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**IMPROVING RESERVOIR
CONFORMANCE USING GELLED POLYMER SYSTEMS**

Annual Report for the Period
September 25, 1994 to September 24, 1995

By
D. W. Green and G. P. Willhite

May 1996

Performed Under Contract No. DE-AC22-92BC14881

The University of Kansas
Lawrence, Kansas

**Bartlesville Project Office
U. S. DEPARTMENT OF ENERGY
Bartlesville, Oklahoma**

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Prepared for
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Abstract

The objectives of the research program are to (1) identify and develop polymer systems which have potential to improve reservoir conformance of fluid displacement processes, (2) determine the performance of these systems in bulk and in porous media, and (3) develop methods to predict their performance in field applications. The research focused on four types of gel systems — KUSP1 systems which contain an aqueous polysaccharide designated KUSP1, phenolic-aldehyde systems composed of resorcinol and formaldehyde, colloidal-dispersion systems composed of polyacrylamide and aluminum citrate, and a chromium-based system where polyacrylamide is crosslinked by chromium(III). Gelation behavior of the resorcinol-formaldehyde systems and the KUSP1-borate system was examined. Size distributions of aggregates that form in the polyacrylamide-aluminum colloidal-dispersion gel system were determined. Permeabilities to brine of several rock materials were significantly reduced by gel treatments using the KUSP1 polymer-ester (monoethylphthalate) system, the KUSP1 polymer-boric acid system, and the sulfomethylated resorcinol-formaldehyde system. The KUSP1 polymer-ester system and the sulfomethylated resorcinol-formaldehyde system were also shown to significantly reduce the permeability to super-critical carbon dioxide. A mathematical model was developed to simulate the behavior of a chromium redox-polyacrylamide gel system that is injected through a wellbore into a multi-layer reservoir in which crossflow between layers is allowed. The model describes gelation kinetics and filtration of pre-gel aggregates in the reservoir. Studies using the model demonstrated the effect filtration of gel aggregates has on the placement of gel systems in layered reservoirs.

Executive Summary

OBJECTIVES

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

The research focused on four types of gel systems — KUSP1 systems which contain an aqueous polysaccharide designated KUSP1, phenolic-aldehyde systems composed of resorcinol and formaldehyde, colloidal-dispersion systems composed of polyacrylamide and aluminum citrate, and a chromium-based system where polyacrylamide is crosslinked by chromium(III).

The laboratory research is directed at the fundamental understanding of the physics and chemistry of the gelation process in bulk form and in porous media. This knowledge will be used to develop conceptual and mathematical models of the gelation process. Mathematical models will then be extended to predict the performance of gelled polymer treatments in oil reservoirs.

The project is divided into five major tasks. These are:

- Development and Selection of Gelled Polymer Systems
- Physical and Chemical Characterization of Gel Systems
- Flow and Gelation in Rock Materials
- Mathematical Modeling of Gel Systems
- Sponsor International Forums on Gelled Polymer Treatments

A summary of progress for Year 3 of the program is described in the following sections.

SUMMARY OF PROGRESS

Development and Selection of Gelled Polymer Systems

Work under this task was completed in Years 1 and 2. Two gelled polymer systems were selected for further study. These systems were the colloidal-dispersion gel system and a phenolic-aldehyde system. A database of gelled polymer systems was prepared and used for the selection process.

Development work on the KUSP1 biopolymer was also completed in Years 1 and 2. KUSP1 is produced by a bacterium. Optimum growth conditions and scale-up of production procedures were determined. Improvements of the gelation characteristics were not achieved through chemical modifications of the KUSP1 polymer.

Physical and Chemical Characterization of Gel Systems

Gelation behavior of the resorcinol-formaldehyde systems and the KUSP1-borate system was examined. Size distributions of aggregates that form in the polyacrylamide-aluminum colloidal-dispersion gel system were determined.

Resorcinol-formaldehyde systems. Two phenolic-aldehyde systems were studied. One was composed of resorcinol and formaldehyde (designated the RF system) and the other composed of sulfomethylated-resorcinol and formaldehyde (designated the SMRF system). The resorcinol-formaldehyde (RF) system has limited applicability for use in gelled polymer treatments in the range of compositions that were studied in bottle tests (41 °C). At salt concentrations less than approximately 1%, the gel time was very sensitive to salt concentration which presents difficulties in controlling the process in the field. At salt concentrations greater than 1%, the gel times are on the order of 10 hours or less. These relatively short gel times would only be applicable for near well-bore treatments in shallow wells. Additionally, the RF system did not gel at pH values less than approximately 7.5.

The sulfomethylated resorcinol-formaldehyde (SMRF) system has improved gelling characteristics and wider field applicability as compared to the RF system. Bottle tests demonstrate that the SMRF system gels over longer time periods and over wider pH ranges (5-8) than the RF system.

KUSP1-boric acid system. The gelation behavior of the KUSP1-boric acid system was characterized. Concentrations studied were 1.0% KUSP1, 0.1 to 0.5 M boric acid, 0 or 1.0% sodium chloride, and pH values between 9 and 13. The effect of temperature on gel times was investigated by conducting bottle tests at 25°C, 45°C and 65°C. Gel times for the KUSP1-boric acid system can be regulated from a few seconds to several days by selection of the boric acid concentration or the pH of the gel solution. At a given pH, a decrease in the boric acid concentration decreased the gel time. Gel times decreased and syneresis increased with increased temperature.

The nature of the gels formed using boric acid is different from the gels formed by reducing the pH of an alkaline KUSP1 solution. Boric acid gels are clear and appear much more resilient than the gels formed without boric acid which are white in color and tend to shatter. It is speculated that the borate crosslinks the polymer molecules to form gels.

Polyacrylamide-aluminum system. The polyacrylamide-aluminum colloidal-dispersion system is different from most gel systems in that a bulk gel is not formed. Instead, colloidal dispersions are claimed to develop in the solution. Colloidal dispersion gels are formulated with relatively low concentrations of polyacrylamide and aluminum. The size of the gel aggregates as they form and grow in the polyacrylamide-aluminum citrate system was determined. A significant effort was required for the development of this procedure.

Size distributions for the polymer and/or aggregates were determined for the polymer solution without crosslinker and for gel samples that had reacted for up to 12 hours. The results showed little-to-no growth of aggregates in the gel samples. Significant development of aggregates and/or aggregate growth in the gel samples was not observed even though other measurements (TGU tests) indicated the development of structure.

Flow and Gelation in Rock Materials

Gelation experiments in porous media were conducted with the sulfomethylated resorcinol-formaldehyde (SMRF) system, the KUSP1-boric acid system, the KUSP1-ester system and the polyacrylamide-aluminum citrate system. The performance of these three systems to reduce the permeability of selected rock materials to subsequent brine flow (waterflooding) was assessed. Permeability reductions to supercritical carbon dioxide were determined for the SMRF system and the KUSP1-ester system.

SMRF system. The SMRF system was very effective in reducing the permeability of limestone, dolomite and sandstone core plugs. Permeabilities to brine were reduced by factors greater than 9000.

KUSP1-boric acid system. Permeability reduction in sandpacks and Berea sandstone cores were determined for a selected gel system at 25 and 45 °C. Gel treatments significantly reduced the permeability. Permeabilities were reduced by factors that ranged from 50 to 3300 in sandpacks and Berea sandstone cores at 25 and 45 °C. Factors by which the permeabilities of brine were reduced were greater in the more permeable sandpacks and at the lower temperature.

KUSP1-ester system. The KUSP1-ester acid system significantly reduced the permeability of sandpacks, Berea sandstone cores and carbonate core-plugs. Permeabilities were reduced by factors greater than 200 in the absence of oil in the media. The presence of a residual oil saturation did not significantly alter the effectiveness of the treatment. Permeabilities were reduced uniformly along the length of the media. The gelled KUSP1-ester system was stable with time and throughput of brine. Little change in permeability was observed during the flow of many pore volumes of brine through the media over periods of many weeks.

Polyacrylamide-aluminum system. Gel solution propagated through a porous medium like a polymer solution when it was injected immediately after mixing in-line. Delaying the entry of the gel solution to allow time for the gel aggregates to develop resulted in retention of polymer at the inlet face. No in-depth development of resistance was observed in this study. Resistance developed at the porous media inlet only.

The colloidal dispersion gel loses its gel-like properties when propagated through porous media. Effluent solutions obtained during both the polymer and gel displacement experiments had reduced viscosities and did not form any structure. Analysis of the effluent solution also indicated significant retention of aluminum.

The colloidal dispersion gel does not appear to be capable of forming a gel-like network in a porous medium even after being shut-in for three weeks. No resistance was observed when brine was injected following the shut-in period.

Permeability reduction to supercritical carbon dioxide. Three systems were tested for their ability to reduce the permeability to supercritical carbon dioxide. In the first system, KUSP1 solutions were gelled in Berea sandstone cores by injecting carbon dioxide. The carbon dioxide reduced the in situ pH resulting in the gelation of the KUSP1. Permeabilities to brine and supercritical carbon dioxide were reduced by approximately 80%.

Permeabilities to supercritical carbon dioxide were reduced by approximately 96% using the KUSP1-ester system. Both KUSP1 systems were stable to the injection of many pore volumes of supercritical carbon dioxide.

The sulfonated resorcinol-formaldehyde (SMRF) system was gelled in situ and was contacted with both brine and supercritical carbon dioxide. Permeabilities were reduced by about 99% with the SMRF system. The permeability reductions were maintained after the injection of many pore volumes of supercritical carbon dioxide and brine.

Mathematical Modeling of Gel Systems

A mathematical model was developed to simulate the behavior of a chromium redox-polyacrylamide gel system that is injected through a wellbore into a multi-layer reservoir in which crossflow between layers is allowed. The model describes gelation kinetics and filtration of pre-gel aggregates in the reservoir.

The model was used to describe the placement of a gel solution into a two-layer reservoir in which the ratio of permeabilities of the layers was 10:1. Three flow regimes which occur during placement were identified. The first encompasses the early reaction time, prior to the formation of aggregates. In the second, aggregates are formed and injection rate drops due to their filtration, but flow into the high permeability layer dominated. In the third flow regime, the high-permeability layer was blocked due to filtration of gel aggregates and flow was diverted into the low-permeability layer. The calculations showed that the treatment process should be terminated before the onset of the third flow regime. Gel placement was improved by using a higher injection pressure, by treating reservoirs with higher permeability contrast and by using gel solutions with lower viscosity. Isolating and injecting into the high permeability layer only, resulted in considerably improved gel placement.

Sponsor International Forums on Gelled Polymer Treatments

We participated in the 1993 Society of Petroleum Engineers Forum on Improvements in Conformance Technology. Professor G. Paul Willhite was on the planning committee of that forum. We are planning to sponsor a forum during fiscal year 1996.

Chapter 1

Introduction

The application of gelled polymer treatments to petroleum reservoirs can improve oil recoveries and reduce fluid-handling costs. This research program consists of laboratory investigation of chemical systems that are applicable for gelled polymer treatments and the development of mathematical models that describe gelled polymer treatments of oil reservoirs. Laboratory research focused on three types of systems - (1) phenolic-aldehyde systems, (2) a polyacrylamide-aluminum citrate system, and (3) KUSP1 biopolymer systems. Mathematical models were developed for a chromium-polyacrylamide system.

Two phenolic-aldehyde systems were investigated. One was composed of resorcinol and formaldehyde (designated the RF system) and the other composed of sulfomethylated-resorcinol and formaldehyde (designated the SMRF system). Results of the investigation of the phenolic-aldehyde systems are presented in Chapter 2.

Two studies of the polyacrylamide-aluminum citrate system were conducted. Results of an investigation to determine the size of aggregates that form and grow in this system are reported in Chapter 3. The performance of the polyacrylamide-aluminum citrate system in reducing permeability is described in Chapter 4.

Two KUSP1 biopolymer systems were studied. An investigation of the permeability-reducing capabilities and long-term stability of the permeability reductions of the KUSP1-ester system is presented in Chapter 5. Gelation behavior of the KUSP1-borate system in bulk form and the performance of treatments using this system in several rock materials were investigated and are reported in Chapter 6.

The sulfomethylated resorcinol-formaldehyde system and KUSP1-biopolymer systems were tested for their ability to reduce permeabilities to supercritical carbon dioxide. The results of this study are presented in Chapter 7.

A mathematical model was developed to simulate a gel treatment at reservoir scale using a polyacrylamide-chromium system. The model was used to study the placement gelant in layered radial system. Chapter 8 presents the results of this study.

Chapter 2

Gelation and Permeability Reduction of Resorcinol-Formaldehyde Gel Systems

Principal Investigators: C.S. McCool, D.W. Green and G.P. Willhite
Research Assistants: Yingfeng Zuang, S.N. Pandey

INTRODUCTION

The placement of gelant in the targeted zones of a reservoir during permeability reduction treatments is vital to the success of the treatment. Viscosity of the injected fluid plays a significant role in determining where that fluid will travel in the reservoir. In most situations, a less viscous solution will penetrate low permeability zones to a lesser extent than a more viscous solution.¹ Thus, gelants with low, or water-like, viscosity are preferred for permeability reduction treatments. In addition, injectivities are greater for less viscous gelants which enables greater volumes of gelant to be injected.

Most gelants used today contain polymers which increase the viscosity of the aqueous solvent by factors on the order of 5 to 30. Phenolic-aldehyde systems are a class of gels in which the initial viscosity of the gelant (before gelation occurs) is slightly above that of the aqueous solvent. This feature makes phenolic-aldehyde systems attractive for use in permeability-reduction treatments due to the enhanced placement potential. Phenolic-aldehyde systems are composed of water-soluble phenols and aldehydes or dialdehydes. A gel is formed through a step-reaction polymerization. Several studies on the performance of phenolic systems have been reported.²⁻¹⁰

Two phenolic-aldehyde systems were studied. One was composed of resorcinol and formaldehyde (designated the RF system) and the other composed of sulfomethylated-resorcinol and formaldehyde (designated the SMRF system). Bottle testing to characterize the RF system revealed the gelation was sensitive to pH, salinity and hardness. At conditions where gelation was less sensitive to these parameters, the gel times were relatively short. The RF system was modified to improve the tolerance to chemical composition by sulfomethylation of the resorcinol. The performance of the SMRF system was determined to be superior to that of the RF system by bottle tests. Gelation of the SMRF was studied in several types of core material.

EXPERIMENTAL

Bottle Testing. RF gel systems were usually prepared as ten gram samples from chemicals and stock solutions of appropriate concentrations. Five grams of brine, 1.00 g formaldehyde solution, 1.00 g of resorcinol and 2.8 g of water were combined in a vial, mixed and the pH of the solution was measured. A combination of 1.0 N or 0.1 N NaOH solutions and water were then added to achieve the selected initial pH value and final weight of 10.00 grams. The time period for initial pH adjustment was critical for reproducibility. pH adjustments were accomplished over a time period of approximately one minute unless otherwise noted. All chemical preparations were done on a weight basis.

SMRF gel solutions were prepared in two steps. The first step was the sulfomethylation of the resorcinol. 18.24 g of a 37 % aqueous formaldehyde solution was mixed with an aqueous sodium sulfite solution composed of 18.91 g of sodium sulfite and 58 g of water. This mixture was then added drop-wise into

a stirred aqueous resorcinol solution (33.0 g resorcinol and 20 g water). pH of the reaction mixture was adjusted to about 9.5 by adding 50% NaOH. The temperature of the reaction mixture was then increased to 60 °C and incubated for 72 hours. Care must be taken during the incubation to minimize evaporation losses. The sulfomethylated-resorcinol solution was used to prepare SMRF gel solutions by the same procedure described for the RF solutions. Composition of SMRF samples are described by the weight percent of resorcinol and the mole ratios, $F_2:F_1:S:R$, where F_1 , S and R are formaldehyde, sodium sulfite and resorcinol used in the sulfomethylation step, and F_2 is the formaldehyde used to prepare the gelant mixture. All values are based on the final gelant mixture.

Gel samples were stored in constant-temperature ovens or water baths at 25, 41 and 52 °C. Most of the work was conducted at 41 °C. Gelation and gel quality (e.g., formation of gel, gelatinous-precipitate or precipitate) were observed visually. Gel time was defined as when the sample would remain at the bottom of the vial when inverted. Viscosity and solution pH was monitored for selected samples. (The elapsed time from mixing at which the viscosity increased rapidly to greater than 100 cp (shear rate of 4.5 sec⁻¹) was defined as the gel time for viscosity measurements. This gel time was approximately 90% of the visually observed gel time.

In-Situ Gelation in Core Plugs. Gelation experiments were conducted in core plugs to determine the reduction in permeability achieved using the SMRF system. Core plugs were cut from samples of Baker dolomite, J-Alpha grainstone (limestone) and Berea sandstone. J-Alpha grainstone samples were reservoir rock and Baker and Berea samples were quarried rock. The plugs were fitted with endcaps, encapsulated with epoxy and equipped with a pressure port that was located at the midpoint of the length of the plugs. The plugs were then saturated with brine and the pore volume (porosity) and initial permeabilities were determined. A tracer test was conducted to check for the presence of flow channels in the plugs. No major flow channels were observed.

Three pore volumes of freshly-prepared gelant were injected into the core plugs. Gelant was injected at a rate of about 1.4 ml/minute in the dolomite and sandstone plugs and at a rate of about 0.63 ml/minute in the limestone plugs. These flow rates were selected to accomplish the gelant injection within time periods that ranged between one-half and one hour, much less than the gel time. Pressure drops across the core plugs and the effluent pH were measured during gelant injection. Gel times of injected-gelant samples and effluent samples were determined.

After gelant injection, the flow lines to and from the plugs were purged with brine and the plugs were shut-in to allow for gelation as determined for samples of the injected gelant and of the effluent. Brine was then injected to determine post-treatment permeabilities. pH of the effluent during brine injection was measured.

Flow experiments were conducted at 41° C. Brine used in these experiments contained 5.0 weight % NaCl and 0.036 wt. % $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.01 % Ca^{++}).

RESULTS AND DISCUSSION

Bottle Tests of the Resorcinol-Formaldehyde (RF) System. Bottle tests were conducted to determine the effect of compositional parameters on the gel time for the RF system. Parameters investigated were resorcinol concentration, mole ratio of formaldehyde to resorcinol, initial pH, salinity and hardness.

Gel times as function of the formaldehyde to resorcinol ratio (F/R) are shown in Figure 2.1 for a system at constant resorcinol and salt concentrations and constant initial pH. The gel time was not significantly affected as the mole ratio of formaldehyde to resorcinol (F/R) was decreased from 4 to 1.5. In this range of mole ratios, the rate of gelation depended on the deficient reactant, resorcinol. Gel times increased significantly as the F/R mole ratio was decreased below the 1.5 value. At these lower mole ratio values, the data indicated that formaldehyde was the deficient reactant and, thus, controlled the rate of gelation.

The data presented in Figure 2.1 are consistent with the statistical polymerization theory. The stoichiometric mole ratio, F/R, for the condensation reaction for formaldehyde and resorcinol is 1.33.¹¹ Steric effects make reaction sites less accessible as molecular size increases which results in a stoichiometric mole ratio to be a value somewhat larger than 1.33. The theoretical stoichiometric mole ratio agrees well with the break in the data presented in Figure 2.1.

Gelation behavior of the RF system was sensitive to the initial pH of the system and to the procedure for adjusting the initial pH. The rate of adding 0.1 N NaOH to the sample affected the amount of base required. This, in turn, affected the pH during gelation, the gelation time and sometimes the gel quality, especially at higher monomer concentrations and higher initial pH. The slower procedure for initial pH adjustment required more base. The additional base was probably consumed by a methylation reaction that occurs quickly on mixing the reactants to yield a series of hydroxymethyl resorcinol molecules that have higher acid strength.

The pH histories for two samples that were adjusted to an initial pH of 9.0 over periods of 1 and 5 minutes are shown in Figure 2.2. For the slow adjustment procedure, more base was required to reach the same "initial" pH and the pH remained higher during gelation. The gel time for the 5 minute adjustment was 8 hours compared to a gel time of 5 hours for the sample that was adjusted to initial pH in about 1 minute.

The pH histories for a gel system at selected initial pH values are presented in Figure 2.3. The pH decreases with time for samples prepared at the lower initial pH values and increases with time for samples prepared at the higher initial pH values.

Gel times and precipitation times for a series of gel solutions that were adjusted initially to selected pH values are shown in Figure 2.4. Gels formed for initial pH values of 7.35 and above. Samples prepared at initial pH values of 7 and below did not form homogenous gels but formed precipitate or gelatinous precipitate. The data shows that the overall reaction rate between resorcinol and formaldehyde was faster at the initial pH range between 7 and 8. This was probably due to the rate dependence of the individual reactions on pH. The rate of the methylation reaction increases and the rate of polycondensation reactions decreases as the hydroxyl ion concentration is increased^{12,13} resulting in a pH range where the overall reaction rate is fastest.

Stronger gels were formed at longer gel times as the initial pH was increased in the range from 8 to 10. For initial pH values higher than approximately 10, formaldehyde undergoes a disproportionation reaction yielding methanol and formic acid (Cannizzaro reaction) which probably inhibited the formation of gel.

Gel times as a function of resorcinol concentration are shown in Figure 2.5 for a series of samples prepared at constant F/R ratio, salt concentration and initial pH. Gel times ranged from 30 minutes to 7 days for the resorcinol concentrations of 10. and 0.5 wt. %, respectively. At resorcinol concentrations less than 0.5 wt. %, gelatinous-precipitate or precipitate formed and the amount of free water in the product

Figure 2.1: Gel Time as a Function of the Mole Ratio of Formaldehyde to Resorcinol for RF System; Gelants contained 0.5% resorcinol, initial pH = 9.5, 1.0% NaCl, 0.36% $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$; 41 °C.

Figure 2.2: Effect of Speed of pH-Adjustment on pH History for RF System;
Gelants contained 3.0% resorcinol, 3.0% formaldehyde, 0.5% KCl; 41 °C.

Figure 2.3: pH History During Gelation for RF System; Gelants contained 3.0% resorcinol, 3.0% formaldehyde, 0.5% KCl; 41 °C.

Figure 2.4: Gel or Precipitation Times as a Function of Initial pH for RF System; Gelants contained 3.0% resorcinol, 3.0% formaldehyde, 0.5% KCl; 41 °C.

Figure 2.5: Gel Times as a Function of Resorcinol Concentration; Gelants contained a mole ratio of formaldehyde-to-resorcinol of 1.3, initial pH= 9.0, 0.5% KCl; 41 °C.

increased with decreasing concentrations. The gel strength determined by visible inspection decreased with decreasing concentration.

The effect of the concentration of salt and salt type on gel times for two series of gel samples are shown in Figures 2.6 and 2.7. These data show that the gelation behavior was sensitive to small changes in salinity at salt concentrations below 1.0% salt. Salt significantly increased the gelation rate and decreased the gel time. The divalent cation Ca^{2+} had an stronger influence^{11,14} than the monovalent ions.

Gelation behaviors for samples prepared with both NaCl and CaCl_2 salts are given in Table 2.1. Series of samples were prepared at three brine formulations and at selected initial pH values and resorcinol concentrations. A constant F/R ratio of 1.5 was used. Entries in Table 2.1 show if and when a gel was formed and if precipitate or gelatinous-precipitate was observed. Again, the effect of small quantities of salt on the gel time is shown by comparing the results for the sample containing no salt and Brine C at 3.0% resorcinol. The data also show the gel system does not tolerate very high concentrations of brines containing both mono- and divalent ions except at the higher initial pH values. This effect might be caused by a change of the solvent-power or dielectric constant of the solutions.

Gel times for the RF system were on the order of ten hours at component concentrations that were considered applicable for use in permeability reduction treatments. Longer gel times would be required for in-depth application. Several chemicals have been suggested¹⁵ as agents to slow the gelation process. 2-propanol was tested and the gel times as a function of 2-propanol concentration are shown in Figure 2.8. Prohibitive amounts of 2-propanol were required to significantly extend the gel time.

Bottle Tests of the Sulfomethylated Resorcinol-Formaldehyde (SMRF) System. Screening experiments were conducted to determine the effects of various parameters on the gelation and gel times of the SMRF system. A problem with the experimental procedure was detected during experiments that were conducted to test the reproducibility of the data. During the sulfomethylation of the resorcinol, evaporation losses occurred during the 72 hour incubation period. Initial experiments were conducted with sulfomethylated resorcinol that was prepared at conditions where evaporation losses occurred. Evaporation losses on the order of 8% were measured. Assuming the loss was water, the concentration of resorcinol, sodium sulfite, and formaldehyde used in the sulfomethylation step are approximately 8.7% greater than the reported values. This was confirmed by the fact that samples prepared at the elevated concentration (without evaporation) showed consistent gelation behavior with samples prepared at the original concentration with evaporation. For example, samples prepared with 2.5 % resorcinol and evaporation gelled at the same time as samples prepared with 2.7% resorcinol without evaporation. Samples where evaporation losses occurred are identified.

The pH values of selected formaldehyde - sulfomethylated resorcinol systems (SMRF) during the gelation process are shown in Figure 2.9. The pH trends were similar to the RF system shown in Figure 2.3.

The effects of initial pH and salt concentration on the gelation of the SMRF system using 3.0% resorcinol are shown in Figures 2.10 and 2.11 for NaCl and CaCl_2 salts, respectively. The data show increased salt concentration and hardness accelerated the gelation process. The initial pH also affected the gel times. SMRF gels were formed at initial pH values that ranged from 5.0 to 10, in contrast to the RF system where gels were not formed at initial pH values between 5.0 and 7.0.

Figure 2.6: Effect of Salt Concentrations on Gel Times for Gelants Containing 3.0 % Resorcinol for RF System; Gelants contained a mole ratio of formaldehyde-to-resorcinol of 1.5, initial pH = 9.0; 41 °C.

Figure 2.7: Effect of Salt Concentrations on Gel Times for Gelants Containing 1.0 % Resorcinol for RF System; Gelants contained a mole ratio of formaldehyde-to-resorcinol of 1.5, initial pH = 9.0; 41 °C.

Table 2.1: Gelation Behavior of Resorcinol-Formaldehyde System.
Gelants contained mole ratio of formaldehyde-to-resorcinol of 1.5; 41°C.

Resorcinol Conc. (%)	NaCl Conc. (%)	CaCl ₂ •2H ₂ O Conc. (%)	Initial pH							
			7		8		9		9.75	
			Physical State	Gel Time (hours)	Physical State	Gel Time (hours)	Physical State	Gel Time (hours)	Physical State	Gel Time (hours)
3.0	0.0	0.0	gel	108	gel	380	gel	460		
	0.1	0.036	gel	13	gel	16			gel	140
	1.0	0.36	precipitate		precipitate		gel	2.8	gel	8
	3.0	0.72	precipitate		precipitate		precipitate		gel	2.3
1.0	1.0	0.36	precipitate		precipitate		gel	6	gel	26
	3.0	0.72	precipitate		precipitate		precipitate		gel	5
0.5	1.0	0.36	precipitate		precipitate		gelatinous precipitate	5.5	gelatinous precipitate	28
	3.0	0.72	precipitate		precipitate		precipitate		gelatinous precipitate	6.3

Figure 2.8: Effect of 2-Propanol Concentration on Gel Time for RF System;
Gelants contained 3.0% resorcinol, a mole ratio of formaldehyde-to-resorcinol of 1.5,
2.0% NaCl, initial pH = 9.0; 41 °C.

Figure 2.9: pH History During Gelation for SMRF System; Gelants contained 3.0% resorcinol, mole ratios of $F_2 : F_1 : S : R = 1.3 : 0.75 : 0.5 : 1$, 5.0% NaCl; 41 °C.

Figure 2.10: Effect of NaCl Concentration on Gel Time for SMRF System;
Gelants contained 3.0% resorcinol, mole ratios of $F_2 : F_1 : S : R = 1.3 : 0.75 : 0.5 : 1$;
41 °C.

Figure 2.11: Effect of CaCl₂ Concentration on Gel Time for SMRF System;
 Gelants contained 3.0% resorcinol, mole ratios of F₂ : F₁ : S : R = 1.3 : 0.75 : 0.5 : 1;
 41 °C.

A comparison of gel times for similar RF and SMRF systems is shown in Figure 2.12 as a function of NaCl concentration. These data show that sulfomethylation of the resorcinol increased the gel time. For example, under the condition of 41°C, 0.5% NaCl and an initial pH of 9.5, the gel time of RF gel solution (3%R, F:R=1.5) was about 3 days; while the gel time of SMRF gel solution (3%R, SMRF F₂:F₁:S:R=1.3:0.75:0.5:1) was more than two months.

Gel times are given in Table 2.2 for a selected SMRF system at initial pH values of 6, 7 and 8 and at several brine compositions. Inspection of these data show that gel times for the SMRF system were on the order of days and that the gel times were not as sensitive to pH and salt concentrations as for the RF system. SMRF gel systems that were prepared at pH values less than 6 or more than 9 gelled at longer times and the gel times were more sensitive to small changes in pH.

Gel times for samples at selected initial pH and temperatures are given in Table 2.3. At initial pH values of 7.0 and below, the gel time decreased with increased temperature and the gels were firm. Samples prepared at a pH of 8.0 and at 2.5% resorcinol formed weaker gels. Increasing the resorcinol concentration to 2.75% (initial pH of 8.0), decreased the gel time and produced firm gels. No gel was formed at initial pH values of 9.0.

The viscosity as a function of time for the samples prepared at initial pH of 8.0 and 41° C are shown in Figure 2.13. Initial viscosity was 0.72 cp, comparable to water viscosity of 0.71 cp. The viscosity remained low for extended period of time and then increased rapidly. Visible gels formed at the time the viscosity was about 300 to 400 cp, while firm gels that did not fall upon inversion of the sample bottle formed at much higher viscosities (above 1000 cp).

The pH of samples were monitored with time and are shown in Figure 2.14 for samples prepared at initial pH of 7.0. In this and all other cases, the pH decreased with time. Final pH values of selected gels are given in Table 2.3. For some cases, a ranges of values is given for replicate runs.

In situ Gelation in Core Plugs. Eight in situ gelation experiments were conducted in selected core plugs using three gel compositions. Properties of the core plugs are given in Table 2.4. Composition of the gelants are given in Table 2.5. Three pore volumes of freshly-prepared gelant were injected into the core plugs over time periods between one-half and one hour. Pressure drops across the core plugs and across two sections of the plugs were measured during gelant injection. Pressure drops were converted to apparent viscosity values by Darcy's law assuming the initial permeability and indicates the flow resistance in the section of the plug over which the pressure drop was measured. The apparent viscosity of the gelant was only slightly higher than the value that would be observed for brine flow demonstrating the low viscosity of the gelant.

pH values of the effluent from the plugs were measured at several times during the sequence of flow experiments and are presented in Table 2.5. The pH of the brine (initially between 7 and 8) was elevated to values of 8.9 and above by the flow through the plugs prior to gelant injection. The pH of the gelant displaced through the plugs at the end of gelant injection was approximately the same as the injected value indicating the capacity of the gelant to resist the pH-altering capability of the rock. pH values during post-gelation brine injection were lower than when brine was injected prior to gelant injection as shown in Table 2.5. The presence of gel in some manner prevented the pH of the injected brine to be elevated to the high pH values that were observed before gelant injection.

Figure 2.12: Comparison of Gel Times Between RF and SMRF Gel Systems; Both systems contained 3.0% resorcinol, mole ratio of formaldehyde-to-resorcinol was 1.5; initial pH = 9.5; 41°C; SMRF system - mole ratios of $F_2 : F_1 : S : R = 1.5 : 0.75 : 0.5 : 1$.

Table 2.2: Gelation Behavior of Sulfomethylated Resorcinol-Formaldehyde System at 41 °C.
Gelants contained 2.5% resorcinol, mole ratios of $F_2 : F_1 : S : R = 1.4 : 0.75 : 0.5 : 1$;

NaCl Conc. (%)	$CaCl_2 \cdot 2H_2O$ Conc. (%)	Initial pH		
		6.0	7.0	8.0
		Gel Time (hours)		
5.0	0.0	50-60	50-60	110-120
5.0	0.036	50-60	36-46	44-54
5.0	0.36	36-46	22-30	22-30
5.0	1.8	13-23	9-13	6-8
4.0	0.036	~288	~175	~202
4.0	0.36	~77	59-69	~120
4.0	1.8	18-22	10-13	6-10
3.0	0.36	312-323	275-285	
3.0	1.8	34-44	10-20	10-20

Table 2.3: Gel Times and Final pH of Sulfomethylated Resorcinol-Formaldehyde Gels at 25, 41, and 52 °C.
Gelants contained mole ratios of $F_2 : F_1 : S : R = 1.4 : 0.75 : 0.5 : 1$, 5.0% NaCl, 0.035% $CaCl_2 \cdot 2H_2O$.

Initial pH	25°C		41°C		52°C	
	Gel Time (hours)	Final pH	Gel Time (hours)	Final pH	Gel Time (hours)	Final pH
5.0	66		43			
6.0	28	5.42	25	5.21	12	5.16
7.0	30-42	5.70-5.89	26-43	5.45-5.64	17	5.46
8.0	64-72	6.48-7.19	120-200	6.30-6.69	216	6.12
8.0*	41	7.25	67	6.45		
9.0	No gel	No gel	No gel	No gel	No gel	No gel

* resorcinol concentration was 2.75% in samples.

Figure 2.13: Viscosity as a Function of Time and Resorcinol Concentration for SMRF Gel System; Gelants contained mole ratios of $F_2 : F_1 : S : R = 1.4 : 0.75 : 0.5 : 1$, 5.0% NaCl, 0.035% $CaCl_2 \cdot 2H_2O$; 41 °C.

Figure 2.14: pH a Function of Time and Temperature for SMRF Gel System; Gelants contained 2.5% resorcinol, mole ratios of $F_2 : F_1 : S : R = 1.4 : 0.75 : 0.5 : 1$, 5.0% NaCl, 0.035% $CaCl_2 \cdot 2H_2O$.

Table 2.4: Physical Properties of Porous Media.

Core Number	Diameter (cm)	Length (cm)	Porosity (%)	Permeability (md)		
				Overall	Section 1	Section 2
DOL-1	3.78	10.20	25.6	163	158	170
DOL-2	3.78	10.10	24.8	161	194	139
DOL-3	3.78	9.50	25.6	113	104	120
DOL-4	3.78	9.90	24.2	128	110	159
LST-1	2.47	5.63	23.6	11.5	10.4	12.4
LST-2	2.47	6.15	27.2	19.7	10.8	106
LST-3	2.47	6.40	26.8	35.3	49.3	33.1
BR-1	3.78	10.20	22.6	500	514	462

Samples of the injected gelant and the effluent gelled during the shut-in time for the plugs (except for DOL-3). Brine was then injected to determine post-treatment permeabilities. The reduction in permeability produced by the gel treatments are presented in Table 2.5. Residual resistance factors are a ratio of the initial permeability to the post-treatment permeability. The treatments reduced the permeabilities of the core plugs by factors greater than 9,000 (except for DOL-3). The three limestone plugs were completely sealed by the gel and no brine could be displaced. For the other plugs, the post-treatment permeabilities were determined only after the pressure drops stabilized. During initial brine injection, the pressure drops decreased with time (at a given flow rate) demonstrating that the permeabilities were even lower initially.

The gel system used for plug DOL-3 did not gel as predicted by the screening experiments. This resulted in no reduction in permeability of the plug by the treatment. It was determined in the screening experiments that the SMRF gel system prepared at an initial pH of 8.0 and resorcinol concentration of 2.5%, a weak gel was formed at times of 120 to 200 hours. The particular sample prepared for the DOL-3 plug formed a weak gel only after many weeks. Brine was injected after 25 days of shut-in and before gelation occurred. It is not known if this *weak* gel would reduce the permeability of core plugs. At an initial pH of 8.0 and a resorcinol concentration of 2.75%, much stronger gels are formed and the permeabilities of core plugs are effectively reduced as shown in Table 2.5 for plugs DOL-1, DOL-4 and LST-3. (The gelant for DOL-1 was prepared at a resorcinol concentration of 2.5%, but evaporation losses during preparation resulted in a resorcinol concentration of approximately 2.75%.)

Table 2.5: Details and Results of Gel Treatments Using the Sulfomethylated Resorcinol-Formaldehyde System.

Core No.	Gelant Composition *	pH of Effluent			Shut-In Time (days)	Initial Permeability (md)			Post-Treatment Permeability			Residual Resistance Factor
	Initial pH Resorcinol Conc.	Pre-Treatment Brine Injection	Gelant Injection	Post-Treatment Brine Injection		Total	Section 1	Section 2	Total	Section 1	Section 2	
DOL-1	pH 8.0 2.5% resorcinol (2.75%)**	9.12	7.80	7.36	10	163	158	170	0.02	0.03	0.01	9050
DOL-2	pH 7.0 2.5% resorcinol	9.43	7.0	7.87	5	161	194	139	0.02	0.06	0.01	9450
DOL-3	pH 8.0 2.5% resorcinol	9.53	8.03		24	113	104	120				
DOL-4	pH 8.0 2.75% resorcinol	9.62	8.10	7.19	11	128	110	159	0.01	0.01	0.01	14500
LST-1	pH 7.0 2.5% resorcinol	8.98	7.17		5	11.5	10.4	12.4	0.0			∞
LST-2	pH 7.0 2.5% resorcinol	8.94	7.16		5	19.7	10.8	106	0.0			∞
LST-3	pH 8.0 2.75% resorcinol	9.09	8.04		11	35.3	49.3	33.1	0.0			∞
BR-1	pH 7.0 2.5% resorcinol	8.94	6.76	7.38	5	500	514	462	0.01	0.01	0.02	34700

* All gelants contained sodium sulfite and formaldehyde at $F_2:F_1:S:R$ mole ratios of 1.4 : 0.75 : 0.5 : 1. See Experimental section for details. Gelants also contained 5.0% NaCl and 0.036% $CaCl_2 \cdot 2H_2O$.

** Evaporation occurred in this resorcinol solution. Concentration was estimated at 2.75% resorcinol.

CONCLUSIONS

1. The sulfomethylated resorcinol-formaldehyde (SMRF) system has improved gelling characteristics and wider field applicability as compared to the RF system. Bottle tests demonstrate that the SMRF system gels over longer time periods and over wider pH ranges (5-8) than the RF system.
2. The SMRF system was effective in reducing the permeability of limestone, dolomite and sandstone core plugs. Permeabilities were reduced by factors greater than 9000.
3. The resorcinol-formaldehyde (RF) system has limited applicability for use in gelled polymer treatments in the range of compositions that were studied in bottle tests (41 °C). At salt concentrations less than approximately 1%, the gel time was very sensitive to salt concentration which presents difficulties in controlling the process in the field. At salt concentrations greater than 1%, the gel times are on the order of 10 hours or less. These relatively short gel times would only be applicable for near well-bore treatments in shallow wells. Additionally, the RF system did not gel at pH values below approximately 7.5.

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Chapter 3

Aggregate Growth in the Polyacrylamide-Aluminum Citrate System

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INTRODUCTION

The polyacrylamide-aluminum citrate "colloidal dispersion" system is different from most gel systems in that a bulk gel is not formed. Instead, colloidal dispersions are claimed^{1,2} to develop in the solution which can penetrate deep into reservoirs and then be retained to reduce permeabilities. The development of colloidal dispersion, or gel aggregates, has been inferred by the determination of the transition pressure using a TGU apparatus.³ The transition pressure is a measure of gel strength and is based on the measurements of flow rates through a screen pack. The development/growth of gel aggregates in the solution was inferred from increased transition pressures.

Colloidal dispersion gels are formulated with relatively low concentrations of polyacrylamide and aluminum. The development of transition pressure with time for a typical concentration of 300 ppm polyacrylamide and 15 ppm aluminum is shown in Figure 3.1. The transition pressure increased rapidly with most of the development occurring within the first 12 hours.

The objective of this work was to measure the size of the gel aggregates as they form and grow in the polyacrylamide-aluminum citrate system. The information derived from this study will then be used to determine the mechanisms by which the polyacrylamide-aluminum system affects fluid flow in porous media. A significant effort was required to develop the procedure to measure aggregate size for this system.

EXPERIMENTAL

The formulation studied contained 300 ppm polyacrylamide, 15 ppm aluminum and 0.5% KCl. The polymer (HiVis 350) and the aluminum citrate solution (TIORCO 677) were obtained from TIORCO, Inc., Englewood, CO.

A procedure to determine the size of gel aggregates for another system⁴ was modified to be applicable to the polyacrylamide-aluminum citrate system. The modified procedure consisted of the following steps. A gelant was prepared and stored at 25 °C. A sample of the gelant was removed at selected times and the reactions quenched by diluting the sample with solvent (0.5 % KCl brine) at a 9:1 solvent-to-sample weight ratio. The diluted sample was then contained in 12,000 MW-cutoff dialysis tubing and placed in additional solvent (0.5% KCl brine) for two days to remove a large percentage of the free aluminum. The amount of solvent used was six times the amount of diluted sample. After these steps, the polymer concentration was reduced by a factor of 10 and the concentration of free aluminum was reduced by a factor of 60. It was assumed that these reductions in concentrations effectively quenched the reactions.

Figure 3.1: Development of Transition Pressure for Polyacrylamide-Aluminum Citrate Gel System.

The principal step of the procedure was to separate the aggregates by size using membrane dialysis. Dialysis cells were constructed from Teflon stock. Each half-cell was 1.5 inches in diameter and 0.125 inches deep. Half-cells were separated by polycarbonate membranes (Nucleopore) that contained precision cylindrical pores. Membranes with pore diameters of 0.1, 0.4, 1.0, 2.0, 3.0 and 5.0 microns were used.

Five milliliters of sample were placed in the retentate half-cell and five milliliters of solvent (0.5% KCl brine) were placed in diffusate half-cell. The cells were placed in a 25 °C waterbath for a period of five or six weeks. The retentate and diffusate were removed from the cells after the dialysis period and analyzed for polymer concentration. The analytical procedure for polymer concentration used Hyamine 1622 reagent and was automated using a Technicon AutoAnalyzer. Details of the procedures are given in Reference 6.

A material balance on the polymer charged and removed from the cells was performed to insure the integrity of the experimental procedure. Aggregate sizes were determined by assuming that the polymer aggregates greater than the pore size remained on the retentate side of the cell and that the polymer aggregates less than the pore size evenly distributed between the half-cells.

The modified procedure for determining the size of gel aggregates was the result of problems encountered with applying the original procedure to the HiVis 350-TIORCO 677 gel system. Polymer analysis using UV absorption after separating the polymer from debris using size-exclusion chromatography failed because the HiVis 350 polymer was retained in the column and was not eluted as a distinct peak. Several column packings were tested without success although the columns work fine for other polyacrylamide samples. The results indicated that the HiVis 350 polyacrylamide contained some very large molecules that would not flow through the columns in the desired manner. These results were consistent with the reported viscosity-averaged molecular weight of 27 million for HiVis 350. A second method for polymer analysis, the bleach method,⁵ also failed due to the interference of TIORCO 677 (aluminum citrate solution) with the precipitation reactions.

Experiments were conducted to show that little separation occurred after the five-week membrane-dialysis period. Efforts to reduce the equilibrium time by rotating the cells during the dialysis period resulted in apparent loss of polymer. Material balances showed that 30% of the polymer was lost after two days of rotation and that the polymer mass balances decreased with time. The results indicated that the rotation corrupted the polymer analysis rather than a loss of polymer. Similar problems in the polymer analysis occurred when the gelant sample was continuously stirred before samples were taken. During polymer analyses of these samples, turbidity signals from the detector were distorted. It was speculated that the shear induced by stirring the gelant or by rotating the dialysis cells altered the polymer and/or aggregates in solution resulting in analysis errors.

RESULTS AND DISCUSSION

Size measurements of aggregates were conducted on a sample of the polymer solution (without aluminum citrate) and on gelant samples that were aged for 4, 8 and 12 hours before quenching the reactions. Experiments were conducted on two different samples that were aged for 8 hours. Polymer concentrations measured in the retentate and diffusate half-cells and the polymer material balance for each cell are presented in Tables 3.1 through 3.5. Experiments were conducted for selected membrane-dialysis time periods and with several different membrane pore sizes. The results in Table 3.2 show that the net transfer of polymer across the membrane was essentially complete by five weeks of dialysis time. Material balances were calculated as the percentage of polymer measured with respect to the amount charged to

Table 3.1 Polymer Concentrations and Material Balances for Dialysis Cells
- Polymer Solution without Crosslinker.

Pore Diameter of Membrane (microns)	Time (weeks)	Retentate Concentration (ppm)	Diffusate Concentration (ppm)	Material Balance (%)
0.1	2	30.7	2.65	111
	6	30.1	1.58	106
0.4	2	27.2	3.94	104
	6	23.9	9.01	110
0.8	2	24.0	8.46	108
	6	20.7	14.9	119
1.0	2	22.4	8.79	104
	5	19.2	14.1	110
2.0	2	22.6	9.43	107
	5	17.6	14.9	108
3.0	2	19.4	11.7	104
	5	16.0	15.5	105
5.0	2	19.4	14.3	112
	5	16.4	15.7	107

Table 3.2 Polymer Concentrations and Material Balances for Dialysis Cells
- Gel Solution at 4-hour Reaction Time.

Pore Diameter of Membrane (microns)	Time (weeks)	Retentate Concentration (ppm)	Diffusate Concentration (ppm)	Material Balance (%)
1.0	2	18.1	11.4	98.3
	3	18.1	13.5	106
	3	16.3	14.3	102
	4	17.2	12.6	99.3
	5	17.9	14.1	107
2.0	2	18.8	12.0	102
	3	16.6	12.9	98.3
	3	16.2	13.7	99.7
	4	15.7	14.4	100
	5	17.1	14.1	104
5.0	2	16.3	13.8	100
	3	16.4	13.8	101
	3	16.8	14.7	105
	4	15.4	15.4	102
	5	16.2	16.2	108

Table 3.3 Polymer Concentrations and Material Balances for Dialysis Cells
- Gel Solution at 8-hour Reaction Time (Run A).

Pore Diameter of Membrane (microns)	Time (weeks)	Retentate Concentration (ppm)	Diffusate Concentration (ppm)	Material Balance (%)
0.1	3	29.7	1.55	104
	5	29.3	1.76	103
0.4	3	23.9	6.20	100
	5	23.1	7.92	103
0.8	3	20.7	10.4	104
	5	18.6	11.2	99.3
1.0	3	20.0	10.6	102
	5	18.2	13.3	105
2.0	3	19.0	11.6	102
	5	18.6	9.97	95.2
3.0	3	18.2	12.9	103
	5	16.1	14.1	101
5.0	3	16.6	13.7	101
	5	16.1	15.7	106

Table 3.4 Polymer Concentrations and Material Balances for Dialysis Cells
- Gel Solution at 8-hour Reaction Time (Run B).

Pore Diameter of Membrane (microns)	Time (weeks)	Retentate Concentration (ppm)	Diffusate Concentration (ppm)	Material Balance (%)
0.4	3	21.0	7.79	96.0
	5	22.2	8.92	104
0.8	3	19.4	9.79	97.3
	5	18.4	12.8	104
1.0	3	17.8	13.8	105
	5	16.6	13.0	98.6
2.0	3	20.2	11.6	106
	5	17.4	14.0	104
3.0	3	20.2	11.2	105
	5	15.8	14.6	101

Table 3.5 Polymer Concentrations and Material Balances for Dialysis Cells
- Gel Solution at 12-hour Reaction Time.

Pore Diameter of Membrane (microns)	Time (weeks)	Retentate Concentration (ppm)	Diffusate Concentration (ppm)	Material Balance (%)
0.4	3	23.0	6.29	97.8
	5	22.2	8.29	102
0.8	3	18.3	10.3	95.1
	5	18.3	12.3	102
1.0	3	16.3	12.3	95
	5	16.7	13.1	99.1
2.0	3	18.3	11.5	99.1
	5	16.3	13.1	97.7
3.0	3	16.3	12.3	95.1
	5	16.3	14.3	102

each cell. The balances in most cases were within a few percent of the amount charged. Experiments were conducted with gel samples that were aged longer than 12 hours but the polymer analyses of these samples were not consistent.

Size distributions for the polymer and/or aggregates are presented in Figure 3.2 for the polymer solution without crosslinker and for gel samples that had reacted for up to 12 hours. The distributions are presented as the cumulative mass of polymer that is smaller than the indicated diameter. The datum for one of the 8-hour gel samples at 2.0 microns was obviously in error. The data show little-to-no growth of aggregates in the gel samples. Possible growth was indicated by the data taken with the 3 micron membranes where all the gel samples contained less polymer that had a size smaller than the polymer sample without crosslinker. Significant development of aggregates and/or aggregate growth in the gel samples was not observed even though TGU measurements indicated the development of structure as shown in Figure 3.1.

The HiVis 350- TIORCO 677 gel system may not form aggregates without an imposed shear deformation. During the TGU measurement, the sample is subjected to significant shear during flow through the screen pack and a visible structure is formed that separates from excess solvent. The same phenomenon occurs when a aged gelant is rapidly shaken. During this study, the polymer analysis were corrupted when the gel samples were stirred for long periods after preparation and when the dialysis cells were rotated. We speculate that the aggregates were formed by these motions and that the separation of aggregates from excess solvent produced the problems with the polymer analysis. Further work is required to determine the role of aggregate development and growth in the HiVis 350-TIORCO 677 system.

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Figure 3.2: Size Distributions for Polymer and Gel Aggregates in a Polyacrylamide-Aluminum Citrate Gel System as a Function of Reaction Time.

Chapter 4

Permeability Modification by In Situ Gelation of a Polyacrylamide-Aluminum Citrate Colloidal Dispersion Gel

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INTRODUCTION

The amount of oil recoverable by displacement in waterflooding and other enhanced recovery operations in heterogeneous reservoirs containing zones of high permeability can be significantly improved by application of gelled polymer treatments. A mobile solution of high-molecular-weight polymer is injected along with a multivalent metal ion into the high permeability zones of the reservoir, which react in situ to form a relatively immobile gel and increases resistance to injection of fluids through these zones.

A major factor influencing the success of such treatments is the extent to which the gel solution can be propagated into the reservoir before onset of gelation and formation of an immobile gel structure. Simulation of waterfloods¹ following gelled polymer treatments has shown that in-depth placement of gels can significantly improve incremental oil recoveries. A major objective of research in gelled polymer treatment is to find suitable systems capable of in-depth permeability modification. The use of a partially hydrolyzed polyacrylamide-aluminum citrate "colloidal dispersion" gel has been claimed^{2,3} to produce long-term in-depth permeability modification in certain reservoirs resulting in significant incremental oil recoveries.

The objective of this study was to investigate and understand the mechanisms governing the propagation and in situ gelation behavior of colloidal dispersion gel in porous media. Flow experiments were conducted where gel was injected into the porous media, and the pressure behavior across the porous media was observed during the displacement. Analytical experiments were performed to determine polymer and aluminum concentrations in the effluent fractions collected during displacements to aid in the interpretation of gel behavior in porous media.

BACKGROUND

Colloidal dispersion gel is a modified version of the layered aluminum citrate gel system developed in 1974. It was observed by Needham et al.⁴ that injection of alternate slugs of polymer and aluminum solutions resulted in permeability reduction. It was claimed⁴ that layers of polymer were retained on the rock and were bound together by crosslinking with aluminum forming a network of gel. It was further claimed that the network continued to build up layers and increase resistance to flow as the alternate injection of polymer and aluminum was continued. Laboratory experiments conducted to investigate the layered aluminum citrate gels showed^{5,6} that the gel was not capable of developing in-depth resistance to flow. Flow resistance developed only at the inlet of porous media in laboratory studies. Reduction in permeability was also observed to occur abruptly rather than gradually as proposed by Needham et al.⁴ Rocha et al.⁷ showed that aluminum was retained by the reservoir rock and becomes unavailable for in-depth crosslinking.

Colloidal dispersion gel was developed at Tiorco, Inc. while conducting experiments to study bulk form of the layered aluminum citrate gel. It is claimed^{2,3} to be capable of in-depth permeability modification based on its application in certain reservoirs. However, no laboratory studies were performed to support

these claims. Such studies are essential to develop an understanding of the mechanisms governing the behavior of the gel system in porous media and to design successful gel treatments. Seright⁸ examined the colloidal dispersion gel and found that gel aggregates could not be propagated through a sandstone core and that filtration of gel aggregates at the inlet face resulted in resistance factors which were impractical to obtain under field conditions. Seright also examined the reports of Mack and Smith² and Fielding et al.³ and found certain anomalies. He concluded that the formation where the gel solutions were injected would have to be fractured in order to obtain the high injectivities that were reported.

EXPERIMENTAL

Colloidal dispersion gel consists of 300 parts-per-million (ppm) polymer, 15 ppm aluminum, and 5000 ppm potassium chloride. Polymer used in this study was HiVis 350[®], a partially hydrolyzed anionic copolymer of acrylamide, and the aluminum was Tiorco 677[®], a chelated aluminum citrate solution, both obtained from Tiorco, Inc. Deionized water was used in the preparation of both polymer and gel solutions as the solutions were found to be extremely sensitive to the purity of water. It was found that presence of chlorine to the extent of one-quarter ppm was sufficient to degrade the solutions⁹. The mixing procedure followed in the preparation of the gel solution is presented in Figure 4.1.

The schematic diagram of the experimental setup used for conducting porous media displacements is shown in Figure 4.2. Unconsolidated sandpacks, prepared with acid washed Wedron silica sand having a grain fineness of 144.3, were used as the porous media. Sandpack holders were constructed out of acrylic plastic stock. The main body of the sandpacks had an ID of 1.5" and a length of 4 feet. Pressure ports were attached along the length of the sandpacks in such a way that they divided the sandpacks into eight sections of 6 inches length each. The sections were labeled A through H, inlet to outlet. A layer of 50 mesh coarse sand was placed at the two ends of the sandpack and was retained in place by a 40 mesh Teflon[™] screen.

The sandpack was saturated with 5000 ppm potassium chloride brine. Pressure differentials were measured across the sections and across the total length of the porous media by flowing brine at three different flow rates. The pressure differentials were then used to calculate permeabilities of the porous media and its sections. A dispersion test was conducted by introducing a step change in the salt concentration of the injected brine and monitoring the effluent concentration using a differential refractometer. Results of the dispersion test were used to check the relative homogeneity of the porous media and to determine the dispersion coefficient of the porous media.

Polymer or gel solution was injected into the porous media at a frontal velocity of 2 feet/day. This allowed an in situ residence time of 48 hours for the gel solution. It has been shown⁹ that the colloidal dispersion gel develops most of its screen flow resistance in TGU apparatus within 48 hours. TGU apparatus¹⁰ provides an empirical measure of gel strength based on the time required to flow gel solution at different pressures through a screen pack. Pressure differentials across the total length of the porous media and across its sections were monitored during the displacement. The displacement experiments were terminated if it was felt that adequate amount of solution has been injected or if it was necessitated by development of extremely high flow resistances. Effluent fractions were collected during the displacement to monitor pH, flow rate, and to determine aluminum and polymer concentrations. Technicon Autoanalyzer II was used to determine the polymer concentration. The method consisted of precipitating the samples with Hyamine[®] 1622 reagent and measuring the resulting turbidity in a spectrophotometer. Aluminum concentrations in the effluent samples were determined by spectrophotometry using Perkin-Elmer Model 460 atomic adsorption spectrophotometer.

Gel Mixing Procedure

Figure 4.1: Mixing procedure for a 300 ppm HPAM, 15 ppm aluminum gel solution.

Figure 4.2: Schematic diagram of the setup for displacement experiments.

The saturated porous media was left for two to three weeks in a water bath maintained at 25°C. A few pore volumes of 5000 ppm potassium chloride brine was then injected through the porous media to displace resident gel solution. Pressure differentials were measured at three flow rates to determine permeabilities and to calculate the residual resistance factor (RRF) in the sandpack. Residual resistance factor of a sandpack subsequent to a polymer or gel displacement is defined as the ratio of *permeability to brine before the displacement to permeability to brine after the displacement*.

RESULTS AND DISCUSSION

Results of four displacement experiments are presented in this section. A polymer solution displacement experiment was conducted in sandpack SP5 to provide the basis for analyzing and interpreting the results of the gel solution displacement experiments in sandpacks SP6 and SP7. In the case of sandpack SP7, the gel solution was mixed in-line and injected immediately into the sandpack. In the case of sandpack SP6, a tubing placed between the in-line mixer and the sandpack inlet. This delayed entry of the gel solution into the sandpack by 2 hours after it was mixed in-line, and simulated field conditions where the gel solution flows through surface pipelines and wellbore injection tubing before reaching the reservoir being treated. Residence time of two hours also resulted in considerable progress in crosslinking between HPAM molecules and aluminum ions.

Pressure differentials measured during displacements were converted to apparent viscosities using Darcy's law as in Equation 4.1. Apparent viscosity determined for a particular section of the sandpack is a measure of flow resistance in that section. Apparent viscosity is equivalent to average viscosity of the fluid flowing in the section, assuming the permeability of the section does not change.

$$\mu_{app} = \frac{k A \Delta p}{Q L}$$

.....Equation 4.1

where,

μ_{app}	=	apparent viscosity
k	=	initial brine permeability
A	=	cross-sectional area
Δp	=	pressure differential across a section
Q	=	volumetric flow rate
L	=	section length

Polymer solution displacement experiment in sandpack SP5. Porosity of the sandpack SP5 was calculated as 34.6% based on a pore volume of 474 mL. Permeability to brine for the sections and the total length of the sandpack is given in Table 4.1. Polymer solution injected into the sandpack consisted of 300 ppm HiVis 350[®] HPAM prepared in a 5000 ppm potassium chloride brine. An average injection rate of 0.16 mL/min. equivalent to a frontal velocity of 1.9 ft./day was achieved.

Apparent viscosity profiles for all the sections and the overall sandpack during the polymer displacement are presented in Figure 4.3. The behavior is typical of polymer displacements, and shows that apparent viscosity increases as the polymer bank displaces the resident brine solution and then stabilizes. Only Section "A" showed a different behavior where the initial resistance is higher than other sections. Spikes in pressure data was due to capillary pressure effects of a trapped air bubble in the pressure sensing tubing connected to the pressure transducer and pump pulsations. Displacement was discontinued after about 6 pore volumes of polymer solution were injected. Apparent viscosities in the different sections varied

Figure 4.3: Apparent viscosities in sandpack SP5 during polymer displacement.

between 10 and 20 cP. Although no unusual behavior was noticed, it was still decided to inject an additional pore volume of the 300 ppm HiVis 350° HPAM solution through the sandpack after solving the problems associated with the pump and with the air bubble trapped in the pressure sensing tubing. Apparent viscosity profiles for the overall sandpack and other sections during this displacement are presented in Figure 4.4. Results were comparable to the previous experiment.

Residual resistance factors are presented in Table 4.1. It is interesting to note that, if the apparent viscosity (18 cP) observed during polymer displacement is divided by the residual resistance factor (2.8), we get 6.4 cP which is similar to the viscosity of the 300 ppm polymer solution recorded in a viscometer. However, the effluent solutions were found to have a less viscous appearance than the injected solution.

Gel solution displacement experiment in sandpack SP7. Average porosity of the sandpack was 34.7% based on a pore volume of 483 mL. Permeabilities of the sections and the overall sandpack are given in Table 4.2. Gel solution consisted of 300 ppm HiVis 350° HPAM and 15 ppm aluminum citrate prepared in a 5000 ppm potassium chloride brine. Gel solution was injected into the sandpack immediately after mixing it in-line.

Table 4.1: Initial and final permeabilities in millidarcies, and residual resistance factors of the sections and overall sandpack SP5.

Section	Overall	A	B	C	D	E	F	G	H
Initial permeability	3445	4223	3371	3731	3098	3501	3486	3206	3289
Final permeability	1217	1217	1348	1192	1192	1006	880	864	806
RRF	2.83	3.10	2.55	3.13	3.81	3.48	3.96	3.71	4.08

Table 4.2: Initial and final permeabilities in millidarcies, and residual resistance factors of the sections and overall sandpack SP7.

Section	Overall	A	B	C	D	E	F	G	H
Initial permeability	3138	2193	2363	4059	3016	3427	3711	3298	3411
Final permeability	1868	4138	1641	2537	2170	2052	2196	1346	950
RRF	1.68	0.53	1.44	1.60	1.39	1.67	1.69	2.45	3.59

Figure 4.4: Second phase of polymer displacement in sandpack SP5.

Apparent viscosity profiles for the overall sandpack and the sections are presented in Figure 4.5. After injecting about 2.2 pore volumes, displacement was suspended because Pressure Port #1, demarcating sections A and B, was not communicating pressure. Apparent viscosity trends in sections B through H are similar to those obtained with polymer displacement. In section A the apparent viscosity started increasing after one pore volume indicating development of resistance. Injection was resumed after cleaning pressure port #1. A sharp build-up of resistance in section A was noticed after 0.07 pore volumes of the gel was injected. The sandpack was opened to examine the inlet section. A disk of filter cake had formed at the interface between the coarse sand placed at the inlet end and the regular sand making up the sandpack. Examination of sand underneath this disk revealed no cohesive gel structure or rigidity.

Polymer and aluminum concentrations in the effluent fractions are presented in Figure 4.6. Aluminum was found to have been retained by the sandpack. Physical appearance of the effluent fractions was unlike those seen with the gels in beaker tests. The effluent fractions appeared to be thinner and less viscous. It was also observed that the effluent samples did not develop any gel-like structure. The experiment was discontinued due to high pressure after 0.11 pore volumes. Subsequent attempts at displacing the gel solution resulted in the development of a similar filter cake and flow resistance.

Residual resistance factors are presented in Table 4.2. The factors are somewhat lower than those obtained with polymer displacement in sandpack SP5. Two factors can explain this. One, presence of filter cake at the inlet and corresponding increase in resistance indicate that gel aggregates were retained. This is confirmed by the analytical results of the effluent fractions showing polymer and aluminum were retained. Second, only 2 pore volumes were injected in this displacement compared with 7 pore volumes in the polymer displacement in sandpack SP5. The lower resistance factors were, therefore, a result of the porous media being contacted by lower amount of polymer. The significant findings of this displacement experiment are summarized below:

1. No in situ gelation was observed in spite of providing adequate residence time for the gel structure to form. Resistance developed only at the inlet face where a thin disk-like filter cake formed. Gel solution propagated through the downstream sections in a manner similar to the polymer solution.
2. Aluminum was retained by the porous media.
3. In spite of letting the porous media saturated with the gel solution sit in a water bath maintained at 25°C for 3 weeks, no flow resistance developed in any of the sections.

Gel solution displacement experiment in sandpack SP6. Average porosity of the sandpack was 34.2% based on a pore volume of 479 mL. Permeability of the sections and the overall sandpack are given in Table 4.3. Gel solution consisted of 300 ppm HiVis 350[®] HPAM and 15 ppm aluminum citrate prepared in a 5000 ppm potassium chloride brine. As indicated earlier, a 1/4" tubing loop was inserted between the in-line mixer and the sandpack inlet to delay entry of gel solution by two hours. Frontal velocity of 1.8 feet/day was achieved.

Resistance in the inlet section started increasing early. After about 2.5 pore volumes were injected, there was a sharp pressure increase in the inlet section. Correspondingly, the apparent viscosities in the other sections dropped below their peak values. It is believed to be due to filtration of gel aggregates across the inlet end resulting in solution with lower polymer and aluminum concentrations flowing through the downstream sections. Displacement was discontinued after 3.2 pore volumes were injected. Examination of the sandpack inlet revealed that gel aggregates were filtered by the inlet end screen and by the 50-mesh coarse sand layer at the inlet. The filtration and retention had resulted in the formation of a thick gelatinous structure at the inlet end. Interestingly, sand making up the porous medium underneath the filter cake disk was clean with no evidence of gel structure. The gelatinous disk was fairly strong, and had a well developed structure.

Figure 4.5: Apparent viscosities in sandpack SP7 during gel solution displacement.

Figure 4.6: Polymer and aluminum concentration in the effluent fractions for sandpack SP7.

Displacement was resumed after cleaning the sandpack inlet. Apparent viscosity showed a sharp increase during injection of one-half pore volume and seemed to have levelled off thereafter. At the same time, a gelatinous structure similar to the one described in the previous paragraph was beginning to form at the inlet end and extended along a gap between the main sand body and the sandpack holder. The gelatinous structure was beginning to plug the pressure ports and the pressure communication was established by poking needle holes through them. However, it was found that a blob of gel had formed inside those needle holes with continued displacement of gel solution. Displacement was discontinued after injection of 5.5 pore volumes. Polymer and aluminum concentrations in the effluent fractions are presented in Figure 4.7. The loss of polymer and aluminum in the effluent is 240 ppm and 12 ppm respectively. This, interestingly, is the same ratio at which the gelant was prepared and injected, i.e. 20:1 polymer to aluminum. This indicates that gel aggregates had formed in the delay loop and were filtered out as a whole at the inlet face. As in the case of sandpack SP7, it was observed that the effluent fractions did not develop any gel-like structure.

Residual resistance factors are presented in Table 4.3. The factors are similar to those obtained with the polymer displacement in sandpack SP5. Unlike gel displacement in sandpack SP7, nearly 5.5 pore volumes were injected in this displacement.

Table 4.3: Initial and final permeabilities in millidarcies, and residual resistance factors of the sections and overall sandpack SP6.

Section	Overall	A	B	C	D	E	F	G	H
Initial permeability	3746	3996	3783	3999	3445	3814	3535	3559	3790
Final permeability	1504	2562	1461	1932	1168	1128	1219	1310	1813
RRF	2.49	1.56	2.59	2.07	2.95	3.38	2.90	2.71	2.09

The significant findings of this displacement experiment are summarized below.

1. Delaying injection of gel solution by two hours after mixing it in-line results in stripping of crosslinked gel aggregates at the inlet face. The mechanism of stripping is akin to deep bed filtration.
2. Analysis of effluent fractions indicate that most of the polymer and aluminum were stripped out.
3. The gelatinous structure that resulted from the stripping of gel aggregates was fairly strong and had well developed structure.
4. In spite of letting the porous media saturated with gel solution sit in a water bath maintained at 25°C for 3 weeks, no flow resistance developed in any of the sections.

SUMMARY

1. Gel solution propagated through like a polymer solution if it was injected immediately after mixing it in line (sandpack SP7). Delaying the entry of the gel solution to allow adequate time for the gel aggregates to develop resulted in retention of gel aggregates at the inlet face (sandpack SP6). From the

Figure 4.7: Polymer and aluminum concentrations in the effluent fractions for sandpack SP6.

results of this study, therefore, it appears that either the solution would not flow through the porous media or if it flows through it will not develop any resistance downstream. No in-depth development of resistance was found in this study. Resistance developed at the porous media inlet only.

2. When propagated through porous media, the colloidal dispersion gel seems to lose all gel-like properties. Effluent solutions obtained during both the polymer and gel displacement experiments were found to have very low viscosities. Also, the gel effluent samples never formed a gel-like structure. Analysis of the effluent solution indicated that aluminum was heavily retained.

3. The colloidal dispersion gel does not appear to be capable of forming a gel-like network in the porous media even when allowed to remain there for as long as three weeks. No resistance was noticed in this study when a brine flush was initiated following the static rest period.

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Chapter 5

Permeability Modification by In Situ Gelation of a KUSP1-Ester System in Porous Media

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INTRODUCTION

The gel system investigated was composed of the KUSP1 biopolymer and monoethylphthalate ester (MEP). An alkali solution of the KUSP1 polymer forms a gel when the pH of the solution is lowered to a value of about 10.8 or below. Gelation was controlled by the hydrolysis reaction of the MEP ester which produces acid and reduces the pH of the KUSP1 solution.

The primary purpose of this work was to determine the magnitude of permeability reduction produced by the gelation of the KUSP1-ester system in selected rock samples. The effectiveness and long-term stability of the gel treatments in sandpacks, Berea cores and field cores were investigated. The effect of residual oil saturation on permeability reduction was also determined.

EXPERIMENTAL

Flow experiments were conducted in sandpacks, Berea sandstone cores and plugs cut from carbonate field cores. Sandpacks were packed with Wedron Silica sand (SP1) or Oklahoma #1 sand (SP2). Berea cores were fitted with endplates and coated with epoxy. Pressure ports were installed along the length of the sandpacks and Berea cores at 2" intervals. Carbonate core plugs were cut from the J-Alpha Grainstone interval of the Lansing-Kansas City formation. The plugs were fitted with endplates, epoxy coated and equipped with a pressure port at the midpoint of their length. The dimensions of the porous media are presented in Table 5.1.

The media were saturated with brine and the porosity was determined gravimetrically. Permeabilities of the medium and of each section were determined. A tracer test was conducted to evaluate the flow characteristics of the medium. The tracer was a step change in salt concentration during brine injection.

The media were saturated with 0.1 N NaOH solution prior to injection of gelant. Approximately two pore volumes of gel solution were injected through the porous medium over a period of about an hour. The injection was completed in much less time than the bulk gelation time of approximately 35 hours. Solutions injected in the Berea cores and the carbonate rocks contained 1.0% NaCl. No salt was added to the solutions injected in the sandpacks. Flow experiments were conducted at 25 °C.

The media were shut-in for three to four days to allow gelation to occur. Brine (water for sandpacks) was injected to determine the post-treatment permeabilities. A tracer test was conducted to assess changes in the flow characteristics of the medium produced by the treatment.

The long-term stability of the treatment was assessed by determining the permeability as a function of time over a period of many weeks. Fluid was flowed through the media using a constant head of fluid (3 psi) and the flow rate was measured.

Table 5.1 Porous Media Properties and Results of Flow Experiments.

Experiment Code	Porous Medium Type	Dimensions length x diameter (cm x cm)	Overall Permeability (mD)		Residual Resistance Factor	Post-Treatment Pore Volume (% of orig. PV)
			Before Treatment	After Treatment		
SP1	Sandpack	30.5 x 3.81	7750	34	230	0.97
SP2	Sandpack	30.5 x 3.81	9470	2.1	4500	0.85
SP3	Sandpack	30.5 x 3.81	7340	4.3	1700	0.90
BC1	Berea SS	30.5 x 5.1 x 5.1*	157	0.54	290	0.96
BC2	Berea SS at residual oil saturation (S_{or})	30.5 x 3.81	45 (at S_{or})	0.59	76	0.67 at S_{or} , 0.66 after treatment
BC3	Berea SS	30.5 x 3.81	600	1.3	460	0.98
JAG1	Limestone	6.5 x 2.6	115	0.18	640	0.86
JAG2	Limestone at residual oil saturation (S_{or})	5 x 2.4	14.3 (at S_{or})	0.04	360	0.74 at S_{or} , 0.62 after treatment
JAG3	Limestone	5 x 2.4	145	0.41	350	0.92

* square cross-section.

RESULTS and DISCUSSION

Nine gel treatments were conducted using a gel solution that contained 2.0% KUSP1 polymer, 0.1 N NaOH and 0.06 M MEP ester. The gelant was filtered through a 5-micron membrane before injection. Gelant injected into the Berea cores and carbonate rocks also contained 1.0% NaCl. The gel time for this gelant was between 30 and 35 hours as shown in Figure 5.1 where the pH and viscosity as a function of time are presented. Media BC2 and JAG2 were flooded to residual oil (normal dodecane) prior to the gel treatment. Specifications of the porous media are presented in Table 5.1.

Flow resistance in the porous media during the injection of gelant was measured. Increased flow resistance was observed only in the first section of the media BC3 and JAG3. The cause of the increased flow resistance was not determined. Samples of the injected solution and effluent samples collected after one pore volume had been injected gelled at approximately the same time as depicted in Figure 5.1. After the gelation of these samples, post-treatment permeabilities were measured. The permeabilities of the media were reduced significantly by the gel treatments as shown in Table 5.1. The factor by which the permeabilities were reduced, or residual resistance factor (RRF), are also presented in Table 5.1. Pressure drops measured across 2-inch long sections of the porous media showed that the permeability reduction was uniform along the length. The lower RRF for SP1 as compared to SP2 was attributed to changes in the preparation technique of the polymer stock.

Treatments in BC2 and JAG2 were conducted in the presence of a residual oil saturation. Inspection of the permeabilities in Table 5.1 indicate that the residual oil saturation did not significantly alter the effect of the treatment process.

Tracer tests conducted before and after the gel treatment were compared to determine the pore volume contacted by the injected brine after the treatment. Tracer concentrations in the effluent are presented in Figure 5.2 for SP3. The data show that the brine contacted 90% of the pore volume during post-treatment injection. Tracer tests were conducted in BC2 with the core saturated with brine, with the core at residual oil saturation and after the treatment. The tracer concentrations in the effluent are shown in Figure 5.3 and show that the tracer contacted 99% the non-oil-saturated pore volume during post-treatment injection. The pore volume contacted by the tracer during post-treatment injection are given in Table 5.1 for all the experiments. These results indicate that the gel was permeable to brine.

The stability of the permeability-reduction treatments was assessed in six of the media by continuously flowing brine under a constant pressure differential of 3 psi across the media. Permeability as a function of time is shown in Figure 5.4. The results demonstrate the long-term stability of the KUSP1-ester system in the three types of porous media. Permeabilities of the individual sections of the media were determined at the end of the study are presented in Table 5.2. The gel system was stable along the length of the porous media.

CONCLUSIONS

1. The KUSP1-ester acid system significantly reduced the permeability of sandpacks, Berea sandstone cores and carbonate core-plugs. Permeabilities were reduced by factors greater than 200 in the absence of oil in the media. The presence of a residual oil saturation did not significantly alter the effectiveness of the treatment. Permeabilities were reduced uniformly along the length of the media.

2. The gelled KUSP1-ester system was stable with time and throughput of brine. Little change in permeability was observed during the flow of many pore volumes of brine through the media over periods of many weeks.
3. The results indicated that the gel was permeable to brine. Tracer injected after gelation contacted large percentage of the pore volume even though the permeability was reduced significantly.

Figure 5.1: Viscosity and pH Behavior of Gelant System;
2.0% KUSP1 polymer, 0.1N NaOH, 0.06 M MEP ester, 25 °C.

Figure 5.2: Results of Tracer Tests for Sandpack SP3.

Figure 5.3: Results of Tracer Tests for Berea Sandstone BC3.

Figure 5.4: Permeability as a Function of Time for Long-Term Stability Tests.

Table 5.2: Results of Stability Test of KUSP1-Ester System in Porous Media.

Experiment #		SP1	SP2	SP3	BC1	BC2	JAG1
Duration (days)		117	175	156	200	90	23
Pore Volumes Injected		270	18	42	6	5	8
	Section	Permeability (md)					
After treatment	overall	34	2.1	4.3	0.54	0.59	0.18
After stability test	overall	43	3.8	5.8	0.41	0.71	0.26
	1 st	82	3.2	6.5	0.38	1.1	0.15
	2 nd	57	3.4	6.3	0.39	0.86	0.95
	3 rd	51	4.1	5.6	0.39	0.65	-
	4 th	38	2.6	5.4	0.39	0.64	-
	5 th	31	4.2	5.4	0.42	0.62	-
	6 th	24	6.1	5.8	0.47	0.59	-

Chapter 6

Gelation Behavior and Permeability Reduction for the KUSP1 Biopolymer-Boric Acid System

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INTRODUCTION

The objectives of this study were to characterize the gelation behavior of the KUSP1-boric acid system and to determine the permeability reduction produced by treatments of this system in selected rock material. Bottle tests were conducted to determine gelation behavior. Concentrations studied were 1.0% KUSP1, 0.1 to 0.5 M boric acid, 0 or 1.0% sodium chloride, and pH values between 9 and 13. The effect of temperature on gel times was investigated by conducting bottle tests at 25°C, 45°C and 65°C.

Results from the bottle tests were used to select a suitable composition of the gel system for testing the performance in porous media. Permeability reduction in sandpacks and Berea sandstone cores were determined for a selected gel system at 25°C and 45°C.

EXPERIMENTAL

Preparation of gelant and measurement of gel times. Stock KUSP1 was obtained in two forms, as an alkaline polymer solution or as an aqueous gel. Alkaline polymer solutions typically had a concentration of approximately 2.0% KUSP1 and a sodium hydroxide concentration that ranged between 0.6 to 1.0 N. Stock KUSP1 gel contained approximately 4.0% KUSP1 and was at neutral pH values. Stock gel also contained 200 ppm sodium azide as a biocide. Both stocks were refrigerated.

Gelant samples were prepared by weight. Stock polymer solutions were first diluted with water or stock gel was diluted and dissolved with water and NaOH. Solid orthoboric acid was dropped into the stirred, diluted polymer solution and allowed to dissolve. The pH of the solution was monitored and adjusted to the desired value using a combination of concentrated and 1 N hydrochloric acid. Occasionally, sodium hydroxide solutions were used to adjust pH values. Care was exercised on addition of acid to the stirred gel solution. Gel would form around the acid droplet on its addition to the stirred solution. The gel droplet was allowed to dissolve and the pH of the solution was allowed to stabilize before another drop was added. After the pH was adjusted to a selected value, the samples were placed in constant-temperature water baths or ovens. Gel times were determined by visual inspection. Syneresis of the formed gel was also noted.

An alternate preparation procedure was tested to determine whether the pH-adjustment technique had an effect on the gel time. The pH (or sodium hydroxide concentration) of the polymer solution was adjusted prior to boric acid addition. Gel did not form around the droplets during this procedure due to the higher pH. It was determined that the procedure used for pH adjustment did not affect the gelation behavior. This alternate procedure was not followed due to difficulty in targeting the pH of the gel solution after addition of boric acid (the initial pH of the gelant).

Alkaline KUSP1 solutions turned yellow and then brown over a period of many days when stored at room temperature. The color change was expedited at 40 °C and retarded considerably under refrigeration at approximately 4 °C. Testing showed that the gel time was not affected by the color change for polymer solutions that were stored at 25 °C for up to 7 days. Longer periods of storage during which the polymer solutions developed a dark brown color diminished the gelling ability of the solution.

It was discovered that storing 1.0% KUSP1 solutions with 0.2 M boric acid and at a pH of approximately 13 resulted in no color change and no gelation for several weeks at 25 °C. Samples prepared with a polymer solution stored under these conditions did not affect the gelation behavior. The shelf life of KUSP1 solutions can be extended by this technique.

Rheological experiments were performed on a Bohlin CS (controlled stress) Rheometer for selected gelants at 25 °C. Oscillation tests were conducted at a stress of 0.5 Pascals and a frequency of 0.1 Hz using a cone-and-plate geometry (4-cm diameter, 1° cone). The storage modulus, loss modulus and dynamic viscosity were monitored as a function of time.

Procedure for gel treatments. Flow experiments were conducted in sandpacks and Berea sandstone cores. Sandpack holders were one foot in length, had a diameter of 1.5 inches and were packed with Oklahoma #1 sand. Berea cores were one foot in length with a 2 inch square cross-section. The cores were fitted with endplates and encapsulated with epoxy. Pressure ports were spaced 2 inches apart along the length of each media. The media were saturated with 1% NaCl brine and the porosity determined. Permeabilities were determined and a tracer test was conducted prior to the gel treatment.

Gel treatments were conducted by injecting approximately three pore volumes of gelant into the medium over a period between two and three hours. The media were shut-in for 24 hours to allow for gelation. Brine was injected to determine post-treatment permeabilities. A post-treatment tracer test was also conducted.

RESULTS AND DISCUSSION

Bottle testing. Gel times for the KUSP1-boric acid system were determined to be a function of the boric acid concentration and the initial pH. Gel times as a function of initial pH are shown in Table 6.1 for a series of gelants which contained 1.0% KUSP1 and 0.5 mole boric acid per kg of solution. The results show that the gel time was sensitive to initial pH. A change in initial pH from 9.6 to 10.0 increased the gel time by a factor of 16. It was also determined that a NaCl concentration of 1.0% added to the gel system did not affect the gelation behavior.

Several series of gelants were prepared and monitored to investigate the effect of boric acid concentration, initial pH and temperature on the gel time. Values of these parameters are presented in Table 6.2. KUSP1 concentration was held constant at 1.0%. Gel times are shown in Figures 6.1, 6.2 and 6.3 for these series of experiments. The results show that the gel time for the KUSP1-boric acid system can be regulated from instantaneous to several days by selection of boric acid concentration and initial pH.

Figures 6.1, 6.2 and 6.3 show that at constant initial pH, the gel time decreased with a decrease in boric acid concentration. This observation was counter to the intuitive thought that a higher concentration should decrease the gel time. This observation demonstrates the interrelationship between pH and boric acid concentration has on the gelation of KUSP1.

Table 6.1: Gel time as a function of initial pH for the 1.0% KUSP1 and 0.5 mol/kg boric acid at 25°C.

pH	Gel Time
9.6	6 hours
10.0	4 days
10.1	5 days
10.2	6 days

Table 6.2: Matrix of gel solution concentrations investigated to study the effect of boric acid concentration and pH. The solutions contained 1.0% KUSP1 polymer and 1.0% sodium chloride.

Boric acid concentration (mole/kg)	Initial pH	Temperature °C
0.5	10.0	25 45 65
0.4	10.5	
0.3	11.0	
0.2	11.5	
0.1	12.0	

Gel times were reduced as the temperature was increased as shown by comparing the results in Figures 6.1, 6.2 and 6.3. Syneresis of the gels increased with increased temperature and decreased pH. At 25 °C, syneresis (less than 10% solvent expulsion) was observed only at a pH of 10.0. At 45 °C, syneresis occurred at pH values of 11.0 and lower. Syneresis was observed at all pH values for samples maintained at 65 °C. Gels shrank to less than 25% of their original volume at 65 °C and at pH values less than 11.0

The nature of the KUSP1-boric acid gels was different from gels prepared by pH reduction without boric acid present. KUSP1 solutions without boric acid gel when the pH of the solution is dropped to a value of approximately 10.8 and the gel is white in color and has a tendency to shatter. Gels prepared at a boric acid concentration of 0.5 mole/kg solution were transparent and more resilient. As the boric acid concentration was decreased, the gels exhibited the same resiliency but they developed a white tinge.

Experiments showed that alkaline KUSP1 polymer solutions gelled when the pH of the solution was decreased. These experiments were conducted by titrating an alkaline KUSP1 solution with a HCl solution. The pH values at which the solution gelled as a function of boric acid concentration are shown in Figure 6.4. A gel is formed in a KUSP1 solution without boric acid at a pH of 10.8. Increasing the boric acid concentration lowered the pH value at which a gel was formed.

Figure 6.1: Gel times as a function of pH and boric acid concentration for the KUSP1-boric acid gel system at 25°C.

Figure 6.2: Gel time as a function of pH and boric acid concentration for the KUSP1-boric acid gel system at 45°C.

Figure 6.3: Gel time as a function of pH and boric acid concentration for the KUSP1-boric acid gel system at 65°C.

Figure 6.4: pH at which gelation occurs immediately as a function of the boric acid concentration for the KUSP1-boric acid gel system at 25 °C.

Figures 6.5 and 6.6 show the storage modulus and dynamic viscosity as functions of time for a gel system at three boric acid concentrations. The storage modulus and dynamic viscosity increased faster at lower boric acid concentrations supporting the results obtained for the bottle tests.

Gel treatments in porous media. The performance of the KUSP1-boric acid system was determined in sandpacks and Berea sandstone cores at 25 and 45 °C. The gelant was composed of 1.0% KUSP1 and 0.5 mole of orthoboric acid per kg of gelant. A gel time of 24 hours was controlled by adjusting the pH of the gelant to 9.9 at 25 °C and to 10.5 at 45 °C.

During the injection of gelant, flow resistance in the media did not exceed that due to the viscosity of the gelant which indicated no problems with the injectivity of the gelant. Atypical behavior was observed during post-treatment brine injection in that several pore volumes of brine were injected before pressure drops stabilized. Pressure drops declined at a given flow rate demonstrating an increase in permeability with volume of brine injection. Post-treatment permeabilities were determined after more than 400 hours of injection which corresponded to more than four pore volumes of brine injected. Pre- and post-gelation permeabilities are given in Table 6.3. The residual resistance factors, which is the ratio of these permeabilities, show that the permeabilities were reduced by factors greater than 50. Permeabilities were reduced less at 45 °C than at 25 °C, possibly due to more syneresis occurring at the higher temperature. At a given temperature, permeabilities were reduced by larger factors in sandpacks than in Berea sandstone cores.

Data from tracer tests conducted before and after the gel treatment were used to determine the fraction of pore volume that was contacted by the displacing tracer. Values of the fraction of pore volume contacted by the tracer during the post-treatment tracer test are given in Table 6.3. The results show that the gel reduced the volume contacted by the tracer. Similar experiments conducted with the KUSP1-ester system (see Chapter 5) showed that most of the pore volume was contacted by tracer. These results indicate the differences between the two KUSP1 system in how the gel reduces the permeability of porous media.

SUMMARY

Gel times for the KUSP1-boric acid system can be regulated from a few seconds to several days by selection of the boric acid concentration or the pH of the gel solution. At a given pH, a decrease in the boric acid concentration decreased the gel time. Gel times decreased and syneresis increased with increased temperature.

The nature of the gels formed using boric acid is different from the gels formed by reducing the pH of an alkaline KUSP1 solution. Boric acid gels are clear and appear much more resilient than the gels formed without boric acid which are white in color and tend to shatter. It is speculated that the borate crosslinks the polymer molecules to form gels.

Gel treatments using the KUSP1-boric acid treatment can significant reduce the permeability of porous media. Permeabilities were reduced by factors that ranged from 50 to 3300 in sandpacks and Berea sandstone cores at 25 and 45 °C. Permeability reduction was greater in the more permeable sandpacks and at the lower temperature.

Table 6.3: Results for Gel Treatments in Porous Media.

Exp. Code	Porous Media Type	Temp. (°C)	Initial Permeability (md)	Post-Treatment Permeability (md)	Residual Resistance Factor	Post-Treatment Pore Volume (% of orig. PV)
SP1	sandpack	25	6700	2	3300	-
SP2	sandpack	25	6800	2.6	2600	-
SP3	sandpack	45	7000	112	62	20
BC1	Berea Sandstone	25	560	1.2	470	44
BC2	Berea Sandstone	45	610	12.5	50	22

Figure 6.5: Development of storage modulus as a function of time and boric acid concentration for the KUSP1-boric acid gel system at 25°C.

Figure 6.6: Dynamic viscosity as a function of time and boric acid concentration for the KUSP1-boric acid gel system at 25°C.

Chapter 7

Gel Systems for Controlling CO₂ Mobility in Carbon Dioxide Miscible Flooding

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INTRODUCTION

Carbon dioxide miscible flooding is one of the most important tertiary oil recovery techniques employed in the United States. However, the process experiences major difficulties in field application because of reservoir heterogeneity due to high permeability contrast. CO₂ tends to finger through the high permeability zones and bypass the oil. Early CO₂ production occurs with increased recycling and other operating costs.

Different methods have been investigated for improving the overall efficiency of CO₂ flooding process. In almost all these methods, attempts have been made to achieve a favorable mobility ratio by affecting the CO₂ relative permeability. Examples of these methods are: 1) water alternating gas (WAG) process,¹ 2) carbon dioxide-foam process,² and 3) viscosified carbon dioxide process.³

Another technology which is under study is permeability reduction by in-depth placement of polymer gels. The objective of this research is to reduce the permeability in high permeability zones so that the CO₂ will flow in the low permeable zones of the reservoir. Reduction of matrix permeability in the CO₂ process has been studied by other investigators.^{4,5} No systems were found that gave satisfactory permeability reduction when exposed to prolonged injection of CO₂.

Three new in situ gel systems developed and tested in our laboratory are described in this paper. Two of these systems are based on a biopolymer termed KUSP1.^{6,7} The third system is based on a modification of a previously reported organic crosslinking system.

KUSP1 (Kansas University Super Polymer One) is an acronym for a biopolymer developed at the University of Kansas. The polymer is a β -1,3-polyglucan and is produced by fermentation of a bacteria known as *Alcaligenes faecalis* and certain species of *Agrobacterium*.⁶ The polymer grows on the surface of the bacteria. During the fermentation process, the polymer laden bacteria aggregate and settle out from the growth medium. Polymer is extracted from the bacteria by suspension in dilute alkali. Neutralization of the alkaline polymer solution produces a hydrogel. The gelation process is reversible and the hydrogels are stable at high temperatures in neutral solutions. The polymer degrades in alkaline solution with time and at elevated temperatures.

Earlier investigations^{8,9} revealed the potential of this biopolymer for permeability reduction in sand packs as well as Berea sandstones. In situ gelation was achieved by injecting acid to reduce the pH of the alkaline polymer solution to the level below the gelation point, i.e., pH = 10.8. In the studies reported in this paper, two methods of gelling the biopolymer solution were studied: 1) in-situ gelation by injection of carbon dioxide and 2) neutralization of the alkaline polymer solution using an ester.

Sulfomethylated resorcinol-formaldehyde (SMRF) gel system has shown promising characteristics for reducing the permeability of porous media during an earlier laboratory test.¹⁵ This gel system revealed applicability in high salinity environments, temperatures up to 41°C, and a wide range of pH. Therefore, it seems to be applicable under CO₂ supercritical conditions. Data presented in this paper will support this conjecture.

KUSP1 - CO₂ System: This system is based on neutralization of the alkaline polymer solution by controlled injection of CO₂. Initial experiments¹⁰ were conducted in sandpacks under atmospheric conditions to investigate the possibility of in situ gelation by CO₂ injection in porous media saturated with the KUSP1. In the first experiment, early gas breakthrough occurred with no permeability reduction. This was attributed to a high CO₂ injection rate (1 ml/min), which caused CO₂ fingering through the sand pack without sufficient reaction with the polymer solution. A second experiment, conducted at lower CO₂ injection rates, led to permeability reduction on the order of 98%. It was not possible to restore the permeability to its original state by injection of concentrated NaOH. This may be because of inability of NaOH to contact all the gel formed.

KUSP1 - Ester System: The second system uses the hydrolysis of an ester to control the rate of neutralization. The ester is slowly hydrolysed and causes pH reduction to the level for the KUSP1 alkaline solution to gel. The ester used in this study was monoethylphthalate. Figure 7.1 shows the structure of monoethylphthalate ester and the reaction which produces ethanol and hydrogen ion.¹¹ The rate of hydrolysis is controlled by the concentration of the ester and the initial pH of the solution. There are two mechanisms contributing to the reduction of pH. A rapid, irreversible neutralization reaction takes place as soon as the ester is added to the alkaline solution. It releases H⁺ ions resulting in a fast, initial pH drop. The second reaction is the hydrolysis reaction that is rate determining.

Figure 7.2 shows pH-versus-time data for the KUSP1-monoethylphthalate system used in this research.¹¹ The pH drops with time, causing the polymer solution to gel at about pH 10.8. Thus, through control of the hydrolysis reaction, it is possible to control gel time of a KUSP1 system injected into a porous medium. The gelation system has been studied and results have been reported in detail elsewhere.¹²

SMRF System: The third gel system developed and studied in this work for application to CO₂ flooding is the SMRF (sulfomethylated resorcinol formaldehyde) system. This is an organic gel system based on modification of the resorcinol formaldehyde system which was used commercially for a limited period of time and abandoned due to extreme sensitivity to salinity and solution pH.¹³ Tolerance for both pH and a broad range of salinity was obtained by sulfomethylating the resorcinol.¹⁴ The resulting gel system tolerates a high salinity environment, temperatures up to about 45°C, and the range of solution pH anticipated in carbonate reservoirs. Gel time is controlled by the composition of the reactants. The injected solution has a low viscosity (1.1cp at 41°C) and is easily injected into porous rocks. Figure 7.3 shows a typical viscosity time plot for a SMRF gel system which has a nominal gel time of 23 hours.¹⁵

EXPERIMENTAL

The experimental program consisted of gelling each polymer system in a one-foot Berea core which was mounted in a core holder and determining the permeability of the treated rock to brine and carbon dioxide at supercritical conditions. Five separate tests were conducted. Dispersion tests were run in some tests to estimate the pore volume contacted by the injected fluids after treatment with a gelled polymer system.

Figure 7.1: Chemical structure for monoethylphthalate and the hydrolysis reactions leading to consumption of hydroxide ion and reduction of pH.

Figure 7.2: A representative pH versus time plot for the gelation of KUSP1-ester system.

Figure 7.3: Viscosity time graph for the gelation of SMRF at 41°C.

EQUIPMENT AND MATERIALS

Experimental Apparatus: Figure 7.4 is a schematic presentation of the experimental apparatus used in this work. An ISCO syringe pump was used for injecting CO₂, brine, and gel solutions into the core. All the experiments were conducted at constant rate. A TEMCO high-pressure core holder equipped with pressure ports was used. The rubber sleeve was filled with water and the injection pressure was kept at 500 psi below the sleeve pressure because higher sleeve pressures caused the rubber sleeve around the pressure taps to deform and seal off the pressure ports.

One-foot Berea cores, 2 inches in diameter, were used in all experiments. Pressure ports were located such that the core was divided into four sections. The first and fourth sections were 5 cm in length and sections two and three were 10 cm long. The pressure difference for each section, as well as overall pressure difference, was measured by pressure transducers and recorded via a computer based data gathering system. The effluent of the core, after passing through the back pressure regulator, was collected by a fraction sample collector for further analysis. The apparatus was placed in an air bath in which the temperature of the core and the injected fluids was kept constant. The pressure of the core was maintained by a TEMCO back-pressure regulator connected to a cylinder containing nitrogen at high pressure. The back pressure was maintained at 1200 psi. Details of the experimental set up are presented elsewhere.¹⁰

Solution Preparation: KUSPI- CO₂ System: Concentration of the KUSP1 polymer solution was 1 % by weight. The solution was prepared by dissolving 4 g of dry KUSP1 polymer and 4 g of NaCl in 392 g of 1N NaOH solution. The solution was stirred continuously using a magnetic stirrer for about 2 hours until a clear and consistent solution was obtained. KUSP1 polymer contains some proteinaceous impurities such as cell debris.¹² Biopolymers are known to form microgels in the presence of salt and free proteins. To remove the impurities, the polymer solution was filtered through a 5 micron nylon filter using a vacuum filtration apparatus. Approximately 2g of carbon black and 2g of diatomaceous earth were added to the solution to help the filtration process. The carbon black absorbed proteins in the polymer. Care was taken to ensure that the filter cake formed was not disturbed or cracked while pouring the solution into the beaker. The final pH of the solution was 13.6.

KUSPI-Ester System: The KUSP1 polymer solution was prepared as described above. An ester solution was added to the filtered polymer solution. The ratio of number of moles of mono ethyl phthalate to sodium hydroxide was 1:0.6. Special care was taken while adding ester solution to prevent gel globules from forming in the region where the ester came in contact with the polymer solution.¹¹ The ester solution was added drop by drop, giving each drop sufficient time to dissolve into the polymer solution before the next drop was added. Gelation time was adjusted by adding concentrated hydrochloric acid to reduce the pH to the required value. This was done just before injecting the solution into the core to ensure a reasonable gelation time for the experiment to be carried out.

SMRF System: A fresh solution of SMRF was prepared in the laboratory. Sulfomethylation was carried out by initially reacting sodium sulfite with formaldehyde and subsequently reacting it with resorcinol¹⁴ at 60°C. The composition of the SMRF was maintained at a mole ratio of F/S/R = 0.75/0.5/1; where, F is formaldehyde, S is sodium sulfite, and R is resorcinol. The pH of the final solution was adjusted to 9.8 by adding 50% NaOH solution at the initiation of the reaction.

SMRF gelling solution was prepared by adding brine (10% NaCl + 0.072% CaCl₂) and formaldehyde solution to the SMR solution. Twenty grams of brine and 1.032g of 37% aqueous solution of

Figure 7.4: Schematic presentation of experimental equipment.

formaldehyde were added to 4.6g of SMR solution. Solution pH was adjusted to approximately 7 by adding 20% acetic acid solution.

EXPERIMENTAL PROCEDURE

KUSP1 - CO₂ System: Once the core was mounted in the coreholder, the air in the core was displaced by CO₂ under atmospheric conditions at room temperature (circa 25°C). Brine was injected to saturate the core with a 2% solution. Porosity was determined by material balance. A dispersion run was carried out by displacing 2% brine with 2.2% brine and *vice versa* to check the pore volume as well as the heterogeneity of the core. The core was then saturated with 1 N NaOH solution. This ensured that the system pH was above 11 to avoid possible gelation at the interface between the injected polymer and the fluid inside the core. In experiments on Berea Core #3, CO₂ was injected into the core saturated with NaOH to determine the permeability to CO₂ in the presence of a trapped liquid saturation. The core was resaturated with NaOH before injection of alkaline polymer solution.

The alkaline polymer solution was prepared 5 hours before injection. The solution was injected under atmospheric conditions. The pressure data were recorded continuously while injecting the polymer solution into the core. After injecting about two pore volumes of the polymer solution the core was pressurized to 1300 psi. This was done by increasing the injection pressure gradually in three steps. First the pressure was increased to 500 psi, then to 900 psi and finally to 1300 psi and the system was maintained at that pressure. The inlet and the outlet valves were closed in preparation for CO₂ injection.

Some preparation was required before CO₂ was injected into the core. First, the temperature of the air bath was raised to 90° F. Lines connecting the pump to the inlet of the core were flushed with water to avoid gelation in the lines during CO₂ injection. The pump was charged with CO₂ from a cylinder and allowed to equilibrate. The pressure of CO₂ in the pump at this stage was in the vicinity of 900 psi. Since the core pressure was always above 1200 psi, the pump pressure was increased to a value just above the core pressure to ensure that the CO₂ was injected at supercritical conditions. Temperature was maintained at 90°F.

The CO₂ pressurization was accomplished by letting the CO₂ flow through the bypass line to build the pressure of CO₂ gradually. When the injection pressure reached the core pressure, flow through the bypass line was discontinued and the inlet valve to the core was opened to let CO₂ flow into the core. Pump limits were set to appropriate values and CO₂ injection was started at the predetermined flow rate.

The experiment was carried out under constant flowrate conditions. At the effluent end, an in-line pH electrode was used to record the variation in effluent pH and to determine the gas breakthrough time. Pressure data were collected continuously during the experiment. The effluent was observed continuously for possible presence of gas bubbles which would indicate gas breakthrough. Effluent was collected at a predetermined frequency in glass tubes mounted on a fractional collector. Gas breakthrough could also be detected by a sharp change in effluent pH from about 13.5 to 8. After gas breakthrough occurred, injection of CO₂ continued until the pressure drops across all the sections remained constant.

Brine (10000 ppm NaCl) was injected to determine the liquid permeability after gelation and the persistence of the permeability reduction. Trapped and dissolved CO₂ were displaced from the core before permeability measurements to eliminate relative permeability effects due to trapped gas saturation. A dispersion run was carried out before disassembling the core.

KUSP1 - Ester System: The core was prepared using the same procedures as for the KUSP1-CO₂ system. Before injecting the polymer-ester solution, the core was saturated with 0.1 N NaOH. Polymer-ester solution was injected into the core at 5 ml/min. A small sample of the solution was kept in a bottle under the same temperature as the core. This was done to verify the time of gelation. The polymer solution gelled after 114.5 hours. The polymer-ester solution was allowed to gel in situ at atmospheric pressure before injecting CO₂. Liquid permeability was measured after the completion of in situ gelation. This was followed by permeability measurement with CO₂ under supercritical conditions. Five pore volumes of CO₂ were injected before initiating brine injection. Brine injection was resumed after CO₂ injection to determine the effect of CO₂ on gel structure. Temperature was maintained at 93°F for all runs.

SMRF System: The core preparation procedure was identical to the KUSP1-ester experiments except the core was saturated with brine having the same composition as the gelling solution (i.e. 5% NaCl and 0.036% CaCl₂) and the temperature was maintained at 41°C(105.8°F). SMRF solution was injected in place of KUSP1-ester. Around three pore volumes of SMRF solution at pH = 7 were injected into the core. A small sample of effluent was collected before injection stopped and kept in a bottle under the same temperature as the core to verify gelation time. After the sample gelled in the bottle, the core was left for another 48 hours to make sure that the gelation process was complete in the core. In situ gelation was done at atmospheric pressure and the permeability to brine was determined. Because of our earlier experience with the system, a permeability in the range of microdarcies was expected after gelation was complete. Therefore, the transducers were replaced with larger range transducers and the injection rate of brine was reduced to 0.007 ml/min in order to remain in the pressure measuring range of the transducers. The core was pressurized to 1200 psi and permeability to brine was determined. Then, CO₂ was injected at a constant rate to determine the permeability of the gelled core to CO₂ and the persistence of the permeability reduction under continued injection.

RESULTS AND DISCUSSION

KUSP1- CO₂ System: Four Berea cores were used to investigate CO₂-induced gelation of KUSP1. Table 7.1 presents the initial permeabilities of the cores as measured by injecting brine and measuring pressure drop for each section and for the entire core. Permeabilities of the cores varied from 72 md to 384 md. Three CO₂ injection rates of 0.5, 0.1, and 0.005 ml/min were studied with one replication(Cores 1 and 2). Brine permeabilities after CO₂ injection are given in Table 7.2. Permeability reductions on the order of 78% to 93% were observed after CO₂ injection into the core saturated with KUSP1 in alkaline solution. The highest permeability reduction occurred for the lowest CO₂ injection rate.

The effective permeability for carbon dioxide in the presence of a trapped liquid saturation was determined in Berea Core #3 by displacing the initial alkaline solution with carbon dioxide. Effective permeabilities to CO₂ for the CO₂-NaOH system are presented in Table 7.3. Also presented in Table 7.3 are the effective permeabilities for the KUSP1-CO₂ system after the pressure stabilized. Inspection of Table 7.3 shows that in situ gelation of KUSP1 caused a reduction of 85% in the overall effective permeability to CO₂. A reduction of 85% in overall CO₂ effective permeability is comparable to the 88% reduction in overall brine permeability reported in Table 7.2 for Berea core No. 3.

Brine was injected to determine the brine permeability after the treatment and to investigate the gel stability under brine injection. A total of 12 pore volumes was injected into the core and the permeability was evaluated after every 2 pore volumes injected. Results for Berea core No. 1 are presented in Table 7.4. Data clearly support that the gel was stable under the operating conditions.

Table 7.1: Properties of Berea Sandstone Cores

Initial Brine Permeabilities (md)				
	Berea Core #			
	1	2	3	4
Overall	384	163	72	93
Section 1	331	154	68	72
Section 2	423	174	70	97
Section 3	384	163	73	106
Section 4	332	161	53	101
Porosity (%)	21.4	26.3	17.5	—

Table 7.2: Brine Permeabilities after CO₂-Induced Gelation

Brine Permeabilities (md)				
	Berea Core #			
	1	2	3	4
Overall	86	34	9	6
Section 1	88	30	7	4
Section 2	92	38	11	5
Section 3	78	41	11	10
Section 4	90	43	7	13
CO ₂ Injection Rate (ml/min)	0.5	0.5	0.1	0.005
Permeability Reduction (%)	78	79	88	93

Table 7.3: Comparison of CO₂ Effective Permeability for Berea Core 3

CO ₂ Effective Permeability (md)			
	CO ₂ -NaOH system	CO ₂ -KUSP1 System	Reduction (%)
Overall	3.65	0.56	85
Section 1	4.83	1.20	75
Section 2	6.05	0.95	84
Section 3	4.84	0.32	93
Section 4	1.21	0.48	60

Table 7.4: Gel Stability Study for Berea Core 1

Brine Permeability (md) after Injecting Indicated Pore Volumes					
	4 PV	6 PV	8 PV	10 PV	12 PV
Overall	90	90	93	85	86
Section 1	89	91	94	91	88
Section 2	89	92	93	93	92
Section 3	85	84	85	72	78
Section 4	103	103	103	98	90

KUSP1-Ester System: After confirming that gelation had occurred, brine was injected into the core at 0.1 ml/min under atmospheric conditions to determine the reduced permeability of the core. The core was then pressurized to 1200 psi and brine injection was resumed. Permeabilities to brine are presented in Table 7.5. Missing values in the table are due to plugging of pressure ports. An overall permeability reduction of the order of 99% was obtained. Permeabilities after gelation under high pressure are slightly higher than those under atmospheric condition. This suggests that gel shrinkage might have occurred as a result of pressurizing the system. This was further substantiated by measuring brine permeabilities under different back pressures as reported in Table 7.6.

The effective permeability of the KUSP1-ester gel to CO₂ under supercritical conditions of 1200 psi was 4.15 md which is 97% of the initial permeability to brine. The permeability was evaluated after injecting about five pore volumes of CO₂ into the core after gas breakthrough. Brine injection was resumed after injecting about five pore volumes of CO₂ under supercritical conditions. Brine permeabilities were evaluated under different back pressure values. No significant changes were observed. For example, the overall brine permeability at 1200 psi back pressure was 7.64 md before the gel was exposed to supercritical CO₂ and its value changed to 7.9 md (95% of the initial brine permeability) after injecting about five pore volumes of CO₂ under supercritical conditions. Thus, the gel is quite stable under the conditions studied in these experiments.

SMRF System: The initial brine permeabilities measured at two different brine flow rates are given in Table 7.7. The average permeability of the core was 700 md. Permeabilities after in situ gelation are presented in the last column of Table 7.7. The effective permeability to brine after in situ gelation was 0.049 md, a reduction of over 99% in the initial brine permeability. It is clear from Table 7.7 that the SMRF gel effectively shuts off the flow of brine and reduces the effective brine permeability of the core to almost zero.

The core was pressurized to 1200 psi and its permeability to brine was determined again. The permeability to brine increased due to pressurizing the core, but still remained below 1 md. For example, the overall permeability increased from 0.049 md to 0.9 md.

Nine pore volumes of CO₂ under supercritical conditions, i.e., 1200 psi and 41°C, were injected following brine injection at 1200 psi. Permeability of the core to the CO₂ was determined when the pressure reading became stable. This produced an overall effective permeability to CO₂ of 0.557 md. The injection rate of CO₂ was raised to 0.4 ml/min and 12 more pore volumes of CO₂ were injected. The effective permeability to CO₂ was 0.64 md and did not change significantly. This is a reduction of over 99% of the initial brine permeability. The CO₂ injection rate was reduced to 0.2 ml/min and three more pore volumes of CO₂ were injected. The effective permeability to CO₂ was 0.61 md. Thus, the gel treatment remained intact after 24 pore volumes of supercritical CO₂ were injected. At the end of the CO₂ injection, the overall brine permeability was 1.7 md which is 0.2% of the initial overall brine permeability of 700 md.

Table 7.5: Permeability Modification for KUSP1-Ester System

Brine Permeability (md)			
Porosity = 0.23	Initial	After Gelation (Low Pressure)	After Gelation (High Pressure)
Overall	144	1.08	2.64
Section 1	167	0.56	0.40
Section 2	186	0.63	--
Section 3	164	0.31	--
Section 4	76	1.44	--

Table 7.6: Effect of Pressure on KUSP1-Ester Gel System

Brine Permeability (md)				
Back Pressure Applied:	0 psi	400 psi	800 psi	1200 psi
Overall	5.58	5.70	6.05	7.64
Section 1	0.97	0.99	1.00	1.05
Section 2	--	--	--	--
Section 3	--	--	--	--
Section 4	--	--	--	--

Table 7.7: Permeability Modification for SMRF Gel System

Brine Permeability (md)			
Porosity - 0.23	Initial (2 ml/min)	Initial (5 ml/min)	After Gelation (0.007 ml/min)
Overall	705	695	0.049
Section 1	531	567	0.060
Section 2	776	744	0.085
Section 3	638	622	0.034
Section 4	716	707	0.042

CONCLUSIONS

The following conclusions apply to the three gel systems studied to control CO₂ mobility in Berea sandstone cores:

1. Injection of supercritical CO₂ into Berea cores saturated with KUSP1 solution causes in situ gelation. The amount of permeability reduction was about 85% of the original permeability. The reduction in effective permeability of CO₂ (86%) was very close to that of brine (84%) and the permeability reduction was uniform throughout the length of the cores.
2. The KUSP1-CO₂ induced gel was stable under prolonged brine injection at supercritical conditions.
3. KUSP1 was gelled in porous media by hydrolysis of monoethylphthalate ester with a gelation time of over 100 hours at 90°F. Permeabilities to brine and CO₂ were reduced to 95-97% of the initial brine permeability. The permeability reduction was stable after injecting several pore volumes of CO₂ under supercritical conditions.
4. The SMRF system effectively shuts off the flow of brine in Berea sandstone and is equally effective in reducing the mobility of the CO₂ under atmospheric and under supercritical conditions. Effective permeability was less than 1 md for a Berea core with an initial brine permeability of 700 md. Effectiveness of the permeability reduction did not deteriorate with the flow of supercritical CO₂ through the treated core.

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Chapter 8

Modeling the Effect of Filtration of Pre-Gel Aggregates on Gel Placement in Layered Reservoirs with Crossflow

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INTRODUCTION

Flow experiments with the polyacrylamide/chromium system show a build-up of resistance in a localized region some distance behind the front of the gelant.^(1,2) Several pore volumes of gelant flow through this region till complete plugging of the sandpack occurs. The age of solution flowing through the zone of flow resistance is significantly lower than the "gel time" of the solution in a beaker. These trends suggest that the build-up of flow resistance during in-situ gelation does not result from a simple bulk gelation at the displacement front. On increasing the flowrate, the gelant penetrates further into sandpacks, but also plugs the sandpacks at a faster rate.

Previous models simulate in-situ gelation of polyacrylamide/chromium system in porous media by relating a lumped "resistance factor" to the kinetics of the redox reaction.^{3,4,5,6} These models do not predict the characteristic features of the experimental results with the polyacrylamide system. More importantly, these models do not show the effect of flow rate on the rate of build-up of flow resistance. This dependance is essential for an accurate scale-up of laboratory experiments to field-scale conditions.

Todd et al. proposed a model based on the hypothesis that build-up of resistance for the polyacrylamide/chromium system is due to the filtration of pre-gel polymer aggregates by the porous medium.⁷ The crosslinking ions released by the redox reaction are attached to the polymer molecules and lead to the formation of aggregates of crosslinked polymer molecules. The attached chromium ions enhance the filtration properties of the aggregates by their ability to form crosslinks with polymer deposited on the walls of the pores. The zone of flow resistance is characterized by a rapid reduction in porosity and permeability of the porous medium well before a gel structure is formed.

Since the redox reaction is a slow, kinetically-controlled process, at high flow rates it is possible to inject the gelling solution deep into the sandpack before significant amounts of crosslinking ions are released. Once chromium-ions are attached to the polymer molecules, the rate of filtration is a function of the interstitial velocity of the aggregates through the pores. Higher interstitial velocities lead to faster rates of filtration and plugging. The model of Todd et al.⁷ successfully matched experimental results over a range of flow rates suggesting the validity of the underlying filtration mechanism.

This work extends the filtration hypothesis for the polyacrylamide/chromium system to simulate permeability-modification treatments in layered reservoirs with crossflow. A description of the radial flow-geometry around the wellbore is necessary not only for an accurate prediction of the radius of penetration of the gelant, but also in determining the magnitude of the build-up of flow resistance. In addition, most reservoirs are characterized by some degree of crossflow between the high-permeability and low-permeability regions. The effects of filtration of polymer aggregates on crossflow behavior are yet to be investigated.

In this work, a two-dimensional numerical model for simulating in-situ gelation of the polyacrylamide/chromium system is developed. The model is used to study the effects of the injection pressure, which constitutes an important operating parameter, and reservoir characteristics such as the permeability contrast between the layers, the vertical permeability and height of the reservoir. Once the favorable reservoir characteristics are identified, the effects of gelant viscosity and zonal isolation for improving the performance of a permeability-modification treatment are examined.

The emphasis in the main body of the paper is on this analysis. The detailed model description is in the Appendix. The model basically consists of differential equations describing Darcy flow, mass transfer of the different chemical species, chromium and gelation reaction kinetics and filtration of gel aggregates. The equations are solved numerically using a procedure described in the Appendix.

PHYSICAL DESCRIPTION

Gel placement in an idealized, two-layered reservoir, as shown in Figure 8.1, is examined. Each layer is assumed to be homogenous in nature. Table 8.1 summarizes a base set of parameters for all the simulations. These conditions represent typical field-scale conditions for a near-wellbore, permeability-modification treatment. The concentrations and reaction parameters for the chromium/polyacrylamide gelling system correspond to those used to simulate experimental results of Marty et al., in linear sandpacks.¹ The pore structure characteristics for the two layers are scaled according to the Cozeny-Karman model.⁸ Variations from the set of conditions in Table 8.1 are indicated in the description of the individual runs.

In the simulations, each layer is assumed to be at a uniform relative pressure of zero prior to gel-solution injection. Gel-solution injection occurs at a constant wellbore pressure (500 psi in base case) and for some specified time period. Crossflow between layers in the reservoir is allowed. Parameters calculated in the model are pressure, flowrate, concentrations, and localized flow resistance.

RESULTS AND DISCUSSION

A key mechanism governing gel-placement behavior in reservoirs is the build-up of the resistance to flow during in-situ gelation. The build-up of resistance may be due to two mechanisms; an increase in gelant viscosity by the formation of crosslinks between the polymer molecules, and the filtration of polymer aggregates which reduces the permeability of the porous medium. In this study, the evolution of the "apparent viscosity" in the reservoir is used to characterize both effects during gelation processes. Apparent viscosity is defined as

$$\text{apparent viscosity} = \mu \left(\frac{k^0}{k} \right) \dots \dots \dots (1)$$

where μ is the viscosity of the gelant, k_0 is the initial permeability and k is local value of the permeability during the treatment. In the model, both the radial and vertical permeabilities are effected equally by the filtration mechanism and either value may be used in Equation A-1.

Base Case. The base case represents a direct scale-up of the laboratory experiments by Marty¹ to field-scale conditions shown in Table 8.1. The gel-placement behavior in this set of results is representative of a typical permeability-modification treatment in heterogenous reservoirs with crossflow.

Figure 8.1: Physical system examined in simulations.

Table 8.1: Base set of parameters for the simulations.

I Reservoir Description		
wellbore pressure		500 psi
wellbore radius		0.66 ft
exterior radius		500 ft
reservoir height		32 ft
initial viscosity		1 cp
injected viscosity		10 cp
compressibility		$5 \cdot 10^{-6}$ psi ⁻¹
II Porous Media Characteristics		
	layer 1	
height		0 - 16 ft
radial permeability		100 mD
vertical permeability		100 mD
porosity		0.24
average grain diameter		91 microns
average pore length		86 microns
median pore throat diameter		11 microns
	layer 2	
height		16 - 32 ft
radial permeability		10 mD
vertical permeability		10 mD
porosity		0.16
average grain diameter		51 microns
average pore length		48 microns
median pore throat diameter		6 microns
III Reactant Concentrations		
injected polyacrylamide concentration		5000 ppm
injected dichromate concentration		400 ppm
injected thiourea concentration		1500 ppm

Figure 8.2 shows the profile of the total rate of injection of gelant as a function of time. Figure 8.3 shows the corresponding profile of the fraction of the total gelant injected into the high-permeability layer. These profiles are compared to the case where the flow behavior of the gelant is governed solely by viscous flow of the polymer solution without filtration. Comparison of the two profiles is used to differentiate the effects of viscous crossflow from the effects of filtration during the treatment. Additionally, the profiles with only viscous flow represent the behavior of the gel system under two possible conditions - when filtration is not an important characteristic of the gelling system, or, fluid-rock interactions in the reservoir inhibit the effects of filtration to insignificant levels.

Figure 8.2: Rate of injection in the presence of filtration compared to the rate of injection with only viscous flow of gelant.

Figure 8.3: Fraction of total gelant injected into the high-permeability layer in the presence of filtration and compared to the case with only viscous flow of gelant.

In order to understand the dynamics of the placement behavior, the total injection period may be approximately divided into three regimes.

Regime I. The first regime occurs in the initial period of the treatment in which the redox reaction has not progressed significantly and little release of crosslinking ions (Cr^{3+}) occurs in the solution. Figures 8.2 and 8.3 indicate that this period lasts till approximately 30 hours of injection at the given reservoir conditions. The total flowrate in Figure 8.2 shows a rapid decline akin to that of viscous flow of the polymer under transient conditions. The fraction of the gelant injected into the high-permeability layer is also similar for the two cases.

Figure 8.4 shows the apparent viscosity contour of the gelant after 24 hours of injection and is representative of flow behavior during this regime. A small fraction of pre-gel aggregates are retained in the porous medium by interception and result in the deposition of a thin layer of polymer on the walls of the pores. This process causes a slight decrease in the permeability of the reservoir and the apparent viscosity of the advancing gelant is above the injected viscosity of 10 cp. Consequently, the total flowrate of the gelant into the reservoir with filtration is less than that for pure viscous flow of the polymer solution into the reservoir (Figure 8.2).

Crossflow behavior during this period is dominated by viscous forces. Figure 8.4 shows that the front of the gelant in the low-permeability layer is altered by crossflow from the high-permeability layer. Similarly, the front of the gelant in the high-permeability layer is modified by crossflow from the low-perm layer. Both effects reduce the effectiveness of the gel-placement in the reservoir.

Understanding the flow behavior during the first regime is critical since the bulk of the gelant is injected into the reservoir during this period. The profiles in Figures 8.3 and 8.4 show that a significant fraction of this gelant is injected into the low-permeability layer. This fraction is a function of the permeability contrast between the layers, the viscosity of the gelant and the degree of crossflow in the reservoir. Examining the effects of these parameters, therefore, constitutes an important objective of this study.

Regime II. The second regime represents the gel-placement behavior during the period from 30 to 60 hours of injection. Figure 8.2 shows that this regime is characterized by a rapid drop in the total flowrates compared to pure viscous flow of gelant. Figure 8.3 indicates that the gelant is preferentially injected into the high-permeability layer during this regime.

The time period represented by the second regime is long enough for significant reaction between the dichromate and thiourea, but is shorter than the nominal "gel time" of 72 hours observed for the system in static beaker tests. Considerable amounts of Cr^{3+} ions are released into the solution and are subsequently attached to the polymer molecules by the uptake reaction. The attached chromium-ions enhance the efficiency of capture of the pre-gel aggregates by forming crosslinks with the polymer deposited on the walls of the pores. Thus, the dominant mechanism for the build-up of resistance during in situ gelation of the polyacrylamide/chromium system consists of the rapid reduction of permeability due to the filtration of pre-gel aggregates. Filtration of these aggregates decreases the concentration of polymer in the solution which offsets any increase in viscosity by the crosslinking reaction.

Figure 8.5 shows the apparent-viscosity contours in the two layers after 48 hours of injection. The profiles show a significant build-up of resistance in both the high-permeability and the low-permeability layers. The peaks in apparent-viscosity profiles in the two layers occurs some distance behind the front. This

Figure 8.4: Apparent viscosity profiles after 24 hours of injection (Base Case).

Figure 8.5: Apparent viscosity profiles after 48 hours of injection (Base Case).

behavior is characteristic of filtration processes observed in laboratory experiments with the polyacrylamide/chromium system.^{1,2}

Crossflow, during this period, is due to a combination of viscous forces and the filtration mechanism. The crossflow behavior may be divided into three distinct regions.

(1) In the region between the wellbore and the peak in resistance in the low-permeability layer, crossflow is directed from the low-permeability layer towards the high-permeability layer. Since the peak in resistance in the low-permeability layer is located close to the wellbore, gelant is preferentially injected into the high-permeability layer during this period (Figure 8.3). Although the presence of gelant in the low-permeability layer will eventually reduce the injectivity of the well after the shut-in period, it is beneficial during the process of placement of the gelant.

(2) In the region intermediate to the peaks of resistance in the two layers, crossflow is directed from the high-permeability layer into the low-permeability layer. Build-up of resistance by the filtration mechanism, however, limits this front to a relatively small region near the interface of the two layers. This crossflow also results in the formation of peaks in the Cr^{3+} ion concentration and the apparent viscosity profiles in the low-permeability layer near the interface.

(3) In the vicinity of the peak in resistance in the high-permeability layer, crossflow is directed from the low-permeability layer into the high-permeability layer.

The high-permeability layer is characterized by higher interstitial velocities than the low-permeability layer. Figure 8.5 shows that the difference in velocities has two important consequences regarding the filtration behavior. First, significant concentrations of Cr^{3+} are extended over a larger region in the high-permeability layer. Filtration of polymer aggregates and ensuing build-up of resistance occurs over a larger region in the high-permeability layer than the low-permeability layer. Second, since the rate of filtration is proportional to the interstitial velocity of the pre-gel aggregates, the high-permeability layer is characterized by faster rates of filtration than the low-permeability layers.

The contrast in the rates of filtration is complicated by the following effects.

(1) The low-permeability layer is characterized by pores with smaller pore-throat diameters and pore lengths which favor the higher rates of filtration. The difference in the rates of filtration in the two layers, therefore, is reduced by the differences in the pore structure in the two layers.

(2) The radial flow-geometry around the wellbore also plays a significant role in determining the rates of filtration in the two layers. Cr^{3+} ions are released further into the reservoir in the high-permeability regions where the radial velocities decrease with increasing radius. Thus, the difference in the rates of filtration in the two layers in a radial flow-geometry is less than that expected with a linear flow-geometry.

(3) For the given system, the difference in velocities due to the permeability contrast of 10:1 between the two layers dominates over the two previously listed effects. Consequently, the high-permeability regions of the reservoir are affected by the filtration mechanism more than the low-permeability regions.

Regime III. The third regime is the period after 60 hours of injection in which the total flowrate levels off after the rapid drop in Regime II (Figure 8.2). This trend is deceptive as the levelling in flowrate does not imply a cessation in the filtration of the polymer aggregates. Figure 8.3 shows that this period is characterized by a precipitous drop in the fraction of gelant injected into the high-permeability layer.

Figures 8.6 shows the apparent viscosity profiles after 96 hours of injection. In order to understand the gel-placement behavior during this period, the fronts of the polymer solution are plotted as a function of

Figure 8.6: Apparent viscosity profiles after 96 hours of injection (Base Case).

time in Figure 8.7. Although the shape of the fronts is altered by filtration, these profiles demonstrate the following important features.

During the first 60 hours of injection, increasing amounts of polymer are lost from solution due to the filtration mechanism, but the polymer front still advances deeper into the reservoir. Onset of the third regime is characterized by the following behavior:

(1) In the region intermediate to the peaks of resistance in the two layers, this period is characterized by significantly more crossflow from the high-permeability layer into the low-permeability layer. This is evident from the polymer fronts at 72 and 96 hours of injection shown in Figure 8.7.

(2) As a result of the low flowrates characterizing Regime III, large amounts of Cr^{3+} ions are released near the wellbore. The rate of filtration in these regions eventually exceeds the rate of injection of the polymer and the front of the polymer in the solution recedes closer to the wellbore rather than further into the reservoir. The injected solution is rapidly stripped of polymer aggregates by filtration and the peaks in apparent viscosity in the high-permeability layer move toward the wellbore. Consequently, increasing amounts of gelant are diverted into the low-permeability region at the wellbore (Figure 8.3).

Clearly, the gel placement behavior during Regime III is detrimental for an effective permeability-modification treatment of a well. The transitional period from regime II to regime III represents the optimal time for stopping the injection of gelant. This transition is characterized by a levelling off in the flowrate profile. For the given set of conditions, this time is approximately 60 hours in Figure 8.2. Injection of gelant beyond this period results in more diversion of gelant into the low-permeability layer without increasing the penetration of the gelant in the high-permeability layer.

Effect of Injection Pressure or Flow rate. The experiments of Marty et al.¹ with the polyacrylamide/chromium system showed that higher flow rates resulted in deeper penetration of gelant into sandpacks but also caused a faster build-up of resistance. Both trends may be explained by the filtration mechanism which couples the rate of build-up of resistance to the kinetics of the redox reaction and the velocity of the polymer aggregates through the porous medium. Extension of the filtration mechanism to field-scale conditions indicates that the flow rate, or the injection pressure, is an important operating variable in a permeability-modification treatment.

Figure 8.8 compares the total flow-rate profiles for injection pressures of 1000 psi and 250 psi to the base case of 500 psi. Figure 8.9 shows the corresponding profiles of the fraction of gelant injected into the high-permeability layer. The gel-placement behavior at the three different injection pressures is similar and may be divided into the three regimes discussed earlier.

During the first regime, the filtration mechanism is insignificant and the flow behavior of the gelant is governed by viscous forces. During this period, higher injection pressures result in the injection of greater volumes of gelant into the reservoir. Figure 8.9 shows that the distribution of this gelant between the two layers is similar for the range of injection pressures investigated. For higher flow rates, a minor increase in the fraction of gelant injected into the high-permeability layer under transient conditions is observed.

Figures 8.10 and 8.11 show the apparent viscosity profiles after 48 hours of injection at 1000 psi and 250 psi respectively. The corresponding profiles for the base case were shown earlier in Figure 8.4 and show trends intermediate to the results in Figure 8.10 and 8.11. These profiles are representative of the behavior during Regime II.

Figure 8.7: Profiles of the polymer front in the solution during gelation (Base Case).

Figure 8.8: Rate of injection in the presence of filtration for different injection pressures.

Figure 8.9: Fraction of gelant injected into the high-permeability layer for different injection pressures.

Figure 8.10: Apparent viscosity profiles after 48 hours of injection at 1000 psi.

Figure 8.11: Apparent viscosity profiles after 48 hours of injection at 250 psi.

The values of the apparent viscosities at 48 hours indicate faster rates of filtration at higher flow rates. The increase in the rate of filtration is a consequence of the higher interstitial velocities of the pre-gel aggregates in the reservoir at higher injection pressures. The difference in the rates of filtration, however, is less than that expected with a linear flow-geometry. The build-up of resistance occurs further into the reservoir at higher injection pressures with the radial velocities decreasing with increasing radius. As a result, the onset of the behavior in Regime III occurs at approximately the same time of 60 hours despite the difference in the injection pressures. Therefore, in the presence of radial flow-geometry, the kinetics of the redox reaction is the critical mechanism in determining the amount of gelant which can be injected into the reservoir.

In conclusion, it is possible to inject greater volumes of gelant into the reservoir by increasing the injection pressure. The rates of filtration increase with increasing flowrate, but this effect is mitigated by the radial flow behavior around the wellbore. Unfortunately, increasing the injection pressure does not alter the injectivity pattern significantly, i.e. more polymer is injected into both layers with increasing injection pressure. The advantages of injecting large volumes of gelant into the reservoir, therefore, may be offset by the loss in injectivity of the well after the shut-in period.

Effect of Permeability Contrast. Previous results show that a significant amount of gelant is injected into the low-permeability region. After shut-in of the well, this gelant lowers the injectivity of the well and the overall effectiveness of the treatment. The ratio of radial permeabilities is an important parameter in determining the distribution of gelant in the two layers. A case in which the permeability of the high-perm layer is changed from 0.1 D to 1.0 D is examined. The resulting permeability ratio of 100:1 represents a reasonable upper limit of the contrast in absolute permeabilities expected in unfractured reservoirs. The ratio of the effective permeabilities of the layers, however, may be enhanced by the presence of unswept oil in the low-permeability regions of the reservoir. Therefore, a permeability ratio of 100:1 is representative of cases characterized by severe channeling problems during waterflooding.

Figures 8.12 and 8.13 show profiles of the total flowrate and the fraction of gelant injected into the high-permeability layer as a function of time. The initial period essentially consists of viscous flow of gelant into the reservoir. Due to the higher permeability contrast, the flowrate of the gelant into the high-permeability layer in Figure 8.12 is considerably greater than the base case (Figure 8.2) at the same injection pressure. More importantly, the fraction of the total gelant injected into the high-permeability layer is considerably higher in Figure 8.13 than that in Figure 8.3. Thus, it is possible to inject gelant into the reservoir with a more favorable distribution as the permeability contrast between the layers increases.

Regime II represents the period in which the filtration processes become significant. Figure 8.14 shows the apparent-viscosity profiles after 48 hours of injection. Due to the higher injection rates, the penetration of gelant into the high-permeability layer region is significantly deeper than for the corresponding profile in Figure 8.5. The difference in the rates of filtration in the two layers increases as the permeability contrast increases. For the permeability contrast of 100:1, the build-up of resistance near the wellbore in the low-permeability layer is not sufficient to diverting significant amounts of gelant into the high-permeability layer. Consequently, for a higher permeability contrast, preferential flow into the high-permeability layer during Regime II is reduced.

Build-up of resistance limits the crossflow of gelant from the high-permeability layer into the low-permeability layer to a relatively small distance near the interface. This result is significant since considerably more gelant is injected into the reservoir than for the base case.

Figure 8.12: Rate of injection in the presence of filtration for a permeability contrast of 100:1.

Figure 8.13: Fraction of gelant injected into the high-permeability layer for a permeability contrast of 100:1.

Figure 8.14: Apparent viscosity profiles after 48 hours of injection for a permeability contrast of 100:1.

During Regime III, higher flow-rates hasten the plugging of the high-permeability layer by filtration. The drop in the fractional flow profile shown in Figure 8.13 occurs about 10 hours earlier than for the base case. Clearly, the radial-flow geometry around the wellbore plays a major role in reducing this time differential. For the given conditions, therefore, injection of gelant should be stopped after approximately 50 hours.

In conclusion, a more effective treatment is possible in reservoirs with high-permeability contrast. Permeability-modification treatments, therefore, are expected to be more effective in severe cases of water channeling as opposed to mild cases of water channeling during the waterflooding stage.

Vertical Permeability and Aspect Ratio. Previous results show that the bulk of the total gelant is injected into the reservoir during Regime I. During this period, crossflow is due to viscous forces only. After the onset of filtration in Regime II, further crossflow of gelant from the high-permeability layer into the low-permeability layer is retarded by the filtration mechanism. Hence, crossflow due to viscous forces is a critical mechanism determining the effectiveness of gel placement in a reservoir.

The degree of crossflow during gel placement is determined by the aspect ratio of the treatment and the ratio of the vertical permeability to the radial permeability. The aspect ratio is defined as the ratio of a characteristic radius of penetration defining the region of treatment (R) around the wellbore to the height of the layers (H). The degree of crossflow, G, is defined as ^{9,10}

$$G = \frac{R}{H} \sqrt{\frac{k_z}{k_r}} \quad (2)$$

Thus, crossflow is significant in relatively thin reservoirs characterized by high vertical permeabilities. The degree of crossflow in layered reservoirs is bounded by two limiting cases. A zero value of G indicates a reservoir without crossflow representing a layered system with each layer separated by an impermeable shale layer. As G approaches infinity, the crossflow between the layers increases and approaches vertical equilibrium.

Previous results indicate that the radius of penetration for the polyacrylamide/chromium system, is confined to within 10 to 30 ft of the wellbore for typical reservoir and operating conditions. In all the simulations shown earlier, the value of the ratio of the vertical permeability to the horizontal permeability of a reservoir is unity which represents the maximum amount of crossflow expected for that particular geometry. Therefore, the typical value of the degree of crossflow for near-wellbore treatment with this system is expected to be of the order of unity. The simulated apparent viscosity profiles show that crossflow of gelant is confined to a relatively small region near the interface of the layers.

In order to study the effect that filtration has in the presence of significant amounts of crossflow, injection of gelant into a reservoir with thickness (H) of 3 ft is examined. Although this case has little practical importance for the polyacrylamide/chromium system, the degree of crossflow in this case is representative of a system in which a deeper treatment of reservoir is possible. It may also be noted that the aspect ratio of the treatment in this example is closer to some laboratory experiments used to simulate of flow in layered reservoirs.⁹

Figure 8.15 shows the apparent viscosity profiles after 24 hours of injection. The movement of the front of the solution in the low-permeability layer is accelerated by crossflow from the high-permeability layer.

Figure 8.15: Apparent viscosity profiles after 24 hours of injection into a reservoir with height of 3.2 ft.

The movement of the front of the gelant in the high-permeability layer is retarded by crossflow from the low-permeability layer. The net effect of viscous crossflow, therefore, is to bring the fronts in the two layers closer together.

Figure 8.16 shows the apparent viscosity profiles after 48 hours of injection. Filtration of pre-gel aggregates results in a build-up of resistance in both layers. In addition, there is a build up of resistance intermediate to the peaks in the layers by crossflow. This front penetrates a significant distance into the low-permeability region.

Although viscous crossflow has a relatively small effect during typical near-wellbore treatments, the effects of viscous crossflow may become significant in deeper treatments by gelants with long gel times. In these cases, the bulk of the crossflow occurs before the onset of filtration and the filtration mechanism does not help to keep gelant from penetrating into the low-permeability regions.

Clearly, gel-placement is most effective in reservoirs characterized by low crossflow. It may be noted that reservoirs with significant amounts of crossflow may not exhibit severe problems of channeling during waterflooding. Based on crossflow behavior, therefore, it may be concluded that gel placement will be more effective in cases characterized by severe water channeling problems.

Effect of Gel Solution Viscosity. The initial viscosity of the polyacrylamide/chromium system in all the previous results was a relatively high value of 10 cp. Simulations were conducted by decreasing the gelant viscosity to 1 cp and maintaining the same reaction parameters. Although this reduction in viscosity is not physically possible for the polyacrylamide/chromium system, the results provide insight into the role of gelant viscosity on the flow behavior and filtration mechanism. These results also lead to general conclusions regarding the design of gelant systems.

Figures 8.17 and 8.18 show the total flowrate and fractional flowrate into the high-permeability layer as a function of time. During the first regime, the injection rate of the gelant shown in Figure 8.17 is considerably higher than for the base case (Figure 8.2) at the same injection pressure. Comparison of Figures 8.18 and 8.3 indicates that the fraction of the total gelant injected into the high-permeability layer is higher for low-viscosity gelants. The ratio of volume flowing in the two layers is equal to the ratio of the permeabilities for a unit-viscosity gelant and approaches the square root of the permeability ratio as the viscosity of the gelant increases.⁹

The apparent viscosity contours after 48 hours of injection are shown in Figure 8.19. The values of the apparent viscosity in this figure reflect significantly more filtration for the unit viscosity gelant than for the base case. This behavior is due to the following effects.

- (1) The low-viscosity gelant is injected at a considerably higher flowrate than for the base case. These higher flowrates result in faster rates of filtration in the two layers.
- (2) A characteristic of the filtration mechanism in the model is that Brownian motion of the pre-gel aggregates is more pronounced at lower viscosities. This Brownian motion results in more collisions of the pre-gel aggregates with the walls of the pores. Thus, when the Cr^{3+} ions are attached to the polymer aggregates, filtration is more rapid for low-viscosity gelants. It may be noted that Brownian motion is the dominant mechanism for the typical aggregate size of the injected polyacrylamide solution (0.1 microns). As the aggregate size increases, streamline interception begins to dominate. Streamline interception is a function of the ratio of the aggregate size to the pore diameter and is independent of the viscosity of the gelant. Thus, for gelants characterized by large molecules, the effect of viscosity on the rate of filtration may not be significant.

Figure 8.16: Apparent viscosity profiles after 48 hours of injection into a reservoir with height of 3.2 ft.

Figure 8.17: Rate of injection in the presence of filtration for a unit-viscosity gelant.

Figure 8.18: Fraction of gelant injected into the high-permeability layer for a unit-viscosity gelant.

Figure 8.19: Apparent viscosity profiles after 48 hours of injection of a unit-viscosity gelant.

As a consequence of the higher rates of filtration, Figures 8.17 and 8.18 show that the onset of Regime III is hastened. The optimal time of injection of the gelant is about 45 hours which is less than the corresponding time for the base case. However, since the bulk of the gelant is injected during the first regime, it is possible to inject larger volumes of gelant into the reservoir with low-viscosity gelants.

In the case of a unit-viscosity gelant, viscous forces are absent and crossflow is due to the filtration mechanism alone. Crossflow is directed from the low-permeability to the high-permeability layer in the region before the front in the low-permeability layer. In the region intermediate to the fronts in the two layers, crossflow is directed from the high-permeability layer towards the low-permeability layer. This crossflow causes plugging at the interface of the two layers. In the vicinity of the front in the high-permeability layer, crossflow is directed from the low-permeability layer into the high-permeability layer.

In conclusion, as the viscosity of the gelant is lowered, it is possible to inject larger amounts of gelant into the reservoir with a more favorable distribution between the two layers. Although viscous crossflow is reduced as the viscosity of the gelant is reduced, crossflow of gelant may occur due to build-up of resistance by the filtration mechanism.

Zonal Isolation. Previous results show that significant amounts of gelant are injected into the low-permeability regions during conventional permeability-modification treatments. This gelant reduces both the overall effectiveness of the gel placement in the high-permeability layer and the injectivity of the low-permeability regions after the shut-in period. Simulations were conducted to study permeability-modification treatments in reservoirs where it is possible to mechanically isolate the layers and inject gelant into the high-permeability layer alone. Base case conditions were used.

Figure 8.20 shows the apparent viscosity profiles after 24 hours of injection into the high-permeability layer only. In addition to viscous crossflow, there is a considerable amount of crossflow into the low-permeability layer close to the wellbore. This crossflow is due to the significant amount of time required for the pressure transient to equilibrate across the height of the low-permeability layer. Note that this crossflow is not due to viscous forces and is present even in case of injection of a unit-viscosity gelant.

Figure 8.21 shows the apparent viscosity profiles after 48 hours of injection into the high permeability layer only. The values of the apparent viscosity and the volume of gelant injected into the high-permeability layer are similar to the case with injection in both layers (Figure 8.5). Injection of gelant into the low-permeability layer, however, is avoided by zonal isolation and results in a more effective gel placement than conventional treatments. There is some penetration of the gelant into the low-permeability layer by crossflow. Filtration of polymer aggregates at the front, however, confines this gelant to a small region near the interface of the layers.

The effects of viscous crossflow and filtration on gel placement with zonal isolation are similar to the case with injection into both layers. In the case of zonal isolation, however, crossflow near the wellbore is an additional mechanism limiting the volume of gelant which can be injected into the reservoir. As the injection pressure is increased, it is possible to inject larger volumes of gelant into the high-permeability layer before the onset of Regime III (Figures 8.22 and 8.23). Since most of the crossflow occurs before the onset of the filtration mechanism, increase in injection pressure also increases crossflow near the wellbore.

As in the case of conventional treatments, favorable gel-placement behavior is achieved when the permeability contrast between the layers is large. This is seen by comparison of Figures 8.24 and 8.21 (Figure 8.21 is for the base-case parameters). The significance of crossflow increases as the aspect ratio

Figure 8.20: Apparent viscosity profiles after 24 hours of injection into the high-permeability layer only.

Figure 8.21: Apparent viscosity profiles after 48 hours of injection into the high-permeability layer only.

Figure 8.22: Apparent viscosity profiles after 48 hours of injection at 1000 psi only into the high-permeability layer:

Figure 8.23: Apparent viscosity profiles after 48 hours of injection at 250 psi only into the high-permeability layer.

Figure 8.24: Apparent viscosity profiles after 48 hours of injection into the high-permeability layer of a reservoir with a permeability contrast of 100:1.

and vertical permeability increase. Figure 8.25 shows apparent viscosity profiles in a system with a height of 3.2 ft where crossflow near the wellbore renders the treatment ineffective. Low-viscosity gels minimize the effects of viscous crossflow, but, as a result of the higher flow rates, tend to penetrate more into the low-permeability layers before filtration becomes dominant. This is shown by a comparison of the behavior for injection of a unit-viscosity gelant (Figure 8.26) and the base-case gelant (Figure 8.21).

CONCLUSIONS

The gel-placement behavior of the polyacrylamide/chromium system in layered reservoirs was examined. The following points summarize the major conclusions from this study:

- (1) For a given set of reservoir conditions, there exists an optimal time for stopping the injection of gelant. This period is characterized by a levelling off in the flowrate profile. Injection of gelant beyond this period results in more diversion of gelant into the low-permeability layer without increasing the penetration of the gelant in the high-permeability layer.
- (2) It is possible to inject more volume of gelant into the reservoir by increasing the injection pressure. The rates of filtration increase with increasing flowrate, but this effect is mitigated by the radial flow behavior around the wellbore. Unfortunately, increasing the injection pressure results in injection of more gelant into both the high-permeability and the low-permeability layers.
- (3) Although viscous crossflow has a relatively small effect during typical near-wellbore treatments, its effects may become significant in deeper treatments with gelants characterized by long gel times. In these cases, the bulk of the crossflow occurs before the onset of filtration.
- (4) Gel-placement is most effective in reservoirs characterized with high-permeability contrast and low crossflow between layers. Permeability-modification treatments, therefore, are expected to be more effective in severe cases of water channeling as opposed to mild cases of water channeling during the waterflooding stage.
- (5) As the viscosity of the gelant is lowered, it is possible to inject large amounts of gelant into the reservoir with a more favorable distribution between the two layers. Although viscous crossflow is reduced as the viscosity of the gelant is reduced, crossflow of gelant may occur due to build-up of resistance by the filtration mechanism.
- (6) Isolation of the low-permeability layer results in a considerably more effective gel placement compared to conventional treatment. Filtration may aid in minimizing crossflow of gelant from the high-permeability regions into the low-permeability regions of the reservoir.

NOMENCLATURE

C_i	:	concentration of component "i", moles/cm ³ .
C_{id}	:	concentration of component "i" after it is deposited by filtration in the porous medium, moles/cm ³ .
C_t	:	compressibility, psi ⁻¹ .
D_r	:	radial dispersion coefficient, cm ² /sec.
D_z	:	vertical dispersion coefficient, cm ² /sec.
F	:	fraction of hydrolyzed repeat units on a polyacrylamide chain
g	:	matching parameter in the G' equation, dimensionless.

Figure 8.25: Apparent viscosity profiles after 48 hours of injection into the high-permeability layer of a reservoir with a height of 3.2 ft.

Figure 8.26: Apparent viscosity profiles after 48 hours of injection of a unit-viscosity gelant into the high-permeability layer only.

G'	:	shear modulus of a gelling fluid, dynes/cm ² .
G'_{en}	:	initial shear modulus due to polymer entanglements, dynes/cm ² .
G'_{max}	:	maximum shear modulus of a gelling fluid, dynes/cm ² .
K	:	Boltzmann's constant.
K_1, K_2	:	reaction rate constants for the reduction reaction.
K_{upt}	:	reaction rate constant for chromium uptake.
k_r	:	radial permeability of the reservoir, darcy.
k_z	:	vertical permeability of the reservoir, darcy.
l_p	:	average length of pore, °A.
p	:	pressure, psi.
MW_p	:	molecular weight of polymer
MW_{ru}	:	molecular weight of a polymer repeat unit
n	:	crosslink density, crosslinks/cm ³ .
PSR	:	matching parameter for the interception efficiency equation.
r	:	radius, cm.
R_i	:	kinetic reaction term, moles/cm ³ .s
R_k	:	rate constant for the shear modulus equation
T	:	temperature, K.
t	:	time, sec.
v_r	:	radial velocity, cm/sec.
v_z	:	vertical velocity, cm/sec.
v_{tot}	:	magnitude of total velocity, cm/sec.
z	:	height, cm.

Greek Characters

α	:	probability that a particle will collide with the pore walls, dimensionless.
ϵ	:	the fraction of collisions that result in the deposition of the particle, dimensionless.
Γ^i	:	interception rate coefficient
Γ^s	:	straining rate coefficient
ϕ^0	:	initial porosity
ϕ	:	current value of porosity
σ	:	total fraction of initial porosity occupied by deposited polymer.
μ	:	viscosity, cp.

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APPENDIX - Governing Equations

In order to simplify the formulation of the mathematical model, the following set of assumptions are adopted in the continuity equations.

- (1) Flow is assumed to be symmetric around the wellbore. Two-dimensional Darcy flow of the gelant is considered in the radial and vertical directions.
- (2) Only single-phase flow is considered during the process of gel placement. Oil is assumed to be immobile and its effects on the gelation processes are neglected.
- (3) A single-well model is developed in which the well is isolated from all effects of surrounding wells.

Pressure Equation. Based on the above assumptions, the overall equation of continuity for a fluid with a small and constant compressibility is given by

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{k_r}{\mu} \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{k_z}{\mu} \frac{\partial p}{\partial z} \right) = \phi_0 c_f \frac{\partial p}{\partial t} \quad \text{..... (A-1)}$$

The radial and vertical components of the fluid velocity are given by

$$v_r = - \frac{k_r}{\mu} \frac{\partial p}{\partial r}, \quad \text{..... (A-2)}$$

$$v_z = - \frac{k_z}{\mu} \frac{\partial p}{\partial z}, \quad \text{..... (A-3)}$$

The mobility terms in Equation A-1 are a function of the gelation process of the polyacrylamide/redox system. Both the radial and vertical permeabilities of the reservoir vary as the pre-gel aggregates of polymer are filtered by the porous medium. Similarly, the viscosity of the gelant is usually greater than the viscosity of the initial fluid and the fluid viscosity in Equation 1 undergoes a rapid drop at the front of the injected solution. The gelant viscosity increases as crosslinks between the polymer molecules are formed.

Initial and Boundary Conditions. The selection of boundary and initial conditions for Equation A-1 deserves some discussion. Well operation may be modelled for two conditions- injection of gelant at a constant flow-rate, or, injection of gelant at a constant injection pressure. At constant flow-rate conditions, the flow rate of gelant into the individual layers with constant permeabilities may be obtained by simply dividing the total flow-rate in proportion to the radial permeabilities of the layers. However, in the presence of the filtration mechanism, the radial permeability of the reservoir varies as a function of both position and time. In order to avoid iterative calculations of the varying flow rates across the height of the wellbore, this study is restricted to the relatively straightforward case of well operation at constant-pressure conditions alone. The boundary condition for Equation 1 at the wellbore, therefore, is given by

$$p = p_{inj} \quad \text{at } r = r_w \quad \text{..... (A-4)}$$

Since the model is restricted to near-wellbore treatments only, the boundary condition at the exterior radius is developed by assuming that the well is isolated from the surrounding wells. The exterior radius is typically far enough from the wellbore that the exterior boundary-condition does not significantly effect flow behavior near the wellbore. The exact form of the boundary condition for the pressure equation is developed in conjunction with the initial condition for Equation A-1.

The initial condition must be selected so as to represent the pressure distribution around the wellbore after an extended period of waterflooding. Two sets of initial and boundary conditions may be envisioned. The first set of conditions physically represents steady-state operation of the well in which pressure has equilibrated across the height of reservoir:

$$p = \frac{p_{inj} \ln\left(\frac{r}{r_{ext}}\right)}{\ln\left(\frac{r_w}{r_{ext}}\right)} \quad \text{at } t = 0 \dots\dots\dots (A-5)$$

$$p = 0 \quad \text{at } r = r_{ext} \dots\dots\dots (A-6)$$

This boundary condition is representative of the pressure distribution in laboratory experiments simulating flow through layered reservoirs. For field-scale conditions, however, this set of conditions is oversimplified since it neglects the presence of unswept oil in the low-permeability regions of the reservoir. Simulated pressure contours after an extended period of waterflooding by Scott et al.⁽⁶⁾ show that pressures in the high-permeability layer are greater than the corresponding pressures in the low-permeability layer. An additional complication arises in practical cases as permeability-modification treatments usually require some period of shut-in of the well before injection of the gelant is initiated.

In this study, pressure behavior is described by a second set of conditions which represent the transient operation of the well after a shut-in period.

$$p = 0 \quad \text{at } t = 0 \dots\dots\dots (A-7)$$

$$\frac{\partial p}{\partial r} = 0 \quad \text{at } r = r_{ext} \dots\dots\dots (A-8)$$

Pressure transients are propagated faster in the high-permeability regions than the low-permeability regions of the reservoir. After a relatively short period, the pressure distribution in the reservoir becomes similar in nature to that shown by Scott et al.⁶ This set of initial conditions also enables a direct comparison between conventional treatments with injection of gelant into both layers and treatments with zonal isolation where gelant is injected into the high-permeability layer alone.

Numerical results for the two sets of conditions show that the choice of initial conditions effects the flow behavior near the wellbore only for a short period (typically less than 10 hours) during the early stages of the treatment. During this period, the transient initial conditions produce considerably higher flow-rates than the steady-state conditions and result in a greater cumulative volume of gelant being injected into the reservoir. The overall gel placement behavior and the effects of parameters, however, are quite similar for the two sets of conditions.

Mass Transport. Based on the velocity field given by Equation A-1, in-situ gelation of the polyacrylamide/chromium system is described by the transport of the following chemical species:

1. sodium dichromate
2. thiourea (reducing agent)

3. ionic chromium (III)
4. chromium attached to polymer
5. cross-links between polymer chains
- 6.-10. five size categories of polyacrylamide aggregates

Mass transport of the "ith" chemical species is given by

$$\frac{1}{r} \frac{\partial}{\partial r} [r (-v_r C_i + D_r \frac{\partial C_i}{\partial r})] + \frac{\partial}{\partial z} [-v_z C_i + D_z \frac{\partial C_i}{\partial z}] - \phi_0 C_{i(d)} \frac{\partial \sigma}{\partial t} + R_i \phi = \frac{\partial (\phi C_i)}{\partial t}, \quad \dots \dots \dots (A-9)$$

which accounts for transport of mass by convection, dispersion, filtration and chemical reaction. $C_{i(d)}$ is the concentration of the "ith" species deposited on the walls of the pores by filtration and is related to the local concentration of "i" in the solution. The dispersion coefficients in Equation 1 are linear functions of the velocity vectors. The reaction and filtration terms for the different chemical species are described below.

Reaction Kinetics. The kinetics of the chromium reactions are assumed to be independent of the flow geometry. Hence, both the form of the kinetic expressions and the reaction parameters used in this model are identical to those used by Todd et al. to match linear core-flood experiments. A detailed description of the reaction kinetics is available in Reference 7 and only a brief summary is presented here.

The gelation kinetics of the polyacrylamide/chromium system is described as a three step process:

1. The reduction of dichromate by thiourea to liberate free Cr^{3+} ions into the solution. This reaction is modeled by the following rate equation proposed by ⁽¹¹⁾

$$\frac{d[Cr_2O_7^{2-}]}{dt} = -\frac{1}{2} [k_1 [HCrO_4^-] [H_4N_2CS] [H^+] + k_2 [HCrO_4^-] [H_4N_2CS] [H^+] [COOH]_{PAAm}] \quad \dots \dots \dots (A-10)$$

The concentration of the bichromate ion in Equation 10 is calculated from the dichromate-ion concentration using equilibrium relationships.

2. The free Cr^{3+} ions in the solution are attached to the reactive sites on the polymer molecules. The rate of Cr^{3+} uptake by the polymer is given by Hunt et al., as ¹²

$$\frac{d[Cr^{3+}]_{upt}}{dt} = k_{upt} \frac{[Cr^{3+}]^{1.32}}{F^{0.8} [H^+]} [F[PAAm] - [Cr^{3+}]_{upt}]^{0.8} \quad \dots \dots \dots (A-11)$$

3. As a result of the attached chromium ions, the polymer molecules crosslink to form large chains or aggregates of polymer molecules. This step is characterized by the evolution shear modulus (G') of the gelling solution by the following empirical relation ¹³

$$\frac{dG'}{dt} = R_k [Cr^{3+}]_{\text{opt}} G' \left[1 - \frac{G'}{G_{\text{max}}}\right] \dots \dots \dots (A-12)$$

Based on the value of the shear modulus, the crosslink density of the gelling solution is estimated using Graessley's equation ¹⁴

$$G' = gnkT + G'_{\text{en}} \dots \dots \dots (A-13)$$

where n is crosslink density in crosslinks per unit volume. The crosslink density increases as the crosslinking reaction proceeds in time and causes an increase in gelant viscosity and the formation of aggregates of polymer molecules.

The size distribution of the polymer aggregates in the solution is estimated by Flory's equation ¹⁵. This relation provides the weight distribution of aggregate sizes in gelling solutions based on the crosslink density. For computational purposes, the overall size distribution is divided into five discrete categories according to size ⁷.

Deep Filtration. The pore structure of reservoir rock is typically characterized by pore lengths of the order of 100 microns and pore-throat diameters ranging from 0-20 microns .⁸ The gelling solution flowing through these pores consists of aggregates of polyacrylamide molecules ranging from 0.1-2.5 microns in diameter. Under these conditions, two mechanisms for the filtration of polymer aggregates predominate.^{16,17} Straining of particles occurs in the smaller pores when the particle diameter exceeds the diameter of the pore throats. In the larger pores, the aggregates may be intercepted by the walls of the pores due to the nature of the streamlines of flow, or, by the Brownian motion of the particles. The trapped particles by both filtration mechanisms reduce the porosity and the permeability of the porous medium and result in a build-up of flow resistance in the regions of high deposition.

The filtration model in this work is an extension of existing one-dimensional filtration models. ^{7,17} In order to incorporate the effects of crossflow on filtration, the rate of filtration of the polymer aggregates is assumed to be proportional to the magnitude of the flux of particles through the pores. The rate of filtration of the polymer in the straining and interception pores is given by

$$\frac{d\sigma_i}{dt} = [\Gamma_s(\phi_s - \phi_0 \sigma_s) + \Gamma_i(\phi_i - \phi_0 \sigma_i)] \frac{v_{\text{tot}} C_i}{\phi_0 (1 - \sigma)} \dots \dots \dots (A-14)$$

where σ is the fraction of initial porosity occupied by deposited polymer. v_{tot} is defined as the magnitude of the total velocity of the particles through the porous medium

$$v_{\text{tot}} = \sqrt{v_r^2 + v_z^2} \dots \dots \dots (A-15)$$

The filtration coefficients Γ 's and Γ_i in Equation 14 are of the form

$$\Gamma = \frac{\alpha \epsilon}{l_p} \dots \dots \dots (A-16)$$

where α is the probability that a particle will collide with the walls of pore, ϵ is the fraction of the collisions by which the particle sticks to the pore walls and l_p is the average pore length of the pore throat. The quantities α and ϵ incorporate the effects of the straining and interception mechanisms of filtration.

The collision probability and the collision efficiency for the small straining pores are assumed to be unity. In the large interception pores, collisions with the pore walls may be due to the constriction of the streamlines of flow, or, by the Brownian motion of the particles. The collision probability due to streamline interception is dependant only on the ratio of the particle diameter to the grain diameter of the porous medium. The collision probability due to Brownian motion, however, is a function of various parameters including the particle diameter, temperature and the solution viscosity. The total collision probability is the sum of the contributions due to the two mechanisms and is calculated using the sphere-in-cell models.⁷

The polymer intercepted by the pores is retained by two mechanisms. Initially, the injected polymer is deposited into a thin dense layer which has little effect on the permeability. The efficiency of these collisions is given by the expression

$$\epsilon_i = \epsilon_0 \left(1 - \frac{\sigma_i}{\sigma_{\max}}\right) \dots \dots \dots (A-17)$$

As the chromium/redox reaction progresses, polymer aggregates are retained in the pores by virtue of their ability to form crosslinks with previously deposited polymer

$$\epsilon_i = \left(PSR \frac{MW_{\text{polymer}}}{MW_{\text{rx}}} \frac{[Cr^{3+}]_{\text{upl}}}{[PAAm]} \right)^2 \dots \dots \dots (A-18)$$

where PSR is a matching parameter estimated from laboratory core-flood experiments at different flow-rates.

The total rate of filtration is computed as the sum of the rates of filtration of all the size fractions of the polymer aggregates. The decrease in porosity due to the filtration of polymer aggregates is related to the decrease in the permeability of the porous medium by the simplified relation

$$\frac{k_r}{k_r^0} = \frac{k_z}{k_z^0} = \left(\frac{\phi}{\phi^0}\right)^3 \dots \dots \dots (A-19)$$

Thus, the model allows for porous medium to be anisotropic in nature, but, both the radial permeability and the vertical permeability are assumed to be effected equally by the decrease in porosity.

In summary, the filtration model differs from other models for in-situ gelation since it couples the effects of flow rate and reaction kinetics to the build-up of flow resistance. In addition, the rate of filtration of

the polymer aggregates is a function of the aggregate size and the pore structure of the porous medium. Since the low-permeability regions are characterized by smaller pores than the high-permeability regions, the rate of filtration of polymer aggregates under similar conditions is greater in low-permeability regions of the reservoir.

Numerical Model. Single-well models are particularly subject to instability due to the sharp diverging/converging nature of flow near the wellbore. Numerical models for coning type problems show that implicit treatment of mobility terms in the pressure equation for implicit-pressure explicit-saturation (IMPES) type algorithms is more efficient than explicit treatment of the mobility terms.^{18,19} Similarly, fully implicit numerical models with simultaneous solution of all variables perform better than IMPES type algorithms. Although implicit techniques require more work for each time-step, they become computationally efficient by allowing substantially larger time steps than explicit techniques thereby reducing the total number of required time-steps.

In this study, the governing set of equations are solved numerically using the Method of Lines.²⁰ The spatial derivatives of the partial differential equations (PDEs) are substituted by corresponding finite-difference approximations. This step converts each PDE into a set of ordinary differential equations (ODEs). The resulting set of ODEs for the model are solved simultaneously using an implicit ODE integrator, LSODES.

Evaluation of the spatial derivatives is performed using first-order finite-difference approximations based on non-uniform spacing of grid points.²¹ One-point upstream weighting is employed for the non-linear component of the mobility terms in the pressure equation. Similarly, the convection terms in the mass-transfer equations are evaluated using one-point upstream finite-difference approximations. Since the direction of flow is not known a priori, the upstream direction in the radial and vertical directions is dictated by the direction of the corresponding pressure gradients.

Non-uniform spacing of the spatial grid is essential for maintaining the accuracy of the finite-difference approximations and minimizing the overall size of the model. In the radial direction, 31 grid points are used to capture the flow behavior and gelation process near the wellbore. An additional 10 grid points are then logarithmically spaced to the exterior radius to evaluate the progress of the pressure transients into the reservoir. In the vertical direction, a total of 14 grid points are used with 9 grid points in the low-permeability layer and 6 grid points in the high-permeability layer. For each layer, the mesh is refined near the interface of the two layers. Convergence studies confirm that this grid is sufficiently accurate for studying the gel-placement and crossflow behavior in the two-layered reservoir.

The temporal derivatives of the ODEs are evaluated in LSODES by variable time-step, variable order, backward-difference formulas.^{20,22} The time-stepping procedure is adaptive in nature with the maximum time-step size selected to meet stability requirements and specified error tolerances. At each time-step, the resulting set of non-linear algebraic equations are solved iteratively by Newton's method. Since the non-linear nature of the original equations remains undisturbed, Newton's method avoids linearizations or lagging of the non-linear terms in the governing equations. Simulations showed that incorporation of Newton's method typically increased the size of the permissible time steps by a factor of 1000.

The LSODES integrator incorporates the Yale sparse-matrix solver for evaluating the Jacobian matrix required for Newton's method. Since the Jacobian matrix for the problem is more than 99% sparse, the sparse-matrix solver minimized the storage requirements for the model considerably and enabled efficient solution of the Jacobian matrix. Further details about LSODES are available in References 20 and 22.

The MOL technique, therefore, results in a fully implicit numerical scheme for solving the governing equations. Numerical simulations were performed on a Digital Alpha 7000-610 computer and typically required 3-8 CPU hours depending on the flow rate and degree of crossflow.