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Improved Oil Production Using Economical Biopolymer-Surfactant Blends for Profile
Modification and Mobility Control

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*IMPROVED OIL PRODUCTION USING ECONOMICAL BIOPOLYMER-SURFACTANT
BLENDS FOR PROFILE MODIFICATION AND MOBILITY CONTROL*

ABSTRACT

A two-year research project funded by the United States Department of Energy (DOE) has identified new materials for use in oil field production technology. The program, funded through a subcontract to BDM Oklahoma, identified these new materials found to be effective alternates to partially hydrolyzed polyacrylamides, copolymers, and xanthan gum polymers as water shutoff agents in fractures and in matrix flow configurations.

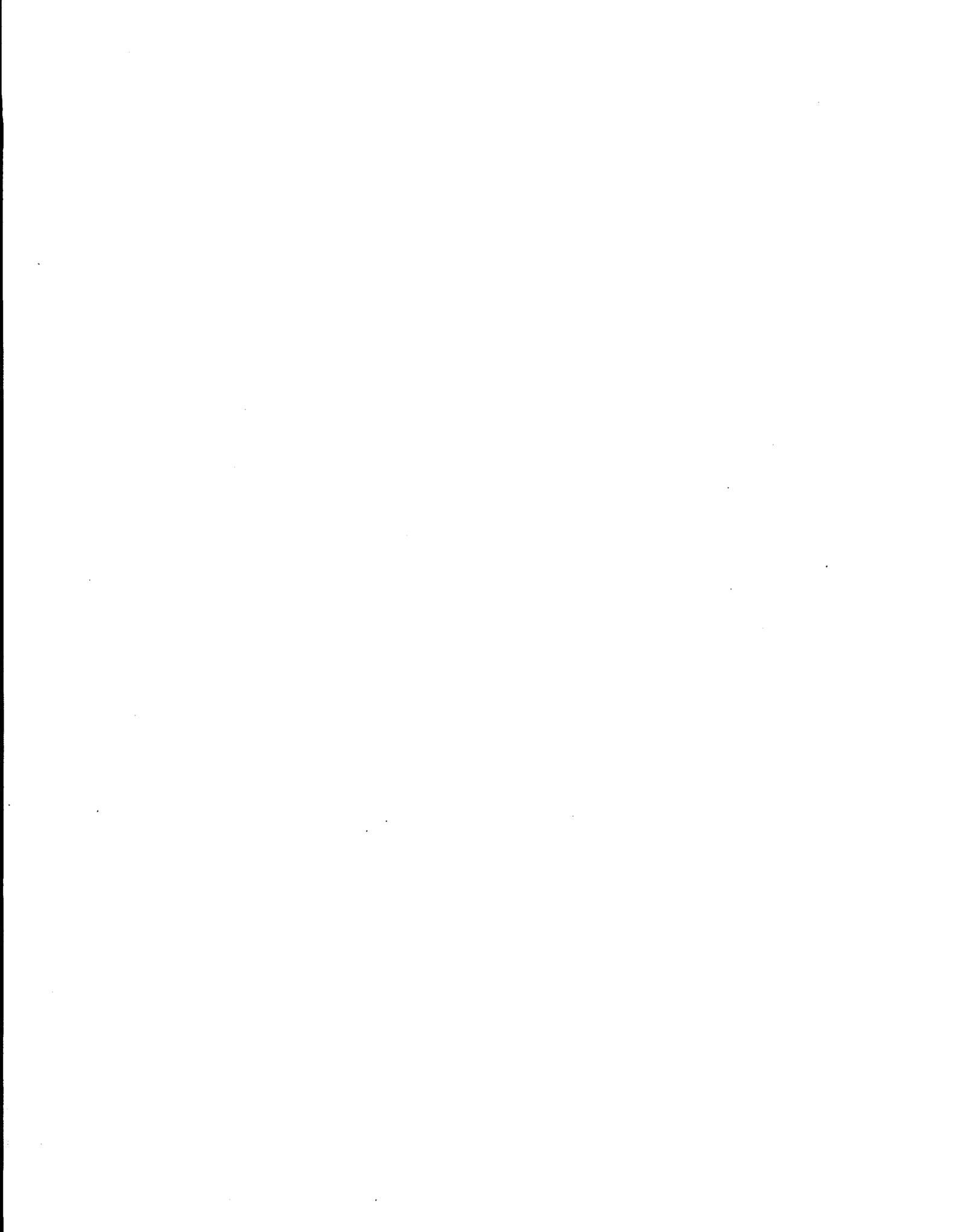
In the past, the oil industry has found that poor injectivity and questionable stability of starch products prevented their use in profile control applications. However, in recent years, the demands of the oil and gas drilling industry have led to the development of new modified starches for drilling, drill-in, and completion fluids. The properties of the new products lend themselves to applications in improved recovery.

Scientists from Prairie View A&M University and Texas A&M University have found that chemically modified starches have properties suitable for improved recovery technology. The materials, derived from inexpensive agricultural products, do not hydrolyze in harsh saline environments, are made more resistant to biodegradation, and because of their wide spectrum of molecular weight distributions can be tailored to specific lithologies. The development of new materials with superior functionality and reliability has been an important technological advance that can significantly increase oil and gas reserves, and reduce production costs.

Among the various applications where modified starches were tested, two areas were identified with significant promise for improvement in technology, specifically (1) low temperature environmentally approved gel packages and (2) high temperature delayed gel packages. Modified starches offer an alternative to currently used polyacrylamide, particularly for lower temperature systems, because of faster reaction times and adequate retention properties in porous media and in fractured core systems. Such systems compare favorably to commercially available systems used in soil consolidation and soil barrier treatments and are environmentally safe as well.

Likewise, the program has identified starch materials that offer advantages in high temperature delayed gel applications. Delayed gel times are essential in high temperature applications because of the difficulty in placing gelant materials in formations where temperature accelerates reaction rates and gel times. Currently, the standard practice is to use retarding agents so that systems can be placed in reservoirs.

The principal investigators for the research effort are Dr. Jorge Gabitto of Prairie View A&M University and Dr. Maria Barrufet of Texas A&M University. The work was supported in part by grants from Chemstar Inc. and Staley Manufacturing Inc.



IMPROVED OIL PRODUCTION USING ECONOMICAL BIOPOLYMER-SURFACTANT BLENDS FOR PROFILE MODIFICATION AND MOBILITY CONTROL

EXECUTIVE SUMMARY

In the past, starch hydrocolloids have not been effective alternates to partially hydrolyzed polyacrylamides, copolymers, and xanthan gum polymers as water shutoff agents in fractures and in matrix flow configurations. Poor injectivity and questionable stability have usually prevented their use in profile control applications. However, in recent years, the demands of the oil and gas drilling industry have led to the development of new drilling, drill-in, and completion fluids with improved functionality. New types of modified starches have contributed to these new "drill in fluid" (DIF) products. It was felt that the properties of the new products would lend themselves to applications in improved recovery.

Objectives

The objective of this project has been to evaluate the use of agricultural starch biopolymers for gelled and polymer applications in oil recovery processes. We believe that there is great potential for finding new functional starch products because of their chemical and structural flexibility, low cost, and wide availability. The goals of this project have been, therefore, to systematically investigate how the physical properties and chemical composition of relatively inexpensive agricultural starch products will influence their use as effective selective permeability control agents or as gels for water shut-off.

Summary of Research Efforts

Chemically and/or physically modified starch polymer samples were subjected to preliminary screenings involving rheological tests, sedimentation tests, and stability tests at varying pH and temperature. The samples passing these tests were selected for core flow testing. The functionality of a new generation of modified starches was evaluated for profile control applications in matrix and in fracture flow configurations. Sandpack coreholders and a new type of fractured core cell were designed and constructed for testing the polymer samples. Computer models were run to compare the benefits of inexpensive conformance improvement treatments to the more expensive processes that are commercially available.

Studies were performed with crosslinking agents and modified starches to develop effective gel packages. Stability tests and kinetic reaction rate test results were compared to select promising candidates. Core flow studies were performed in consolidated porous media and in fractured core test cells. Specific materials were identified that have the necessary stability under reservoir conditions for extended periods.

Testing in porous media indicated that certain types of polymers have sufficient injectivity to allow propagation out into the reservoir matrix. Delayed gelation times in certain systems were developed so that gelant placement could be achieved in high temperature

applications. In summary, we have proven that the concept of utilizing modified starch polymers as inexpensive substitutes for polyacrylamides and xanthan gum is valid.

Significant Results from Research

Results of our research show that chemically modified starches have properties suitable for improved recovery technology. They do not hydrolyze in harsh saline environments, are made more resistant to biodegradation, and because of their wide spectrum of molecular weight distributions can be tailored to specific lithologies. The development of new materials with superior functionality and reliability has been an important technological advance that can significantly increase oil and gas reserves and reduce production costs.

Among the various applications where modified starches were tested, two areas were identified with significant promise for improvement in technology. Those areas are:

- **Low temperature environmentally approved gel packages**
- **High temperature delayed gel packages**

Crosslinked polymer gel systems indicate that the modified starches offer an alternative to currently used polyacrylamide, particularly for lower temperature systems, because of faster reaction times and adequate retention properties in porous media and in fractured core systems. Such systems compare favorably to commercially available systems used in soil consolidation and soil barrier treatments. When compared to a representative starch/crosslinker package with a well known¹ polyacrylamide-chrome acetate system at 25° C, the crosslinked starch systems offer systems that react up to 90% faster.

Gelation times of more than 48 hours are required for low molecular weight hydrolyzed polyacrylamide (HPAM) and chrome acetate with no accelerator chemical addition. Depending on the type of starch, gelation times from 1 to 24 hours are observed for modified starch materials with zirconium crosslinkers. The starch packages are also more acceptable environmentally because of the substitution of zirconium salts for chrome acetate.

Likewise, the program has identified starch materials that offer advantages in high temperature delayed gel applications. Delayed gelation times are essential in high temperature applications because of the difficulty in placing gelant materials in formations where temperature accelerates reaction rates and gel times. Currently, the standard practice is to use retarding agents so that systems can be placed in reservoirs.

The significance of the performance of the starch/HMT (hexamine hydroquinone) gel package is realized when it is compared with a new copolymer/organic crosslinker system just recently introduced by Hardy et. al.² as an alternative to chromium crosslinked polymer systems. The new copolymer/organic crosslinker system is expected to extend the use of conformance improvement treatments to temperatures beyond 100° C. However, some of these products may not propagate into the target zones because of their reactivity.

Our work has found that there are modified starch/HMT gel packages that provide similar gelation characteristics as the new technology described by Hardy. While the modified starch packages have not shown the long term thermal stability of the synthetic polymer systems, the opportunity to employ low cost materials for treatments is intriguing. Further work is needed.

Presentations, Publications and Educational Activities

The progress and results of this DOE funded program were presented twice in international meetings. The paper 976007, entitled "*Rheology of starch polymers for enhanced oil recovery*" was presented in the American Society of Agricultural Engineers, 1997 Annual International Meeting held in Minneapolis, Minnesota (see Appendix I). Similar results corresponding to this research program were also presented in Copenhagen, Denmark at a 1997 DOE/World Bank sponsored workshop. These presentations described our research findings and progress in the six tasks of our proposal. These opportunities have served to widen the interest in the use of agricultural products for use in the industry and the potential utility of modified starches in particular.

The experimental results of the two-year study have been summarized in a SPE paper³ presented at the SPE/DOE Improved Recovery Conference in Tulsa Oklahoma in April 1998 (SPE 39692 "*Screening and Evaluation of Modified Starches as Water Shutoff Agents in Fractures and in Matrix Flow Configurations*"). It was well received and should serve as a springboard to carry this technology into commercial application.

Mr. Gerald Emesih graduated from the Petroleum Engineering Department at TAMU during 1997. He completed the Ph. D. Dissertation entitled "*Characterization of Agricultural Starch Based Biopolymers for Use in Oil and Gas Field Production Processes.*" Mr. Norman Alban is scheduled to graduate with a PVAMU Master degree in General Engineering in December 1998. Mr. Alban is completing work on his Master Thesis entitled "*Simulation of Polymer Floods in Enhanced Oil Recovery.*" Several graduate and undergraduate students from Petroleum Engineering and Agricultural Engineering Departments at TAMU, and Chemical Engineering Department at PVAMU participated part-time in work related to this research project.

Mr. Xun Zhou, a graduate student at PVAMU, worked assembling the injectivity test workstation at the Chemical Engineering Department at PVAMU during 1997. Mr. David Burnett designed and supervised the set-up of the injectivity test workstation. The assembly of this workstation is a significant asset to the Enhanced Oil Recovery Program at PVAMU. Mr. David Burnett also completed the assembly of the apparatus to conduct injectivity tests in fractured pores media. This apparatus that allows the researcher to control the fracture opening in flow tests, significantly improves the experimental capabilities at Petroleum Engineering Department (TAMU).

Because of the research programs that have proven the concept of using modified starches in improved recovery applications, and our efforts to disseminate the technology developed from them, we are finding support from industry. As a result, we are planning to develop new processes designed for field application. This new effort is designed to be an industry-government partnership with funding sources from each.

Improved Oil Production Using Economical Biopolymer-Surfactant Blends for Profile Modification and Mobility Control

INTRODUCTION: THE POTENTIAL & NEED FOR NEW TECHNOLOGY

The industry has benefited greatly from new technology, the new knowledge that increases the energy reserves of the United States while at the same time decreases the finding costs of oil and gas. Innovations such as multi lateral wells, splitter technology, extended reach wells, downhole motors, and coil-tubing technologies have all contributed to this increased efficiency to find and produce oil and gas. The International Energy Outlook 1997⁴ made projections through 2015 for oil, natural gas, coal, nuclear power, and electricity. Analysis showed that growing understanding of the world's oil resource base and improved recovery methods will allow large gains in future oil supplies at relatively stable development and production costs so that world oil prices will rise only modestly, to about \$21 per barrel in 2015 (1995 dollars).

Unfortunately, while other areas of well technology advance, there have been fewer developments in the area of improved recovery technology. Currently, more than 30 billion barrels of oil and gas equivalent are unreachable in the US because of inadequate technology to produce the reservoir economically. Most of these reserves are in mature fields operated with severe economic constraints by companies without the resources to develop improved technology themselves.

The Need for New Products and Processes in Conformance Improvement

Improvements in technology are critically needed in the area of secondary recovery. Almost every oil field where secondary recovery has been implemented faces the problem of high water cuts or excessive gas-oil ratios (GORs). Economic and environmental considerations are increasing costs of operations. It is becoming increasingly expensive to provide disposal facilities for excess water or for re-injection of excess produced gas. Downhole fluid separation is difficult. Profile control through application of water and gas shutoff agents is widely used. However, these treatments are expensive, and in themselves have certain drawbacks. Industry experience indicates that there is real need for less expensive choices in improved recovery.

Texas A&M University's Departments of Agricultural Engineering and Petroleum Engineering have been evaluating modified starches since 1993⁵. The evaluation and characterization of agricultural starch based biopolymers for enhanced oil recovery operations rests on the identification and analyses of the fundamental properties of the starch biopolymers that play a role in their selection and use as effective mobility control agents. Different starch products provide a way to vary the properties of polymer solutions. The structures of two basic starch molecules are shown in Figure 1. Starch owes much of its functionality as a thickening or binding agent to the two major carbohydrate components, amylose and amylopectin, as well as the physical organization

of these macromolecules into the granular structure. Thus, altering the inter- and intramolecular hydrogen bonding or the ratio of these polymer units through chemical or thermal modification methods will alter the rheological and other functional properties of the starch biopolymer⁶⁻⁹.

Modified starches are processed to alter the physical and/or chemical properties of native starch to achieve the desired viscosity, paste clarity, freeze-thaw stability, and shear stability desired for the specific application. The more common modifications and how they alter starch properties include physical modifications, non-degradative and degradative chemical modifications.

Linear molecular structures are more injectable, but do not have the same rheological properties that the branched molecules have. Derived products provide even more variation in solution properties. The properties that affect technical and economic feasibility of agricultural starch use are, rheological behavior of polymers and surfactant blends, starch chemistry, chemical interaction with oil field brines, transport properties in porous media, mobility reduction per unit cost, water solubility, retention properties, shear, chemical and biological stability, etc⁵. The type and condition of the starch material affect these properties. Results of the aforementioned research indicate that the potential for developing new materials is great although more work is needed.

The Potential of New Technology

Improved recovery technology accounts for approximately 3% of the worldwide production of oil and significantly more of total US production of oil and gas, not counting waterflooding technology⁹. When waterflooding is included, more than 25% of our nation's petroleum production is derived from improved recovery technology. Most of the production from these "augmented" fields is associated with production of excess oil and gas. For example, the volume of produced water from the North Slope is greater than the oil and gas production. It is estimated that more than \$100,000,000 worth of chemicals is spent annually on field production problems attributed to excess water and gas production on the Slope and in the lower 48 states of the United States¹⁰.

The benefit of new technology that is less expensive, yet effective, is two-fold. It reduces the cost of chemicals used in producing this resource. Second, because the new technology is more economical, there are more projects that are economically justifiable even in times of depressed petroleum prices. Based on studies of commercial development of new technology, mature field lifetimes could be extended by more than 25% by implementation of improved operating and recovery practices.

Research Program Background

In 1992 Dr. Rosana Moreira of the Agricultural Engineering Department and Dr. Maria Barrufet of the Department of Petroleum Engineering, both at Texas A&M University, collaborated on a project to investigate the properties of starch agricultural products. This

work began a long-term project at Texas A&M to investigate the potential for inexpensive agriculture derived products which could be used in the petroleum industry and in particular as improved oil recovery agents. In 1994 Mr. Gift Ngo graduated with a Master of Engineering degree at the Chemical Engineering Department, Prairie View A&M University. Mr. Ngo simulated waterflooding processes in fractured media using an averaging technique. Mr. Ngo worked under Dr. Jorge Gabitto's direction. BDM Oklahoma Inc. awarded in 1996 a subcontract (G4S60329 under DOE prime DE-AC22-94PC91008) to Prairie View University to evaluate the potential for modified starches as water and gas profile control agents ("Improved Oil Production Using Economical Biopolymer-Surfactant Blends for Profile Modification and Mobility Control". A research team comprising Drs. Moreira, Barrufet, Burnett and Gabitto carried out the project.

This report describes the results of the investigation.

PROGRAM DESCRIPTION

Goals and Objectives

This project proposed the use of agricultural starch biopolymers for gelled and polymer applications in oil recovery processes because of their chemical and structural flexibility, low cost, and wide availability. Thus, the main goals of this project have been to investigate systematically how the physical properties and chemical composition of relatively inexpensive agricultural starch products will influence their use as effective selective permeability control agents or as gels for water shut-off.

Technical Approach to Evaluation of Modified Starches

The use of polymer and gels for profile modification, mobility control, and gas and water shut-off technology is well documented¹¹⁻¹⁸. In the last ten years, gelled polymer treatments have been the most common treatment involving these polymers. Such treatments have used partially hydrolyzed polyacrylamides and xanthan gum biopolymers for the most part, since other materials have lacked the properties required for efficient water and gas blocking gel designs.

In order to place and to utilize these materials at significant distances from the well bore, there is a need to identify polymer solutions that are pumpable, injectable and functional.

Starch materials can be used in un-crosslinked form or also possibly in gel packages. Starches can also form strong gels in the formation. Gel technology therefore requires a knowledge of the polymer/crosslinker combinations and concentrations that can form good (ringing) gels, with gelation properties that can be delayed or retarded, and one that has prolonged consistency (lack of retrogradation or syneresis) under reservoir temperature conditions. This determination is important because gels encounter different types of formation fluids and are supposed to be efficient for a sufficient length of time.

Separately, it is necessary to show that the systems tested are functional under reservoir conditions for extended time periods. Thus, the research program that was devised took a multi-task approach to proving the concept that these materials would be acceptable alternatives to current commercial products in many applications.

Description of Tasks Comprising the Project

The plan for evaluating modified starches relied heavily upon early screening studies to evaluate starch functionality in oil field brines. Recognizing that some products would be superior to others, a multi-task program was established to organize work and allow screening protocols to continue while more definitive testing was also planned. Specifically the following tasks were scheduled,

Task 1: Determination of Starch Polymer Properties at Wellbore Conditions

Task 2: Measurement of Performance in Porous Media

Task 3: Evaluation of Injectivity in Porous Media

Task 4: Analyze Interaction of Starch Polymer and Formation Rock

(Adsorption/retention studies)

Task 5: Performance of Starch Polymer in Simulated Well Treatments

Task 6: Investigation of Performance of Combinations of Starch Polymers

With Surfactants and other Polymers.

Specialists from the Department of Agricultural Engineering at Texas A&M University in College Station led the screening studies program with the aid of partners in the starch industry. Prairie View A&M led the work to perform computer simulations scheduled for the project while the Department of Petroleum Engineering at A&M in College Station performed the core flow studies.

PROGRAM REVIEW

Characterization and Screening

Introduction

Sixteen modified starch polymer samples were obtained from three different companies. Table 1 lists nine materials that are representative of the products screened. Manufacturer's specifications for these samples are similar. Laboratory testing is required to differentiate performance. Accordingly, samples that were representative of different types of products were subjected to rheological tests, sedimentation tests, stability tests at varying pH values, and gelation tests for crosslinked starch polymer systems.

Gelation tests were performed at temperatures ranging from 165°F to 200°F and included gel stability measurements for extended time periods. Polymer samples that were not stable at elevated temperatures for an extended time period were eliminated from the screening program.

Rheological Studies

The viscoelastic behavior of several modified starch products as function of polymer concentration, brine concentration, shear rate and time was evaluated. Four different starches were used for these tests, Mira-sperse 623, Mira-Thick 603, Instant Jel C and tapioca (Binasol 90C), listed in Table 1. For these studies, 1 % and 3 % weight/volume (w/v) starch solutions were prepared by mixing the starch powders in distilled water, 3 % and 6 % (w/v) NaCl solutions.

For the rheological tests, a Brookfield DVIII viscometer equipped with a sampler adapter and a SC4-18 spindle was used. Two different test methods were used,

- 1). In the first test, the apparent viscosity of starch samples for different brine concentration was obtained by measuring torque on a spindle rotating at a constant rate (100 sec⁻¹). Measurements were repeated every 30 minutes to observe viscosity changes with time.
- 2). In the second test time-dependent thinning behavior (thixotropic) was determined for the starch solutions. Viscosity changes were recorded at different speeds (30 to 100 rpm). The degree of thixotropy is indicated by a comparison of viscosities at different speeds.

Pseudoplastic model parameters were calculated from the experimental results using the following equation,

$$\eta = K \{ \dot{\gamma} \}^{n-1} \quad (1),$$

where η is the apparent viscosity (Pa sec.), K is the consistency coefficient (Pa sec.ⁿ), n is the flow behavior index, and $\dot{\gamma}$ is the shear rate (sec.⁻¹). The apparent viscosity and other viscosity parameters are shown in Table 2.

The shear thinning index (STI) was obtained by dividing the apparent viscosity measured at low rotational speed by the viscosity at a speed three times higher, e. g., 40 and 120 sec.⁻¹. The degree of thixotropy (Thix) was estimated using a ratio of the lowest speed (30 rpm) viscosities for both increasing and decreasing speeds. An estimate of one (1) implies lack of thixotropy.

Figure 2 shows typical viscosity behavior as a function of shear rate for different brine concentrations for Instant Jel C starch samples. Similar plots were developed for the other starch types tested.

A shift from Newtonian to pseudoplastic behavior from the 1 % concentration samples to the 3 % concentration starch solutions was observed for all the samples analyzed. Considerable differences were observed between the rheological characteristics of Binasol and Instant Jet C on one hand and the other samples on the other hand (Table 2). The Mira Sperse 623 (MS 623) and Mira Thik (MT 603) exhibit higher degree of thixotropy, lower shear-tinning characteristics and are very easily miscible in water. A variation in viscosity values of about 5 % was observed for all the starch samples at different saline concentration. It could therefore be concluded that all the starch samples used in this study are stable within the saline concentration range used.

Sedimentation Tests

The mechanical stability of several modified starch samples was studied by measuring the rate and extent of solid sedimentation in solutions prepared in various saline solvents and pH levels. The four solutions used in the rheological studies were tested. Two concentrations, 1% and 3% w/v, were prepared in 0%, 3%, 6% and 9% NaCl solutions. The solutions were dispersed in cylindrical glass tubes, the liquid level measured, the tubes were corked and stored at room temperature.

The ability of the starch solutions to maintain their spatial and structural integrity is related to the size, shape and interactions between polymer molecules. The sedimentation of suspended particles in a medium depends upon the physical properties of the particles and the chemical and rheological properties of the medium. The stability of these polymers under static conditions is an indication of their suitability in oil recovery operations.

Sedimentation time is the elapsed time before a clear supernatant solution is observed in the container. The sedimentation levels were monitored daily for a period of two weeks or until no further change in sedimentation level was observed. If no sedimentation occurred the liquid height in the tube (4.25 in.) was recorded. The obtained sedimentation levels were normalized as the ratio of the percent height of the sample to the percent polymer concentration.

Typical results are shown in Figure 3. The results show a greater degree of sedimentation in the 1 % polymer solutions than in the 3 % samples. It is important to notice that the level in Figure 3 represents measured liquid level no deposited solid level. Therefore, the higher the level the smaller the degree of sedimentation, e. g., there was no sedimentation at all in Instant Jel C solutions. The cold-water swelling polymers (MS 623 and MT 603) showed a faster rate of sedimentation than the pre-gelatinized starches (Binasol 90C and

Instant Jel C). In addition to less sedimentation, the pre-gelatinized polymers exhibited less fluctuation in sedimentation levels across the range of saline concentration tested. This was considered an indication of saline stability of the starch samples. After these first screening Binasol 90C and Instant Jet C were considered suitable materials for use in future test involving, pH, injectivity and displacement.

Two sets of solutions at starch concentrations of 0%, 0.5%, 1% and 2% in distilled water were prepared for observation at high temperature and low pH. All the solutions were prepared by dissolving completely the powder starch in distilled water. The ones used in the temperature studies were heated up to a temperature near the boiling point of the solution. The sedimentation volume (height) was measured every five minutes for the first hour. The samples were left overnight for observation of any long term change.

The pH of the starch solutions was lowered by adding 0.1 N HCl solution until the pH was approximately 3.

Some samples did not show sedimentation at room temperature. The ones which showed sedimentation were used in the high temperature studies. All solutions tested showed less sedimentation at high temperature than at room temperature. Sedimentation disappeared completely in two of the tested solutions. These results suggest that heat contributes significantly to starch solubility.

The same samples that showed sedimentation at room temperature were used in the pH studies. The low pH conditions did not reduce appreciably the sedimentation levels.

In conclusion the experimental results showed that temperature significantly reduces the sedimentation degree while low pH does not affect the sedimentation levels. Samples that do not exhibit significant amount of sedimentation at reservoir conditions are the most stable. Those samples were selected for injectivity tests.

Flow Performance in Porous Media

Introduction

Solution performance in porous media is a requirement for polymer performance in profile control applications. Recognizing that water shutoff applications are needed in a range of reservoir conditions, we tested polymer samples under three kinds of conditions: (1) injectivity into consolidated porous media (Berea cores), (2) injectivity into fractured core systems and (3) injectivity into unconsolidated porous media (simulated Frio formation sand).

At Prairie View A&M University, a core facility was designed and constructed to test injectivity of starch polymer samples to be submitted from vendors. A schematic of the work station is shown in Figure 4. This work station is the duplicate of the equipment at Texas A&M University in College Station.

Flow Experiments through Berea Cores

The objectives of these experiments were, first to determine maximum polymer concentration that can be used to obtain flow through specific cores and, second, to evaluate mobility and permeability reduction characteristics for the different starch biopolymer solutions used.

The experiments were done in two steps, first samples of MS 623, MT 603, Instant Jel C and Binasol 90 C were tested. Then, samples of Starpak, Starpak II and Starpark DP were used. The experimental procedures were similar in both cases. Brine saturated Berea core samples 1.5 in. to 2.4 in. (length) and 1 in. (diameter) with an average porosity of 20% were used for the tests. The injection fluids consisted of 2% NaCl solution and various concentrations of the selected starch polymers prepared in this solvent. A positive displacement Ruska pump was used for fluid injection at a constant flow rate of 0.109 cc/sec. The overburden was maintained at 300 psi while the pore pressure was 50 psi. Differential pressure transducers, located 1 in. apart, were used to measure the pressure drop across the core. The apparatus was maintained at room temperature.

Starch solutions with polymer concentrations of 3%, 2%, 1%, 0.5%, 0.25%, 0.1% and 0.05% were prepared in both cases. Core samples 2.5 in. length and 6.5 cm³ pore volume were used. The following experimental procedure was used. After each of the plugs was vacuum saturated and its pore volume was measured, the core was placed in the core holder. The system was brought to operating pressure and temperature. The core was flooded with brine until reaching steady-state. Then the core was polymer flooded until approximately 28 PV or a maximum pressure of 80 psi was reached. The core was then flushed with brine. The absolute liquid permeability of the cores was determined using Darcy's law, from the steady state differential pressure across the entire core length (ΔP_1).

Representative results of the first starch set are shown in Figure 5. This figure shows a representative plot for the 0.2% MT 603 polymer injection. A steady state response is attained after a few brine PVs injected. A subsequent injection of starch polymer shows a sharp increase in pressure over time. Limitations in the transducer prevented us from reaching steady state during polymer injection. Instead we stopped polymer injection and evaluated the permeability reduction effects upon subsequent brine flow.

Estimations of polymer penetration were made for each solution concentration in order to determine whether plugging existed. The experimental results showed that only the 0.05% polymer concentration solutions did not result in pore plugging. Therefore, mobility and permeability reduction for this starch set can only be determined using 0.05% (w/v) polymer concentrations.

The suitability of these four polymers as water shut-off materials was studied by determining the mobility and permeability reduction characteristics of their 0.05% polymer solutions. Mobility reduction or resistance factor (F_r), is the ratio of water mobility to polymer solution mobility in the porous medium at the same oil saturation,

$$F_r = \frac{(k_w / \mu_w)}{(k_p / \mu_p)} \quad (2),$$

where k is the permeability, and μ is the viscosity. The subscripts w and p refer to water and polymer solution, respectively. This ratio can be estimated experimentally from differential pressure measurements (ΔP_1) before and during polymer flooding at constant flow rate¹⁹,

$$F_r = \frac{\Delta P_1 \text{ (polymer flow)}}{\Delta P_1 \text{ (brine before polymer flow)}} \quad (3).$$

Permeability reduction or residual resistance factor (F_r) is a measured of the resistance to brine flow after the polymer solution is displaced from the porous media. It may be expressed as a ratio of brine mobility before and after polymer flow. From Darcy's law this ratio can be obtained experimentally from differential pressure ratios, before and after polymer flow, at constant flow rate¹⁹,

$$F_r = \frac{\lambda_b \text{ (before polymer flow)}}{\lambda_b \text{ (after polymer flow)}} = \frac{\Delta P_1 \text{ (brine after polymer flow)}}{\Delta P_1 \text{ (brine before polymer flow)}} \quad (4),$$

where λ_b is the mobility of the brine solution.

Table 3 summarizes our experiments for the first four starch samples tested. Binasol 90 C shows the best promise as a water control agent because of its higher mobility and permeability reductions.

The second set of injectivity tests were done using Starpak, Starpak DP, and Starpak II starch samples. Some characteristic results of these experiments are indicated in Figures 6 and 7 for samples of Starpak II and Starpak, respectively. Figure 7 shows results of injection of approximately 60 pore volumes of starch material into a 200 md Berea core. While injectivity was acceptable, F_r was not as good as a corresponding polyacrylamide polymer.

The F_r (resistance factor) and F_r (residual resistance factor) values corresponding to these tests are reported in Table 4. These values correspond to the steady state flow rates at constant pressure (40 psi). Mobility reductions (F_r) greater than 20 were obtained with Starpak II and Starpak DP. By observing the percentages of mobility and permeability reduction (F_r and F_r), Starpak II appears to be more effective, followed by Starpak DP, and finally Starpak.

The lower the water/oil mobility ratio (λ_w/λ_o) the closer the water velocity approaches that of the oil and, consequently, the displacement is more efficient²⁰. Decreased mobility ratio is obtained with polymer solutions by increased viscosity or decreased permeability of the aqueous phase, or both. The nature of the polymer and the electrolyte content of the aqueous phase dictate which effect predominates. For example, hydrolyzed polyacrylamide (HPAM) solutions show both effects while xanthan gum acts by increasing viscosity without significant reduction of permeability. The results shown in Table 2 proved that biopolymers can significantly increase the viscosity of their aqueous solutions. The results shown in Tables 3 and 4 proved that biopolymers can significantly reduce the aqueous phase permeability. Therefore, the biopolymers studied in this work lower the water/oil mobility ratio by increasing aqueous phase viscosity and decreasing permeability.

Flow Experiments through Fractured Cores

One key application for polymer gels used as water and gas shutoff agents has been in fractured reservoirs. Seright has extensively studied the problem of gel placement (Seright²¹, Seright et al.²²). Several modified starches were evaluated as possible substitutes for currently used gelants. There is need for materials acting as permeability modifiers in fractured zones of sandstone and carbonate reservoirs. Existing testing methods do not allow the researcher to control the fracture aperture in the rock. A new core flow cell has been designed to correct this limitation (Burnett and Mamora²³). Figure 8 shows a schematic of the core holder. A reservoir core fits within a metal sheath and a rubber boot serving to enclose the material. A small hole is drilled at the entrance end of the core. A small hydraulic ram assembly fits within the hole with a 0.125 in. high pressure tube extending through the end piece of the core assembly. The entire assembly is placed within an aluminum or titanium core holder that allows pressurization of the material. The assembly is pressurized to force the rock matrix together, including the faces of the fracture. The key component of the apparatus is the hydraulic fracture expander device inserted in the core. This device opens the fracture by exerting a force superior than the confining pressure of the sand, thus, stabilizing the fracture and holding it open.

A test is performed by first opening the fracture hydraulically. Baseline permeability is then established using filtered brine. The modified starch sample is loaded into a piston and injected into the core at constant pressure. The effluent flow rate is measured as a function of the total throughput. Depending upon the fracture width, the dimensions of the flow path are known and pressure and flow data can be converted into permeability data directly.

Testing was performed at constant injection pressures ranging from 20 to about 90 psi. The pressure was 10 psi for the fractured cores. Some characteristic results of these injectivity experiments are presented in Figure 9. The Figure shows results corresponding to 1% Starpak solution in a 0.5 mm fractured core for a 6% NaCl concentration. The material was present in uncrosslinked form and the results suggest that was not retained in the fracture and was washed out by the subsequent brine injection.

Table 5 shows F_r and F_{rr} results for fractured systems. The average fracture width in these cases was about 0.5 mm. The same pattern of results is observed as with consolidated systems. Permeability reductions are, overall, much smaller than with consolidated cores. The effectiveness of the polymers was studied by observing the values of mobility and permeability reduction (F_r and F_{rr}). At 1% concentration Starpak appears to be more effective, followed by Starpak DP, and finally Starpak II. At higher starch concentrations the order is reversed.

Flow Experiments through Sandpacks

The objective of sandpack operation injector mode testing was to characterize the degree of injectivity in a sandpack resulting from polymer injection. After each run the sandpack column was disassembled and discarded. A new column was prepared prior to each experiment. Brine at 1 ml/min. was injected through the sandpack to start the test. After

several PVs have eluted through the column, brine permeability (k_{w1}) is calculated by measuring differential pressures, flow rates and brine viscosity. Then, oil is injected into the column. After differential pressures have stabilized oil permeability (k_{o1}) is calculated from differential pressures, flow rates and oil viscosity. After recording the brine and oil volumes eluted re-injection of brine started. After differential pressure had stabilized the new brine permeability (k_{w2}) is calculated from appropriate values of recorded pressures and flow rates.

Figure 10 shows typical results for injectivity tests for several polymer concentrations. No sandpack plugging was observed until polymer concentrations were higher than 3%. There is significant decrease in the flow rate as the polymer concentration increases, up to two order of magnitudes for the 1% solution. All sandpacks gave a very high value of residual resistance factor (almost infinity). At the beginning of the test, the polymer flow rate in the sandpack was close to the brine flow rate, but after injection of less than one PV the flow rate started to decrease for the same displacement pressure. The flow rate continued decreasing up to a negligible value, which indicates phase plugging. The pore volumes of polymer that could be injected into a sandpack depends upon the polymer concentration. For example, for a 1% concentration, only about 1 PV of starch solution could be injected for any given pressure. This amount increased as the starch concentration decreased.

Computer Simulation Studies

Introduction

Research efforts were directed toward establishing a set of data for a hypothetical reservoir treatment with a profile control agent. Preliminary work was performed with a BEST-GEL²⁴ simulator using data of a known profile control process with properties of a starch polymer material. Treatments were compared with similar treatments using polyacrylamide technology. Starch polymer systems outperformed the polyacrylamide solutions in terms of oil produced and oil production rates. Final simulation studies were done using a copy of the UTCHEM²⁵ simulator. UTCHEM is a more powerful and complete simulator than BEST-GEL. The reported results were computed using UTCHEM.

A chemical flooding simulator (UTCHEM) has been used to compare two different polymer flooding products, a synthetic polymer and a starch biopolymer. In order to study permeability contrast the reservoir had two vertical layers with different permeabilities. Water floods and polymer floods with and without crosslinkers were simulated. Pressure distribution, oil saturation, oil production rates, water-oil ratios, water production rates and chemical distributions were computed. The other phase pressures are computed by adding the capillary pressures between phases. Phase trapping functions and adsorption of both surfactant and polymer were modeled as a function of permeability.

Polymer adsorption can be an important mechanism for a chemical recovery project since it causes retardation and polymer consumption. The effective salinity for polymer (SEP) was allowed for in the calculations. Liquid phase viscosities were modeled in terms of pure component viscosities and the phase concentrations of the organic phase, water, and chemicals. In the absence of polymer, water and oil phase viscosities are reduced to pure water and oil viscosities. The viscosity of the polymer solution depends on the concentration of polymer and on salinity.

The gel properties modeled in UTCHEM²⁵ include the effect of gel on aqueous phase viscosity, and aqueous phase permeability reduction. The effect of gel on aqueous phase permeability reduction is taken into account through a residual resistance factor commonly used for polymer flooding. The kinetics of polymer/chromium chloride gel was modified, and gel reactions of polymer/chromium malonate gel and silicate are modeled. Appendix II contains a more detailed description of the simulation studies used for the evaluation.

Permeability Modification Calculations

The three dimensional permeability simulation runs were conducted on a one-quarter 5-spot, two layers 1,000 x 1,000 x 30 ft reservoir model with an injection well and a production well located at opposite corners of the model. This system is equivalent to a 46 acres well spacing, which approximates typical field waterflooding well spacing. Each layer was 15 ft thick. Horizontal permeabilities in the x and y directions were 100 md in the top layer and 1000 md in the bottom layer. The top (low permeability) and bottom (high permeability) layers will be referred to as number one and two, respectively. Consequently, a vertical/horizontal permeability contrast value of 0.1 is achieved. Original oil in place was 0.8075×10^6 bbl. Okessa sandstone samples were used as reservoir material. The relative permeability, capillary pressure tables, viscosity data, permeability reduction factors and other biopolymer properties were experimentally determined, see Tables 6 and A2 for a summary of reservoir parameters used in the simulation. Constant injection rates were used in this project. A hydrolyzed polyacrylamide polymer (HPAM) was used as synthetic chemical while a corn starch represented the biopolymer.

The polymer flooding injection sequence without crosslinkers was: waterflooding (0-90 days), polymer flooding (90-180 days) and waterflooding, without polymer or other chemicals, up to 500 days (1 Pore Volume or PV). The gel treatment injection sequence was: waterflooding (0-90 days), polymer and crosslinkers flooding (90-92 days) and waterflooding, without polymer or other chemicals, up to 500 days (1 PV).

Simulation Results

Figure 11 shows typical results for polymer flooding without crosslinking agents. Simulation results show that the biopolymer produces slightly better oil recovery (7%) than the polyacrylamide polymer. Simulation results also show that the oil production rate increases significantly after the end of the polymer flood (180 days). The oil production rate then decreases. Figure 12 shows a water viscosity contour plot. The biopolymer produces a big increase in the water phase viscosity, up to 20 times the value of pure water. Similar results computed using synthetic surfactant showed that the chemical

polymer produces an even higher increase (50%) in water phase viscosity (see Appendix II).

Figure 13 shows a typical permeability reduction factor (F_{rr}) contour plot for biopolymer in layer 2. The biopolymer produces a big decrease in the permeability value, more than two orders of magnitude in some zones. Similar calculations for the chemical polymer showed less permeability reduction. The biopolymer produces permeability reduction factors that are four times bigger, e.g., 240 vs. 60, than the synthetic polymer.

Figure 14 shows permeability reduction factor values for the less permeable layer (top). A comparison of Figures 13 and 14, shows that the biopolymer produces a lower permeability reduction in the less permeable (top) layer than in the more permeable layer (bottom). Figure 14 shows that there is no permeability reduction at all in most of the top layer.

Our production results suggest that the biopolymer decreases the aqueous phase mobility more than the synthetic polymer. The phase mobility is the ratio of relative permeability and viscosity. Therefore, the biopolymer lower mobility is produced because the higher relative permeability decrease, compared to the synthetic polymer, offsets the lower viscosity increase, compare to the synthetic polymer. The mobility reduction is inversely proportional to the product of the viscosity times the permeability reduction factor. The higher this product, the smaller the mobility. The water-oil ratio at the production well will vary accordingly. Cumulative oil recovered vs. time before and after gel treatment are discussed in Appendix II.

Conclusions

The synthetic and the biopolymer significantly increased the oil recovery after polymer flooding with and without crosslinker addition. The biopolymer produced higher recovery and higher residual resistance factors and decreased the oil saturation more than a synthetic polymer in the model reservoir. A long-term polymer treatment (90 days) produced only slightly better results than a two-day gel treatment.

The biopolymer produced significantly higher residual resistance factors than the chemical polymer. There is no complete agreement on the exact mechanism of mobility reduction with polymeric materials. Polymer adsorption on small pores seems to be responsible for the increased resistance²⁰. The desired effects are obtained by the retention of very small amount of polymer even though there may be a larger but unproductive retention of polymer by adsorption on the rock surfaces. Since the retained polymer affects the permeability to water but does not usually affects the permeability to oil, it may be presumed that the polymer is associated with the rock surface at critical points in the flow paths for the water which are not necessarily the same as the oil flow paths²⁶.

The synthetic polymer solutions increased the viscosity more (50%) than the biopolymer solutions. The biopolymer solutions presented lower mobilities despite having lower viscosities than the chemical polymer solutions. Decreased mobility is obtained with polymer solutions by increased viscosity or decreased permeability of the aqueous phase, or both. The simulation results show that both, the synthetic polymer and the biopolymer, increase viscosity and decrease permeability (Figures A8 and A9, Appendix II). The

mobility reduction is a combination of both effects. The lower value of polymer solutions viscosity, compared to similar synthetic polymer solutions, is more than compensated by an even lower value of permeability.

The biopolymer treatment reduced the permeability in the high permeability layer more than in the low permeability layer. Despite this fact, more recovery comes early from the high permeability layer than from the low permeability layer. After depletion of the high permeability layer, significant amounts of oil remain in the low permeability layer.

Phase Behavior and Interfacial Tension of Oil/Brine/Polymer/Surfactant Blends

Introduction

One of our research tasks was to evaluate the phase behavior and interfacial tension of oil/brine/polymer/surfactant blends and the determination of their salinity ternary diagrams. From stability analysis of various starch samples we selected the most promising candidates in terms of viscosity and solubility for the interfacial tension (IFT) measurements.

After reviewing preliminary work, we concentrated on investigating the behavior of five different starches upon the air/polymer solution interfacial tension and the oil/polymer solution interfacial tension. Over 500 experimental IFT data points were collected in a matrix of parameters that includes, (a) five polymer types, (b) four polymer concentration levels (when possible), (c) two brine concentration levels, and (d) three temperature levels.

The IFT's were measured for air/polymer solution and for oil (n-decane)/polymer systems with and without surfactant. The surfactant employed was an ionic product AKZO NOBEL (Isoproponal, quaternary ammonium salt). The surface tensiometer used was Model 21 from Fisher Scientific.

Temperature, Polymer, and NaCl Concentration Effects on Air/Polymer Solutions IFT's

Samples of Starpak, Starpak DP, and Starpak II solutions (CHEMSTAR starches) had similar behavior. At 25, 50 and 75° C with 0.5% polymer concentration the three starches had IFT values between 43-36 dynes/cm. There was some IFT variation with some of the starch concentrations above 1% concentration.

The effect on IFT's of increasing the NaCl concentration was mixed. For Starpak and Starpak DP, a higher salt concentration increased the IFT at essentially all polymer concentrations and temperatures, while for Starpak II, Binasol, and Instant Gel the effects were the opposite and some crossovers were observed. Figure 15 is an example of the data collected for the samples. The chart illustrates the salt effect for Starpak DP at 75° C; a higher salt concentration lowers the IFT for the entire polymer concentration range (C_p).

Temperature, Polymer, and NaCl Concentration Effects on Oil/Polymer Solutions IFT's

The same experimental matrix of parameters was used for this second set of experiments. The general results regarding the polymer and salt concentration effects also apply for the IFT's of oil/polymer systems. The main difference is that all IFT's, as expected, are about 20 dynes/cm lower than those for air/polymer systems.

Figures 16 and 17 compare the behavior of Starpak and Starpak II at temperatures of 25, 50, and 75° C and NaCl concentration of 3%. Starpak is the polymer that exhibits the lowest IFT of the five samples tested. This is consistent with our previous findings, that Starpak is the best permeability reducer polymer.

Temperature, Polymer, and NaCl Concentration Effects on the IFT's of Oil/Polymer/Surfactant Solutions

The same experimental matrix of parameters was used for this third set of experiments. The general results regarding the polymer and salt concentration effects also apply for the IFT's of oil/polymer/surfactant systems. The main difference is that all IFT's, as expected, are lowered from about 25 dynes/cm for oil/polymer systems to about 2-5 dynes/cm. The final polymer solution contained about 0.26% of Arquad 18-50 (surfactant), which is in the range of the critical micellar concentration²⁷.

The interfacial tension data show that the modified starches lower values of IFT between oil and water. However, the value of approximately 2 dynes/cm is thought to be insufficient to mobilize trapped oil in a traditional "Low IFT" process. As an alternate, such materials would help to lower oil saturation near a wellbore where flow velocities are higher and IFT lowering is not as critical a parameter.

Relative Permeability Modification in Gravelpacked Completions

Laboratory tests were planned to measure the performance of samples of modified starch polymer in production well treatments. The polymer is designed to reduce the relative permeability to brine without affecting oil production. The treatment would not require zone isolation, therefore, it could be used in gravelpacked completions. Tests were designed to provide the following:

- Test modified starch products in consolidated cores.
- Measure end point relative permeability before and after polymer injection in single core tests at reservoir temperature.

The results of the single core end point relative permeability experiments show that the polymer system is effective in reducing brine permeability to a greater degree than oil permeability. Table 7 shows these results. The higher concentration polymer in the higher permeability core gave better results. No evidence of core plugging was observed.

Well bore model tests were modeled after a series of experiments performed by D. B. Burnett at Westport Technology for Statoil Oil Company for the Statfjord Field in the North Sea. Test data with starches were to be compared to data with commercially available products offered by industry.

A preliminary test was performed with outcrop Berea/Brady cores to test out equipment and procedures. Testing was at 65° C. The polymer treatment was, 200 ml of polymer mixed at a concentration of 1,000 ppm containing 1,500 ppm crosslinker. Here the permeability of two cores with the high oil permeability are combined (oil zone). In the same manner, the permeability data of the two high water saturation cores are combined as well (water zone). Results showed that the flow capacity of the water zone was significantly reduced by the polymer treatment (from 925 md to 162 md). Oil permeability was not severely affected (84% retained).

The results of the gravelpacked model test using two cores from the Statfjord Field testing at 70° C using 1,000 ppm polymer with 1,500 ppm crosslinker are also summarized in Table 8. In this test, the brine permeability was not reduced as much as before. Permeability dropped from 358 md (Erady) & 266 md (Statfjord) to 94 and 188 md respectively. As was found in the preliminary experiment, retained oil permeability was acceptable, with an average of 80% of the flow capacity regained. No plugging material was observed, either on the gravelpack sand, the screen or the core sample.

In this experiment, it was difficult to determine the amount of polymer actually passing through the core samples and the cores may have been undertreated. After this experiment, to better determine polymer volumes, we made the decision in any subsequent experiments to use dye in the polymer slug to track injection better.

The test data show that the polymer treatment does lower the permeability to brine to a greater degree than the oil permeability. Specific conclusions drawn from the test are:

- Polymer clearly reduced the brine relative permeability more than the oil relative permeability as shown in single core tests.
- Polymer was effective in both types of core material at 70° and 90° C temperatures, respectively, and brine permeability in watered out zones was clearly reduced to a greater extent than was oil permeability reduction.
- In wellbore model tests, polymer penetrated into all cores, regardless of saturation and permeability.

Research on Gel Packages

Introduction

Different gel systems using organic and metallic crosslinkers were evaluated. At selected intervals during the gelling and aging periods the samples were tested for gel strength. The gel volume versus time was recorded to determine their stability. This was

accomplished by observing color and changes in the gel structure, separation of water from the gel body (syneresis) or swelling due to solvent adsorption.

Standard protocols were applied for the visual reading of gel strength. These are inherently subjective but for those practiced in the art, they provide the basis for gel strength conformance. Companies used to work with their own gels have developed these codes. We translated this code to an equivalent scale from 0 to 100 to indicate gel strength. The table of gel codes shown in Table 9 provides description for the reading of gel strength against a percentage of gel strength on the left hand side, using the Marathon, Unocal and Philips Petroleum Gel codes.

Specific starch materials have been identified that have the necessary stability under reservoir conditions for extended time periods. The greatest potential for the modified starch materials tested to date has been for applications where strong crosslinked gels are required. Therefore, in identifying suitable starch biopolymers for water shutoff, this project's objectives have been to perform screening tests on various combinations of polymer, cross-linker and, if necessary, retarder concentrations that will produce the right conditions of pumpability, gelation, thermal and chemical stability.

The gelation process is affected by many variables. Among these are temperature, concentration and type of crosslinking agent, concentration and type of polymer, pH, concentration and type of retarder/accelerator. The proper selection of these variables is well established for commercial products, however, those general guidelines may fail with these new products and therefore we must investigate larger matrices of experimental operating conditions (temperature, pH, polymer and crosslinker concentration, etc.) to find the suitable product.

Efforts have been focused on screening gels using various organic and inorganic crosslinkers.

Characterization of Starches as Polymer Precursors in Crosslinked Gels

Efforts were made to identify a range of field applicable crosslinking systems that are thermally stable, demonstrate sufficient gel strength, and have reaction times reasonable for possible field use. Previous studies had been conducted on the following:

- Starpak (a carboxymethyl ether starch),
- Glucostar C500XP (a corn starch carboxymethyl ether),
- Glucostar 1748 (a potato starch ether),
- Chemstar 6425 (a modified starch),
- Starpak DPP (a corn starch ether),
- Binasol and Instant Jel (highly viscous products not biocide treated), and
- Aqualon (a hydroxyethyl cellulose starch).

Crosslinking agents used were chrome acetate (inorganic) and a hydroquinone complex (HMT). All samples were prepared using standard procedures. After complete mixing of the polymer solution, the appropriate amounts of the polymer solution, brine and the

crosslinker were mixed using a magnetic stirrer. Gel formulations were mixed for 5-15 minutes to ensure uniformity. The formulation is then placed in vials.

All gels were made up with a brine containing 55,000 ppm of dissolved solids. For core injectivity tests, brines were filtered through 1.2 micrometer membrane filters before testing.

The majority of the gel systems succeeded, at 90-100%, in the temperature range from 70° F to 250° F. Syneresis was observed in chromium crosslinking systems at temperatures above 70° F.

All organic crosslinking systems made with hydroquinone gave gels with 90-100% strength. The gel times ranged from four hours to twenty-four hours for temperatures between 200° F and 250° F. No syneresis was observed; however, all of these gel tests must be repeated with flame sealed glass ampoules for long term testing and stability.

All modified starches required lower crosslinker concentration (about three times lower) to make gels than did commercial products.

Significant Results from Gel Screening Experiments

Testing showed that certain modified starches gave robust gels when crosslinked with chrome acetate, the crosslinker most often employed in field applications of polyacrylamide gels. Certain starches gave different gel characteristics as measured by Sydansk's gel strength code.

The majority of the gel systems succeeded at 90-100% in the temperature range from 70° F to 250° F. Strong gels were obtained with chrome acetate in a manner similar to those of low molecular weight polyacrylamides. For example, ringing gels were obtained at 100° F with Starpak at chrome acetate concentrations increasing of 500; 1,000; 1,500; and 2,000 ppm. The 2,000 ppm tube exhibited 5% syneresis after 14 weeks of storage.

Syneresis was observed in chromium crosslinking systems at temperatures above 70° F. Tests used chrome acetate crosslinker at 2,000 ppm and 70° F, with measurements for 16 weeks of storage, see Figure 18. All gels formed were type J, except Glucostar type I.

All organic crosslinking systems made with hydroquinone, gave gels with 90-100% strength. The gel times ranged from four hours to twenty-four hours for temperatures between 200° F and 250° F. No syneresis was observed. However, all of these gel tests must be repeated with flame sealed glass ampoules for long term testing and stability. Table 10 shows the stability of modified starch gels after 16 weeks of storage using the crosslinker Hexamine:Hydroquinone (1:1) at 250° F with 2,000 ppm of crosslinker.

All modified starches required lower crosslinker concentration (about three times lower) to make gels than commercial products.

Binasol and Instant Jel 5-7% concentrations were not successful because the resulting solution was too thick (non-pumpable). Therefore, 3% and 4% solutions provided better results. Instant Jel stored at 150° F transformed from a flowing gel (C grade) to a non-flowing (G and H) and rigid (I) gel in the first two hours, irrespective of crosslinker

concentration. It remained a rigid non-flowing gel, but non-ringing thereafter. At a higher temperature (250° F), the Instant Jel formulations were not temperature stable as shown by viscosity decrease and subsequent occurrence of syneresis. A similar behavior was also observed for the Binasol formulations at 250° F. A gel was not formed at 150° F for this starch solution. These gels appeared to be more stable at lower temperatures.

Chemstar 6425 (a modified starch) and Starpak DPP formed rigid gels (I) after about 2 hours of storage. Starpak DPP subsequently formed a ringing gel (J) after 3 and 4 hrs for the 2,000 and 1,500 ppm crosslinker concentrations, respectively.

After 1 day of storage, slight syneresis (~5%) was observed in the samples prepared in 2,000 ppm crosslinker concentration. On the other hand, this level of syneresis was observed after about 5 days of storage for the 1,500 ppm crosslinked samples. These results suggest that the rate of syneresis may be faster at higher crosslinker concentrations. In addition, our results showed that at lower crosslinker concentrations, the gelation was slightly delayed.

The results from these preliminary investigations with chrome acetate crosslinker show that the samples were not thermally stable at 250° F. The gelation times are longer, and the stability is better at lower temperatures (<150° F). These results open a large market of new applications for these starch-based biopolymers.

In addition, lower concentrations of the polymer and crosslinker were shown to reduce the gelation time and the occurrence of syneresis.

Low Temperature Gels with New Crosslinkers

The results from preliminary investigations with chrome acetate crosslinker showed that the samples were not thermally stable at 250° F. The gelation times were longer, and the stability was better at lower temperatures (<150° F). Results also showed the significant differences in performance among the various starches, so more experiments were scheduled with new crosslinking agents.

Zirconium is an effective and widely used crosslinking agent in oil field fracturing operations. It is environmentally benign and readily available. Two Zirconium salts, Zirconium Acetate and Zirconium Lactate, were screened in tests to duplicate work performed earlier. Materials tested were Starpak DPP, Glucostar, Binasol, and Instant Jel. The latter two materials were evaluated at two concentration levels after encouraging gels were formed with the 5% concentration of product. Testing was conducted at 70° F to test the efficacy of these products as gel agents for low temperature applications.

Results are shown in Table 11. Results indicate that two products, the Binasol and the Instant Jel starches, would be suitable for gel formation at low temperatures. Crosslinking times (less than 24 hours) would allow acceptable pumping and placement. The relatively strong gels formed (H+) would be suitable for blocking of fluids in a porous matrix.

The reaction kinetics for the modified starch and Zirconium crosslinker are very favorable when compared to commercially available systems. Conventional chrome acetate HPAM systems have gel reaction rates too slow for many applications at temperatures below 75°.

For such applications, chemical accelerators are required which add expense and complexity to a normally simple gel package. The starch/Zirconium gel package also is more environmentally acceptable than the chrome/HPAM systems.

However, further work is needed to determine if these gels are of sufficient strength to withstand high drawdown pressures in a near wellbore environment.

High Temperature Delayed Gels

A series of long-term tests was performed to measure the stability of certain gels for longer time periods. Tests were performed with Starpak DP, Glucostar C500, Binasol, and Instant Jel using the organic crosslinking agent HMT/HQ (hexamine hydroquinone). This crosslinking agent has been extensively studied by industry² and offers an acceptable alternative to chrome acetate systems with a product that is more environmentally acceptable than this product.

Test results are shown in Table 12. Significantly, the Instant Jel system developed stable gels (H gels), with Binasol gels nearly as strong (G). Also significant was the delayed reactivity of the gel package.

In elevated temperature applications, it is vitally important to have relatively slow reacting gel packages for shutoff treatments. A long reaction time allows adequate pumping times so that the gelant can be placed within the high temperature formation without resorting to wellbore cooling. The industry has been working to develop new products and processes for this type of high temperature application. Hardy et. al.² discuss the development of a new copolymer and organic crosslinker for high temperature conformance improvement treatments. Their system is promising, and although field results have not yet been released, it is reported that the system can be propagated better than conventional chrome crosslinked systems.

The modified starch products and crosslinkers used in these tests have comparable reaction kinetics. At 250 °F, however, the systems have begun to degrade after approximately two weeks at temperature. Results are available to approximately 30 days for the crosslinked systems. Further work is needed in sealed ampoules to test long term stability.

RESULTS AND CONCLUSIONS DRAWN FROM THE TWO-YEAR PROGRAM

Starch materials and certain modified forms of starches have the functionality to be used in improved recovery applications. There is no one type of modified starch that offers the most promise. In fact, one of the advantages of this family of materials is the ability to develop different variants with properties suited for particular application.

The modified starches do not seem to be of particular benefit in low tension flooding types of recovery processes. In addition, while injectivity is adequate, the materials do not seem to offer advantages in mobility control type of application. The low molecular weights of the samples tested did not provide a range of rheological properties adequate to this type of process.

The most promising application for the modified starches seems to be in conformance improvement. Tests have shown that the materials can be crosslinked in a fashion similar to the xanthans and the polyacrylamide polymers. In particular, the reaction rates of some of the products differ from polyacrylamide systems and that difference may be significant in certain applications

Tests in cores indicate that crosslinked gel systems in fractured (2D) flow conditions hold promise as materials that could be used in injection well water or gas diverting applications. Strong gel systems placed in consolidated cores and in sandpacks showed the ability to shut off the flow of brine. These promising properties make us believe that new commercial development of modified starches as shutoff agents should be considered.

TECHNOLOGY TRANSFER ACTIVITIES

The progress and results of this DOE funded program were presented twice in international meetings. The paper 976007, "Rheology of starch polymers for enhanced oil recovery" was presented in the American Society of Agricultural Engineers, 1997 Annual International Meeting held in Minneapolis, Minnesota (Appendix I). Results corresponding to this research program were also presented in Copenhagen, Denmark at a 1997 DOE/World Bank sponsored workshop. These presentations described our research findings and progress in the six tasks of our proposal. These opportunities have served to widen the interest in the use of agricultural products in the oil industry and the potential applications of modified starches.

A paper describing the results of this research program was presented at the SPE/DOE Eleventh Symposium on Improved Oil Recovery held in Tulsa, Oklahoma, on 19-22 April, 1998. The paper (SPE 39692, "Screening and Evaluation of Modified Starches as Water Shutoff Agents in Fractures and in Matrix Flow Configurations") discussed chemically and/or physically modified starch polymer samples that were subjected to preliminary screening and to subsequent core flow testing. It was well received and should serve as a springboard to development of this technology into commercial applications.

Dr. Gabitto has submitted one abstract describing the preliminary simulation program results to the Sixth Latin American and Caribbean Petroleum Engineering Conference to be held in Caracas, Venezuela, on April, 1999. He has also sent another abstract describing complete results from the simulation studies to the Mathematical and Computational Issues in the Geosciences Conference to be held on San Antonio, Texas on March 1999.

Drs. Barrufet and Gabitto are also preparing a paper describing the most significant results of the program to be presented in a suitable future SPE meeting. This paper will describe ongoing simulation research on gel placement, especially using the experimental zirconium crosslinker results.

EDUCATIONAL ACTIVITIES

The programs at Prairie View A&M University (PVAMU), Chemical Engineering Department, and Texas A&M University (TAMU), Petroleum Engineering and Agricultural Engineering Departments, significantly benefited from the educational activities originated from this research program.

Mr. Norman Alban is scheduled to graduate with a PVAMU Master degree in General Engineering in December 1998. Mr. Alban is completing work on his Master Thesis entitled "Simulation of Polymer Floods in Enhanced Oil Recovery." Several undergraduate students also participated in research work done on this project. They prepared many of the starch biopolymer solutions used in the injectivity tests. Mr. Xun Zhou, a graduate student at PVAMU, worked assembling the injectivity test workstation at the Chemical Engineering Department at PVAMU during 1997. Mr. David Burnett designed and supervised the set-up of the injectivity test workstation. Four high-school students participated during summer 1997 in the NASA Young Scholars Program at the Chemical Engineering Department at PVAMU. They conducted injectivity tests under Mr. Zhou's direction. The assembly of this workstation is a significant asset to the Enhanced Oil Recovery Program at PVAMU.

Mr. Gerald Emesih graduated from the Petroleum Engineering Department at TAMU during 1997. He completed the Ph. D. Dissertation entitled "Characterization of Agricultural Starch Based Biopolymers for Use in Oil and Gas Field Production Processes." Other graduate and undergraduate students from Petroleum Engineering and Agricultural Engineering Departments at TAMU participated part-time in work related to this research project.

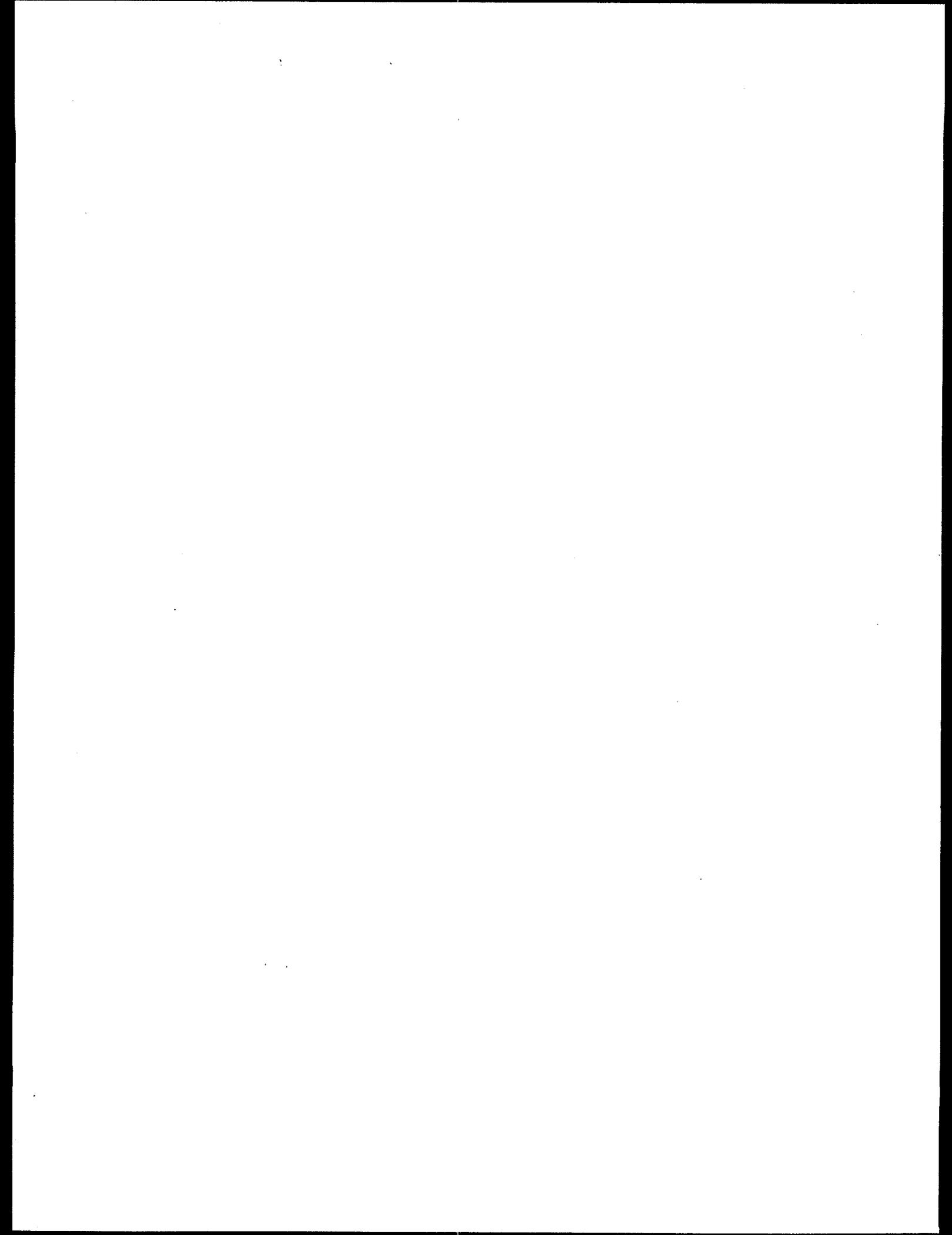
Mr. David Burnett completed the assembly of the apparatus to conduct injectivity tests in fractured porous media. This apparatus that allows the researcher to control the fracture opening in flow tests, significantly improves the experimental capabilities at Petroleum Engineering Department (TAMU). Mr. Burnett also completed an experimental procedures manual²⁸. This manual describes in great detail all the experimental procedures used in this research program.

THE WAY FORWARD: PLANS FOR FUTURE WORK

As a result of the research programs that have proven the concept of using modified starches in improved recovery applications, and of our efforts to disseminate the technology developed from them, we are finding support from industry. Accordingly, we are planning to develop new processes designed for field application. This new effort is designed to be an industry-government partnership with funding sources from each. A proposed research program has been submitted to the US Department of Energy Oil Technology R & D Program (Area of Interest #2: Production Research) in response to their solicitation Number DE-RA-26-98BC15200. Additionally, a proposal to industry for cost sharing of the development program was presented to the Completion Engineering Association on May 7, 1998 (CEA 110 " New Modified Starch Material for Use in Water & Gas Shutoff Applications").

ACKNOWLEDGEMENTS

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Table 1: Examples of modified starch samples used in powder form.

| Sample Name | pH Range | Chemical or Physical Modification | Density (lb/ft ³) |
|-----------------|----------|---|-------------------------------|
| Starpak | 5-7 | Pre-gelatinized Potato Starch (Biocide treated) | 25-35 |
| Starpak DP | 10-10 | Corn Starch Ether | 30-40 |
| Starpak II | 9-10.5 | Corn Starch Carboxymethyl Ether | 30-45 |
| Glucostar CH4 | 7-8 | Hydroxipropyl Starch Ether | 25-30 |
| Chemstar | 9-10 | Carboxymethyl Corn Starch Ether | 35-40 |
| Mira-Sperse 623 | 9-10 | Waxy Corn Derivatized | 11-16 |
| Mira-Thik 603 | 6 | Waxy Corn Derivatized | 33 |
| Instant Jel C | 5-7 | Waxy Corn Derivatized | 30-40 |
| Binasol 90 C | 5-6 | Tapioca | N/A |

Table 2. Rheological parameters for 3% concentration starch samples.

| Starch | NaCl Conc. (%) | K | n | η (Pa s) | STI | Thix |
|-----------------|----------------|-------|-------|---------------|-------|------|
| Binasol 90 C | 0 | 451.2 | 0.682 | 104.3 | 1.436 | 1.02 |
| Binasol 90 C | 3 | 481.2 | 0.686 | 113.3 | 1.421 | 1.01 |
| Binasol 90 C | 6 | 341.3 | 0.703 | 86.92 | 1.400 | 1.03 |
| Instant Jel C | 0 | 1040. | 0.546 | 128.4 | 1.660 | 1.02 |
| Instant Jel C | 3 | 728.4 | 0.578 | 104.32 | 1.600 | 1.01 |
| Instant Jel C | 6 | 1090. | 0.543 | 132.87 | 1.660 | 1.00 |
| Mira-Thik 603 | 0 | 30.5 | 0.897 | 18.98 | 1.130 | 1.05 |
| Mira-Thik 603 | 3 | 35.2 | 0.918 | 24.13 | 1.260 | 1.33 |
| Mira-Thik 603 | 6 | 30.9 | 0.908 | 20.23 | 1.130 | 1.05 |
| Mira-Sperse 623 | 0 | 57.9 | 0.814 | 24.59 | 1.39 | 1.29 |
| Mira-Sperse 623 | 3 | 72.7 | 0.805 | 29.62 | 1.30 | 1.09 |
| Mira-Sperse 623 | 6 | 57.2 | 0.848 | 28.41 | 1.23 | 1.10 |

Table 3. Flow parameters for injection of 0.05% starch solutions into Berea sandstone cores.

| Property | MT 603 | MS 623 | Binasol 90 C | Instant Jel C |
|---------------------------------------|--------|--------|--------------|---------------|
| $\Delta P_{1(\text{brine } 1)}$ (psi) | 6.445 | 7.852 | 5.625 | 6.133 |
| $\Delta P_{1(\text{polymer})}$ (psi) | 15.665 | 12.695 | 29.922 | 16.133 |
| $\Delta P_{1(\text{brine } 2)}$ (psi) | 25.586 | 17.383 | 31.211 | 21.25 |
| $K_{(\text{brine } 1)}$ (md) | 201 | 164 | 227 | 211 |
| $K_{(\text{polymer})}$ (md) | 83 | 101 | 43 | 80 |
| $K_{(\text{brine } 2)}$ (md) | 51 | 74 | 41 | 61 |
| F_r | 2.42 | 1.60 | 5.28 | 2.64 |
| F_{rr} | 3.97 | 2.21 | 5.55 | 3.46 |

Table 4: Resistance factors for various concentrations of starch biopolymers in 6% NaCl injected into consolidated matrix cores.

| Starch Type | Polymer Conc. (w/v) % | Porosity | F_r | F_{rr} |
|-------------|-----------------------|----------|-------|----------|
| Starpak | 0.25 | 0.18 | 3 | 1.95 |
| | 0.5 | 0.18 | 3.13 | 2.3 |
| | 1 | 0.20 | 5.41 | 2.07 |
| | 2 | 0.20 | 2.85 | 1.31 |
| | 3 | 0.19 | 5.88 | 3.83 |
| Starpak II | 0.25 | 0.17 | 17.49 | 9.52 |
| | 0.5 | 0.22 | 10.19 | 6.67 |
| | 1 | 0.21 | 24.64 | 13.46 |
| | 2 | Plugged | ** | ** |
| | 3 | Plugged | ** | ** |
| Starpak DP | 0.25 | 0.17 | 6.51 | 1.27 |
| | 0.5 | 0.18 | 7.89 | 1.41 |
| | 1 | 0.19 | 19.28 | 2.43 |
| | 2 | Plugged | ** | ** |

Table 5: Resistance factors for various concentrations of starch biopolymers in 6% NaCl injected into fractured sandstone cores.

| Starch Type | Polymer Conc. (w/v) % | Porosity | F_r | F_{rr} |
|-------------|-----------------------|----------|-------|----------|
| Starpak | 0.50 | 0.15 | 1.72 | 1.41 |
| | 1.00 | 0.18 | 2.98 | 1.42 |
| | 2 | 0.18 | 2.06 | 1.1 |
| | 3 | 0.19 | 2.15 | 1.29 |
| | 5 | 0.19 | 2.53 | 1.23 |
| Starpak II | 0.50 | 0.21 | 2.07 | 1.19 |
| | 1.00 | 0.18 | 1.62 | 1 |
| | 2 | 0.18 | 8.81 | 1.64 |
| | 3 | 0.17 | 16.46 | 2.25 |
| Starpak DP | 0.50 | 0.21 | 3.95 | 2.55 |
| | 1.00 | 0.19 | 2.83 | 1.77 |
| | 2 | 0.19 | 2.4 | 1.09 |
| | 3 | 0.16 | 6.09 | 1.78 |
| | 5 | 0.17 | 16.57 | 5.11 |

Table 6. Reservoir parameters for numerical simulation.

| Dimensions | $L_x = 1,000$ ft | $L_y = 1,000$ ft | $L_z = 30$ ft |
|---------------------------|-------------------|----------------------|--|
| Top layer permeability | $k_x = 100$ md. | $k_y = 100$ md. | $k_z = 100$ md. |
| Bottom layer permeability | $k_x = 1,000$ md. | $k_y = 1,000$ md. | $k_z = 1,000$ md. |
| Thickness | Top layer = 15 ft | Bottom layer = 15 ft | Volume of oil in place = 0.8075×10^6 bbl. |

Table 7: Single Core relative permeability tests.

| Before Polymer ¹ | After Polymer ¹ | | | | |
|-----------------------------|----------------------------|----------|----------|---------------|-------------------------------|
| Ko @ Swr | Kw @ Sor | Kw @ Sor | Ko @ Swr | Retained Ko % | F _{rr} (to water) |
| 1286 | 358 | 94 | 1015 | 79% | 3.81 |
| 4101 | 266 | 188 | 3825 | 93% | 1.42 |

[1] permeabilities are in md

Table 8: Summary of gravelpacked core tests.

| Sample | Before Polymer | | After Polymer | | | |
|----------------------------|----------------|---------|---------------|----------|--------------------|---------------------------------|
| | Ko @ Swr | Kw @Sor | Kw @Sor | Ko @ Swr | Retained Ko % | F _{rr} (to water) |
| Reservoir Core (Statfjord) | 609 | | | 575 | 94 % (oil zone) | |
| Reservoir Core (Statfjord) | | 266 | 188 | | | 2.21 (average in water zone) |
| Brady 3 | | 358 | 94 | | | |
| Brady 4 | 742 | | | 527 | 71 % (oil zone) | |
| Berea (Oil zone) | 75 | | | 63 | 84 % | |
| Berea (Water zone) | | 925 | 162 | | | 5.71 |

Table 9: Gel Strength Codes-Cross-Reference and General Guidelines.

| % of Gel Strength | Marathon | Unocal | Philips | Detailed Gel Description |
|-------------------|----------|--------|---------|--|
| 0 | A- | 1 | 0 | Waterlike |
| 0 | A | 1+ | 0 | Viscosity similar to base polymer |
| 5 | A+ | 2- | 5 | Viscosity increased |
| 10 | A/B | 2 | 10 | Some gel Structure, easily Pourable |
| 20 | B | 2+ | 20 | Highly flowing gel, pours with difficulty detectable |
| 30 | B+ | 3- | 30 | Gel Structure, most gel flows to bottle cap |
| 40 | C | 3 | 40 | flowing gel, gel tongue length greater than "6" |
| 45 | C+ | 3+ | 45 | Flowing gel, gel tongue length between "4" - "6" |
| 50 | D | 4- | 50 | Moderately Flowing , gel tongue length between "2- 4" |
| 55 | D+ | 4 | 55 | Moderately Flowing , gel tongue length between "1- 2" |
| 60 | E | 4+ | 60 | Barely Flowing, gel tongue less than "1" |
| 65 | E+ | 4++ | 65 | Gel tongue just exits vial, major portion doesn't flow |
| 70 | F | 5- | 70 | Gel tongue will not exit vial, just short of reaching vial cap |
| 75 | F+ | 5-/5 | 75 | Gel tongue flows 3/4 down the vial, towards the cap |
| 80 | G | 5 | 80 | Gel tongue flows 1/2 down the vial, towards the cap |
| 85 | G+ | 5/5+ | 85 | Gel tongue flows 1/4 down the vial, towards the cap |
| 90 | H | 5+ | 90 | Gel surface flows only slightly, very short tongue length |
| 95 | H+ | 5+/5++ | 95 | Deformable non flowing gel, slight surface movement |
| 100 | I | 5++ | 100 | Rigid Gel, gel will not move upon inversion |
| 100+ | J | 6 | 100+ | Ringing Gel, vibration felt after tapping vial |
| syn | syn | syn | syn | syneresis, shrinkage of gel |

Table 10: Resulting biopolymer gels after 16 weeks of storage using Hexamine:Hydroquinone (1:1) at 250°F with 2,000 ppm of crosslinker.

| <i>Starpak DP</i> | | <i>Glucostar C500</i> | |
|-------------------|--------------|-----------------------|--------------|
| Cp (w/v) % | Gel Strength | Cp (w/v) % | Gel Strength |
| 2 | H+ | 2 | I |
| 3 | H+ | 3 | I |
| 4 | G | 4 | F |
| 5 | F | 5 | C |

Table 11: Results of Gel Screening Tests at 70°F, 5% NaCl: 0.5% CaCl₂.

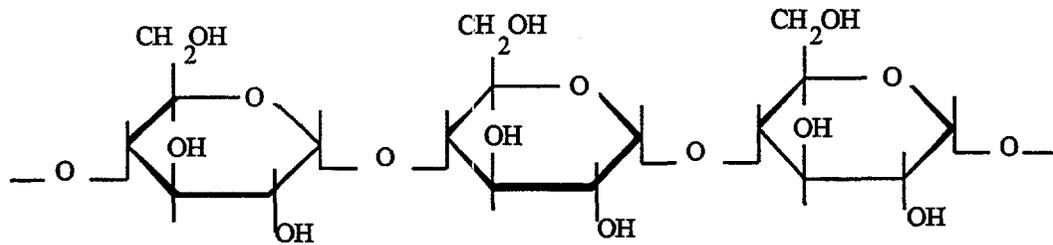
| Crosslinker | Gel System | Observations |
|--------------------------|----------------|---|
| Zirconium Lactate | - | |
| 0.5% | 5% Starpak DPP | Instant gelation (G ⁺ to H gel) Clear reaction, no ppt. Stable H gel after 9 days |
| 0.5% | 5% Glucostar | No ppt. No gelation |
| 0.5% | 5% Binasol | No ppt. No gelation |
| 0.5% | 5% Instant Jel | No ppt. No gelation |
| | | |
| Zirconium Acetate | | |
| 0.5% | 5% Starpak DPP | Rapid rxn. Phase separation, ppt. |
| | 5% Glucostar | Rapid rxn. Phase separation, ppt. |
| | 5% Binasol | H+ gel (non-flowing) in 24 hrs. Stable H+ gel after 10 days (will flow if shaken) |
| | 7% Binasol | H+ gel (non-flowing) in 24 hrs. Stable H+ gel after 10 days (will flow if shaken) |
| | 5% Instant Jel | Compatible fluids. H+ gel within 24 hrs Stable H+ gel after 10 days (will flow if shaken) |
| | 7% Instant Jel | Compatible fluids. H+ gel within 24 hrs Stable H+ gel after 10 days (will flow if shaken) no perceptible increase in gel strength |

Table 12: High Temperature Gel Stability.

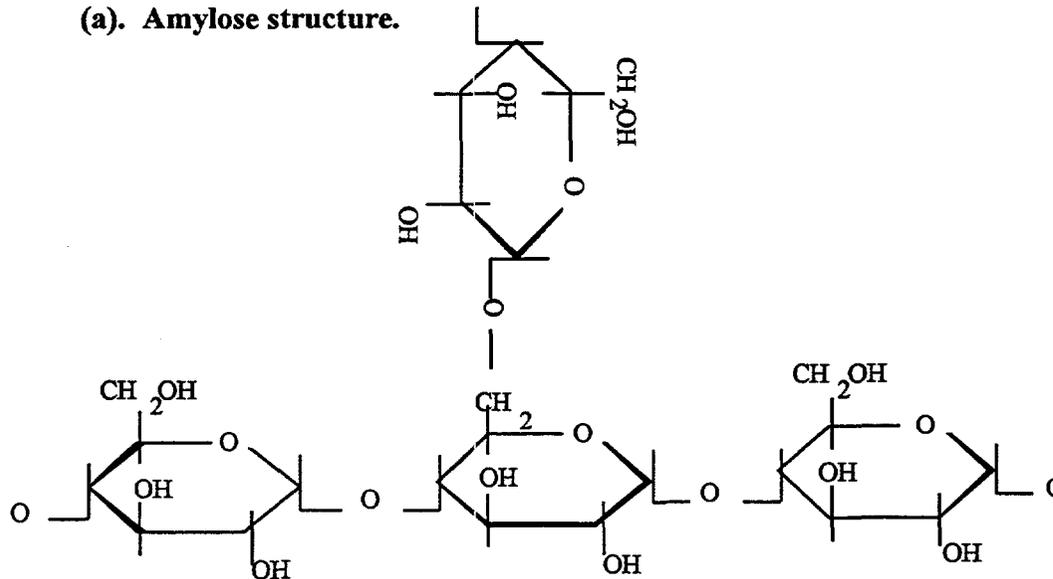
Temperature: 200°F

XL : HMT/HQ (1:1)

| Gel Screen | Starpak DP | | | Glucostar C 500 | | | Binasol | | | Instant Gel | | | | | |
|------------|---------------|--------------------|--------------|-----------------|--------|--------|---------|--------|--------|-------------|--------|--------|--------|--------|--------|
| | Polymer (ppm) | Cross-Linker (ppm) | Elapsed time | Gel 1 | Gel 2 | Gel 3 | Gel 4 | Gel 5 | Gel 6 | Gel 7 | Gel 8 | Gel 9 | Gel 10 | Gel 11 | Gel 12 |
| 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 30,000 | 40,000 | 40,000 | 40,000 |
| 1,500 | 2,000 | 3,000 | 1,500 | 2,000 | 3,000 | 1,500 | 2,000 | 3,000 | 1,500 | 2,000 | 3,000 | 1,500 | 2,000 | 3,000 | |
| 0 | A | A | A | A | A | A | A | A | A | A | A | A | A | A | A |
| 1 hour | A | A | A | A | A | A | A | A | A | A | A | A | A | A | A |
| 2 hours | A | A | A | A | A | A | A | A | A | A | A | A | A | A | A |
| 4 hours | A | A | A | A | A | A | A | A | A | A | A | A | A | A | A |
| 6 hours | A | A | A | A | A | A | A | A | A | A | A | A | A | A | A |
| 24 hours | A | A | A | A | A | A | A | A | A | A | A | B+ | A | D | G |
| 48 hours | A | A | B | A+ | A+ | B | B+ | E | G | G+ | H | H+ | | | |
| 5 days | A | A | B | A | A | A | D | F | G | G+ | H | H+ | | | |
| 8 days | A | A | A/B | A | A | A | E | F | G | G+ | H | H+ | | | |
| 12 days | A | A | A | A | A | A | E | F | G | G+ | H | H+ | | | |
| 23 days | A | A | A | A | A | A | E | F | G | G+ | H | H | | | |
| 30 days | A | A | A | A | A | A | E | F | G | G+ | H | H | | | |



(a). Amylose structure.



(b). Amylopectin structure.

Fig. 1- Structures of Amylose and Amylopectin starch components.

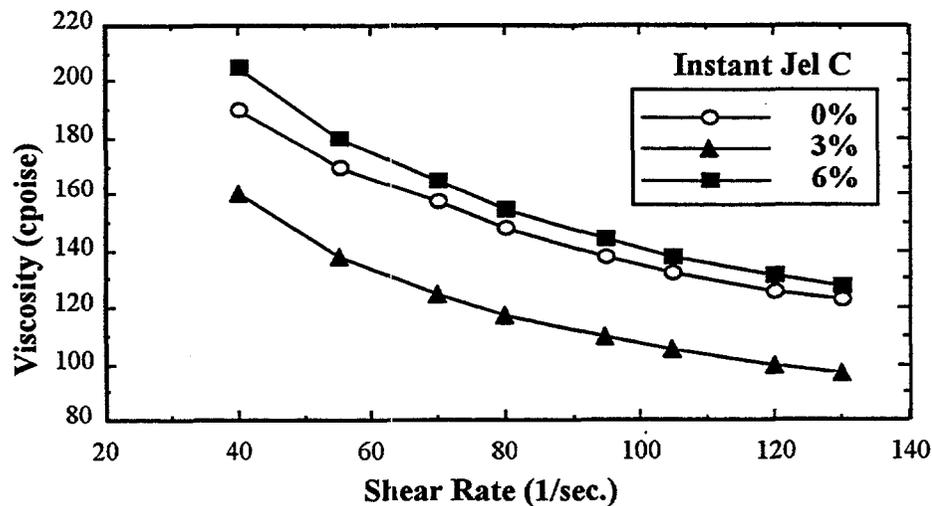


Fig. 2- Viscosity dependence on shear rate for 3% Instant Jel C starch solutions prepared in various brine concentrations.

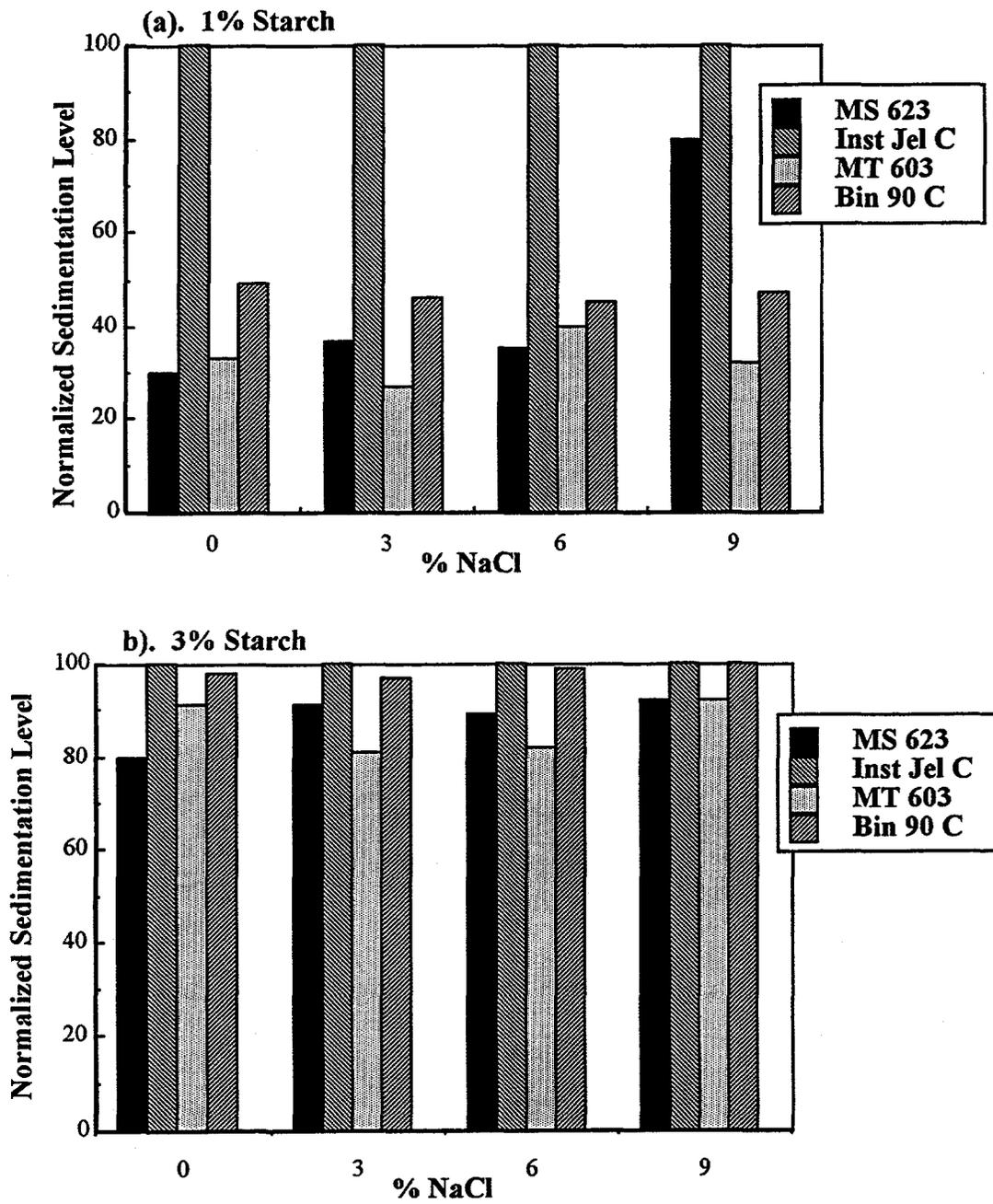


Fig. 3- Normalized sedimentation levels after two weeks storage for 1% and 3% starch solutions prepared in various brine concentrations.

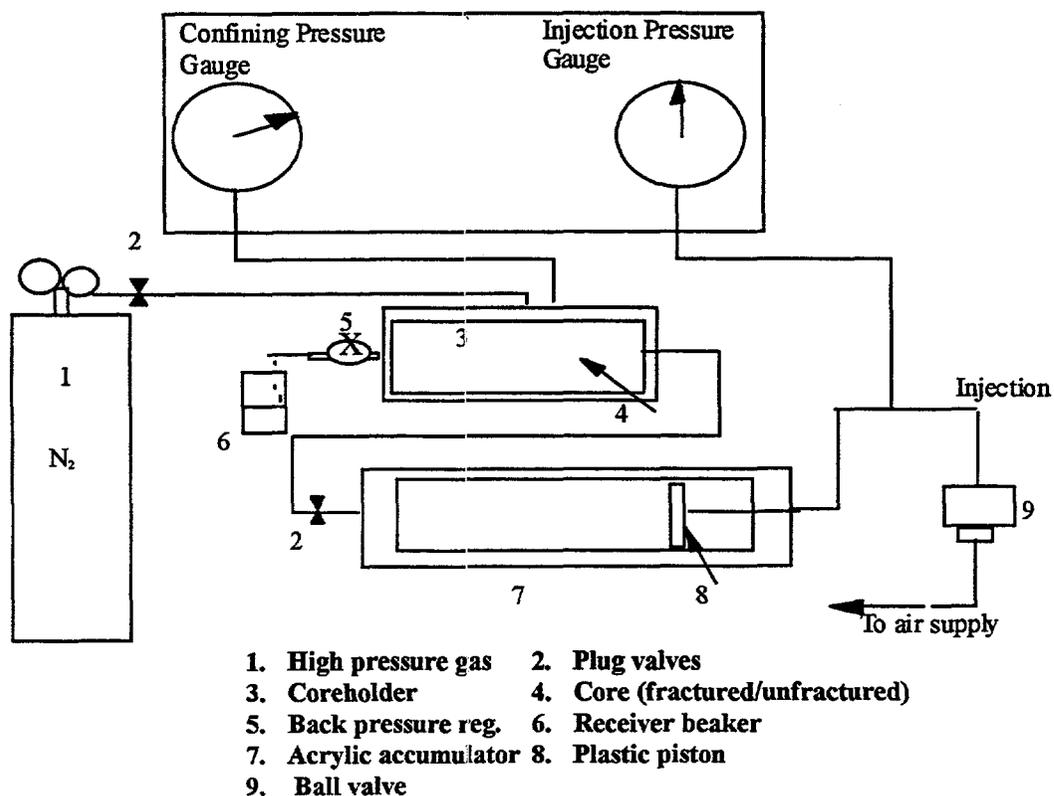


Fig. 4- Constant pressure injection tests apparatus.

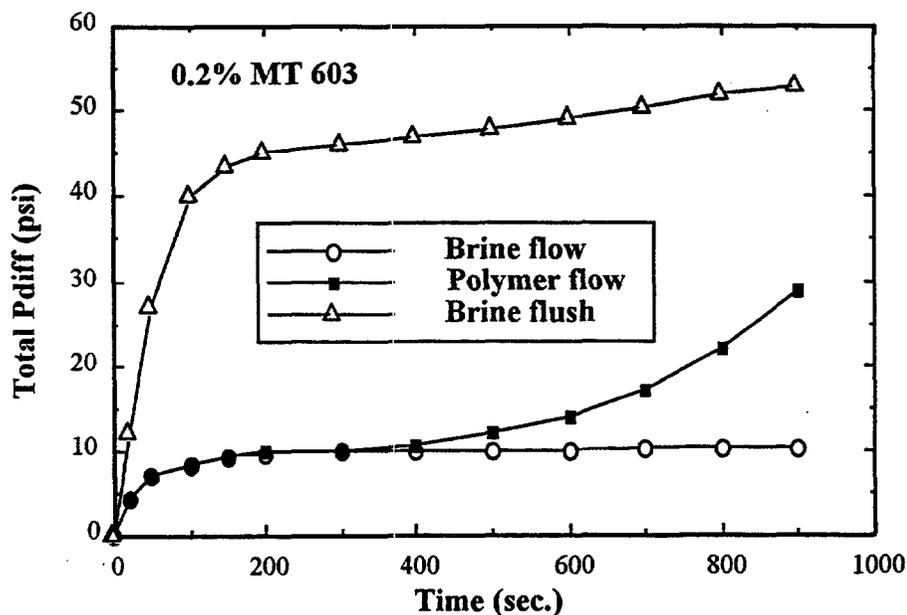


Fig. 5- Total differential pressure profiles before, during and after polymer injection through a Berea core.

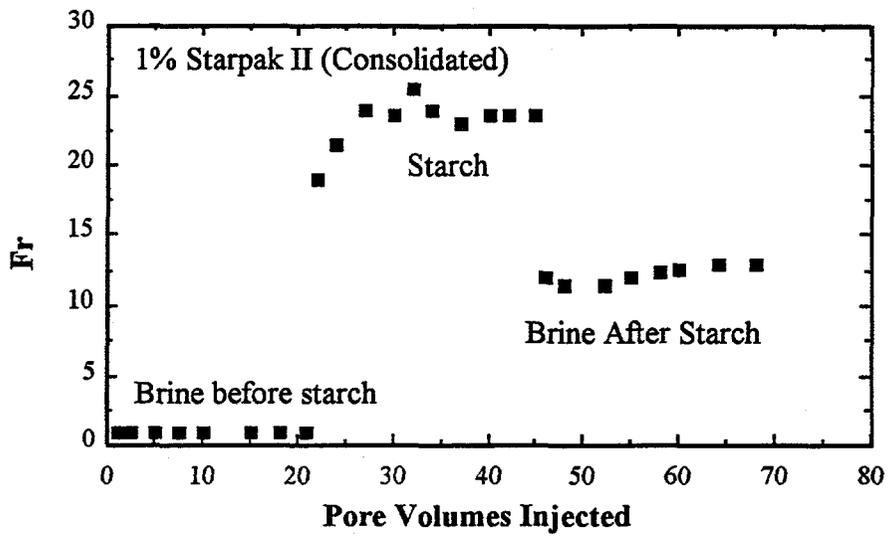


Fig. 6- Permeability reductions obtained using 1% Starpak II through a consolidated Berea core.

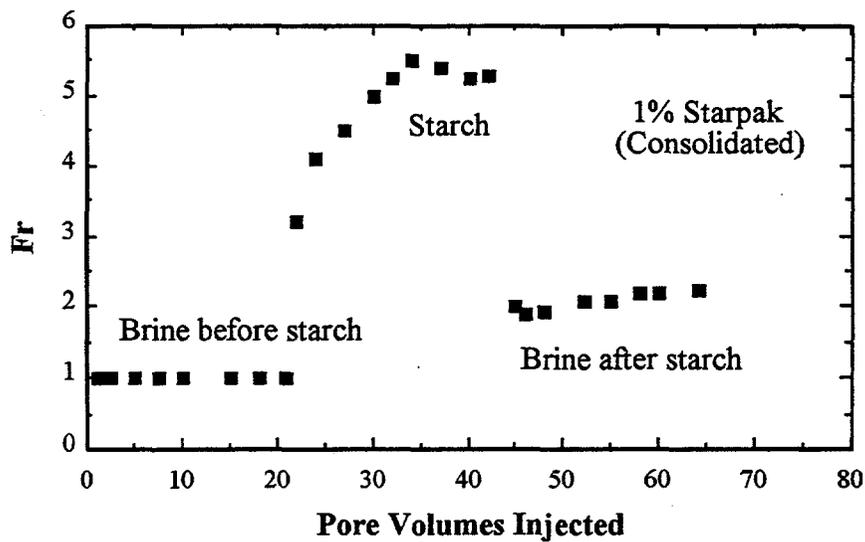


Fig. 7- Permeability reductions obtained using 1% Starpak through a consolidated Berea core.

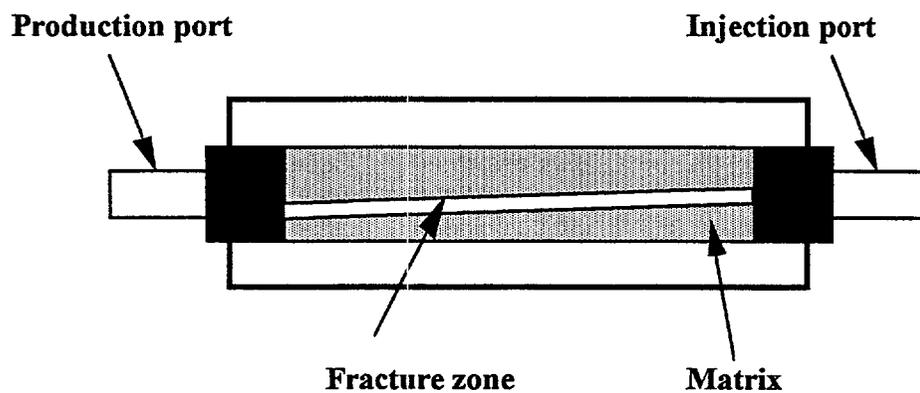


Fig. 8- Fractured core flow test cell.

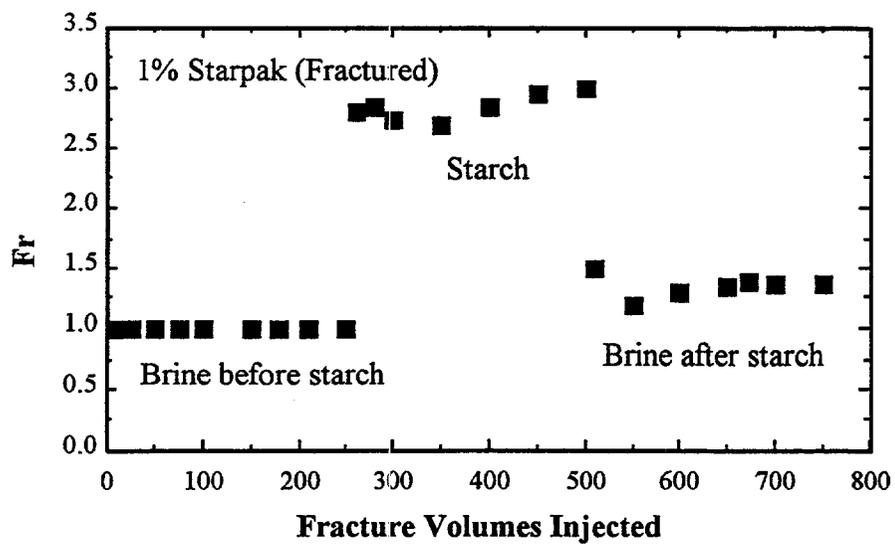


Fig. 9- Permeability reductions obtained using 1% Starpak through a fractured Berea core.

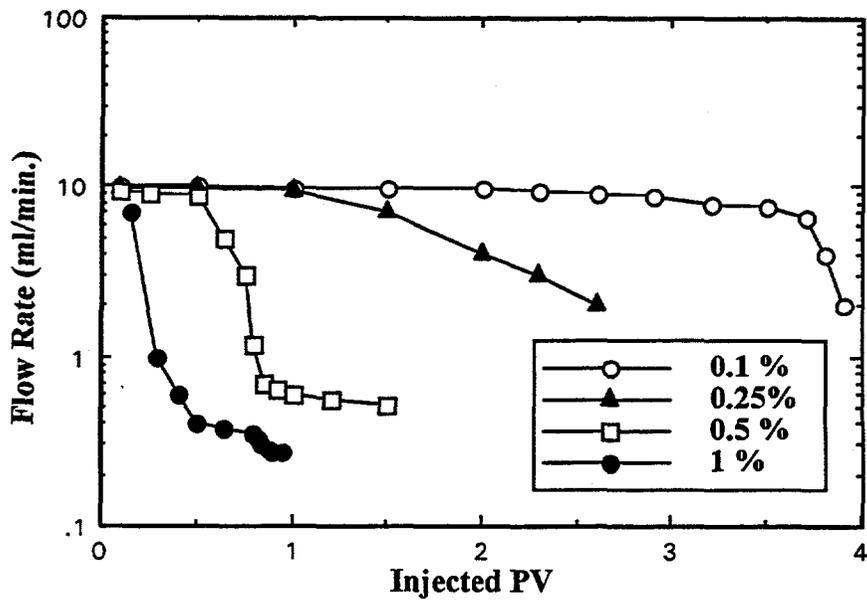


Fig. 10- Flow rate time evolution for Starpak at different concentrations.

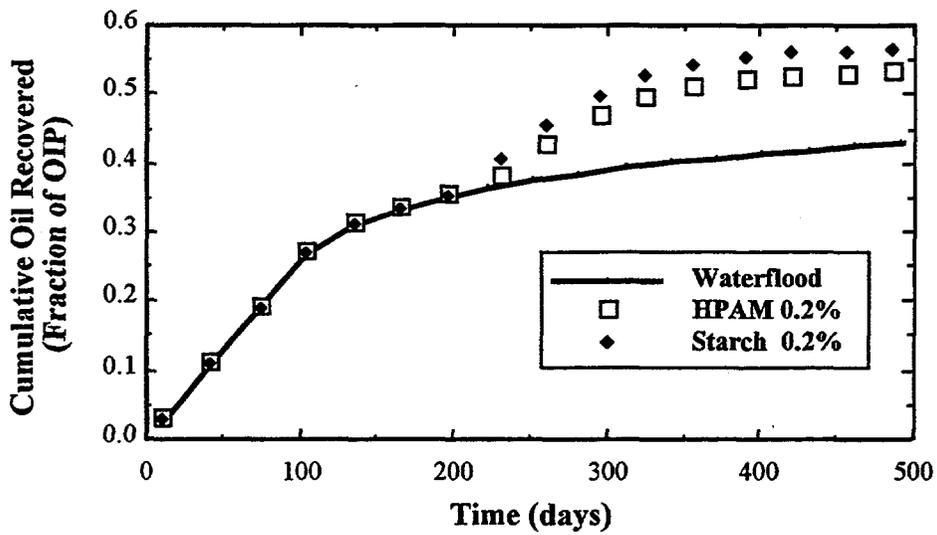


Fig. 11- Cumulative oil recovered vs. time before and after polymer treatment.

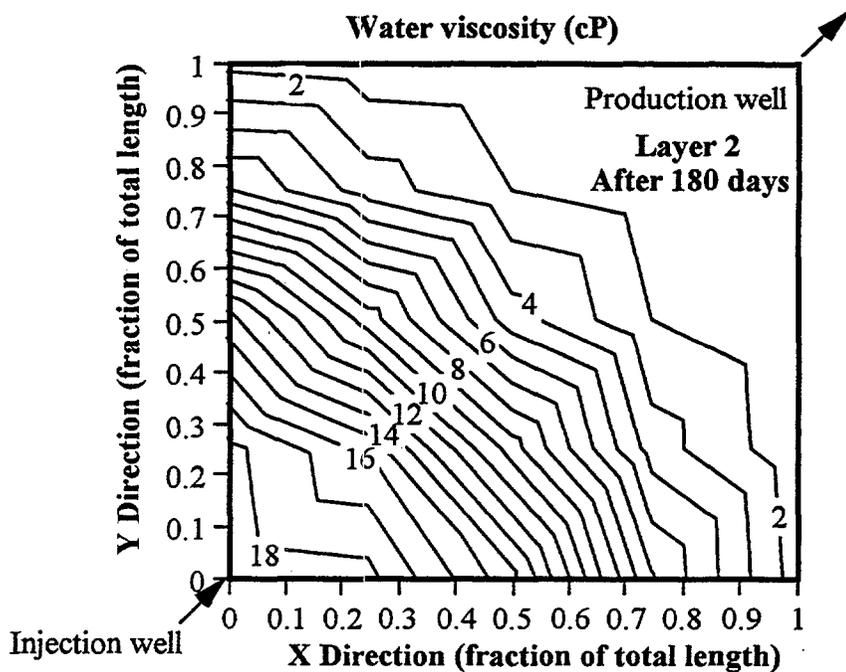


Fig. 12- Water phase viscosity (cP) contour for Starch biopolymer treatment.

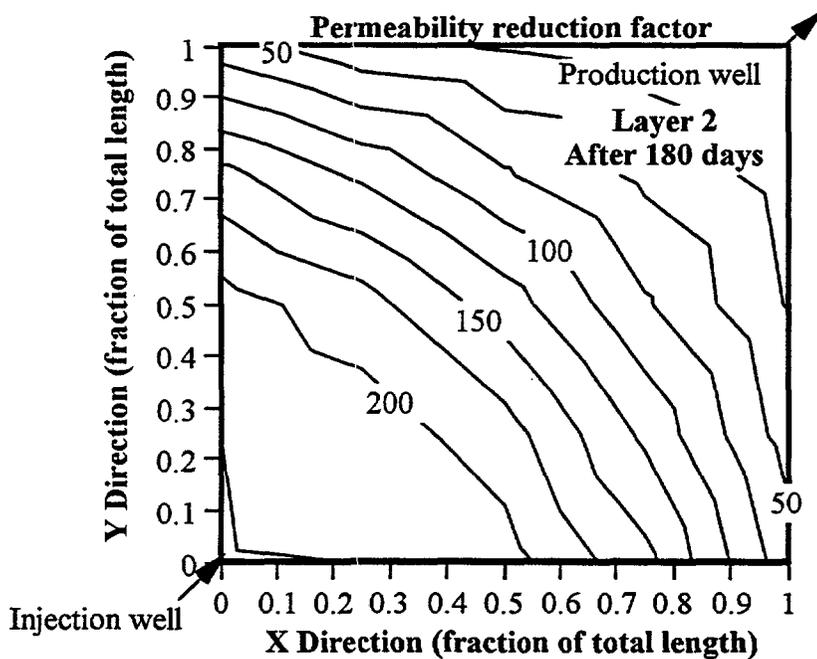


Fig. 13- Permeability reduction factor (F_{rr}) contour for Starch biopolymer treatment.

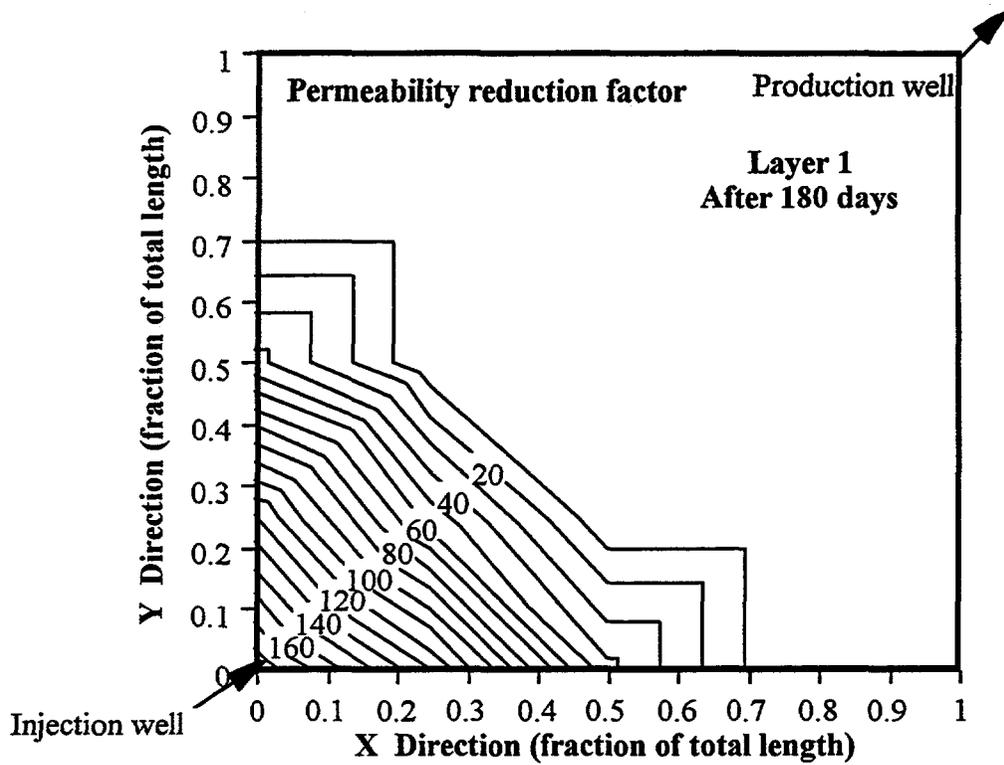


Fig. 14- Permeability reduction factor (F_{rr}) contour for Starch biopolymer treatment in layer 1.

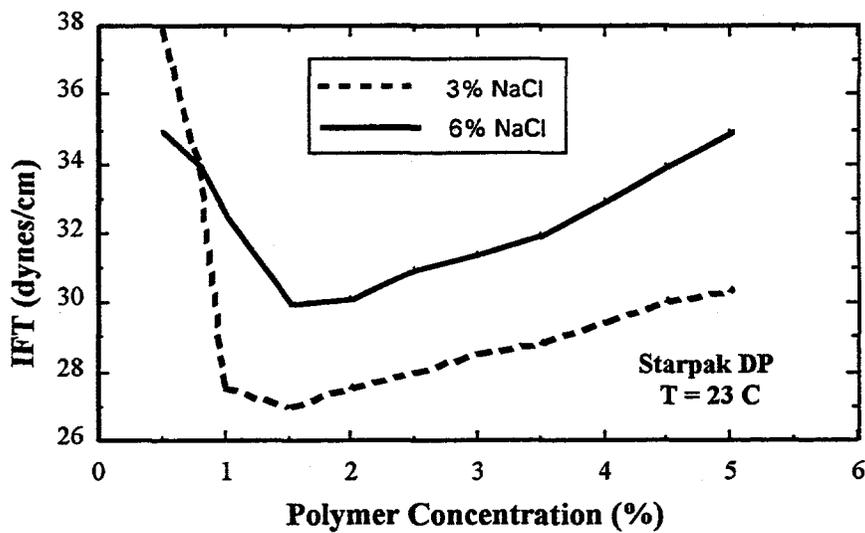


Fig. 15- Air/Polymer interfacial tension of Starpak solutions at 3% and 6% NaCl for different polymer concentrations (no surfactant added).

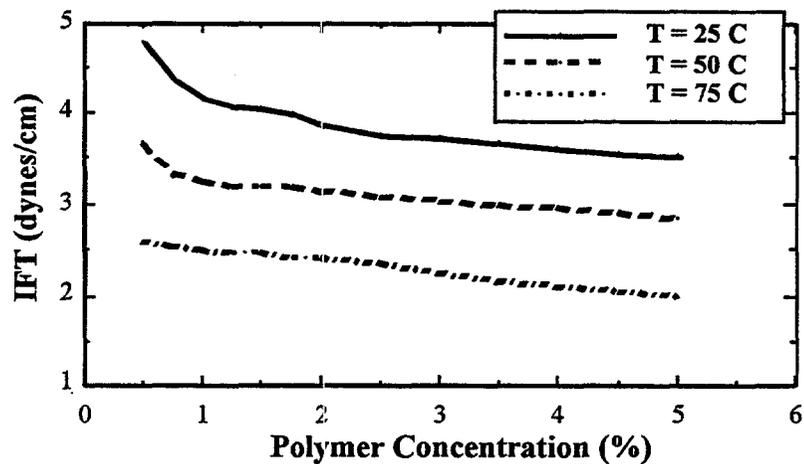


Fig. 16- Decane/Polymer IFT of Starpak II solutions at 3% NaCl for different polymer concentrations (no surfactant added).

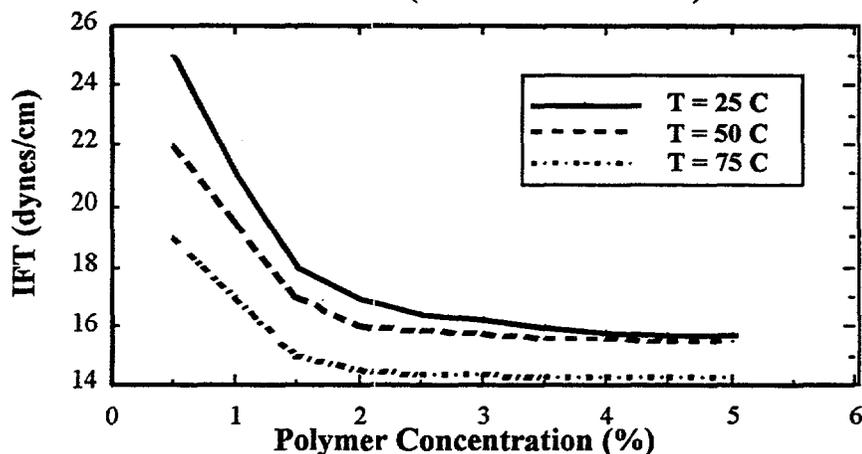


Fig. 17- Decane/Polymer IFT of Starpak solutions at 3 % and 6% NaCl concentrations, 0.26% surfactant added.

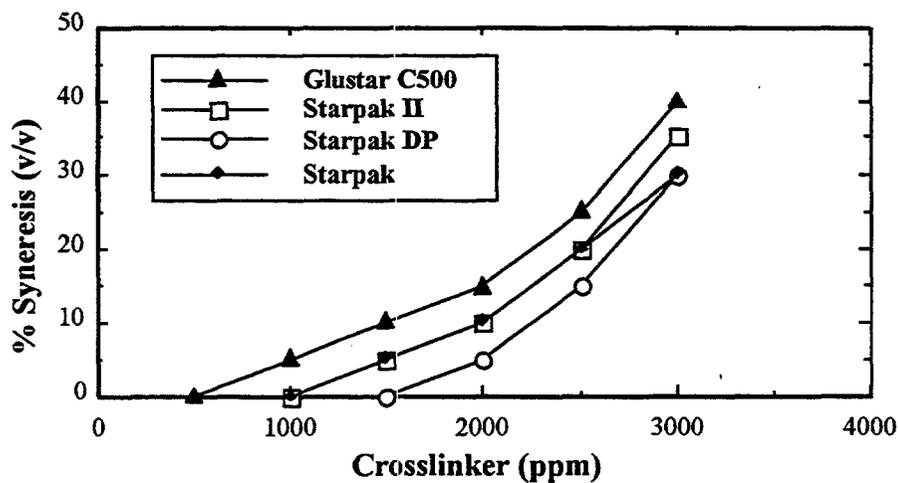


Fig. 18-. Degree of syneresis obtained with chrome acetate crosslinker at 2,000 ppm and 70 °F, after 16 weeks of storage.

APPENDIX I

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APPENDIX II

SIMULATION PROGRAM

Abstract

A chemical flooding simulator (UTCHEM) has been used to compare two different polymers flooding products, a synthetic polymer and a starch biopolymer. A typical one-quarter 5-spot domain with one injection and one production well was simulated. In order to study permeability contrast the reservoir had two vertical layers with different permeabilities. Water floods and polymer floods with and without crosslinkers were simulated. Pressure distribution, oil saturation, oil production rates, water-oil ratios, water production rates, and chemical distributions were computed. The results were analyzed and conclusions drawn.

Simulator Background

UTCHEM, a chemical simulator developed by researchers at the University of Texas at Austin¹, has been used for the simulation program. UTCHEM is a multicomponent, multiphase, three-dimensional compositional with variable temperature simulation model². The basic equations are as follows:

- 1) the mass balance equations, which are solved up to 21 species;
- 2) the aqueous phase pressure, which is obtained by an overall mass balance on volume occupying species (water, oil, surfactant, alcohol, and gas). The other phase pressures are computed by using the capillary pressures between phases;
- 3) the energy balance equation, which includes heat flow between the reservoir and the overburden rocks.

The flow equations allow for compressibility of rock and fluids, dispersion and molecular diffusion, chemical reactions, and phase behavior and are complemented by constitutive equations. The model includes options for multiple wells completed either horizontally or vertically. Aquifer boundaries are modeled as constant potential surfaces or as closed surfaces.

The flow equations are solved using a block-centered finite-difference scheme. The solution method is implicit in pressure and explicit in concentration (IMPES-like). Either one, two-point upstream, or third-order spatial, discretization is used. A brief description of the equations used in the code is provided below.

Mass Conservation Equations

The assumptions imposed when developing the flow equations are:

- 1) local thermodynamic equilibrium, except for tracers;
- 2) immobile solid phases;

- 3) slightly compressible rock and fluids;
- 4) Fickian dispersion;
- 5) ideal mixing; and
- 6) Darcy's law.

The boundary conditions are no flow and no dispersive flux across the impermeable boundaries.

The mass continuity for component k in association with Darcy's law is given in terms of overall volume of component k per unit pore volume (\tilde{C}_k) as,

$$\frac{\partial}{\partial t}(\phi \tilde{C}_k \rho_k) + \underline{\nabla} \cdot \sum_{j=1}^{n_p} r_k (C_{kj} \underline{u}_j - \underline{\nabla} \cdot \underline{\underline{D}}) = R_k \quad (1),$$

where the overall volume of component k is the summation over all phases including the adsorbed phases,

$$\tilde{C}_k = \left\{ 1 - \sum_{k=1}^{n_{cv}} \hat{C}_k \right\} \sum_{j=1}^{n_p} S_j C_{kj} + \hat{C}_k, \quad \text{for } k=1, \dots, n_{cv} \quad (2),$$

n_{cv} is the total number of volume occupying components. These components are water, oil, surfactant, and gas, n_p is the number of phases, \hat{C}_k is the adsorbed concentration of species k, and ρ_k is the density of pure component k at a reference phase pressure P_r relative to its density at reference pressure P_{r0} , usually taken at a surface condition of 1 atm.

The phase flux from Darcy's law is given by,

$$\underline{u}_j = - \frac{k_{rj} - k}{\mu_j} \cdot (\underline{\nabla} P_j - \gamma_j \underline{\nabla} h) \quad (3),$$

where \underline{k} is the intrinsic permeability tensor and h is the vertical coordinate, k_{rj} , μ_j , and γ_j are the relative permeability, viscosity, and specific weight for phase j. The source terms R_k are a combination of all rate terms for a particular component.

Pressure Conservation Equations

The pressure equation is developed by summing the mass balance equations over all volume occupying components, substituting Darcy's law for the phase flux terms, using the definition of capillary pressure, and noting that $(\sum_{k=1}^{n_{cv}} C_{kj}) = 1$. The pressure equation in terms of the reference phase pressure (phase 1) is given by,

$$\phi C_t \frac{\partial P_j}{\partial t} + \nabla \cdot \underline{k} \cdot \lambda_{rTc} \nabla P_j = -\nabla \cdot \sum_{j=1}^{n_{cv}} \underline{k} \cdot \lambda_{rTc} \nabla h +$$

$$+ \nabla \cdot \sum_{j=1}^{n_{cv}} \underline{k} \lambda_{rTc} \cdot \nabla P_{C_{jw}} + \sum_{j=1}^{n_{cv}} Q_k \quad (4),$$

where the total relative mobility including the correction for fluid compressibility is given by $\lambda_{rTc} = \sum_{k=1}^{n_{cv}} \lambda_{rjc}$, and $\lambda_{rjc} = \frac{k_{rj}}{\mu_j} \sum_{k=1}^{n_{cv}} r_k C_{kj}$. C_t is the total compressibility calculated as the volume weighted sum of matrix and component compressibilities.

Fluid and Soil Properties

Geological heterogeneities are the key factor that reduces the effectiveness of chemical enhanced recovery processes because their success depends on the delivery of injected chemicals and water into the subsurface. In order to capture some of the geological features, reservoir properties such as formation permeability, porosity, residual phase saturation, phase relative permeability, and phase capillary pressure are allowed to vary spatially in UTCHEM. Phase trapping functions and adsorption of both surfactant and polymer are modeled as a function of permeability.

Polymer Adsorption

Polymer adsorption can be an important mechanism for a chemical recovery project since it causes retardation polymer consumption. The retention of polymer molecules in permeable media is due to both adsorption onto solid surfaces and trapping within small pores. UTCHEM uses a Langmuir-type isotherm to describe the adsorption level of a polymer, which takes into account the salinity, polymer concentration, and soil permeability³. The adsorption is irreversible with concentration and reversible with salinity. The adsorbed concentration (\hat{C}_p) is given by,

$$\hat{C}_p = \min \left\{ \tilde{C}_p, \frac{a_p (\tilde{C}_p - \hat{C}_p)}{1 + b_p (\tilde{C}_p - \hat{C}_p)} \right\} \quad (5).$$

The minimum is taken to guarantee that the adsorption is no greater than the total polymer concentration. Adsorption increases linearly with effective salinity and decreases as follows,

$$a_p = (a_{p1} + a_{p2} C_{SEP}) k^{-0.5} \quad (6).$$

The adsorption parameters a_{p1} , a_{p2} and b_p are found by matching laboratory polymer adsorption data. The effective salinity for polymer (C_{SEP}) is,

$$C_{SEP} = \frac{C_{s1} + (\beta_p - 1) C_{c1}}{C_{w1}} \quad (7),$$

where C_{s1} , C_{c1} , and C_{w1} are the anion, calcium, and water concentrations in the aqueous phase and β_p is experimentally determined.

Viscosity

Liquid phase viscosities are modeled in terms of pure component viscosities and the phase concentrations of the organic, water and chemicals,

$$\mu_k = C_{wk} \mu_k e^{\alpha_w (C_{ok} + C_{chk})} + C_{ok} \mu_k e^{\alpha_o (C_{wk} + C_{chk})} + C_{chk} \mu_k e^{\alpha_{ch} (C_{wk} + C_{ok})} \quad (8),$$

for $k = \text{water, oil or chemical}$.

The α parameters are determined by matching laboratory microemulsion viscosities at several compositions. In the absence of polymer, water and oil phase viscosities are reduced to pure water and oil viscosities. When polymer is present μ_w is replaced by μ_p defined below.

The viscosity of the polymer solution depends on the concentration of polymer and on salinity,

$$\mu_p^0 = \mu_w \{ 1 + (A_{pw} C_{pw} + A_{po} C_{pw}^2 + A_{pch} C_{pw}^3) C_{SEP}^{Sp} \} \quad (9),$$

where C_{pw} is the polymer concentration in water, μ_w is the water viscosity, A_{pi} are constants. The factor C_{SEP}^{Sp} allows for dependence of polymer viscosity on salinity and hardness.

The reduction in the viscosity of the polymer solution is a function of shear rate (γ) and is modeled by using Meter's equation⁴,

$$\mu_p = \mu_w + (\mu_p^0 - \mu_w) / (1 + \{ \gamma / \gamma_{1/2} \}^{P\alpha-1}) \quad (10),$$

where $\gamma_{1/2}$ is the shear rate at which viscosity is the average of μ_p^0 and μ_w , and $P\alpha$ is an empirical coefficient.

Gelation Reaction Kinetics

Permeability modification by gel formation is an important mechanism to improve chemical enhanced oil recovery. Gels are formed either on the surface before injection or in situ, by controlled release of an ionic crosslinking agent or by buildup of crosslinked polymer layers. The three aforementioned mechanisms can be simulated in UTCHEM. The gel properties modeled in UTCHEM¹ include:

- 1) effect of gel on aqueous phase viscosity;
- 2) gel retention on matrix; and
- 3) aqueous phase permeability reduction.

The viscosity of an aqueous solution containing gel is modeled using the following equation:

$$\mu_p = \mu_w \{ 1 + (A_{pw} C_{pw} + A_{po} C_{pw}^2 + A_{pch} C_{pw}^3) C_{SEP}^{Sp} + A_{gw} C_{pw} + A_{go} C_{pw}^2 \} \quad (11).$$

Gel retention modeling is done using a Langmuir-like isotherm. The effect of gel on aqueous phase permeability reduction is taken into account through a residual resistance factor (F_r) commonly used for polymer flooding,

$$F_r = 1 + \frac{[F_{rmax} - 1] A_g C_{gw}}{1 + B_g C_{gw}} \quad (12).$$

Gel reactions are implemented in the source term as gel kinetic equations and the mass conservation equation is solved with reacted amounts of each gel component. Polymer molecules are crosslinked by Cr(III), which is known to be one of the most widely used crosslinkers. Three types of gel reactions and kinetics are used in UTCHEM. The kinetics of polymer/chromium chloride gel was modified, and gel reactions of polymer/chromium malonate gel and silicate are modeled. Two sets of reactions and kinetics for polymer/chromium chloride gel are implemented in the simulator. The first set uses in-situ gelation of polymer with sodium dichromate with reducing agent thiourea, and the second employs gelation of Cr(III) with polymer to form gel. The influence of pH is implemented in the computer program for more realistic simulation. The first set of reactions was used in our simulation studies. Suitable values for the three reaction schemes used were proposed.

Permeability Modification Calculations

The three dimensional permeability simulation runs were conducted on a one-quarter 5-spot, two layers 1,000 x 1,000 x 30 ft reservoir model with an injection well and a production well located at opposite corners of the model. This system is equivalent to a 46 acres well spacing, which approximates typical field waterflooding well spacing. Each layer was 15 ft thick. Horizontal permeabilities in the x and y directions were 100 md in the top layer and 1,000 md in the bottom layer. The top (low permeability) and bottom (high permeability) layers will be referred to as number one and two, respectively. Consequently, a vertical/horizontal permeability contrast value of 0.1 is achieved. Original oil in place was 0.8075×10^6 bbl. Okessa sandstone samples were used as reservoir material. Rock properties were determined experimentally, using procedures described previously in this report, see Table A1 for a summary of reservoir parameters used in the simulation. Constant injection rates were used in this project. This means that the pressure will vary to maintain the constant production rate. The amount of oil and aqueous phases produced is a function of the two phases' mobilities.

This system was selected for comparison with the results presented by Gao et al.⁵ These researchers used the BEST-GEL⁵ simulator developed at NIPER to study permeability modification.

Computations were made for three kinds of treatments: waterflooding, and polymer flooding with and without gel formation. These computations were repeated using a hydrolyzed polyacrylamide polymer (HPAM) and a starch biopolymer (unmodified waxy corn starch). The relative permeability, capillary pressure tables, viscosity data, permeability reduction factors, and other biopolymer properties were experimentally determined. The relative permeability curve determined for a linear Okessa sandstone core is shown in Figure A1. Other system properties used in the simulations are presented in Table A2.

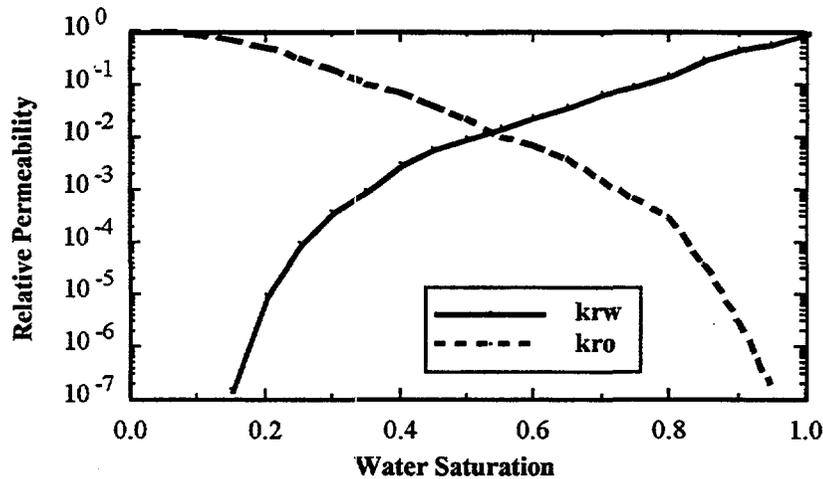


Figure A1. Relative permeability curve for Okessa Sandstone Core.

The water flood involved water injection for 1 pore volume (PV) for 500 days. Breakthrough was observed at approximately 90 days (0.19 PV). The polymer flooding injection sequence without crosslinkers was waterflooding (0-90 days); polymer flooding (90-180 days); and waterflooding, without polymer or other chemicals, up to 500 days (1 PV). The gel treatment injection sequence was waterflooding (0-90 days); polymer and crosslinker flooding (90-92 days); and waterflooding, without polymer or other chemicals, up to 500 days (1 PV). Dichromate and thiourea were used for gel treatments. Injection polymer concentration was 2,000 ppm while dichromate and thiourea concentrations were 1,000 and 1,400, respectively. The polymer and/or crosslinkers were injected into the bottom (most permeable) layer in order to improve the process effectiveness. The chemicals reached the top (less permeable) layer by crossflow.

Ten grid blocks in the x and y directions, and 6 blocks in the z direction were used in all the floods. Some water and polymer floods were repeated with a 20 x 20 x 10 grid to test the effect of grid block size change. The results were not sensitive to change in grid block size.

Table A1. Reservoir parameters.

| | | | |
|---------------------------|-------------------|----------------------|--|
| Dimensions | $L_x = 1,000$ ft | $L_y = 1,000$ ft | $L_z = 30$ ft |
| Top layer permeability | $k_x = 100$ md | $k_y = 100$ md | $k_z = 100$ md. |
| Bottom layer permeability | $k_x = 1,000$ md | $k_y = 1,000$ md | $k_z = 1,000$ md. |
| Thickness | Top layer = 15 ft | Bottom layer = 15 ft | Volume of oil in place = 0.8075×10^6 bbl. |

Table A2. Parameters Used in Starch Biopolymer Simulations.

| | | | |
|---|--------------------------------|--------------------------------|---|
| Adsorption Parameters {Eqn. (7)} | $a_{p1} = 1.0$ | $a_{p2} = 0.5$ | $b_p = 1,000.0$ |
| Liquid Viscosity Parameters {Eqn. (8)} | $\alpha_w = 3.4$ | $\alpha_o = 1.0$ | $\alpha_{ch} = 3.0$ |
| Polymer Viscosity Parameters {Eqn. (9)} | $A_{pw} = 52$ | $A_{po} = 2,430$ | $A_{pch} = 4.0E+4$ |
| Residual Resistance Factor Parameters {Eqn. (12)} | $F_{rr\ max} = 45.0$ | $A_p = 1.17$ | $B_g = 1.01E-4$ |
| Gelation Reaction Constants ⁵ | $k_1 = 1.0E-4$ s ⁻¹ | $k_2 = 1.0E-4$ s ⁻¹ | $k_3 = 1,000$ meq m ⁻³ sec ⁻¹ |
| Meter eqn. Parameters {Eqn. (10)} | $\mu_p^o = 1.17$ cp. | $P\alpha = 1.1$ | $\gamma_{1/2} = 4.0$ |

Results and Discussion

Comparison between our computed results and those of Gao et al.⁵ using the BEST-GEL simulator were used to validate our calculations. Good agreement was found in all the tests conducted. Figures A2 and A3 show typical results for polymer flooding without crosslinking agents. There is a significant increase (approximately 40%) in the amount of oil recovered after the polymer treatment both for the polyacrylamide polymer and the biopolymer with respect to the water flood.

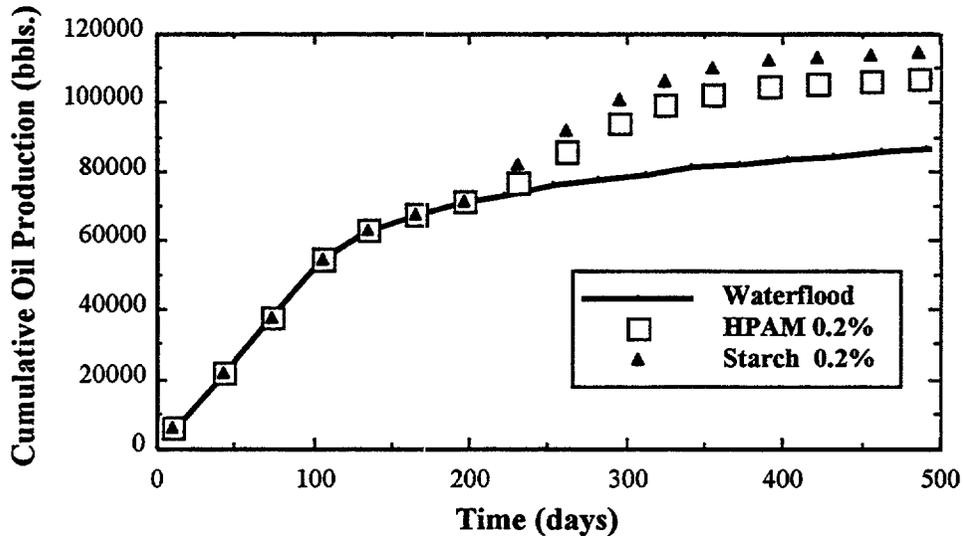


Figure A2. Cumulative oil production vs. time before and after polymer treatment.

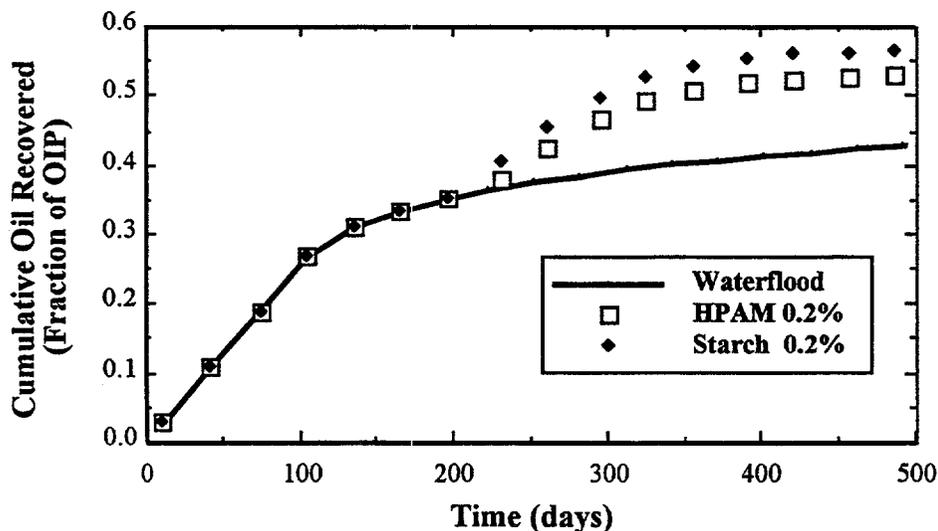


Figure A3. Cumulative oil recovered vs. time before and after polymer treatment.

Simulation results show that the biopolymer produces slightly better oil recovery than the polyacrylamide polymer (approximately 7%). Simulation results showed that the oil

production rate increases significantly after the end of the polymer flood (180 days). This increase remains continuous until approximately 270 days. Then, the oil production rate decreases.

The influence of treatment on oil saturation was studied analyzing contour plots similar to Figure A4. The oil saturation contour in the second (deepest) layer after 180 days is shown in this Figure. There is one injection well on the bottom left corner and one production well on the top right corner. Inspection of a similar contour plot for the top, less permeable, layer, shows higher values of in-situ oil saturation. The polymer concentration in layer two, after 180 days, is shown in Figure A5. The polymer concentration is higher closer to the injection well and decreases from there to the production well. The corresponding contour plot for the top layer shows significantly smaller values (4 to 5 times smaller) everywhere. The contour plots for 180 days show approximately the same difference (4 to 5 times) in the residual resistance factors for both layers.

These results show that the relative permeability in the most permeable layer will decrease more than the relative permeability in the less permeable layer. The relative permeability of the reservoir varies proportionally to the residual resistance factor (F_{rr}). The residual resistance factor is a function of the adsorbed polymer concentration as shown by equation (12).

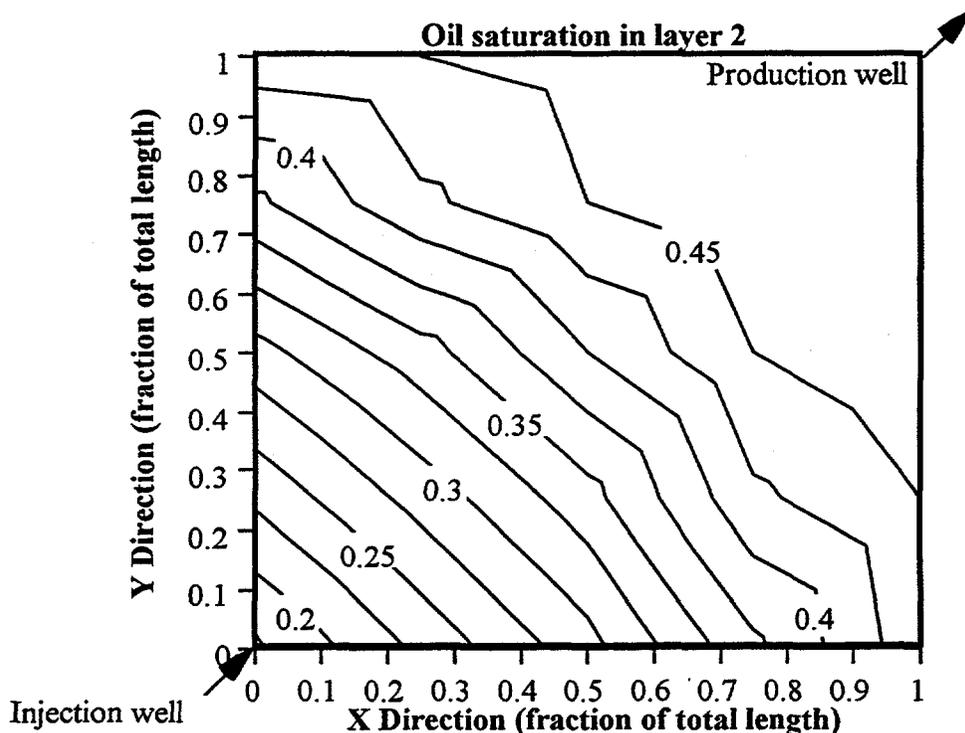


Figure A4. Oil saturation distribution for layer 2 after polymer treatment.

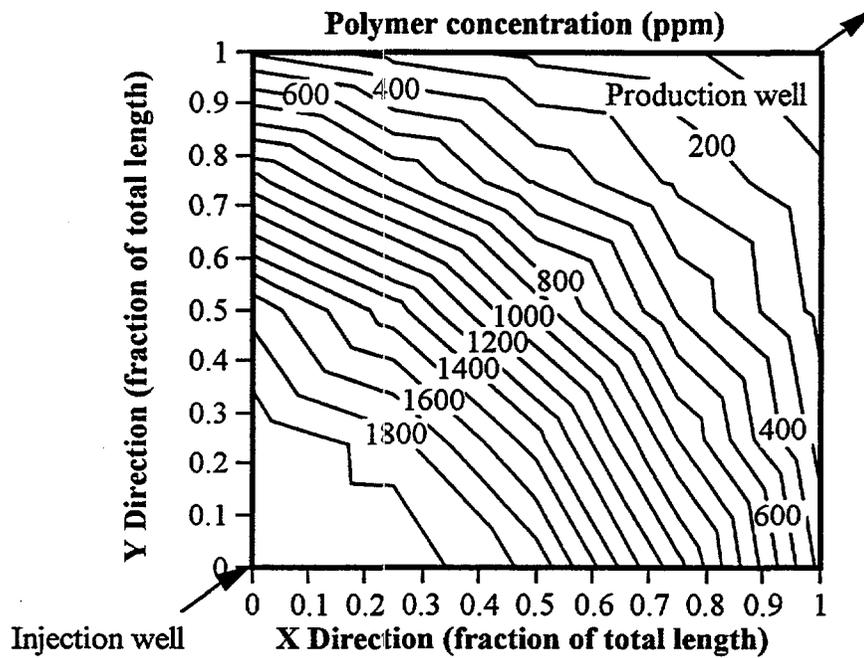


Figure A5. Polymer concentration contour for layer 2 after polymer treatment.

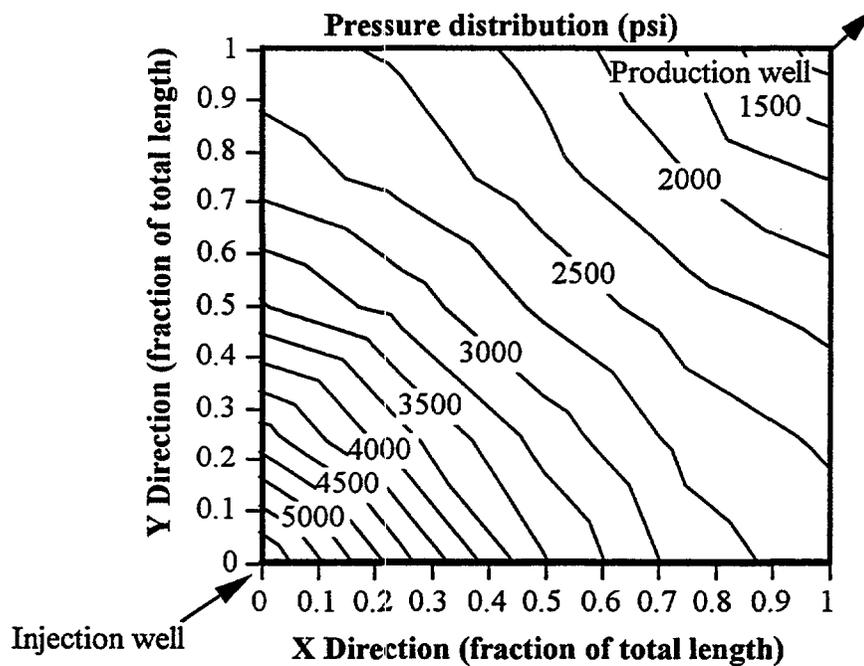


Figure A6. Pressure distribution contour for layer 2 (180 days).

The pressure distribution values are significantly higher after polymer treatment than the ones calculated for the water flood. Typical pressure distribution values for layer two are shown in Figure A6. Corresponding results for layer one are slightly lower than those for layer two.

Figure A7 shows the cumulative oil fraction recovered after a two-day gel treatment. A significant increase in the amount of oil recovered is shown. Simulation results also show that the biopolymer performed slightly better than the polyacrylamide polymer. The same kinetic data were used for both types of polymers. Contour plots for the gel showed higher concentration on the high permeability layer than in the top layer.

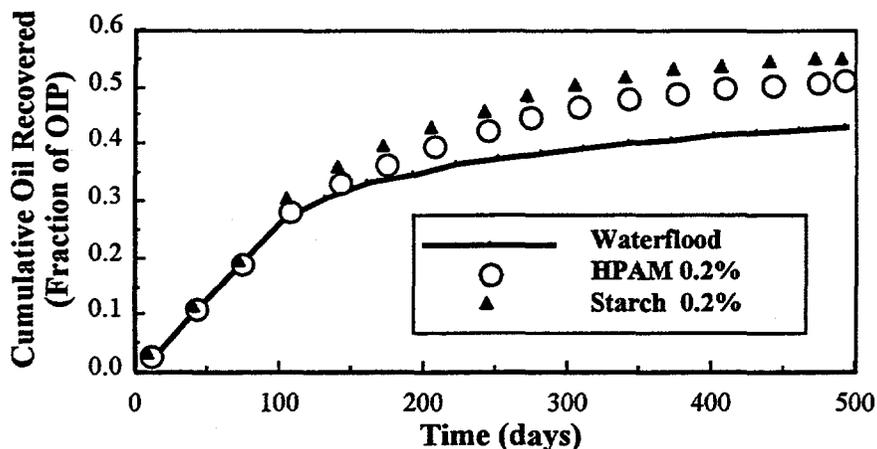


Figure A7. Cumulative oil recovered vs. time before and after gel treatment.

A good sweep should lower the displacing phase mobility in order to decrease fingering. Figures A8a and A8b show typical water phase viscosity contours for polymer floods conducted using HPAM and starch biopolymer. The water viscosity values produced by adding the synthetic polymer are approximately 50% higher than the corresponding values for the biopolymer solutions. Figures A9a and A9b show permeability reduction factors produced by the HPAM polymer addition and the corresponding values for biopolymer solutions. The biopolymer produces permeability reduction factors that are four times bigger, e.g., 240 versus 60, than the synthetic polymer. Therefore, the biopolymer lower relative mobility is produced because the higher relative permeability decrease, compared to the synthetic polymer, offsets the lower viscosity increase compared to the synthetic polymer.

A comparison of Figures A9b and A10, shows that the biopolymer produces a lower permeability reduction in the less permeable (top) layer than in the more permeable layer (bottom). Figure A10 shows that there is little permeability reduction in most of the top layer. This fact is explained if we consider that the relative permeability reduction is produced by the polymer concentration within the porous media pores. A comparison of Figures A6 and A11 show that most of the polymer circulates through the high permeability zones (bottom layer) practically by-passing the low permeability zones (top layer). A comparison of Figures A10 and A11 also shows a direct relation between polymer concentration and permeability reduction. The areas with high polymer concentration correspond exactly to areas with high permeability reduction factors.

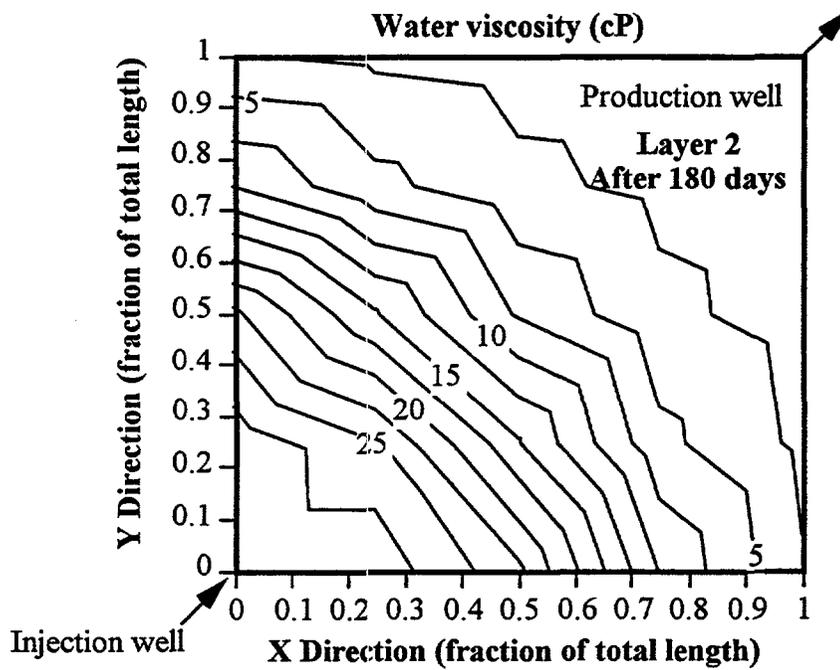


Fig. A8a- Water phase viscosity (cP) contour for HPAM polymer treatment.

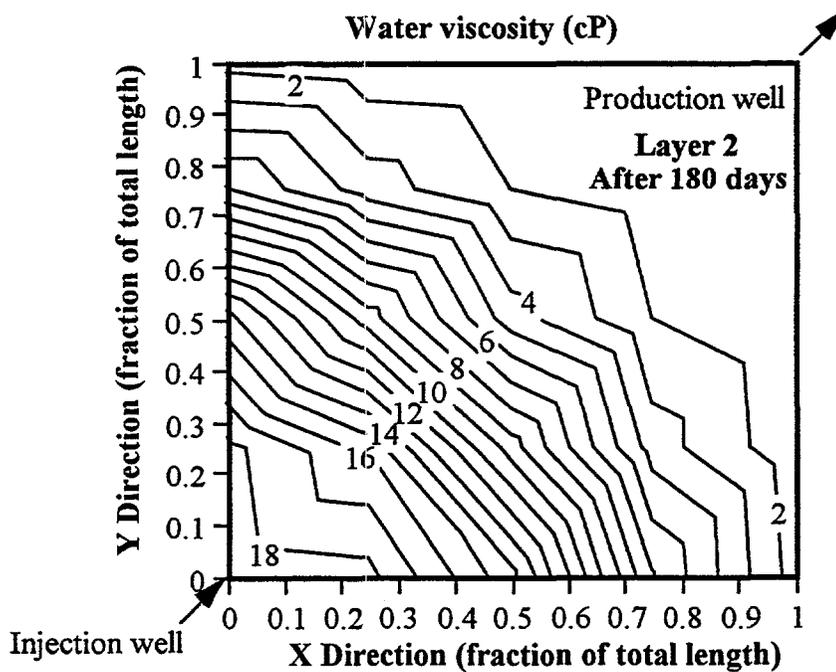


Fig. A8b- Water phase viscosity (cP) contour for Starch biopolymer treatment.

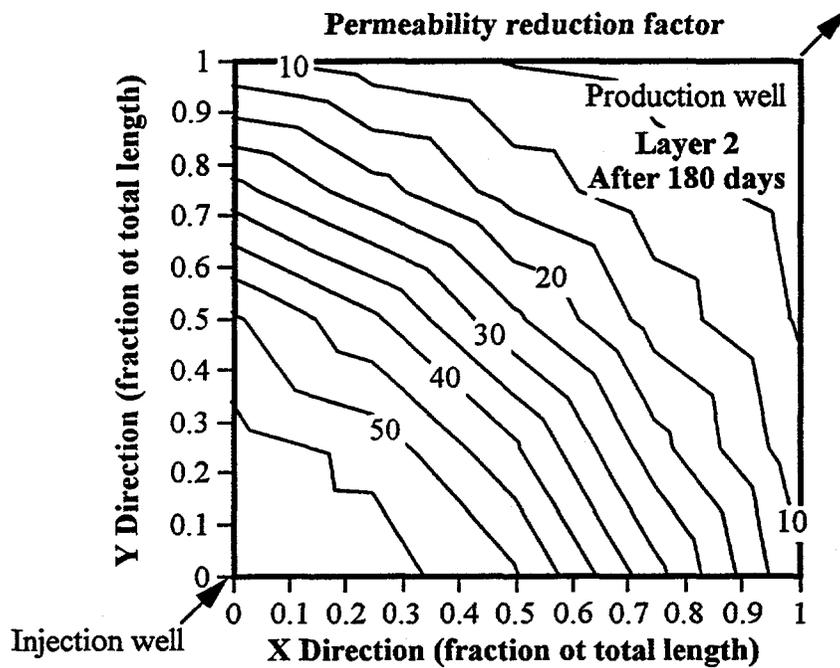


Fig. A9a- Permeability reduction factor contour for HPAM polymer treatment.

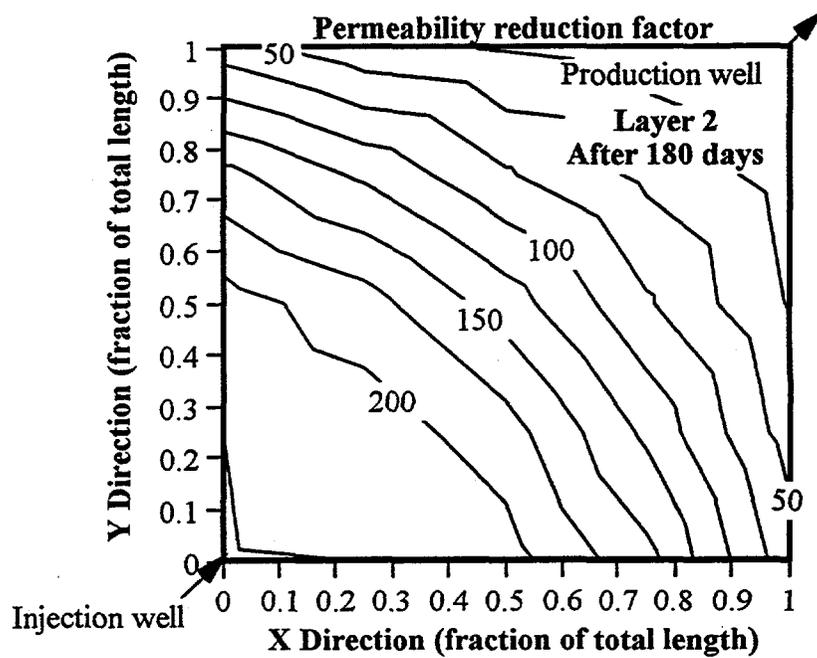


Fig. A9b- Permeability reduction factor contour for Starch biopolymer treatment.

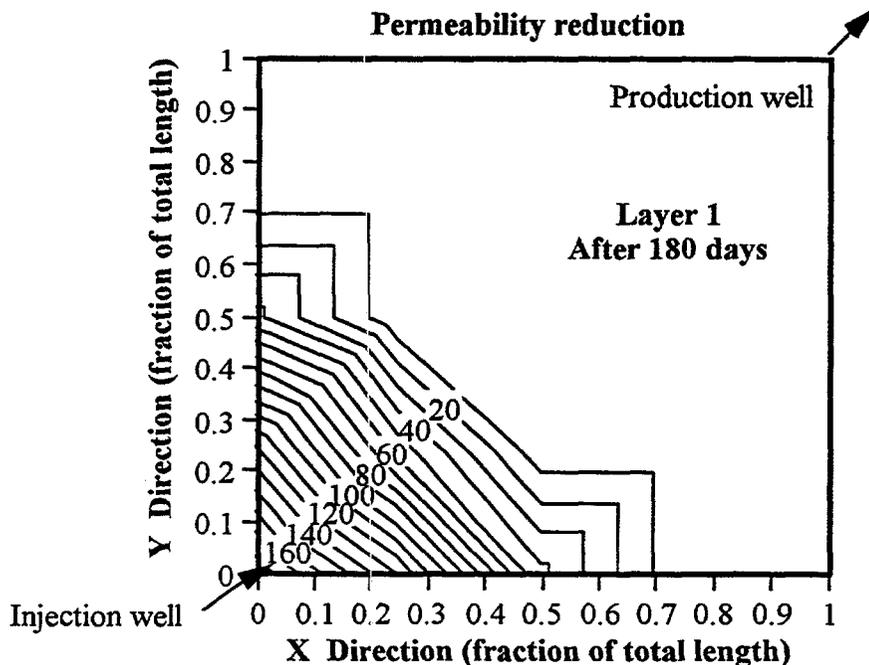


Fig. A10- Permeability reduction factor contour for Starch biopolymer treatment in layer 1.

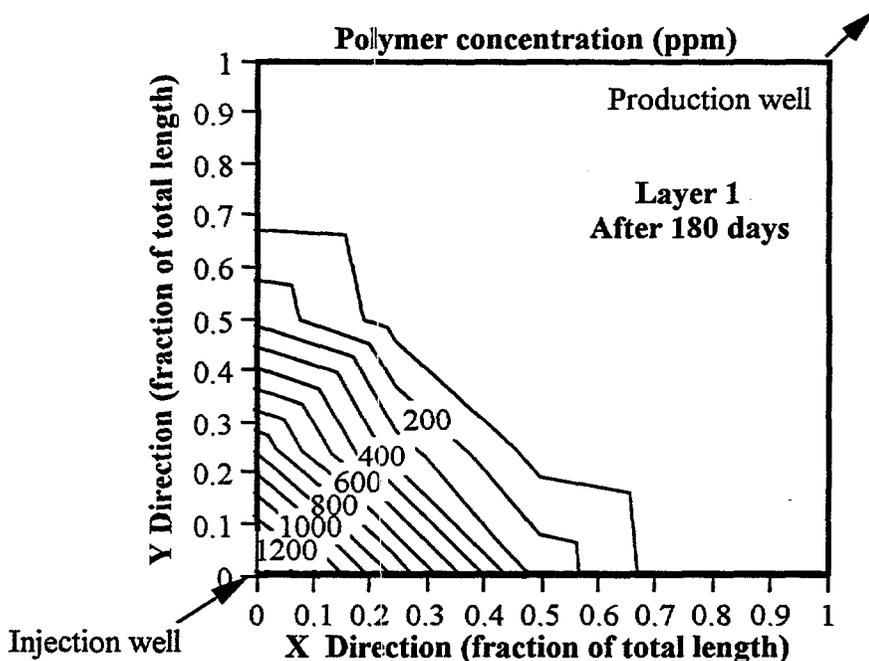


Fig. A11- Polymer concentration contour for layer 1 after polymer treatment.

The simulation runs performed during this project involved only two phases, aqueous and oil, and constant injection rates. Therefore, a decrease in the oil production rate implies an increase in the water production rate. The relative amount of water and oil produced is a ratio of their respective mobilities at the production well. The water-oil ratio at the

production well will vary accordingly. The treatment that produces the highest oil production rate will produce the lowest water-oil ratio and the reverse is also true.

Conclusions

A numerical simulator was used to compare behavior of two different polymers, a synthetic and a biopolymer. Both polymers significantly increased the oil recovery after polymer flooding with and without crosslinker addition. The biopolymer produced higher recovery and higher residual resistance factors and decreased the oil saturation more than a synthetic polymer in the model reservoir. However, the synthetic polymer solutions have higher viscosities than equivalent biopolymer solutions. A long-term polymer treatment (90 days) produced only slightly better results than a two-day gel treatment. Therefore, the gel treatment is recommended.

The biopolymer produces higher recovery because its solutions have lower mobilities despite higher increases in viscosity produced by the chemical polymer. The biopolymer treatment reduces the permeability in the high permeability layer more than in the low permeability layer. Despite this fact, more recovery comes early from the high permeability layer than from the low permeability layer. After depletion of the high permeability layer, significant amounts of oil still remain in the low permeability layer.

In conclusion, the calculations show good potential for the use of starch biopolymers in chemically enhanced oil recovery.

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Nomenclature

- a_p adsorption parameter used in eqn. (5)
- a_{kj} adsorption parameters used in eqn. (6)
- A_{kj} constants for viscosity calculations used in eqn. (9)
- A_g gel constant used in eqn. (12)
- b_p adsorption parameter used in eqn. (5)
- B_g gel constant used in eqn. (12)
- C_k concentration of species k (m^3/m^3)
- C_{kj} concentration of species k in phase j (m^3/m^3)
- \tilde{C}_k total concentration of species k (m^3/m^3)
- \hat{C}_k adsorbed concentration of species k (m^3/m^3)
- C_{SEP} effective salinity for polymer (m^3/m^3)
- C_{SEP}^{SP} salinity factor used in eqn. (11)
- C_t total compressibility
- $\underline{\underline{D}}$ diffusivity tensor (m/s^2)
- F_{rr} residual resistance factor defined eqn. (12)
- h height (m)
- k absolute permeability (m^2)
- k_i gelation specific reaction rates (1/s)
- k_x x direction permeability (m^2)
- k_y y direction permeability (m^2)
- k_{rj} relative permeability for phase j
- n_{cv} number of volume occupying components
- P_j phase j pressure (Pa)
- P_α empirical coefficient used in eqn. (10)
- PC_{jw} capillary pressure of phase j with respect to water (Pa)

| | |
|-------|--------------------------------------|
| Q_k | production and injection wells (1/s) |
| R_k | Source terms |
| S_j | phase j saturation |
| u_j | phase j Darcy velocity (m/s) |

Greek Letters

| | |
|-----------------|--|
| α_k | experimental parameters used in eqn. (8) |
| β_p | experimental parameter used in eqn. (7) |
| γ | shear rate (N/m^3) |
| γ_j | phase j specific weight (N/m^3) |
| $\gamma_{1/2}$ | shear rate at average viscosity (N/m^3) |
| ϕ | porosity |
| μ_k | viscosity of species k ($kg\ m^{-1}\ s^{-1}$) |
| μ_p^o | initial polymer viscosity ($kg\ m^{-1}\ s^{-1}$) |
| λ_{rjc} | relative mobility including compressibility correction |
| λ_{rTc} | relative total mobility including compressibility correction |

Subscripts

| | |
|-----|-----------|
| ch | chemical |
| g | gel |
| j | phase |
| k | component |
| max | maximum |
| o | oil |
| p | polymer |
| w | water |