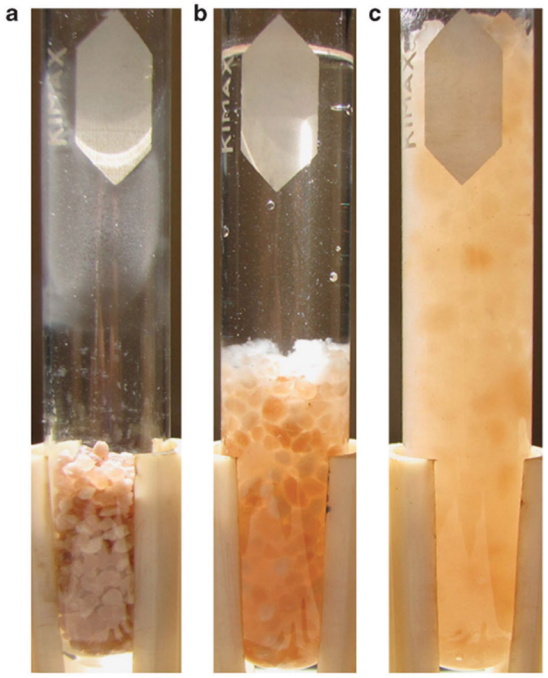

Figure 1. *Photographs showing the swelling behavior of a gel in production water (i.e., reservoir brine). The gel comprises acrylamide/vinylpyrrolidone/sodium 2-acrylamido-2-methylpropane sulfonate, crosslinked with N,N′-methylenebisacrylamide. (a) Dry gel. (b) Gel at the beginning of the swelling process. (c) Gel at the end of the swelling process (i.e., after 24 hours).*[1]

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provide thermal and ionic strength resistance, respectively, thereby improving the mechanical properties of the resultant polymer.[2] For the synthesis of such polymeric materials, standardized procedures are necessary to enable an understanding of the optimal proportion of reagents and to achieve a proper cause-and-effect evaluation.

We first developed and implemented an integral and comprehensive procedure for evaluating and selecting the polymer structures that are suitable for harsh conditions in a carbonate reservoir. Our technical procedure includes an analysis of the oil field information, a problem diagnosis, the establishment of reaction conditions, and a polymer-structure synthesis and characterization (via elemental analysis, attenuated-total-reflectance Fourier-transform infrared spectroscopy, solid-state carbon-13 nuclear magnetic resonance spectroscopy, calorimetric techniques, and rheology). We also implement aging tests (i.e., for stability and compatibility) and performance evaluation tests (i.e., oil-recovery factor, adsorption, resistance factor, and residual resistance factor) at reservoir conditions.

Based on this work, we synthesized a gel (shown in Figure 1) that can act as a water flow-pattern modifier within a reservoir.[1] We synthesized this gel by using AAm, AMPSNa, and VP monomers (with a molar ratio of 1:1:1), N,N′-methylenebisacrylamide at 0.5wt.% as a crosslinking agent, clay (2wt.%) to improve the mechanical properties of the material, ammonium persulfate (0.1wt.%) as an initiator, and tetramethylenediamine (0.05wt.%) as a redox agent. Our gels are stable to high temperature (up to 130°C), at high salinity (up to 250,000ppm total dissolved solids, TDS), and under high concentrations of divalent cations (up to 50,000ppm). We also developed a polymer—using a different molar ratio of monomers (2:1:1 of AAm:AMPSNa:VP) and 0.01wt.% of ammonium persulfate—that maintains its functionality as a viscosity control agent under temperatures of up to 92°C,

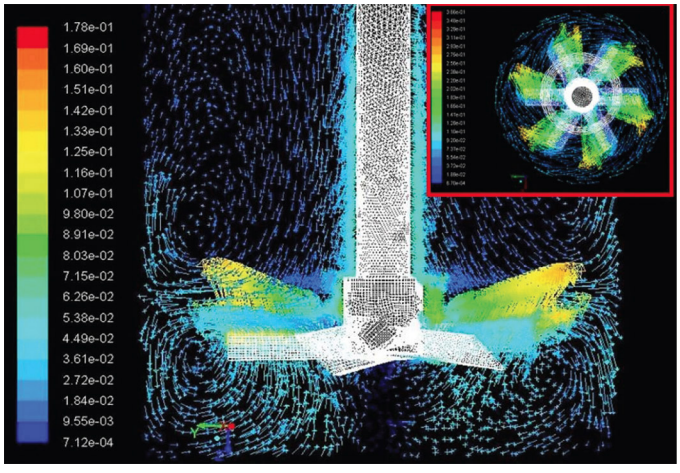

Figure 2. *Flow patterns, simulated by computational fluid dynamics, of a stirred batch reactor.[4] Values shown are velocity (in ms^{-1}).*

Figure 3. *The high-pressure continuous tubular reactor used for the synthesis of polyacrylamide-based polymers.*

salinity of 28,443ppm TDS, and under divalent-cation concentrations of 2000ppm.[3]

To achieve synthesis of these materials, we implemented two of the most common polymerization processes at laboratory scale (i.e., solution and inverse emulsion, and thermal and redox catalysis). Solution polymerization is a simple technique, but polymers with high molecular weights synthesized using this approach can exhibit heat- and mass-transfer problems. Emulsion polymerization represents an alternative method that can reduce these problems and can also control the molecular weight dispersity, thus improving the quality of the final product. We also implemented batch and continuous reactors for fabrication. To understand these processes, we used computational fluid dynamics (see Figure 2) and tracer technology,[4] and found that the polymers synthesized in the batch reactor exhibit local mass-transfer problems (i.e., dead zones) due to deficient mixing. Using a continuous tubular reactor (shown in Figure 3) for synthesis minimizes this effect, but requires the use of complicated high-pressure systems.[5]

In summary, we have developed a (cause-and-effect) general procedure to provide solutions for industrial problems associated with the harsh conditions of oil reservoirs. Our procedure enables control over the polymeric structure and its final performance by emulating reservoir conditions (pressure, temperature, and ionic strength) during laboratory evaluation. Furthermore, to ensure the successful synthesis of these polymeric structures, we have developed solution and inverse-emulsion polymerization processes that can be carried out in batch reactors or continuous reactors. This approach has enabled us to develop several novel structures (i.e., associative polymers, and polyampholytic and double-network gels) that offer a broad spectrum of technological alternatives for the oil industry. Based on our results, we are currently working on developing materials with improved mechanical strength, water affinity, and thermal and ionic-strength stability.

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