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IMPROVING RESERVOIR CONFORMANCE USING GELLED POLYMER SYSTEMS

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Program Manager
G. Paul Willhite
University of Kansas
Lawrence, Kansas

Principal Investigators
Don W. Green
G. Paul Willhite

Co-Investigators
C. Buller, S. McCool, S. Vossoughi, M. Michnick

Contracting Officers's Representative
Jerry Casteel
Bartlesville Project Office

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Objectives

The general objectives are to 1) to identify and develop gelled polymer systems which have potential to improve reservoir conformance of fluid displacement processes, 2) to determine the performance of these systems in bulk and in porous media, and 3) to develop methods to predict the capability of these systems to recover oil from petroleum reservoirs.

This work focuses on three types of gel systems - an aqueous polysaccharide (KUSP1) system that gels as a function of pH, the chromium(III)-polyacrylamide system and the aluminum citrate-polyacrylamide system. Laboratory research is directed at the fundamental understanding of the physics and chemistry of the gelation process in bulk form and in porous media. This knowledge will be used to develop conceptual and mathematical models of the gelation process. Mathematical models will then be extended to predict the performance of gelled polymer treatments in oil reservoirs.

Summary of Technical Progress

Task I : Development and Selection of Gelled Polymer Systems

I.2 Selection of organic crosslinking system to be investigated

A database of gel polymer systems was constructed and three systems were identified as candidates to be studied in detail. Screening experiments indicated problems with the piperazine di-HCl-polyacrylamide system and the sodium aluminate-polyacrylamide system. Gelation was not observed in samples prepared at selected pH values and concentrations of piperazine di-HCl and polyacrylamide. It is suspected that the piperazine di-HCl does not crosslink polyacrylmides as claimed in patent literature. Piperazine di-HCl was the only organic crosslinker that was identified to less hazardous than chromium. The sodium aluminate-polyacrylamide system is prepared at pH values of approximately 12 and gels upon reduction of pH below a value of 10. Screening experiments took the form of identifing and testing chemical agents, e.g. esters, that can reduce the pH of solutions from 12 to 10 over a period of several days. Mono-ethyl phthalate met this requirement but produced precipitates when added to the sodium aluminate-polyacrylamide system.

The third candidate was the aluminum citrate-polyacrylamide system and this system was selected to be investigated in detail. Aluminum citrate and polyacrylamide were rated less toxic than at least one of the components in all of the organic crosslinked systems. Another factor that influenced the selection of the aluminum citrate-polyacrylamide system was the renewed interest of the oil industry which was due in part to its reputation as a low-toxicity system.

Task II : Physical and Chemical Characterization of Gel Systems

II.2 Chemical Reaction Kinetics

A study was conducted to determine chemical kinetics of the Cr(III)-polyacrylamide system. Rate data were obtained on the uptake reactions of Cr(III) monomers, dimers and trimers with polyacrylamide. Oligomer uptake was determined by separating the unreacted Cr(III) by equilibrium dialysis, oxidizing the Cr(III) to Cr(VI) and measuring the Cr(VI) concentration by UV spectroscopy. Slopes of storage

moduli-time data obtained from dynamic rheological measurements were used as a measure of the gelation rate.

Uptake rate and gelation rate increased with oligomer size, oligomer concentration, polymer concentration and pH. The gelation reaction, as indicated by the value of storage modulus, generally tracked the Cr(III)-uptake data for the monomer and trimer species as shown in Figures 1 and 2. This tracking suggests that the gelation or crosslinking reaction occurred at short but finite time after the chromium first reacts with the polymer (the uptake reaction). A kinetic model was developed that described very well the uptake data for the monomer, but fit the dimer data less well and the trimer data poorly.

Task IV : Mathematical Modelling of Gel Systems

IV.2 Develop of mathematical model(s) of laboratory in situ gelation

The kinetics of gelation of polymers is usually related to the pH of the polymer solution. The pH of polymer solutions, in turn, is affected by chemical interactions with the reservoir rock. The effects of sodium/hydrogen ion exchange in simple core-flood experiments with high pH NaCl brine solutions were modeled. A mechanism proposed by Bunge and Radke[1] was used to describe the ion-exchange reaction on the surface of the rock. This mechanism was incorporated into a flow model by assuming local equilibrium between the fluid-phase concentrations and the adsorbed-phase concentrations.

Figures 3 and 4 show the simulated concentration profiles of the Na^+ species and the pH as the injected solution advances along the length of the core. The trends shown by the results may be rationalized on the basis of the study of cation-exchange reactions by Lake and Helfferich[2,3].

Each profile shows the formation of two distinct fronts:
1) The first front travels at the interstitial velocity with no retardation. This front simply entails the displacement of the initial solution and is termed as the *salinity wave*.
2) The second front moves at a velocity less than the interstitial velocity and involves a change in both the solid-phase composition and the fluid-phase concentrations. This front is termed as the *ion-exchange wave*. The region before the ion-exchange wave corresponds to the injected fluid-phase composition and solid-phase concentrations in equilibrium with the injected concentrations.

The velocity and shape of the ion-exchange wave is a function of the sodium/hydrogen ion-exchange equilibrium and the dispersion in the core. The Langmuir-like nature of the ion-exchange equilibria produces fronts which continuously sharpen as they propagate through the core. Dispersion, however, tends to smother the sharp concentration gradients and opposes the sharpening character of the wave fronts. These competing phenomena balance each other and the resultant ion-exchange waves are indifferent with respect to sharpening behavior as they progress through the core.

Since the velocities of the salinity wave and the ion-exchange wave are different, an intermediate plateau in the concentration profiles is formed. This plateau consists of a modified fluid-phase composition in equilibrium with the initial solid-phase composition. As the sodium-ion concentration in the intermediate region is less than its injected value, the model predicts an overall uptake of sodium ions from the injected solution.

REFERENCES

1. Bunge, A.L. and Radke, C.J.,"The Origin of Reversible Hydroxide Uptake on Reservoir Rock", SPEJ, (Oct. 1985), 711-718.
2. Pope, G.A., Lake, L.W. and Helfferich, F.,"Cation Exchange in Chemical Flooding: Part 1-Basic Theory Without Dispersion", SPEJ, (Dec. 1978), 418-434.
3. Lake, L.W. and Helfferich, F.,"Cation Exchange in Chemical Flooding: Part 2-The Effect of Dispersion, Cation Exchange, Polymer/Surfactant Adsorption in Chemical Flood Environment", SPEJ, (Dec. 1978), 435-444.

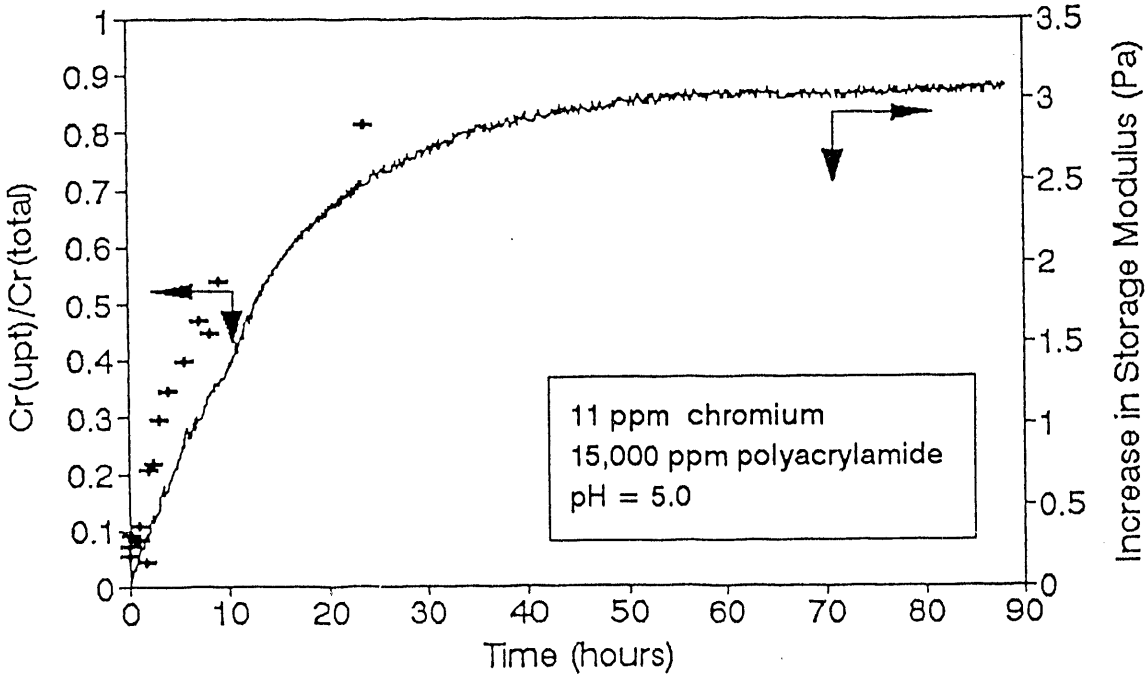

Figure 1 : Comparison of Cr(III)-uptake data and gelation data for the chromium monomer species.

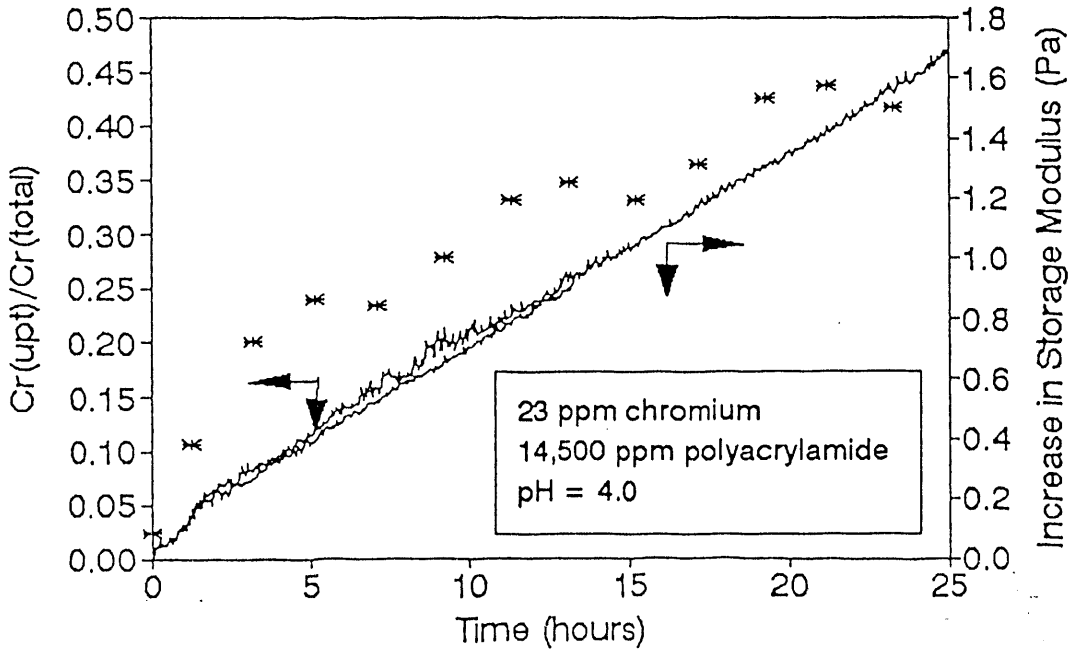

Figure 2 : Comparison of Cr(III)-uptake data and gelation data for the chromium dimer species.

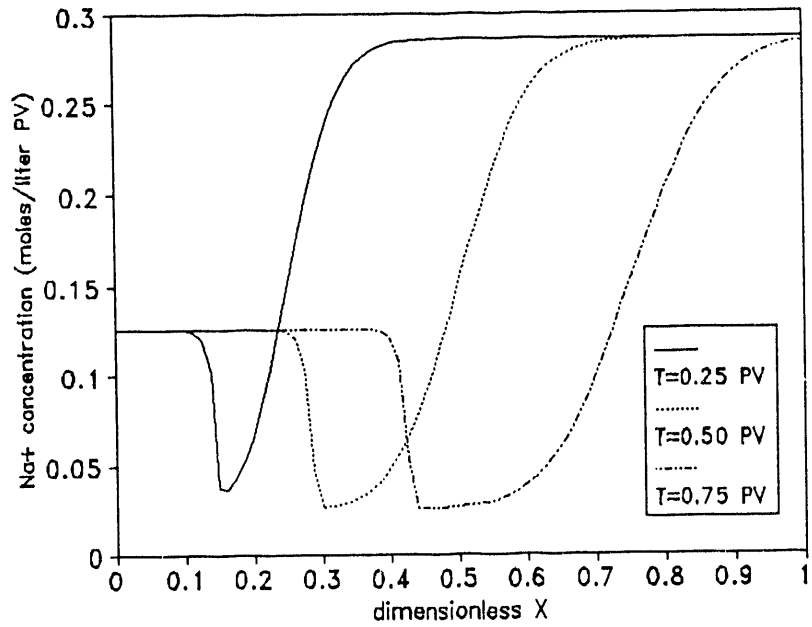

Figure 3: Na^+ concentration profiles along the length of the core as a function of pore volumes of injection.

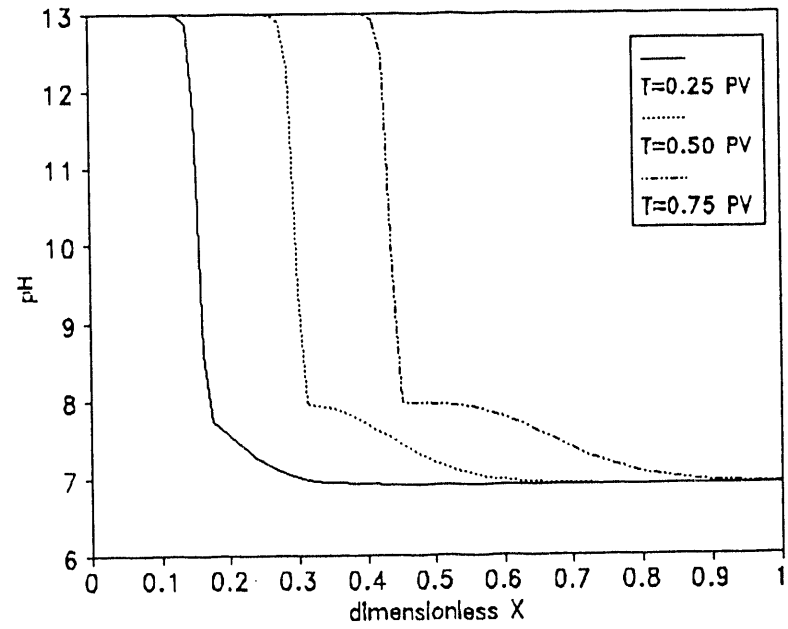

Figure 4: pH profiles along the length of the core as a function of pore volumes of injection.

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