IN SITU PERMEABILITY MODIFICATION USING GELLED POLYMER SYSTEMS

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September 1998

Performed Under Contract No. DE-AC22-94PC91008

The University Of Kansas
Lawrence, Kansas

National Petroleum Technology Office
U. S. DEPARTMENT OF ENERGY
Tulsa, Oklahoma

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Prepared for
U.S. Department of Energy
Assistant Secretary for Fossil Energy

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Executive Summary

Results from a research program on the application of gelled polymer technology for in situ permeability modification are presented in this report. The objective of this technology when used with displacement processes such as waterflooding is to reduce the permeability in fractures and/or high permeability matrix zones to improve volumetric sweep efficiency of the displacement process. In production wells, the objective is to reduce water influx.

The research program focused on five areas:
- Gel treatment in fractured systems
- Gel treatment in carbonate rocks
- In-depth placement of gels
- Gel systems for application in carbon dioxide flooding
- Gel treatment in production wells

The research program is primarily an experimental program directed toward improving the understanding of gelled polymer systems and how these systems can be used to increase oil recovery from petroleum reservoirs. A summary of progress for research conducted in the second 12 month period of a 28 month program is described in the following sections.

Summary of Progress

Gel treatment in fractured systems. Results were obtained from displacement of a partially hydrolyzed polyacrylamide (HPAAm)-Cr(III) gelant in a physical model of a fracture and a study of the behavior of the gel after treatment. During displacement of the gelant (mixed in-line) through the fracture, the gelant behaved like a viscous fluid. There was little change in pH or chromium concentration of the gelant flowing in the fracture. A substantial volume of gelant leaked from the fracture into the matrix. Chromium retention was high in the matrix and the gelant that leaked off was not capable of forming a gel. The mature gel was extruded from the fracture on application of a small pressure gradient. Brine permeabilities of the matrix after contact with the gelant were reduced. Residual resistance factors varied from 70-200 near the fracture to 7.4-11, a distance of about 0.5 ft from the fracture. Values of residual resistance factors from the injection of polymer alone were estimated to be 2.0. Leakoff was simulated by treating the gelant as a viscous fluid flowing through the matrix under a constant pressure drop.

Experiments were conducted to determine the amount of leakoff from gelants of various ages into Berea sandstone cores (1 ft in length) when a constant pressure drop was maintained across the core during placement. Leakoff was significant but decreased as the age of the injected gelant increased from 0 to 6 hours of delay. During gel placement, the pH of the gelant rose from 4.8 at the inlet to 8.0 at the effluent. Chromium retention was high and the effluent did not form a gel. The apparent viscosity increased rapidly with time near the inlet of each core and quickly exceeded the viscosity of the base polymer solution at the same flow rate. Filtration of gel aggregates is believed to be responsible for the high flow resistance developed in the front of the cores. Aging of the gelant prior to displacement causes a faster buildup of flow resistance near the inlet face of the core. A model describing leakoff during gel placement in a linear system with deep filtration of gel aggregates was developed.
Gel treatment in carbonate rocks. In previous research, we discovered that sulfomethylation of resorcinol led to increased salinity and pH tolerance of a gel system based on the reaction of sulfomethylated resorcinol (SMR) with formaldehyde. This system provided superior permeability reduction in carbonate rocks compared to current systems.

The focus of our research was to eliminate formaldehyde from the system because of environmental and safety concerns. It was determined that formaldehyde was not present in the SMR even though it was a reactant to produce SMR. Hexamethylenetetramine (HMTA) was studied as a potential substitute for formaldehyde in the resorcinol-formaldehyde and SMRF gel systems. The studies show that the R-HMTA formed gels at 40, 70 and 100°C. The gel system has significantly longer gel times than those observed in the RF or SMRF gel systems due to the hydrolysis of HTMA to form formaldehyde. SMR-HTMA formed hydrogels but higher concentrations were required than in previous research on the SMRF system. The SMR-HMTA gels were thermally sensitive, decomposing at temperatures higher than 40°C, possibly due to the reaction of excess sulfite ion with the polymer. Hydroxymethanesulfonate was investigated as a substitute for formaldehyde in the preparation of SMR, but this did not perform well.

Propagation of chromium in carbonate rock is a limitation of gel systems based on chromium acetate and partially hydrolyzed polyacrylamide. Precipitation of chromium occurs if the pH of the injected fluid increases due to fluid rock interactions. Results from a study of the precipitation of Cr(III) from aqueous solutions are presented in this report. This study includes the effects of pH, temperature and salinity on chromium precipitation. The study covers a range of pH values from 7 to 11 and temperatures between 25°C and 45°C. Our data show that chromium precipitates faster as pH increases. The induction time and precipitation rate are functions of pH, temperature and salinity of the solution. The precipitation rate is first order with respect to aqueous chromium concentration after onset of precipitation. The precipitation rate increases with increasing temperature and salinity. Precipitated chromium does not cause the polymer to gel.

In-depth placement of gels. Gel systems used to treat a porous matrix are composed of a polymer and a crosslinker. As these components react, pre-gel aggregates are formed and grow in size. The depth of treatment is limited by the filtration of aggregates from solution as they flow through the reservoir rock. Three studies are in progress related to in-depth placement of gels. The first study concerns the rate that gel aggregates grow to form a three-dimensional gel structure. The remaining studies involved two gel systems that were investigated to study in-depth treatment of matrix rock to reduce permeability. These systems were the chromium acetate-polyacrylamide system and an aluminum citrate-polyacrylamide system.

An experimental program was initiated to determine the size distribution of gel aggregates as they grow from polymer molecules to form a gel. A critical part of the study is the development of methods to determine the size distribution of pre-gel aggregates. During this year, the method used to determine size distribution was equilibrium dialysis. Aggregates were separated by diffusion through a set of membranes that have selected pore sizes. The concentration of polymer in the dialysate was determined by size-exclusion chromatography (SEC) with an UV detector. Aggregate growth with reaction time was observed for a polyacrylamide-chromium acetate gelant. Procedures to determine aggregate size distributions using equilibrium dialysis were
developed and tested. Equipment to determine the size of polymer aggregates using Field Flow Fractionation (FFF) was evaluated and ordered.

Development of the chromium acetate-polyacrylamide system for in-depth permeability modification requires control of the rate of aggregate growth to slow down the rate of permeability reduction due to filtration of gel aggregates. A study was completed in which the gelation time of chromium-polyacrylamide systems was increased by adding acetate ions to reduce the rate of crosslinking between chromium and polyacrylamide. Bulk gelation data were obtained for a range of acetate/chromium ratios. Displacement experiments were conducted in unconsolidated sandpacks of various lengths to determine the effect of acetate/chromium ratio on in-depth placement. Adding acetate ions as sodium acetate or acetic acid increased gel times of HPAAm-chromium acetate systems. Gel times in the range of a few hours to several days at 25°C were attained by varying the acetate/chromium ratio from 3 to 91 in solutions containing 5000 ppm Alcoflood 935 and 109 ppm chromium. Acetate/chromium ratios greater than 260 inhibited gelation for more than a year. Gelation delays were significant beyond a threshold acetate/chromium concentration of about 80 mole/mole for this gel composition. Gel solutions prepared from aged chromium stock had significantly shorter gel times than fresh stock samples. High concentrations of acetate ions in solution were found to offset the effect of chromium stock age.

Sandpacks were conditioned to pH 5 prior to treatment using an acetic acid/sodium acetate buffer. Increasing acetate/chromium ratios delayed the development of flow resistance (and thus aggregate filtration) during gel injection into sandpacks. High acetate concentrations (acetate/chromium =600) completely inhibited in situ gelation. The time available for gel injection using reasonable injection pressures was significantly shorter than the gel times measured in beakers. This was probably due to filtration of pre-gel aggregates.

Experimental work was initiated to determine the flow behavior of HiVis 350, a partially hydrolyzed polyacrylamide, in a sandpack. This work was done prior to studying the in situ behavior of a gelant consisting of a solution of aluminum citrate and HiVis 350. Experiments completed this year were conducted to determine the effect of flow rate on the apparent viscosity of HiVis 350 in unconsolidated sandpacks. All work was done using a 300 ppm concentration of polymer at 25°C. Displacement experiments were conducted in one foot long unconsolidated sandpacks equipped with pressure ports to determine the pressure drop at specific locations along the sandpack. The 300 ppm solution of HiVis 350 exhibited shear thickening behavior over the range of frontal advance rates between 2.3 and 58 ft/d. Polymer retention was a function of flow rate. Increased amounts of polymer were retained with each increase in flow rate. Some polymer was expelled when the flow rate was reduced indicating hydrodynamic retention. Polymer degradation was observed during displacement experiments at low flow rates.

**Gel treatment in production wells.** Gels placed in a production well to reduce water production are subjected to pressure gradients of oil and/or water for long periods of time after placement. A series of exploratory experiments was completed to determine the permeability and the amount of dehydration that can occur after placement when a gel is under a pressure gradient of either oil or water. Gel systems studied include KUSP1-ester, KUSP1-boric acid, SMRF and Cr(III) acetate-HPAAm. All gels were permeable to water with permeabilities
ranging from 5 – 130 microdarcies. Both KUSP1 gel systems dehydrated extensively under pressure gradients from 35 psi/ft to 76 psi/ft. The SMRF gel did not dehydrate under pressure gradients ranging from 76 psi/ft to 305 psi/ft. Cr(III)-acetate-HPAAm gels can be dehydrated by applying a pressure gradient across the gel with either brine or oil. Oil dehydrated Cr(III)/HPAAm gels at pressure gradients as low as 30.5 psi/ft. In Cr(III)-HPAAm gels at low-pressure gradients, the brine flows through the gel and dehydration is low. Dehydration causes a decrease in the permeability of the gel.

Experiments were completed to simulate the effect of a gel treatment in a production well to reduce water production. The experiments were conducted in a Berea sandstone slab (60 cm in length by 10 cm wide) which was divided into four equal lengths. Relative permeabilities to oil and water were determined prior to treatment. Water saturations were measured using a microwave apparatus. A quarter of the length of the slab was treated with a polyacrylamide-chromium(VI)-thiourea gelant and relative permeability measurements were repeated after gelation. Microwave saturation measurements could not distinguish between gel and water after treatment.

Relative permeabilities to water and oil were decreased significantly by the gel treatment in the treated section. Residual resistance factors for oil and water were about the same. Thus, there was no disproportionate permeability modification for this gelant. The range of mobile oil and water saturation in the treated section decreased significantly after gel treatment. Permeabilities to both phases were functions of flow rates. The effective permeability of each phase increased with increasing flow rate of that phase. The relationship between effective permeability and flow rate of each phase was correlated with a power law function. There was no effect of the gel treatment on permeabilities in the untreated sections.
Abstract

The research program is directed at improving the understanding of gelled polymer systems and how these systems can be used to increase oil recovery from petroleum reservoirs. The research is focused on five areas: (1) Gel treatment in fractured systems; (2) Gel treatment in carbonate rocks; (3) In-depth placement of gels; (4) Gel systems for application in carbon dioxide flooding; (5) Gel treatment in production wells. Results were obtained from displacement of a Cr (III)-acetate-partially hydrolyzed polyacrylamide (HPAAm) gelant in a physical model of a fracture and a study of the behavior of the gel after treatment. Substantial gel leakoff occurred during treatment. The mature gel was extruded from the fracture on application of a small pressure gradient. Data were obtained on the leakoff of gelant of different ages in Berea sandstone cores. A model describing leakoff during gel placement in a linear system with deep filtration of gel aggregates was developed. Hexamethylenetetramine (HMTA) was studied as a potential substitute for formaldehyde in resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde (SMRF) gel systems. Gels were formed using HMTA over a restricted range of conditions. The precipitation of chromium from chromium acetate solutions was studied and rates of precipitation were determined for a range of pH values from 7 to 11 and temperatures between 25°C and 45°C. The rate of precipitation increased with pH, temperature and salinity. A study was initiated to determine the size of gel aggregates as they grow from polymer molecules to form a gel. Procedures to determine aggregate size distributions using equilibrium dialysis were developed and tested. Equipment to determine the size of polymer aggregates using Field Flow Fractionation (FFF) was evaluated and ordered. A study was completed in which the gelation time of chromium acetate-polyacrylamide gel systems was increased by adding acetate ion to reduce the rate of crosslinking between chromium and polyacrylamide. Displacement experiments in unconsolidated sandpacks verified results expected from bulk gelation tests. In depth placement was possible by increasing the acetate to chromium ratio above a critical value. Experimental work was initiated to determine the flow behavior of HiVis 350, a partially hydrolyzed polyacrylamide, in a sandpack. A 300-ppm solution of HiVis 350 exhibited shear-thickening behavior over a range of frontal advance rates between 2.3 and 58 ft/d. Polymer retention was a function of flow rate and hydrodynamic retention was observed. Polymer degradation occurred at low flow rates. A series of exploratory experiments was completed to determine the permeability and the amount of dehydration that occurs after placement when a gel is under a pressure gradient of either oil or water. Gels studied had permeabilities to water ranging from 5 – 130 microdarcies. Applying a pressure gradient across the gel with either brine or oil dehydrated Cr (III)-acetate-HPAAm gels. Oil dehydrated these gels at pressure gradients as low as 30 psi/ft. Dehydration caused a decrease in the permeability of the remaining gel. Experiments were completed to simulate the effect of a gel treatment in a production well to reduce water production. The experiments were done in a Berea sandstone slab (60 cm long by 10 cm wide) which was divided into four equal length segments. The end segment was treated with a chromium (VI)-thiourea-polyacrylamide gel. Relative permeabilities to water and oil were decreased significantly by the gel treatment in the treated section. The range of mobile oil and water saturation decreased significantly after gel treatment. Permeabilities to both phases were functions of flow rates in the treated section. The effective permeability of each phase increased with increasing flow rate of that phase. The permeability data were correlated with flow rate with a power law function.
Chapter 1

Introduction

Research was conducted on the application of gelled polymer technology for in situ permeability modification. The objective of this technology when used in injection wells is to reduce the permeability of fractures or high permeability zones in order to improve the volumetric sweep efficiency of oil recovery processes. In production wells, the objective is to reduce water influx.

The chemistry of resorcinol-formaldehyde and sulfomethylated resorcinol-formaldehyde gels was studied to determine the possibility of substituting hexamethylenetetramine (HMTA) for formaldehyde in the formulation of the gel. Results of this study are presented in Chapter 2.

In-depth permeability modification in a porous matrix is limited by the rate that gel aggregates are formed and removed from the gelant as it flows through the pore space. Chapter 3 describes a study to determine the size distribution of pre-gel aggregates as they form in the gelation of a Cr (III)-partially hydrolyzed polyacrylamide (HPAAm) solution. A method to extend the application of the Cr (III)-acetate-HPAAm gel system to in-depth treatment of porous rocks by adding acetate ions was developed. Results of beaker and displacement experiments are summarized in Chapter 7. Chapter 6 summarizes research to determine the flow behavior of HiVis350, a partially hydrolyzed polyacrylamide, which is used with aluminum citrate to obtain in-depth permeability modification. This gel system is claimed to be a “colloidal dispersion” gelant. The study focused on determining the conditions under which permeability modification occurs.

Gel placement in the porous matrix of carbonate rocks is influenced by fluid-rock interactions where the calcium and magnesium are dissolved with a corresponding increase in pH of the gelant. Chapter 4 describes a study of the precipitation of Cr (III)-acetate solutions as a function of pH, temperature and salinity.

Cr (III)-acetate-HPAAm gelants are widely used to treat fractured formations. During placement of these gelants, an unknown amount of the gelant leaks off from the fracture into the adjacent formation. A study to determine leakoff of gelant is described in Chapter 8. This study includes both experimental measurements of leakoff in a physical model of a fracture and development of models to correlate leakoff during gel placement in a linear system with deep filtration of gel aggregates.

Gels placed in fractures and the porous matrix are subjected to pressure gradients after placement. Results from a series of exploratory experiments to determine the permeability and the amount of dehydration that can occur after placement when a gel is under a pressure gradient of either oil or water are reported in Chapter 5.

Experiments were completed to simulate the effect of a gel treatment in a production well to reduce water production. Changes in relative permeability relationships that occurred after the treatment of a Berea sandstone slab with a chromium (VI)-thiourea-polyacrylamide gelant are presented in Chapter 9.
Chapter 2

Resorcinol-Formaldehyde Based Gel Systems

Graduate Research Assistant: Jeff Botts

Introduction

Resorcinol-formaldehyde (RF) and sulfomethylated resorcinol-formaldehyde (SMRF) based hydrogels are being developed as an alternative to the chromium-polyacrylamide gel system. Hexamethylenetetramine (HMTA) was studied as a potential substitute for formaldehyde in the RF gel system. These studies showed that the R-HMTA gel system has significantly longer gel times than those seen in the RF and SMRF gel systems due to the time necessary for hydrolysis of HMTA to occur. Hydroxymethanesulfonate (HMS) was studied as a potential substitute for formaldehyde in the sulfomethylation reaction, but it was found that this compound would not work under conditions utilized in this reaction. Also, it was determined that formaldehyde was not present after the sulfomethylation reaction was completed. SMR and HMTA also formed hydrogels; the gelation times were the longest observed in the phenolic hydrogel systems studied. The SMR-HMTA gels were thermally sensitive, decomposing at temperatures higher than 40°C. This decomposition may result from the reaction of the sulfite ion with the polymer.

Background

Resorcinol polymerizes readily with formaldehyde to produce polymers. In the neat phase, these polymers tend to be hard, highly crosslinked resins [Ravve, 1967]. However, in dilute solutions, resorcinol forms hydrogels with formaldehyde under both acidic and basic conditions. This property allows for the gel to be used as a substitute for the highly utilized chromium-polyacrylamide gel system in the oil recovery process.

Under acidic conditions, the RF polymer produced is initially a gel precipitate. However, under basic conditions, firm gels are produced. It was determined that the gels could form even when the monomer concentration was as low as 1%. Previous researchers also found that the RF gel system possessed a high degree of brine sensitivity [Zuang et al., 1997]. This property, along with the use of formaldehyde, prompted more research in the area.

To combat the brine sensitivity, the SMRF gel system was developed. In the SMRF gel system, the resorcinol was pre-treated with formaldehyde and sodium sulfite. This mixture was made in the ratio of 2 resorcinol : 1.5 formaldehyde : 1 sodium sulfite as shown in Figure 2.1.

![Figure 2.1 - Sulfomethylation of resorcinol.](image-url)
The solution was maintained at 60°C for 72 hours. The gelation step involved taking an aliquot of this solution, mixing in a brine solution and additional formaldehyde, and incubating. The SMRF gel system was determined to be superior to the RF gel system. It displayed significantly reduced brine sensitivity and longer gelation times. Interestingly, it also displayed apparent reverse kinetic behavior since the gelation process was longer at higher temperatures [Zuang et al., 1997]. The SMRF system still used formaldehyde in both the SMR preparation step and the gelation step. Elimination of the formaldehyde reactant is desirable based on environmental considerations.

Hexamethylenetetramine (HMTA) is known to be a source of formaldehyde. One mole of HMTA theoretically can supply six moles of formaldehyde as shown in Figure 2.2 [Blazevic and Kolbah, 1979].

\[
\text{HMTA} + \text{H}_2\text{O} \rightarrow 6 \text{HCHO} + 4 \text{NH}_3
\]

Figure 2.2 - Hydrolysis of hexamethylenetetramine.

Therefore, substitution of HMTA for formaldehyde in the gelation process is a potential route to eliminate formaldehyde from the gel system. Also, hydroxymethanesulfonate (formaldehyde-sodium bisulfite addition compound) is reported to be the intermediate in the sulfomethylation reaction [Alaburda et al., 1987; Bordwell et al., 1945]. Therefore, this material is considered to be a potential substitute for the formaldehyde and sodium sulfite in the SMR preparation step.

**Experimental**

**R-HMTA Gels.** Resorcinol-HMTA hydrogels were developed as a substitute for the RF gel system. Gelants were prepared as 20 gram solutions in a 50 mL beaker or Erlenmeyer flask. Each gelant contained 2.5% NaCl, 0.018% CaCl₂, resorcinol, HMTA, and 18 MΩ-cm⁻¹ water. The molar ratio of HMTA to resorcinol varied from 0.33:1 to 0.67:1. The ingredients were added in the order of brine solution (5.0% NaCl, 0.038% CaCl₂), resorcinol, HMTA, and water. The solutions were adjusted to the desired pH using a 1 N NaOH solution. The amount of NaOH added was included in the total amount of water added. Bottles containing approximately 5 grams of this mixture were placed into constant temperature oil or water baths for incubation during the gelation process. Gel times were based on the amount of time necessary to form a solid.

The experiment to test if oxygen affected the R-HMTA gel properties involved preparing aqueous solutions containing either brine solution (5.0% NaCl, 0.036% CaCl₂) and HMTA or resorcinol and 1 N NaOH. Solution A was prepared by mixing 2.0 g brine solution and 1.0 g HMTA in a bottle. The density of this solution was found to be 1.09 g/mL. Solution B was prepared by mixing 1.0 g resorcinol, 0.5 g 1 N NaOH, and 3.1 g 18 MΩ-cm⁻¹ water in a second bottle. The density of solution B was found to be 1.05 g/mL. 2.25 g brine solution, 1.45 g 18 MΩ-cm⁻¹ water, 0.24 g 1 N NaOH, and 0.66 mL solution B were mixed in the testing bottle. Two control bottles were prepared by immediate addition of 0.35 mL of solution A. The two
experimental bottles were prepared by addition of solution A after 20 minutes of purging with oxygen free nitrogen. Both solution A and the testing solution were purged. The final concentration of the gelants was 2.5% NaCl, 0.018% CaCl₂, 3.0% resorcinol, and 2.6% HMTA. The pH of one experimental (purged) bottle and one control (non-purged) bottle were found to be 8.65 and 8.58, respectively. The other two bottles were placed in a 40°C constant temperature bath for gelation. The cap of the experimental (purged) bottle was covered with parafilm to ensure that no oxygen entered the system.

**Sulfomethylation Reaction.** Sulfomethylation of resorcinol using hydroxymethanesulfonate (HMS) was attempted under both basic and acidic conditions. A solution consisting of 33.0 g resorcinol, 20.1 g HMS, and 69.5 g 18 MΩ-cm⁻¹ water was prepared. The pH was adjusted to either 9.5 or 10.5 with 50% NaOH or the pH was adjusted to 0.5 with concentrated HCl or H₂SO₄. These solutions were then incubated at 60°C for three days or refluxed for one week. The products of these experiments were analyzed visually and by NMR spectroscopy (after drying the mixture for several hours by vacuum and re-dissolving the solid in D₂O.)

Chemical tests to determine if formaldehyde remained after completion of the sulfomethylation reaction involved the Jones’ test, the Tollen’s test, and the 2,4-DNP test. The Jones’ reagent, Tollen’s reagent, and 2,4-DNP reagent were prepared according to the standard method described by Landgrebe [1993]. SMR was prepared by dropwise addition of a mixture containing 18.2 g of a 37% w/w solution of formaldehyde and 76.9 g of a saturated sodium sulfite solution (32% w/w) to a stirred aqueous solution of 33.0 g of resorcinol in 20.0 g of 18 MΩ-cm⁻¹ water. The pH of this solution was adjusted to 9.5 with 50% NaOH and incubated at 60°C for 72 hours. Once the reaction was completed, a portion of the SMR solution was dried on a vacuum line, and the solvent was frozen in a liquid nitrogen trap. The tests involved taking approximately ten drops of the solution in a test tube and diluting with nanopure water to about two mL. About five drops of the test reagent were then added to the test tube.

Studies to determine the effect of hydroxide, sulfite, or ammonia on the stability of RF polymers were performed. RF polymers were prepared by either HCl catalyzed polymerization of a 1:1.33 mixture of resorcinol to formaldehyde or NaOH catalyzed polymerization of a 1:1.33 mixture of resorcinol to formaldehyde. In the acid catalyzed system, the polymer was adjusted from a pH of below 1 to a pH of 9 with 50% NaOH. To test the effects of hydroxide, additional NaOH was added until the pH was around 11. For the sulfite tests, aqueous sodium sulfite (in a two fold molar excess based on resorcinol) was added to the mixture. When ammonia was used, a two to five fold molar excess of the concentrated reagent was added. These suspensions were then heated at reflux for four hours. In the base catalyzed system, the polymer was prepared in bottles. After gelation, the testing material (in a two fold molar excess) was added to the bottle and maintained at 70°C for one week.

**SMR-HMTA Gels.** The SMR-HMTA gel system was developed as a substitute for the SMRF gel system. Gelants were prepared as 20 gram solutions in either 50 mL beakers or Erlenmeyer flasks. Each gelant contained 2.5% NaCl, 0.018% CaCl₂, SMR, HMTA, and 18 MΩ-cm⁻¹ water. The molar ratio of HMTA to resorcinol varied from 0.33:1 to 6:1. The ingredients were added in the order of brine solution (5.0% NaCl, 0.038% CaCl₂), SMR, HMTA, and water. The pH was
adjusted (if necessary) to the desired pH using 1N NaOH. Then, ten gram portions of this pre-gel mixture were placed into bottles for testing. The bottles were placed in either 40°C or 70°C constant temperature baths. Gel times were based on the amount of time necessary to form a solid.

To model the reactivity of SMR, 2-methylresorcinol, pyrogallol (1,2,3-trihydroxybenzene), or phloroglucinol dihydrate (1,3,5-trihydroxybenzene dihydrate) were used. 10%, 5%, 3%, or 1% solutions of these monomers were prepared. Gelant compositions matched those typically used in the SMR system in which SMR was simply substituted with the test monomer. The solutions were adjusted to a pH around 9 to 10 (or possibly 11) using 1 N NaOH. The solutions were either placed in a constant temperature bath maintained at 70°C or left out at room temperature for gelation.

**Results and Discussion**

**R-HMTA Gels.** The results of the bottle tests are shown in Table 2.1. At 10% resorcinol and a 0.33:1 HMTA to resorcinol ratio, gel times ranged from 30 minutes at 100°C to 12 days at 40°C. Increasing the concentration of HMTA to a 0.67:1 ratio increased the rate of gelation. These gels formed overnight at 40°C. Decreasing the amount of resorcinol significantly increased the time for gelation to occur. At 3% resorcinol, gelation required about one week even at 100°C.

The removal of oxygen affected the appearance of the gels that formed (e.g. the color of the gels). After 30 minutes at 40°C, the control (the one that was not purged with nitrogen) was a rusty orange color, while the sample purged of oxygen was colorless. By the next day, the non-purged gelant was a dark blue solution, while the purged gelant was still colorless. Both gelled by the third day; the non-purged sample was a dark blue gel while the purged sample was a pink gel. No adverse effects of oxygen were seen on the gel times or gel characteristics in the R-HMTA gel system.

**Sulfomethylation Reaction.** Experiments to sulfomethylate resorcinol using HMS yielded no SMR product based on the NMR spectra of the isolated product. Under basic conditions, the solution remained a rusty brown color, even after a week of refluxing the mixture. This was indicative of the oxidation of resorcinol to a quinone, but not of the production of SMR. The peaks (in the NMR spectrum) for the product were at δ 6.88 (t), δ 6.05 (d), and δ 5.87(s). This pattern was significantly different from those obtained in the known sulfomethylation reaction [Zuang et al., 1997]. The pattern was indicative of unreacted resorcinol. Acidic conditions also yielded no SMR (peaks were at δ 7.05 (t), δ 6.35 (d), and δ 6.30(s).

The results of the chemical tests to verify the presence or absence of formaldehyde are summarized in Table 2.2. Direct testing of SMR for formaldehyde with the test reagents was inconclusive. This was due to the ability of the Jones’ reagent to oxidize methylene groups bound to an aromatic ring and the Tollen’s reagent to oxidize resorcinol. However, tests involving the solvent that was trapped in liquid nitrogen showed no signs of a positive test. This verified that all the formaldehyde reacted with resorcinol in the sulfomethylation reaction.
Table 2.1 - Gelation times for the R-HMTA gel system.

<table>
<thead>
<tr>
<th>Resorcinol (wt%)</th>
<th>HMTA (wt%)</th>
<th>Molar Ratio</th>
<th>pH</th>
<th>Temp. (°C)</th>
<th>Gelation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>4.2</td>
<td>0.33:1</td>
<td>8.00</td>
<td>40</td>
<td>12 days</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>0.5:1</td>
<td>?</td>
<td>40</td>
<td>3 days</td>
</tr>
<tr>
<td></td>
<td>8.5</td>
<td>0.67:1</td>
<td>?</td>
<td>70</td>
<td>2 hours</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>?</td>
<td>100</td>
<td>30 minutes</td>
</tr>
<tr>
<td>5.0</td>
<td>2.1</td>
<td>0.33:1</td>
<td>8.17</td>
<td>40</td>
<td>12 days</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.17</td>
<td>70</td>
<td>1 day</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>0.33:1</td>
<td>8.58</td>
<td>40</td>
<td>5 days</td>
</tr>
<tr>
<td></td>
<td>1.9</td>
<td>0.5:1</td>
<td>8</td>
<td>40</td>
<td>4 days</td>
</tr>
<tr>
<td></td>
<td>2.6</td>
<td>0.67:1</td>
<td>8.47</td>
<td>40</td>
<td>4 days</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>0.33:1</td>
<td>8.86</td>
<td>40</td>
<td>no gel formed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8.86</td>
<td>70</td>
<td>6 days</td>
</tr>
<tr>
<td></td>
<td>1.7</td>
<td>0.67:1</td>
<td>8.31</td>
<td>40</td>
<td>6 days</td>
</tr>
<tr>
<td>1.0</td>
<td>0.4</td>
<td>0.33:1</td>
<td>9.19</td>
<td>40</td>
<td>no gel formed</td>
</tr>
</tbody>
</table>

Note: some of the pH data is missing due to solubility problems
Reactions of RF polymers with sulfite, hydroxide, or ammonia indicated that sulfite and ammonia had negative effects on the polymer. After four hours of refluxing the polymer in the presence of sodium sulfite at a pH of about 9.0, the solid in the flask dissolved. This may be due to the reaction of sulfite with the polymer to produce smaller, more water-soluble molecules. The pH of this solution after refluxing showed a dramatic increase in the concentration of hydroxide. The final pH of the solution was around 11.0. This indicated that a large amount of hydroxide was being produced from the reaction. The same result was seen when sulfite was added to a bottle containing an RF gel. The question of whether it was actually the sulfite ion or the hydroxide ion that was causing the breakdown of the polymer was answered by refluxing the polymer at a pH of 9.0 and 11.0 without sulfite present. In both cases, the polymer formed a purple gelatinous material within one hour. This material did not breakdown, even after refluxing for a week. In the bottle test, all that occurred was swelling of the gel. Since HMTA produces ammonia (the pH of the R-HMTA and SMR-HMTA gels increased during the gelation period indicating the production of ammonia), the question of whether ammonia effected the gels was answered by the following tests. Refluxing an RF polymer at a pH of around 9 to 10 in the presence of ammonia resulted in a much finer suspension of the polymer. The bottle tests, however, showed the same behavior as that seen in the hydroxide test. This indicated that ammonia had a negative effect on the polymer, but not as much of an effect as the sulfite ion.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Test</th>
<th>Result</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>formaldehyde</td>
<td>2,4-DNP Test</td>
<td>yellow precipitate</td>
<td>Positive</td>
</tr>
<tr>
<td></td>
<td>Jones' Test</td>
<td>greenish solution</td>
<td>Positive</td>
</tr>
<tr>
<td></td>
<td>Tollen's Test</td>
<td>gray precipitate</td>
<td>Positive</td>
</tr>
<tr>
<td>resorcinol</td>
<td>2,4-DNP Test</td>
<td>orange precipitate</td>
<td>Positive</td>
</tr>
<tr>
<td></td>
<td>Jones' Test</td>
<td>black solution</td>
<td>Positive</td>
</tr>
<tr>
<td></td>
<td>Tollen's Test</td>
<td>gray precipitate</td>
<td>Positive</td>
</tr>
<tr>
<td>SMR direct</td>
<td>2,4-DNP Test</td>
<td>yellow solution</td>
<td>Negative</td>
</tr>
<tr>
<td></td>
<td>Jones' Test</td>
<td>dark solution</td>
<td>Positive</td>
</tr>
<tr>
<td></td>
<td>Tollen's Test</td>
<td>gray precipitate</td>
<td>Positive</td>
</tr>
<tr>
<td>trapped solution</td>
<td>2,4-DNP Test</td>
<td>orange-yellow solution</td>
<td>Negative</td>
</tr>
<tr>
<td></td>
<td>Jones' Test</td>
<td>orange solution</td>
<td>Negative</td>
</tr>
<tr>
<td></td>
<td>Tollen's Test</td>
<td>colorless solution</td>
<td>Negative</td>
</tr>
</tbody>
</table>

SMR-HMTA Gels. SMR does not readily gel with HMTA at concentrations of SMR lower than 5% resorcinol. At both 10% and 5% SMR, gels formed at 40°C (within 1 day at 10% SMR and 3 days at 5% SMR.) These gels form at low concentrations of HMTA (0.33:1 to 0.67:1 HMTA to SMR ratios.) However, only at 10% SMR will gels form at elevated temperatures at these HMTA concentrations. Also, a 5% SMR gel that formed at 40°C will decompose if heated to 70°C. This solution will not "re-gel" if maintained at 40°C. The cause for this behavior was attributed to residual sulfite that may be remaining in the solution after the SMR preparation step. The formula may be modified to force SMR to gel with HMTA at SMR concentrations as low as
3% resorcinol. This requires the increase in HMTA content to around 19%, however. No gels have ever formed at SMR concentrations lower than 3% resorcinol content. The results of the model studies showed that removal of the most reactive site on resorcinol significantly increased the time required for gelation. 2-methylresorcinol was originally thought to be a good model for SMR. The question of SMR having longer gelation time could be explained simply by assuming that the sulfomethyl group is "blocking" the most reactive site on resorcinol (the 2-position.) 2-methylresorcinol, however, is highly insoluble. Only at 3% monomer concentration and a pH of about 11 will this compound dissolve in water. Once dissolved, though, the time for gelation is increased greatly. In fact, after nearly two weeks at 70°C, the only product obtained was a gel precipitate. Pyrogallol was chosen as another model for SMR since this compound has comparable solubility as resorcinol. At 10% pyrogallol (at a pH of 8.42 and temperature of 65°C), gelation took about an hour. At 3% pyrogallol and under similar conditions, gelation takes about a week. To contrast the removal of the most reactive site to the addition of two more sites, phloroglucinol was used. At 10% phloroglucinol (at a pH of 8.48) gelation took 1 minute 57 seconds at 20°C. This shows that the longer gelation times seen with SMR is due at least partly to the removal of the most reactive site on the resorcinol monomer.

**Conclusions**

1. Resorcinol forms hydrogels with HMTA at resorcinol concentrations as low as 1% resorcinol. These gels form at 40°C, 70°C, and 100°C.

2. R-HMTA gels have longer (approximately 100 times longer) gel times than those observed in the RF and SMRF systems. This is due to the time necessary for hydrolysis of the HMTA to occur and the production of unreactive side products [Blazevic and Kolbah, 1979; Nielsen et al., 1979].

3. Oxygen does not adversely effect the R-HMTA gel times and the R-HMTA gel’s physical characteristics.

4. “SMR” is a complex mixture of sulfomethylated products, oligomers, and unreacted resorcinol. The composition of the products is quite sensitive to reaction conditions.

5. Formaldehyde is not present after sulfomethylation of resorcinol in completed based on chemical tests.

6. Substitution of formaldehyde and sodium sulfite with hydroxymethanesulfonate (formaldehyde-sodium bisulfite addition complex) in the reaction results in no sulfomethylation of resorcinol. HMS, which had been proposed as an intermediate in the reaction, will not work as a substitute for formaldehyde in the preparation of SMR under the conditions used.

7. Sulfomethylated resorcinol will gel with HMTA at concentrations of SMR as low as 3%.
8. SMR-HMTA gels are more thermally sensitive than R-HMTA gels since gels form at 40°C, but not at 70°C. Gels that are pre-formed at 40°C decompose when heated to 70°C. This is not thermotropic behavior since the solutions will not re-gel when placed back in a 40°C constant temperature bath. The apparent reverse kinetics behavior that SMR based gels exhibit is due to the action of residual sulfite on the polymer at higher temperatures. This reaction is also the cause for SMR being unable to gel with HMTA at temperatures higher than 40°C. Formulations must be modified to develop SMR-HMTA gels that do not exhibit this thermal sensitivity.

9. Model studies show that SMR gelation kinetics can also be attributed to the removal of the most reactive site on the resorcinol monomer.

**Current and Future Research**

1. The extent of sulfomethylation in the current SMR formulation will be determined using ion chromatography.

2. Based on current results from ion chromatography, the current SMR formulation contains 2.0% residual sulfite. Alternative formulations for sulfomethylation will be developed that have the lowest possible concentration of sulfite while still displaying the decreased brine sensitivity.

3. The mechanism of the reaction between the sulfite ion and the polymer will be investigated. An NMR study using a commercially available dimer of the phenol-formaldehyde polymer and sulfite will be performed.

4. The oligomer sizes obtained during gelation experiments will be determined in order to improve the gelation characteristics in the SMR-HMTA gel system.
Chapter 3

Determination of Aggregate Size during Gelation

Principal Investigators: G. Paul Willhite, Don W. Green, and C.S. McCool
Graduate Research Assistant: Pau Ying Chong

Introduction

Gel treatments are used to control fluid movement in oil reservoirs by reducing the permeability of selected zones. The injected gelant is composed of polymer molecules and crosslinker. As they react, pre-gel aggregates are formed and grow in size. During injection, the aggregates are filtered from solution as they flow through reservoir rock, affecting the gel placement and creating flow resistance.

In order to understand and improve the application of gelled polymer treatments, it is necessary to know the size of gel aggregates as they grow from polymer molecules to form a gel. The objective of this study is to develop methods to determine the size distribution of pre-gel aggregates.

The method used to determine size distributions is equilibrium dialysis. The aggregates are separated by diffusion through a set of membranes that have selected pore sizes. The concentration of polymer in the dialysate products is determined by size-exclusion chromatography (SEC) with a UV detector. Size distributions are calculated knowing the amount of polymer that passes through a given pore size.

An alternative method to determine size of polymer aggregates is Field Flow Fractionation (FFF) with a UV detector. The elution time of the aggregates depends on the size. The mass of the eluted sample is detected by a UV detector. The FFF equipment will be used in future studies.

Experimental

The gel system selected for study contained Alcoflood 935 polyacrylamide and chromium acetate crosslinker. A gel solution was prepared by mixing polymer and chromium acetate solutions to obtain concentrations of 5000 ppm polymer and 100 ppm chromium. The solution had a gel time of approximately 12 hours. All solutions contained 1% potassium chloride. Brine solutions were filtered through 0.22 μm membranes.

The gel aggregates were separated using a membrane dialysis technique. The technique was modified from one developed by McCool [1988]. After a specified reaction time, the reacting mixture was quenched by a factor of 10 by adding 1% KCl brine. The concentration of the non-reacted chromium in the diluted sample was reduced using tubing dialysis. In the tubing dialysis step, the diluted sample was placed into 12,000-to-14,000 molecular weight cutoff dialysis tubing and dialyzed against KCl brine for two days. The sample to solvent ratio was 1:30. After these steps, the concentration of polymer was reduced to 500 ppm and the non-reacted chromium concentration was reduced by a factor of 300. It is assumed that these steps quenched the crosslinking reactions.
After the tubing dialysis step, the sample was charged to dialysis cells that were constructed from Teflon stock in house. The chamber in each half-cell was 1.5 inches in diameter and 0.125 inches deep. Polycarbonate membranes with pores having diameters of 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 microns-separated the chambers. One side of the cell was charged with 2.5 mL of sample, and the other side was charged with 1% KCl brine. The cells were sealed by plugs and placed into a 30°C waterbath. After dialysis, the solutions from both sides of the cell were removed and the polymer concentration determined using a size-exclusion chromatography column equipped with a UV detector.

Aggregates in the sample that were larger than the membrane pores were assumed to remain on the sample side during dialysis. Aggregates smaller than the membrane pores would diffuse until the concentration of the smaller aggregates on both sides of the cell became equal. Assuming equilibrium of the smaller aggregates, a quantitative size distribution was determined. A material balance on the sample charged and removed from the cells was also performed to insure the integrity of the experimental procedure.

Results and Discussion
The time required for the dialysis to attain equilibrium was determined for three pore sizes. The results are presented as the amount of polymer dialyzed as a function of time in Figure 3.1. The amount of polymer that crossed the membrane increased and then leveled off at long dialysis times, indicating an approach to equilibrium. The equilibrium time was longer for larger membrane pore sizes. Since most of the equilibrium was achieved in about 350 hours, a two-week period (336 hours) for cell dialysis was used in subsequent dialysis experiments in order to obtain data in a reasonable time frame.

Size distributions were determined for the polymer solution (without crosslinker) and for gelants that were allowed to react for 10 minutes and for nine hours (approximately 75% of the gel time). The distributions are given in Table 3.1 and in Figure 3.2. The results show that there was little difference in aggregate size between the polymer solution and the 10-minute old gel. Aggregate growth was observed in the 9-hour old gel sample. Material balances of the amount of polymer measured after dialysis compared to the amount of polymer charged averaged 102%±3% where 100% represents a perfect material balance.

Summary
Aggregate growth with reaction time was observed for a polyacrylamide-chromium-acetate gelant. Procedures to determine aggregate size distributions using equilibrium dialysis were developed and tested. Equipment to determine size distribution by the Flow Field Flow Fractionation technique was specified and ordered.
**Figure 3.1** – Weight percent of polymer dialyzed as a function of time.

**Table 3.1** – Size distributions measured with equilibrium-dialysis technique.

<table>
<thead>
<tr>
<th>Size range (µm)</th>
<th>Size Distribution (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Polymer solution</td>
</tr>
<tr>
<td>0.0--0.1</td>
<td>15</td>
</tr>
<tr>
<td>0.1--0.2</td>
<td>24</td>
</tr>
<tr>
<td>0.2--0.4</td>
<td>36</td>
</tr>
<tr>
<td>0.4--0.6</td>
<td>18</td>
</tr>
<tr>
<td>0.6--0.8</td>
<td>2</td>
</tr>
<tr>
<td>&gt;0.8</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 3.2 - Aggregate size distribution measured with the equilibrium-dialysis technique.
Chapter 4

A Preliminary Experimental Study of the Precipitation of Chromium

Principal Investigators: G.P. Willhite, D.W. Green, C.S. McCool
Graduate Research Assistant: Bin Zou

Introduction
Systems utilizing Cr(III) as crosslinker, such as Cr(III)-polyacrylamide or Cr(III)-xanthan, are frequently used systems in permeability modification treatments. Studies indicate that polymer propagates through sandstone or carbonate rock [Sorbie, 1991]. On the other hand, studies on the transport of Cr(III) in porous rock [McCool et al., 1995; Seright, 1992; Stavland et al., 1993] have shown poor propagation of chromium, especially for deep displacement in carbonate formations. The retention of chromium can be caused by ion exchange, chemical adsorption, physical adsorption, and precipitation. This report concerns the precipitation of Cr(III) which is an important factor impairing the propagation in carbonate rock. Chromium precipitation is initiated by an increase of the pH in the injected solution due to the fluid-rock interaction after the solution has been injected into a carbonate formation. It is generally thought that the precipitation of chromium is a slow irreversible formation of insoluble Cr(III) colloids of the form Cr(OH)$_3$(H$_2$O)$_3$ [Bryant et al., 1996].

There are many factors affecting the precipitation rate of chromium. In this work, the effects of pH, temperature, and salinity on chromium precipitation were studied using pH-stat titration. The pH range studied was between pH 7 and 11, and the temperature range between 25 to 45°C.

Background
Earlier work in this contract investigated the chemical interactions between injected brine and a dolomite core [Zou et al., 1998]. The pH in the effluent exhibits a three-stage behavior when the pH of the injected solution increases from 1 to 13. Previous studies [McCool et al., 1995; Seright, 1992; Stavland et al., 1993] on chromium propagation show that pH change of the injected solution correlates with poor propagation of Cr(III) in carbonate cores or sandstone cores containing carbonate as the solution flows through porous rock. McCool et al. [1995] studied the interaction between a dolomite core and a xanthan-Cr(III) gel system. Solutions containing chromium chloride or chromium acetate were injected through a 10.2-cm long dolomite cores. Only 0.5 ppm (which corresponded to 1% of the chromium concentration in the injected solution) was detected in the effluent after four pore volumes of solution were injected as a chromium chloride solution. Significant amounts of Cr(III) precipitated when chromium was injected as a chromium acetate solution. McCool et al. [1995] concluded that the chromium was retained due to precipitation at elevated in-situ pH levels. Seright [1992] studied the propagation of chromium acetate or chromium chloride through 14-cm long Indiana limestone cores. Cr(III) concentration in the effluent never reached the injected concentration after injecting about 10 pore volumes of chromium solution. Chromium propagated more rapidly when the counterion was acetate as opposed to chloride. No chromium was detected in the effluent after injecting 10 pore volumes of chromium chloride solution through a limestone core, indicating that chromium was removed from solution by precipitation.
Stavland et al. [1993] studied the retention of chromium in Brent and Berea sandstone cores (with about 2% carbonate content). They found precipitation was the most important reason for chromium retention in cores. Precipitation was caused by the dissolution of carbonate minerals that increased the pH of the injected solution. Their experiments also revealed that the retention rate of Cr(III) was lower with less carbonate present in the cores.

Though chromium precipitation is an important mechanism involved in chromium transport in porous media, the kinetics of chromium precipitation have not been well studied. The available information in literature includes the hydrolysis equilibrium constants of hydrated chromium complexes and the kinetic studies of the early stage of the hydrolysis of monomeric Cr(III) solution. The solubility of Cr(OH)$_3$ is a function of the solution pH and the concentration of ligands. The solubility curves for Cr(OH)$_3$ in 1% KCl brine and in 1% KCl brine with 0.01M acetate anion are displayed in Figure 4.1 (The curves were calculated using constants from Rai et al. [1987].) A characterization study of aqueous chromium acetate [Rai et al., 1987] showed that dissolving solid chromic triacetate in water producing a complex mixture in which bridge-structured trimers were the dominant species, including both cyclic and linear trimers. The base hydrolysis of the trimers led to the substitution of hydroxyl groups for the bridging acetate groups, and a break of the polynucleic bond. It is not known if the chromium precipitated from solution directly in the polymeric format or first forming monomer-based solid Cr(OH)$_3$.

**Experimental**

**Materials.** The chromium triacetate used in the pH-stat precipitation experiments was obtained from Alfa Products. The empirical formula of the material is Cr(OAc)$_3$·H$_2$O. The chromic chloride, CrCl$_3$·6H$_2$O, was obtained from Fisher Scientific. The titrant was 0.1M NaOH (Fisher Scientific). Reagent grade potassium chloride was used to adjust the ionic strength in the solution. Millipore super-pure water (>18 x 10$^6$ Ω-cm) was used to prepare all solutions. Except for those specified otherwise, all chromic acetate solutions were prepared by dissolving solid Cr(OAc)$_3$·H$_2$O in 1% KCl brine. The pH of 200ppm Cr(OAc)$_3$ solution was 4.50, which remained unadjusted prior to titration.

**Apparatus and Procedure.** A Fisher trimeter II titration system, which consisted of an electrometer, a titrate demand, and a burette/dispenser, was used for the pH-stat titration. A motor driven adjustable stirrer was used to provide a constant stirring speed. A 250 mL double-walled glass reaction jacket was used to contain the chromium triacetate solution. Water was circulated through the jacket to provide a constant temperature. Nitrogen blanket was used to minimize the invasion of CO$_2$ from the atmosphere. pH was monitored by a Fisher pH electrode, and recorded by either a chart recorder or a computer. A schematic of the apparatus for the titration system is shown in Figure 4.2.

The turbidimetric change in solution during titration was measured using a Perkin Elmer UV/VIS spectrometer Lambda 20. The chromium concentration in solution was measured using a Perkin Elmer 460 atomic absorbency spectrophotometer.

For each run, 223 grams of a 200ppm chromium-acetate solution was charged to the jacketed beaker. The solution was kept for 30 minutes prior to titration, to allow the solution to
Figure 4.1 - Solubility curves of chromium hydroxide in 1% KCl and in 0.01M NaOAc.

Figure 4.2 - Schematic diagram of the titrator apparatus.
attain the desired temperature. The experiment was initiated by titrating 0.1M NaOH into the reaction beaker. The addition rate of NaOH, which was dependent on the difference between the solution pH and the desired value, was remotely controlled by a dispenser. Generally, it takes about 1-3 minutes to bring the pH to the desired value.

Samples were taken periodically from the reaction jacket for turbidimetric and chromium concentration analysis. Samples taken for measuring turbidity were processed and measured within 30 seconds. Turbidity was measured at 900nm wavelength. Samples taken for determining aqueous chromium concentration were pre-processed to separate precipitated solids from liquid phase. The separation methods were filtering the solution through 220nm filter or centrifuging at 14000 rpm for 3 minutes. Samples were then acidified to around pH 2 by addition of 1M hydrochloric acid to stop additional precipitation.

Results and Discussion
Precipitation was defined for this study in terms of loss of dissolved chromic ion from solution. Under this definition, precipitation includes any or all of the following processes: hydrolysis of complexed Cr(III), formation of initial small polymers (nucleation), and growth to spherical or thread-shaped colloidal-sized particles. Direct measurement of the amount of precipitated chromium hydroxides in solution is experimentally difficult. Instead, the rate of precipitation was determined by measuring the loss of chromium from solution. Several studies [Grundl and Delwiche, 1993] have identified the separation of colloidal particles as the primary obstacle to obtaining accurate measurement of concentration in solution. The two separation methods used in this study, namely, micro-filtration by filtering the solution through a 220 nm filter and centrifuging the solution at 14000 rpm for 3 minutes, were equally effective to separate the precipitated solids from solution as indicated from results obtained in ancillary experiments.

Figure 4.3 shows typical results from a chromium precipitation experiment. The temperature was 25°C and the pH was 10. Two distinct stages were observed during the precipitation, an induction period (or nucleation period) and a growth period. During the nucleation period, there was no separable chromium hydroxide formed. During the growth period, chromium concentration decreased markedly within a short time. The chromium concentration profile exhibited an S-shape curve. The onset of increased turbidity occurred almost simultaneously with the loss of chromium in solution, which suggests that turbidity is a direct index of the precipitation. However, quantitative correlation of turbidity with the amount of precipitated chromium is difficult because the size, shape and refractive index of the particle affect the light scattering properties of the suspension.

The effect of pH on chromium precipitation is shown in Figure 4.4. The pH of the experiments was controlled at values between 8 and 11 (at 25°C). All four runs show an induction period that was shortened between 8 to 10. Between pH 10 and 11, both the length of induction period and the chromium concentration profiles were similar, which indicates that rate of nucleation is not a strong function of pH. According to the turbidimetric measurement at 1000 minutes and over, it was observed that turbidity was lower if the pH was controlled at a higher value. A possible explanation is that precipitation under high-super-saturation conditions favors nucleation over growth processes and will result in smaller particles at the earlier stage and this has an effect on the later growth.
Figure 4.3 - Typical chromium concentration profile and turbidimetric history in pH-stat titration experiment (T=25°C, pH=10).

Figure 4.4 - Effect of pH on chromium precipitation at pH between 8 and 11.
The chromium profiles in Figure 4.4 are re-plotted in Figure 4.5 in terms of normalized concentration and precipitation time after onset of precipitation. The x-axis \( t' \) is time from the onset of precipitation, \( t' = t - t_i \). \( t \) is the elapsed reaction time which begins from the start of titration, \( t_i \) is the length of the induction period. The y-axis is the normalized chromium concentration at time \( t \), \( C_i^* \), which is defined as

\[
C_i^* = \frac{C_i - C_{eq}}{C_0 - C_{eq}},
\]

where \( C_i \) is the measured concentration at time \( t' \) after onset of precipitation, \( C_0 \) the initial Cr(III) concentration, and \( C_{eq} \) is the calculated equilibrium chromium concentration at the experiment controlled pH value. The data fall onto three straight lines, indicating that the precipitation reaction is first order with respect to aqueous Cr(III) concentration. The slope of the curves increases with an increase of pH from 8 to 10, indicating that the chromium precipitation rate increases as the pH increases.

Figure 4.6 shows the influence of 1% KCl on chromium precipitation. All the three experiments were conducted at 25°C and controlled at pH 9. It was observed that the turbidity shot up much earlier in the experiment in which the chromium solution was prepared by dissolving solid Cr(OAc)_3*H_2O into 1% KCl than in the experiments in which the chromium solutions were prepared by dissolving solid Cr(OAc)_3*H_2O into Millipore water. It implies that the chromium precipitation happened much faster in the solution with 1% KCl.

Figure 4.7 shows the effect of temperature on chromium precipitation. The temperature is controlled at 25°C and 35°C (at pH 9). There was no or a very short induction period at 35°C compared to an over 120 minute induction time at 25°C. The chromium profile is steeper at 35°C than at 25°C, indicating the precipitation rate is more rapid at higher temperature. A similar dependence on temperature was observed in the precipitation when the pH of the solutions was controlled at 8.

In the studies of McCool et al. [1995] and Seright [1992], the retention of chromium in the rock samples was much greater when the solution was prepared with chromic chloride than when it was prepared with chromic acetate. Two experiments were performed (at 25°C, pH=8) to compare the precipitation rate of chromium from chromic chloride solution and from chromic acetate solution. The results shown in Figure 4.8 indicate that precipitation occurred immediately in the chromium chloride solution. Most of the chromium precipitated from solution within 10 minutes. The concentration of chromium in the chromium acetate solution, however, showed no significant change until 400 minutes.

Additional experiments were performed to understand the characteristics of precipitated chromium hydroxide from chromic acetate. In one experiment, precipitated chromium hydroxide from the previous titration experiments of chromium triacetate was removed from solution by filtration on a 0.45μm filter. The precipitate was rinsed with water three times. The precipitate was divided into three portions. One portion was mixed with 5000 ppm polyacrylamide solution. The estimated chromium concentration in the mixture is 200 ppm and the pH of the mixture was 6.2. The mixture did not gel in 6 months. It was observed that the
Figure 4.5 - Rate data for precipitation of chromium at different pH; Temperature = 25°C.

Figure 4.6 - Effect of 1% KCl on turbidimetric history during pH stat titration.
Figure 4.7 - Effect of the temperature on chromium precipitation at 25°C and 35°C.

Figure 4.8 - Comparison of chromium precipitation rate of different chromium sources.
added precipitate was still present as a solid. The second and third portions of the precipitate were added into pH 2 and pH 13.3 solutions. The precipitate was found to dissolve at both high and low pH values, confirming that chromium hydroxide is amphoteric.

Conclusions
1. Chromium precipitates faster as pH is increased. The induction time and precipitation rate are functions of pH, temperature and salinity of the solution.
2. The precipitation reaction is first order with respect to aqueous chromium concentration after onset of precipitation.
3. The precipitation rate increases with increasing temperature.
4. The presence of 1% KCl in the solvent favors chromium precipitation.
5. Precipitated Cr(OH)₃ in solid phase was not directly available for crosslinking.
Chapter 5

Permeability and Dehydration of Polymer Gels after Placement

Principal Investigators: G. P. Willhite, D.W. Green, C.S. McCool, M.J. Michnick, S. Vossoughi
Graduate Research Assistants: Koorosh Asghari, Praveen Krishnan

Introduction
In injection wells, aqueous gelants are injected into high permeability regions and/or in fractured formations to reduce the permeability of water with the expectation that water injected after the treatment will flow through less permeable portions of the reservoir and displace oil. In production wells, gelants are placed to reduce water production without affecting oil production. In both situations, the gelled polymer is subjected to a pressure gradient of oil and/or water for a long period of time after placement.

In a recent paper by Dawe and Zhang [1994], the flow of oil and water through a chromium xanthan gel was investigated using micromodels. One observation in this paper was that oil could be displaced relatively easy through their gel, creating its own flow path. This could occur only if the oil displaced water from the gel structure (dehydrating the gel) as the flow path was created. In contrast, brine flowed through the gel indicating that the gel was permeable to brine. The behavior of gels subjected to pressure gradients is not understood.

The research presented in this chapter was carried out in two separate sets of experiments. The first set consisted of exploratory experiments designed to investigate, for different gels, gel permeability and dehydration under a pressure gradient. Results from these experiments indicated that several gels could be dehydrated under pressure gradients of the magnitude expected in field applications. The second set of experiments was a systematic study of the dehydration and gel permeability of a chromium acetate-polyacrylamide gel. This set of experiments is not yet complete.

Background
When an aqueous gelant is placed in most porous rocks or fractures, the gelant displaces the aqueous phase and fills the volume that is accessible to the aqueous phase. There is no observable change in volume of the gelant upon gelation. If the gel does not swell or shrink (synerese), the permeability to brine after treatment is determined primarily by the permeability of brine in the gel and its ability to resist deterioration when a pressure gradient is applied across the gel. Because most gels used in oil recovery applications contain from 90% to 99.5% (by weight) water, the reduction in brine permeability is attributed to the immobilization of water by the three dimensional, crosslinked polymer network that forms when gelation occurs. When a stable gel forms, the permeability to brine is often quite low.

In laboratory experiments in porous rocks, a high-pressure gradient is usually required to initiate brine flow after placement of a gel. When the injection rate is constant, the pressure gradient declines with time as flow channels are developed in the gel, usually reaching a stable value at a specified injection rate. Flow channels are created by deterioration of the gel under the imposed...
pressure gradient. Aqueous gels have no permeability to oil when they remain intact. However, permeability can be developed as the oil phase creates its own flow channels through the gel [Dawe and Zhang, 1994].

**Gel Permeability.** The permeability of a gel to the flow of brine determines the initial flow resistance of a region filled with a gel. The permeability of aqueous gels (hydrogels) has been studied by a few investigators. Permeability of a polyacrylamide gel copolymerized in an aqueous solution with methylenebisacrylamide was measured and reported by White [1960]. He found that the permeability decreased from 0.38μD to 0.02μD as polymer concentration increased from 5wt% to 35wt%. Tokita and Tanaka [1991] measured the permeabilities of polyacrylamide gels over a concentration range of 2.85wt% to 20 wt%. Permeabilities decreased from 6.3 μD to 0.34 μD over this range of concentration. Seright and Martin [1991] determined the permeability of selected gels to brine after placement in micromodels that were 10.83 cm in length, 2000 microns wide by 200 microns thick. Gel permeabilities were on the order of 6-60 microdarcies when pressure drops between 5 psi and 25 psi were applied. Their data are presented in Table 5.1.

<table>
<thead>
<tr>
<th>Gel System</th>
<th>Permeability, μD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol-formaldehyde</td>
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</tr>
<tr>
<td>3% resorcinol,3%formaldehyde, 0.5% KCl, pH=9</td>
<td></td>
</tr>
<tr>
<td>Cr(III)-xanthan</td>
<td>50</td>
</tr>
<tr>
<td>4000 ppm Flocon 4800, 154 ppm Cr+3(as CrCl₃)</td>
<td></td>
</tr>
<tr>
<td>0.5% KCl, pH=4</td>
<td></td>
</tr>
<tr>
<td>Chromium(redox)-polyacrylamide</td>
<td>30</td>
</tr>
<tr>
<td>2.8% Cynamid Cyanagel 100,500 ppm Na₂CrO₄,</td>
<td></td>
</tr>
<tr>
<td>1500 Na₂S₂O₄, 0.5% KCl, pH=5</td>
<td></td>
</tr>
<tr>
<td>Cr³⁺(acetate)-polyacrylamide</td>
<td>42</td>
</tr>
<tr>
<td>1.39% polyacrylamide,360ppm Cr+3(as acetate)</td>
<td></td>
</tr>
<tr>
<td>1%NaCl,pH=5.0</td>
<td></td>
</tr>
<tr>
<td>Colloidal silica</td>
<td>60</td>
</tr>
<tr>
<td>10 sts% DuPont Ludox SM,® 0.7% NaCl, pH=8.2</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl alcohol-glutaraldehyde</td>
<td>Syneresed-no stable gel</td>
</tr>
<tr>
<td>2.5% PVA,3%HOAc,0.25% GTA,0.5% KCl, pH=5</td>
<td></td>
</tr>
</tbody>
</table>

These permeabilities suggest that gelants placed in porous rocks and fractures will reduce the permeability to microdarcy levels if the pore space or fracture volume is filled with gel and the gel remains intact when subjected to pressure gradients.

**Gel Dehydration.** The deterioration of a gel after placement has not been studied extensively. Some aqueous gels undergo syneresis with time, spontaneously expelling solvent and shrinking in volume [Gales et al.,1988]. Syneresis creates liquid filled volume that may be accessible to the flow of fluids, thereby increasing the brine permeability. Experimental data [Eggert et al., 1992]
show that gels provide significant permeability reduction in porous rocks even after syneresis. However, gels that do not exhibit syneresis can also be deformed under a pressure gradient to create flow channels.

Dehydration of a gel occurs when the solvent (brine/water) is removed from the gel under a pressure gradient or when the gel structure is destroyed. Dawe and Zhang [1994] used a glass micro model to study the reason(s) for disproportionate permeability reduction in flow through gelled porous media. Their findings showed that while water flows through the gel, oil creates channels and pathways in the gel. As a result of the formation of channels in the gel during the flow of oil, the gel dehydrates and loses some of its structural water. This observation stimulated the study of gel dehydration and its effect on gel performance in the porous medium reported in this chapter. The only other research on gel dehydration was done by Seright [1996] who observed gel dehydration while injecting gel into capillary tubes and fractures.

**Exploratory Permeability and Dehydration Experiments**

**Experimental Procedure.** The initial experiments to determine gel permeability and investigate dehydration were done using KUSP1-boric acid [McCool et al., 1998], KUSP1-ester [McCool, 1998], and sulfomethylated resorcinol formaldehyde [Zhuang et al., 1997] gel systems which were studied earlier in this program. Experiments were conducted using the apparatus as shown in Figure 5.1. The apparatus consists of a gel cell connected to a capillary tube filled with brine (same composition as the original gel). The capillary tube (0.5mm I.D.) is connected to a source of air maintained at a constant pressure.

In these experiments, a gelant was placed in a gel cell (10-mm I.D. glass chromatographic tube) and allowed to gel. The gel was confined to the tube by a 10-micron Teflon filter that was placed at the end of the gel. After gelation, the remaining volume of the gel cell was filled with brine and connected to the capillary tube. Since flowrates through gels are small, the flow rate was determined by positioning the air-brine interface in the capillary tube and measuring the location of the air-brine interface at different times. A constant air pressure was set. All experiments were done at a constant temperature of 25°C.

The experimental procedure for measuring gel permeability and gel dehydration is as follows. About 1.6 mL of gelant (mixture of polymer and crosslinker) was placed in the gel cell and allowed to gel. Length of the gel was about 20mm. The remainder of the volume in the gel cell, as well as the capillary tube and connection tubing, were filled with water. The desired displacement pressure was applied to the capillary tube and the change in the level of the water in the capillary tube with time was recorded to determine the water flow rate through the gel. At various times, the length of the gel was measured to determine the volume change due to dehydration. The permeability of the gel was calculated using Darcy’s Law and the measured length of the gel, neglecting the pressure drop in the capillary tube and in the brine above the gel-brine interface. The pressure drop across the 10-micron filter was not measured separately but was assumed to be small compared to the pressure drop in the gel.

**Results and Discussion – Exploratory Experiments.** Results from exploratory experiments on three different gel systems follow. These systems are described elsewhere [McCool et al., 1998; Zhuang et al., 1997].
**Figure 5.1** - Schematic diagram of the apparatus used for measuring the gel permeability.

**Figure 5.2** - Inherent gel permeability for sulfomethylated resorcinol-formaldehyde (SMRF) gel system at 25°C and different applied pressures.
**Sulfomethylated resorcinol formaldehyde (SMRF).** Sulfomethylated resorcinol reacts with formaldehyde to form a rigid gel [Zhuang et al., 1997]. Figure 5.2 presents permeabilities determined for the SMRF system as a function of pressure drop. The permeability of the SMRF gel system is 26 microdarcies at an applied pressure of 5 psi (pressure gradient is 76.2 psi/ft) and decreases with increasing pressure gradient. The decrease in the measured permeability with increasing applied pressure is attributed to the compression of the gel structure. Dehydration of SMRF was not measurable under the pressure gradients studied (76.2 psi/ft to 305 psi/ft).

**KUSP1-ester gel system.** KUSP1 is a biopolymer that is soluble in alkaline solutions and forms a gel when the pH is decreased to 10.8 [McCool, 1998]. In this system, the pH is dropped by hydrolysis of the ester monoethylphthalate. The gel composition used for this experiment was 2.4 wt.% KUSP1 with 0.6 moles of ester/moles of NaOH. Water at 5 psi was applied at the gel-water interface. The volume of the gel decreased slowly with time as water was “squeezed” from the gel and flowed out of the gel cell. Dehydration was nearly complete as a thin gel film remained on the 10-micron filter at the end of the experiment. Since this gel exhibited nearly total dehydration under a pressure of 5 psi, the permeability of another KUSP1-ester gel was measured by using a constant head of water as the pressure source (0.253 psi) and collecting the effluent under oil. The gel sample was 2.3 cm long and the pressure gradient was 3.35 psi/ft. The permeability of KUSP1-ester gel was 0.13 md.

**KUSP1-boric acid gel system.** KUSP1 can also be gelled with borate [McCool et al., 1998]. Two compositions were used to investigate dehydration of the gel. In the first three experiments, the gelant composition was 1 wt% KUSP1 and 0.5 moles boric acid/kg gelant in 1% sodium chloride brine. In the first experiment, the gel was contacted with air at 5 psi as depicted in Figure 5.3. The initial pressure gradient was about 76 psi/ft. An air-gel interface was maintained throughout the experiment. The progressive dehydration of the gel is shown in Figure 5.3. The gel lost most of its volume and dehydrated to a thin filter cake that was retained on the filter at the end of the tube. During the experiment, the exit tube was put into water. No bubbles were formed in the water, which indicates that air did not create flow paths as the gel was dehydrated. However, as depicted in Figure 5.3c, air channeled through when the gel was exposed to air pressure for a long period of time.

In the second experiment, water was used to dehydrate the gel. Strong syneresis was observed and the experiment was terminated. The third experiment was done to determine brine permeability. Figure 5.4 shows the change in permeability with time for this gel at constant pressure of 2 psi. The permeability of the gel decreases with time and finally levels off. This behavior shows the effect of constant pressure on compressing the gel because of the dehydration of the gel. These measurements were conducted in a very short time because of the severe syneresis behavior of KUSP1-boric acid at 0.5 mole boric acid/kg gelant.

A fourth KUSP1-boric acid gel was studied that would not synerese when contacted with brine. The gelant contained 1 wt% KUSP1 and 0.2 mol boric acid/kg gelant in 1 wt% sodium chloride brine. The dehydration experiment was done by injecting water at 2 psi. In this experiment, the initial length of gel was 17 mm but decreased to 9 mm when exposed to the initial pressure gradient of 35.2 psi/ft. This gel lost 47% of its volume as the pressure gradient increased from 35.2 psi/ft to 67 psi/ft. Permeabilities are shown in Figure 5.5 as a function of time.
Air source

a. Before applying air pressure. No bubbles were observed in the effluent collector.

b. During applying air pressure. No bubbles were observed in the effluent collector.

c. After applying air pressure for sufficiently long time. Air bubbles were observed in the effluent collector.

Figure 5.3 - Dehydration behavior observed for KUSP1-boric acid gel when applying air pressure of 5 psi.

Figure 5.4 - Gel permeability for KUSP1-boric acid gel with 0.5 mol boric acid per kilogram of gel at 25°C and 2 psi.
These exploratory experiments demonstrated that some gels are dehydrated under pressure gradients that might be expected in field applications. All gels had some brine permeability. Permeability to brine was low which is consistent with previous work of Seright and Martín [1991] discussed earlier in this chapter. Data on the dehydration of gels under a pressure gradient have not been reported in the petroleum literature. These results lead to the study of gel dehydration and permeability of chromium acetate-polyacrylamide gels described in the next section.

Dehydration and Permeability of Chromium Acetate-Polyacrylamide Gels

The dehydration of chromium acetate-polyacrylamide gels was studied in a series of experiments in which both brine and oil were used to apply pressure to the gel. The experimental apparatus depicted in Figure 5.6 is essentially the same as in Figure 5.1 except the air pressure is applied to a transfer cylinder that contains either water or oil. Use of a transfer cylinder to maintain constant pressure in the brine or oil allowed the running of several gel dehydration experiments simultaneously.

Experimental Setup and Procedure. Polymer stock solution was made by mixing polyacrylamide polymer (Alcoflood 935, batch 3243A) in 1 wt% potassium chloride solution. Chromium stock solution was made from a commercially available 50% chromium acetate solution (McGean-Rohco Inc., Lot-40014806). The two stock solutions were mixed in the ratio 3:1 by weight. The pH of this mixture is in the range of 4.5-4.6. The pH was adjusted to 5.00 using 1N sodium hydroxide solution and the solution was placed in a water bath maintained at a
Figure 5.6 - Schematic sketch of setup to study dehydration of HPAAm/Cr(III) gel system.

temperature of 25°C. The gel composition was 5000ppm polymer, 200ppm chromium(III) and 1%KCl when brine was used to dehydrate the gel. A gel composition having 5000ppm polymer, 200ppm chromium, 1% KCl and 7500ppm polymer, 300ppm chromium, 1% KCl was used when oil was used to dehydrate the gel.

Gels were made and placed in glass chromatographic columns (Omnifit) capable of high-pressure operations. Columns with an inside diameter of 10mm were used for most of the research. Some experiments were conducted in columns with an inside diameter of 35mm. A special end plug with the same dimensions as the end cap with filter was inserted into one end of the column. About 1.6 cm³ of gelant was placed in the 10 mm column so that the length of the gel was about 25mm. The glass columns were then placed in a water bath maintained at 25°C and allowed to gel for 24 hours. After gelation, the end plug was removed and replaced with the endcap containing a 10-micron Teflon filter, saturated with brine. This procedure was developed to eliminate penetration of the gelant into the filter during gelation. Brine permeabilities of the 10 micron Teflon filters were usually in the range of 0.5-2 md before contact with gel and 0.2 – 0.9 md after the experiment. Some of the experiments were conducted using 25-micron filters, which resulted in gel penetrating into the filter. The use of these filters was discontinued.

Each column was mounted on a rack and connected to a constant pressure source as shown in Figure 5.6. A constant pressure was applied to a transfer cylinder containing brine or oil connected to a bottle of compressed air. The pressure measurements were made using a Validyne transducer (Model CD-15). The effluent was collected at regular intervals of time and weighed to calculate the flowrate. Two types of experiments were conducted. In the first set of
experiments, brine was injected into the gel. In the second set of experiments, oil was used to dehydrate the gel.

**Results and Discussion - Brine Dehydration and Permeability Experiments.** The brine experiments were conducted at constant pressure with pressures ranging from 50 to 450 psi. Flow rates are low and these experiments took several days to complete. When the pressure in the brine is increased at the front of the gel, brine flows through the gel. The color of the gel gradually changes from bluish-green to colorless indicating that the excess chromium is displaced by brine flowing through the gel. In one experiment a water-soluble dye was added to the injected brine. A visible displacement front was observed to propagate through the gel, demonstrating that the entire gel was permeable to water.

The behavior of the gel when the brine pressure at the front of the gel is constant can be described in terms of the appearance of the gel depicted in Figure 5.7. As pressures increase, a "brine-finger" forms along the central axis of the tube. This brine finger is difficult to detect because the refractive index of brine is essentially the same as the refractive index of the gel. Addition of particulates (i.e. dust particles) at the gel-brine interface allows visualization of the shape of the finger. The brine finger is quite irregular in shape. However, the existence of this finger indicates that the gel no longer occupies the volume in the “finger.” This volume, which is difficult to determine for brine injection, is the volume of the gel that is dehydrated. At brine pressures less than 150 psi, the “brine finger” stabilizes and brine flows through the gel at a constant rate. At pressures greater than 150 psi, the brine finger propagates through the gel until it reaches the filter cake that forms above the 10-micron filter at the end of the tube. The dehydration of gel when brine pressure exceeds 150 psi is shown in Figure 5.8.

**Behavior of HPAAm/Cr (III) Gel System at Pressures Equal To or Less Than 150psi When Brine Is Used to Dehydrate the Gel.** When brine is used to dehydrate the gel at pressures less than 150psi, the finger reaches a constant length. The brine flow rate becomes steady meaning that there is no further dehydration of the gel. It is possible to estimate the permeability of the remaining gel in the tube if the following assumptions are made. At steady state, assume that the brine flows uniformly across the cross section of the gel in the region below the finger. The pressure within the finger is constant with small variations due to fluid head. The gel length is taken as the distance between the tip of the finger and the top of the filter and the thickness of the filter is known.

The permeability of the gel and filter combination is calculated using Darcy’s law. Values of the combined gel/filter permeability are plotted against time for runs conducted at 100 and 150psi in Figures 5.9 and 5.10. The combined gel and filter permeability decreases with time but attains a steady state value. This permeability was on the order of a few microdarcies. Since the permeability of the 10-micron Teflon filters was found to be on the order of few millidarcies, the permeability obtained from the data is primarily the permeability of the dehydrated gel. Although a filter cake does not form on the 10 micron Teflon filter, much of the dehydration probably occurs in the region above the filter where a structured gel layer forms. The polymer concentration increases in this region. Thus, the composition of the dehydrated gel is probably not uniform.
Figure 5.7 - Gel behavior at pressures less than 150psi when brine (1% KCl) is used to displace the gel.

Figure 5.8 - Gel behavior at pressures greater than 150psi when brine is used to displace the gel.
Figure 5.9 - Permeability of gel and filter combination vs time at 100psi when brine is used to dehydrate the gel. Gel composition – 5000ppm polymer, 200ppm chromium and 1% KCl.

Figure 5.10 - Permeability of gel and filter combination vs time at 150psi when brine is used to dehydrate the gel. Gel composition – 5000ppm polymer, 200ppm chromium and 1% KCl.
In the results described above, the permeability of the sample was a combination of the permeability of both the structured gel layer and the remaining gel in the tube. An experiment was conducted to determine the individual permeabilities of the structured gel layer and the remaining gel. A gelant was prepared with a composition of 750 ppm Alcoflood 935, 300 ppm chromium (from a 50% chromium acetate solution McGean-Rohco Inc.) in 1 wt% KCl. A 10-micron Teflon filter was inserted in the endcap at the exit side of the gel cell to keep the gelant in place. This procedure is different from the dehydration experiments discussed above where the endcap containing the filter was installed after gel placement. This experiment was conducted in a stainless steel cell rather than a glass cell.

After gelation, the water reservoir, connecting tubing, and the rest of the gel cell were filled with water. A pressure of 50 psi was applied to the water. Effluent water was collected in a bottle. Knowing the amount of effluent collected with time, a water flow rate was calculated as $0.00039 \text{ mL/min}$. This corresponds to an overall permeability (gel and filter) of 24.8 $\mu$D. The filter was removed and it was observed that a "structured gel layer" of about 2 mm thick formed on the surface of filter. After the rest of the gel was removed from the gel cell, the filter+structured gel layer was put back in the gel cell and the cell was filled with water. The steady state flowrate of water through the filter+structured gel layer was $0.00068 \text{ cm}^3/\text{min}$ when 50 psi pressure was applied across the filter+structured gel layer. The permeability of the filter+structured gel layer was calculated as 1.8 $\mu$D. The gel and filter+structured gel layer can be considered to be two resistance’s in series. Thus, the permeability of the gel was calculated from Equation 5.1

$$\frac{L_1}{k_{fg}} + \frac{L_2}{k_g} = \frac{(L_1+L_2)}{k_{eff}}.$$  
Eq. 5.1

where:
- $L_1$ = thickness of the filter and structured gel layer (0.4 cm).
- $L_2$ = thickness of the gel not including the structured gel layer (9.8 cm).
- $k_{fg}$ = permeability of the filter+structured gel layer (1.8 $\mu$D).
- $k_g$ = permeability of the gel not in the structured gel layer.
- $k_{eff}$ = overall permeability of gel-filter+structured gel layer (24.8 $\mu$D)

The permeability of the gel not in the structured gel layer was calculated to be 55.9 $\mu$D.

The structured gel layer was scraped off the filter surface and the permeability of the filter was determined from Darcy’s law by measuring the steady state flowrate of water at a pressure drop of 50 psi across through the filter. The filter permeability was about 5.0 $\mu$D. Using this value, the permeability of the structured gel layer was estimated to be 1.02 $\mu$D.

Applied pressure through this experiment was 50 psi, and the flow rate during the experiment of flowing water through the gel was measured at 0.00039 mL/min. Analysis of this data shows that from a total of 50 psi applied pressure, 4.86 psi pressure drop occurred in the filter, 23.8 psi pressure drop in the structured gel layer with 2 mm thickness, and 23.8 psi pressure drop in the rest of the gel. The permeabilities were in the range expected.

**Behavior of HPAAm/Cr (III) Gel System at Pressures Greater Than 150 psi When Brine is Used to Dehydrate the Gel.** When the experiment was conducted at pressures greater than 150 psi the brine finger reached the filter and formed a channel that widened with time as shown in
Figure 5.8. The volume of this channel is the volume of gel that has been dehydrated. A filter cake formed on the filter, which indicated that polymer was being retained on the filter. The permeability of the gel and filter combination was found to be much lower when compared to experiments conducted at low pressures. It was observed that as the pressure increased the permeability decreased. The resistance to flow of brine through the gel at the brine-gel interface increases at high pressure thereby favoring the propagation of the “brine-finger” through the gel which results in dehydration of the gel. The permeability of the Teflon filter was measured at the end of the experiment and found to be two to three orders of magnitude higher than the permeability of the gel and filter combination. The changes in permeability with time for the gel and filter combination at 250 and 400 psi are shown in Figures 5.11 and 5.12.

The permeability of the gel and filter combination at the end of the experiment was measured for pressures from 50 to 450 psi and is shown in Figure 5.13. The decrease in permeability with increase in pressure may be due to the more compact nature of the filter cake at higher pressures.

Oil dehydration experiments. Experiments were conducted with oil as the displacing fluid. As noted earlier, the gel is not permeable to oil. Oil fingered through the gel as shown in Figure 5.14 until the oil reached the filter cake that formed on the 10-micron Teflon filter. Once the oil reaches the filter cake it cannot pass through it so it moves laterally and widens into a hourglass shape as shown in Figure 5.14d. Brine can flow through those portions of the filter cake not covered with oil. Flow of brine ceased and the oil finger was stable. The volume of the dehydrated gel is equal to the volume of the oil in the finger. We observed that dehydration occurred at pressures as low as 2 psi applied across a gel that was 2 cm in length. This is equivalent to a pressure gradient of 30.5 psi/ft. This pressure gradient is well within gradients observed in the reservoir, particularly around the production well. The chromium acetate-polyacrylamide gel is much more susceptible to dehydration by the oil phase than by the brine phase.

The time taken for dehydration decreases as the pressure increases. The experiment was initially conducted with a gel composition of 5000ppm polymer, 200ppm chromium and 1% KCl. It took about 50 hours for complete dehydration to occur at 50psi. Later the gel composition was changed to 7500ppm polymer, 300ppm chromium and 1% KCl but the dehydration time remained the same at about 50 hours at a pressure of 50psi. The volumes of gel dehydrated as a fraction of the original gel volume at three different pressures, 5, 10 and 50 psi are shown in Figure 5.15. The dehydration rate and the amount of dehydration depend on the pressure and these two parameters increase as the pressure increases. The experiments were also conducted in glass columns with an inside diameter of 35mm. The volume of gel dehydrated was close to 70% (Figure 5.16) of the original volume compared to 50-60% in the case of the columns with inside diameters of 10mm. This indicates that the effect of adhesion of the gel to the walls of the column is reduced as the diameter of the glass column increases.

Once the hourglass-shaped oil finger formed, the dehydration was complete because oil covered the surface of the filter cake. Now the oil in the glass cell was poured into a measuring cylinder and the volume of oil was measured. Then, the gel sticking to the sides of the glass wall was cleaned out and the empty cell volume was measured. The difference between this volume and
Figure 5.11 - Permeability of gel and filter combination vs time at 250psi when brine is used to dehydrate the gel. Gel composition – 5000ppm polymer, 200ppm chromium and 1% KCl.

Figure 5.12 - Permeability of gel and filter combination vs time at 400psi when brine is used to dehydrate the gel. Gel composition – 5000ppm polymer, 200ppm chromium and 1% KCl.
Figure 5.13 - Permeability of gel and filter combination at the end of the experiment v pressure.

Figure 5.14 - Gel behavior when oil is used to displace the gel.
Figure 5.15 - Dehydration as a fraction of the original gel volume vs. time when oil is used to displace the gel in glass column with inside diameter 10mm at 50 and 10 and 5psi. Gel composition – 7500ppm polymer, 300ppm chromium and 1% KCl.
Figure 5.16 - Dehydration as a fraction of the original gel volume vs. time when oil is used to displace gel in a glass column with inside diameter of 35mm. Gel composition – 7500ppm polymer, 300ppm chromium and 1% KCl.

the previously measured volume gives the volume of undehydrated gel. This, when subtracted from the original volume of gel sample, gives the volume of the oil finger or the volume of dehydrated gel. The weight of polymer in the dehydrated volume is estimated based on the initial concentration of polymer in the gel sample and was compared to the weight of polymer in the filter cake. The filter cake was carefully peeled off from the Teflon filter and dried in an oven and weighed at regular intervals of time to a constant weight. This weight was usually within 5% of the weight calculated from the volume of dehydrated gel, as shown in Table 5.2 for experiments at 50 psi. This indicates that most of the polymer is being retained on the surface of the filter.
Table 5.2 - Comparison of estimated and measured weight of polymer in filter cake; Experiments conducted at 50 psi.

<table>
<thead>
<tr>
<th>Estimated weight of polymer. (grams)</th>
<th>Measured weight of filter cake (grams)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0117</td>
<td>0.0096</td>
<td>17.9</td>
</tr>
<tr>
<td>0.011</td>
<td>0.01</td>
<td>9.1</td>
</tr>
<tr>
<td>0.011</td>
<td>0.0105</td>
<td>4.5</td>
</tr>
<tr>
<td>0.0102</td>
<td>0.0102</td>
<td>0.0</td>
</tr>
<tr>
<td>0.0095</td>
<td>0.0091</td>
<td>4.2</td>
</tr>
<tr>
<td>0.0091</td>
<td>0.01</td>
<td>-9.9</td>
</tr>
<tr>
<td>0.008</td>
<td>0.009</td>
<td>-12.5</td>
</tr>
<tr>
<td>0.0058</td>
<td>0.0068</td>
<td>-17.2</td>
</tr>
<tr>
<td>0.01</td>
<td>0.0098</td>
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</tr>
<tr>
<td>0.0101</td>
<td>0.0097</td>
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</tr>
<tr>
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<td>0.0098</td>
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<td>0.009</td>
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</tr>
<tr>
<td>0/0102</td>
<td>0.0104</td>
<td>-2.0</td>
</tr>
<tr>
<td>0.0087</td>
<td>0.0087</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Conclusions

The conclusions are based on the gel systems studied in this chapter at temperatures of about 25°C.

1. The KUSP1-ester and KUSP1-boric acid gels dehydrate extensively under pressure gradients imposed in this work, from 35.2 psi/ft to 76.2 psi/ft.
2. The SMRF gel did not dehydrate under pressure gradients from 76.2 psi/ft to 305 psi/ft.
3. Cr(III)-acetate/HPAAm gels can be dehydrated by applying a pressure gradient across the gel with either brine or oil. Oil dehydrates Cr(III)/HPAAm gels at pressure gradients as low as 30.5 psi ft. With brine flow at relatively low-pressure gradients, the brine flow through the Cr(III)/HPAAm gels dominates and dehydration is small.
4. The dehydration rate and degree of dehydration increase as the pressure gradient increases.
5. All gels studied were permeable to water with permeabilities ranging from 5 μD to 130 μD.
6. Dehydration results in a decrease in the permeability of the gel.
Chapter 6

An Experimental Study of the Effect of Rate on the Flow of a HiVis 350 Polymer Solution Through a Sandpack

Principal Investigators: G.P. Wilhite, C.S. McCool, and D.W. Green
Graduate Research Assistant: Abdulwahed Al-Assi

Introduction
Partially hydrolyzed polyacrylamides (HPAM) are used in the petroleum industry to improve oil recovery. Flooding with solutions of high molecular weight HPAMs is used for mobility control in displacement processes. The application of HPAMs at low concentration and crosslinked with aluminum has been used to modify in-depth permeability variation in oil reservoirs to improve oil recovery [Mack and Smith, 1994].

This chapter presents experimental work on the flow behavior of a partially hydrolyzed polyacrylamide, HiVis 350, in a sandpack. The aim of the study was to examine the effect of flow rate on HiVis 350 solutions without a cross-linker and to examine the effect of flow rate on polymer retention. Laboratory polymer displacement experiments were conducted to accomplish the objectives. This work provides a basis for a study of the HiVis 350-aluminum citrate gel system.

Experimental
Displacement equipment. A schematic diagram of the experimental apparatus is presented in Figure 6.1. The sandpack holder was made of a acrylic tubing that was 1 ft long and 1.5 inch in diameter. Pressure ports were attached along the length of the sandpack at intervals of 2 inches dividing the sandpack into 6 sections. Pressure drops were measured across the sections that were labeled A through F. The pressure drop across the entire length was also measured and labeled as T. The transducer for the entire sandpack had a 100 psi diaphragm while those for the individual sections had 10 psi diaphragms.

An automatic packer was used to pack the tube with Wedron Silica sand. Ottawa sand (20-30 mesh) was placed at the inlet and outlet of the sandpack holder. The sandpack was saturated with 0.5% potassium chloride (KCl) brine. Brine was flowed through the pack resulting in some settling of sand. Sand was added to the pack until no more settling was observed.

The porosity of the SP1 was 35.6% based on a pore volume of 124 mL determined by weight. Permeabilities to brine for the individual sections and the overall sandpack length are given in Table 6.1. The permeability of the sandpack was relatively uniform.

Table 6.1 - Permeability in millidarcies for sandpack SP1.A.

<table>
<thead>
<tr>
<th>Section</th>
<th>T</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Permeability</td>
<td>4800</td>
<td>4500</td>
<td>4800</td>
<td>4710</td>
<td>4580</td>
<td>5410</td>
<td>5730</td>
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</table>
Polymer solution. The polymer used in this study was HiVis 350 (TIORCO, Inc., Denver, CO). HiVis 350 has a viscosity-average molecular weight of 28 million and average percent hydrolysis of 23%. The polymer stock solution consisted of 3000 ppm HiVis 350 and 5000 ppm potassium chloride (KCl). The polymer stock solution was stirred for 24 hours and then stored for a minimum of 2 days before use. The 3000 ppm polymer stock solution was diluted with a 5000 ppm potassium chloride solution to a final polymer concentration of 300 ppm.

Displacement procedure. The 300 ppm HiVis 350 was injected into the sandpack column and the pressure drops in each section and across the sandpack column were monitored by pressure transducers. The sandpack was maintained at a constant temperature of 25°C in a water bath. Effluent samples were collected in approximately 30 mL fractions by an automated collector. Polymer concentrations of the injected solution and effluent fractions were measured. The viscosity of each sample was measured at shear rates of 225 and 450 sec⁻¹. All viscosity measurements were taken at the temperature of 25°C.

Polymer analysis. The polymer concentrations of the injected and effluent samples were determined with a Technicon Autoanalyzer II. The method consisted of precipitating the polymer samples with Hyamine 1622 reagent (0.4 % by wt) and measuring the resulting turbidity in a spectrophotometer [Allison et al., 1978].
Results and Discussion
Experiments were conducted to determine the effect on pressure drop of rate of flow of HiVis 350 solutions (without cross-linker). Two sets of runs, SP1.A and SP1.B, were conducted in the same sandpack. The principal parameter varied was the frontal advance velocity. The flow conditions that were used for 300-ppm HiVis 350 displacement experiment for SP1.A and SP1.B are shown in Table 6.2. The difference between SP1.A and SP1.B was that in SP1.A the flow was stopped for a period of time between different flow rates. In SP1.B, the flow rate was changed without stopping the pump.

The flow resistance in the sandpack during the polymer displacement experiment was monitored by measurement of pressure differentials along the sandpack length and across sections labeled A through F (see Figure 6.1). Pressure differentials were converted to apparent viscosities using Darcy’s equation:

\[ \mu_{\text{app}} = \frac{k A \Delta p}{245 q \Delta L} \]  

\[ \mu_{\text{app}} = \text{apparent viscosity (cp)} \]
\[ k = \text{initial deionized distilled water permeability (md)} \]
\[ \Delta p = \text{pressure differential across a section (psi)} \]
\[ q = \text{flow rate (mL/min)} \]
\[ \Delta L = \text{section length (cm)} \]
\[ A = \text{cross-sectional area (cm}^2) \]

Run SP1.A. The flow rates in the SP1.A series ranged from 0.20 mL/min (frontal advance velocity = 2.33 ft/day) to 5.01 mL/min (frontal advance velocity = 58.32 ft/day) and then back to 1.04 mL/min (frontal advance velocity = 12.11 ft/day). The SP1.A series runs were labeled as SP1.A1 to SP1.A5 and are described in Table 6.2. The injected solution contained 300 ppm HiVis 350 and 5000 ppm KCl.

The flow rate for SP1.A1 was 0.20 mL/min which corresponded to a frontal advance velocity of 2.33 ft/day. The apparent viscosity profiles during the polymer displacement of SP1.A1 are presented in Figure 6.2. At this flow rate, section A experienced a higher flow resistance which was increased linearly as the polymer solution was displaced through the sandpack. The high flow resistance in section A indicated face plugging and only occurred at this, the lowest, flow rate. The flow resistances in the remaining sections leveled off after 1.25 pore volumes were injected. The pressure data for Sections E and F were combined due to a problem at the common pressure port. The polymer displacement was discontinued after the injection of 10.8 pore volumes.

The sandpack was shut-in with no flow for 50 hours before SP1.A2 was initiated. The flow rate for SP1.A2 was 1.67 mL/min which corresponded to frontal advance velocity 19.4 ft/day. The initial condition for SP1.A2 was that the sandpack was saturated with polymer from the previous run SP1.A1. The apparent viscosity profile for SP1.A1 showed section A had an apparent
Table 6.2 - Flow Conditions for HiVis 350 Displacement Experiments.

<table>
<thead>
<tr>
<th>Run</th>
<th>Injection Flow Rate (mL/min)</th>
<th>Frontal Advance Velocity (ft/day)</th>
<th>Residence Time (hrs)</th>
<th>Pore Volumes Injected</th>
<th>Shut-Down Time after Run (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP1.A1</td>
<td>0.2</td>
<td>2.33</td>
<td>10.5</td>
<td>10.8</td>
<td>50.0</td>
</tr>
<tr>
<td>SP1.A2</td>
<td>1.67</td>
<td>19.4</td>
<td>1.24</td>
<td>3.67</td>
<td>1.2</td>
</tr>
<tr>
<td>SP1.A3A</td>
<td>4.03</td>
<td>46.9</td>
<td>0.51</td>
<td>3.91</td>
<td>0.5</td>
</tr>
<tr>
<td>AP1.A3B</td>
<td>4.29</td>
<td>49.9</td>
<td>0.48</td>
<td>2.43</td>
<td>0.82</td>
</tr>
<tr>
<td>SP1.A4</td>
<td>5.01</td>
<td>58.3</td>
<td>0.41</td>
<td>1.66</td>
<td>1.67</td>
</tr>
<tr>
<td>SP1.A5</td>
<td>0.88</td>
<td>10.2</td>
<td>2.34</td>
<td>6.24</td>
<td>140.0</td>
</tr>
</tbody>
</table>

![Table 6.2](image1)

**Figure 6.2** - Apparent viscosity profiles as a function of pore volumes injected - Run SP1.A1.

\[ Q = 0.20 \text{ ml/min (2.33 ft/day)} \]
\[ PV = 123.76 \text{ ml, ID = 3.81 cm} \]
\[ L = 30.48 \text{ cm, dL = 5.08 cm, Porosity = 0.356} \]
viscosity of about 45 cp and the remaining sections had apparent viscosities that ranged from 4 to 10 cp. The apparent viscosity profiles of SP1.A2 at a flow rate of 1.67 mL/min are presented in Figure 6.3 for each section and for the overall length of the pack. The flow resistance in the sandpack showed a transition behavior during the first 1.5 pore volumes of polymer injected. The apparent viscosity profiles for SP1.A3a, SP1.A3b, and SP1.A4 were similar to SP1.A2 run with the transition behavior becoming less pronounced as the flow rate increased.

The flow rate for SP1.A5 was 0.88 mL/min which corresponds to a frontal advance velocity of 10.2 ft/day. The sandpack was shut-in for 1.67 hours before SP1.A5 was initiated. The apparent viscosity profiles of SP1.A5 for the sections and the overall of the sandpack are presented in Figure 6.4. Reduction in the injection flow rate from 5.01 to 1.04 mL/min produced high flow resistance, during the initial injection time, which later declined. The transition period lasted for about one pore volume. This behavior was different than when the flow rate was increased after a shut-in period. SP1.A5 was terminated after 6.24 pore volumes were injected.

The apparent viscosities at the end of each run were plotted as function of frontal advance velocity in Figure 6.5 on a log-log scale. The flow resistance increased with increased frontal advance velocity exhibiting shear-thickening type behavior over the range of the flow rates studied. Two apparent viscosities at 2.33 ft/day were not consistent with the other data, the result of face plugging in the front section of the pack.

Run SP1.B. The series of runs for SP1.B were conducted at flow rates that ranged from 1.04 mL/min (frontal advance velocity = 12.11 ft/day) to 4.08 mL/min (frontal advance velocity = 47.49 ft/day) and then back to 0.89 mL/min (frontal advance velocity = 10.36 ft/day). The runs in SP1.B were labeled SP1.B1 to SP1.B5 and the experimental parameters are presented in Table 6.1. The injected solution contained 300 ppm HiVis 350 and 5000 ppm KCl. SP1.B was performed with continuous flow while adjusting the injection flow rate.

Figure 6.6 shows the apparent viscosity profiles as a function of pore volumes injected for SP1.B1 through SP1.B5. The flow resistance in SP1.B increased as the injection flow rate increased. The transition behavior in SP1.B is less pronounced than that of SP1.A. This might be due to the continuous flow used during SP1.B.

The apparent viscosity as a function of frontal advance velocity of the 300-ppm HiVis 350 solution in SP1.B is presented in Figure 6.7. The 300 ppm HiVis 350 solution exhibits shear-thickening behavior in the range of flow velocity of 20 to 50 ft/day. The apparent viscosities for SP1.B runs were a little higher than for the SP1.A runs.

Polymer concentration. The polymer concentrations in the effluent from the SP1.A series of runs are presented in Figure 6.8 as a function of the pore volumes injected. Changing the flow rate affected the polymer concentration in the effluent. Polymer breakthrough was at approximately one pore volume injected. Thereafter, the effluent polymer concentration reached the injected polymer concentration. It appears that there was negligible polymer retention during the SP1.A1 run between two and ten pore volumes injected. The sandpack was shut-in for 50 hours before Run SP1.A2 which was conducted at a higher flow rate. The shut-in time and the
Figure 6.3 - Apparent viscosity profiles as a function of pore volumes injected during Run SP1.A2.

Figure 6.4 - Apparent viscosity profiles as a function of pore volumes injected during Run SP1.A5.
Frontal Advance Velocity (ft/day)

Figure 6.5 - Apparent viscosity as a function of frontal advance velocity during Run SP1.A.

L = 30.48 cm, dL = 5.08 cm
ID = 3.81 cm, PV = 123.76 ml
Porosity = 0.356

Figure 6.6 - Apparent viscosity as a function of pore volumes injected for SP1.B.
Figure 6.7 - Apparent viscosity as a function of frontal velocity for SP1.B.

Figure 6.8 - Effluent polymer concentration as a function of pore volumes injected for SP1.A.
change in flow rate resulted in a decrease in the polymer concentration during the initial injection of Run SP1.A2. Each increase in the flow rate caused additional polymer retention as shown in Figure 6.8 suggesting hydrodynamic retention. Hydrodynamic retention was reversible as seen by the increase in polymer concentration from 300 ppm to 400 ppm when the frontal advance rate was decreased to 10.2 ft/day in Run A5. A reduction in flow rate in Run SP1.A5 resulted in a higher polymer concentration at the beginning of the run before the polymer concentration leveled out at the injected polymer concentration. The lower and higher polymer concentrations observed during the initial injection periods correlated with lower and higher flow resistance in the packs (see Figures 6.3 and 6.4) Similar results were observed in the SP1.B series as shown in Figures 6.6 and 6.9.

Effluent viscosity. The viscosities of the injected and effluent solution for SP1.A are shown in Figure 6.10 as a function of pore volumes injected. Viscosities were measured at shear rates of 225 s⁻¹ and 450 s⁻¹. The HiVis 350 solutions exhibited shear-thinning behavior in that the viscosities were lower at the higher shear rate. This behavior was in contrast to the flow experiments where higher apparent viscosities were observed at higher flow rates (Figures 6.5 and 6.7). This indicated that retention and/or other phenomena were affecting the flow behavior of HiVis 350 solution in the sandpack.

The effluent viscosity was always less than the injected viscosity with the largest difference observed at the lower flow rates. At the higher flow rates, the polymer concentration in the effluent reached the injected concentration but the effluent viscosity was lower than the injected value. These observations indicated that the polymer was degraded during the flow through the pack, confirming results reported earlier [Ranganathan, 1997]. Similar results were observed in run SP1.B.

Conclusions
The following conclusions were drawn from and are applied to the flow of a HiVis 350 polymer solution under the conditions studied.

1. A 300-ppm HiVis 350 solution in a sandpack exhibited shear-thickening behavior over the range of frontal advance rates between 2.3 and 58 ft/day.

2. Polymer retention was a function of flow rate. Increased amounts of polymer were retained with an increase in flow rate. Hydrodynamic retention was observed.

3. Polymer degradation was observed, particularly at low flow rates
Figure 6.9 - Polymer concentration as a function of pore volumes injected for SP1.B.

Figure 6.10 - Comparison of injected and effluent viscosities for SP1.A.
Chapter 7

A Study of Gelation and Injection Characteristics of a Polyacrylamide–Chromium Acetate System in the Presence of Added Acetate Ions

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Graduate Research Assistant: Dilip Natarajan

Introduction
Chromium acetate-polyacrylamide gel systems have been used primarily to treat fracture systems, casing leaks and near wellbore regions in matrix rock [Sydansk, 1993] where short gel times are acceptable. The application of this technology to in-depth treatment of matrix rock is limited because the chromium acetate-polyacrylamide reaction is rapid. Pre-gel aggregates form during the gelation reaction increasing the viscosity of the solution. Some of these aggregates are filtered from the solution, building up high flow resistance and limiting the depth of penetration into the porous matrix. Development of the chromium acetate-polyacrylamide system for in-depth permeability modification in matrix rock requires control of the rate of aggregate growth to control both the rate of increase in solution viscosity and filtration.

The objective of this study was to increase the gelation time of chromium-polyacrylamide systems by adding acetate ion to reduce the rate of crosslinking between chromium and the polymer. Measurements were conducted on bulk gel samples to study the effect of sodium acetate concentration on the gel time of partially hydrolyzed polyacrylamide (HPAAm)–chromium acetate (CrOAc) gel systems. The effect of sodium chloride concentration on the gel times of PAAm–CrOAc–NaOAc gel systems was also studied. Displacement experiments were conducted to investigate the injection characteristics of this gel system.

Background
Sydansk [1990], Sydansk, Argabright [1987], Sydansk [1997] developed that a family of chromium(III)–polyacrylamide gels ranging from highly flowing to rigid rubbery gels, with a wide range of gel times. Burrafato and Lockhart [1989] and Burrafato et al. [1990] proposed that the chromium uptake from chromium-carboxylate complexes is a ligand exchange reaction in which a carboxyl group on the polyacrylamide displaces ligands (i.e. acetate). Crosslinking occurs when a second polyacrylamide molecule reacts with the attached chromium. The chemistry of the reaction between chromium(III) and polyacrylamide is complex because the structure of chromium and the attached ligands vary with pH and temperature. Eq.7.1 and Eq.7.2 describe chromium uptake and crosslinking reactions. The symbol P-CO₂ indicates a polymer with a carboxyl group and OAc⁻ indicates an acetate ion.

Uptake Reaction

\[ \text{Cr}_3\text{O(OAc)}_6^{+1} + \text{P-CO}_2^- \Leftrightarrow \text{Cr}_3\text{O(OAc)}_5(\text{PCO}_2)^{+1} + \text{OAc}^- \]  
Eq. 7.1

Crosslinking Reaction

\[ \text{Cr}_3\text{O(OAc)}_5(\text{PCO}_2)^{+1} + \text{P-CO}_2^- \Leftrightarrow \text{Cr}_3\text{O(OAc)}_4(\text{PCO}_2)_2^{+1} + \text{OAc}^- \]  
Eq. 7.2
When Eq.7.1 and Eq.7.2 are depicted as equilibrium relationships, addition of acetate to a gel solution would limit the amount of chromium uptake and reduce the amount of crosslinking. The chemistry represented by Eq. 7.1 and 7.2 suggests that added ligand as well as the type of ligand control the rate of gelation.

Several researchers have explored the use of competing ligands for delaying gelation. Albonica et al. [1993] demonstrated that organic chromium salts and added organic ligands like salicylate and malonate prevented gelation of chromium-polyacrylamide systems at low temperatures and delayed gelation at elevated temperatures. They also demonstrated that chromium-polyacrylamide gels can be “degelled” by adding a solution containing a ligand that is stronger than the carboxyl group on the partially hydrolyzed polyacrylamide such as glycolate or malonate.

Green et al. [1993] studied the effect of various ligands like chloride, nitrate, acetate etc. and their concentrations as free ligands in solution on the gel times of HPAAm - chromium (III) system. These studies showed that the use of chromium acetate and the presence of free acetate in solution could delay gelation significantly at 25°C.

Bottle tests conducted as a part of this research and their results were presented in a previous report [Green et al., 1997] along with a few preliminary displacement experiments. Gel solutions were prepared from different polymer and chromium acetate sources and the effect of added acetate (provided as sodium acetate), sodium chloride and chromium stock age on the gel times, were studied. Increasing concentrations of sodium acetate were shown to delay gelation. Delays in gel times were significant beyond a certain threshold acetate concentration. Figure 7.1 shows the effect of sodium acetate and chromium stock age on the gel times of HPAAm–CrOAc systems. Aging the chromium stock significantly reduced the gel times of this system. The effect of sodium chloride on HPAAm–CrOAc–NaOAc systems is shown in Figure 7.2. Sodium chloride at high concentrations relative to the acetate salt reduced gel times of HPAAm–CrOAc–NaOAc gel systems. Preliminary displacement experiments showed that increasing acetate concentrations delayed the development of flow resistance during gelant injection in the porous media. However, the flow resistance development was significantly faster than the gelation rates observed in bottle tests.

The objective of this research was to demonstrate in packs of different dimensions that increasing acetate ion concentrations would delay in-situ gelation of chromium acetate-polyacrylamide systems. Delayed in-situ gelation would improve the injection characteristics of the system by allowing deeper penetration of gelant before the development of significant flow resistance.

**Experimental**

Displacement experiments were designed to study the injection characteristics of the gel system in porous media. The composition of the gel solution used in the displacement experiments was 5000 ppm polyacrylamide (Alcoflood 935, 10% hydrolyzed), 109 ppm Cr(III) (McGeane Rohco) and an initial pH of 5.0. Parameters like concentration of sodium acetate, sodium chloride and age of the chromium stock were studied along with the reproducibility of the injection characteristics.
Figure 7.1 - Effect of NaOAc and Cr(III) stock age on gel times of PAAm - CrOAc system. [polymer (Alcoflood 935) - 5000 ppm, Cr(III) (Mceane & Rohco)-109 ppm and initial pH - 5.0 at 25°C]. Sample with no NaOAc estimated at shear rate of 4.5/s while the rest were at 11.25/s.

Figure 7.2 - Effect of NaCl on the gel times of PAAm - CrOAc - NaOAc system. [polymer (Alcoflood 935) - 5000 ppm, Cr(III) (Mceane & Rohco) - 109 ppm and initial pH - 5.0 at 25°C]. Gel times estimated at shear rate of 11.25/s.
The experiments were conducted in unconsolidated sandpacks with lengths of 1, 4 and 6 feet. The sandpack holders were 1.5" and 1" ID acrylic tubes and were fitted with ports for measurement of pressure. The holders had six sections (2" long) in case of the 1-foot long packs, 6 sections (1 ft long) for the 6 foot long pack and 8 sections (6 " long) for the 4-foot long packs. Figure 7.3 is a schematic of the experimental setup. Silica sand obtained from Wedron Silica Company (nominal grain size of 144 mesh) was acid washed to remove the iron particles, rinsed in distilled water, dried and was packed using a pneumatic packer. Screens were placed at the ends and in the pressure port fittings to avoid sand washout. Pressure ports were connected to transducers to measure the differential pressure across sections. Pressure data were collected with a computer-based data acquisition system. The pressure in the sandpacks was limited to 80 psi for experimental and safety considerations.

The sandpack was flushed with carbon dioxide and water was injected at a constant flow rate with a back-pressure of 40 psi applied to the exit end of the pack. Pore volume and the porosity were calculated from the dry weight and the weight after saturation. The porosity was verified by a tracer test. Brine permeability of the individual sections were obtained at different flow rates and averaged.

Figure 7.3 - Schematic of the experimental set-up.
A buffer solution at a pH of 5.0 (±0.1) containing sodium acetate and acetic acid at an acetate concentration corresponding to that in the gel solution was injected into the sandpack to stabilize pH. Stock solutions of polymer and crosslinker were pumped and mixed in-line at a 3:1 ratio, respectively. Chromium stock solutions were used fresh or aged for a month depending on the experiment. The pH of the polymer stock solutions was adjusted so that the gel solution pH was 5.0 (± 0.1) at the entrance of the sandpack. The injection rate was maintained around a darcy velocity of 2.49 ft/day, which correspond to a frontal advance velocity of 7.5 Wday. Effluent samples were collected at regular intervals using an automatic sample collector. Pressure was measured during gel injection using the transducer setup. Bulk samples, effluent samples and in-line mixed samples were collected for measurement of pH and viscosity. Gel injection was terminated when a specified volume of gelant was injected or when the overall injection pressure increased to 80 psi. For runs where bulk gel time was less than 21 days, the sandpack was shut-in at 25°C for a period equal to or greater than its bulk gel time. Brine injection at constant pressure was used to determine the post-treatment permeabilities.

**Results and Discussion**

A listing of the displacement experiments is given in Table 7.1. Runs B2 and SP11 were conducted in 4 ft long packs with 1.5” ID and Runs SP14 and SP15 were conducted in 6 ft long packs with an ID of 1”. All the other runs were conducted in 1-ft long packs with 1.5” ID. The porosity of the sandpacks was in the range of 30-35%. The pore volume of 1 ft packs were in the range of 100-120 mL while the 4 ft packs had a pore volume of 460 mL. The 6 ft packs had a pore volume of 400-410 mL. Fresh chromium stock was used in most of the experiments except SP2 and SP3 where the crosslinker solution was aged for one month before gel injection.

The acetate/Cr ratios provided in Table 7.1 are about 30% higher than the values corresponding to the added sodium acetate, due to the addition of acetic acid for pH adjustment. At least 1 PV of gelant was injected into each sandpack with the exception of Run B2 where the pressure limitation was reached after 0.65 PV of gelant was injected. Effluent samples were collected in most of the experiments and their viscosity, pH and the flow rate were measured. The pH of the gelant was quite stable due to the buffering effect of sodium acetate and acetic acid. However, a slight drop in the effluent viscosity and the flow rate was observed after the development of increased flow resistance in Runs SP5, SP6, SP11, SP13, SP14 and SP15. All sandpacks were shut-in at 25°C for a time corresponding to the gel times of the gelant injected and post-treatment permeabilities were estimated by injecting brine. The post-treatment permeabilities of the packs were in the range of 30 - 40 micro-darcies, except in SP3. No permeability reduction was observed in SP3 when brine was injected after 4 months of shut-in time.

Pressure drop data collected during injection of gelant are presented as apparent viscosities as a function of pore volumes injected. Apparent viscosities were calculated from the pressure differentials and the initial permeabilities using Darcy’s law (Eq.7.3). Apparent viscosity is a measure of the average flow resistance in the sandpack over which the pressure differential was measured.
\[ \mu_{app} = \frac{k \cdot A \cdot \Delta p}{q \cdot L} \]  

where,

- \( \mu_{app} \) = apparent viscosity
- \( k \) = permeability
- \( A \) = cross-sectional area
- \( \Delta p \) = pressure differential across a section
- \( q \) = volumetric flow rate
- \( L \) = section length

Table 7.1 - Summary of displacement experiments.

<table>
<thead>
<tr>
<th>Run #</th>
<th>NaOAc conc. (m)</th>
<th>OAc/Cr ratio</th>
<th>Bulk gel times</th>
<th>Pore volumes injected</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 1</td>
<td>No NaOAc</td>
<td>3.05</td>
<td>48 hrs</td>
<td>5</td>
</tr>
<tr>
<td>B 2</td>
<td>No NaOAc (1% NaCl)</td>
<td>3.00</td>
<td>24 hrs</td>
<td>0.65</td>
</tr>
<tr>
<td>SP2</td>
<td>0.12</td>
<td>81</td>
<td>20 hrs</td>
<td>1.2</td>
</tr>
<tr>
<td>SP3</td>
<td>1.0</td>
<td>600</td>
<td>&gt; 1 year</td>
<td>3.75</td>
</tr>
<tr>
<td>SP5</td>
<td>0.088</td>
<td>60</td>
<td>148 hrs</td>
<td>7</td>
</tr>
<tr>
<td>SP6</td>
<td>0.104</td>
<td>71</td>
<td>200 hrs</td>
<td>7.3</td>
</tr>
<tr>
<td>SP8</td>
<td>0.14</td>
<td>91</td>
<td>17-18 days</td>
<td>7.5</td>
</tr>
<tr>
<td>SP9</td>
<td>0.14</td>
<td>91</td>
<td>17-18 days</td>
<td>8</td>
</tr>
<tr>
<td>SP10</td>
<td>0.14 (0.7 m NaCl)</td>
<td>91</td>
<td>13-14 days</td>
<td>7.5</td>
</tr>
<tr>
<td>SP11</td>
<td>0.14</td>
<td>91</td>
<td>17-18 days</td>
<td>2</td>
</tr>
<tr>
<td>SP14</td>
<td>0.104</td>
<td>71</td>
<td>200 hrs</td>
<td>1.2</td>
</tr>
<tr>
<td>SP15</td>
<td>0.14</td>
<td>91</td>
<td>17-18 days</td>
<td>1.8</td>
</tr>
</tbody>
</table>
**Base Case(s).** Runs B1 and B2 were conducted as baseline runs in that the injected gelant contained no added acetate. The gel solution used in Run B1 contained no added salts except for a small amount of acetic acid that was used to adjust pH. The initial viscosity of the gelant was higher than in the other runs because the low ionic strength permitted the polyacrylamide molecules to elongate in solution. Apparent viscosities along the pack for Run B1 (acetate/chromium ratio of 3.05) are shown in Figure 7.4 as a function of pore volumes of gelant injected. The apparent viscosity increased with distance from the inlet becoming uniform after about 10 cm of penetration. The increase in the apparent viscosities was not significant with additional injection of gelant. The apparent viscosity was about 300 cp after 5 pore volumes of gelant were injected. The high initial and apparent viscosities were not considered suitable for matrix applications.

Run B2 was a more appropriate base-line run to judge the effect of added acetate has on the injectivity of the polyacrylamide-chromium acetate system. The gelant for Run B2 was the same as in Run B1 except KCl (1.0% concentration) was added to give a similar initial solution viscosity as in the runs that contained added acetate. The apparent viscosity in the first foot of the pack (sections 1 and 2) increased rapidly to about 200 cp with the injection of about 300 mL as shown in Figure 7.5. Apparent viscosities of sections 2-4 increased rapidly after the arrival of the gel front, reaching values in the range of 170-180 cp when the pressure limit on the differential transducers was exceeded. The overall pressure drop exceeded 80 psi by 0.65 PV and injection was terminated. The gelant penetrated about 2.8 ft. of the pack.

**Effect of added acetate ions.** The effect of added acetate ions on the injection characteristics in the first foot of the porous media is demonstrated by a comparison of Runs B2, SP3, SP5, SP6, and SP8 (OAc/Cr ratios were 3, 60, 71, 91 and 600).

The overall apparent viscosities in the foot long packs i.e. SP3, SP5, SP6 & SP8 and the first one-foot of the four-foot long pack B2 are shown in Figure 7.6. The data show that increasing concentrations of added acetate ions delayed the development of flow resistance during gel injection in the porous medium. In B2 (OAc/Cr = 3), the flow resistance development was significant and the apparent viscosity across the first foot of the pack increased rapidly to about 200 cp with the injection of about 300 mL. At an OAc/Cr ratio of 60 (Run SP5), about 500 mL (4.5 PV for the foot long pack) was injected before the apparent viscosity increased to 200 cp. An acetate/Cr(III) ratio of 71 was used in SP6 and 700 mL of gel solution was injected before the apparent viscosity increased to 200 cp. Only small increases in apparent viscosities were observed when the OAc/Cr ratios were 91 and 600. In these runs, the OAc/Cr ratios were sufficiently high to inhibit development of high apparent viscosities in the sandpack during gel placement. Brine was injected in SP8 (OAc/CR = 91) after 20 days of shut-in. The permeability was approximately a few microdarcies, indicating gelation. Brine was injected into SP3 (acetate/Cr = 600) after about 4 months of shut-in. The brine fingered through the pack at very low pressure differentials, indicating that the high acetate concentration inhibited gelation. Permeability reduction did not occur.

In all cases where flow resistance development was observed during injection (i.e. SP2, SP5, SP6, and SP11), the flow resistance developed much sooner than the respective gel times observed in the bottle tests. For example, the gel solution used in SP5 had a gel time of about
Figure 7.4 - Apparent viscosity against the length of the pack in B1. Gel solution containing 5000 ppm polymer, 109 ppm Cr(III), pH = 5.0 (±0.1) was injected at a darcy velocity of 2.49 ft/day at 25°C.

Figure 7.5 - Apparent viscosity profiles during gel injection in B2. Gel solution containing 5000 ppm polymer, 109 ppm Cr(III), 1% NaCl, pH = 5.0 (±0.1) was injected at a darcy velocity of 2.49 ft/day at 25°C.
Figure 7.6 - Effect of added acetate on injection characteristics. Comparison of apparent viscosities across the first foot of sandpack in runs SP3, SP5, SP6, SP8 and B2.

150 hours but showed significant flow resistance within an injection time of 24 hours. The probable reason for this behavior is the formation of aggregates and the filtration of pre-gel aggregates as the gel progressed through the pack. This combination of progressive crosslinking and filtration probably had a compounding effect that resulted in a near exponential increase in the resistance development. Hence the injection time before the development of substantial flow resistance is a function of the residence time (or flow rate), gelation kinetics (influenced by the added acetate) and properties of the porous media.

The effect of acetate ions in delaying the development of flow resistance within the first foot of the porous medium was clearly demonstrated in SP2, SP3, SP5, SP6, and SP8. The injection characteristics of this gel system in 4 ft packs, at different OAc/Cr ratios are presented in Figure 7.7. The plot shows that increasing the ratio from 3 to 91 increased the time to reach an apparent viscosity of 150 cp by a factor of about 4. The effect of added acetate on the injection into 6-foot long packs is shown in Figure 7.8. OAc/Cr ratios of 71 and 91 were used in these runs. This comparison shows that increasing the OAc/Cr ratio from 71 to 91 facilitated the injection of about 70% more gelant for the same flow resistance development.

Gelant propagation. Figures 7.9, 7.10 and 7.11 show the effect that added acetate ions have on the apparent viscosity profiles along the length of the pack. Figure 7.9 is a plot of the apparent viscosities along the foot-long packs SP5 and SP6 after equivalent gelant injection. It is evident that in the runs SP5 and SP6 the zone of high flow resistance was formed towards the end of the
Figure 7.7 - Effect of added acetate on injection characteristics. Comparison of overall apparent viscosities across 4 ft in runs SP11 and B2.

Figure 7.8 - Effect of added acetate on injection characteristics. Comparison of overall apparent viscosities across 6 ft in SP14 and SP15.
**Figure 7.9** - Comparison of apparent viscosities along the foot long packs SP5 and SP6.

**Figure 7.10** - Comparison of apparent viscosities along the 4 ft packs in SP11 and B2.
pack, which was about 1 foot from the inlet end. The higher concentration of added acetate ions in SP6 resulted in slower development of flow resistance. In Figure 7.10, apparent viscosities encountered in the four foot packs, SP11 and B2, are plotted against the length. The gel solution with added acetate (SP11) showed slower resistance build-up when compared to gel solutions without added acetate (B2). In SP11, about 2 PV were injected before significant increase in the apparent viscosities was observed, while only 0.5 PV was injected in B2, when injection was terminated due to excessive resistance. In both these runs, the zone of high flow resistance was near the second section which was also about 1 foot from the inlet. It is probable that resistance zones might have formed at greater distances from the inlet face, at higher flow rates. From Figure 7.11, it is seen that gel solution with a lower added acetate concentration resulted in faster flow resistance development. In Run SP14, the point of highest flow resistance was about 2 ft from the inlet end, while it was about 3 ft from the inlet in Run SP15. However, the zone of flow resistance development started about 1 ft from the inlet end in both the runs. These plots show that by increasing the OAc/ Cr ratios, one can delay the development of flow resistance and improve gelant propagation for a given injection pressure limitation.

An interesting observation in Runs SP11, SP14 and SP15 was that the apparent viscosities started increasing after the second section and were uniform along the rest of the pack. This behavior is unique and different from what was reported for the redox gel systems by McCool [1988] and the chromium-xanthan system studied by Hejri et al. [1993] where rapid buildup of flow resistance occurred in a localized region.
Effect of sodium chloride. A displacement experiment using a gel solution with an acetate/Cr ratio of 91 and a sodium chloride concentration of 0.7 m was conducted to verify bottle test results which showed a 20% reduction in gel times of this system in the presence of high sodium chloride concentrations. Figure 7.12 is a comparison of the injection characteristics in Runs SP8 and SP10. The gel solution used in SP10 was similar to that of SP8, except the gelant also contained 0.7 m sodium chloride. The data indicates that sodium chloride did not affect the injection characteristics of this system within 1 ft of the porous medium in spite of the reduction in bulk gel time. The effect of sodium chloride might have been more pronounced at distances greater than 1 ft from the inlet.

Effect of chromium stock age. The effect of chromium stock age that was observed in bottle tests was also studied in the porous media. SP2 was a displacement experiment in a foot-long pack, where a gel solution was made from a month-old chromium stock with an acetate/Cr ratio of 81. The results are provided in Figure 7.13 along with the apparent viscosity in the first foot of the base-case run (B2). It is seen from the plot that in spite of the presence of added acetate ions in SP2, the use of old chromium stock significantly increased the rate of gelation and hence the rate of resistance development. The delaying effect of the added acetate ions was completely offset by the use of aged chromium stock. Fresh chromium solution is likely to be used in field applications so gel times would not be affected by solution age.

Reproducibility. The reproducibility of the results obtained in this study was evaluated. Gel times in bottle tests were reproducible to within 10%. Gel times and viscosity behavior with time for bulk samples and in-line samples prepared during the displacement runs were also consistent with the bottle samples. Four displacement experiments were conducted using an OAc/Cr ratio of 91. Two runs (SP8 and 9) were in sandpacks one foot in length while SP11 was 4 ft and SP15 was a 6 ft pack. All parameters like injection velocity, chromium stock age etc were maintained constant in the four runs except different sandpacks were used. Figure 7.14 is a plot of the overall apparent viscosities for SP8, SP9, and the apparent viscosities for the first foot of SP11 and SP15. Figure 7.15 is a comparison of SP11 and the first 4 ft of SP15. The reproducibility is considered good. Small differences in the apparent viscosities are attributed to the different physical characteristics of each sandpack. Figure 7.16 is a comparison of runs SP6 and SP14, where similar gel solutions were studied in packs of different lengths. The apparent viscosities in the first foot of SP14 compare well with the overall apparent viscosities encountered in the foot-long pack SP6.

Conclusions
The conclusions are limited to the chromium acetate-polyacrylamide system studied at 25°C under conditions where the pH was controlled at pH 5±0.1 with displacement experiments conducted in unconsolidated sandpacks.

1. The gel times of HPAAM–chromium acetate gel systems can be increased by adding acetate ions. Gel times in the range of a few hours to several days were achieved by varying the OAc/Cr ratios from 3 to 91 in gel solutions containing 5000 ppm polymer and 109 ppm chromium. OAc/Cr ratios greater than 260 inhibited gelation for more than a year.
2. Gelation delays were significant beyond a threshold acetate ion concentration. The threshold OAc/Cr(III) ratio for the gel composition studied was about 80.
3. Gel solutions prepared from aged chromium stock had significantly shorter gel times than fresh stock samples. High concentrations of acetate ions in solution were found to offset the effect of chromium stock age.

4. Increasing concentrations of sodium chloride were found to reduce the gel times of the HPAAm–CrOAc–NaOAc system.

5. Increasing OAc/Cr ratios were found to delay the development of flow resistance during gel injection in unconsolidated sandpacks.

6. The use of aged stock significantly reduced the time available for gel injection at reasonable pressures.

7. The time available for gel injection using reasonable injection pressures was significantly shorter than the gel times in most of the displacement experiments which was probably due to filtration of pre-gel aggregates.

8. High acetate ion concentrations (OAc/Cr(III) = 600) completely inhibited \textit{in situ} gelation and hence any permeability modification.

9. Gel times and injection characteristics for this system were reproducible within acceptable limits.

\textbf{Figure 7.12} - Effect of sodium chloride on the apparent viscosities in packs SP8 and SP10.
Figure 7.13 - Effect of chromium stock age. Comparison of apparent viscosities at the end of 1 ft in runs SP2 and B2.

Figure 7.14 - Reproducibility. Comparison of apparent viscosities at the end of 1 foot in runs SP8, SP9, SP11 and SP15
Figure 7.15 - Reproducibility. Comparison of apparent viscosities across 4 ft of SP11 and SP15.

Figure 7.16 - Reproducibility. Comparison of apparent viscosities at the end of 1 foot in runs SP6 and SP14.
Chapter 8

Gel Behavior in Fractured Media

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Graduate Research Assistant: S. Ganguly

Introduction
Many oil reservoirs are fractured to some extent. In addition to naturally occurring fractures, reservoir rocks are hydraulically fractured at production wells to improve production rates. Thermal stresses and over-pressure at injection wells also create fractures. These fractures can cause a severe water channeling problem during enhanced oil recovery processes. One method for water control is a gelled polymer treatment.

During placement of a gelant into a fracture within a porous matrix, some of the gelant leaks off to the adjoining matrix. "Leakoff" of gelant into the matrix adjoining the fracture contributes to flow dynamics during placement. It affects fracture gel strength, and may be responsible for additional resistance in matrix after placement.

This chapter reports results from a study of the displacement of Cr(III)-partially hydrolyzed polyacrylamide (HPAAm) gelant in a physical model of a fracture, and the behavior of the gel after treatment. A model, accounting for simultaneous flows in fracture and matrix was developed to describe the flow of a viscous solution displacing resident brine. A model was also developed to describe the flow and pressure profile for gelant leakoff in unfractured cores when the injection pressure is constant. The primary objectives of this research are to study the behavior of gels in a fracture and in adjacent matrix during placement (with leakoff), and during brine injection after placement.

Background
The application of gelled polymer treatments to fractured systems was investigated by Seright [1996; 1994]. Seright studied the performance of several immature, preformed, and mechanically degraded gels by displacing them through fractured cores without any significant leak off into the adjacent matrix. For the purposes of this report, an immature gel is a gelant with an age less than the gel time measured in a quiescent bottle. Immature gels are usually characterized by the amount of time from mixing.

Injection of bulk mixed Cr(III) acetate HPAAm gelant / gel under constant pressure is reported by Seright [1994] and Sydansk [1988]. Sydansk found that the mature gel (gel with age exceeding gel time) did not penetrate into a Mid-Continent carbonate core plug, whereas immature gel penetrated to some extent. Seright observed an increase in resistance factor after injection of one pore volume of immature gelling solution. Build up of resistance eventually stopped the displacement before two pore volumes could be injected. With a matured gel, rapid increase in resistance factor was observed, and only half a pore volume of gel could be injected into the core under constant pressure of 100 psi. The effect of gelant leakoff on gel placement and gel displacement has not been studied.
Experimental Fracture Model. A physical model of a fracture was developed to study the behavior of gel in controlled experiments. Provisions were made to control leak off from the fracture face into the matrix. Design of the physical model, its characterization with brine, and its testing with glycerol (simulating a viscous gelling solution) were presented in the last annual report [Green et al., 1997].

A schematic of the fracture model is shown in Figure 8.1. A Berea slab (24"x10"x1") was fractured into two halves by a hydraulically operated fracturing blade. The two halves were held together and the entire assembly was coated with epoxy. Flow into the fracture enters through a small compartment and exits the fracture through a similar compartment. The rest of the inlet and outlet faces were sealed with epoxy. Leak off from the fracture into the matrix exited the model from the two sides. Each side was divided into two compartments. Pressure ports were drilled at different positions on the top of the assembly, and their locations are shown by squares on the top view. Carbon dioxide displaced air from the assembly. Next the assembly was saturated with 1% NaCl solution. The fracture permeability, fracture aperture width, matrix permeability and matrix porosity were determined from a series of flow tests.

Figure 8.1 – Schematic of fracture model.
Permeability of the fracture was determined by closing the matrix outlets and flowing brine through the fracture. Flow rate and pressure differentials across fracture sections were measured. Darcy's law (Equation 8.1) and theory of ‘flow between two parallel plates [Iwai, 1976; Bird, et al., 1960] (Equation 8.2) were used to compute the aperture width of the fracture.

\[
\frac{q}{(2h)w} = \frac{k_f \Delta p}{\mu L} \quad \text{Eq. 8.1}
\]

\[
k_f = \frac{(2h)^2}{12} \quad \text{Eq. 8.2}
\]

Matrix permeability was determined by injecting brine into the fracture and measuring flow rate at the matrix outlets. Pressure differentials were measured between the ports, which divide the matrix into sections.

A tracer test was conducted in each half of the cell assembly to determine the pore volume of the matrix. A step change in influent concentration was introduced and effluent concentrations of the two matrix segments (front and back) were monitored with time. The matrix outlets were held at the same hydrostatic head to reduce crossflow between the front and the rear sections. Analysis of the reduced concentration with effluent volume provided an estimate of the matrix pore volume of the front and back sections of each side of the assembly. Typical data for a quadrant is presented in Figure 8.2. The permeability and the pore volume of the fracture model, used for gel displacement are presented in Figure 8.3.

Cr(III)-HPAAm gelant was displaced through the fracture model. The polymer used for this study was hydrolyzed polyacrylamide (Alcoflood 935, molecular weight 5(10^6) daltons, degree of hydrolysis 5-10%). Chromium tri acetate (McGean Rhoco) was the crosslinker. The composition of the gelant was 5000 ppm polymer, 417 ppm chromium triacetate, and 1% NaCl. pH of the mixture was 4.78 (unadjusted). The gel time for this composition at 25°C was 12-16 hours. The viscosity of the polymer solution (5000 ppm HPAAm, with 1% NaCl) was measured on a Bohlin rheometer. Viscosity as a function of shear rate is presented in Figure 8.4.

A schematic diagram of the equipment and set up used for the gel displacement experiment is shown in Figure 8.5. Oil displaced polymer from the transfer cylinder. The polymer solution was mixed with the crosslinker solution in the ratio of 2:1 in an in-line mixer, prior to entering into the fracture. Matrix outlets were open to atmospheric pressure. The pressure at the fracture outlet was set at a specified value by the back-pressure regulator. The effluents from the fracture and matrix outlets were collected in graduated cylinders. Volume in the cylinders was recorded with time. Samples of the fracture and matrix effluents were collected at specified intervals for analyses.

**Leak off experiments (unfractured core).** During injection of a Cr(III)-HPAAm gelant into a long fracture, the pressure drop in the fracture is small at injection rates observed in field applications. Thus, the injection pressure in the fracture remains constant with time and the fracture acts as a line source extended from the well. As the gelant travels down the fracture, the age of the gelant increases. Leakoff experiments that simulate these effects were performed in
Figure 8.2 - Tracer response from one of the quadrants of the fracture model.
<table>
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<th>Section No.</th>
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</thead>
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<table>
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**Figure 8.3** - Permeability and pore volume of different sections of the fracture model.
Figure 8.4 - Viscosity of HPAAm solution as a function of shear rate.
Figure 8.5 – Flow schematics for gelant displacement in the fracture model.
unfractured Berea cores as a part of this research. In the experiments, the injection pressure was constant and the in-line mixed gelants were allowed to age by displacing them through a tubing section prior to injection.

Berea sandstone cores of square cross section (2 inches X 2 inches) and of 1 ft length, were used to study leakoff of gelant under constant pressure. Each core was fitted with end caps and was coated with epoxy. Five equal distant pressure ports along the length were installed to divide the core into six sections. Carbon dioxide was used to displace air out of the core and the core was saturated with 1% NaCl. Weights of the core before and after saturation were used to calculate the pore volume.

Permeability of each section was determined to be 60-65 md from measurement of pressure differentials at five different flow rates. A tracer test was conducted to estimate the pore volume. Influent to the core, flowing at 3 mL/min, was given a step change in concentration. Effluent concentration was monitored using a manual RI meter. Porosities of the cores were found to be 0.17-0.18.

Four displacement experiments were performed with Cr(III)-HPAAm gelling solutions. For the first displacement experiment, polymer and crosslinker were mixed in bulk using a magnetic stirrer, and the mixture was loaded in a transfer cylinder connected to the core. An air source displaced the gelling solution from transfer cylinder into the core at constant pressure of 70 psi. In the other three runs, gel was mixed inline in the ratio of 2:1. After inline mixing, the gelant flowed (@ 1.8 mL/min) through 3/8 " O.D. tube of pre designed length for aging. The tube was held with an upward gradient to avoid formation of a stagnant pocket of gelant inside the tube. Three ages of gelant were studied: 1) zero age (no delay between inline mixing and injection), 2) three hours of flow between inline mixing and injection and 3) six hours of flow between inline mixing and injection. The injection pressure of 70 psi was limited by the epoxy coating.

Figure 8.6 describes the flow schematics followed for displacement with in line mixing. A back pressure regulator, used in parallel to the main flow, maintained constant pressure of 70 psi at the inlet face of the core. The length of the tube between the purging point from the main flow line and the inlet face was kept minimum (< 1 inch) so that the inlet face could be exposed to gelant of same age, even if the flow rate changed significantly.

For constant pressure displacement, the flow rate dropped significantly within a short time. Therefore, most of the gelling solution flowed through the back pressure regulator to maintain a constant pressure by this approach. A transfer cylinder was installed after the delay loop to minimize this problem. The transfer cylinder was pressurized by nitrogen source to a constant pressure of 70 psi. A small volume of influent was pushed into the transfer cylinder just before the displacement in the core. When the gate valve at the core inlet was opened for displacement in the core, the resident fluid in the transfer cylinder provided for extra flow during the initial period (typically on the order of 5 minutes). When flow is registered at the outlet of back pressure regulator, the transfer cylinder was taken off line.
Figure 8.6 – Flow schematics for leakoff experiments in unfractured cores.
Pressure transducers, attached to various sections of the core, continuously measured the pressure differential, through a demodulator assembly. Cumulative volume, collected at the effluent end was measured with time. Samples were drawn from the effluent for subsidiary measurements (viscosity, pH, Cr content).

About one pore volume of bulk mixed gelant was injected before the flow rate dropped to zero. A similar situation happened with inline mixed gelants. More than two pore volumes of gelant could be injected with no prior aging, one and half pore volumes of gelant could be injected with three hours of prior aging, and three quarters of a pore volume of gelant could be injected for six hours of prior aging.

A separate set of displacement experiments was performed with uncrosslinked polymer to estimate the viscosity of the gelling solution as a function of flow rate. These experiments also provided an estimate of permeability reduction caused by retention of uncrosslinked polymer. In these experiments, 5000 ppm partially hydrolyzed polyacrylamide (with 1% NaCl) was displaced through a core at constant flow rate. A cylindrical Berea core, 4 inches long and 1.25 inches in diameter was used for the displacement. The core was fitted with end caps and was coated with epoxy. Two pressure ports, embedded in the core, divided the core into three sections of equal length. Permeability of the three sections was found to be between 515 md to 530 md.

After saturation with 1% NaCl, polymer was injected into the core at a constant flow rate by oil displacing the polymer from the transfer cylinder. Pressure drop stabilized within a short time after break through. However to ensure no further build up of flow resistance due to filtration, four pore volumes of polymer solution were injected before the flow rate was varied for viscosity measurements. Flow rate was increased in steps from 0.02 mL/min to 3 mL/min and then reduced back to 0.08 mL/min. Pressure differentials along the three sections were continuously measured with time.

After the polymer displacement, 35 pore volumes of brine were injected into the core to flush out polymer. Post flush permeability of the core was estimated by measuring pressure drop across the core, while displacing brine at various flow rates.

Results and Discussion

Gel displacement in fracture model. Cr(III) HPAAm gelant was injected into the fracture at a constant flow rate of 4.6 mL/min. The back pressure, set at the fracture end, was 50 psi. More than an hour of injection was required for the fracture pressure to rise to 50 psi, and flow to begin at fracture end. Displacement continued for nearly 14 hours. The fraction of injected fluid that leaked off into the matrix during this period is plotted as a function of time in Figure 8.7.

Cumulative flow at fracture and matrix outlets is plotted in Figure 8.8. For first 1.25 hours, there was no flow at the fracture outlet. All the influent went out of the matrix at constant flow rate. Beyond this period, fracture flow increased for a short period, with matrix flow dropping significantly. Then both fracture and matrix flow gradually approached a steady value.
Figure 8.7 - Fraction of injected gelant that has leaked off (cumulative) with time.
Figure 8.8 - Cumulative flow at fracture and matrix outlets with time.
Pressure gradients (psi/inch) for the three fracture sections are plotted in Figure 8.9. There was a short initial plateau during the pressure build up period in the fracture, when injection rate into the fracture was constant and there was no gelant leaving the fracture outlet. Beyond this period, flow started at the fracture outlet and the pressure drop at three fracture sections changed discretely. A slow increase in pressure differential (which gradually flattened out) was due to increase in fracture flow rate with time. The maximum pressure gradient was observed in the first section, followed by second and third sections. This is in agreement with the fracture pressure profile (convex downward) deduced theoretically in Appendix 8A.

Pressure profiles for the matrix sections were nearly the same for all the four quadrants. Figure 8.10 represents pressure profile for one of the quadrants. For the first 1.25 hours, the leakoff rate remained constant with time. During this period, the overall pressure drop across the matrix quadrant, as well as pressure differential across the first two sections increased linearly with time. Once the gelant front crossed the first section, the pressure differential for that section became constant. All sections registered an immediate rise in pressure differential as the flow started. The maxima in the pressure profile for each section corresponds to the arrival of the viscous front. However the rise for the section adjacent to the fracture was significantly higher than the rise in pressure for other sections due to the contribution from viscous gelant. No second build up of pressure (expected for significant filtration) was observed during the course of the displacement experiment.

Fracture effluent gelled just like influent. Matrix effluent did not gel. Matrix effluent was colorless with a pH of 8.0, though it had the same viscosity as the injected gelant. A portion of the matrix effluent was mixed with 5% sodium hypochloride solution in the ratio of 2:1, and was left overnight to destroy the polymer. Atomic absorption spectrophotometry was used to determine chromium concentrations. The matrix effluent contained 3 ppm of chromium compared to 100 ppm in the injected gelant. Chromium was retained extensively in the matrix.

Gel was allowed to mature in the flow cell for seven days. Brine was then injected into the fracture, with the matrix outlets closed and the fracture outlet open to atmosphere. Air from a constant pressure source was used to displace the brine into the fracture. Pressure at the injection port was raised in steps of 5 psi. At each step, the pressure was held for 15 minutes. At a pressure of 10 psi, a sudden surge of brine flow began at the fracture outlet. Within a couple of minutes a gelatinous mass was extruded from the fracture and uninhibited fracture flow continued. Fracture permeability was found to be the same as it was before gel displacement.

Subsequently, the fracture end was closed, and matrix outlets were opened to atmosphere. Brine was injected into the fracture at constant pressure. Pressure profile for the matrix sections went through a transient phase, and a polymer solution was displaced from the matrix. When the pressure profile reached a steady state, flow rates from the matrix outlets were measured to estimate the permeability of the matrix sections. Pre and post gelation permeability values are presented in Figure 8.11. The permeability values suggest that there was a moderate reduction permeability throughout the matrix, and a significant reduction of permeability near the fracture face.
Figure 8.9 - Pressure differentials across the fracture sections during displacement.
Figure 8.10 - Pressure differentials across the matrix sections during displacement.
<table>
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<td>12</td>
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**Figure 8.11** - Permeability reduction in the fracture model after gelant displacement.
Leak off studies in unfractured core. The first leakoff experiment was conducted with bulk mixed gelant. This created uncertainty in the experiment because the gel was injected over a period of several hours and gelation was occurring in the bulk solution during injection. Inline mixed gelant was used to provide gelant with a constant age.

Figure 8.12 compares the cumulative flow of gelant for the four displacements at constant injection pressure of 70 psi. Decline in flow rates with time is evident for all the four cases. Maximum cumulative flow was observed for the displacement with no prior crosslinking, followed by displacements with three and six hours of prior crosslinking respectively. Cumulative flow for bulk mixed gelant showed up as an intermediate between all these three cases at different phases of displacement because the age of the injected gelant increased with time during placement.

Figures 8.13a,b,c,d compare the evolution of pressure differential across different sections of the core. Initial build up of pressure in each section represents the arrival of gel front in that section. Later, there was a sharp rise in pressure differential across the first section. The rise in pressure differential for the first section was delayed as the age of the immature gel increased.

The injected gelant had a pH of 4.8, and the pH of displaced brine was 8.7. After the break through of the gelant, the effluent had the same viscosity as that of the gelant, though the pH dropped gradually to a minimum of 8.0 for the case with no prior aging. The effluent was colorless, and never gelled. Atomic absorption spectrophotometry was performed on the degelled effluent to determine the chromium concentration. Chromium concentration in the effluent was 3 ppm while the injected concentration was 100 ppm. Thus, most of the chromium was stripped from the displacing gelant. Prior aging did not influence the chromium content in the effluent.

Gel was allowed to mature for seven days. Then, brine was injected at constant pressure (90 psi) to establish a brine flow through the core and to measure its permeability. Flow rate was transient as polymeric solution was displaced from the core (a quarter of a pore volume). Once a steady flow was reached, a reduction of over all permeability by three orders of magnitude was observed, with most of the flow resistance, contributed by the first two sections. In contrast, the post-flush permeability to brine was reduced by half in all the sections of the core when polymer (without the crosslinker) was displaced through Berea core.

Flow rate and pressure drop data were combined to obtain apparent viscosity using the following equation

\[ \mu_{app} = \frac{k\Delta p}{uL} \]  

Eq. 8.3

For polymer (without crosslinker) displacement, apparent viscosity of the displacing fluid in the three sections of the core is plotted against frontal advance rate in Figure 8.14. The power law exponent for the shear thinning region was found to be 0.23 – 0.25. Shear thickening began at a frontal advance rate of about 15 ft/day.
Figure 8.12 - Cumulative leakoff with time in unfractured cores.
Figure 8.13a – Pressure differentials across the sections of the unfractured core during leakoff of bulk mixed gelant.

Figure 8.13b - Pressure differentials across the sections of the unfractured core during leakoff of inline mixed gelant with no delay.
Figure 8.13c - Pressure differentials across the sections of the unfractured core during leakoff of inline mixed gelant with three hours delay.

Figure 8.13d - Pressure differentials across the sections of the unfractured core during leakoff of inline mixed gelant with six hours delay.
Figure 8.14 - Apparent viscosity of uncrosslinked polymer in the sections of Berea core at various frontal advance rates.
For the four displacement experiments with gelant, apparent viscosity is presented in Figures 8.15a,b,c,d, as a function of time and distance from the inlet face. There was a sharp gradient in apparent viscosity along the length of the core for all the four displacement experiments. The steep gradient in apparent viscosity is believed to be due to deep filtration of gel aggregates. Filtration was more extensive and filtration resistance was contained more near the inlet face when the gelant was aged prior to injection. For six hours of prior crosslinking, the gel front could travel only half way down the core.

Models of leakoff from the hydraulic fracturing literature [Penny, Conway, 1989] were used to analyze the displacement data. In these models, the cumulative volume that leaks off during hydraulic fracturing increases linearly with the square root of time over certain regions of the leakoff. Figure 8.16 is a typical plot of cumulative flow due to leakoff from a hydraulic fracture. Two linear segments are visible on Figure 8.16. The first linear segment represents viscous flow in the matrix. The slope of this segment is $2C_v$, where $C_v$ is the leakoff coefficient for viscous flow in the matrix. The cumulative flow during the viscous flow regime is given by Equation 8.4

$$V_{\text{cum}} = 2C_v \sqrt{t}$$

Eq. 8.4

The second linear region accounts for wall building at the fracture face. The cumulative flow during this period is expressed as Equation 8.5 where $C_w$ is the leakoff coefficient for wall building and $V_{\text{spurt}}$ is the spurt loss. The spurt volume, $V_{\text{spurt}}$, represents the amount of leakoff that is needed before filtration (wall building) begins at the face of the fracture.

$$V_{\text{cum}} = V_{\text{spurt}} + 2C_w \sqrt{t}$$

Eq. 8.5

The non linear region between viscous and wall building regions is where there is a transition from viscous displacement to wall building. In this region, the leakoff volume is approximated by Equation 8.6 where the total leakoff coefficient, $C_t$, is the harmonic mean of $C_v$ and $C_w$.

$$V_{\text{cum}} = 2C_t \sqrt{t}$$

Eq. 8.6

Figure 8.17 shows the cumulative flow for the three experiments plotted against the square root of time. The viscous leakoff region is present for each run and values of $C_v$ for each run were determined.

The linear regions in Figure 8.17 decrease in length as the gelant age increases. This reveals the shift of regime from viscous displacement to another leakoff mechanism. An attempt was made to fit Equation 8.5 to the data but a second linear region (characteristic of wall building) was not found because at the end of each experiment the flowrate was approaching zero. Values of $C_w$ and $V_{\text{spurt}}$ were estimated from the last data points and a combined leakoff coefficient ($C_t$) was estimated for each experiment. This model did not agree with the experimental cumulative flow-time data. Thus, the leakoff models used in hydraulic fracturing calculations do not adequately represent the leakoff process during injection of a gelant.
Figure 8.15a - Apparent viscosity in the sections of the unfractured core during leakoff of bulk mixed gelant.

Figure 8.15b - Apparent viscosity in the sections of the unfractured core during leakoff of inline mixed gelant with no delay.
Figure 8.15c - Apparent viscosity in the sections of the unfractured core during leakoff of inline mixed gelant with three hours delay.

Figure 8.15d - Apparent viscosity in the sections of the unfractured core during leakoff of inline mixed gelant with six hours delay.
Figure 8.16 - Typical plot of cumulative flow with square root of time.

Figure 8.17 - Cumulative leakoff in unfractured core with square root of time.
The apparent viscosity plots obtained from the pressure data show that the flow resistance behind the viscous gelant front increased continuously with time. Deep filtration of gel aggregates could explain these observations. Consequently, a comprehensive model of gelant leakoff with deep filtration was developed and used to match the experimental flow and apparent viscosity data. The model is described in the next section.

Theoretical Modeling

Displacement of viscous solution in fracture model. A theoretical model was developed to predict cumulative flow and pressure profile for displacement of a viscous solution through a fractured slab. First an analytical solution was obtained for simultaneous linear flows along fracture and matrix with the same viscosity for displacing and displaced fluids. Next the injection of a viscous fluid was modeled by assuming piston-like displacement with no dispersion. Details of this model are presented in Appendix 8A.

Glycerol was displaced through a fracture model similar to the one used for gelant displacement. Glycerol-brine solution of viscosity of 20 cp was injected through the fracture inlet at a flow rate of 15 mL/min and at a set back pressure of 25 psi at the fracture end. Injection into the fracture inlet was accomplished by an oil pump and a transfer cylinder. The fracture was flushed with glycerol just before the displacement run. Other experimental details were presented in the last annual report [Green et al., 1997]. The comparison of experimental data with prediction from theoretical model is presented in this section.

After injection started through the fracture inlet, about 5 minutes were required for the fracture pressure to rise to the selected back pressure. Flow at the fracture outlet started after this time period and matrix flow rate declined rapidly. Cumulative flow from the fracture outlet is compared with the flow from the simulation in Figure 8.18 as a function of time. Cumulative matrix flow in four quadrants is compared with the simulated cumulative flow in Figure 8.19.

The profiles approached to linearity with time indicating stabilization of leakoff rate as the viscous front traveled down the matrix.

Due to the linear front in the matrix, the pressure profile in the matrix was almost the same for all the quadrants. Figure 8.20 compares the pressure drop for matrix sections of one of the quadrants with the simulated pressure drop. All sections responded with an immediate build up of pressure differential as the flow started, followed by a drop for a short period of time because the matrix flow rate declined. However the rise in pressure differential for the section adjacent to the fracture was significantly higher than the other sections due to the contribution from the viscous fluid. Subsequently, the pressure differential for the section adjacent to the fracture dropped to a steady value due to the stabilization of leakoff rate. Arrival of the viscous front in other sections is noted by the rise in pressure differential for the respective sections. The mathematical model described well the displacement of brine by a viscous fluid in the fractured slab.
Figure 8.18 - Comparison of experimental and simulated flow (cumulative) from the fracture during glycerol displacement.

Figure 8.19 - Comparison of experimental and simulated flow (cumulative) from the matrix during glycerol displacement.
Figure 8.20 - Comparison of experimental (top) and simulated (bottom) pressure differentials across the matrix sections for Ely convert displacement in fractured core.
Leakoff Model with Deep Filtration of Gel Aggregates: A model was developed to simulate the cumulative flow and apparent viscosity profile from leakoff experiments. A review of apparent viscosity plots suggests movement of a viscous front along with deep filtration of gel aggregates. Displacement of gelant through the core is represented by the following mechanisms:

1. Movement of viscous front through the core at constant pressure. Change in viscosity of the displacing fluid with flow rate due to shear thinning nature of the gelant.
2. Permeability modification behind the gelant front due to deep filtration.

Mathematical expressions for the three mechanisms are given in Eq. 8.7 – 8.10

Darcy velocity of a viscous front displaced through the core at a constant pressure

\[ u = \frac{k \Delta p / \mu_w}{\sqrt{L^2 + 2(\mu / \mu_w - 1)k \Delta pt / \Phi \cdot \mu_w}} \]  

Eq. 8.7

- Shear thinning viscosity
  \[ \mu_{\text{shear}} = Ku^{n_e - 1} \]  
  Eq. 8.8

- Permeability profile within the gelant slug
  \[ \frac{1}{k_u} = \psi(Q, L_1, k_0, r_1, r_2, r_3) \]  
  Eq. 8.9
  with the average permeability across the gelant slug
  \[ \frac{1}{k} = \int_{0}^{L_1} \frac{dL_1}{k_u} \]  
  Eq. 8.10

where \( Q \) is cumulative flow, \( L \) is total length of the core, \( L_1 \) is the length of penetration of the gelant front, \( k_0 \) is the permeability before contact with gelant, \( k_u \) is the updated permeability, \( K \) and \( n_e \) are power law constants, \( \Delta p \) is the overall pressure drop across the core, \( \mu \) and \( \mu_w \) are the viscosity of displacing and displaced fluids, and \( r_1, r_2, r_3 \) are lumped parameters for filtration specific to the gelant of a particular age. The derivation of these relationships is presented in Appendix 8B.

The expression for velocity of the viscous front (Equation 8.7) is explicitly defined. Shear dependence of the viscosity term made Equation 8.7 implicit. Deep filtration modified the upstream permeability. Cumulative flow with time was predicted from integration of \( u \) in Equation 8.7, with the modifications in viscosity and permeability mentioned above. Apparent viscosity profile along the length of the core was predicted from the information on updated permeability and the shear thinning viscosity. Details are in Appendix 8B.

To model the displacement of viscous front at constant pressure by Equation 8.7, the input parameters required were the properties of the core, injection pressure and viscosity of displacing and displaced fluids. They were available from direct measurements. Power law constants for the
polymer were obtained from experimental data on polymer displacement. The deep filtration model required estimates of three parameters (lumped constants characterizing filtration-related properties of the gelant at a specific age) that were not available directly. Experimental data for cumulative flow with time was converted to average permeability of the portion of the core, flooded with gelant. Average permeability data as a function of cumulative flow was regressed with the model to obtain estimates of the lumped constants. The regression was comprised of the following computations.

At a given time / cumulative volume of effluent
A) Length up to which gelant front has penetrated (using cumulative flow with time data and porosity of the core)
B) Length of the brine slug in the core that is yet to be displaced (subtracting the length of the gelant slug from the length of the core)
C) Instantaneous flow rate (differentiating cumulative flow data with respect to time)
D) From B and C, pressure drop across the brine slug (using Darcy’s law)
E) From D, pressure drop across the gelant slug (subtracting the pressure differential across brine slug from the total pressure drop across the core (70 psi))
F) Power law viscosity for the flow rate obtained in C.
G) From E and F, average permeability across the gelant slug (using Darcy’s law).

The above steps were repeated for different times. Cumulative volume of effluent and average permeability across the gelant slug was plotted as a function of cumulative flow. This plot was regressed using Equation 8.7 to obtain estimates of lumped constants r₁, r₂, and r₃. A comparison of experimental and regressed permeabilities is presented in Figure 8.21. A typical set of lumped constants is reported in Table 8.1.

<table>
<thead>
<tr>
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<th>Zero delay</th>
<th>3 hrs delay</th>
<th>6 hrs delay</th>
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<tr>
<td>r₁</td>
<td>9.1e-13</td>
<td>2.7e-12</td>
<td>7.7e-12</td>
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<tr>
<td>r₂</td>
<td>0.07</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>r₃</td>
<td>7.0e+09</td>
<td>3.5e+09</td>
<td>3.01e+09</td>
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The dimension of r₁ is concentration of suspension at inlet per unit volume of porous media (ppm/cc). r₂ is filter coefficient, that has a dimension of inverse of length (per cm). The term r₃ is dimensionless.

A comparison of predicted and experimental cumulative flow as function of time is presented in Figure 8.22. Simulated apparent viscosity profiles for the three cases (representing displacement of gelant of age 0, 3, and 6 hours) are presented in Figures 8.23a,b, 8.24a,b, and 8.25a,b, respectively. The agreement between theoretical prediction and experimental data indicates that leakoff of Cr(III)-HPAAm gelant in Berea sandstone can be described by a displacement model which describes movement of a viscous front of power law fluid, with deep filtration of large particles behind the gelant front.
Figure 8.21 - Comparison of experimental and regressed average permeability in the gelant slug for leakoff experiments in unfractured cores.

Figure 8.22 - Comparison of experimental and predicted cumulative flow for leakoff in unfractured cores.
Figure 8.23a - Apparent viscosity (experimental) in the unfractured core for leakoff with no delay.

Figure 8.23b - Apparent viscosity (predicted) in the unfractured core for leakoff with no delay.
Figure 8.24a - Apparent viscosity (experimental) in the unfractured core for leakoff with three hours delay.

Figure 8.24b - Apparent viscosity (predicted) in the unfractured core for leakoff with three hours delay.
Figure 8.25a - Apparent viscosity (experimental) in the unfractured core for leakoff with six hours delay.

Figure 8.25b - Apparent viscosity (predicted) in the unfractured core for leakoff with six hours delay.
Conclusions
1. During displacement of a viscous fluid through the fracture model at constant pressure, leakoff rate stabilizes rapidly.
2. Cr(III)-HPAAm gelant behaves like a viscous fluid in a fractured Berea slab.
3. A mathematical model was developed that describes the displacement of brine by a viscous fluid in the fractured slab.
4. After maturity, the gel in the fracture extrudes on application of a small pressure gradient.
5. After displacement, permeability of the matrix, adjoining the fracture is reduced moderately all over the matrix, and significantly near the fracture face.
6. During leakoff in Berea sandstone, chromium is retained significantly in the matrix, rendering the leaked off fluid incapable of forming gel. Fracture effluent does not exhibit any loss of chromium.
7. Displacement of Cr(III)-HPAAm gelant in Berea core leads to build up of flow resistance, that has a downward gradient along the length of the core. Aging of gelant, prior to displacement, hastens the build up near the inlet face of the core.
8. Partially hydrolyzed polyacrylamide (5000 ppm Alcoflood 935 in 1% NaCl) in Berea core was found to exhibit lower and upper Newtonian behavior with a power law exponent of 0.23 – 0.25 in shear-thinning region.
9. A mathematical model was developed that describes the leakoff of a gelant into a linear system under a constant pressure drop. The agreement between predicted and experimental data for leakoff of a Cr(III)-HPAAm gelant into a Berea sandstone was satisfactory.

Present research focuses on further understanding of the extrusion of gel from fracture, matured in situ, and flow resistance, developed in the adjacent matrix.
Appendix 8A
Displacement of viscous fluid in fracture model

A theoretical model was developed accounting for two mutually perpendicular linear flows at steady state as shown in Figure 8.A1. One flow is along the fracture and the other flow is leak off into adjacent matrix (outlets open to atmosphere). The model is presented here in two steps.

A) Model for displacing and displaced fluid with same viscosity
B) Modifications to account for displacing fluid of higher viscosity

Figure 8.A1 -- Two linear flows in the fracture model.

When displacing and displaced fluids are of same viscosity, the differential equation that describes the pressure gradient along the fracture is given by Equation A1.

\[ \frac{d^2 p_f(x)}{dx^2} = \frac{k_m (p_f(x) - p_{am})}{k_r h b} \]  

Eq. A1

Boundary conditions are:

Constant flow rate at fracture inlet \[ \frac{dp_f}{dx} \bigg|_{x=0} = -\frac{q_{in} \mu}{2w k_r h} \]  

Eq. A2

Constant pressure at fracture outlet \[ p_f \bigg|_{x=x_f} = p_b \]  

Eq. A3

The analytical solution of Equation A1 with above set of boundary conditions is

\[ p_{id} \bigg|_{x=0} = \frac{\left( p_{bd} - \frac{e^{-\sqrt{A}}}{\sqrt{A}} \right) e^{\sqrt{A} x_f} + \left( p_{bd} + \frac{e^{\sqrt{A}}}{\sqrt{A}} \right) e^{-\sqrt{A} x_f}}{e^{\sqrt{A}} + e^{-\sqrt{A}}} \]  

Eq. A4
\[ p_{mD}|_{x_0,z_0} = p_{m}|_{x_0}[1 - z_D] \]  
Eq. A5

where \( A \) is a dimensionless constant, that characterizes the flow cell and is expressed as:

\[ A = \frac{k_m x_f^2}{k_f b h} \]  
Eq. A6

Other dimensionless variables are

\[ z_D = \frac{z}{b}; \quad x_D = \frac{x}{x_f}; \quad p_D = \frac{p - p_{am}}{\frac{q_{in} \mu x_f}{2 w k_f h}} \]  
Eq. A7

Typical pressure profile for the symmetric half of the fracture model, as obtained from above equation, is presented in Figure 8.A2. Pressure profile along the matrix is linear, however the same along the fracture is curved inside due to leakoff.

**Figure 8.A2 - Pressure profile (theoretical) in the fracture model.**

When displacing fluid has higher viscosity, different types of boundary conditions at fracture inlet and outlet lead to different transient distributions of flow in fracture and matrix, until the resident fluid is displaced completely. Three boundary conditions at fracture inlet and outlet were investigated.

- **BC1** Constant injection flow rate and constant back pressure at fracture outlet
- **BC2** Constant injection pressure and constant back pressure at fracture outlet
- **BC3** Constant injection flow rate and constant differential pressure along fracture
To account for a viscous front in the model, pressure profile in the matrix section was represented by two linear segments meshing each other at the location of the front (as described by lines AB and BC in Figure 8.A3). The extrapolation of linear segment for the viscous fluid (i.e., AB) meets the x-axis at C'. At this position of the front, pressure profile along the fracture and flow along fracture and matrix will be same as the pressure and flow profiles if the width of the matrix half is OC', and the entire matrix is flooded with viscous fluid. As the front moves down the matrix, OC' changes from zero to b.

Figure 8.A3 - Matrix pressure profile for displacement of a viscous solution in the fracture model.

Therefore a solution methodology was developed that uses the Equation A4, for flow through fracture with
i) entire matrix filled with viscous fluid
ii) OC', taken to be the width of the symmetric half of the matrix, changing with time

OC' is related to the length of penetration of the viscous front as follows

Equating the velocity of the displaced and displacing fluids (Figure 8.A3)
Combining Equations A8 and A9

\[
OC' = \frac{\Delta p_1 + \Delta p_2}{\Delta p_1} L_1
\]

Combining Equations A8 and A9

\[
OC' = \frac{\mu_w}{\mu} \left[ b + \left( \frac{\mu}{\mu_w} - 1 \right)L_1 \right]
\]

Accordingly the dimensionless constant A was modified as

\[
A(t) = \frac{k_m x_i^2}{k_r \mu_w \left( b + \left( \frac{\mu}{\mu_w} - 1 \right)L_1 \right) h}
\]

That is, constant A in Equation A4 was allowed to evolve with displacement. Material balance, across the whole viscous slug inside the cell, provided the other necessary specification. The difference between the flow rate at fracture inlet and outlet was equated with the rate of leakoff into the adjacent matrix (Figure 8.A3) for this purpose.

\[
q_{\text{in}} - q_{\text{out}} = A_r \phi \frac{dL_1}{dt}
\]

Where \( A_r \) is the total area on fracture face available for leakoff. For the three sets of boundary conditions at fracture ends, \( q_{\text{in}} \) and \( q_{\text{out}} \) are either specified, or they are expressed in terms of local pressure gradient as follows

\[
q = (2wh)u = -2wh \frac{k_r}{\mu} \left( \frac{q_{\text{in}} \mu}{2wk_r h} \frac{dP}{dx_D} \right)
\]

For BC3, the back pressure at the fracture outlet was to be adjusted such that the differential pressure across the fracture remained constant. Numerically this was accomplished by expressing \( p_b \) as difference between inlet pressure and differential pressure along the fracture, so that \( p_b \) evolved with time appropriately. For BC2 the fracture inlet was held at constant pressure instead of constant flow, that modified Equation A4. However the rate of leakoff for BC2 was practically same as that for constant pressure displacement in linear core (Equation A17 described later).

Finally the above set of equations constituted a nonlinear ordinary differential equation, which was solved numerically using MATLAB routine. Third order Runge-Kutta algorithm was employed for this purpose.
Leak off rate as a function of time for all the three cases is presented in Figure 8.A4. When the viscous solution fully displaces brine from the cell, all the three boundary conditions leads to the same flow. For comparison of the three cases, the boundary conditions had been chosen such that after complete invasion of the adjacent matrix by viscous solution, the injection flow rate became 15 mL/min and the back pressure at the fracture end was 25 psi. Other parameters for the simulation run was influent viscosity = 20 cp, displaced fluid viscosity = 1 cp, fracture aperture = 0.098 cm, matrix permeability = 81 md, matrix porosity = 0.12.

Velocity profile for all the three cases approached each other with rate of approach decreasing with time. Finally the velocity profiles converged to each other when viscous solution swept the flow cell completely. BC1 was implemented experimentally.

For injection at a constant back pressure, all the viscous solution goes into the matrix (and therefore it is a constant flow in the matrix) till the pressure in the fracture builds up to the set back pressure. Once sufficient viscous solution enters into the matrix to give a back pressure higher than the set back pressure at fracture end, fracture flow starts. This was accounted for in the model by meshing together the two regimes, wherever they intersect each other.

For quadrant wise analysis of cumulative flow in matrix, pressure drop along the fracture, and the time for development of pressure along the fracture were noted from the simulation discussed above. For this period, flow was distributed to all the quadrants, in the ratio of their permeabilities next to the fracture. For subsequent period, the same model, discussed before, was applied for each quadrant separately.

Appendix 8B
Leakoff model

Movement of viscous front under constant pressure. Figure 8.A5 describes the constant pressure flooding in an unfractured core. $L_1$ represents the distance up to which the gel front has penetrated into the core at time $t$. There is a break in the pressure profile at the position of the front, and the two linear segments represent pressure profile within the gelant and the brine front.

The velocity of the gel front and the brine front had to be the same for steady displacement. Using Darcy's law, the two fronts were equated as follows.

$$u = \frac{k \Delta p_1}{\mu L_1} = \frac{k \Delta p_2}{\mu_w L_2} = \frac{k(\Delta p_1 + \Delta p_2)}{\mu_w (\mu L_1 / \mu_w + L_2)} = \frac{k\Delta p}{\mu_w (L + (\mu / \mu_w - 1)L_1)}$$  \hspace{1cm} \text{Eq. A14}$$

Next, the front velocity was expressed as the rate of change of $L_1$.

$$\Phi \frac{dL_1}{dt} = \frac{k\Delta p}{\mu_w (L + (\mu / \mu_w - 1)L_1)}$$  \hspace{1cm} \text{Eq. A15}$$

On integration with boundary condition, $L_1 = 0$, @ $t=0$;
Figure 8.A4 - Comparison of leakoff rates for three types of boundary conditions.

Figure 8.A5. - Pressure profile for gelant displacement in the unfractured core.
\[ L_1 = \frac{-L + \sqrt{L^2 + 2(\mu/\mu_w - 1)k\Delta pt / \Phi \cdot \mu_w}}{\mu / \mu_w - 1} \]  
\text{Eq. A16}

And
\[ u = \frac{\Phi \frac{dL_1}{dt} = \frac{k\Delta p / \mu_w}{\sqrt{L^2 + 2(\mu/\mu_w - 1)k\Delta pt / \Phi \cdot \mu_w}}} \]  
\text{Eq. A17}

The cumulative flow with time was obtained by integrating the above expression.

**Power Law behavior of gelling solution.** Viscosity \( \mu \) in Equation A14 was replaced by \( \mu_{\text{shear}} \) to account for shear thinning behavior of polymer

\[ \mu_{\text{shear}} = K_1 \left[ \frac{k_1 \phi_1}{k_2 \phi_2} \right]^{\frac{n_w-1}{2}} u^{n_w-1} \]  
\text{Eq. A18}

Where \( K_1 \) and \( n_w \) are power law constants obtained from experiment with uncrosslinked polymer. \( k_1, \phi_1 \) are permeability and porosity of the medium, used for polymer displacement; \( k_2, \phi_2 \) are the same of the core, used for gel displacement. A detailed review on this expression is available in reference 8.

**Deep bed filtration.** The filtration of gel aggregates from the gelant is analogous to the filtration of particles from suspensions. In accordance with the fundamental hypothesis of deep bed filtration [Tien, 1989], the removal of particles from a suspension with respect to filter depth (here the depth up to which the gelant front has penetrated) is first order with respect to the particle concentration. That is,

\[ -\frac{\partial C}{\partial L_1} = \lambda C \]  
\text{Eq. A19}

Where \( C \) is the particle concentration in fluid, and \( \lambda \) is filter coefficient.

Particles removed from the suspension are deposited in the pores of the bed. That is

\[ -\frac{\partial C}{\partial L_1} = \frac{A_c}{\beta} \frac{\partial \sigma}{\partial Q} \]  
\text{Eq. A20}

Where 
\( \sigma \) is the specific deposit, expressed as volume of the particles deposited per unit filter volume, 
\( Q \) is the cumulative volume of fluid that has passed through the bed, 
\( A_c \) is the cross sectional area of the core, and 
\( \beta \) is a factor, to account for the compaction of the aggregates, as they are deposited on the pore wall.
There are functional forms in literature that relate change of filter coefficient to the specific deposit. These functions have the general form given by Eq. A21.

\[ \frac{\lambda}{\lambda_0} = f_1(\sigma) \]  

Eq. A21

Where \( \lambda_0 \) is filter coefficient at zero flow.

Elimination of \( C \) from Equations A17 and A18, and use of a form for \( f_1 \) from the literature led to

\[ \frac{\sigma}{\phi} = f_2 \left( \lambda_0, \frac{\beta}{\phi}, C_0, \lambda_0, Q, L \right) \]  

Eq. A22

The above expression gave a profile for specific deposit along the length of the gelant slug in terms of initial porosity and cross sectional area of the core, cumulative volume of gelant, that has passed through that location, and other filtration related parameters \((\lambda_0, \beta, C_0 (C \text{ at inlet}))\) characteristic of the gelant for a specific age.

The specific deposit constricts pores and causes the permeability to decrease. Equation A23 is a function that relates permeability to the specific deposit.

\[ \frac{k_u}{k_0} = f_3 \left( \frac{\sigma}{\phi} \right) \]  

Eq. A23

where \( k_0 \) is the permeability at a point in the core already flooded with gelant, and \( k_0 \) is the permeability before contact with gelant. The term \( k_0 \) is taken as \( k/3.5 \) for the three experiments simulated in this chapter. Therefore, Equation A23 provided an expression for the permeability profile along the portion of the core, flooded with gelant.

Average permeability across the gelant slug was obtained by integrating the permeability profile. That is

\[ \frac{1}{k(L)} = \frac{1}{L} \int_0^L \frac{dx}{k_u} \]  

Eq. A24

When the above integration is possible analytically, the above set of equations provides a functional form for average permeability across the whole gelant slug in terms of cumulative flow, properties of the core, and other filtration related parameters characterizing the injected gelant for a specific age. Regression of the functional form for average permeability with experimental data provided the estimate of the filtration related parameters.

Several researchers have proposed different functional forms for \( f_1 \) and \( f_3 \). A detailed listing is available in reference 9. Most of them were investigated for best fit of permeability data, as well as good prediction of apparent viscosity plot. Following forms were selected for the deep filtration model for gelant.
\[ f_1 = 1 - \frac{\lambda}{\lambda_0} \sigma^2 \]  
\[ f_3 = \frac{1}{1 - \beta' \frac{\sigma}{\phi}} \]

\[ \text{Eq. A25} \]
\[ \text{Eq. A26} \]

\( \lambda_1, \lambda_0, \beta' \) are constants. \( f_1 \) accounted for a second order decrease in removal rate with deposition. \( f_3 \) was originally derived for clogging of caverns by predominantly large particles in suspension. Details are available in reference 10.

Use of A25 and A26 led to following expressions for the permeability profile and the average permeability across the slug.

Local permeability within the gelant slug at a distance \( x \) from the inlet face

\[ k_o = \frac{1}{k_u} \left( 1 - \frac{r_3}{\sqrt{1 + \text{Re}^{5x}}} \right) \]

\[ \text{Eq. A27} \]

And average permeability across the slug

\[ \frac{k_o}{k} = \int_0^L k_o \frac{dx}{k_u} = \frac{1}{r_2 L (r_3^2 - 1)} \left[ \ln \left( \frac{1}{\sqrt{1 + \text{Re}^{5x}} - r_3} \right) \right]_{x=0}^{x=L_1} \]

\[ \text{Eq. A28} \]

Where

\[ R = \frac{4e^{5q}}{(e^{5q} - 1)^2}; \quad r_1 = \frac{\lambda_0 \beta C_0}{A_1 \phi}; \quad r_2 = \lambda_0; \quad r_3 = \frac{\lambda_0 \beta'}{\lambda_1 \phi} \]

Values of the lumped constants \( r_1, r_2, \) and \( r_3 \) were obtained by regression of experimental data on average permeability.

**Prediction from the model.** Once the filtration parameters were obtained, the permeability term in the viscous front model (Equation A11) was modified as follows

\[ u = \frac{k \Delta p_1 + k \Delta p_2}{\mu_w \left( L + \left( \frac{\mu_{\text{shear}}}{\mu_w} - 1 \right) L_1 \right)} \]

\[ \text{Eq. A29} \]

Accordingly, the \( \Delta p \) term in Equation A(17) was replaced by
For 6 hours old gel beyond 15 hours of displacement, the above methodology led to prediction of erratic cumulative flow. Cake filtration and contribution of filtrate to cumulative flow was taken to be responsible for this behavior. In accordance with the apparent viscosity plot, the gelant front was stalled externally and discharge of filtrate accounted for the subsequent flow.

The apparent viscosity was obtained from following expression.
\[
\mu_{app} = \frac{k_{old}}{k_{new}} \mu_{shear} = \frac{k}{k_u} \mu_{shear}
\]  
Eq. A30

**Nomenclature**

<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>A</td>
<td>dimensionless constant of the flow cell</td>
</tr>
<tr>
<td>A_r</td>
<td>Area available for flow, L^2</td>
</tr>
<tr>
<td>q</td>
<td>flow rate, L^3 T^-1</td>
</tr>
<tr>
<td>w</td>
<td>height of the cell, L</td>
</tr>
<tr>
<td>2h</td>
<td>fracture aperture width, L</td>
</tr>
<tr>
<td>k</td>
<td>permeability, L^2</td>
</tr>
<tr>
<td>p</td>
<td>pressure, ML^-1 T^-2</td>
</tr>
<tr>
<td>x</td>
<td>length along fracture axis, L</td>
</tr>
<tr>
<td>z</td>
<td>length along matrix axis, L</td>
</tr>
<tr>
<td>v</td>
<td>frontal advance rate (interstitial velocity), LT^-1</td>
</tr>
<tr>
<td>V</td>
<td>Volume, L^3</td>
</tr>
<tr>
<td>2b</td>
<td>flow cell width, L</td>
</tr>
<tr>
<td>L_1</td>
<td>depth of penetration of viscous front in the matrix, L</td>
</tr>
<tr>
<td>P_b</td>
<td>set back pressure, ML^-1 T^-2</td>
</tr>
<tr>
<td>q</td>
<td>flow rate, L^3 T^-1</td>
</tr>
<tr>
<td>Q</td>
<td>cumulative flow, L^3</td>
</tr>
<tr>
<td>k</td>
<td>permeability, L^2</td>
</tr>
<tr>
<td>C</td>
<td>suspension concentration, ML^-3</td>
</tr>
<tr>
<td>C</td>
<td>leakoff coefficient</td>
</tr>
<tr>
<td>t</td>
<td>time, T</td>
</tr>
<tr>
<td>x</td>
<td>distance from inlet face of the core, L</td>
</tr>
<tr>
<td>L</td>
<td>Length of the core, L</td>
</tr>
<tr>
<td>u</td>
<td>darcy velocity, LT^-1</td>
</tr>
<tr>
<td>K</td>
<td>flow constant for shear thinning region</td>
</tr>
<tr>
<td>n_e</td>
<td>power law constant</td>
</tr>
<tr>
<td>\Delta p</td>
<td>pressure drop across the core</td>
</tr>
<tr>
<td>R, r_1, r_2, r_3</td>
<td>lumped constants</td>
</tr>
</tbody>
</table>
Greek Symbols

\( \mu \) viscosity, ML^{-1}T^{-1}
\( \Phi \) porosity
\( \rho \) resistivity L^{-2}
\( \sigma \) specific deposit
\( \beta \) compaction factor
\( \lambda \) filter coefficient L^{-1}
\( \beta' \) factor to account for plugged pores that are not available for flow

Subscripts

\( f \) fracture
\( m \) matrix
\( atm \) atmosphere
\( in \) fracture inlet
\( out \) fracture outlet
\( w \) water
\( app \) apparent
\( o \) initial
\( old \) before gel displacement
\( new \) after gel displacement
\( D \) dimensionless variable
\( u \) updated
\( v \) viscous
\( w \) wall building
\( t \) total
\( shear \) shear dependent term
\( cum \) cumulative
Chapter 9

Gel Treatments in Production Wells

Principal Investigators: G. P. Willhite, D. W. Green and C. S. McCool
Graduate Research Assistant: Zhongchun Yan

Introduction
In an oilfield, crude oil is displaced into production wells by various driving forces. In most cases, oil flow is accompanied by water and the volume of water increases with time. Thus, large amounts of water must be lifted, separated and disposed of as a reservoir is depleted. The costs associated with water production are significant.

Some porous rocks, when treated with polymer solutions, show reduction of the permeability to water (at $S_{ow}$) to a larger extent than the permeability to oil (at $S_{iw}$). This property is termed disproportionate permeability modification, and suggests that the water-oil ratio can be reduced by treating a production well with a polymer solution [Seright and Liang, 1994; Liang et al., 1995; Zaitoun and Kohler, 1989; 1991; 1988; Parsons, 1975; Dawe and Zhang, 1994; Liang et al., 1994; Matre et al., 1995; Seright, 1993; 1996; White et al., 1973; Liang and Seright, 1997; Thompson and Fogler, 1997].

The mechanism of disproportionate permeability modification is not understood. The objective of this research is to simulate gel treatments in production wells and to investigate the effect of gel treatments on the effective permeabilities to water and oil over the range of saturations where two-phase flow exists. The results of this study will be used to examine the mechanisms of disproportionate permeability modification.

The relative permeability experiments were conducted in a Berea sandstone slab. Water saturations in the slab were determined using a microwave apparatus. The gelant used was a polyacrylamide-chromium(VI)-thiourea system. Relative permeabilities to water and oil were measured in the slab before it was treated with gel. A quarter of the length of the slab was then treated with the gel system and relative permeability measurements were repeated. Microwave saturation measurements could not differentiate between water and gel for these latter measurements. The effect of flow rate on relative permeability after gel treatment was also investigated.

Experimental
Apparatus. The principal apparatus for this study was a microwave scanning system shown in Figure 9.1. Microwave energy is absorbed by water to a significant degree, but relatively small amounts of the energy are absorbed by oil and rock. Thus the apparatus can be used to measure local water saturations in a rock-fluid system. Since a gel of the type used here is 99+ per cent water, the microwave measurements cannot differentiate between water and gel. The apparatus used is capable of scanning a slab core that is 6" wide, 3/4" thick by 4' in length during displacement tests. The microwave beam is focused as a one-inch diameter circle that is centered in the middle of the slab width. The microwave equipment is mounted on a trolley so that the device can scan along the length of a slab. Pressure drops during flow tests were measured across
the entire slab and four subsections using five differential pressure transducers. The pumps used for oil and water injection were Model 314 metering pumps supplied by Instrumentation Specialties Company (ISCO). A small-volume oil/water separator, invented by Bretz et al. [1984] was connected on-line to separate the oil and water in the effluent continuously.

Figure 9.1 - Schematic of microwave apparatus.
Materials. A Berea sandstone slab (61.1 cm long, 10.5 cm wide, and 1.74 cm thick) was used. A plexiglass endcap was attached to each end of the slab with epoxy. The endcap was fabricated with a groove on the surface which contacts the sandstone. The groove was made to distribute the oil and water uniformly across the inlet face of the slab during injection and to minimize accumulation of oil and/or water at the effluent end. The slab was evacuated and then saturated with brine to determine the porosity, which was 0.15. The permeability to brine was measured at a flow rate of 200mL/hr. The results are shown in Table 9.1.

**Table 9.1 - Absolute permeability of overall slab and four sections (md).**

<table>
<thead>
<tr>
<th></th>
<th>Overall</th>
<th>190</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section 1</td>
<td>182</td>
<td></td>
</tr>
<tr>
<td>Section 2</td>
<td>233</td>
<td></td>
</tr>
<tr>
<td>Section 3</td>
<td>188</td>
<td></td>
</tr>
<tr>
<td>Section 4</td>
<td>183</td>
<td></td>
</tr>
</tbody>
</table>

The oil-water fluid pair used in all experiments was n-dodecane and 2.0 weight percent NaCl. The densities and viscosities of n-dodecane and brine are shown in Table 9.2.

**Table 9.2 - Properties of 2% NaCl brine and n-dodecane.**

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity (cp)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@ 25°C</td>
<td>@ 30°C</td>
</tr>
<tr>
<td>2% NaCl brine</td>
<td>1.023</td>
<td>0.905</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>1.336</td>
<td>1.290</td>
</tr>
</tbody>
</table>

The gelant solution was 5000 ppm polyacrylamide (AlcoFlood 935)-1500 ppm thiourea-600 ppm sodium dichromate. The gelant composition was chosen by trial and error to obtain a beaker gel time of 40 hours, which was judged to be sufficient to place the gel into the slab before gelation occurred.

**Relative Permeability Measurements – Before Gel Treatment.** A schematic diagram of the apparatus is shown in Figure 9.2. Three pressure taps segmented the slab into four equal-length sections, labeled from 1 to 4. Pressure drops across the entire slab and the four sections were measured using five differential pressure transducers. Relative permeabilities were measured using the steady-state method by injecting water and oil at fixed ratios and measuring pressure drops and saturation after steady state was achieved. Flow was in direction #1 (section 1 → 4). Saturations were measured with the microwave apparatus. Pressure drop was limited to 80 psi across the slab.

Relative permeability curves were determined for both decreasing (drainage) and increasing (imbibition) water saturations. To prepare for relative permeability measurements, an oilflood and then a waterflood were run until steady states were reached. The endpoint permeabilities of water and oil were used to estimate flow rate limitations for relative permeability experiments.
Figure 9.2 - Apparatus for flow experiments.

**Gel Treatment.** The gel treatment procedure was designed to simulate an oilfield situation. Two-phase flow at 60% water and 40% oil fractional flow was run from direction #1 (Section 1→4) until a steady state was reached prior to gel treatment. Gelant (0.13 PV) was injected in direction #2 (Section 4→1) over 27.5 hours. This volume corresponds to 90% of the volume of water in Section 4 when this section is at residual oil saturation. Displaced fluid was separated by the water/oil separator and collected in graduated cylinders.
About 0.20 PV oil overflush followed the gelant solution. The overflush oil was injected to create oil flow channels after gel treatment. Without overflush, the pore space might be completely blocked, thus making oil production impossible after treatment. The slab was shut in for eight days to let the gel set up once the gelant injection and oilflush were completed.

**Relative Permeability Measurements – After Gel Treatment.** The same procedure was used as for the before-gel permeability measurements. Since the microwave apparatus cannot differentiate between free water and gel, measurements in this case reflected free water plus gel saturation.

**Flow Rate Effect on Relative permeability.** The effect of flow rate on relative permeabilities was tested at four different fractional flow conditions after gel treatment of Section 4. The different flow conditions were 1) waterflooding, 2) 25% water fractional flow, 3) 50% water fractional flow, and 4) oilflooding. The experimental procedure was to maintain the fractional flow of water and oil constant while the total flow rate was increased from one run to another. Pressure data were recorded continuously.

**Summary of Experiments.** The sequence of experiments is presented in Table 9.3.

<table>
<thead>
<tr>
<th>Table 9.3 - Experiment Sequence.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I</strong> Preliminary measurement</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>II</strong> Relative permeability before gel treatment</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>III</strong> Gel treatment</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>IV</strong> Relative permeability after gel treatment</td>
</tr>
<tr>
<td>Fractional flow sequence</td>
</tr>
<tr>
<td>b) Imbibition</td>
</tr>
<tr>
<td><strong>V</strong> Flow rate effect on effective permeability</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Results and Discussion

Relative Permeability before Gel Treatment. Relative permeabilities before gel treatment for the entire slab and for the four sections are given in Tables 9.4 and Table 9.5 and graphically shown in Figures 9.3 to 9.7.

Table 9.4 - Effective permeability results in a drainage process before gel treatment.

<table>
<thead>
<tr>
<th>Seq #</th>
<th>$q_w$ [mL/hr]</th>
<th>$q_o$ [mL/hr]</th>
<th>Overall $\Delta p$ [psi]</th>
<th>$S_w$ @ SS</th>
<th>$k_w$ [md]</th>
<th>$k_o$ [md]</th>
<th>Section 1 $\Delta p$ [psi]</th>
<th>$S_w$ @ SS</th>
<th>$k_w$ [md]</th>
<th>$k_o$ [md]</th>
<th>Section 2 $\Delta p$ [psi]</th>
<th>$S_w$ @ SS</th>
<th>$k_w$ [md]</th>
<th>$k_o$ [md]</th>
<th>Section 3 $\Delta p$ [psi]</th>
<th>$S_w$ @ SS</th>
<th>$k_w$ [md]</th>
<th>$k_o$ [md]</th>
<th>Section 4 $\Delta p$ [psi]</th>
<th>$S_w$ @ SS</th>
<th>$k_w$ [md]</th>
<th>$k_o$ [md]</th>
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<td>100%</td>
<td>0%</td>
<td>0</td>
<td>28.10</td>
<td>7.50</td>
<td>6.22</td>
<td>7.37</td>
<td>7.03</td>
<td>0.577</td>
<td>9.6</td>
<td>0</td>
<td>0</td>
<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.30</td>
<td>82%</td>
<td>18%</td>
<td>2.25</td>
<td>18.84</td>
<td>5.24</td>
<td>4.12</td>
<td>5.73</td>
<td>6.41</td>
<td>0.561</td>
<td>5.7</td>
<td>4.8</td>
<td>0</td>
<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10.49</td>
<td>61%</td>
<td>39%</td>
<td>6.72</td>
<td>22.98</td>
<td>5.86</td>
<td>5.00</td>
<td>5.73</td>
<td>6.41</td>
<td>0.561</td>
<td>5.7</td>
<td>4.8</td>
<td>0</td>
<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
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<td></td>
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<tr>
<td>4</td>
<td>4.28</td>
<td>51%</td>
<td>59%</td>
<td>6.08</td>
<td>10.62</td>
<td>2.95</td>
<td>2.07</td>
<td>2.47</td>
<td>3.25</td>
<td>0.555</td>
<td>4.6</td>
<td>8.5</td>
<td>0</td>
<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
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<tr>
<td>5</td>
<td>3.95</td>
<td>21%</td>
<td>79%</td>
<td>15.25</td>
<td>11.56</td>
<td>3.06</td>
<td>2.44</td>
<td>2.61</td>
<td>3.21</td>
<td>0.510</td>
<td>4.3</td>
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<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4.03</td>
<td>5%</td>
<td>95%</td>
<td>77.06</td>
<td>26.04</td>
<td>6.56</td>
<td>5.78</td>
<td>6.48</td>
<td>7.20</td>
<td>0.441</td>
<td>2.0</td>
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<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0%</td>
<td>100%</td>
<td>75.1</td>
<td>9.47</td>
<td>2.29</td>
<td>1.95</td>
<td>2.20</td>
<td>3.12</td>
<td>0.347</td>
<td>0</td>
<td>109.4</td>
<td>0</td>
<td>10.49</td>
<td>5.09</td>
<td>5.39</td>
<td>5.61</td>
<td>6.7</td>
<td>1.9</td>
<td></td>
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</tr>
</tbody>
</table>
Table 9.5 - Effective permeability results in an imbibition process before gel treatment.

<table>
<thead>
<tr>
<th>Seq #</th>
<th>q(_w) [mL/hr]</th>
<th>q(_o) [mL/hr]</th>
<th>Overall 1) Δp [psi] 2) S(_w) @ SS* 3) k(_w) [md] 4) k(_o) [md]</th>
<th>Section 1 1) Δp [psi] 2) S(_w) @ SS 3) k(_w) [md] 4) k(_o) [md]</th>
<th>Section 2 1) Δp [psi] 2) S(_w) @ SS 3) k(_w) [md] 4) k(_o) [md]</th>
<th>Section 3 1) Δp [psi] 2) S(_w) @ SS 3) k(_w) [md] 4) k(_o) [md]</th>
<th>Section 4 1) Δp [psi] 2) S(_w) @ SS 3) k(_w) [md] 4) k(_o) [md]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.0</td>
<td>75.1</td>
<td>9.47 0.337 1.95 0.341 2.20 0.357 3.12 0.347</td>
<td>0.0 144.5 0.0 175.1 0 155.2 0 109.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>4.05</td>
<td>23.18</td>
<td>6.08 0.461 4.97 0.486 5.51 0.493 6.49 0.465</td>
<td>0.0 23.18 0.0 65.0 0 58.7 0 49.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>3.95</td>
<td>14.51</td>
<td>3.72 0.521 3.07 0.545 3.78 0.536 3.98 0.512</td>
<td>0.0 19.9 0.0 23.5 0 19.1 0 18.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>9.94</td>
<td>27.05</td>
<td>7.45 0.538 5.68 0.570 6.43 0.561 7.37 0.539</td>
<td>0.0 19.9 0.0 12.5 0 11.0 0 9.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>10.01</td>
<td>24.18</td>
<td>6.09 0.545 5.37 0.575 6.00 0.568 6.62 0.543</td>
<td>0.0 5.9 0.0 6.5 0 5.8 0 5.3 0 4.8</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>12</td>
<td>10.00</td>
<td>20.62</td>
<td>5.36 0.555 4.56 0.579 5.04 0.567 5.74 0.540</td>
<td>0.0 5.9 0.0 7.7 0 6.9 0 6.4 0 4.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>9.61</td>
<td>17.21</td>
<td>4.96 0.558 3.92 0.582 4.51 0.582 3.97 0.552</td>
<td>0.0 7.8 0.0 8.6 0 7.4 0 8.5 0 0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: SS-Steady State
Figure 9.3 - Relative permeability before gel treatment — Overall;
Absolute permeability = 189.7 md.
Figure 9.4 - Relative permeability before gel treatment --Section 1; Absolute permeability = 182.2 md.
Figure 9.5 - Relative permeability before gel treatment --Section 2; Absolute permeability = 233.2 md.
Figure 9.6 - Relative permeability before gel treatment --Section 3; Absolute permeability = 187.7 md.
Figure 9.7 - Relative permeability before gel treatment —Section 4; Absolute permeability = 182.8 md.
Water permeabilities for the total slab and each section are consistent in the drainage and imbibition paths. For oil permeabilities, however, some hysteresis was observed. At high oil cut (oil fractional flow $>80\%$, water saturation $<0.5$), oil permeabilities in the imbibition path are higher than oil permeabilities in the drainage path. Otherwise, oil permeabilities in the drainage path are higher than oil permeabilities in the imbibition path.

Water saturation profiles measured during the experiments are presented in Figures 9.8 and 9.9. Most of the saturation change occurred at high oil cut both in the drainage and the imbibition paths.

The residual oil saturations for the entire slab and each section do not agree within experimental error. Water saturation at the end of the first waterflood was 0.03 PV higher than water saturation at the end of the second waterflood. The inconsistency in water saturation may be due to the differences of water flow rates. The first waterflood was conducted at the flow rate of 19.4 mL/hr or darcy velocity of 25.4 cm/day. The second waterflood was at the rate of 9.61 mL/hr. Its equivalent darcy velocity was 12.6 cm/day.

**Relative Permeability after Gel Treatment.** Results of effective permeability measurements after gel treatment are presented in Tables 9.6 and Table 9.7 for the drainage process and imbibition process respectively. Relative permeability of section 4, which is the gel-treated section, is shown in Figure 9.10. The hysteresis behavior is similar to that before gel treatment. Oil relative permeabilities at high oil cut in the imbibition path are higher than in drainage path. At low oil cut, oil permeabilities at the drainage path are higher.

Section 4 (after gel treatment) showed the typical behavior of a strongly water-wet medium. End-point permeability to oil is much higher than end-point permeability to water.

Comparisons of relative permeabilities of Section 4 before and after treatment are shown in Figure 9.11. The relative permeabilities to water and oil were both reduced significantly at all saturations. Oil relative permeability was decreased more than the relative permeability to water. The relative permeability curves of Section 4 after gel treatment were obtained at specific flow rates. Latter experiments showed that the relative permeabilities of the gel-treated section were not independent of flow rate.

Residual resistance factors in Section 4 are shown in Table 9.8. In this experiment, the oil residual resistance factor is higher than water residual resistance factor. That is, the oil permeability was reduced more significantly than water permeability.

Water saturation distributions along the slab were monitored during each experiment after gel treatment. Water saturation profiles at steady states for all fractional flows are shown in Figures 9.12 and 9.13. Similar to the water saturation profiles before gel treatment, most of the saturation change also occurred at high oil cut. Saturation of Section 4, compared with other sections, changed over a narrow range after gel treatment.
Figure 9.8 - Water saturation profiles at fractional flows before gel treatment; Drainage path and steady state.

Figure 9.9 - Water saturation profiles at fractional flows before gel treatment; Imbibition path and steady state.
Table 9.6 - Effective permeability of the slab in a drainage process after gel treatment.

<table>
<thead>
<tr>
<th>Seq #</th>
<th>q_w [mL/hr]</th>
<th>q_o [%]</th>
<th>Overall</th>
<th>Section 1</th>
<th>Section 2</th>
<th>Section 3</th>
<th>Section 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>u_o [cm/D]</td>
<td>1)Ap [psi]</td>
<td>2)S_w @ss</td>
<td>3)k_w [md]</td>
<td>4)k_o [md]</td>
<td>1)Ap [psi]</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.530</td>
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</tr>
<tr>
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<td>83%</td>
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<td>0.478</td>
<td>0.490</td>
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<td>0.502</td>
</tr>
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<td>4.76</td>
<td>4.76</td>
</tr>
<tr>
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<td>0.08</td>
<td>0.11</td>
<td>18.10</td>
</tr>
<tr>
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<td>95%</td>
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<td>0.418</td>
<td>0.444</td>
<td>0.478</td>
<td>0.478</td>
</tr>
<tr>
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<td>0.10</td>
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</tr>
<tr>
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<td>100%</td>
<td>0.451</td>
<td>0.404</td>
<td>0.447</td>
<td>0.479</td>
<td>0.479</td>
</tr>
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<td>1.14</td>
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<td>72.0</td>
<td>41.9</td>
<td>29.29</td>
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### Table 9.7 - Effective permeability of the slab in an imbibition process after gel treatment.

<table>
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<tr>
<th>Seq. #</th>
<th>q_w [mL/hr]</th>
<th>q_o [mL/hr]</th>
<th>Overall</th>
<th>Section 1</th>
<th>Section 2</th>
<th>Section 3</th>
<th>Section 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f_w [%]</td>
<td>f_o [%]</td>
<td>(psi)</td>
<td>(psi)</td>
<td>(psi)</td>
<td>(psi)</td>
<td>(psi)</td>
</tr>
<tr>
<td></td>
<td>u_w [cm/D]</td>
<td>u_o [cm/D]</td>
<td>1)Δp</td>
<td>2)S_w @ss</td>
<td>3)k_w [md]</td>
<td>4)k_o [md]</td>
<td>1)Δp</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0.98</td>
<td>15.13</td>
<td>0.08</td>
<td>0.06</td>
<td>0.10</td>
<td>14.68</td>
</tr>
<tr>
<td></td>
<td>0%</td>
<td>100%</td>
<td>0.451</td>
<td>0.404</td>
<td>0.447</td>
<td>0.479</td>
<td>0.473</td>
</tr>
<tr>
<td></td>
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<td>1.28</td>
<td>1.14</td>
<td>54.0</td>
<td>72.0</td>
<td>41.9</td>
<td>0.29</td>
</tr>
<tr>
<td>7</td>
<td>0.05</td>
<td>0.99</td>
<td>18.12</td>
<td>0.08</td>
<td>0.09</td>
<td>0.08</td>
<td>17.56</td>
</tr>
<tr>
<td></td>
<td>5%</td>
<td>95%</td>
<td>0.458</td>
<td>0.419</td>
<td>0.449</td>
<td>0.480</td>
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</tr>
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<td>1.64</td>
<td>1.91</td>
<td>0.009</td>
</tr>
<tr>
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<td>1.41</td>
<td>0.95</td>
<td>56.6</td>
<td>46.4</td>
<td>54.0</td>
<td>0.25</td>
</tr>
<tr>
<td>8</td>
<td>0.20</td>
<td>0.97</td>
<td>26.62</td>
<td>0.15</td>
<td>0.08</td>
<td>0.21</td>
<td>26.08</td>
</tr>
<tr>
<td></td>
<td>17%</td>
<td>83%</td>
<td>0.511</td>
<td>0.503</td>
<td>0.518</td>
<td>0.518</td>
<td>0.502</td>
</tr>
<tr>
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<td>0.26</td>
<td>1.27</td>
<td>0.09</td>
<td>4.08</td>
<td>7.65</td>
<td>2.87</td>
<td>0.02</td>
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<tr>
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<td></td>
<td></td>
<td>0.64</td>
<td>28.5</td>
<td>53.5</td>
<td>20.1</td>
<td>0.16</td>
</tr>
<tr>
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<td>27.15</td>
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<td>0.24</td>
<td>0.31</td>
<td>26.23</td>
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<tr>
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<td>45%</td>
<td>55%</td>
<td>0.520</td>
<td>0.508</td>
<td>0.532</td>
<td>0.531</td>
<td>0.510</td>
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<td>0.66</td>
<td>0.19</td>
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<td>5.20</td>
<td>4.04</td>
<td>0.05</td>
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<td></td>
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<td>0.32</td>
<td>9.04</td>
<td>9.04</td>
<td>7.02</td>
<td>0.08</td>
</tr>
<tr>
<td>10</td>
<td>0.34</td>
<td>0.20</td>
<td>21.71</td>
<td>0.20</td>
<td>0.32</td>
<td>0.20</td>
<td>20.88</td>
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<td>63%</td>
<td>37%</td>
<td>0.535</td>
<td>0.524</td>
<td>0.543</td>
<td>0.549</td>
<td>0.524</td>
</tr>
<tr>
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<td>0.45</td>
<td>0.26</td>
<td>0.20</td>
<td>5.23</td>
<td>3.35</td>
<td>5.22</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.16</td>
<td>4.30</td>
<td>2.76</td>
<td>4.29</td>
<td>0.04</td>
</tr>
<tr>
<td>11</td>
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<td>0</td>
<td>20.29</td>
<td>0.16</td>
<td>0.22</td>
<td>0.14</td>
<td>19.63</td>
</tr>
<tr>
<td></td>
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<td>0%</td>
<td>0.551</td>
<td>0.546</td>
<td>0.567</td>
<td>0.560</td>
<td>0.533</td>
</tr>
<tr>
<td></td>
<td>0.43</td>
<td>0</td>
<td>0.20</td>
<td>6.31</td>
<td>4.66</td>
<td>7.21</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### Table 9.8 - Residual Resistance factors of water and oil --section 4.

<table>
<thead>
<tr>
<th></th>
<th>Pre-treatment</th>
<th>Post-treatment</th>
<th>Residual resistance factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water permeability at oil residual saturation</td>
<td>9.6 md</td>
<td>0.04 md</td>
<td>( F_{rw} = 240 )</td>
</tr>
<tr>
<td>Oil permeability at interstitial water saturation</td>
<td>109.4 md</td>
<td>0.29 md</td>
<td>( F_{ro} = 377 )</td>
</tr>
<tr>
<td>Interstitial water saturation</td>
<td>0.347</td>
<td>0.473</td>
<td></td>
</tr>
<tr>
<td>Residual oil saturation</td>
<td>0.423</td>
<td>0.458</td>
<td></td>
</tr>
</tbody>
</table>
Figure 9.10 - Relative permeability after gel treatment — Section 4; Absolute permeability = 182.8 md (Pre-treatment).
Figure 9.11 - Comparison of relative permeability before and after gel treatment --Section 4; absolute permeability = 182.8 md (Pre-treatment).
Figure 9.12 - Water saturation profiles at fractional flows after gel treatment; Drainage path and steady state.

Figure 9.13 - Water saturation profiles at fractional flows after gel treatment; Imbibition path and steady state.
Flow Rate Effect on Relative Permeability of the Gel-treated Section. Effective permeabilities at the four fractional flows \( f_w = 100\%, 25\%, 50\%, 0\% \) are presented in Figures 9.14 through 9.17. In Section 4, both oil and water permeabilities increase with increasing flow rate. For each fractional flow condition, oil permeability is higher than water permeability at a specified darcy velocity. Oil and water effective permeabilities were correlated with darcy velocity with a power-law relationship presented in Table 9.9.

<table>
<thead>
<tr>
<th>Water fractional flow</th>
<th>Water effective permeability ((\text{md}))</th>
<th>Oil effective permeability ((\text{md}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_w = 1.0 )</td>
<td>( k_w = 0.081 , u_w^{0.67} )</td>
<td>0</td>
</tr>
<tr>
<td>( f_w = 0.25 )</td>
<td>( k_w = 0.064 , u_w^{0.57} )</td>
<td>( k_o = 0.13 , u_o^{0.67} )</td>
</tr>
<tr>
<td>( f_w = 0.50 )</td>
<td>( k_w = 0.096 , u_w^{0.48} )</td>
<td>( k_o = 0.18 , u_o^{0.49} )</td>
</tr>
<tr>
<td>( f_w = 0.0 )</td>
<td>0</td>
<td>( k_o = 0.66 , u_o^{0.47} )</td>
</tr>
</tbody>
</table>

Oil and water permeabilities for the untreated sections, 1 through 3, are also shown in Figures 9.14 through 9.17. No flow-rate effect was observed. Oil and water permeabilities were consistent for the three fractional flows \( f_w = 100\%, 25\%, \) and \( 50\% \). At interstitial water saturation \( f_w = 100\% \), oil permeability increased from one measurement to next one. This may be caused by the observed decrease of water saturation. A small amount of water (approximately 1.0 mL) was produced as the result of oilflooding.

The permeability of Section 1 is not consistent from test 1 to test 5 at 25% water fractional flow (Figure 9.15). This is believed to be caused by a capillary effect. A capillary effect occurred when the fluid phase which directly contacted the pressure port changed from water to oil or vice versa. The fluid phase change affected the pressure reading of the transducer to which the pressure port was connected because of capillary pressure.

Water saturations of the slab were monitored during the tests and are shown in Table 9.10. No significant variation was observed under the four test conditions.

As can be seen in Figures 9.14 through 9.16, there was no significant hysteresis observed at 100%, 25% and 50% water fractional flow when flow rate was varied. When the flow rate was decreased after an increasing path, water and oil effective permeabilities were reproducible. For the data in Figure 9.17, however, the oil end-point permeability is higher when the flow rate was lower. The higher oil permeability may arise from the slight decrease of water saturation during oilflooding.
Figure 9.14 - The effect of flow rate on effective permeability to water; 100% water fractional flow (Post-treatment).
Figure 9.15 - The effect of flow rate on effective permeability to water and oil;
25% water fractional flow (Post-treatment).
Figure 9.16 - The effect of flow rate on effective permeability to water and oil; 50% water fractional flow (Post-treatment).
Figure 9.17 - The flow rate effect on effective permeability to oil, 100% oil fractional flow (Post-treatment).
Comparison with Other Research. The variation of the relative permeability to water at $S_\text{or}$ (or actually $S_\text{or} + S_\text{gel}$) with superficial velocity in the gel treated section is consistent with data reported by Liang et al. [1995]. However, our data show that relative permeabilities of both oil and water vary with flowrate and saturation between the region of 100% water flow and 100% oil flow. In contrast, Liang et al. report that values of residual resistance factors to oil ($F_{\text{no}}$) were Newtonian and thus did not vary with flow rate for the systems they studied. Values of relative permeability at intermediate saturations were not measured by Liang et al.

We did not observe disproportionate permeability reduction for the system studied in this research. Residual resistance factors for oil and water were approximately the same after gel treatment. These experiments require much time to conduct and results from one system are reported. We do not know if the absence of disproportionate permeability modification for this system is due to the composition of the gelant or the placement procedure. Both oil and water phases were mobile when the gelant was placed and a small post placement oil flush was used to insure oil connectivity in the treated region following gelation.

<table>
<thead>
<tr>
<th>$f_w$</th>
<th>Test #</th>
<th>$u_w$ [cm/D]</th>
<th>$u_o$[cm/D]</th>
<th>Overall</th>
<th>Sect. 1</th>
<th>Sect. 2</th>
<th>Sect. 3</th>
<th>Sect. 4</th>
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<td>0.56</td>
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</tr>
<tr>
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<td>0.54</td>
<td>0.52</td>
</tr>
<tr>
<td>25%</td>
<td>5</td>
<td>0.81</td>
<td>2.62</td>
<td>0.52</td>
<td>0.51</td>
<td>0.54</td>
<td>0.53</td>
<td>0.50</td>
</tr>
<tr>
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<td>0.52</td>
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<td>0.50</td>
</tr>
<tr>
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<td>4.73</td>
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<td>0.54</td>
<td>0.53</td>
<td>0.50</td>
</tr>
<tr>
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<td>7.81</td>
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<td>0.52</td>
<td>0.54</td>
<td>0.52</td>
<td>0.49</td>
</tr>
<tr>
<td>50%</td>
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<td>1.18</td>
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<td>0.53</td>
<td>0.56</td>
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<td>0.52</td>
</tr>
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<td>0.53</td>
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<td>0.52</td>
</tr>
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<td>0.55</td>
<td>0.52</td>
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<tr>
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<td>8.62</td>
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<td>0.53</td>
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<td>0.55</td>
<td>0.52</td>
</tr>
<tr>
<td>0%</td>
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<td>0.40</td>
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<td>0.38</td>
<td>0.40</td>
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<td>0.34</td>
<td>0.37</td>
<td>0.39</td>
<td>0.40</td>
</tr>
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</table>
Conclusions
The following conclusions can be drawn for the particular gel system and porous medium used in this study:
1. The relative permeabilities to water and oil were decreased significantly by the gel treatment.
2. The residual resistance factors for oil and water are approximately the same.
3. The range of mobile saturation decreased significantly after gel treatment.
4. The permeabilities to both phases were functions of flow rates in the section of the slab treated by gel.
5. In the treated section, the effective permeability of each phase increased with increasing flow rate of that phase. The relationship between effective permeability and flow rate of each phase is logarithmically linear.
6. Hysteresis of relative permeability occurred both before and after gel treatment.
7. No hysteresis was observed in the gel-treated section due to flow rate changes.

Nomenclature
f  = fractional flow
F_{r} = residual resistance factor
k  = relative permeability
S  = saturation
u  = darcy velocity
Subscripts
o  = oil
w  = water or water and gel
r  = relative
Chapter 10

References

11. Dawe, R., and Zhang, Y.: "Gel micromodel experiment (Video)," (Sept. 1993).


