NUMERICAL SIMULATION OF pH-SENSITIVE

POLYMER INJECTION AS A CONFORMANCE CONTROL

METHOD

by

Ian Phillip Benson, B. S.

Thesis
Presented to the Faculty of the Graduate School of
The University of Texas at Austin
in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in Engineering

The University of Texas at Austin
May 2007
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Approved by
Supervising Committee:

______________________________
Steven L. Bryant

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Mukul M. Sharma

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Chun Huh
DEDICATION

This Thesis is dedicated to Gail, Christian, Clarissa and Callum Benson.
ACKNOWLEDGEMENTS

This work was supported by the Department of Energy grant #DE-FC26-04NT15520. The development and implementation of the pH-sensitive polymer rheological model in the GEM-GHG reservoir simulator that enabled this work can be attributed to the efforts of Dr. Mukul Sharma, Dr. Steven Bryant, Dr. Chun Huh, Dr. Long Nghiem, S. K. Choi, and F. Lalehrokh. The guidance and support of Drs. Sharma, Bryant and Huh is also appreciated.

May 2007
ABSTRACT

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by

Ian Phillip Benson, M.S.E.
The University of Texas at Austin, 2007

Supervisors: Mukul M. Sharma, Steven L. Bryant, Chun Huh

Polymers such as polyacrylic acid hydrogel are microgel solutions that exhibit large viscosity changes as their pH increases above a critical value. The Huh-Choi-Sharma rheological model developed previously for pH-sensitive polymer was successfully implemented in the commercial GEM-GHG reservoir simulator and tested. With the simulator’s ability to model geochemical reactions and to predict fluid pH, the polymer viscosity model allowed estimation of polymer solution viscosity based on the pH, ionic strength, shear rate and polymer concentration of an aqueous solution. Simulations of linear and radial geometry floods were carried out to test the effectiveness of using high-viscosity fluids and pH-sensitive polymers as an in-depth conformance control method in oil reservoirs.
Simulations were performed to history match the observed effluent pH profiles resulting from laboratory corefloods of Berea sandstone. Mineral selection, mineral concentrations, the type of mineral reaction equation used, and the selection of intra-aqueous reaction equations are variables that were changed to obtain suitable history matches. The Damköhler number was defined and employed for acid-mineral reactions for the simulations to group the effects of reservoir geometry, acid flow velocities and mineral reaction-rates. Simulations showed that increasing acid injection velocity, decreasing mineral reaction-rates, using acid preflushes and using weak acids can lower the Damköhler number of a reaction. This is usually desirable and necessary to place pH-sensitive polymer deep into a reservoir at low pH conditions in order to maintain low polymer viscosity.

Simulations and analytical calculations demonstrated that pH-sensitive polymer slug treatments may be a very effective conformance control method in linear and radial geometry floods with and without vertical crossflow. Simulations show that conventional polymer flooding is a better conformance control method in linear and injector-centered radial geometry reservoirs than continuous pH-sensitive polymer flooding. The geochemical history matching procedures described herein and the pH-sensitive polymer modeling capability developed for the GEM-GHG simulator will enable case-specific evaluation of pH-sensitive polymer injection for conformance control and environmental containment applications in the future.
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Chapter 1: INTRODUCTION

High current oil prices combined with the challenges of discovering and developing offshore and remote oil fields has made improving recovery from existing mature oil fields attractive. Eliminating excessive water production in mature fields is fundamental to lowering operating costs, increasing oil recovery, and making enhanced oil recovery (EOR) projects attractive in these fields. Recent estimates suggest that $100 billion is spent annually in the United States (Sharma, 2006) to address water handling expenses. Increasing the sweep efficiency of waterfloods and similar processes combined with lower operating costs to extend field life will improve field oil recoveries. The concept of increasing flooding sweep efficiency while reducing excess water production in oil fields is called conformance control. The purpose of this Thesis is to investigate the use of pH-sensitive polymer as a conformance control agent with numerical simulations employing a newly developed reservoir simulator feature.

Ideal conformance in a waterflood or EOR operation is when the injected fluid completely displaces all the oil in a flood pattern before it breaks through to a producer. Some methods proposed to improve conformance include workovers to plug old perforations and to create new perforations in a wellbore; polymer flooding; near wellbore polymer gel treatments; foams (Kabir, 2001); stimulating microbial growth (Gandler, 2006); downhole controls (Brnak et al., 2006); and chemical precipitation in thief zones (Asghari et al., 2006). Al-Anazi and Sharma (2002) proposed the idea of using pH-sensitive polymer as a conformance control method. The pH-sensitive polymer
process uses a polyelectrolyte polymer gel that exhibits a very large viscosity increase when its pH is raised from a low value to above a critical value. This Thesis investigates this concept using analytical and numerical simulation approaches.

Much work has been done earlier towards the goal of using pH-sensitive polymer as a conformance control method. Al-Anazi and Sharma (2002) demonstrated two requirements necessary to use pH-sensitive polymer \textit{in situ}. First, they showed that acid will react with Berea sandstone to form high pH brine. Second, they demonstrated that pH-sensitive polymer can be propagated some distance into a core. Choi (2005) conducted laboratory acid floods in Berea sandstone cores and measured effluent pH and cation concentrations to characterize the acid-matrix chemical reactions that occur in Berea core. Ermel (2005) modeled the coreflood acid-mineral reactions using the KGEOFLOW simulator (Sevougian \textit{et al.}, 1992).

**Scope of Project**

The goals of this project are threefold. The first is to model the mineral-acid reactions between acid and Berea sandstone using the GEM-GHG simulator to provide the mineralogy and mineral reaction-rate constants necessary to model the behavior of pH-sensitive polymer in a sandstone reservoir. The second is to compare the effectiveness of the use of pH-sensitive polymer as a conformance control method to the use of conventional polymers. The third goal is to identify the conditions that optimize the effectiveness of pH-sensitive polymer injection as a conformance control method. The
GEM-GHG simulator equipped with the pH-sensitive polymer rheological model developed by Huh, Choi and Sharma (2005) was used in this study.

**Mineral-Acid Reaction Modeling**

Acids usually react with petroleum reservoir rocks and alter the pH of reservoir brine. This reaction allows pH-sensitive polymer to be injected into a reservoir in a low pH, low-viscosity state and to achieve high viscosity *in situ* when the acidic polymer solution experiences a pH increase. The GEM-GHG simulator was used to model the matrix mineralogy, mineral concentrations and reaction constants that estimate the pH behavior of acid in Berea core reasonably well. These matrix properties can be used to model the pH and viscosity of the polymer-containing brine in a Berea sandstone reservoir. The Damköhler number is a dimensionless number that describes the ratio of the acid reaction-rate to the convection rate in a reservoir. The Damköhler number is used in this Thesis to describe the complex process conditions in an organized manner since it accounts for many variables including reservoir dimensions, reaction-rates, fluid flow rates and initial acid concentration.

**Comparison Between Uses of Regular Polymer and pH-Sensitive Polymer as Conformance Control Methods**

Polymers can be used for in-depth reservoir conformance control. Polymer floods improve the mobility ratio of a flooding operation which reduces fingering and diverts injected fluid into unswept areas of a reservoir. To investigate the advantages of employing the pH-sensitive polymers, simulations and analytical calculations are also
presented in this Thesis that describe the effect of injecting “conventional” polymers that do not exhibit pH sensitivity into a multiple-layer linear geometry flood that does not have crossflow between zones. Simulation results are given showing the beneficial effect of injecting conventional polymers into a reservoir when crossflow between layers is present. Simulation results are presented showing the effect of injecting pH-sensitive polymer into linear and radial geometry floods. pH-sensitive polymer simulations were run for reservoirs with and without vertical crossflow, and at conditions simulating various acid-matrix Damköhler numbers.

**Optimal Effectiveness of pH-Sensitive Polymer as a Conformance Control Method**

Simulations in this Thesis show that pH-sensitive polymer can effectively divert injected fluid into low-permeability unswept regions of a reservoir. It has been observed that continuous injection of pH-sensitive polymer into a reservoir can give highly variable oil recoveries depending on the reservoir geometry, the presence of crossflow, the Damköhler number, and the final viscosity of the polymer in situ.

**Overview of Simulations Performed**

Many simulations were performed for this Thesis to history match coreflood experiments, to demonstrate several methods to propagate low-pH fluid in a reservoir, to improve sweep efficiency in a single-phase (aqueous) two-layer reservoir, and to improve sweep efficiency in a two-phase (oil-water) two-layer reservoir. This overview of simulation results will help readers locate results and understand the general purpose for the simulations.
Chapter 4 documents history matching simulations performed to model the observed pH effluent observed during three acid corefloods performed by Choi (2005) in Berea cores. A four-mineral model was used for most of the simulations. Sensitivity cases that modeled deviations of one or several model parameters were performed to assess the impact of key parameters on the history match results. The sensitivity cases include usage of a one-mineral model to match observed coreflood effluent pH using a simple model.

Table 1-1: History Match Simulations Using Four-Mineral Model

<table>
<thead>
<tr>
<th>Description</th>
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<tbody>
<tr>
<td>Simulation of Berea Core Flood (Experiment 1)</td>
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<tr>
<td>-Effluent pH</td>
<td>Figure 4-1</td>
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<tr>
<td>Simulation of Berea Core Flood (Experiment 2)</td>
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<td>-Effluent Calcium Concentration</td>
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<td>-Reaction Affinity, Mineral Concentrations and Select Ion Concentration Profiles after 50 Pore Volumes Injected</td>
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<tr>
<td>Simulation of Berea Core Flood (Experiment 3)</td>
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<table>
<thead>
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<tr>
<td>Sensitivity Case Simulations of Berea Core Flood (Experiment 2)</td>
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<tr>
<td>- Effluent pH (Various Calcite Reaction Rates)</td>
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</tr>
<tr>
<td>- Effluent pH (Various Initial Calcite Volume Fractions)</td>
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<tr>
<td>- Effluent pH (Reaction Rates are First Order in Hydrogen</td>
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<tr>
<td>Sensitivity Case Simulation of Berea Core Flood (Experiment 1)</td>
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<td>- Effluent pH (Reaction Rates are First Order in Hydrogen</td>
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<td>- Effluent pH (Reaction Rates are First Order in Hydrogen</td>
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<td>Concentration)</td>
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<tr>
<td>Sensitivity Case Simulation of Berea Core Flood (Experiment 3)</td>
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<tr>
<td>- Effluent pH (Reaction Rates are First Order in Hydrogen</td>
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<tr>
<td>Concentration)</td>
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Chapter 5 documents simulations performed to investigate methods to propagate a low-pH fluid into a Berea sandstone reservoir by lowering the Damköhler number of an acid-matrix reaction. The four-mineral Berea mineralogy determined by history matching (from Chapter 4) was used for most of the simulations, although a one-mineral model was considered too. Chapter 5 simulations showed many in situ pH-profiles for acid
injection cases involving acid injection at different velocities, acid concentrations, acid types, and acid volumes.

**Table 1-4: Simulations Performed to Propagate a Low-pH Front in a Four-Mineral Reservoir**

<table>
<thead>
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<th>Description</th>
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<tbody>
<tr>
<td>In situ pH profiles in a 100-m reservoir</td>
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<tr>
<td>- After 1 PV of HCl injected (Various velocities)</td>
<td>Figure 5-2</td>
</tr>
<tr>
<td>- After 1 PV of HCl injected (Various concentrations)</td>
<td>Figure 5-3</td>
</tr>
<tr>
<td>- Corresponding mineral concentrations</td>
<td>Figure 5-4</td>
</tr>
<tr>
<td>- Corresponding Al+++ and H4SiO4 and H+ concentrations</td>
<td>Figure 5-5</td>
</tr>
<tr>
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<td>Figure 5-6</td>
</tr>
<tr>
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<td>Figure 5-7</td>
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<tr>
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</tr>
</tbody>
</table>

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<table>
<thead>
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<tbody>
<tr>
<td>In situ pH profiles in a 100-m reservoir</td>
<td></td>
</tr>
<tr>
<td>- After 1 molal acid injected (Various acid types)</td>
<td>Figure 5-10</td>
</tr>
<tr>
<td>- After pH=2 acid injected (Various acid types)</td>
<td>Figure 5-11</td>
</tr>
</tbody>
</table>

Chapter 6 investigates conformance control in 1D, water-filled reservoirs using pH-sensitive polymer and conventional polymers. Many of the results generated in this chapter are based on analytical calculations performed in spreadsheets. The simulations documented in this chapter are based on one-mineral mineralogy (calcite) that is not intended to represent a Berea sandstone matrix. The one-mineral reaction-rates were varied by case to present results in terms of Damköhler number of the acid-matrix reaction in the high-permeability layer of the reservoir.
Table 1-6: Simulations of Single-Phase Reservoir Floods

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fractional flow allocation of injected high viscosity fluid into a reservoir layer -Comparison of analytical result to simulation result</td>
<td>Figure 6-4</td>
</tr>
<tr>
<td>Swept volume versus volume of pH-sensitive polymer injected -Effect of Damköhler number on pH-sensitive polymer flood sweep efficiency -Viscosity profile at various times during $N_{Da}=1$ simulation</td>
<td>Figure 6-6 Figure 6-7</td>
</tr>
<tr>
<td>Swept volume versus volume fluid injected -Comparison of pH-sensitive polymer slug treatment sweep efficiency between analytical calculations and simulations</td>
<td>Figure 6-11</td>
</tr>
</tbody>
</table>

Chapter 7 documents two-phase (oil-water) simulations that compare oil recoveries from waterflood, polymer flood, pH-sensitive polymer flood and polymer slug treatment simulations for linear and radial reservoirs.

Table 1-7: Simulations of Linear Oil Reservoir Floods

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil recovery, well injection pressures and rates for a linear reservoir flood -High-viscosity fluid floods: Linear geometry without crossflow -High-viscosity fluid floods: Linear geometry with crossflow -pH-sensitive polymer floods: Linear geometry without crossflow -pH-sensitive polymer floods: Linear geometry with crossflow -pH-sensitive polymer and high-viscosity fluid slug treatments: Linear geometry without crossflow -pH-sensitive polymer and high-viscosity fluid slug treatments: Linear geometry with crossflow -pH-sensitive polymer slug treatment injected into high permeability zone: Linear geometry with and without crossflow</td>
<td>Figures 7-2 to 7-4 Figures 7-5 to 7-7 Figures 7-8 to 7-10 Figures 7-11 to 7-13 Figures 7-14 to 7-16 Figures 7-17 to 7-19 Figure 7-20</td>
</tr>
</tbody>
</table>
Table 1-8: Simulations of Radial Oil Reservoir Floods

<table>
<thead>
<tr>
<th>Description</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil recovery, well injection pressures and rates for a radial reservoir flood</td>
<td>Figures 7-22 to 7-24</td>
</tr>
<tr>
<td>-High-viscosity fluid floods: Radial geometry without crossflow</td>
<td>Figures 7-25 to 7-27</td>
</tr>
<tr>
<td>-High-viscosity fluid floods: Radial geometry with crossflow</td>
<td>Figures 7-28 to 7-30</td>
</tr>
<tr>
<td>-pH-sensitive polymer floods: Radial geometry without crossflow</td>
<td>Figures 7-31 to 7-33</td>
</tr>
<tr>
<td>-pH-sensitive polymer floods: Radial geometry with crossflow</td>
<td>Figures 7-34 to 7-36</td>
</tr>
<tr>
<td>-pH-sensitive polymer and high-viscosity fluid slug treatments: Radial</td>
<td>Figures 7-37 to 7-38</td>
</tr>
<tr>
<td>geometry without crossflow</td>
<td></td>
</tr>
<tr>
<td>-pH-sensitive polymer and high-viscosity fluid slug treatments: Radial</td>
<td>Figure 7-39</td>
</tr>
<tr>
<td>geometry with crossflow</td>
<td></td>
</tr>
<tr>
<td>-pH-sensitive polymer slug treatment injected into high permeability</td>
<td>Figures 7-40 to 7-41</td>
</tr>
<tr>
<td>zone: Radial geometry with and without crossflow</td>
<td></td>
</tr>
<tr>
<td>-pH-sensitive polymer and high-viscosity fluid flood for constant</td>
<td></td>
</tr>
<tr>
<td>reservoir pressure drop conditions: Radial geometry without crossflow</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 2: LITERATURE REVIEW

Waterfloods increase both the oil rate and the volume of recoverable oil from a field, but become very inefficient once the injected fluid channels through the reservoir directly to the production wells. It is desirable to improve the sweep efficiency of flooding operations to lower water treatment costs and to further improve oil recovery. Conformance control attempts to improve the sweep efficiency of a flood and consists of both wellbore workover methods and \textit{in situ} flow diversion methods.

Ideal conformance is when the displacing fluid completely displaces all the oil in a flood pattern before it breaks through to a producer. Such displacements are often referred to as piston-like displacements. Many methods have been attempted to improve conformance as described earlier. All of the methods work by reducing the flow rate through high-permeability thief zones near the injector well, the producer well, or throughout the reservoir. Mechanical workovers, polymer floods, polymer gel treatments and colloidal dispersion gel floods are common conformance control methods used in the field.

A mechanical workover is an operation that changes the configuration of a wellbore using downhole tools and treatments. Plugs, cement squeezes, and straddle packers (Bishop \textit{et al}., 2004) are some of the workover methods used to improve flood conformance. Workovers are most effective when the high-permeability thief zone can be identified and is not in vertical communication with the remaining zones. Water shut-off workovers often prevent any remaining oil in the thief zone from being recovered unless
another workover is performed later to reaccess the isolated reserves. Smart well controls operate in a manner similar to workovers except that smart wells contain downhole valves that control which zones in a completion are produced from or injected into at any given time.

Polymers are good in-depth conformance control because they can be propagated a long distance in the reservoir when adsorption and other polymer transport concerns are addressed in the flood design. They improve conformance in four ways. First, their increased viscosity compared to water alone improves the mobility ratio of a flood. Second, the higher pressure gradient required to propagate high-viscosity polymer compared to water or gas increases the flow rate of the injected fluid into the low-permeability zones in a horizontally layered reservoir. Sorbie and Mackay (2005) suggest that this benefit may not be as large as commonly believed for radial flood geometries and this general issue will be further addressed in Chapters 6 and 7. Third, conformance is improved by crossflow when a fluid with its mobility lower than the resident fluid’s is injected into a horizontally layered reservoir when the layers communicate vertically. Crossflow forces injected fluid from the high-permeability layers into the lower permeability layers to decrease vertical pressure difference between the layers (Zapata and Lake, 1981). Fourth, some polymers reduce the relative permeability of the aqueous phase which also retards polymer flow into the swept zone (Lake, 1989). Polyacrylamides and polysaccharides are the two common types of polymers used in polymer floods (Lake, 1989). Polyacrylamides such as HPAM (partially hydrolyzed polyacrylamide) are relatively inexpensive and resistant to bacterial attack but are
sensitive to water hardness and salinity. Polysaccharides like xanthan gum are susceptible to bacterial attack and are more expensive than polyacrylamide but are less sensitive to hardness and salinity. Polymer flooding field tests have been conducted extensively, e.g. the Chateaurenard field (Takagi et al., 1992).

Gel treatments are used for conformance control to block high-permeability zones. In situ gels are polymers that are injected with a crosslinker to form a stationary plug in the target reservoir zone to force displacing fluid around it into lower permeability zones. Research by Liu (2002) to investigate flow of gels in a reservoir as they crosslink in situ found that steady and unsteady viscous fingers may form as the gels crosslink depending on the Damköhler number of the displacement. Some of the issues with gel treatments include uncertainty regarding the mixing of the crosslinker and the polymer, the reaction time for the gel to set, the penetration depth of the gel, and gel degradation during injection. The crosslinkers used in gel treatments are often environmentally harmful and some are known to be carcinogens (Kabir, 2001). Work done by Raje et al. (1999) resulted in three gels that do not rely on a crosslinker but that decrease reservoir permeability when subjected to a low pH caused by supercritical CO$_2$. Many trials using gel treatments have been performed in the laboratory and in the field. One of many successful field trials of gel treatments is at the Rangely Weber Sand Unit field in Colorado that was treated with chromium polyacrylamide gels (Fullbright et al., 1996) and CO$_2$ gelled foam (Friedmann et al., 1999).
Colloidal dispersion gels (CDG) are gelled polymers that are crosslinked before they are injected into the reservoir. They form a high-viscosity microgel solution that is injected like a polymer flood. CDG flooding has been field tested in the Daqing field (Wang et al., 2006) with favorable results. Industry research such as the Bright Water (Frampton et al., 2004) project is investigating new crosslinked polymers that expand in situ to enhance conformance control.

A polyelectrolyte polymer called polyacrylic acid has recently been proposed for oilfield use as a conformance control agent (Al-Anazi and Sharma, 2002). Polyacrylic acid is attractive for oil field use due to its low cost, availability in industrial quantities and because it is environmentally benign. The novel property of polyelectrolytes is that their viscosity in solution is strongly dependent on the pH of the solution, and that the viscosity change is reversible. The viscosity behavior of the polymer is affected by the ionization of carboxylic (COOH) groups. At high pH values, the ionization of carboxylic groups causes an electrostatic repulsion between ionized groups (COO⁻) which causes the polymer chain to uncoil and expand, causing the polymer solution viscosity to increase. At low pH values, the ionized carboxyl groups are protonated and the repulsion forces are reduced. This causes the polymer chain to coil which lowers the solution viscosity. Many other factors also affect the viscosity of anionic polymers such as ionic strength, temperature, shear rate and polymer concentration. Al-Anazi and Sharma (2001) proposed using the viscosity change feature of polyelectrolytes such as polyacrylic acid and polymethacrylic acid to carry sand for gravel packing operations. The high-viscosity
polymer can carry sand effectively, but the polymer carrying fluid can be produced back after its viscosity has been lowered by an acid flush.

The main objective of this Thesis research is to use a reservoir simulator to assess the incremental oil recovery benefit, if any, of a pH-sensitive microgel flood over a waterflood and conventional polymer flood in a reservoir. It is necessary to model the mineral-acid reactions between acid and Berea sandstone using the GEM-GHG simulator to provide the mineralogy and reaction constants necessary to model the behavior of pH-sensitive polymer in a reservoir. Another objective of this research is to identify the conditions that optimize the effectiveness of pH-sensitive polymer as a conformance control method.

Effective simulation of pH-sensitive polymer floods requires a simulator capable of handling multiple fluid and mineral components, geochemical reactions and the viscosity behavior of the polymer. Aqueous and mineral species are required to model aqueous-mineral reactions, which determine the pH and ionic strength of the polymer solution in situ. The simulator must accurately calculate the viscosity of the pH-sensitive polymer according to the viscosity model (Huh et al., 2005) in order to effectively estimate the incremental oil recovery associated with the use of this polymer. The simulator used for this work is the Computer Modelling Group’s GEM-GHG compositional simulator. This simulator includes a polymer viscosity program implemented by CMG that effectively models the behavior of pH-sensitive polymer.
There has been a great deal of literature published regarding various facets of the processes affecting the viscosity of pH-sensitive polymer *in situ*. Discussion of these processes follows.

Conventional acidizing technology literature discusses the dissolution of minerals into an aqueous phase. Acidizing reactions cause the pH of injected acid to increase, which will serve as a ‘trigger’ for the viscosity of pH-sensitive polymer to increase *in situ*. Economides *et al.* (1994) discuss the common two-mineral model used to describe acidizing reactions. The two-mineral model represents the reservoir as having a fast reacting mineral and a slow reacting mineral, along with a non-reacting matrix. Such models often do not represent the complex geochemistry occurring in a reservoir, and more complex simulation models are often used. Geochemical simulators such as KGEOFLOW (Sevougian *et al.*, 1992), Geochemist’s Work Bench (Bethke, 2006), TOUGHREACT (Xu *et al.*, 2004), PHREEQC (Parkhurst and Appelo, 1999), GEM-GHG (Nghiem, 2002) and others are commonly employed to model mineral reactions and intra-aqueous reactions involving several minerals. Geochemical simulators model complex phenomena such as mineral precipitation and intra-aqueous species equilibrium reactions that conventional reservoir simulators are not designed to handle.

Geochemical reactions consisting of the dissolution or precipitation of minerals in a formation are closely related with the reactions occurring within the aqueous phase. Sevougian *et al.* (1992) presented the partial local equilibrium assumption (PLEA) that simplifies the modeling of geochemical reactions by assuming that kinetically controlled
mineral reactions limit the overall reaction-rate between minerals and an aqueous phase. Partial local equilibrium allows the dissolution of the reactive minerals to be modeled as a kinetic (rate controlled) reaction whereas the reactions between chemical species in the aqueous phase are modeled to achieve equilibrium instantaneously. The PLEA assumption is employed by the GEM-GHG simulator used for modeling pH-sensitive polymer in this Thesis. The critical assumption made in the PLEA is that aqueous reactions occur instantaneously which is not true physically, but is reasonable when the aqueous reactions occur much faster than mineral dissolution and precipitation reactions. It is imperative that all the necessary aqueous reactions be included in a geochemical simulation to produce acceptable results. Ideally all reactions that are possible between H⁺, OH⁻, water, mineral anions and cations, initial brine ions and injected fluid ions should be modeled. Lake et al. (2002) suggest “knowing when and what to neglect comes about only through running the full problem – or through experience.” Nghiem (2003) demonstrated the importance of modeling the correct aqueous reactions by showing significantly different mineral dissolution volumes of a mineral in two geochemical simulation runs that differ only in the number of aqueous reactions modeled.

It is desired to model the reactions of Berea sandstone with injected fluid in this study to model the reaction of acid with sandstone. Ermel (2005) summarized Berea compositions given in the literature which generally include a large proportion of quartz with small proportions of carbonate, feldspars, and clays (illite, smectite, chlorite, kaolinite). Modeling the presence of these minerals requires reaction equations, reaction equilibrium constants and reaction-rate constants. Lake et al. (2002) give solubility products for
common reservoir minerals. Kharaka et al. (1988) give reaction equations for many reservoir minerals. Palandri and Kharaka (2004) give rate constants for Arrhenius-type rate reactions for more than 70 minerals based on an extensive literature review. Arrhenius-type reactions exhibit reaction-rates that change with temperature. Palandri and Kharaka identified rate constants at acid, neutral and basic pH values, demonstrating a reaction-rate dependence on pH.

Ermel (2005) researched the problem of propagating pH-sensitive polymer in a sandstone core using the KGEOFLOW reactive transport simulator. KGEOFLOW was used to history match the pH of effluent from Berea corefloods conducted by Choi (2005). Propagating a low pH fluid front requires consideration of geochemical reactions and the Damköhler number associated with the acid-mineral reactions.

Polymer transport in porous media involves phenomena such as polymer dispersion, excluded/inaccessible pore volume phenomena, adsorption, and viscous fingering. Sorbie (1991) presents both mathematical equations and coreflood results that study these phenomena along with others. Choi et al. (2005) investigated the polymer transport mechanisms of several pH-sensitive polymers. Choi measured microgel particle sizes, microgel settling times, and characterized particle interaction to estimate the degree of pH-sensitive polymer adsorption and straining/filtration in field applications. Polymer transport phenomena are not addressed in this Thesis though they strongly influence the feasibility of polymer usage in a reservoir or geological formation.
Polymer rheology strongly affects the flow behavior of polymer in porous media. Huh et al. (2005) developed a rheological model to describe the viscosity behavior of a pH-sensitive polymer that can be adapted to a reservoir simulator. The Huh-Choi-Sharma rheological model describes polymer viscosity as a function of pH, polymer concentration, shear rate, ionic strength and other factors. A detailed description of this model and how it was implemented in the GEM-GHG simulator for this research is given in the next chapter.
Chapter 3: RESERVOIR SIMULATOR DESCRIPTION AND pH-SENSITIVE POLYMER RHEOLOGY ROUTINE

The GEM–GHG simulator equipped with pH-sensitive polymer viscosity code was used for this research project because it is a compositional reservoir simulator that models geochemical reactions and the rheological behavior of pH-sensitive polymer. This chapter is divided into two sections. The first section describes the Computer Modelling Group’s GEM simulator with additional green house gas (GHG) geochemical reaction capabilities. Equations used in the GEM-GHG simulator pertinent to the simulations performed are also given (from Nghiem, 2002-2006). The second section describes the additional viscosity routine implemented in the simulator that models the rheology of pH-sensitive polymer.

3.1 Description of the GEM-GHG Simulator

GEM, or Generalized Equation of State Model, is a reservoir simulator that can model three-phase multicomponent fluid flow in geologic formations. Separate fluid parameters are required for the aqueous and hydrocarbon phases. The GHG program (version 2004-19a) included in the version of GEM used for this project allows intra-aqueous reactions in the aqueous phase and geochemical reactions between minerals and aqueous species. The chemical reactions are determined by user-defined stoichiometric reactions. This version of the code was developed to model the sequestration of carbon dioxide which can cause geochemical reactions in an aquifer or petroleum reservoir. All equations presented in this chapter assume the use of metric units.
GEM-GHG Calculations and Input Parameters

The GEM-GHG simulator with pH-sensitive polymer capabilities, hereafter referred to as GEM, solves fluid flow and chemical reactions by solving transport and reaction equations for every component each timestep. The principal processes modeled include fluid transport and chemical reactions.

Fluid Properties and Species Definition

GEM requires hydrocarbon and aqueous species to be defined. Water properties are built into the simulator and need not be entered.

GEM models hydrocarbon oil and gas properties using an equation of state. The C7-16 pseudo-component properties characterized by Khan (1992) from a JEMA oil sample were used in the simulations. This oil has a viscosity of 1.09 cp at conditions of 10 MPa and 25 °C.

Table 3-1: Oil Species Properties

<table>
<thead>
<tr>
<th>Hydrocarbon Component</th>
<th>Critical Pressure (atm)</th>
<th>Critical Temperature (K)</th>
<th>Critical Volume (m³/(kg mol))</th>
<th>Accentric Factor</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C7-16</td>
<td>20.6764</td>
<td>611.116</td>
<td>0.58957</td>
<td>0.6386</td>
<td>147.182</td>
</tr>
</tbody>
</table>

Aqueous species must be defined to describe the components that are present in the aqueous phase. These species are initially present in the reservoir, or result from mineral dissolution reactions, intra-aqueous reactions or fluid injection into the model. The
charge and ion-size parameters may be used for calculation of ionic strength of the aqueous phase depending on the ion activity model chosen. The species properties given below are those used for the “final-match” case discussed later in Chapter 4.

Table 3-2: Aqueous Species Properties for Final-Match Simulation

<table>
<thead>
<tr>
<th>Species Label</th>
<th>Molecular Weight (g/mol)</th>
<th>Ion Size (Angstroms)</th>
<th>Ionic Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLM</td>
<td>1500000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H⁺</td>
<td>1.00794</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>40.078</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>K⁺</td>
<td>39.0983</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Na⁺</td>
<td>22.98777</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>26.98154</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>35.453</td>
<td>3</td>
<td>-1</td>
</tr>
<tr>
<td>CO₃⁻</td>
<td>60.0092</td>
<td>4.5</td>
<td>-2</td>
</tr>
<tr>
<td>H₄SiO₄</td>
<td>96.11486</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>61.01714</td>
<td>4.5</td>
<td>-1</td>
</tr>
<tr>
<td>Al(OH)₄⁻</td>
<td>95.0109</td>
<td>4</td>
<td>-1</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>62.02508</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OH⁻</td>
<td>17.00734</td>
<td>3.5</td>
<td>-1</td>
</tr>
</tbody>
</table>

Fundamental Transport Equations

Fundamental transport equations describe the flow of hydrocarbon and aqueous species, and the mineral concentrations, at each point (at the representative elementary volume scale) in a reservoir. The following equations assume constant porosity and velocity:
For each species \(i\) in the hydrocarbon phase:

\[
\phi \frac{\partial C_i}{\partial t} + u \vec{\nabla} \cdot C_i = r_i
\]  

(3-1)

where \(C_i\) is the concentration of species \(i\) (mass of species \(i\) / mass of the hydrocarbon phase), \(\phi\) is porosity, \(t\) is time, \(r_i\) is the rate of transfer of \(i\) to the aqueous phase (\(r_i\) is 0 except when Henry’s law constant is used), and \(u\) is the Darcy velocity of the hydrocarbon phase. Dispersion is not included in Equation 3-1, but can be modeled with GEM if desired.

For each species \(i\) in the aqueous phase:

\[
\phi \frac{\partial C_i}{\partial t} + u \vec{\nabla} \cdot C_i = R_i + r_i + K_i \left[ \vec{\nabla} \cdot C_i \right]
\]  

(3-2)

where \(C_i\) is the concentration of species \(i\) (mass of species \(i\) / mass of the aqueous phase), \(t\) is time, \(\phi\) is porosity, \(R_i\) is the reaction-rate of species \(i\) and \(r_i\) is the rate of transfer from the hydrocarbon phase, \(K_i\) is the dispersion coefficient of species \(i\), \(u\) is the Darcy velocity of the aqueous phase.

For each rock mineral species in the solid phase:

\[
\phi \frac{\partial C_i}{\partial t} = -R_i
\]  

(3-3)

where \(C_i\) is the concentration of mineral species \(i\) (mass of species \(i\) / mass of the solid phase), \(t\) is time, \(\phi\) is porosity, and \(R_i\) is the reaction-rate of species \(i\).
The GEM-GHG simulator solves component mass-balance, finite-difference equations for gas, oil and water components for each grid block in the simulator that have a different form than Equations 3-1, 3-2 and 3-3 (Computer Modelling Group, 2006). The simulator solves equations shown later to determine reactive mineral concentrations in each grid block.

**Chemical Reactions**

GEM models chemical reactions using two methods. The first method is to model homogeneous chemical reactions in the aqueous phase as those that achieve equilibrium instantaneously. The second method is to model mineral dissolution or precipitation reactions with aqueous ions as rate controlled reactions.

The stoichiometric coefficients \((v_k)\) for any reaction must satisfy the requirement:

\[
\sum_{k=1}^{n_s} v_k A_k = 0
\]

(3-4)

where \(A_k\) is the species name, \(k\) is the species number, and \(n_s\) is the total number of species present in the simulation. In GEM, no minerals may be involved in the intra-aqueous equilibrium reactions, and only one mineral component \(A_k\) may be present in a rate controlled reaction.
Intra-Aqueous Equilibrium Reactions

A chemical reaction is in equilibrium if the forward reaction-rate and backward reaction-rates are equal giving a net reaction-rate of zero. GEM models reactions between ionic species in the aqueous phase as equilibrium reactions.

Reactions in equilibrium satisfy the following condition:

\[
Q - K_{eq} = 0
\]  

(3-5)

where \[ K_{eq} = \exp \left( -\frac{1}{RT} \sum_{k=1}^{n_s} \nu_k \left( \Delta G_f^0 \right)_k \right) \]  

(3-6)

and \[ Q = \prod_{k=1}^{n_s} (a_k)^{\nu_i} = \text{activity product of reaction} \]  

(3-7)

where \( n_s \) is the number of species in an intra-aqueous equilibrium reaction, \( a_k \) is the activity of each species in the aqueous phase, \( K_{eq} \) is the equilibrium constant for the chemical reaction, \( R \) is the universal gas constant, \( T \) is the fluid temperature, \( \nu_i \) is the stoichiometric coefficient of a species for the chemical reaction, and \( \Delta G_f^0 \) is the Gibbs free energy for each species.

Activities for each species \( (a_k) \) are related to their concentration in solution. The activities of water and the mineral species can be taken to be unity without introducing significant errors (Helgeson et al., 1970). Activities in ideal cases can be taken to be approximately equal to the concentration of the species (in molality). Such “ideal” activities were used
for the simulations performed, although GEM also offers the Debye-Huckel and B-dot methods to calculate activities.

Modeling intra-aqueous reactions as instantaneous equilibrium reactions neglects their actual reaction times, but this simplification allows increased computational efficiency by permitting the use of an equilibrium-rate-annihilation (ERA) matrix that reduces the number of flow equations (Nghiem, 2002). Neglecting the reaction-rates of intra-aqueous reactions is reasonable assuming that mineral reactions control the net reaction-rates in the brine.

Defining equilibrium reactions in GEM is done by defining the number of equilibrium reactions with the *N-CHEM-EQUIL keyword, defining whether numerical or analytical rate derivatives should be used, and by defining the stoichiometric coefficients for each reaction using the *STOICHIOMETRY keyword

The equilibrium reactions modeled in the history match simulations described in Chapter 4 are given below. These values were taken from Stumm and Morgan (1996). Only the intra-aqueous reactions that included species present in the reservoir minerals were included in the simulations performed in this Thesis.
Table 3-3: Intra-Aqueous Reactions Equilibrium Constant Values

<table>
<thead>
<tr>
<th>Equilibrium Reaction</th>
<th>Log $K_{eq}$ (25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$</td>
<td>-10.329</td>
</tr>
<tr>
<td>$\text{Al}^{+++} + 4 \text{H}_2\text{O} = \text{Al(OH)}_4^- + 4 \text{H}^+$</td>
<td>-22.7</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3 = 2 \text{H}^+ + \text{CO}_3^{2-}$</td>
<td>16.6</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$</td>
<td>-14</td>
</tr>
<tr>
<td>$\text{Mg}^{++} + \text{CO}_3^{2-} = \text{MgCO}_3(\text{aq})$</td>
<td>2.98</td>
</tr>
<tr>
<td>$\text{Mg}^{++} + \text{HCO}_3^- = \text{MgHCO}_3^+$</td>
<td>1.07</td>
</tr>
<tr>
<td>$\text{Mg}^{++} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$</td>
<td>-11.44</td>
</tr>
<tr>
<td>$\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH}(\text{aq}) + \text{H}^+$</td>
<td>-14.18</td>
</tr>
<tr>
<td>$\text{K}^+ + \text{H}_2\text{O} = \text{KOH}(\text{aq}) + \text{H}^+$</td>
<td>-14.46</td>
</tr>
<tr>
<td>$\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$</td>
<td>1.27</td>
</tr>
<tr>
<td>$\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3(\text{aq})$</td>
<td>-0.25</td>
</tr>
<tr>
<td>$\text{Ca}^{++} + \text{CO}_3^{2-} = \text{CaCO}_3(\text{aq})$</td>
<td>3.224</td>
</tr>
<tr>
<td>$\text{Ca}^{++} + \text{HCO}_3^- = \text{CaHCO}_3^+$</td>
<td>1.106</td>
</tr>
<tr>
<td>$\text{Ca}^{++} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$</td>
<td>-12.78</td>
</tr>
<tr>
<td>$\text{Al}^{+++} + \text{H}_2\text{O} = \text{AlOH}^{++} + \text{H}^+$</td>
<td>-5.00</td>
</tr>
<tr>
<td>$\text{Al}^{+++} + 2 \text{H}_2\text{O} = \text{Al(OH)}_2^+ + 2 \text{H}^+$</td>
<td>-10.1</td>
</tr>
<tr>
<td>$\text{H}_4\text{SiO}_4 = \text{H}_2\text{SiO}_4^- + \text{H}^+$</td>
<td>-9.83</td>
</tr>
<tr>
<td>$\text{H}_4\text{SiO}_4 = \text{H}_2\text{SiO}_4^- + 2 \text{H}^+$</td>
<td>-23.0</td>
</tr>
</tbody>
</table>

The log $K_{eq}$ values for each reaction change as a function of temperature, but all simulations performed were assumed to be at 25 °C.

**Rate Controlled Reactions**

Reactions between the aqueous species and the reactive minerals in a reservoir are kinetically controlled. Reactions involving reservoir minerals cause minerals to dissolve
or precipitate when they are not in a state of equilibrium with the ions in the aqueous phase.

Mineral reactions in GEM must be written so the mineral has a stoichiometric coefficient of -1 (Nghiem, 2005), and so there is only one mineral involved per reaction. The dissolution or precipitation rate of a mineral is calculated as:

$$r_\beta = \text{sgn} \left[ 1 - \left( \frac{Q_\beta}{K_{eq,\beta}} \right) \right] \hat{A}_\beta S_w \left( k_\beta + \sum_{i=1}^{n_m} k_{i,\beta} a_{i,\beta} \right)^{\xi_\beta} \left( \frac{Q_\beta}{K_{eq,\beta}} \right)^{\zeta_\beta}$$  \hspace{1cm} (3-8)

where:

\(\hat{A}_\beta\) = reactive surface area of reactant mineral \(\beta\) per unit bulk volume of porous medium \((m^2/m^3)\)

\(S_w\) = water saturation

\(k_\beta\) = rate constant of mineral reaction \(\beta\) \((mol/m^2\cdot s)\). This depends on temperature as shown in Equation 3-9.

\(k_{i,\beta}\) = rate constants of mineral reaction \(\beta\) related to activity of each species (default \(k_{i,\beta} = 0\) in GEM). Index “i” refers to each species (both hydrocarbon and aqueous) in the simulation.

\(a_{i,\beta}\) = activity of ions for mineral reaction \(\beta\)

\(K_{eq,\beta}\) = chemical equilibrium constant of mineral dissolution/precipitation reaction

\(Q_\beta\) = activity product of mineral \(\beta\) dissolution reaction

\(r_\beta\) = dissolution/precipitation rate per unit bulk volume of porous medium \([mol/(m^3\cdot s)]\)

\(R_{mn}\) = number of mineral reactions

\(\xi_\beta\) = parameter (default = 1 in GEM)

\(\zeta_\beta\) = parameter (default = 1 in GEM)
The sgn (signum) function provides only the sign of the expression in brackets. A positive sign for this equation indicates the reaction is a dissolution reaction; a negative sign indicates a precipitation reaction.

Reaction-rates are normally stated at a reference temperature. The reaction-rate constant \( k \) at any desired temperature can be found using the following equation:

\[
\begin{align*}
    k_{\beta} &= k_{0,\beta} \exp \left[ -\frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \\
    \text{(3-9)}
\end{align*}
\]

where \( E_a \) = activation energy for reaction (J/mol), \( k_{0,\beta} \) = reaction-rate constant for reaction at reference temperature, \( R \) = universal gas constant (8.314 J/(mol K)), \( T \) = temperature (K) and \( T_0 \) = reference temperature (K).

The reactive surface area of mineral per unit bulk volume of porous medium changes as the mineral dissolves or precipitates. GEM (Ngheim, 2005) employs the following equation to adjust the reactive surface area of a mineral:

\[
\dot{A} = \dot{A}_0 \cdot \frac{N_{\beta}}{N_{\beta 0}} \\
\text{(3-10)}
\]

where \( \dot{A}_0 \) = reactive surface area at time zero, \( N_{\beta} \) = moles of mineral \( \beta \) per grid block volume at current time, and \( N_{\beta 0} \) = moles of mineral \( \beta \) per grid block volume at time zero.

Equation 3-10 makes the reaction-rate of a mineral in a simulation grid cell a de facto first-order reaction in terms of mineral volume.
The porosity of the matrix should change as minerals are dissolved or precipitated. GEM calculates the effective porosity (Nghiem, 2005) of each grid block using the following:

\[
\phi_{eff} = \phi + \sum_{\beta=1}^{n_{mn}} \left( \frac{N_{\beta} - N_{\beta 0}}{\rho_{\beta}} \right)
\]

where \( n_{mn} \) = number of reactive minerals present in simulation, \( N_{\beta} \) = total moles of mineral \( \beta \) per bulk volume, \( N_{\beta 0} \) = total moles of mineral \( \beta \) per bulk volume initially present, \( \rho_{\beta} \) = molar density of mineral \( \beta \),

and \( \phi \) is the porosity calculated as a function of pressure based on:

\[
\phi = \phi^* \left[ 1 + c_\phi (p - p^*) \right]
\]

where \( \phi^* \) = porosity value at reference pressure \( p^* \), and \( c_\phi \) = rock compressibility (kpa\(^{-1}\)).

GEM can model permeability changes that result from porosity changes using the Kozemy-Carman equation. This feature was not used for any simulations carried out for this Thesis. A representative at the Computer Modelling Group said that use of the *PERM-VS-POR keyword controls both porosity and permeability changes in the simulator when mineral reactions occur. PERM-VS-POR (0) causes no changes in porosity and permeability with mineral dissolution, PERM-VS-POR (-1) causes changes in porosity with mineral dissolution, and PERM-VS-POR (1) causes changes of both porosity and permeability with mineral dissolution.

The *DPORMNR keyword in GEM-GHG shows the change in porosity of each grid cell caused by mineral dissolution and precipitation (Equation 3-11). Use of this keyword
showed that no porosity changes were caused by mineral reactions in the simulation runs in this Thesis. Use of the *POROS keyword in GEM shows the current porosity of a grid cell and revealed that porosity changes caused by changes in pressure (Equation 3-12) is used in GEM and has caused porosity changes of less than 1% in the simulations performed for this Thesis.

### 3.2 pH-Sensitive Polymer Rheological Model

The pH-sensitive polymer code implemented in GEM allows the calculation of the polymer solution viscosity based on the rheological model developed by Huh, Choi and Sharma (2005). Lalehrokr and Choi developed Fortran code to calculate the viscosity of pH-sensitive polymer which was then implemented in the GEM code by the Computer Modelling Group. Polymer viscosity in the simulator is controlled by user defined polymer properties, the polymer concentration, aqueous phase pH, ionic strength, and the shear rate of the fluid in the simulation run. The remainder of this section contains a detailed description of how GEM calculates pH-sensitive polymer viscosity, and provides plots demonstrating pH-sensitive polymer solution viscosity as a function of pH, *in situ* fluid velocity, ionic strength and polymer concentration for given conditions.

The following description of the pH-sensitive polymer viscosity calculations is taken from “A Rheological Model for pH-sensitive Ionic Polymer Solution” (Choi et al., 2006). GEM follows the steps shown below in Figure 3-1 to calculate the polymer viscosity in each grid block for each time step. The input for the polymer viscosity program comes from the GEM input file and internally from data calculated within GEM.
Step 1) Read polymer parameters from input file and read input from GEM simulator (ionic strength, fluid velocity, etc.)

Step 2) Compute equilibrium swelling volume (Q)

Step 3) Calculate intrinsic viscosity (|\eta|)

Step 4) Calculate polymer solution viscosity at zero shear limit (\eta_0)

Step 5) Calculate apparent shear rate in porous media (\gamma_{eff})

Step 6) Calculate effective polymer viscosity in porous media (\eta)

Figure 3-1: Viscosity Code Calculations Flow Chart

Step 1) Read polymer parameters from input file and read input from GEM simulator

The viscosity program requires polymer and reservoir grid data from the GEM input file and calculated values from within GEM itself to calculate the polymer viscosity for each cell in the simulation model. Table 3-4 shows the variables required by GEM to calculate the viscosity of the aqueous phase that contains polymer. The table also gives the sources of the data, the units of the input parameters (usually metric) and the polymer values used for the simulation described later in this Thesis. The polymer input parameters are empirical parameters taken from Huh, Choi and Sharma (2005) for a three weight percent
polymer concentration solution of Carbopol EZ-2 with three weight percent concentration of sodium chloride.

Table 3-4: pH-Sensitive Polymer Properties

<table>
<thead>
<tr>
<th>Variable</th>
<th>Data Source</th>
<th>Units</th>
<th>Value used in Simulations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer specific volume, $\bar{\nu}$</td>
<td>Input file</td>
<td>cm$^3$/g</td>
<td>0.714286</td>
</tr>
<tr>
<td>Polymer dissociation constant, $K_a$</td>
<td>Input file</td>
<td>None</td>
<td>0.0000446684</td>
</tr>
<tr>
<td>Average Polymer Molecular Weight, $\bar{M}_n$</td>
<td>Input file</td>
<td>g/mol</td>
<td>1500000</td>
</tr>
<tr>
<td>Average molecular weight of polymer between crosslinks, $\bar{M}_c$</td>
<td>Input file</td>
<td>g/mol</td>
<td>80000</td>
</tr>
<tr>
<td>Polymer-solvent interaction parameter, $\chi_1$</td>
<td>Input file</td>
<td>None</td>
<td>0.2</td>
</tr>
<tr>
<td>Polymer volume fraction in relaxed state, $\nu_{2,r}$</td>
<td>Input file</td>
<td>None</td>
<td>0.2</td>
</tr>
<tr>
<td>Solvent (water) molar volume, $V_1$</td>
<td>Simulator</td>
<td>cm$^3$/mol</td>
<td>Varies, ~ 18.02</td>
</tr>
<tr>
<td>Ion valence factor (charge), $z_i$</td>
<td>Input file</td>
<td>None</td>
<td>Varies</td>
</tr>
<tr>
<td>Molar Concentration of ionic species, $m_i$</td>
<td>Simulator</td>
<td>mol/litre</td>
<td>Varies</td>
</tr>
<tr>
<td>pH of solution, $pH$</td>
<td>Simulator</td>
<td>None</td>
<td>Varies</td>
</tr>
<tr>
<td>Empirical constant $a$</td>
<td>Input file</td>
<td>None</td>
<td>0.146349970294204</td>
</tr>
<tr>
<td>Empirical constant $b$</td>
<td>Input file</td>
<td>None</td>
<td>1.16589153642437</td>
</tr>
<tr>
<td>Solvent viscosity, $\eta_s$</td>
<td>Simulator</td>
<td>cp</td>
<td>Varies</td>
</tr>
<tr>
<td>Polymer concentration, $C$</td>
<td>Simulator</td>
<td>weight fraction</td>
<td>Varies</td>
</tr>
</tbody>
</table>
### Table 3-4 Continued: pH-Sensitive Polymer Properties

<table>
<thead>
<tr>
<th>Empirical Constant $k''$</th>
<th>Input File</th>
<th>None</th>
<th>0.4</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Polymer viscosity at infinite shear rate, $\eta_\infty$</th>
<th>Input file</th>
<th>cp</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical parameter 1, $e_1$</td>
<td>Input file</td>
<td>None</td>
<td>-0.038</td>
</tr>
<tr>
<td>Empirical parameter 2, $e_2$</td>
<td>Input file</td>
<td>None</td>
<td>0.032</td>
</tr>
<tr>
<td>Empirical parameter 3, $e_3$</td>
<td>Input file</td>
<td>None</td>
<td>0.00</td>
</tr>
<tr>
<td>Empirical parameter 4, $e_4$</td>
<td>Input file</td>
<td>None</td>
<td>0.0000001 (or 0) Note: setting this to zero disables polymer shear-thinning</td>
</tr>
<tr>
<td>Empirical parameter 5, $e_5$</td>
<td>Input file</td>
<td>None</td>
<td>5.842</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aqueous phase velocity in cell, $U_w$</th>
<th>Simulator</th>
<th>cm/s</th>
<th>Varies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell average permeability, $k$</td>
<td>Input file</td>
<td>mDarcy</td>
<td>Varies</td>
</tr>
<tr>
<td>Water relative permeability in cell, $k_{rw}$</td>
<td>Simulator</td>
<td>None</td>
<td>Varies</td>
</tr>
<tr>
<td>Water saturation in cell, $S_w$</td>
<td>Simulator</td>
<td>None</td>
<td>Varies</td>
</tr>
<tr>
<td>Porosity in cell, $\phi$</td>
<td>Input file</td>
<td>None</td>
<td>Varies by case</td>
</tr>
</tbody>
</table>

Several variables are calculated, stored, and read later during the process of calculating the polymer viscosity. Table 3-5 describes these intermediate variables.

### Table 3-5: Internal GEM Polymer Viscosity Code Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer volume fraction in the swollen network, $\nu_{2,s}$</td>
<td>None</td>
</tr>
<tr>
<td>Equilibrium swelling volume, $Q$</td>
<td>None</td>
</tr>
<tr>
<td>Polymer intrinsic viscosity, $</td>
<td>\eta</td>
</tr>
<tr>
<td>Polymer solution viscosity in the zero-shear-limit, $\eta_0$</td>
<td>cp</td>
</tr>
<tr>
<td>Effective polymer shear rate in cell, $\gamma_{\text{eff}}$</td>
<td>$s^{-1}$</td>
</tr>
<tr>
<td>Carreau equation empirical parameter, $n$</td>
<td>None</td>
</tr>
<tr>
<td>Carreau equation empirical parameter, $\lambda$</td>
<td>None</td>
</tr>
<tr>
<td>Ionic strength of polymer solution, $I$</td>
<td>None</td>
</tr>
<tr>
<td>pH of polymer solution, $pH$</td>
<td>None</td>
</tr>
</tbody>
</table>
Step 2) Compute equilibrium swelling volume

The ionic strength, I, of the polymer solution affects the ability of the polymer to swell. Ionic strength is calculated in the GEM viscosity model using Equation 3-13. Note that this calculation is separate from the one used for the activity product calculations in GEM-GHG for the mineral-aqueous reactions. High ionic strength lowers the viscosity of polymer solution. Multivalent ions have a larger effect than monovalent ions on the ionic strength of solution as reflected by the squared charge term in the equation.

\[ I = 0.5 \sum_{i}^{N_{aq}} z_{i}^{2} M_{i} \]  

(3-13)

where \( N_{aq} \) is the number of aqueous species in solution, \( z \) is the charge of an ionic species and \( M \) is the molal concentration of species \( i \).

GEM tracks the concentrations of aqueous species in molality (\( C_{\text{Molality}} \), mol/kg). This approach makes concentrations independent of pressure changes. The polymer viscosity code was developed for concentrations in molarity (\( C_{\text{Molarity}} \), mol/liter) at conditions near standard atmospheric temperature and pressure. The polymer rheological model calculations within GEM are based on concentrations given in molality, not molarity.

\[ C_{\text{Molality}} = \frac{C_{\text{Molarity}}}{\rho} \]  

(3-14)

where \( \rho \) is the solution density (kg/liter).

These two measures of concentrations are equal when the density of the water phase is 1000 kg/m³ (1 kg/liter). The simulations performed for this Thesis contained aqueous
fluids with densities usually ranging from 1030 kg/m$^3$ to 1060 kg/m$^3$. The aqueous phase
density depends mainly on the concentration of polymer and of other species in the fluid.

GEM does not track the pH of a solution. For the purposes of calculating the polymer
viscosity pH is approximated as:

$$\text{pH} = - \log_{10} ([\text{H}^+ \text{ molality}]) \quad (3-15)$$

The equilibrium swelling volume $Q$ is calculated from the equilibrium polymer swelling
volume $\nu_{2,s}$. $\nu_{2,s}$ is solved for using an initial guess of 0.5 and a Newton-Raphson
iterative scheme with an error tolerance of $10^{-10}$.

$$\left( \frac{V_1}{4l} \right) \left( \frac{\nu_{2,s}}{\nu} \right)^2 \left( \frac{K_a}{10^{\text{pH}} + K_a} \right)^2 = \ln(1-\nu_{2,s}) + \nu_{2,s} + \chi I \nu_{2,s}^2 + \left( \frac{V_1}{\nu M_c} \right) \left( 1 - \frac{2M_c}{M_n} \right) \left( \frac{\nu_{2,s}}{\nu_{2,r}} \right)^{1/3} \left[ 1 - \frac{1}{2} \left( \frac{\nu_{2,s}}{\nu_{2,r}} \right) \right]$$

$$Q = \frac{1}{\nu_{2,s}} \quad (3-17)$$

**Step 3) Calculate intrinsic viscosity**

The intrinsic viscosity of the ionic polymer is calculated based on the Mark-Houwink
equation:

$$[\eta] = a Q^b \quad (3-18)$$

where $a$ and $b$ are empirical constants defined in the input file.
Step 4) Calculate polymer solution viscosity at zero shear limit

The polymer solution viscosity in the zero-shear-limit, $\eta_o$, can be determined by the Martin equation. $\eta_o$ has the dominant effect on the solution viscosity.

$$\eta_o = \eta_s + \eta_s C|\eta| \exp\left(k'' C|\eta|\right) \quad (3-19)$$

where $\eta_s$ is solvent (water) viscosity, $C$ is polymer concentration, and $k''$ is an empirical constant.

Step 5) Calculate apparent shear rate in porous media

The Carreau empirical constant $n$ must be calculated before the effective shear rate is determined. Variables $e_1$ and $e_2$ are empirical constants.

$$n = -e_1 - e_2 C|\eta| - 1 \quad (3-20)$$

The effective shear rate applicable for a permeable rock can be calculated using the Cannella equation (Cannella et al., 1988).

$$\gamma_{eff} = 6.0 \left[\frac{3n+1}{4n}\right]^{n(n-1)} \left[\frac{U_w}{\sqrt{kk_{rw}S_w\phi}}\right] \quad (3-21)$$

where $U_w$ is the water phase Darcy velocity, $k$ is the grid cell permeability, $k_{rw}$ is the relative permeability of water, $S_w$ is water phase saturation, and $\phi$ is the grid cell porosity.

Observed values of $\gamma_{eff}$ in the simulations performed for this Thesis range from 0 s$^{-1}$ where there is no flow in a model to as high as 1500 s$^{-1}$ in the grid block adjacent to the
injection well in the high-permeability layer in some of the radial geometry simulations. The shear-thinning feature of the polymer rheological model was usually disabled (by setting $e_4$ equal to zero in the input files) for the polymer simulations in Chapter 6 and Chapter 7 to understand the effect of the polymer viscosity on oil recovery without considering the velocity dependent effect of polymer shear-thinning.

**Step 6) Calculate effective polymer viscosity in porous media**

The Carreau equation calculates the effective polymer viscosity using the effective shear rate of the polymer. The Carreau empirical constant $\lambda$ must first be found using the relation below. Variables $e_3$, $e_4$, and $e_5$ are empirical constants.

$$\lambda = e_3 + e_4 (C_\eta)^{e_3}$$

(3-22)

The Carreau equation is:

$$\eta = \eta_\infty + [\eta_\infty - \eta_\infty] \left[1 + (\lambda \gamma_{\text{eff}})^2\right]^{n-1/2}$$

(3-23)

where $\eta_\infty$ is the polymer viscosity at infinite shear rate. Trial runs with $\eta_\infty = 0$ caused the calculation errors in GEM, so a value of 1 cp was used in the simulator.

$\eta$ is the calculated polymer viscosity (cp) in the simulator grid block that is returned to the GEM simulator. It is likely that the simulator will need to iteratively solve for the viscosity of the polymer solution since its viscosity affects the fluid flow in the rest of the simulation, which in turn affects the viscosity of the polymer solution.
**Polymer Viscosity Code Comparison**

A comparison between the viscosity values calculated from the pH-sensitive polymer rheological model (implemented in a spreadsheet calculation by S. K. Choi) and the GEM simulator was performed to ensure they matched. GEM simulation runs based on polymer concentration, polymer pH, polymer velocity and solution ionic strength showed excellent agreement between the two codes. The relative error in the GEM viscosity values was less than 1% compared to the spreadsheet values for all cases except at high fluid velocity rates (see Figure 3-3). For the high velocity cases shown in Figure 3-3, inspection of the viscosity versus polymer velocity data showed that the absolute differences in viscosity remained small despite the solution viscosity being several orders of magnitude smaller than the zero shear values.

Figure 3-2 shows a comparison of polymer solution viscosity values between the spreadsheet calculations and the GEM simulator as the pH of a polymer solution was varied (3 wt% polymer concentration, 3 wt% NaCl concentration giving a solution ionic strength of 0.5, no fluid flow).

Figure 3-3 shows a comparison of polymer solution viscosity values between the spreadsheet calculations and the GEM simulator as the fluid velocity of a polymer solution was varied (3 wt% polymer concentration, 3 wt% NaCl concentration giving a solution ionic strength of 0.5, solution pH of 5).
Figure 3-2: Polymer Viscosity versus pH (3 wt% Polymer Solution, Ionic Strength of 0.5, No Flow)

Figure 3-3: Polymer Viscosity versus Fluid Velocity (3 wt% Polymer Solution, pH=5, Ionic Strength of 0.5)
Figure 3-4 shows a comparison of polymer solution viscosity values between the spreadsheet calculations and the GEM simulator as the ionic strength of the polymer solution was varied by changing the NaCl concentration of the solution (3 wt% polymer concentration, solution pH of 4, no flow). Figure 3-4 shows that very high polymer viscosities can arise at low ionic strengths. It is important to remember that the input values for the polymer rheological model must be chosen for the appropriate polymer and salt concentrations, to be sure that reasonable polymer viscosities are modeled. Huh et al. (2005) give empirical polymer rheological model parameters for various types of pH-sensitive polymer for various polymer concentrations and salt concentrations.

Figure 3-4: Polymer Viscosity versus Ionic Concentration (3 wt% Polymer Solution, pH=4, No Flow)
Figure 3-5 shows a comparison of polymer solution viscosity values between the spreadsheet calculations and the GEM simulator as the polymer concentration of a solution was varied (3 wt% NaCl concentration giving a solution ionic strength of 0.5, solution pH of 4, no fluid flow).

Figure 3-5: Polymer Viscosity versus Polymer Concentration (pH=4, Ionic Strength of 0.5, No Flow)

Notes About the GEM-GHG Simulator

The GEM User’s Guide (Computer Modelling Group, 2006) available inside the CMG Technology Launcher program describes how to use the regular GEM simulator. A description of the GEM-GHG simulator and instructions for using it was developed by Long Nghiem of the Computer Modelling Group Limited (see Nghiem 2002, 2003,
2005). Descriptions of GEM keywords for the GEM polymer code are also available (Nghiem, 2006). A sample input file with annotated comments is given in Appendix 2 to aid readers in the construction of GEM-GHG input files. Appendix 3 gives a sample GEM-GHG input file for a pH-sensitive polymer flood. The Computer Modelling Group’s WINPROP and BUILDER programs provide windows based graphical user interfaces to aid in the construction of GEM-GHG input files.
Chapter 4: CHARACTERIZATION OF RESERVOIR–BRINE INTERACTIONS USING GEOCHEMICAL SIMULATIONS

Reservoir minerals may react with injected aqueous fluids to alter the composition and pH of the fluid. Such fluid-mineral reactions must be accurately characterized to model the behavior of pH-sensitive polymer in situ. This chapter documents the results of the history matching procedure used to model the reaction of hydrochloric acid with Berea sandstone. Three Berea coreflood experiments conducted by Choi (2005) served as the basis for this work. The GEM-GHG simulator described in Chapter 3 was used to model the corefloods. The chosen final mineralogy and reaction parameters matched the effluent pH measurements of three coreflood experiments reasonably well. Simulations demonstrating sensitivities to various mineral reaction-rates, mineral volumes and to a first-order hydrogen reaction model are given. The dimensionless Damköhler number is defined at the end of this chapter that is used to compare the acid reaction-rate in porous media to the transport rate of the acid.

4.1 Berea Corefloods

Choi (2005) performed three coreflood experiments with Berea sandstone cores to estimate the pH inside Berea sandstone while it is being flooded with acid. A solution of 3 wt% NaCl brine was injected at the start of these corefloods, followed by injection of hydrochloric acid with a pH of 1. The experiments were carried out at a temperature of 24°C. The rate of fluid injection was varied in Experiments 1 and 3, and the rate was held constant for Experiment 2. Shut-in periods occurred during the experiments by design or
to allow refilling of the injection pump. Nearly continuous effluent pH readings were taken for all three experiments. Additional silicon, aluminum, calcium, iron and potassium concentrations were measured in effluent samples taken during Experiment 2. The core dimensions and porosities for the experimental cores are given below, along with fluid injection rates and fluid residence times. More information about the corefloods can be obtained from “A Study of a pH-Sensitive Polymer for Novel Conformance Control Applications” (Choi, 2005).

Table 4-1: Core Dimensions, Core Properties and Fluid Residence Times

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Length</th>
<th>Diameter</th>
<th>Porosity</th>
<th>Fluid Injection Rate (Range)</th>
<th>Fluid Residence Time (Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coreflood 1</td>
<td>0.2247 m</td>
<td>Approx. 0.0249 m</td>
<td>0.20</td>
<td>1 - 5 cc/min</td>
<td>4.4 - 21.9 min</td>
</tr>
<tr>
<td>Coreflood 2</td>
<td>0.2247 m</td>
<td>0.0249 m</td>
<td>0.177</td>
<td>2 cc/min</td>
<td>9.7 min</td>
</tr>
<tr>
<td>Coreflood 3</td>
<td>0.2247 m</td>
<td>0.0248 m</td>
<td>0.1825</td>
<td>1 - 6 cc/min</td>
<td>3.3 - 19.8 min</td>
</tr>
</tbody>
</table>

Note: The core diameter recorded by Choi for Experiment 1 was 1 inch but has been approximated as 0.0249 m in the simulations since the other two “1 inch” diameter cores had a smaller diameter.

**Typical Berea Mineralogy**

Ermel (2005) summarized Berea compositions given in the literature which generally include a large proportion of quartz with small proportions of carbonate, feldspars, and clays (illite, smectite, chlorite, kaolinite). Ermel’s work to match the same three corefloods performed by Choi identified that including anorthite in a simulation of a Berea coreflood can provide a good match of the observed pH values. The following
minerals were included in the author’s attempts to history match the pH effluent behavior exhibited by the corefloods: quartz, kaolinite, anorthite, calcite, potassium feldspar and illite.

4.2 History Matching Procedure

Initial attempts were made by the author to recreate the successful history match that Ermel achieved using the KGEOFLOW simulator for the second coreflood, with kaolinite and anorthite representing the Berea core minerals. The kaolinite-anorthite model showed that the peak effluent pH of a coreflood is 7.84 when given time for pH=1 hydrochloric acid to equilibrate with the rock matrix. This pH is too high compared with maximum effluent pH values observed from the coreflood experiments.

A more methodical approach was taken to model the Berea sandstone using commonly identified constituent minerals, by performing the following steps:

1) Identify minerals that were likely to be present in Berea sandstone based on literature. In this case quartz, kaolinite, calcite, potassium feldspar and illite were selected.

2) Select a primary matching parameter. Matching the observed effluent pH of ~5 when pH=1 hydrochloric acid was being injected into the Berea cores was selected as the primary matching parameter.

3) Perform simulations to identify the equilibrium pH values achieved between pH=1 HCl acid and single minerals and groups of minerals. Equilibrium pH values are the final pH values that a brine-mineral system will attain given infinite time. This was approximated in GEM by injecting acid into a core containing the desired minerals while
either increasing the mineral reaction-rates or the simulation grid length in the flow direction to achieve a very large Damköhler number. The equilibrium pH and ion concentrations were identified when the spent acid composition no longer changed with distance traveled in the core. Mineral combinations that did not raise the pH of the acid to 5 or above were unacceptable representations for Berea.

4) Evaluate model results. Initially a pH of 5 could not be obtained from the coreflood simulations containing the calcite reaction. This did not match analytical calculations for pH=1 strong acid mixed with calcite at atmospheric pressure at 25°C (Stumm and Morgan, 1996). Additional aqueous phase reactions and ionic species (such as H$_2$CO$_3$) were then added to the model. A sample case was run to compare the calcite reaction with pH=1 hydrochloric acid described in a GEM test file with an example from page 375 of Aquatic Chemistry (Stumm and Morgan, 1996) to ensure that the simulated calcite reactions were correct. The GEM simulator results matched the solution given in the textbook. New equilibrium pH values (step 3) were calculated with the new aqueous species reactions.

5) Calcite was considered the prime reactive mineral since it reacted with pH=1 acid to give an effluent pH of 5.4 which was close to the observed effluent pH of ~5. Simulations with calcite combined with quartz and/or potassium feldspar had a similar equilibrium pH.

6) It was recognized that adding anorthite, kaolinite or illite to quartz and potassium feldspar drives the equilibrium pH above 6 in the core. It is desired to have a final pH greater than six or seven to test the concept of pH-sensitive polymer gelling to very high viscosities. The combination of kaolinite, calcite, quartz and potassium feldspar was
chosen for further matching since it closely matches the Berea sandstone composition most often cited in literature.

7) Analysis of the calcite-kaolinite-potassium feldspar-quartz model revealed that many of the intra-aqueous reaction equations (Table 3-3) could be removed from the simulation without materially changing the effluent pH or metal cation concentrations. Only the significant intra-aqueous reactions, namely the dissociation of $H_2O$, $H_2CO_3$, $Al(OH)_4^-$ and $HCO_3^-$ (see Table 4-2), were left in the simulation model to shorten the simulation run times.

**Table 4-2: Intra-Aqueous Reactions Equilibrium Constants for Final-Match Simulations**

<table>
<thead>
<tr>
<th>Equilibrium Reaction</th>
<th>$\log K_{eq} @ 25^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HCO_3^- = H^+ + CO_3^{2-}$</td>
<td>-10.329</td>
</tr>
<tr>
<td>$Al^{+++} + 4 H_2O = Al(OH)_4^- + 4 H^+$</td>
<td>-22.7</td>
</tr>
<tr>
<td>$H_2CO_3 = 2 H^+ + CO_3^{2-}$</td>
<td>16.6</td>
</tr>
<tr>
<td>$H_2O = H^+ + OH^-$</td>
<td>-14</td>
</tr>
</tbody>
</table>

8) A simulation of Experiment 2 was run using (i) the kaolinite, calcite, quartz and potassium feldspar mineralogy; (ii) a best guess for approximate mineral grain fractions (6%, 3%, 88% and 3%, respectively); and (iii) published reaction-rate constants ($10^{-13}$, $10^{-8.8}$, $10^{-13.9}$, $10^{-12}$ mol·m$^{-2}$·s$^{-1}$, respectively) compiled by Xu *et al.* (2001). The simulation revealed that the minerals did not react fast enough to raise the effluent pH of the injected acid given the core properties and flow rates of Experiment 2. The mineral reaction-rates for the four minerals were changed to $10^{-7.2}$, $10^{-4.07}$, $10^{-6.22}$, and $10^{-5.98}$ mol·m$^{-2}$·s$^{-1}$,
respectively, and the mineral fractions were changed to those given in Table 4-5 to give a reasonable initial match for the effluent pH and ion concentrations for the second coreflood.

9) The chosen mineralogy and reaction-rates from the last step, now referred to as the “initial match” parameters determined for Experiment 2 were used to simulate coreflood Experiments 1 and 3. It was necessary to increase the calcite reaction-rate by a factor of 5 to prevent the simulated effluent pH from dropping during the high acid injection rates in Experiment 3. The high injection rates were up to 3 times greater than the acid injection rate (2 cc/min) in Experiment 2. The quartz, kaolinite and potassium feldspar reaction-rates were decreased by a factor of 2 to match the number of pore volumes of pH=1 acid that had to be injected before the effluent pH from the coreflood dropped from about 5 to about 1.5. The close relationship between the reaction-rate, the concentration of the minerals and the number of pore volumes of acid required to lower the effluent pH is discussed later in this chapter. The resulting “final-match” core mineralogy is given in Table 4-5 and reaction parameters are given in Tables 4-3 and Table 4-4.

**Simulation Input**

The following table gives the mineral reactions and associated equilibrium constants used during the history matching process. The equilibrium constants were not changed during the history matching and all simulations were run using values at 25°C.
Table 4-3: Mineral Reactions and Equilibrium Constants (at 25°C)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reaction</th>
<th>log $K_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>$\text{SiO}_2(s) + 2 \text{H}_2\text{O} = \text{H}_4\text{SiO}_4(aq)$</td>
<td>-3.98</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(s) + 6 \text{H}^+(aq) = 2 \text{Al}^{3+}(aq) + 2 \text{H}_4\text{SiO}_4(aq) + \text{H}_2\text{O}$</td>
<td>7.435</td>
</tr>
<tr>
<td>Calcite</td>
<td>$\text{CaCO}_3(s) = \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$</td>
<td>-8.42</td>
</tr>
<tr>
<td>Potassium feldspar</td>
<td>$\text{KAlSi}_3\text{O}_8(s) + 8 \text{H}_2\text{O} = \text{K}^+(aq) + \text{Al(OH)}_4^-(aq) + 3 \text{H}_4\text{SiO}_4(aq)$</td>
<td>-20.573</td>
</tr>
<tr>
<td>Illite</td>
<td>$\text{K}<em>{0.6}\text{Mg}</em>{0.25}\text{Al}<em>{2.3}\text{Si}</em>{3.5}\text{O}_{10}(\text{OH})_2(s) + 8 \text{H}^+(aq) + 2 \text{H}_2\text{O} = 0.6 \text{K}^+(aq) + 0.25 \text{Mg}^{2+}(aq) + 2.3 \text{Al}^{3+}(aq) + 3.5 \text{H}_4\text{SiO}_4(aq)$</td>
<td>9.8</td>
</tr>
<tr>
<td>Anorthite</td>
<td>$\text{CaAl}_2\text{Si}_2\text{O}_8(s) + 8 \text{H}^+(aq) = \text{Ca}^{2+} + 2 \text{Al}^{3+} + 2 \text{H}_4\text{SiO}_4(aq)$</td>
<td>21.81</td>
</tr>
</tbody>
</table>

Table 4-4 contains mineral reaction constants for quartz, kaolinite, calcite and potassium feldspar from Palandri and Kharaka (2004) of the U.S.G.S. and from the history matching exercise. The literature value of $k$ for calcite is a dominantly first-order constant with respect to hydrogen concentration, and it causes a very fast reaction just like the history matched calcite reaction-rate constant ($10^{-3.37}$ mol·m$^{-2}$·s$^{-1}$) suggested. The history matched reaction constants for quartz, kaolinite and feldspar are much larger than those found in literature. The rate constants for these minerals were selected primarily to prevent the effluent pH from the second coreflood from decreasing to 1 after the calcite was consumed in the model to match measured pH values. Complex mineral interactions arose in the simulation due to the presence of kaolinite which raises concerns discussed later in this chapter (Section 4).
### Table 4-4: Mineral Reaction Constants (at 25°C) from Literature and History Matching

<table>
<thead>
<tr>
<th>Mineral Reaction</th>
<th>$k$ – U.S.G.S. moles m$^{-2}$ s$^{-1}$</th>
<th>$k$ – initial match moles m$^{-2}$ s$^{-1}$</th>
<th>$k$ – final-match moles m$^{-2}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>$10^{-13.4}$</td>
<td>$10^{-6.22}$</td>
<td>$10^{-6.52}$</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>$10^{-13.2}$</td>
<td>$10^{-7.2}$</td>
<td>$10^{-7.5}$</td>
</tr>
<tr>
<td>Calcite</td>
<td>$10^{-0.3} [H^+] + 10^{-5.81}$</td>
<td>$10^{-4.07}$</td>
<td>$10^{-3.37}$</td>
</tr>
<tr>
<td>Potassium feldspar</td>
<td>$10^{-12.4}$</td>
<td>$10^{-5.98}$</td>
<td>$10^{-6.28}$</td>
</tr>
</tbody>
</table>

The mineral concentrations, initial reactive surface areas and activation energies used for the final history match simulations are given in Table 4-5. The quartz, kaolinite and potassium feldspar reaction rates constants were changed as a group (of slow reaction minerals) during the history matching, not individually. The relative difference in their mineral reaction-rate constants is based on the published U. S.G. S. reaction-rate constants. The mineral concentrations given in the Table 4-5 are given as a fraction of grain volume and must sum to one. They must be multiplied by (1-porosity) to give the concentrations in terms of volume fraction before they are entered into the GEM-GHG input file. The specific reactive areas given in Table 4-5 are defined similar to those calculated by Xu *et al.* (2001).
Table 4-5: Mineral Compositions, Reactive Areas, and Activation Energies

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Grain Composition</th>
<th>Volume Fraction</th>
<th>Specific Reactive Area (m²/[m³ of Bulk Volume])</th>
<th>Activation Energy (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>0.846</td>
<td>0.696</td>
<td>10000 * Volume Fraction</td>
<td>87500</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>0.061</td>
<td>0.05</td>
<td>1000000 * Volume Fraction</td>
<td>62760</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.057</td>
<td>0.047</td>
<td>10000 * Volume Fraction</td>
<td>41870</td>
</tr>
<tr>
<td>Potassium feldspar</td>
<td>0.036</td>
<td>0.03</td>
<td>10000 * Volume Fraction</td>
<td>67830</td>
</tr>
</tbody>
</table>

4.3 Comparison of Experimental and Simulated Effluent Concentrations

Comparison of the effluent hydrogen (pH) and other measured cation concentrations between the simulation runs and the experimental observations served as the basis for selecting the mineralogy and reaction-rates required to describe the acid-mineral reactions between Berea sandstone and acid. Primary importance was placed on matching the pH of the effluent since the ultimate goal of this work is to model the behavior of pH-sensitive polymer \textit{in situ}. Secondary importance was placed on matching the presence of certain cations, and tertiary importance was placed on matching the actual observed cation concentrations.

The simulation results presented do not include any shut-in time although the experimental results include shut-in time. Simulation of shut-in time caused excessively high pressures to be generated in the model despite water and pore compressibility being included. This problem was not fully investigated, but it was expected that the default
PERM-VS-POR (0) setting should have not allowed porosity to change during the shut-in times. GEM-GHG does not output ion concentrations at the producer wells so the ion concentrations in the effluent side grid cell were plotted as the effluent concentrations.

Figures 4-1, 4-2 and 4-3 show the effluent pH versus pore volumes of fluid injected for Experiments 1, 2, and 3, respectively.

Figure 4-1: Effluent pH for Experiment 1
Figure 4-2: Effluent pH for Experiment 2

Figure 4-3: Effluent pH for Experiment 3
Figures 4-1 (168-226 pore volumes injected) and 4-3 (43-68 pore volumes injected) both show times when the simulated effluent pH values using the initial effluent pH match values decreased significantly below the measured effluent pH values. This problem arose at these times when the pH=1 acid injection rate was increased to values above 2 cc/min because the initial calcite reaction-rate constant chosen was too small. The increased calcite mineral reaction-rate constant used for the final effluent pH match cases eliminated this problem. Use of an increased mineral reaction-rate constant allows a mineral reaction to proceed more quickly in a simulation. The final match case included a decrease in kaolinite, quartz and potassium feldspar reaction-rate constants to match the length of time that the pH~5 effluent was observed in Experiment 2.

Figures 4-4, 4-5, 4-6 and 4-7 show the effluent concentrations of calcium, silicon, aluminum and potassium for the second coreflood, respectively. Although iron was measured in the experimental effluent, iron was not present in the minerals in the simulation. The simulated effluent ion concentration values did not match experimentally measured values or trends very well, and resulted from complex mineral interactions in the simulations that are not suggested by the experimental effluent analyses. Simulation sensitivity runs discussed later in this chapter suggest that one or two-mineral simulations using mineral reaction-rates that are first-order in hydrogen concentration may provide better history matches without undesirable mineral interaction effects.
Figure 4-4: Effluent Calcium Concentration for Experiment 2

Figure 4-5: Effluent Silicon Concentration for Experiment 2
Figure 4-6: Effluent Aluminum Concentration for Experiment 2

Figure 4-7: Effluent Potassium Concentration for Experiment 2
4.4 Mineral Interactions in the Coreflood Simulations

The effluent calcium concentration profiles for Experiment 2 shown in Figure 4-4 qualitatively match the experimentally measured values except between the times when 70-150 pore volumes of fluid were injected. Figure 4-5 and 4-6 show simulated effluent silicon and aluminum concentrations that vary dramatically from the measured results. Figure 4-7 shows that the simulated effluent potassium concentration matches the measured values well. Complex mineral-ion relationships explain the observed effluent behaviors.

Figure 4-8 shows the mineral concentration (fraction of initial volume), the mineral reaction affinity (driving force) of the mineral reactions and select ion concentration profiles from the simulation of Experiment 2 after 50 pore volumes of fluid (PVI) were injected. Analysis of this simulated core cross section aids in the interpretation of the simulated effluent concentrations shown in Figures 4-4, 4-5, 4-6 and 4-7.

The simulated variations of mineral concentrations observed in the core and shown in Figure 4-8 resulted from the mineral reactions shown in Table 4-3 and the intra-aqueous reactions shown in Table 4-2. It is believed that the calcite reaction and kaolinite reactions dominated the reaction behavior in the core. The reaction affinity values shown in Figure 4-8 are the calculated values of

\[1 - \left( \frac{Q_\beta}{K_{eq,\beta}} \right)\]

from Equation 3-8 for each mineral reaction based on the ion activity product, \(Q_\beta\), calculated for each mineral reaction (Equation 3-7) and the equilibrium constant, \(K_{eq,\beta}\), for each mineral reaction.
(Table 4-3). The reaction affinity term is positive for mineral dissolution and negative for precipitation, and the magnitude of this term directly affects the rate of the mineral reaction. All the species included in Table 4-2 are included in the simulations, but only H\(^+\), H\(_4\)SiO\(_4\), K\(^+\), Ca\(^{++}\) and Al\(^{+++}\) concentrations in molality (mol/kg) are shown in Figure 4-8.
Figure 4-8: Reaction Affinity (for Mineral Reactions), Mineral Concentrations and Select Ion Concentration Profiles for Experiment 2 After 50 Pore Volumes Injected (Using Final-Match Reaction Parameters)
An analysis of the data in Figure 4-8 for each mineral explains the simulated mineral profiles and the ion concentration profiles and the effluent ion concentrations.

- Calcite is dissolving at high rates in the core between the acid inlet to a point 3.5 inches (from the inlet) in the core. Calcite is dissolving very slowly at positions from 3.5 to 7 inches in the core. Most of the calcite is dissolving in the core in positions up to 3 inches from the inlet as suggested by the Ca$^{++}$ concentration increase and by the decrease in H$^{+}$ concentration. The high calcium concentrations observed before 70 PVI (pore volumes injected) in Figure 4-4 correspond to the observed calcite behavior in Figure 4-8 from 7 to 9 inches from the inlet where the calcite is nearly in equilibrium with the core but slightly precipitating. The low calcium concentrations observed after 150 PVI in Figure 4-4 correspond to the near inlet conditions in Figure 4-8 where little calcite has reacted due to previous consumption of the calcite in that region.

- It is conjectured that the kaolinite reaction behavior is controlled by the calcite reaction through the change in H$^{+}$ concentration that the calcite reaction causes. The determination of the kaolinite affinity term includes hydrogen concentration to the negative sixth power from the kaolinite reaction equation in Table 4-3

\[
\text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4(s) + 6 \text{H}^+(aq) = 2 \text{Al}^{3+}(aq) + 2 \text{H}_4\text{SiO}_4(aq) + \text{H}_2\text{O}.
\]

This causes decreases in H$^+$ concentration to cause a strong kaolinite precipitation reaction. Such a reaction is shown in Figure 4-8 between about 3 inches and 6.7 inches in the core, which is past the region at 3 inches from the inlet where the H$^+$ concentration stabilizes near 4x10$^{-6}$ mol/kg (this corresponds to a pH of 5.4 which is the equilibrium pH of pH=1 HCl acid fully reacted with calcite). Kaolinite dissolution is shown from
0 to 3 inches in the simulated Berea core, and slight kaolinite precipitation is observed from 6.7 to 9.0 inches in the core. The presence of both kaolinite dissolution and precipitation causes the kaolinite concentration to drop near the inlet of the core and to form a peak further in the core. Figure 4-6 shows the simulated aluminum concentration of the coreflood effluent which is controlled mainly by the kaolinite mineral reaction and slightly by the potassium feldspar reaction. The low aluminum concentrations before 70 PVI correspond to times when most aluminum ions liberated by kaolinite dissolution near the core inlet are precipitated in the core as kaolinite before they can exit the core. Between 70 and 150 PVI the kaolinite precipitation zone moves towards the end of the core as the calcite and kaolinite are being consumed by the acid and increasing amounts of aluminum exit the core since there is not enough time or surface area to precipitate the liberated Al$^{+++}$ ions (and Al(OH)$_4^-$ ions). The aluminum concentration in the effluent falls after 150 PVI when kaolinite is no longer being precipitated in the core and a decreasing amount of kaolinite exists in the core. Huge fluctuations in aluminum are not observed in the experimental data suggesting that kaolinite should not be included in the simulation model although it is frequently measured in Berea sandstone analyses. Simulations with only calcite, quartz and potassium feldspar do not show pH increases above that caused by calcite alone (pH~5) when pH=1 acid is fully reacted with the core.

- Potassium feldspar (K-feldspar on Figure 4-8) continuously dissolves in the simulation despite the large changes in H$^+$ and Al$^{+++}$ concentrations (Al$^{+++}$ and H$^+$ concentration affect the concentration of Al(OH)$_4^-$ which participates in the potassium feldspar reaction through the Al$^{+++}$ + 4 H$_2$O = Al(OH)$_4^-$ + 4 H$^+$ intra-aqueous...
reaction). This explains the relative constant simulated potassium concentration in the coreflood effluent shown in Figure 4-7.

- The quartz concentration shown in Figure 4-8 changes little from its initial value because there is a lot of it in the simulation (0.696 volume fraction). The quartz does react in the simulation primarily in response to the direction of the kaolinite reaction. Quartz strongly precipitates when kaolinite dissolves as observed from 0 to 3 inches in Figure 4-8, and quartz strongly dissolves from 3.0 to 7.4 inches roughly where kaolinite is precipitating. This is shown by the quartz and kaolinite reaction affinities in Figure 4-8. Both quartz and kaolinite slightly precipitate in the core from about 7 inches to the end of the core suggesting other mineral interactions exist too. Simulated effluent silicon concentrations shown in Figure 4-5 show equilibrium effluent levels (0.0001 mol/kg) of silicon (H₄SiO₄ in simulation) before 50 PVI when the H₄SiO₄ is able to achieve equilibrium with the quartz before it reaches the end of the core. Silicon is not observed between 70 and 150 PVI in the simulated coreflood effluent corresponding to times when kaolinite precipitation near the effluent end of the core consumes any available H₄SiO₄ in solution. The high concentrations of silicon simulated after 150 PVI in Figure 4-5 correspond to the times when kaolinite is being dissolved but is not precipitated near the effluent end of the core; liberated H₄SiO₄ created by the kaolinite dissolution exits the core rather than being precipitated in the core. The relatively constant measured silicon concentrations from Choi’s Experiment 2 suggest that the silicon concentration should generally remain near equilibrium levels (0.0001 mol/kg) rather than be coupled so closely with other mineral reactions in a simulation model.
4.5 Simulation Sensitivity Analysis

The calcite reaction-rate and the volume fraction of calcite in the Berea simulations appear to dominate the pH behavior of the coreflood effluent in the simulation models. Sensitivities were performed to demonstrate the effect of changing the calcite reaction-rate constant and the volume fraction of calcite in the cores. These sensitivities were performed using the “final-match parameters” given in the sample file in Appendix 3. Simulations were also performed to test the effect of using mineral reactions that are first-order in hydrogen concentration and of using a single-mineral model rather than a four-mineral model.

Simulation runs of Experiment 2 were performed for cases when the calcite reaction-rate constant is increased (to $10^{-2.67}$ moles m$^{-2}$ s$^{-1}$) and decreased (to $10^{-4.07}$ moles m$^{-2}$ s$^{-1}$) by a factor of five from the final-match value ($10^{-3.37}$ moles m$^{-2}$ s$^{-1}$). Figure 4-9 shows the effluent pH profile for these cases.
Figure 4-9 shows that increasing the calcite reaction-rate by a factor of five increases the number of pore volumes of acid that must be injected until the effluent pH falls to about one, whereas decreasing the reaction-rate decreases the volume of acid required to lower the effluent pH. Increasing the reaction-rate also makes the effluent pH drop more quickly, whereas decreasing the reaction-rate makes the effluent pH decrease more slowly than in the base case.

Simulations of Experiment 2 were performed to demonstrate the effect of changing the initial volume fraction of calcite from the final history matched calcite volume fraction 0.047 by increasing it ten percent to 0.0517 and by decreasing it ten percent to 0.0423. Figure 4-10 shows the effluent pH for these cases.
The results given in Figure 4-10 show that the volume fraction of calcite in the simulation can directly affect the volume of pH=1 acid required to lower the effluent pH from about 5.4 to about 1. Increasing the volume fraction of calcite increases the amount of acid required before the effluent pH decreases, and decreasing the volume fraction of calcite does the opposite.

It can be observed from Figure 4-9 and Figure 4-10 that the reaction-rate constant and the volume fraction of a mineral affect the effluent pH profile for an acid coreflood. Since both factors strongly affect the volume of acid required until the effluent pH drops, various combinations of these two factors can achieve a reasonable effluent pH profile match. The effluent concentration of other ions can be examined to select the mineral concentrations and reaction-rates that yield the best overall match between measurements.
and the simulation. Changes of the reaction-rates and mineral volume fractions has been observed during history matching to cause the presence of a pH=3 plateau in the effluent pH which arises from the complicated mineral interactions within the Berea coreflood simulation.

Sensitivities to a different reaction-rate model were performed to test the effect of using reaction constants that are first-order in terms of hydrogen concentration. This sensitivity was performed using the final-match reaction-rate $k$ (Table 4-4) values as $k_{H^+,\beta}$ values in Equation 3-8, and by setting $k_\beta$ to zero (used 1E-60 instead to prevent run crashes) and by changing the hydrogen activity exponent, $\omega_{H^+,\beta}$, to 1 to make the reaction first-order in hydrogen. These changes caused the resulting form of the modeled mineral reactions (for any mineral $\beta$) to be simplified from that of Equation 3-8 to that of Equation 4-1.

\[
 r_\beta = \text{sgn}\left[1 - \left(\frac{Q_\beta}{K_{eq,\beta}}\right)\hat{A}_\beta S_w\left(k_{H^+,\beta} \cdot a_{H^+}^{eq}\right)\right] 1 - \left(\frac{Q_\beta}{K_{eq,\beta}}\right) \tag{4-1}
\]

where $k_{H^+,\beta}$ are the rate constants of mineral reaction $\beta$ related to first-order hydrogen activity and $a_{H^+}$ is the hydrogen activity (assumed to equal hydrogen concentration by using ideal activity feature in GEM). All other parameters are the same as defined for Equation 3-8.

Figure 4-11 shows the simulated effluent pH for the second coreflood using the final-match mineral reaction-rate constants from the final-match case as the hydrogen activity reaction-rate constants (first-order reactions case in Figure 4-11). This case did not allow the reactions to proceed quickly enough; so another case was run with higher reaction-
rate constants. Figure 4-11 shows the effluent pH for the high reaction-rates sensitivity case when the first-order mineral reaction-rate constants for calcite, kaolinite, potassium feldspar and quartz reaction constants were increased from those used in the first-order reactions case by a factor 100 to $10^{-1.37}$, $10^{-5.5}$, $10^{-4.28}$ and $10^{-4.52}$ mol·m$^{-2}$·s$^{-1}$, respectively.

![Figure 4-11: Effluent pH for Mineral Reactions that are First-Order in Hydrogen Concentration (Experiment 2)](chart)

Cases with calcite volume fractions of 0.015, 0.018 and 0.021 were run to achieve a better match using the first-order reactions and the high reaction-rate constants. The results of these simulations are shown in Figure 4-12.
The first-order reactions allow a decreasing pH trend that cannot be created using the fixed reaction-rate mineral reactions that were used for the history matching process. Figure 4-12 shows that decreasing the calcite volume fraction allowed a very good effluent pH match compared to experimentally measured values. Further improvements to the best matching case shown in Figure 4-12 (calcite volume fraction = 0.018 case) may result if a reaction-rate that is first-order in hydrogen concentration is used for calcite only, and if fixed reaction-rates are used for kaolinite, potassium feldspar and quartz as suggested by Palandri and Kharaka (2004). This has not been attempted. All three sensitivity cases shown in Figure 4-12 show a slight irregularity during the effluent pH decrease at values close to pH=3. This is likely caused by the mineral interactions within the simulations that are observed in Figure 4-8.
A sensitivity case was performed to model the second coreflood using a first-order mineral reaction with only calcite present. The one-mineral model was created by eliminating the kaolinite, potassium feldspar and quartz minerals and mineral reactions from the final-match model and by adjusting the first-order reaction-rate constant and calcite volume fraction to best match the effluent pH of the second coreflood. The best fit run has a calcite volume fraction of 0.051 and a reaction-rate constant of $10^{1.37}$ mol·m$^{-2}$·s$^{-1}$. The effluent pH match was very good so similar runs were made for coreflood Experiments 1 and 3. Figures 4-13, 4-14, and 4-15 show the simulation results for these runs.

![Figure 4-13: Effluent pH for Calcite Model with First-order Calcite Reaction (Experiment 1)](image-url)
Figure 4-14: Effluent pH for Calcite Model with First-order Calcite Reaction (Experiment 2)

Figure 4-15: Effluent pH for Calcite Model with First-order Calcite Reaction (Experiment 3)
The simulated effluent pH for the single-mineral calcite models matched measured values very well for all three coreflood simulations despite the simplicity of the model. The ability of this model to respond to the acid injection rate increases during Experiment 3 between when 40 and 90 pore volumes were injected is impressive.

The results shown in Figure 4-13, 4-14 and 4-15 are for calcite reactions that depend on the first-order calcite reaction-rate constant ($k_{H^+,calcite}$), the hydrogen activity in the model, and the value of the reaction affinity term, $1 - \left( \frac{Q^\beta}{K_{eq,\beta}} \right)$ as shown in Equation 4-1.

Further sensitivity cases were made using the one-mineral calcite model to examine the effect of the reaction affinity term in equation 4-1. The TST-PARAM2 exponent, $\zeta$ (default is one in GEM), was changed to values of 0.75, 0.5, 0.25, 0.05, and 0. When $\zeta$ equals zero the affinity term is effectively removed from the simulation and the mineral reaction become exclusively first-order in hydrogen activity (concentration) and on the reactive surface area, $\hat{A}$. Equation 4-2 shows the effective mineral reaction-rate used in the simulations results given in Figure 4-16.

$$r_\beta = \text{sgn} \left[ 1 - \left( \frac{Q^\beta}{K_{eq,\beta}} \right) \right] \hat{A} \cdot \beta \cdot S_w \left( k_{H^+,\beta} \cdot a_{H^+} \right) \left[ 1 - \left( \frac{Q^\beta}{K_{eq,\beta}} \right)^\zeta \right]$$

(4-2)

Simulation results showed absolutely no change in effluent pH profiles for the calcite simulations using the different TST-PARAM2 values, and these results are not shown here. Simulations of the second coreflood with the four-mineral model with first-order mineral reaction-rates (in hydrogen concentration) with a calcite volume fraction of 0.018 (Figure 4-12 also shows this simulation) were performed for various reaction affinity exponent values. Figure 4-16 shows the results. The exponent value of 0 and 0.05 cases
both crashed, but it seems that the use of low exponents does change the mineral reaction-rates as expected.

Figure 4-16: Effluent pH for Calcite-Kaolinite-Potassium Feldspar-Quartz Model with First-order Mineral Reactions for Various Reaction Affinity Term Exponents (Experiment 2, Calcite VF = 0.018)

Discussion of Chosen Berea Core Mineralogy and Reaction Coefficients

The history matching procedure used to identify the minerals reacting in the Berea sandstone core and their reaction-rates was enlightening with regards to the interaction of the minerals, their concentrations and their reaction-rates. The main issues identified by the author are:
A single-mineral model consisting of calcite can nearly describe the effluent pH measurements for the three corefloods when a mineral reaction-rate that is first-order in hydrogen concentration is used. Such a model requires more calcite than one would expect in a Berea core (0.051 volume fraction = 0.062 grain volume fraction) and will not increase the pH of acid once all the calcite is dissolved.

It is apparent that the mineral concentrations and reaction-rates are interrelated. Multiple combinations of mineral concentrations and mineral reaction-rates are likely to yield a reasonable history match for the pH profile. Examination of ion concentrations other than hydrogen concentration provides another means to choose the best mineral reaction-rate and volume fraction parameters for a coreflood simulation.

The presence of calcite and a clay mineral (such as kaolinite) together causes a significant precipitation-dissolution reaction involving the clay mineral. This precipitation-dissolution reaction can cause a temporary effluent plateau at pH=3 if slower calcite reaction-rates are used or if faster clay reaction-rates are used in the four-mineral model.

The reaction area equation (Equation 3-10) used in GEM slows the dissolution rate of minerals as they deplete. This leaves mineral present behind the dissolution front that dissolves away over time as more acid is injected.

Future acid injection coreflood experiments should also have the effluent concentrations of magnesium and sodium measured, along with any possible measurements to identify complex ions in solution. Such detailed measurements may
be useful to identify the reactive clays and ionic species that should be included in geochemical simulations.

- Representation of the geochemical reactions as a first-order reaction in hydrogen concentration offers a better effluent pH trend compared to using a constant reaction-rate like was used for the four-mineral final-match simulations.

4.6 Improved Performance of Geochemical and Polymer Injection Simulations

Modeling acidizing reactions between pH=1 hydrochloric acid and various minerals presented several numerical challenges to the GEM-GHG simulator. The following actions improved the numerical behavior of the simulator during the history matching and pH-sensitive polymer simulations:

- The use of very small timesteps is required to simulate mineral reactions with high reaction-rates. Maximum timestep sizes are controlled using the *DTMAX keyword.

- Simulation of geochemical reactions that involve large numbers of protons, such as the reaction of anorthite with hydrogen cations (\(\text{CaAl}_2\text{Si}_2\text{O}_8(s) + 8 \text{H}^+_{(aq)} = \text{Ca}^{2+} + 2 \text{Al}^{3+} + 2 \text{H}_2\text{SiO}_4(aq)\)), has been found by the author to be difficult to model when pH=1 acid was injected into the model unless very small timesteps are used. Increasing the pH of the injected acid eliminated this problem but was not the desired case to simulate.

- Use of GEM’s fully implicit solution scheme is often necessary to model acid-matrix reactions and to model polymer injection scenarios.

- Injection of aqueous fluids that contain zero concentrations of some aqueous species can lead to crashed runs. This may be caused by division by zero errors when the
activity product of mineral and intra-aqueous reactions are calculated. Injecting aqueous fluid with small concentrations (such as 1E-60 moles/kg) of the absent species rather than zero concentrations was found to eliminate this problem and did not affect any results.

- Use of larger simulation blocks improved the runtime of all simulations greatly. Use of local grid refinement (near the injection well) in the low-permeability layer of the polymer injection simulations increased the accuracy of those models substantially.

- Correspondence with representatives at the Computer Modelling Group suggests that use of the pH-sensitive polymer viscosity model and the presence of low ion concentrations may cause convergence problems in some simulations. Use of tighter convergence criteria and increasing the minimum and maximum number of Newton iterations in the model has improved model performance (use *CONVERGE, *ITERMIN, and *ITERMAX keywords).

4.7 Definition of the Damköhler Number

The Damköhler number, \( N_{Da} \), is a dimensionless number used to compare the reaction-rate of acid with a mineral to the acid convection rate. The Damköhler number groups the effects of mineral-acid stoichiometry, kinetics, acid concentration and Darcy velocity into one value. Use of this value allows comparison of the acid-matrix reactions between coreflood experiments or simulations without having to refer to case-specific reaction parameters and fluid flow conditions. Typically a large \( N_{Da} \) (greater than 10) indicates a fast acid reaction compared to the transport rate, whereas a small \( N_{Da} \) (less than 1) indicates a relatively slow acid reaction-rate. The Damköhler number can be defined in
several ways, but in this Thesis, it is defined based on the maximum mineral dissolution rate, $r_\beta$, used by GEM-GHG. For a linear reservoir layer the Damköhler number is:

$$ N_{Da} = \frac{LAr_{H}^+}{1000qa} \quad (4-3) $$

where $L =$ length of medium (m), $A =$ area perpendicular to flow (m$^2$), $q =$ acid flow rate (m$^3$/s), $a =$ $H^+$ molality (mol/kg), $r_{H^+} =$ reaction-rate of $H^+$ (mol/m$^3$·s, given by Equation 4-6).

Porosity ($\phi$) is absent in Equation 4-3 because the hydrogen reaction-rate is given as a function of bulk volume, not pore volume, which causes the porosity to cancel out in the derivation of this equation shown in Appendix 1. The acid molality ($a$) in Equation 4-3 should be used to calculate the Damköhler number of an acid-matrix reaction for acidizing purposes. It may be desirable to use Equation 4-4 first to calculate “a” when calculating the Damköhler number for pH-sensitive polymer viscosity calculations, since this gives the proton concentration change that will control the behavior of the polymer in situ. This was not done for calculations in this Thesis.

$$ a = \left[ \text{acid } H^+ \text{ concentration} \right] - 10^{-\text{Trigger}} \quad (4-4) $$

where Trigger is the maximum pH at which a solution of pH-sensitive polymer has low viscosity.

For a radial reservoir layer, the Damköhler number is:
\[ N_{Da} = \frac{\pi \cdot R_e^2 \cdot h \cdot r_{H^+}}{1000qa} \]  

(4-5)

where \( R_e \) is the outer radius of the reservoir layer (assuming \( R_e \gg R_{wellbore} \)).

The Damköhler number can be calculated for any shape of reservoir by changing the numerator of the above equation to include the bulk volume of the desired reservoir. The reaction-rate of \( H^+ \) is directly proportional to the mineral reaction-rate by the ratio, \( \nu_{H^+} / \nu_{\text{mineral}} \). This is the ratio of the number of moles of \( H^+ \) ions consumed per mole of mineral consumed.

\[
r_{H^+} = \frac{v_{H^+}}{v_{\text{mineral}}} = \frac{v_{H^+}}{v_{\text{mineral}}} \left( \text{sgn} \left[ 1 - \left( \frac{Q_{\beta}}{K_{eq,\beta}} \right) \right] \right) \hat{A}_\beta S_w \left( k_{\beta} + \sum_{i=1}^{n_{eq}} k_{i,\beta} a_{i,\beta}^{eq} \right) \left[ 1 - \left( \frac{Q_{\beta}}{K_{eq,\beta}} \right) \right] \zeta_{\beta} \phi_{\beta}
\]

(4-6)

Sample calculations for the Damköhler number and a mineral reaction-rate are given in Appendix 1.

Approximate Damköhler numbers have been calculated for coreflood Experiments 1, 2 and 3 for given flow rates assuming maximum mineral dissolution rates using the final-match reaction constants (Table 4-4) and the initial reactive surface areas (Table 4-5). These values are given in Table 4-6.
Table 4-6: Approximate Damköhler Numbers for the Coreflood Experiments

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Acid Injection Rate (cc/min)</th>
<th>Fluid Flow Area (m²)</th>
<th>Core Length (m)</th>
<th>Injected H+ Concentration (mol/liter)</th>
<th>Total H+ Reaction Rate (mol/(m³*s))</th>
<th>Approximate Damköhler Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>4.870E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>4.870E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>5.4</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4.870E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.831E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.831E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>13.4</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>4.831E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>4.831E-04</td>
<td>0.2247</td>
<td>0.1</td>
<td>0.4117</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Table 4-7: Calculation of Hydrogen Ion Reaction-Rate for Coreflood Experiments Based on Final-Match Parameters and Initial Reactive Surface Areas

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineral Reaction Rate Constant (mol/(m²*s))</th>
<th>Reactive Surface Area (m²/m³)</th>
<th>S_w (fraction)</th>
<th>Ratio of ( \nu_{H+}/\nu_{Mineral} )</th>
<th>Maximum H+ Consumption Rate (mol/(m³*s))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcite</td>
<td>0.00042658</td>
<td>470</td>
<td>1</td>
<td>2</td>
<td>0.4010</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>3.16228E-08</td>
<td>50000</td>
<td>1</td>
<td>6</td>
<td>0.0095</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>5.24807E-07</td>
<td>300</td>
<td>1</td>
<td>8</td>
<td>0.0013</td>
</tr>
<tr>
<td>Quartz</td>
<td>3.01995E-07</td>
<td>6960</td>
<td>1</td>
<td>0</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Total H⁺ Reaction Rate: 0.4117 (mol/(m³*s))

Equation 4-3 was used to calculate the Damköhler numbers for Table 4-6, and Equation 4-6 was used to calculate the total maximum H⁺ consumption rate for the corefloods in Table 4-7. The mineral reactions used for the Table 4-7 calculations came from Table 4-3 except for the net calcite reaction. The two possible net calcite reactions in the simulations are “calcite + 2 H⁺ = H₂CO₃ + Ca²⁺”, which results from the combination of the calcite reaction from Table 4-3 with the H₂CO₃(aq) intra-aqueous reaction from Table 4-2, and “calcite + 1 H⁺ = HCO⁻ + Ca²⁺”, which results from combining the calcite
reaction from Table 4-3 with the $\text{HCO}_3^-(aq)$ intra-aqueous reaction from Table 4-2. The
simulated coreflood effluent from Experiment 2 shows that there is more $\text{H}_2\text{CO}_3(aq)$ than
$\text{HCO}_3^-(aq)$ in the effluent so the “calcite + 2 $\text{H}^+ = \text{H}_2\text{CO}_3(aq) + \text{Ca}^{2+}$” reaction was used for
calculations in Table 4-7. Note that the quartz mineral reaction from Table 4-3 does not
consume hydrogen thus it was not included in the hydrogen reaction-rate calculation in
Table 4-7.
Chapter 5: PROPAGATING AN ACIDIC FLUID FRONT IN REACTIVE POROUS MEDIA

It is desirable to inject pH-sensitive polymer into reservoirs as a low-viscosity acidic fluid for several reasons. It will be shown in Chapters 6 and 7 that injecting this polymer as a low-viscosity fluid can improve flood conformance. Injecting pH-sensitive polymer as a low-pH fluid also increases the injectivity of the polymer. This chapter describes several strategies to place low-pH (acidic) fluids in a reservoir by lowering the Damköhler number of the acid-matrix reactions that occur in situ. The strategies described are increasing the injection velocity, using an acid preflush to consume fast-reacting minerals, using a high acid concentration, and using the pH buffering effect of weak acids. The analysis presented is from simulations containing the geochemical reaction-rates and mineral concentrations found from the history matching process described in Chapter 4 except for the sensitivity cases at the end of that chapter that use a first-order mineral reaction.

Propagating Acidic Fluids in Reactive Porous Media

Chapter 4 showed that hydrochloric acid reacts with Berea sandstone to increase the pH of the injected fluid while metal cations are liberated from the sandstone. Acid-matrix chemical reactions cause a low-pH front to travel slower than the injected fluid front. Injection of acidic pH-sensitive polymer into a reservoir may experience a large viscosity increase in situ unless the Damköhler number of the matrix-acid reaction is reduced to a low value to allow the polymer to travel at its minimum viscosity. The Damköhler number (Equation 4-3) can be reduced by increasing the acid velocity or proton
concentration or by decreasing the acid or polymer transport distance or the net hydrogen consumption rate \( r_{H^+} \). The net hydrogen consumption rate can be effectively reduced by using an acid preflush to consume the fast reacting mineral(s), such as carbonate minerals and clays in the case of sandstones, which leaves the slow reacting minerals behind. The net hydrogen consumption rate can be reduced while the geochemical reaction-rates stay constant by injecting a high concentration of a weak acid like acetic acid or citric acid that releases protons as it is consumed by the reservoir minerals. Numerical simulation should be favored over Damköhler number calculations to assess the \textit{in situ} pH of a polymer treatment. This is because a low Damköhler number can be calculated for an acid-matrix reaction even if the injected acid has a pH close to or above that required to swell pH-sensitive polymer (unless Equation 4-4 is used to calculate “a”). Another reason is because the assumption of constant hydrogen reaction-rate used in the derivation of Equation 4-3 is likely incorrect for real reactions.

**Simulations**

The simulation results presented in this chapter are based on the “final-match” mineralogy, aqueous species and reaction coefficients determined in Chapter 4 unless otherwise specified. A 1-D grid consisting of 200 cells (X-direction) was used. Each cell has a porosity of 0.177 and dimensions of 0.5 m, 2.377 m, and 2.377 m in the x, y, and z directions, respectively. The total pore volume of the model is 100 m³ (0.5 m³ per cell) and there is a constant-rate acid injector in cell 1 and a constant-pressure producer in cell
All cases start with a brine-filled reservoir with a pH of 10.23. Figure 5-1 shows a schematic of the 1-D simulation grid.

**Figure 5-1: Schematic of One-Dimensional Simulation Grid**

**Effect of In situ Acid Velocity**

Changing the acid flow velocity by modifying the injection rate is a way of changing the Damköhler number of a reaction. The figure below demonstrates the effect of varying the flow velocity of pH=1 hydrochloric acid flowing through the linear grid. The dimensionless distance shown is the distance from the injection well divided by the reservoir length (100 m). The dimensionless concentration of non-reactive chloride is shown to demonstrate the mixing effect between the acid and reservoir brine near the end of the reservoir in the 0.3 m/d velocity run. Dispersion and diffusion cause mixing in real single-phase fluid displacements similar to the acid injection modeled here, but only numerical dispersion (common to reservoir simulators) is responsible for the mixing of
the acid and the reservoir brine that is observed in the simulation results shown in this chapter. Theoretically no chloride tracer should remain in the simulation grid after one pore volume of acid is injected if numerical dispersion is absent.

![Diagram showing pH profiles for different velocities with Damköhler numbers](image)

**Figure 5-2: In situ pH Profiles for Velocity Sensitivities (After One Pore Volume of pH=1 HCl Acid Injected)**

Figure 5-2 shows that the pH profile in a linear geometry flood is greatly affected by the acid flow rate in the flood. The Darcy velocities of 0.3, 4.425, 17.70 and 88490 m/d shown correspond to injection rates of 1.7, 25, 100, and 500 000 m$^3$/d and to approximate Damköhler numbers of 1.18x10$^5$, 8040, 2010, and 0.4, respectively. The approximate Damköhler numbers were calculated similarly to those shown in Table 4-6. The large pH increase for the high velocity case (88490 m/d) at dimensionless distances above 0.8 is caused by fluid mixing rather than by chemical reactions.
Effect of Acid Concentration

The Damköhler number of an acid-matrix reaction can be decreased by increasing the concentration of the acid injected for a given acid injection rate. Figure 5-3 shows the *in situ* pH profile in the acid flood as a function of dimensionless distance for various concentrations of hydrochloric acid injected at 25 m$^3$/d (Darcy velocity of 4.425 m/d). Injected acid concentrations of 1 molal, 0.1 molal and 0.01 molal were simulated, giving acid pHs of 0, 1, and 2, respectively. Dimensionless Cl- tracer concentration is shown for the pH=2 acid injection case. Approximate Damköhler numbers are shown.

![Figure 5-3: *In situ* pH Profiles for Various Acid Concentrations (After One Pore Volume Injected)](image)

The unusual local pH increase at dimensionless distances from 0.05 to 0.10 for the pH=0 acid injection case is caused by mineral precipitation of the kaolinite in the simulation.
This can be confirmed by Figure 5-4 that shows the mineral concentrations as a fraction of their initial values. From the equation in Table 4-3, the precipitation reaction for kaolinite is: 

$$2 \text{Al}^{3+} \text{(aq)} + 2 \text{H}_4\text{SiO}_4\text{(aq)} + \text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5\text{(OH)}_4\text{(s)} + 6 \text{H}^+ \text{(aq)}.$$ 

Figure 5-5 shows the falling $\text{Al}^{3+}$ and $\text{H}_4\text{SiO}_4\text{(aq)}$ concentration associated with the precipitation reaction.

**Figure 5-4: In situ Dimensionless Mineral Concentration Profiles (After One Pore Volume Injected)**
Figure 5-5: *In situ* $\text{Al}^{+++}$, $\text{H}_4\text{SiO}_4$ and $\text{H}^+$ Species Concentrations (After One Pore Volume Injected)

**Effect of an Acid Preflush**

A low-pH fluid front can be propagated by injecting a large volume of acid to consume the fast reacting mineral(s) in the reservoir. A simulation was performed with pH=1 hydrochloric acid being injected continuously into a linear reservoir at 25 m$^3$/d (Darcy velocity of 4.425 m/d). The pH stair-step profiles observed in Figure 5-6 are caused by the simulated calcite, kaolinite and potassium feldspar mineral dissolution fronts moving through the reservoir as acid is injected. The continued presence of pH=3 effluent was not observed in the experimental corefloods described in Chapter 4; but they can be expected based on the simulated pH profiles shown in Figure 5-6. This discredits the four-mineral Berea model.
Comparison of Strong Acid to Weak Acid

Strong acids ionize almost completely in water whereas weak acids only partially dissociate into protons and ligands. Simulations were performed to examine the pH profile resulting from injecting a strong acid (hydrochloric acid) and two different weak acids (acetic acid and citric acid). The dissociation reactions and equilibrium constants below are employed in the simulations (at 25°C). Equation 5-2 was added to the acetic acid simulation, and Equations 5-3, 5-4 and 5-5 were added to the citric acid simulation.

**Hydrochloric Acid**

\[ \text{HCl}_{(aq)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)} \quad \text{Assumed fully dissociated} \quad (5-1) \]

\( \text{H}^+_{(aq)} \) and \( \text{Cl}^-_{(aq)} \) were injected directly into reservoir in the aqueous phase

**Acetic Acid**

\[ \text{CH}_3\text{COOH}_{(aq)} \rightarrow \text{H}^+_{(aq)} + \text{CH}_3\text{COO}^-_{(aq)} \quad K_{eq} = 10^{-4.756} \quad (5-2) \]
Citric Acid
\[ C_6H_8O_7(aq) \rightarrow H^+_{(aq)} + C_6H_7O_7^{2-}_{(aq)} \quad K_{eq} = 10^{-3.128} \]  
(5-3)

\[ C_6H_7O_7^{2-}_{(aq)} \rightarrow H^+_{(aq)} + C_6H_6O_7^{3-}_{(aq)} \quad K_{eq} = 10^{-4.761} \]  
(5-4)

\[ C_6H_6O_7^{3-}_{(aq)} \rightarrow H^+_{(aq)} + C_6H_5O_7^{4-}_{(aq)} \quad K_{eq} = 10^{-6.396} \]  
(5-5)

Figure 5-7 shows the *in situ* pH profile for three cases after one pore volume of acid was injected at a rate of 25 m³/d (Darcy velocity of 4.425 m/d). The three cases shown involve the injection of 1 molal concentration solutions of hydrochloric acid (pH=0), acetic acid (pH=2.4) and citric acid (pH=1.6) into the linear flood.

![In situ pH Profiles](image)

**Figure 5-7: In situ pH Profiles After Injecting Various Types of Acid (1 Molal Concentration, After One Pore Volume Injected)**

Stronger acids are better suited for maintaining a low pH in the reservoir compared to weak acids with similar concentrations. Figure 5-8 shows the *in situ* pH profile after
injecting pH=2 solutions of hydrochloric acid, acetic acid and citric acid into Berea (at a rate of 25 m³/d) that have acid concentrations of 0.010 molal, 5.71 molal and 0.144 molal, respectively. The weaker acids maintain a low pH for a longer distance but require much higher concentrations than the strong acid (hydrochloric acid).

The injector in the pH=2 acid injection runs was shut-in after one pore volume of acid was injected, and the simulations were continued to monitor the pH in the reservoir as a function of time after the shut-in time. Figure 5-9 shows the pH in grid cell 100 (dimensionless distance of 0.4975) as a function of time. It took 0, 60 and 76 days for the hydrochloric, acetic and citric acid to approach equilibrium with the Berea reservoir, with final brine pHs of 7.38, 4.46 and 5.56, respectively.

Figure 5-8: *In situ* pH Profiles After Injecting Various Types of Acid (pH=2 Acid, Profile After One Pore Volume Injected)
Comparison of Strong Acid to Weak Acid in a Single-Mineral Model with a First-Order Mineral Reaction

It was shown in Chapter 4 (Section 5) that a single-mineral model, being calcite in the cases simulated (with a mineral reaction-rate that is first-order in hydrogen concentration), can closely match the effluent pH profile observed in three laboratory Berea corefloods. Use of a single-mineral model prevents unwanted mineral interactions that were observed using the four-mineral, final-match model parameters used for simulations presented to this point in this chapter. It is possible that use of a mineral reaction that is first-order in hydrogen concentration will alter the ability of weak acids to propagate a low pH fluid front compared to a strong acid. Single-mineral simulations were run using the 100-m long 1-D grid. Only calcite (0.051 volume fraction) is present.
in the simulation model and a calcite mineral reaction-rate constant \((k)\) of \(10^{-1.37}\ \text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}\) is used for the mineral reaction that is first-order in hydrogen concentration.

Figure 5-10 shows the \textit{in situ} pH profile for three cases after one pore volume of acid is injected at a rate of 25 \(\text{m}^3/\text{d}\) (Darcy velocity of 4.425 \(\text{m/d}\)). The three cases shown involve the injection of 1 molal-concentration solutions of hydrochloric acid (pH=0), acetic acid (pH=2.4) and citric acid (pH=1.6) into the linear flood.

![Figure 5-10: In situ pH Profiles After Injecting Various Types of Acid into a One-Mineral Model (1 Molal Acid Injection; Profile After One Pore Volume Injected)](image)

Figure 5-10: \textit{In situ} pH Profiles After Injecting Various Types of Acid into a One-Mineral Model (1 Molal Acid Injection; Profile After One Pore Volume Injected)

Stronger acids are better suited for maintaining a low pH in the reservoir compared to weak acids with similar concentrations in the one-mineral model. Figure 5-11 shows the \textit{in situ} pH profile after injecting pH=2 solutions of hydrochloric acid (0.010 molal), acetic
acid (5.71 molal) and citric acid (0.144 molal) into a one-mineral calcite model (at a rate of 25 m³/d). The weaker acids maintain a low pH for a longer distance but require much higher concentrations than the strong acid (hydrochloric acid).

**Figure 5-11: In situ pH profiles After Injecting Various Types of Acid into One-Mineral Model (pH=2 Acid Injection; Profile After One Pore Volume Injected)**

**Summary and Conclusions**

Several factors can be adjusted in an acid-polymer flood, such as varying the injected acid rate, concentration and type; and using a large acid preflush.

- Each factor affects the Damköhler number of a displacement but may have other effects on the *in situ* pH of reservoir brine. Considerations such as the lowest pH possible using a given acid type and concentration, and the final resulting pH upon completion of the geochemical reactions, should be made to ensure that an
acid injection strategy provides the desired low-pH environment and high final pH to propagate and gel pH-sensitive polymer *in situ*.

- Simulations using a four-mineral model with fixed mineral reaction-rate constants and a one-mineral model with a mineral reaction-rate first-order in hydrogen concentration both show similar results regarding the injection of weak and strong acids. Injection of strong acids provides a longer low-pH fluid region near the injection well compared to weak acids when the injected acid concentrations are equal. Injection of weak acids provides a longer low-pH fluid region near the injection well compared to strong acids when the injected acid pHs are equal.

- The four-mineral and one-mineral simulations shown in this chapter are based on the best-fit models from Chapter 4 chosen to represent Berea sandstone. The acid-matrix reactions and *in situ* pH profiles may be very different for acid injection into a matrix with a different mineralogy.
This chapter investigates conformance control for 1-D floods with multiple-layers using high-viscosity fluids and pH-sensitive polymer. Flooding patterns in petroleum reservoirs are rarely linear but such a model easily lends itself to analysis using analytical equations. Poor sweep efficiency results from flooding operations conducted in reservoirs comprised of multiple-layers with varying permeabilities. The effects of relative permeability, residual saturations and vertical crossflow that are often present in oil reservoirs are neglected in this chapter by using only aqueous fluids in the simulations and analytical calculations. These simplifications permit increased focus on the ability of high-viscosity fluids and pH-sensitive polymer slug treatments to increase conformance by diverting injected fluid from higher-permeability layers into lower-permeability layers using viscous forces. Comparisons are made between simulation results and analytical results in this chapter; but simulation results are used exclusively for two-phase analyses in Chapter 7. The GEM-GHG simulator is used to model continuous pH-sensitive polymer floods using a single-mineral model. All calculations and simulations shown in this chapter assume that the fluids have Newtonian rheology, and all fluid volumes shown are in terms of reservoir pore volumes.

**Simplified Reservoir Model**

Permeability variations in a reservoir often lower reservoir sweep efficiency from flooding operations, due to early breakthrough of the injected fluid to the producing well(s) before all the resident reservoir fluid is recovered. The porosity and permeability in real reservoirs vary spatially creating complex fluid flow paths that are often difficult
to model. Simplified linear reservoir models comprised of two horizontal layers arranged in a stack are used to represent permeability variations in a reservoir for analysis in this chapter. Each layer is assumed to have homogenous permeability (k) and porosity (Φ) throughout, although they may have a different permeability, porosity and height (h). An injection well is assumed to be completed into all the layers at one end of the reservoir and a production well is assumed to be completed into all the layers at the other end of the reservoir.

Figure 6-1: Simplified Linear Geometry Reservoir with Two Layers

A constant fluid injection rate of 25 m³/d is used for the simulations and analytical calculations in this chapter. All sweep efficiency plots and fractional flow allocation plots presented are plotted as a function of the pore volumes of fluid injected. Reznik et al. (1983) have shown that presenting results in this manner for multiple-layer linear reservoirs without vertical crossflow (vertical flow between layers) gives identical results for both constant injection rate and constant reservoir pressure drop conditions when
Newtonian fluids are injected. These authors warn that results generated for constant injection rate and constant reservoir pressure drop will vary greatly when presented as a function of time unless the flood mobility ratio is one. Constant injection rate and constant reservoir pressure drop results are not equivalent if time-dependent properties such as shear-thinning polymer rheology or acid-matrix reactions are involved in the simulations or calculations.

Effect of Permeability Heterogeneity on Oil Recovery

Water is a common flooding agent due to its availability and low cost. A two-layer linear simulation model similar to that shown in Figure 6-1 was constructed to show the impact of permeability variations between zones on the linear flood sweep efficiency. The linear grid properties given in Table 6-1 are used for the calculations and simulations performed in this chapter. There is no crossflow between zones and flow in the X-direction only.

Table 6-1: Reservoir Grid Properties for Single Phase Linear Simulations

<table>
<thead>
<tr>
<th>Reservoir Property</th>
<th>Layer 1 (top)</th>
<th>Layer 2 (bottom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.177</td>
<td>0.177</td>
</tr>
<tr>
<td>Height</td>
<td>9 m (Z-direction)</td>
<td>1 m (Z-direction)</td>
</tr>
<tr>
<td>Length</td>
<td>100 m (X-direction)</td>
<td>100 m (X-direction)</td>
</tr>
<tr>
<td>Width</td>
<td>56.497 m (Y-direction)</td>
<td>56.497 m (Y-direction)</td>
</tr>
<tr>
<td>X-dir Permeability, k</td>
<td>10 md or 100 md</td>
<td>varied by case</td>
</tr>
<tr>
<td>Y-dir Permeability</td>
<td>equals X-dir permeability</td>
<td>equals X-dir permeability</td>
</tr>
<tr>
<td>Z-dir Permeability</td>
<td>0 md</td>
<td>0 md</td>
</tr>
<tr>
<td>Initial Fluid Properties</td>
<td>$S_w = 1$, $\mu_{res} = 1$ cp</td>
<td>$S_w = 1$, $\mu_{res} = 1$ cp</td>
</tr>
<tr>
<td>Reservoir Pore Volume</td>
<td>10000 m$^3$ total</td>
<td></td>
</tr>
</tbody>
</table>
The cases modeled for both Chapters 6 and 7 using GEM assume that the reservoir is composed of only calcite with a calcite volume fraction of 0.047. The use of a one-mineral model was chosen to facilitate the calculation of Damköhler numbers of the acid-matrix reactions in the cases that involve pH-sensitive polymer. The calcite mineral reaction was modeled using the fixed reaction-rate constant like the final-match Berea simulations described in Chapter 4, and not using a first-order reaction approach, even though that can also be used if desired.

The simulation models or calculations used in this chapter assume that reservoir and injected fluids are single phase (water) to exclude relative permeability and residual saturation effects. The reservoir fluid has a viscosity of 1 cp. Table 6-2 shows the primary ("primary" species are those whose initial concentrations must be defined by the user in the GEM input file) ion concentrations present in the reservoir at time zero for water or high-viscosity fluid injection simulations and for pH-sensitive polymer injection simulations. The ion concentrations used for the water injection and the pH-sensitive polymer injection cases are the values that result when pH=7 brine (with 0.5 mol/kg NaCl) and pH=1 brine (with 0.5 mol/kg NaCl), respectively, equilibrate with the calcite-only reservoir. Use of different initial fluid conditions for the pH-sensitive polymer cases mimics a pH=1 acid preflush ahead of the injected polymer bank, that prevents poor simulation results caused by mixing of pH-sensitive polymer with high-pH reservoir brine (the use of preflush conditions made little difference for linear simulations, but they prevented unnatural fractional flow allocation oscillations in the radial geometry simulations in Chapter 7). Additional species exist in the aqueous phase (called “secondary” species in GEM documentation) whose initial concentrations do not need to be entered into the simulation file because GEM calculates their concentrations using the
primary species concentrations and the intra-aqueous chemical reactions (Table 4-2) used in the model.

**Table 6-2: Initial Primary Aqueous Species Concentrations (mol/kg) Used for Chapter 6 and 7 Simulations**

<table>
<thead>
<tr>
<th>Simulation Case</th>
<th>pH-Sensitive Polymer</th>
<th>H⁺</th>
<th>Ca⁺⁺</th>
<th>Na⁺</th>
<th>Cl⁻</th>
<th>CO₃²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water or High-Viscosity Fluid Injection</td>
<td>0</td>
<td>5.84E-11</td>
<td>9.24E-5</td>
<td>0.5</td>
<td>0.5</td>
<td>4.11E-5</td>
</tr>
<tr>
<td>pH-Sensitive Polymer Injection</td>
<td>0</td>
<td>4.06E-6</td>
<td>0.0531</td>
<td>0.5</td>
<td>0.5</td>
<td>7.16E-8</td>
</tr>
</tbody>
</table>

Figure 6-2 shows the swept volume (in pore volumes) of the reservoir (calculated using a spreadsheet) as a function of the volume of 1-cp water injected as the high-permeability (layer 2) zone permeability is varied. It can be observed that permeability variations between the layers cause the sweep efficiency to decrease dramatically. The unit slope observed on the plot for all cases shown (before 0.1 pore volumes injected) results at times before the injected fluid breaks through the high-permeability layer.
Figure 6-2: Swept Volume vs. Pore Volumes Injected for Two-Layer Linear Reservoir for Various Layer Permeability Ratios (Calculated Values, $Q_{inj} = 25 \text{ m}^3/\text{d}$)

Figure 6-2 demonstrates how permeability variations between layers can lower sweep efficiency. Analytical equations are presented next that predict fractional flow allocation, which affects sweep efficiency, into each layer when injection of high-viscosity fluid is used to improve flood conformance. The insight gained from the single-phase analytical equations improves interpretation of the two-phase, no crossflow simulation results shown in Chapter 7.

**Fractional Flow Allocation (FFA)**

When fluid is injected into an injection well (Figure 6-1) the fluid will flow into different zones at different rates depending on the reservoir layer properties and the viscosity of
the injected fluid and of the fluid in each layer. Since the fluid rate into each layer \((q_i)\) for an \(n\)-layer system) may change over time, it is useful to calculate the fractional flow allocation, \(f_i\), into each layer at any given time. This is the fraction of the total injected fluid rate \((Q)\) that is injected into any given layer in an \(n\)-layer reservoir:

\[
f_i = \frac{q_i}{Q} = \frac{q_i}{\sum_{j=1}^{n} q_j}
\]  

(6-1)

If it is assumed that the injected fluid (viscosity of \(\mu_{\text{inj}}\)) and reservoir fluid (viscosity of \(\mu_{\text{res}}\)) have the same viscosity, (and relative permeability is neglected for a single-phase flow), then the fractional flow into each layer can be calculated using Darcy’s law to get the following result:

\[
f_i = \frac{k_i h_i}{\sum_{j=1}^{n} k_j h_j}
\]  

(6-2)

This result is valid for all times for multi-layered reservoirs with linear and radial geometry and no crossflow (if the density of the reservoir fluid and the injected fluid is the same, this result is true for the crossflow case too). It can be observed that layers with a high-\(kh\) (permeability-height product) will take more of the injected fluid at the expense of the low-\(kh\) layers. It is in these cases that the higher-permeability layers are called thief zones and where a conformance control method is desired to divert fluid into the lower-permeability layers to increase oil recovery.
Ideal conformance of a flooding operation is when the injected fluid travels at an equal velocity \(v_{\text{ideal}}\) in each layer. In such a case all the reservoir fluid will be recovered with no early breakthrough of the injected fluid and with a piston-like fluid displacement. The fractional flow allocation for each layer corresponding to ideal conformance is related to the height of each layer:

\[
f_{i,\text{ideal}} = q_{i,\text{ideal}} = \frac{(v_{\text{ideal}})(\text{width})}{(v_{\text{ideal}})(\text{width})} \frac{h_{i,\text{ideal}}}{\sum_{j=1}^{n} h_{j}} = \frac{h_{i,\text{ideal}}}{\sum_{j=1}^{n} h_{j}}
\]  

This applies to multi-layered reservoirs of linear and radial geometry.

### 6.1 High-Viscosity Fluid Injection as a Conformance Control Method (No Crossflow)

The use of polymers like HPAM and xanthan gum to increase the viscosity of the injected fluid helps divert flow from high-permeability zones to low-permeability zones and increases the flood’s conformance. Some published polymer flooding field tests have been conducted, e.g. Chateaurenard field (Takagi et al., 1992) and Hankensbuettel field (Baviere, 1991). The effect of injecting a high-viscosity polymer (relative to the reservoir fluid viscosity) on the fractional flow allocation into each layer in the absence of crossflow can be calculated for a multi-layer linear reservoir by assuming piston-like displacement of the reservoir fluid by the polymer and by employing Darcy’s law. These calculations and the associated assumptions are given in Appendix 4 and yield the following result at times before the injected fluid breaks through at the producer:
The $\int \Delta P \, dt$ integral reduces to $\Delta P \cdot t$ for the case of the reservoir pressure drop remaining constant. For situations when the reservoir injection rate is held constant and $\Delta P$ changes with time, it is easiest to numerically integrate $\int \Delta P \, dt$. Appendix 4 explains how the ‘constant injection rate’ case is related to the ‘constant reservoir pressure drop’ case. Theoretically, maximum conformance control using a viscous fluid can be achieved by injecting a fluid with infinite viscosity. The limiting fractional flow allocation into each layer of a linear reservoir while an infinitely viscous Newtonian fluid is being injected can be calculated by taking the limit as the injected fluid viscosity approaches infinity. The result is that the fractional flow allocation approaches the following limit for layer $i$:

$$
\lim_{\mu_{\text{inj}} \to \infty} f_i = \frac{h_i \sqrt{\phi_i k_i}}{\sum_{j=1}^{n} h_j \sqrt{\phi_j k_j}}
$$

A similar result has been found by Sorbie and Mackay (2005) in terms of layer flow velocities except that their result did not include the layer porosities. Equations 6-4 and 6-
Analytical calculations were performed for a two-layer 1-D flood to obtain the fractional flow allocation between layers for a waterflood and a high-viscosity fluid flood. Figure 6-3 shows the fractional flow allocation effect of injecting fluids of various viscosities into the low-permeability zone of the model using analytical equations. For ideal conformance in this sample case, Equation 6-3 says that 90% of the injected flow rate must be allocated to the low-permeability zone. The plotted results came from Equation 6-4, with an adjustment made for post-breakthrough times. When the 100-cp and 1000-cp Newtonian fluids are injected, the fractional flow allocation into the low-permeability layer approaches the value of 0.4737 calculated for this layer from Equation 6-5, before the injected fluid breaks through to the producing well after about 0.2 pore volumes have been injected.
The 100-cp fluid injection case was also modeled using the GEM-GHG simulator. Figure 6-4 shows the calculated and simulated fraction flow allocation of fluid into each zone when 100-cp Newtonian fluid is injected into the two-layer linear reservoir. Newtonian high-viscosity fluid was simulated in GEM by setting the e4 parameter in the pH-sensitive polymer rheological model to zero to disable shear-thinning rheology, and by injecting water that had the same composition as the reservoir fluid (Table 6-2) except that it also contained enough pH-sensitive polymer ($6.251 \times 10^{-6}$ mol/kg) to increase the injected fluid viscosity to 100 cp. There is close agreement between the two methods. Both show the large amount of flow rate diversion from the high-permeability layer to the low-permeability layer at early times.
Two Layer Linear Reservoir:
Length = 100 m, width = 56.497 m
Layer 1: h=9 m, Φ = 0.177, k₁ = 100 md
Layer 2: h=1 m, Φ = 0.177, k₂ = 10000 md

Figure 6-4: Fractional Flow Allocation Comparison Between Simulation and Analytical Calculations (100-cp Fluid Injected, Q_{inj} = 25 m³/d)
Cumulative Swept Volume

Table 6-3 shows the effect of permeability variations and of injected fluid viscosities on the swept volume of the two-layer linear model after injecting one pore volume of displacing fluid (water or high-viscosity fluid). The low-permeability zone (layer 1) had a permeability of 100 md and the permeability of the high-permeability layer varied as a factor of 100 md. Table 6-3 gives results from analytical calculations, and the results of GEM simulations conducted for the same cases using the fluids with viscosities up to 1000 cp differed only by up to 1% swept volume, and are not listed.

Table 6-3: Swept Volume of a Two-Layer Linear Geometry Flood

<table>
<thead>
<tr>
<th>Permeability Ratio $k_2/k_1$</th>
<th>Swept Volume After 1 PV of Fluid Injected</th>
<th>$\mu_{injected}/\mu_{reservoir}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1.00 1.00 1.00 1.00 1.00 1.00</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.57 0.75 0.77 0.77 0.77 0.77</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.18 0.37 0.41 0.42 0.42 0.42</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0.11 0.16 0.21 0.22 0.22 0.22</td>
</tr>
</tbody>
</table>

Figure 6-5 shows the swept volume as a function of the volume of fluid injected at a rate of 25 m$^3$/d into a reservoir with Layer-1 permeability of 100 md and Layer-2 permeability of 10000 md (i.e., $k_2/k_1 = 100$) when fluids of various viscosities are injected. The main point is that increasing the viscosity of the injected fluid only helps improve the swept efficiency of a multi-layer linear flood to a limit if there is no vertical crossflow between zones.
Results have not been generated for cases where a constant pressure drop condition was imposed across the reservoir to inject viscous fluids into a flood. In such a case, it will take much longer to inject a fixed volume of high-viscosity fluid than to inject the same volume of low-viscosity fluid. Chapter 7 presents cumulative oil production plots versus injected volume and versus time for cases where high-viscosity aqueous fluids are used to displace oil using a target injection rate of 25 m$^3$/d, but where a maximum reservoir pressure drop limitation (5 MPa) across the reservoir is imposed.
6.2 pH-Sensitive Polymer Flooding as a Conformance Control Method (No Crossflow)

Polyacrylic-acid polymer microgel exhibits a viscosity dependence on its pH. This polymer can be injected into a reservoir in a low-viscosity acidic state. The injection viscosity in the simulation model (at 25°C) depends mainly on the concentration of the polymer, the pH of the solution, the ionic strength of the polymer solution and the shear rate of the polymer. Table 6-4 shows the viscosity of pH-sensitive polymer at initial conditions of pH=1 with 3 wt% NaCl (0.5 mol/kg) in solution, and at the final in situ conditions (pH = 5.39) when it is at equilibrium with the calcite reservoir. The values in Table 6-4 are at zero shear conditions.

**Table 6-4: Estimated Viscosity of pH-Sensitive Polymer in a Calcite Reservoir**

<table>
<thead>
<tr>
<th>Polymer Concentration (Molality)</th>
<th>Viscosity (pH 1) (Injected State, cp)</th>
<th>Viscosity (pH 5.39) (Final In Situ State, cp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.44E-06</td>
<td>1.2401</td>
<td>10</td>
</tr>
<tr>
<td>8.05E-06</td>
<td>1.6323</td>
<td>100</td>
</tr>
<tr>
<td>1.34E-05</td>
<td>2.2112</td>
<td>1000</td>
</tr>
<tr>
<td>1.93E-05</td>
<td>3.014</td>
<td>10000</td>
</tr>
<tr>
<td>2.53E-05</td>
<td>4.0947</td>
<td>100000</td>
</tr>
</tbody>
</table>

Simulation cases were run for the two-layer linear model with Layer-1 having a permeability of 10 md and Layer-2 having a permeability of 1000 md. The Damköhler number and the maximum final in situ polymer viscosity are the two values that characterize the cases. The Damköhler number values calculated used the following assumptions:

- The Damköhler number of the high-permeability zone is shown, although it can also be calculated for the low-permeability zone.
• The reservoir is modeled as containing calcite only, with a mineral volume fraction of 0.047 and a reactive surface area of 470 m$^2$/m$^3$. This represents only the calcite mineral reaction from the final-match parameters from Chapter 4.

• The fixed reaction-rate constant, $k$, was varied to give the desired approximate Damköhler number for a fluid injection rate of 25 m$^3$/d. Damköhler numbers of 0.01, 0.1, 1, 10 and 100 in the high-permeability layer were modeled by changing the fixed calcite reaction-rate constant to $10^{-10.278}$, $10^{-9.278}$, $10^{-8.278}$, $10^{-7.278}$, $10^{-6.278}$ moles·m$^{-2}$·s$^{-1}$, respectively. See Appendix 1 for detailed calculations.

• The flow rate into the high-permeability zone for the purpose of calculating the acid-matrix Damköhler number was calculated using the $kh$ product method given in Equation 6-2. In reality this flow rate changes as the polymer viscosity changes in situ while the polymer flows in the reservoir.

• Equation 5-1 assumes that the acid reacts at its maximum rate (which is not true.) This overestimates the Damköhler number.

• Assumed that two moles of H$^+$ are consumed per mole of calcite consumed for the reason discussed in Chapter 4 (Section 7).

Figure 6-6 shows the simulated swept volume of the reservoir as a function of volume of pH-sensitive polymer injected at 25 m$^3$/d into the model.
Inspection of Figure 6-6 suggests that for most cases the resulting swept volume curve for a 1-D pH-sensitive polymer flood is approximately bounded by the recovery from a waterflood (at very low Damköhler numbers) and by the recovery from a conventional polymer flood with a viscosity equal to the fully reacted viscosity of pH-sensitive polymer (at high Damköhler numbers.) In the case where the Damköhler number of the acid-matrix reaction is approximately one in the thief zone, a short period of increased oil recovery results at the expense of ultimate recovery.

Figure 6-7 shows the viscosity profile of the aqueous phase across layer 1 and layer 2 for the $N_{Da} = 1$ case (At time zero: $N_{Da} = 1$ for layer 2 and $N_{Da} = 100$ for layer 1, and $N_{Da}$
changes with time for each layer as the flow allocation changes) after 0.1, 0.2, 0.3, 0.4 and 0.5 pore volumes of pH-sensitive polymer (maximum viscosity of 1000 cp *in situ* given polymer concentration of $1.34 \times 10^{-5}$ mol/kg) have been injected. Notice that the displacement becomes unstable since the low-viscosity polymer is displacing high-viscosity polymer. This does not harm recovery in this simulation because there is only one grid cell in the z and y directions in each of the non-communicating horizontal layers, but may negatively affect 2-D and 3-D simulations.

![Viscosity Profiles](image)

**Figure 6-7:** Aqueous Phase Viscosity Profile in Each Layer during pH-Sensitive Polymer Flood after 0.1, 0.2 and 0.5 PVI ($N_{Da} = 1$, No Crossflow, $k_2/k_1=100$)
Figure 6-7 shows why the $N_{Da} = 1$ case shows excellent recovery in Figure 6-6 before 0.4 pore volumes of fluid is injected, and why the swept volume remains virtually unchanged after 0.5 pore volumes of pH-sensitive polymer are injected (PVI). Figure 6-7 shows:

- After 0.1 PVI, the injected polymer viscosity (2.21 cp at pH=1 from Table 6-4) in the reservoir starts to increase to 250 cp in layer 2 (high-permeability layer) as the polymer front approaches the production well (at 100 m).

- After 0.2 PVI, the polymer has formed a 1000-cp blockage in the high-permeability layer (layer 2) while only a small amount of polymer has a high-viscosity in the low-permeability layer. The presence of the blockage in the high-permeability layer forces polymer to invade the low-permeability zone (layer 1). The Damköhler number in layer 1 will decrease as the flow velocity increases, however, it will remain above 1 in this example case.

- After 0.3 PVI, the polymer viscosity in layer 1 has increased to 1000 cp at one location, and the 1000-cp polymer slug in layer 2 has been pushed towards the production well.

- After 0.4 PVI, nearly all the pH sensitive polymer in layer 1 has attained its final viscosity of 1000 cp. This caused low-viscosity acidic polymer to displace most of the high viscosity slug in layer 2.

- By the time 0.5 pore volumes have been injected into the reservoir, the flow path of any subsequently injected fluid has been altered greatly from the initial conditions. At 0.5 PVI and afterwards, the low-permeability layer is almost completely plugged by 1000-cp polymer (this final viscosity can be varied by changing the injected polymer concentration). At times greater than 0.5 PVI any more low-viscosity polymer that is injected quickly flows through the high-permeability layer before its viscosity increases (because the Damköhler number...
is now less than 1 due to higher fluid velocity), and the swept volume of the low-permeability zone barely increases. This observation applies to 1-D pH-sensitive polymer floods where the increase in polymer viscosity ratio ($\mu_{\text{MAXIMUM IN SITU}} : \mu_{\text{INJECTED FLUID}}$) is greater than the permeability ratio ($k_{\text{HIGH}} : k_{\text{LOW}}$).

6.3 pH-Sensitive Polymer Slugs as a Conformance Control Method (No Crossflow)

The most effective way to use pH-sensitive polymer to improve conformance when there is no reservoir crossflow is to inject it only into the thief zones at a very low-viscosity, then to let a slug of the polymer react with the formation to achieve very high-viscosity in these zones. This can be accomplished by using packers during the injection phase to force the polymer fluid into the thief zone perforations. Alternatively when crossflow is present, it may be possible to inject the polymer into thief zones using packers and to inject a non-geling fluid like water into the low-permeability zones simultaneously to maintain high pressures in the low-permeability zones. This will help prevent plugging of the low-permeability zones from the gelled polymer. Such ideal cases have not been modeled or analyzed here. The cases described next assume that a slug of pH-sensitive polymer is injected into all the layers in a linear geometry flood as a low-viscosity fluid before its viscosity is allowed to increase.

Determination of pH-Sensitive Polymer Slug Effectiveness Using Analytical Equations (No Crossflow)

It has been observed that continuous injection of pH-sensitive polymer into all layers of a linear geometry flood (Figure 6-6) may improve oil recovery compared to conventional polymer flooding (Figure 6-5), when small volumes of polymer have been injected
(before 0.25 PVI in Figure 6-5). The long term advantage of using the pH-sensitive polymer, however, was not substantial compared to conventional polymer flooding. Analytical calculations were performed using a spreadsheet to test the effect of injecting a slug of pH-sensitive polymer into a linear reservoir followed by waterflooding of the reservoir. The calculations described in Appendix 5 were performed for small time increments to solve for fluid front positions (pH-sensitive polymer slug front and subsequent waterflood front) as a function of time. The calculations assumed Newtonian fluid rheology, no polymer dispersion, no viscous fingering and single-phase fluid behavior (i.e., no relative permeability or residual fluid saturations). Figure 6-8 shows the idealized pH-sensitive polymer slug displacement analyzed with the spreadsheet calculations.
The procedure used to estimate the swept volume of the two-layer reservoir follows:

- Solve for the final position of the injected pH-sensitive polymer front in each linear layer after a slug of a given size was injected. It was assumed that the polymer was injected at its pH=1 viscosity from Table 6-4 and that the reservoir was initially filled with 1-cp fluid. Equation A4-7 (Appendix 4) could have been used to find the pH-sensitive polymer front positions instead at times before the polymer reached the production well in any zone.

- The viscosity of the injected pH-sensitive polymer in the spreadsheet was replaced by the corresponding final in situ viscosity from Table 6-4 for the given polymer concentration. This emulates the polymer reacting with the matrix to cause an increase in polymer viscosity.

- It was assumed that 1-cp water continuously flooded the reservoir after the polymer slug was at its maximum viscosity. The final positions of the pH-sensitive polymer...
fronts in each layer, and the corresponding reservoir swept volume, were calculated after one pore volume of fluid was injected (polymer and water combined).

The analytical calculations give qualitative support for sizing and using polymer slugs in field applications as will be explained.

The swept volume of reservoir fluid was determined after one pore volume of water and pH-sensitive polymer combined was injected into a linear reservoir for different polymer slug sizes with different final viscosities. Figure 6-9 shows the results for a two-layer 1-D reservoir.

![Graph showing theoretical swept volume for pH-sensitive polymer slug treatments](image)

**Figure 6-9: Theoretical Swept Volume for pH-Sensitive Polymer Slug Treatments After One Pore Volume of Fluid Injected**
Interestingly, there appears to be an optimal slug size that depends on the final viscosity of the polymer slug in situ. Injecting a polymer slug followed by a waterflood is less effective at recovering oil than a continuous conventional polymer flood (Table 6-3) when the pH-sensitive viscosity ratio ($\mu_{\text{IN SITU MAX POLYMER}} : \mu_{\text{RES FLUID}}$) is less than the ratio of ($K_{\text{HIGH}} : K_{\text{LOW}}$). When the ratio of ($\mu_{\text{IN SITU MAX POLYMER}} : \mu_{\text{RES FLUID}}$) was greater than the ratio of ($K_{\text{HIGH}} : K_{\text{LOW}}$), the slug of polymer followed by a waterflood achieved higher theoretical oil recovery than continuous polymer floods with very high viscosities.

It can also be observed from Figure 6-9 that the higher the final pH-sensitive polymer slug viscosity in situ, the smaller the polymer slug required.

The position of the trailing fronts (back of slug) of the polymer slugs in both the high-permeability layer and the low-permeability layer are plotted as a function of fluid volume injected in Figure 6-10 for a case where a 0.035 PV slug is injected that has a final in situ viscosity of 1000 cp. The plot shows that nearly all the oil recovered by the slug occurs between the time when the slug is injected and the time when all the polymer is produced from the high-permeability layer. This length of time can be extended by injecting a smaller slug volume of pH-sensitive polymer and by having the polymer achieve higher in situ viscosity to make the fractional flow allocation of the waterflood more ideal.
The mechanisms that cause optimal pH-sensitive polymer slug sizes in multiple-layer linear floods are the beneficial viscosity increase of the polymer in situ and the detrimental effect of producing the polymer slug from the reservoir. It can be shown that if polymer is injected all layers of a linear reservoir with no crossflow with the same viscosity as the reservoir fluid then the slug has a front position in each layer given by Equation 6-6 when it is placed. It will be assumed for following calculations that the polymer is injected into the injector well, and that it does not break through to the producing well before it is allowed to gel to high-viscosity.

Figure 6-10: Position of pH-Sensitive Polymer Slug vs. Volume of Fluid Injected
\[ X_i = t_D \cdot L \cdot \frac{\sum_{j=1}^{n} h_j \phi_j}{\phi_i \sum_{j=1}^{n} k_j h_j}, \quad X_i \leq L \]  

(6-6)

where \( X_i \) is the front position of the injected fluid, \( t_D \) is the number of pore volumes of fluid injected, \( L \) is the length of the linear reservoir, \( k \) is permeability, \( h \) is height, \( \phi \) is porosity, and \( n \) is the number of layers in the reservoir.

When this polymer achieves high viscosities in situ, \((\mu_{\text{IN SITU MAX POLYMER}} : \mu_{\text{RES}})\) is greater, at least 10 times for example, than the ratio of \( K_{\text{HIGH}} : K_{\text{LOW}} \) due to acid-matrix reactions, then the fractional flow into each layer of an \( n \)-layer system approaches the following limit when a fluid with the same viscosity as the reservoir fluid (i.e., waterflood) is injected afterward.

\[ \lim_{\mu_{\text{polymer}} \to \infty} f_i = \frac{h_i \phi_i}{\sum_{j=1}^{n} h_j \phi_j} \]  

(6-7)

This is very close to the desired ideal conformance fractional flow allocation given in Equation 6-4 except that the porosity of each layer is included. If porosities are the same for each layer, Equation 6-7 reduces exactly to the ideal fractional flow allocation.

When the polymer slug is followed by a flooding agent with the same viscosity as the reservoir fluid and viscous fingering is neglected, then the near ideal fractional flow allocation is maintained until the polymer slug reaches the producer in any of the layers. Upon breakthrough of the polymer slug, the fractional flow into the high-permeability
layer increases and the initial reservoir fluid production rate from the reservoir declines as shown in Figure 6-10. Hence, it is desirable from a theoretical standpoint to inject a small slug of pH-sensitive polymer because it will recover the most oil until the front of the slug in the high-permeability layer reaches the producer. On the other hand, it is desirable to inject a larger pH-sensitive polymer slug that can achieve high viscosities so the limit given in Equation 6-7 can be achieved.

Simulations of pH-Sensitive Polymer Slug Treatments (No Crossflow)
GEM simulations were performed to verify the effectiveness of using pH-sensitive slugs to improve flood recovery in conjunction with subsequent waterflooding. Analytical calculations showed that slug treatments are an effective conformance control method but such calculations did not explicitly model the chemical reactions that caused pH-sensitive polymer to increase its viscosity \textit{in situ}, nor did they consider any fluid mixing effects or shear-thinning polymer rheology effects that will affect polymer behavior in a reservoir.

GEM simulations were performed to model the swept volume curve associated with injecting a pH-sensitive polymer slug into a two-layer linear model (layer 1 permeability is 100 md, layer 2 permeability is 10000 md) followed by waterflooding. Each horizontal layer was divided into 200 cells in the X-direction. Additional grid refinement of the cells near the injection well (1 large cells refined to 5 or 10 smaller ones) improved the modeling of the flow diversion effect caused by the slug treatment. A pH=1 solution of pH-sensitive polymer \( \left( C_{\text{polymer}} = 1.34 \times 10^{-5} \text{ mol/kg}, C_{\text{NaCl}} = 0.5 \text{ mol/kg}, \text{see Table 6-4} \right) \) was injected at a constant rate of 25 m\(^3\)/d into the single-mineral calcite reservoir (fixed reaction-rate constant of \( 10^{-9.278} \text{ moles m}^{-2} \text{ s}^{-1} \) to give acid-matrix \( N_{Da} \) of 0.1 for the given injection rate). A Damköhler number of the acid-matrix reaction of 0.1 was selected to
ensure that the polymer did not experience a large viscosity increase during injection. Models simulating 0.035 and 0.05 PV slug size treatments were run. Once the polymer slug was injected, the injector was shut-in for 1000 days to let the pH-sensitive polymer reach its final viscosity of 1000 cp, and then 1-cp, pH=7 brine (0.5 mol/kg NaCl) was injected afterwards. Figure 6-11 shows simulated and calculated swept volume curves for 0.035 and 0.05 PV pH-sensitive polymer treatments followed by waterflooding. The simulated results shown in Figure 6-11 assume the polymer behaves as a Newtonian fluid ($e_4 = 0$).

It was convenient to vary the calcite mineral reaction-rate constants in the simulations to achieve the desired Damköhler number for a simulation, but such reaction-rate constants likely cannot be changed in a reservoir. It is probable that one would choose to vary the acid injection rate to achieve a desired Damköhler number. It would require an acid injection rate of approximately $28.8 \times 10^9$ m$^3$/d to inject a pH-sensitive polymer slug treatment into a reservoir comprised of the final-match Berea minerals (overall $r_{H^+} = 0.4117$ mol/(m$^3$·s) from Table 4-7) at a Damköhler number of 0.1. It is likely that pH-sensitive polymer slug treatments will only be suitable for reservoirs comprised of very slow reacting minerals, or those where a small acid preflush before a treatment will consume all fast reacting minerals like clays and calcite.
Figure 6-11: Calculated and Simulated Swept Volume Curves for pH-Sensitive Polymer Slug Treatments

Figure 6-11 shows that the simulated slug treatments achieved much higher sweep efficiencies than analytical calculations predicted. Fluid mixing caused by numerical dispersion in the low-permeability zone in the simulations caused the 1000-cp polymer slug initially in that zone to dilute to very low concentrations. This lowered the slug viscosity as it moved in the low-permeability layer. The slug velocity in the high-permeability layer was much lower, and thus the polymer effectively prevented flow through the thief zone.

The pH-sensitive polymer slug simulations shown in Figure 6-11 were changed to include the effect of shear-thinning in the pH-sensitive polymer rheology code by
changing the e4 parameter to the value of 0.0000001, as determined by Huh et al. (2005), in Table 3-4 for EZ-2 polymer. The ultimate swept volume curve did not improve over the cases that modeled the polymer as a Newtonian fluid. Shear-thinning did cause the slug viscosity in layer 1 and 2 to decrease to 960 cp and 720 cp, respectively, from 1000 cp when waterflooding was initiated. The layer flow velocities in layer 1 and 2 corresponding to the decreased viscosities were 0.03 m/d and 0.046 m/d, respectively.

Summary and Conclusions

In this chapter it has been shown that injection of high-viscosity fluids can improve flood sweep efficiency in layered linear reservoirs with permeability variations between layers.

- Continuous injection of high viscosity fluid, like conventional polymers, improves sweep efficiency over waterflooding. Increasing the viscosity of the injected fluid helps improve oil recovery only to a limit, and use of very high-viscosity fluids is unlikely to be technically or economically feasible in a reservoir when injectivity concerns are considered.

- Injection of pH-sensitive polymer as a flooding agent has been shown to be beneficial in linear reservoirs with no crossflow early in the flood when the Damköhler number of the acid-matrix reaction that controls the polymer viscosity is about 1 in the high-permeability layer. Given the geological variability in a reservoir it may be hard to design a flood with a Damköhler number of exactly one, but the result from that case suggests that injection of slugs of pH-sensitive polymer can be beneficial.

- Analytical calculations made using an excel spreadsheet showed that very high reservoir swept volumes can be achieved in a waterflood when a slug of pH-
sensitive polymer is placed in a linear geometry reservoir or flood pattern before waterflooding commences.

- Simulations of pH-sensitive polymer slug treatments showed improved oil recoveries compared to the analytically calculated values. This gives strong support for the use of pH-sensitive polymer slug treatments as an in-depth conformance control method in waterfloods with linear flow geometry.
Chapter 7: IN-DEPTH CONFORMANCE CONTROL IN LINEAR AND RADIAL GEOMETRY OIL RESERVOIRS

This chapter shows simulation results for the injection of water, high-viscosity aqueous fluids such as polymer, and pH-sensitive polymer into oil reservoirs with linear and injector-centered radial flood geometries. All results presented are from GEM-GHG simulations and include relative permeability effects and residual saturation effects that were neglected in Chapter 6 analyses. Continuous polymer injection and polymer slug treatment results are presented for cases of linear and radial flood geometries, with and without vertical crossflow. All produced oil volumes shown are in terms of the initial hydrocarbon pore volume of the model. All injected fluid volumes shown are in terms of reservoir pore volumes. The simulations do not include shear-thinning rheology, dispersion and polymer adsorption that are associated with polymer floods.

Common Simulation Inputs

Each simulation performed contained similar initial fluid saturations, oil properties, oil-water relative permeability curves, mineralogy and well parameters.

The reservoir models were initialized with 80% oil saturation, and 20% (connate) water saturation. The oil properties used are given in Table 3-1. The oil has a viscosity of 1.09 cp at 10 000 kPa (initial reservoir pressure). The reservoir water has a viscosity of 1 cp and contains the primary aqueous-species concentrations shown in Table 6-2. The pH=1 acid preflush species concentrations shown in Table 6-2 were used for the pH-sensitive polymer flood and slug treatment cases. As described later, an actual acid preflush was not included in the simulations, rather, the initial reservoir brine aqueous species equivalent to a pH=1 HCl preflush having occurred were used to minimize fractional
flow allocation oscillations between the reservoir layers due to fluid mixing effects. The simulations that include pH-sensitive polymer allow the polymer viscosity to increase to 1000 cp unless otherwise stated.

Figure 7-1 shows the oil-water relative permeability curves used in the simulations and the equations used to generate the curves. The resulting water fractional flow curve for a waterflood (1 cp water, 1.09 cp oil) is also shown.
The reservoirs modeled contain 0.047 volume fraction calcite, as estimated for Berea (from the four-mineral, final-match model) from the history-matching exercise described in Chapter 4. The models do not include kaolinite, potassium feldspar or quartz, nor the associated intra-aqueous chemical reactions related to these minerals. The mineral reaction-rate was varied as was done in Chapter 6 to simulate different Damköhler numbers associated with acid-matrix reactions when pH-sensitive polymer was injected into the reservoir models. Given a fixed injection rate of 25 m³/d, Damköhler numbers of 0.01, 0.1, 1, 10 and 100 were modeled in the high-permeability layer for both the linear and radial cases by changing the fixed calcite reaction-rate constant to $10^{-10.447285}$, $10^{-9.447285}$, $10^{-8.447285}$, $10^{-7.447285}$, $10^{-6.447285}$ moles·m⁻²·s⁻¹, respectively. Appendix 1 shows an example calculation of Damköhler numbers. The reaction constants for calcite corresponding to the various Damköhler numbers modeled in Chapters 6 and 7 differ slightly due to different water saturations in the flooded regions ($S_w = 1$ in Chapter 6 simulations, $S_w = 0.7$ in Chapter 7 simulations). Results presented in terms of Damköhler number are of broad significance since the acid concentration, acid type, mineralogy and acid injection rate are all factors that influence the Damköhler number associated with pH-sensitive polymer injection.

Each model contains one water/polymer injection well and one production well. Figure 6-1 shows the well positioning for the linear simulations, and Figure 7-20 shows the well positioning for the radial simulations. Each well is modeled as a vertical well that has a wellbore radius of 0.1 m, no skin, and is fully completed in each horizontal layer in the simulation models. For all the models the target injection rate into the reservoir is 25 m³/d unless a 15000 kPa maximum bottom hole pressure (bhp) limit was reached. A 25 m³/d injection rate gives an average fluid Darcy velocity of 0.02 m/d (0.7 ft/d) in the linear
floods and an average Darcy velocity of 1.99 m/d (6.5 ft/d) at the injection well sandface in the radial floods. The 15000 kPa pressure limit is meant to represent a fracture pressure limitation. An injection pressure limit was not used for the pH-sensitive polymer flood cases since any variation in injection rate would alter the approximate Damköhler number of the flood. The injection pressures corresponding to these cases are shown.

Crossflow
Crossflow is the vertical movement of fluids between zones caused by viscous and/or gravity forces. Zapata and Lake (1981) discuss the major differences between crossflow and no crossflow displacements which include:

- Injecting a fluid with a higher viscosity than the reservoir fluid viscosity (endpoint mobility ratio $M^0 < 1$) causes improved vertical sweep efficiency over the no crossflow case.

$$M^0 = \frac{k_w^0 \cdot \mu_o}{k_o^0 \cdot \mu_w}$$

where $\mu_w$ is aqueous phase viscosity, $\mu_o$ is oleic phase viscosity, and $k_w^0$ and $k_o^0$ are the endpoint relative permeabilities of water and oil, respectively.

- The ordering of the layered reservoirs with three or more layers causes different vertical sweep efficiencies.

- The injected fluid-oil fronts in each layer must have self-sharpening waves for vertical equilibrium crossflow to increase vertical sweep efficiency.

- The effective length ratio, $R_L$, should exceed 10 for the vertical equilibrium assumption that allows a large degree of crossflow to be valid.
\[ R_L = \frac{L}{H_t} \left( \frac{\bar{k}}{k} \right)^{1/2} \]  

(7-2)

where \( L \) is the reservoir length, \( H_t \) is the total reservoir height, \( \bar{k}_z \) is the harmonically-averaged vertical permeability, and \( k \) is the arithmetically-averaged vertical permeability (Lake, 1989).

The use of a simulator allowed the effect of crossflow on oil recovery to be analyzed. All the simulation models have a thick, low-permeability oil zone above a thin, high-permeability oil zone. The simulation cases that do not have crossflow have two horizontal layers with vertical permeabilities of 0 md. The two-layer, no-crossflow cases represent the reservoir layers as 1-D models in parallel. The cases with crossflow have 15 horizontal layers with vertical permeabilities one-tenth of their horizontal permeabilities. When crossflow is permitted, the low-permeability zone (18 m thick) is vertically divided into 10 layers with the thicker blocks being at the top of the zone. The high-permeability zone is vertically divided into 5 layers with heights of 0.4 m. The 15-layer crossflow models represent a 2-D reservoir. The presence of vertical permeability and the additional vertical resolution allows viscous channeling in the horizontal direction and crossflow in the vertical direction to occur.

### 7.1 Linear Reservoirs

Simulation models representing a linear geometry flood as shown in Figure 6-1 were developed to compare oil recoveries resulting from water injection, conventional polymer injection, pH-sensitive polymer injection and slug treatments. Table 7-1 shows the grid properties for the models. The simulations had one cell in the horizontal \( Y \) direction and
100 cells in the horizontal (X) flow direction with additional grid refinements near the injection well (often 10 refined cells per simulation cell) to improve the accuracy of the models.

### Table 7-1: Linear Simulation Grid Properties

<table>
<thead>
<tr>
<th>Reservoir Property</th>
<th>Layer 1 (top)</th>
<th>Layer 2 (bottom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
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<td>0.177</td>
</tr>
<tr>
<td>Height</td>
<td>18 m (Z-direction)</td>
<td>2 m (Z-direction)</td>
</tr>
<tr>
<td>Length</td>
<td>100 m (X-direction)</td>
<td>100 m (X-direction)</td>
</tr>
<tr>
<td>Width</td>
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<td>56.497 m (Y-direction)</td>
</tr>
<tr>
<td>X-direction Permeability</td>
<td>100 md</td>
<td>10000 md</td>
</tr>
<tr>
<td>Y-direction Permeability</td>
<td>100 md</td>
<td>10000 md</td>
</tr>
<tr>
<td>Z-direction Permeability</td>
<td>0 md or 10 md</td>
<td>0 md or 1000 md</td>
</tr>
<tr>
<td>Hydrocarbon Pore Volume</td>
<td></td>
<td>16000 m³ total</td>
</tr>
<tr>
<td>Reservoir Pore Volume</td>
<td></td>
<td>20000 m³ total</td>
</tr>
</tbody>
</table>

#### 7.1.1 High-Viscosity Fluid Floods: Linear Geometry Without Crossflow

Newtonian aqueous fluids were injected into the reservoir in the simulations by setting the polymer rheological model e4 parameter to zero. 10-cp, 100-cp and 1000-cp high-viscosity aqueous fluids were emulated by adding $2.66 \times 10^{-6}$, $6.251 \times 10^{-6}$ or $1.0434 \times 10^{-5}$ mol/kg concentrations of pH-sensitive polymer into the injected pH=10.23 brine. Chemical reactions did not occur in these simulations since the injected fluid was at equilibrium with the reservoir mineral. Comments included at the end of the GEM input file in Appendix 2 give the aqueous compositions injected in all of the simulations.
Figure 7-2 shows the volume of oil recovered versus the volume of fluid injected into the linear flood when there is no crossflow between the two horizontal layers.

![Graph shows oil recovery versus pore volumes injected for different fluid viscosities.]

**Figure 7-2: Oil Recovery versus Volume of Fluid Injected Using High-Viscosity Fluids (Linear Case, No Crossflow)**

Figure 7-3 shows oil recovery versus time for the same linear simulations without crossflow. The presence of the 15000 kPa injector pressure limit lowered the injection rate in the 100-cp and 1000-cp fluid floods as depicted in Figure 7-4. Figure 7-2 shows that the 1000-cp fluid flood recovers oil most efficiently in terms of fluid volume injected, but Figure 7-3 shows that the 10-cp fluid flood recovers oil the fastest.
Figure 7-3: Oil Recovery versus Time Using High-Viscosity Fluids (Linear Case, No Crossflow)

Figure 7-4 shows the injected fluid rates and injection pressures for the linear floods. The 1000-cp fluid injection well immediately reached its pressure limit, and the 100-cp fluid injection well reached its limit after 80 days of injection. The injectors in the 1-cp and 10-cp fluid flood cases could have injected fluid at much higher rates before reaching their pressure limit. Injecting at higher limits would allow the 1-cp and 10-cp fluid floods to recover oil even faster than the recovery curves shown in Figure 7-3.
Figure 7-4: Injection Well Bottom Hole Pressures and Rates versus Time Using High-Viscosity Fluids (Linear Case, No Crossflow)

7.1.2 High-Viscosity Fluid Floods: Linear Geometry With Crossflow

Linear flood cases were run where vertical crossflow was permitted. The presence of crossflow substantially improved recovery over the no-crossflow cases. All the recoverable oil (0.625 hydrocarbon pore volumes) was produced shortly after 0.8 PV of 100-cp or 1000-cp fluid was injected into the linear reservoir with crossflow. Figure 7-5 shows oil recovery versus volume of fluid injected, and Figure 7-6 shows oil recovery versus time. Figure 7-5 shows that the 1000-cp fluid flood recovers oil the most efficiently in terms of volume of fluid injected, but Figure 7-6 shows that the 100-cp fluid flood recovers oil the most quickly.
Figure 7-5: Oil Recovery versus Volume of Fluid Injected Using High-Viscosity Fluids (Linear Case, With Crossflow)

Figure 7-6: Oil Recovery versus Time Using High-Viscosity Fluids (Linear Case, With Crossflow)
Figure 7-7: Injection Well Bottom Hole Pressures and Rates versus Time Using High-Viscosity Fluids (Linear Case, With Crossflow)

Figure 7-7 shows the injected fluid rates and injection pressures for the linear floods with vertical crossflow. The 1000-cp fluid injection well immediately reached its 15000 kPa pressure limit, and the 100-cp fluid injection well reached its limit after 106 days of injection. The injectors in the 1-cp and 10-cp fluid cases could have injected fluid at much higher rates before reaching their pressure limit. Injecting at higher limits would allow these floods to recover oil even faster than the recovery curves shown in Figure 7-6.

7.1.3 pH-Sensitive Polymer Floods: Linear Geometry Without Crossflow

Injection of acidic pH-sensitive polymer (polymer with pH=1 hydrochloric acid and 3 wt% NaCl) was modeled for linear reservoirs without crossflow for various Damköhler
numbers. The GEM input file in Appendix 2 shows the input data for the $N_{Da} = 1$ case, and Appendix 1 shows the Damköhler calculation procedure used to calculate the appropriate calcite reaction-rate constant for each case. The Damköhler numbers shown are approximated for the acid-matrix reactions in the high-permeability layer as discussed in Chapter 6.

Figure 7-8 shows the volume of oil recovered versus the volume of fluid injected as pH-sensitive polymer is injected for various Damköhler numbers when there is no crossflow. The oil recovery curves for 1-cp and 1000-cp fluid floods (from Figure 7-2) are shown for comparison. Acidic pH-sensitive polymer was injected into the simulations at a constant rate of 25 m$^3$/d. No pressure limitation was used for the pH-sensitive polymer injection wells since reductions in the injection rate could significantly change the approximate Damköhler number of the acid-matrix reactions. The simulations that generated the 1-cp and 1000-cp fluid flood recovery curves that are also shown for comparison did include a 15000 kPa injection well bhp limit.
Figure 7-8: Oil Recovery versus Volume of Fluid Injected Using pH-Sensitive Polymer (Linear Case, No Crossflow)

Figure 7-9 shows oil recovery versus time for the linear pH-sensitive polymer floods without crossflow. Figure 7-8 shows that the $N_{Da} = 100$ case recovered oil most efficiently in terms of volume of pH-sensitive polymer injected. Figure 7-9 shows recovery versus time, and that the $N_{Da} = 1$ case recovered the most oil of all the pH-sensitive polymer flood cases in the first 675 days, and that the $N_{Da} = 0.01$ case recovered the most oil of all the pH-sensitive polymer flood cases between 675 and 1000 days. Notice that the continuous 10-cp fluid flood recovered oil faster than the pH-sensitive polymer cases except for the $N_{Da} = 1$ case at times before 400 days.
Target $Q_{\text{inj}} = 25 \text{ m}^3/\text{d}$ for all cases
- Only 1 cp, 10 cp and 1000 cp fluid cases subject to 15000 kPa injection well pressure limit

Figure 7-9: Oil Recovery versus Time Using pH-Sensitive Polymer (Linear Case, No Crossflow)

Figure 7-10 shows the pH-sensitive polymer injection well bottom-hole pressures as the polymer was injected at 25 m$^3$/d. Injection well pressures in excess of 15000 kPa were modeled for the cases with Damköhler numbers of one and greater.
The oil recovery versus volume of fluid injected plot shown in Figure 7-8 for the two-phase oil reservoir appears similar to the swept volume versus volume of fluid injected plot results shown in Figure 6-6 for a single-phase pH-sensitive polymer flood. Figure 7-8, suggests that the injection of pH-sensitive polymer into a linear reservoir shows oil recoveries roughly bounded by the recoveries from the injection of water and of a fluid with the viscosity equal to the final in situ viscosity of pH-sensitive polymer (1000 cp in these simulations). At low Damköhler numbers (less than one) the oil recovery from a pH-sensitive polymer flood is similar to that of a waterflood. This is reasonable since the injected pH-sensitive polymer in this simulation has a viscosity of only 2.2 cp and does not increase viscosity much at low Damköhler numbers. At high Damköhler numbers (>1) the oil recovery from the pH-sensitive polymer flood is similar to the recovery from injection of a high-viscosity fluid. In this situation the viscosity of the injected pH-
sensitive polymer may reach its final viscosity (1000 cp in this example) shortly after it contacts the reservoir. pH-sensitive polymer floods conducted with a Damköhler number of 1 in a linear reservoir exhibit very high oil recoveries at the start of the flood, but experience little incremental oil production after a certain point. This behavior, discussed in Chapter 6 and depicted by Figure 6-7, is caused by the pH-sensitive polymer nearly invading the entire high-permeability layer before its viscosity starts to increase. The viscosity increase in the high-permeability layer forces the subsequent injected pH-sensitive polymer into the low-permeability zone for effective conformance control. As the polymer is forced into the low-permeability zone much oil is recovered, but eventually the injected polymer begins to plug the low-permeability zone too. Once the low-permeability zone becomes plugged, fluid is forced back into the high-permeability zone, and little incremental oil is recovered from the low-permeability zone afterward.

**7.1.4 pH-Sensitive Polymer Floods: Linear Geometry With Crossflow**

pH-sensitive polymer floods for various Damköhler numbers were simulated for a two-layer linear flood geometry with crossflow. The linear flood cases have 15 vertical layers (representing two different permeability zones) and a vertical to horizontal permeability ratio of 0.1. These linear flood cases are the first ones described in this Thesis that allow viscous fingering to occur due to the presence of crossflow and due to the large number of thin layers in the simulation. Viscous fingering was observed in some of the linear pH-sensitive polymer flood cases when acidic low-viscosity polymer would finger into the high-viscosity polymer bank, but the oil recovery plots from the simulations suggest that this does not harm recovery significantly.
Figure 7-11 shows oil recovery versus the volume of pH-sensitive polymer injected at various Damköhler numbers, along with 1-cp and 1000-cp fluid flood results. The main difference between these results and those for the no crossflow cases (Figure 7-8) is that the crossflow increased oil recovery for all cases. Fluid was injected into the pH-sensitive polymer models at 25 m$^3$/d and no injection well pressure limits were applied for the pH-sensitive polymer injectors, although the 1-cp and 1000-cp fluid flood cases shown for comparison included injection well pressure limits.

![Figure 7-11: Oil Recovery versus Volume of Fluid Injected Using pH-Sensitive Polymer (Linear Case With Crossflow)](image)

Figure 7-12 shows results from the same cases with respect to time since the flood began. In strong contrast with the results shown in Figure 7-9 for the no-crossflow case, the $N_{Da} = 10$ and $N_{Da} = 100$ cases with crossflow recovered oil faster than any of the high-viscosity fluid flood cases. Inspection of Figure 7-13, which shows the injection well
bottom hole pressures for the pH-sensitive polymer simulations, indicates why this happened. The peak injection pressures for the $N_{Da} = 10$ and $N_{Da} = 100$ cases reached 54000 kPa and 75000 kPa, respectively. These correspond to reservoir pressure drops of 44000 kPa and 65000 kPa, respectively, which is many times larger than the maximum 5000 kPa reservoir pressure drop allowed for the 1-cp, 10-cp, 100-cp and 1000-cp cases. If a 15000 kPa injection well pressure limit was applied to the pH-sensitive polymer flood simulations then only the $N_{Da} = 1$ case would exceed the oil recovery versus time curve for the 100-cp flood case at some times before 200 days.

Figure 7-12: Oil Recovery versus Time Using pH-Sensitive Polymer (Linear Case With Crossflow)
Figure 7-13: Injection Well Bottom Hole Pressures versus Time Using pH-Sensitive Polymer (Linear Case, With Crossflow)

All the linear pH-sensitive polymer flood results with and without crossflow showed that injection of a high-viscosity fluid could generally recover oil more efficiently in terms of volume of fluid injected or more quickly in terms of time than a pH-sensitive polymer flood when subject to a similar maximum reservoir pressure drop limitation between all the cases. Simulations were performed to test the effectiveness of pH-sensitive polymer slug treatments to improve oil recovery in oil reservoirs.

7.1.5 pH-Sensitive Polymer and High-Viscosity Fluid Slug Treatments: Linear Geometry Without Crossflow

Chapter 6 showed that small pH-sensitive polymer slug treatments can greatly improve flood conformance for a waterflood in a linear geometry flood. Analytical calculations in
Chapter 6 showed that there may be an optimal pH-sensitive polymer slug size to maximize sweep efficiency from a waterflood, and that pH-sensitive polymer slug treatments are most effective when the polymer viscosity increases by a much greater ratio than the permeability contrast between the high-permeability and low-permeability zones. Chapter 6 showed that simulation results of slug treatments in linear geometry floods yield more optimistic results than analytical results because of fluid mixing effects that lower the polymer slug viscosity in the low-permeability layer(s).

Simulations were carried out to test the concept of injecting a slug of 10-cp fluid, 100-cp fluid, 1000-cp fluid and of pH-sensitive polymer before waterflooding to increase conformance in the two-layer reservoir. The injected slugs have a volume of 800 m$^3$, which is 5% of the hydrocarbon pore volume (HCPV). The pH-sensitive polymer slug case involves the injection of a 2.2-cp acidic (pH=1, 3 wt% NaCl) polymer slug at a Damköhler number of 0.1, followed by a shut-in period when the polymer viscosity increases to 1000 cp, then subsequent waterflooding with 1-cp brine (pH=7, 3 wt% NaCl). A target injection rate of 25 m$^3$/d was used for all the slug simulations, and a 15000 kPa injection well pressure limit was enforced.

Figure 7-14 shows the results when 0.05 HCPV (800 m$^3$) slugs of 10-cp, 100-cp, and 1000-cp Newtonian fluid, and a pH-sensitive polymer slug (that results in 1000-cp viscosity) were used as a conformance control method in a linear reservoir with no crossflow. Figure 7-14 shows oil recovery versus the volume of fluid injected, and Figure 7-15 shows oil recovery versus time. The 1000 day shut-in time included in the simulation, to allow the pH-sensitive polymer slug to reach 1000-cp viscosity, was not shown in Figure 7-15. The shut-in time is only required in these simulations because the
calcite reaction-rate constant \( (10^{-9.447285} \text{ moles m}^{-2} \text{ s}^{-1}) \) used to simulate a \( N_{Da} = 0.1 \) pH-sensitive polymer slug injection is 6 orders of magnitude lower than the final-match history matched value of \( 10^{-3.37} \text{ moles m}^{-2} \text{ s}^{-1} \) for Berea sandstone.

**Figure 7-14: Oil Recovery versus Volume of Fluid Injected Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Linear Case, No Crossflow)**

Both Figure 7-14 and 7-15 show that a 1000-cp Newtonian fluid slug or pH-sensitive polymer slug can improve oil recovery greatly. Both slug treatments recovered oil faster, and using less injected fluid, than any of the high-viscosity fluid floods. The pH-sensitive polymer slug recovered oil faster than the 1000-cp fluid slug; but this requires a treatment design that minimizes flood shut-in time. Injection of the slug at a higher Damköhler number, or injection of the polymer into the reservoir at very high rates along with use of a faster mineral reaction-rate constant are two approaches to minimize or prevent shut-in time.
Figure 7-15: Oil Recovery versus Time Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Linear Case, No Crossflow)

Figure 7-16 shows the viscosity distribution of the pH-sensitive polymer immediately after the 0.05 HCPV (800 m³) slug viscosity reached 1000 cp due to geochemical reactions, and after a total of 0.5 pore volumes of fluid has been injected. It can be seen that the slug viscosity remains high in the high-permeability layer (bottom) whereas fluid mixing has caused the polymer in the low-permeability layer to decrease from an initial value of 1000 cp to very low values. This mixing effect explains why the slug treatments are very successful in the linear simulations.
7.1.6 pH-Sensitive Polymer and High-Viscosity Fluid Slug Treatments: Linear Geometry With Crossflow

Slug treatments were simulated for the linear geometry floods where vertical crossflow was allowed. Cases modeled 0.05 HCPV slug treatments of 10-cp, 100-cp and 1000-cp Newtonian fluids, and of 5000-cp pH-sensitive polymer (injected viscosity was 2.75 cp; and $N_{Da} = 0.1$ during injection) before the reservoir was subsequently injected with water.
(pH=7, 3 wt% NaCl). Figure 7-17 shows oil recovery versus volume of fluid injected for the cases, and Figure 7-18 shows oil recovery versus time. The 1000-day shut-in period used to allow the pH-sensitive polymer to attain its final viscosity of 5000 cp was not included in the results shown in Figure 7-18 for the same reasons given for the no-crossflow slug simulations.

![Figure 7-17: Oil Recovery versus Volume of Fluid Injected Using 0.05 PV Slug Treatment Followed by Waterflooding (Linear Case, With Crossflow)](image-url)
Figure 7-18: Oil Recovery versus Time Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Linear Case, With Crossflow)

Figure 7-17 and 7-18 show oil recoveries from a waterflood after a 0.05 HCPV slug treatment. The oil recoveries resulting from the very high-viscosity slug treatments (100-cp or greater) in the linear reservoir with crossflow are significantly lower than for the no-crossflow cases (Figures 7-14 and 7-15). Two observations explain this. First, the 15-layer crossflow simulations allow viscous fingering of the water to penetrate the slugs, whereas the no-crossflow simulations do not allow this. Second, the presence of crossflow causes more of the injected slug to be allocated to the low-permeability zone which lowers recovery when waterflooding begins. A third phenomenon has been observed for the pH-sensitive polymer cases. When a slug of 2.2-cp acidic pH-sensitive polymer was injected into the reservoir then shut-in to allow the polymer viscosity to rise to 1000 cp, vertical flow was observed to cause the top portion of the polymer slug in the high-permeability zone near the injection well to become diluted with water. It is unclear
what caused this. The final 1000-cp pH-sensitive polymer slug did not completely block the high-permeability zone, hence the case was run using a 5000-cp pH-sensitive polymer. The final aqueous-phase viscosity distribution after the polymer slug reached its maximum viscosity. Figure 7-19 shows the aqueous-phase viscosity distribution in the reservoir with crossflow immediately after the pH-sensitive polymer slug was fully reacted, and after 0.5 pore volumes of fluid injected.

**After pH Sensitive Polymer Slug Fully Reacted**

**After 0.5 Pore Volumes Injected**

Figure 7-19: Aqueous Phase Viscosity Distribution in Linear Reservoir During 5000 cp pH-Sensitive Polymer Slug Treatment Simulation (Linear Case, With Crossflow)
The simulations show that slugs of pH-sensitive polymer effectively improve conformance of a waterflood using a small amount of polymer. Analysis from Chapter 6 suggests that there may be an optimal slug size for a given polymer slug viscosity but no efforts were made to determine the optimum size for the sample linear geometry reservoir used in this chapter.

7.1.7 pH-Sensitive Polymer Slug Treatment Injected into High-Permeability Layer: Linear Geometry

The slug treatment simulations shown in Sections 7.1.5 and 7.1.6 model the injection of polymer slugs into both layers of a two-layer linear reservoir before waterflooding. Simulations of pH-sensitive polymer slug treatments injected into the high-permeability zone before waterflooding have been performed. Polymer can be injected into high-permeability zones in the field by using packers and other equipment. The simulations used 1000 cp pH sensitive polymer slugs (injected at pH=1 conditions) with a volume of 1600 m$^3$ (0.1 HCPV). This volume of polymer was chosen to completely fill the high-permeability layer with polymer.

Figure 7-20 shows oil recovery versus the volume of fluid injected for a linear reservoir with and without vertical crossflow. The high-permeability zone slug treatment was much more effective for the crossflow case than the slug treatment that was injected into both zones. The no-crossflow case slug treatment results were similar with those shown in Figure 7-14. The volume of the slug and the final viscosity of the slug will affect the performance of the treatment.
Simulations were performed to compare oil recoveries resulting from water injection, polymer injection, pH-sensitive polymer injection and slug treatments into injector-centered radial reservoirs. Radial simulations represent the high pressure drops that occur near an injection well but they do not represent the flow near the production well realistically. The two-zone radial model selected for analysis has a permeability contrast of 100 between the two horizontal zones, and the same hydrocarbon pore volume and zone heights as the linear models described earlier.

Figure 7-21 shows a schematic of the radial geometry reservoir model.
Table 7-2 gives the grid properties used for the radial simulations. There are 61 blocks in the radial flow direction. The radial grid sizes were based on a 50 cell radial grid with logarithmically increasing radial direction cell thicknesses, with the outer few grids subdivided (to give a total of 61 cells in the radial direction) to address saturation change errors from the simulator near the production well. Similar to the linear cases described, two horizontal layers were modeled in the no crossflow cases and 15 horizontal layers were modeled in the simulations where crossflow is permitted.
Table 7-2: Radial Simulation Grid Properties

<table>
<thead>
<tr>
<th>Reservoir Property</th>
<th>Layer 1 (top)</th>
<th>Layer 2 (bottom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.177</td>
<td>0.177</td>
</tr>
<tr>
<td>Height</td>
<td>18 m</td>
<td>2 m</td>
</tr>
<tr>
<td>Radial Dimensions</td>
<td>$R_w = 0.1$ m, $R_e = 42.4072$ m</td>
<td></td>
</tr>
<tr>
<td>Radial-Direction Permeability</td>
<td>100 md</td>
<td>10000 md</td>
</tr>
<tr>
<td>Z-dir Permeability</td>
<td>0 md or 10 md</td>
<td>0 md or 1000 md</td>
</tr>
<tr>
<td>Hydrocarbon Pore Volume</td>
<td>16000 m$^3$ total</td>
<td></td>
</tr>
<tr>
<td>Reservoir Pore Volume</td>
<td>20000 m$^3$ total</td>
<td></td>
</tr>
</tbody>
</table>

7.2.1 High-Viscosity Fluid Floods: Radial Geometry Without Crossflow

Simulations with injection of 1-cp, 10-cp, 100-cp and 1000-cp Newtonian fluids at the center of the two-layer radial reservoir were performed. The fluids were injected at a target rate of 25 m$^3$/d, but the rates were less if the 15000 kPa bhp limit was reached for the injector. The production well adhered to a fixed 10000 kPa bhp constraint. Figure 7-22 shows the volume of oil recovered versus the volume of fluid injected into the radial flood when there is no crossflow between the two horizontal layers. Figure 7-23 shows the volume of oil recovered versus time. Figure 7-24 shows the injection rates and injection well bottom hole pressures for the flood cases.
Figure 7-22: Oil Recovery versus Volume of Fluid Injected Using High-Viscosity Fluids (Radial Case, No Crossflow)

Figure 7-23: Oil Recovery versus Time Using High-Viscosity Fluids (Radial Case, No Crossflow)
Figure 7-24: Injection Well Bottom Hole Pressures and Rates versus Time Using High-Viscosity Fluids (Radial Case, No Crossflow)

Figure 7-22 shows that increasing the injected fluid viscosity improves oil recovery efficiency in terms of the volume of fluid injected. Figure 7-23 shows that the 100-cp flood recovers oil the most quickly compared to the other cases. Figure 7-24 shows that only the 1000-cp fluid injection well reached its 15000 kPa pressure limit, which says that the other floods could have proceeded with higher injection rates and recovered oil faster.

7.2.2 High-Viscosity Fluid Floods: Radial Geometry With Crossflow

Figures 7-24, 7-25, and 7-26 show the oil recovery curve versus volume of fluid injected, the oil recovery curve versus time, and the injection well rates and bottom hole pressure
for high-viscosity fluid floods in the radial reservoir with vertical crossflow. These plots show that crossflow in the radial cases increases oil recovery compared to no crossflow cases, and improves the injectivity compared to the no crossflow cases.

The oil recoveries in terms of the volume of fluid injected observed for the radial simulations without crossflow (Figure 7-22) and with crossflow (Figure 7-25) are lower than for the equivalent linear cases shown in Figure 7-2 and Figure 7-5. Sorbie and Mackay (2005) explain that viscous fluid injection causes more flow diversion from high-permeability layers into low-permeability layers in linear reservoirs than in radial reservoirs.

![Figure 7-25: Oil Recovery versus Volume of Fluid Injected Using High-Viscosity Fluids (Radial Case, With Crossflow)](image-url)
Figure 7-26: Oil Recovery versus Time Using High-Viscosity Fluids (Radial Case, With Crossflow)

Figure 7-27: Injection Well Bottom Hole Pressures and Rates versus Time Using High-Viscosity Fluids (Radial Case, With Crossflow)
7.2.3 pH-Sensitive Polymer Floods: Radial Geometry Without Crossflow

The continuous injection of pH-sensitive polymer into radial geometry reservoirs for various Damköhler numbers was modeled. The polymer was injected at a constant rate of 25 m$^3$/d with no injection well pressure limit. The resulting oil recovery curves differ significantly from the linear geometry cases previously shown. Figure 7-28 shows the oil recovery versus volume of fluid injected for the radial cases without crossflow. The oil recovery curves for the injection of water and 1000-cp fluid are included for comparison.

![Figure 7-28: Oil Recovery versus Volume of Fluid Injected Using pH-Sensitive Polymer (Radial Case, No Crossflow)](image)

Figure 7-29 shows oil recovery versus time for the radial pH-sensitive polymer flood cases. The 1-cp, 100-cp and 1000-cp flood results shown on Figures 7-28 and 7-29 had target injection rates of 25 m$^3$/d, but were subject to a 15000 kPa injection limit.
Figure 7-29: Oil Recovery versus Time Using pH-Sensitive Polymer (Radial Case, No Crossflow)

Figure 7-30: Injection Well Bottom Hole Pressures versus Time Using pH-Sensitive Polymer (Radial Case, No Crossflow)
Figure 7-30 shows the injection well bottom hole pressures for the pH-sensitive polymer radial floods without crossflow. It is expected that the $N_{Da} = 10$ and $N_{Da} = 100$ cases have high injection pressures since the polymer viscosity increases to 1000 cp in the model, but the stepwise pressure decreases are unusual. Models of similar single-phase radial cases showed the same feature. Experience with radial models showed that the pH of the initial reservoir brine has the greatest effect on the injection well pressures and zonal flow allocations in the radial pH-sensitive polymer flood cases, followed by the effect of changing the number of radial direction grid cells used. Simulations performed showed that use of high-pH brine initial conditions cause large fractional flow allocation fluctuations between the horizontal zones, but using an acid preflush greatly diminishes the pressure and zonal flow rate oscillations. Use of radial grids with more blocks (e.g., 100) with smaller radial direction thicknesses caused more pressure steps and fractional flow allocation changes than use of fewer (e.g., 25 grid blocks). The radial grids shown in this chapter have 61 radial gridblocks.

### 7.2.4 pH-Sensitive Polymer Floods: Radial Geometry With Crossflow

Simulations were performed for the cases of continuous pH-sensitive polymer (injected viscosity of 2.2-cp; maximum viscosity of 1000-cp) floods into a two-layer radial reservoir where crossflow was permitted. The calcite reaction-rate constant was varied to simulate different acid-matrix reaction Damköhler numbers. The polymer was injected into the center of the radial grid at a constant rate of 25 m$^3$/d with no injection well pressure limit. Figure 7-31 shows oil recovery versus the volume of fluid injected. Figure 7-32 shows oil recovery versus time, and Figure 7-33 shows the injection well bottom hole pressure versus time for the simulations.
The 1-cp, 100-cp and 1000-cp flood results shown on Figures 7-31 and 7-32 had target injection rates of 25 m³/d, but were subject to a 15000 kPa injection limit. The presence of vertical crossflow increased oil recovery for the radial pH-sensitive polymer floods. Similar to the no-crossflow cases, the best high-viscosity fluid flood proved to offer higher recovery compared to any of the pH-sensitive polymer runs in terms of volume of fluid injected or in terms of time. Figure 7-34 shows the stepwise pressure changes also observed for the no-crossflow radial simulations (Figure 7-30).
Figure 7-32: Oil Recovery versus Time Using pH-Sensitive Polymer (Radial Case, With Crossflow)

Figure 7-33: Injection Well Bottom Hole Pressures versus Time Using pH-Sensitive Polymer (Radial Case, With Crossflow)
7.2.5 pH-Sensitive Polymer and High-Viscosity Fluid Slug Treatments: Radial Geometry Without Crossflow

Simulations were performed to test the concept of injecting a slug of 10-cp, 100-cp, 1000-cp fluids and pH-sensitive polymer before waterflooding to increase conformance in the two-layer radial reservoir. The injected slug volume was 800 m$^3$ (5% HCPV). The pH-sensitive polymer slug case involves the injection of a 2.2-cp viscosity acidic (pH=1, 3 wt% NaCl) polymer slug at a Damköhler number of 0.1; a shut-in period for the polymer viscosity to increase to 1000 cp; then subsequent waterflooding with 1-cp brine (pH=7). A target injection rate of 25 m$^3$/d was used for all the slug simulations, and a 15000 kPa injection well pressure limit was used.

Figure 7-34 shows oil recovery versus the volume of fluid injected, and Figure 7-35 shows oil recovery versus time. The 1000-cp pH-sensitive case recovered oil most efficiently in terms of volume of fluid among the slug treatments, and the slug treatments did not improve recovery much compared to the waterflood (1-cp fluid) case. The 100-cp fluid case shown in Figure 7-35 shows faster oil recovery compared to any of the slug cases for the radial simulations without crossflow. Figure 7-36 shows the aqueous-phase viscosity distribution in the radial reservoir for different times during the 1000-cp pH-sensitive polymer slug simulation. The slug reaches high-viscosity near the injection well in both layers due to geochemical reactions, but the slug does not remain stationary in the high-permeability layer but is forced out by waterflooding. The viscosity profile after 0.1 PV injected shows that high-viscosity fluid remains in the low-permeability zone which explains why slug treatments tend to lower oil recovery.
Figure 7-34: Oil Recovery versus Volume of Fluid Injected Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Radial Case, No Crossflow)

Figure 7-35: Oil Recovery versus Time Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Radial Case, No Crossflow)
After pH Sensitive Polymer Slug Fully Reacted

After 0.1 Pore Volumes Injected

Figure 7-36: Aqueous Phase Viscosity Distribution in Radial Reservoir During 1000-cp pH-Sensitive Polymer Slug Treatment Simulation (Radial Case, No Crossflow)
7.2.6 pH-Sensitive Polymer and High-Viscosity Fluid Slug Treatments: Radial Geometry With Crossflow

Similar radial-geometry slug-treatment cases were modeled with vertical crossflow-permitted in the model. Each slug treatment is 0.05 HCPV and is followed by 1-cp waterflooding.

Figure 7-37 shows oil recovery versus volume of fluid injected for slug treatments of 10-cp, 100-cp, 1000-cp Newtonian fluids and of 1000-cp pH-sensitive polymer. Figure 7-38 shows oil recovery versus time for the slug treatments. None of the slug treatments improved recovery significantly over the 1-cp fluid flood case, and the 100-cp and 1000-cp slug treatments lowered oil recovery.

Figure 7-37: Oil Recovery versus Volume of Fluid Injected Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Radial Case, With Crossflow)
Figure 7-38: Oil Recovery versus Time Using 0.05 HCPV Slug Treatment Followed by Waterflooding (Radial Case, With Crossflow)

7.2.7 pH-Sensitive Polymer Slug Treatment Injected into High-Permeability Layer: Radial Geometry

The slug treatment simulations shown in Sections 7.2.5 and 7.2.6 model the injection of polymer slugs into both layers of a two-layer radial reservoir before waterflooding. Simulations of pH-sensitive polymer slug treatments injected into the high-permeability zone before waterflooding have been performed. The simulations used 1000-cp (maximum \textit{in situ} viscosity) pH sensitive polymer slugs (injected at pH=1 conditions) with a volume of 1600 m$^3$ (0.1 HCPV).

Figure 7-39 shows oil recovery versus the volume of fluid injected for radial cases with and without vertical crossflow. These pH-sensitive polymer treatments significantly
improved oil recovery over the cases where polymer was injected into both layers. This suggests the slug treatments can be effective for radial reservoirs when they are applied to the high-permeability thief zones only. The volume of the slug and the final viscosity of the slug will greatly affect the performance of the treatment. Crossflow appears to lower the effectiveness of the high-permeability zone treatments considerably.

![Figure 7-39: Oil Recovery versus Volume of Fluid Injected Using 0.1 HCPV Slug Treatment Followed by Waterflooding (Radial Case)](image)

### 7.2.8 pH-Sensitive Polymer and High-Viscosity Fluid Injection for Constant Injection Pressure Conditions (Radial Case)

Improved polymer injectivity provides an opportunity to increase the oil rate from a field. A simulation was performed where the injection well BHP was 15000 kPa while the producer BHP was 10000 kPa. The two-layer radial reservoir model without crossflow was used for the simulations. One case had 100-cp Newtonian fluid injected and the other
had pH-sensitive polymer with a final viscosity of 100 cp at fully reacted conditions. The pH-sensitive polymer run had a calcite reaction-rate constant of $10^{-5.447285}$ moles·m$^{-2}$·s$^{-1}$ and the injected fluid was pH=1 acid containing 6.251E-6 mol/kg of pH-sensitive polymer. Figure 7-40 shows that the pH-sensitive polymer demonstrated improved fluid injectivity and a higher oil rate versus time compared to the 100-cp fluid flood. Figure 7-41 shows that the 100-cp fluid flood recovered fluid more efficiently in this case. While the pH-sensitive polymer flood is less efficient at recovering oil volumetrically with the two-layer model, it may be as effective as a Newtonian fluid in a one-layer radial model where the only goal is to use the polymer to improve the displacement efficiency of the flood.

![Figure 7-40: Injection Rate and Oil Production Rate vs. Time for Flood With Fixed Injection Well Pressure (Radial Case, No Crossflow)](image-url)
Figure 7-41: Oil Recovery vs. Volume of Fluid Injected for Flood With Fixed Injection Well Pressure (Radial Case, No Crossflow)

The pH-sensitive polymer flow rate fluctuated as shown in Figure 7-40. It is unclear if this is likely to occur in reactive porous media or if it a numerical artifact of the simulation.

Summary and Conclusions

Injection of high-viscosity fluids can improve the conformance of linear and radial floods significantly. Continuous injection of pH-sensitive polymer has not been observed to improve oil recovery compared to polymer flooding except early in the life of a flood. Use of pH-sensitive polymer slug treatments in conjunction with waterflooding has been observed to be an effective way to improve the conformance of a waterflood. Polymer slug treatments appear to be very effective in linear floods whether applied to all the layers or just the thief zone. In injector-centered radial floods, pH-sensitive polymer slug
treatments appear to be very effective when injected into the high-permeability zone, but not when injected into the entire reservoir.
Chapter 8: CONCLUSIONS AND RECOMMENDATIONS

The GEM-GHG simulator was successfully used to model geochemical reactions and the rheology of pH-sensitive polymer in brine-filled and oil-filled reservoirs. The simulator is versatile and allows the modeling of acid-matrix reactions for many different minerals and acids. The pH-triggered viscosity increase caused by acid-matrix reactions in situ can greatly improve vertical conformance in two-layer linear reservoirs when used for polymer slug treatments. Simulations showed that pH-sensitive polymer slug treatments can improve conformance in radial reservoir floods when the polymer is injected into the thief zone(s) only. pH-sensitive polymer can be an effective conformance control method in some situations but careful analysis is recommended since the use of pH-sensitive polymer in a flood does not guarantee improved conformance control.

8.1 Conclusions

- History matching the effluent analysis of an acid coreflood provides a means to estimate the mineralogy and mineral reactions rates in a rock sample. It is difficult to determine the exact composition of a core sample, and history matching suggests several suitable matches rather than one specific answer. History matching provides the necessary geological information to characterize the acid-matrix geochemical reactions that cause the viscosity of pH-sensitive polymer to increase in situ. The inclusion of the correct intra-aqueous reactions involved in the acid-matrix reactions, and use of the proper mineral reaction equation for an acid-matrix reaction is critical to accurately model in situ fluid pH.
- The use of conventional high-viscosity polymers and pH-sensitive polymer improves vertical conformance in linear reservoirs with and without vertical
crossflow. Continuous injection of pH-sensitive polymer in these reservoirs is not recommended since this can plug the low-permeability zones in a reservoir. Simulations suggest that the use of pH-sensitive polymer slug treatments is the preferred way to improve vertical conformance in linear geometry reservoirs during waterflooding. A comparison in Chapter 6 concludes that simulation results for such cases may be optimistic compared to analytical equation analysis. Viscous fingering and pH-sensitive polymer dilution effects have been observed in some of the simulations and should be carefully considered during treatment design.

- The use of conventional high-viscosity polymers and pH-sensitive polymers to improve conformance in injector-centered radial geometry floods is generally less effective than in linear geometry floods. pH-sensitive polymer slug treatments can improve conformance in radial waterfloods when the polymer is injected only into high-permeability zone, but not when it is injected into all the reservoir zones.

### 8.2 Recommendations

Results of this Thesis suggest that further research into the use of pH-sensitive polymers as a conformance control method is warranted. The recommendations from this Thesis are:

- Geochemical modeling of coreflood effluent results provides the needed geochemical properties required by a simulator to model the behavior of pH-sensitive polymer *in situ*. Detailed coreflood effluent results are required to history match acid-matrix reactions in a core. Such tests should measure most of
the ions in the effluent, and should be carried out at different acid injection rates to predict the rate constants associated with geochemical reactions in the core.

- History matching sensitivities shown in Chapter 4 suggest that a one-mineral model with the proper design can approximately describe the effluent pH profile for Berea corefloods. Consideration of basic one or two-mineral models for future history matching efforts may prove to be effective and quick for analysis of pH-sensitive polymer viscosity behavior in reactive porous media.

- The disparity in results between the effectiveness of pH-sensitive polymer in linear and radial geometry floods suggests that detailed simulation studies should be undertaken when designing polymer floods or polymer slug treatments to improve conformance in a reservoir. pH-sensitive polymer may be a very effective conformance control method for one reservoir and ineffective in another. Factors such as reservoir mineralogy (including composition, acid-reaction rates) and reservoir fluid flow paths are key considerations when evaluating the effectiveness of pH-sensitive polymer floods and slug treatments.

- An acid preflush should be considered before injecting pH-sensitive polymer into a reservoir to prevent fluid mixing between the acidic polymer solution and the reservoir brine. Simulation runs that included initial reservoir conditions to mimic the presence of a preflush before pH-sensitive polymer injection gave more predictable viscosity changes and fluid flow allocation between different reservoir zones than those without one.

- Investigation of flow rate fluctuations observed in some radial flood models involving pH-sensitive polymer may lead to modeling improvements.
Appendix 1: SAMPLE DAMKÖHLER NUMBER CALCULATION

The Damköhler number, $N_{Da}$, represents the ratio of acid reaction-rate (with a mineral) to the transport rate. The following equation estimates $N_{Da}$ using the initial acid concentration and initial porous media porosity and surface area.

$$
N_{Da} = \frac{(BV) \phi \cdot r_H^+}{1000qa\phi} = \frac{BV \cdot r_H^+}{1000qa}
$$

where BV is the bulk volume of the desired layer. $BV = L \cdot A = L \cdot w \cdot h$ for linear and five-spot reservoirs layers, and is $\pi (R_e)^2 \cdot h$ for radial reservoir layers

where

$L = \text{length of medium (m)}$

$w = \text{width of reservoir (m)}$

$\phi = \text{initial porosity of porous medium}$

$q = \text{acid flow rate (m}^3/\text{s})$

$a = \text{proton molarity (mol/liter), consider using equation 5-2 when Damköhler number drives the viscosity change of pH-sensitive polymer}$

$R_e = \text{Outer radius of reservoir (m), assuming } R_e >> R_w$

$h = \text{height of radial reservoir (m)}$

$r_H^+ = \text{reaction-rate of } H^+ \text{ (mol/m}^3\cdot\text{s})$

The reaction-rate of $H^+$ is proportional to the mineral reaction-rate

$$
r_{H^+} = \frac{V_{H^+}}{V_{\beta}} \cdot r_{\beta} = \frac{V_{H^+}}{V_{\min}} \cdot \text{sgn} \left[ 1 - \left( \frac{Q_{\beta}}{K_{eq,\beta}} \right) \right] \hat{A}_\beta S_w \left( k_{0,\beta} + \sum_{i=1}^{n_{eq}} k_{i,\beta} a_i^{\alpha_{i,\beta}} \right) \left[ 1 - \left( \frac{Q_{\beta}}{K_{eq,\beta}} \right) \right]^{\frac{x_{\beta}}{2}}
$$

where

$\frac{V_{H^+}}{V_{\beta}} = \text{stoichiometric ratio of } H^+ \text{ consumed per mineral species consumed}$

$\hat{A}_\beta = \text{reactive surface area of reactant mineral } \beta \text{ per unit bulk volume of porous medium (m}^2/\text{m}^3)$

$S_w = \text{water saturation}$

$k_{0,\beta} = \text{rate constant of mineral reaction } \beta \text{ (mol/m}^2\cdot\text{s})$

$k_{i,\beta} = \text{rate constants of mineral reaction } \beta \text{ related to activity (default = 0 in GEM)}$

$a_i^{\alpha_{i,\beta}} = \text{activity of ions for mineral reaction } \beta$

$K_{eq,\beta} = \text{chemical equilibrium constant of mineral dissolution/precipitation reaction}$

$Q_{\beta} = \text{activity product of mineral } \beta \text{ dissolution reaction}$
$r_\beta = \text{dissolution/precipitation rate per unit bulk volume of porous medium \([\text{mol/}(m^3 \cdot s)]\)}$

$\xi_\beta = \text{parameter (default = 1 in GEM)}$

$\zeta_\beta = \text{parameter (default = 1 in GEM)}$

The hydrogen reaction-rate used to calculate the Damköhler numbers shown in this Thesis assumed that $Q_\beta = 0$ to give the maximum mineral dissolution rate and that $\hat{A}_\beta$ was the initial mineral reactive surface area entered into the simulations. The $V_{H^+}^{\beta}$ for the dominant mineral reaction was used if a net mineral reaction could proceed in more than one way (Chapter 4, Section 7). If there is more than one mineral present then the hydrogen reaction-rate from all the reactions should be added together as shown in Table 4-7.

**Example: Reaction of pH=1 hydrochloric acid with calcite**

There are two possible net reactions based on the chemistry used in the GEM-GHG simulator in this Thesis:

A) Calcite + $H^+$ = $Ca^{++}$ + $HCO_3^-$

B) Calcite + $2 H^+$ = $Ca^{++}$ + $H_2CO_3$

Concentrations of $HCO_3^-$ and $H_2CO_3$ from the simulator show that 94% of the reacted calcite is converted to $H_2CO_3$ for the conditions given in the simulator, so the Damköhler calculation below assumes the use of reaction B.

Given:

$L = 100 \text{ m}$

$A = 2m \times 56.497m = 112.994 \text{ m}^2 \text{ (for high-permeability layer)}$

$\phi = 0.177$

$q = 25 \text{ m}^3/d \times (d / 86400 \text{ s}) \times [1m*1000md/(9m*10md+1m*1000md)] = 2.655 \times 10^{-4} \text{ m}^3/s$

The flow rate $q$ at unit mobility ratio conditions were used, hence, the inclusion of the permeability-height product for each of the two layers in the model.

$v = 2 \text{ moles of } H^+ \text{ consumed per 1 mole of calcite consumed} = 2 \text{ (based on reaction B alone)}$

$S_w = 0.7 \text{ (This amount of pore space is filled with acidic polymer, } 1-S_w)$

$\hat{A}_\beta = 10000 \text{ m}^2/\text{m}^3 \times 0.0470 \text{ volume fraction of calcite} = 470 \text{ m}^2/\text{m}^3$

$k_\beta = 3.570377 \times 10^9 \text{ mol/ m}^2 \cdot \text{s} @ 25^\circ\text{C} \text{ (This is incorrect but was used to simulate Damköhler number equals one cases for the high-permeability layer)}$

$k_{i,\beta} = 0 \text{ for all species}$

$\xi_\beta = \xi_\beta = 1$
Assuming:

\[ a = 0.1 \text{ mol/liter (for pH=1 acid)} \]
\[ Q_{\beta} = 0 \text{ (when activity product is zero then reaction-rate is at maximum value)} \]

Solving for \( r_{H^+} \) gives:

\[
r_{H^+} = 2 \cdot \text{sgn} \left( 1 - \left( \frac{0}{K_{eq,\beta}} \right) \left( 470 \frac{m^2}{m^3} \right)(0.7)(3.570377 \times 10^{-9}) \right) \left( 1 - \left( \frac{0}{K_{eq,\beta}} \right) \right)
\]

\[ r_{H^+} = 2.3493 \times 10^{-6} \text{ mol/m}^3 \cdot \text{s} \]

Solving for \( N_{Da} \) gives:

\[
N_{Da} = \frac{LAr_{H^+}}{1000qa} = \frac{(100m)(112.994m^2)(2.3493 \times 10^{-6} \text{ mol/m}^3 \cdot \text{s})}{(1000 \text{ liters/m}^3)(2.655 \times 10^{-4} \text{ m}^3/\text{s})(0.1 \text{ mol/liter})}
\]

\[ N_{Da} = 1 \]

Such calculations were used to determine the Damköhler number of the acid-matrix reactions in Chapter 6 and Chapter 7. The reaction constants were increases by orders of magnitudes to simulate higher Damköhler number reactions.
Appendix 2: SAMPLE GEM-GHG INPUT FILE

*FILENAMES *OUTPUT *SRFOUT *INDEXOUT *MAINRESULTOUT **Output files
*TITLE1 'Calcite-Only Reservoir Model'
*TITLE2 'Linear Geometry, pH-sensitive Polymer Injection'
*TITLE3 'Calcite reaction constant chosen to give Damköhler Number of 1'

**NOTE: Double asterisks indicate the start of comment lines

*INUNIT *SI **All units given in this file are metric
*RESULTFILE *SR2

**The following 12 lines declare which variables should be included in output files
*OUTSRF *GRID *SW *DENW *VISW *VISO *SO *SG *KRW *VELOCRC *PRES
*MOLALITY 'PLM'
*MOLALITY 'H+'
*MOLALITY 'Ca++'
*MOLALITY 'Na+'
*MOLALITY 'Cl-'
*MOLALITY 'OH-'
*MOLALITY 'CO3--'
*MOLALITY 'H2CO3'
*MOLALITY 'HCO3-'  
*MOLALITY 'tracer'
*MINERAL 'Calcite'

**Next 4 lines declare output data frequency (in number of timesteps)
*WSRF *WELL 25
*WSRF *GRID 25
*WPRN *GRID 25
*DIM *MDIMPL 100

**-------------------------------------RESERVOIR & GRID DATA----------------
**This section defines the linear 1-D simulation grid
**Local grid refinements (REFINE) used to improve accuracy near injection well

*GRID *CART 100 1 2
*DI 200*1
*DJ *CON 56.497
*DK 100*18 100*2
*KDIR *DOWN
*DEPTH 1 1 1 1000
*POR *CON 0.177
*PERMI 100*100 100*10000 **top layer has 100 md perm, bottom layer has 10000 md perm
*PERMJ 100*100 100*10000 **top layer has 100 md perm, bottom layer has 10000 md perm
*PERMK *CON 0 **No vertical crossflow allowed between layers
*REFINE 1:50 1 1 INTO 10 1 1
*REFINE 1:2 1 2 INTO 10 1 1
*CPOR 1E-10 **small compressibility included, default is 4.5E-7 (1/kPa)
*PRPOR 10000
**-------------------------------------FLUID PROPERTY DATA--------------**

This section defines 1 component oil, C7-16 pseudocomponent from Khan dissertation

*MODEL  *PR  **Use Peng Robinson EOS
*NC    1    1
*TRES        25  **Temperature, degrees C
*COMPNAME
   'C7-16'

*PCRIT      2.0676400E+01
*VCRIT      0.58957324
*TCRIT      611.116
*AC         6.3860000E-01
*MW          1.4718200E+02
*HCFLAG         0
*BIN
*VSHIFT        0.064
*PCHOR       439.1472
*VISCOR   *MODPEDERSEN
*VISCOEFF   1.3040000E-04  2.3030000E+00  7.3780000E-03  1.8470000E+00  5.1730000E-01
*OMEGA      4.5723553E-01
*OMEGB      7.796074E-02

**---------------------------------------------------------------------**

**GEM settings follow**

*DER-CHEM-EQUIL  *ANALYTICAL  **use analytical derivatives
*DER-REACT-RATE  *ANALYTICAL  **use analytical derivatives
*PERM-VS-POR   0  **Do not adjust permeability as porosity changes
*ACTIVITY-MODEL  *IDEAL  **Use ideal activities: ionic activity is equal to ion concentration
*AQUEOUS-DENSITY  *LINEAR  **Use linear water density model
*VISW 1  **Water has viscosity of 1-cp
*AQFILL  *OFF

**----------------------AQUEOUS SPECIES DEFINITION---------------------**

Following data defines aqueous species in model. pH-sensitive polymer must be first

*NC-AQUEOUS    10  **Number of aqueous species in model
*COMPNAME-AQUEOUS **Names of species in model
   'PLM'  'H+'  'Ca++'  'Na+'  'Cl-'  'CO3--'  'tracer'  'HCO3-'  'H2CO3'  'OH-'  

**NOTE that tracer was added, although it does not react in the model
*MW-AQUEOUS **molecular weight of species in g/mol
1500000  1.00794  40.078  22.98977  35.453  18.02  96.11486  61.01714  62.02508  17.00734
*ION-SIZE-AQUEOUS **Ion size in Angstroms for Debye-Huckel activities (Not used in this run)
0 9 6 4 3 0 0 4.5 0 3.5
*CHARGE-AQUEOUS **Ionic charge of aqueous species. Used for ionic strength calculation
0 1 2 1 -1 0 0 -1 0 -1

**----------------------RESERVOIR COMPOSITION--------------------------**

**All minerals in the model are defined here
*NC-MINERAL    1  **Number of reactive minerals in model. Exclude non-reactive minerals
*COMPNAME-MINERAL **Name of mineral(s) in model
   'Calcite'  **Calcite is CaCO3(s)
*MW-MINERAL  **Molecular weight of each mineral in model (g/mol)
**INTRA-AQUEOUS EQUATIONS AND MINERAL REACTION EQUATIONS**

---

**Intra-aqueous (equilibrium) reactions defined first, geochemical (rate controlled) reactions after**

*N-CHEM-EQUIL  3 **Number of equilibrium reactions within aqueous phase
*N-RATE-REACT  1 **Number of geochemical reactions (Only one mineral per reaction)

**NOTE:** All reaction coefficients follow the same order:

**Hydrocarbon components coefficients are first (C7-16 in this case)
**Water component coefficient next
**Aqueous component coefficients defined next
**Mineral component coefficients defined last

**When there are more than of the same type of components, they are entered in the order defined
**Reactants are given negative stoichiometric coefficients, products are given positive coefficients
**Mineral reactants must have coefficient of negative one, only one mineral per reactions
**Minerals cannot be involved in equilibrium reactions

**FIRST THREE REACTIONS ARE EQUILIBRIUM REACTIONS**

**RXN  1  'H+\textsuperscript{+}' + 'CO3\textsuperscript{2-}' = 'HCO3\textsuperscript{-}'**

*STOICHIOMETRY

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<th>'PLM'</th>
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*LOG-CHEM-EQUIL-CONST **This is logarithm (base 10) of equilibrium constant for reaction 10.329

**RXN  2  2 'H+\textsuperscript{+}' + 'CO3\textsuperscript{2-}' = 'H2CO3'**

*STOICHIOMETRY

| 0 | 0 | 0 | -2 | 0 | 0 | 0 | -1 | 0 | 0 | 1 | 0 |

0

*LOG-CHEM-EQUIL-CONST 16.6

**RXN  3  'H2O' = 'H+\textsuperscript{+}' + 'OH\textsuperscript{-}'**

*STOICHIOMETRY

| 0 | -1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |

0

*LOG-CHEM-EQUIL-CONST -14

**THIS IS A RATE CONTROLLED GEOCHEMICAL REACTION**

**They require extra information to define reaction-rate of reaction**

**RXN  4: 'Calcite' = 'Ca\textsuperscript{++}' + 'CO3\textsuperscript{2-}'**

*STOICHIOMETRY

| 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |

-1

*REACTIVE-SURFACE-AREA 470.0 **given in m\textsuperscript{2} reaction area/m\textsuperscript{3} of bulk volume
**Surface area defined calculated by taking 10000 m\textsuperscript{2}/m\textsuperscript{2} x 0.047 bulk volume = 470 m\textsuperscript{2}/m\textsuperscript{3}
**Bulk volumes are defined later in input file

*ACTIVATION-ENERGY 41870.0
*LOG-CHEM-EQUIL-CONST -8.42
*LOG-TST-RATE-CONSTANT -8.447285 **This is NOT from literature. It was calculated to give
**an acid-matrix reaction-rate Damköhler number of 1 in the high-perm layer when pH=1 HCl acid is injected into
**this linear reservoir at 25 m3/day
**NOTE: the rate constant was adjusted to give the followin Damköhler numbers for the same injection rate
**in other runs:
**log k  Approximate Damköhler number in high-permeability zone
**-10.447285  0.01
**-9.447285  0.1
**-8.447285  1
**-7.447285  10
**-6.447285  100

*REF-TEMP-RATE-CONST 25.0

**The reaction section requires an annihilation matrix for the equilibrium reactions
**See GEM-GHG literature to define this matrix

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0  0  0  0  0  0  0  0  0  0  0  1

*PHASEID *CRIT
*CW  1E-10 **Default compressibility is 4.35E-7 (1/kPa)
*REFPW 10000
*OGW_FLASH *NO_H2OVAP
*DERIVATIVE METHOD *ANALYTICAL

**-------------------PH-SENSITIVE POLYMER INPUT COEFFICIENTS---------------------
**This should be changed to reflect the concentration and type of polymer used
**Coefficients given are for 3wt% EZ-2 polymer in 3wt% brine. See SPE 96914

** Activate the Huh, Choi and Sharma (SPE 96914) polymer solution viscosity model
*PLM-VISCOSITY *HCS
** Polymer specific volume in cm3/g
*PLM-SPCVOL 0.714286
** Polymer dissociation constant
*PLM-DISCST 4.46684E-05
** Polymer average molecular weight. This value will overwrite the molecular weight of
** the polymer entered as the first entry with *MW-AQUEOUS
*PLM-MW 1.5E+06
** Polymer average molecular weight
*PLM-CLMW 8.0E+04
** Polymer-solvent interaction parameter
*PLM-INTPAR 0.2
** Polymer volume fraction in the relaxed state
*PLM-VOLFR 0.2
**Polymer specific empirical constant "a"
*PLM-PARA 0.146349970294204
**Polymer specific empirical constant "b"
*PLM-PARB 1.16589153642437
**Empirical constant k''
*PLM-SCST 0.4
** Polymer limiting viscosity at high shear limit
*PLM-VISINF 1.0
**Alpha appears to be assumed to be 2 in the model
**Five polymer empirical constants
*PLM-PARE1 -0.038 **was -0.038
*PLM-PARE2  0.032   **was 0.032
*PLM-PARE3  0.000  **was 0.0000001, no shear-thinning when this is 0.000
*PLM-PARE5  5.842

**-------------------------------------ROCK FLUID DATA------------------
**The water-oil relative permeability, and gas relative permeability  tables follow

*ROCKFLUID
*RPT
*SWT
**Sw    krw      krow
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0.20600  0.0000432  0.6833008
0.20900  0.0000972  0.6750268
0.21200  0.0001728  0.6668032
0.21500  0.0002700  0.6586300
0.21800  0.0003888  0.6505072
0.22100  0.0005292  0.6424348
0.22400  0.0006912  0.6344128
0.22700  0.0008748  0.6264412
0.23200  0.0012288  0.6132672
0.23700  0.0016428  0.6002332
0.24200  0.0021168  0.5873392
0.24700  0.0026508  0.5745852
0.25200  0.0032448  0.5619712
0.25700  0.0038988  0.5494972
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0.27200  0.0062208  0.5129152
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**SGT**

** This table is not really used in simulation since no gas phase
** is generated in the simulation runs

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*SIGMA  7. 0. 7.  **IFT values used to distinguish gas and oil near critical point
*ROCKDENR 2650.0 **Rock density not including porosity

**-------------------------------------INITIAL RESERVOIR CONDITION------**
**INITIAL**

*SEPARATOR  101.325 15.56 **separator conditions*

*VERTICAL *OFF

*PRES  100*10000 100*10074.1 **Initial pressure in top and bottom layers*

*SW  *CON 0.2000 **Initial water saturation*

*ZGLOBAL  *CON 1  **mole fraction of each oil component in reservoir oil*

**MOLALITY-AQUEOUS-PRIMARY**

**Define the initial water composition in the reservoir at time zero.**

**Only the 'primary' species are defined. The rest are calculated using the equilibrium reaction equations**

**PLM' 'H+' 'Ca++' 'Na+' 'Cl-' 'CO3--' 'tracer'

0.0  4.056E-6  0.0531  0.5  0.5  7.16E-8  0.0

**NOTE: the above composition was used when pH-sensitive polymer was injected into the model**

**to prevent viscosity increases by fluid mixing. Values determined by letting pH=1 HCl with**

**0.5 molality NaCl come to equilibrium with calcite reservoir**

**NOTE: In cases where pH-sensitive polymer was not used the following primary species concentrations**

**were used:**

**PLM' 'H+' 'Ca++' 'Na+' 'Cl-' 'CO3--' 'tracer'

**  0.0  5.84269E-11  9.24104E-5  0.5  0.5  4.11414E-5  0.0

**VOLUMEFRACTION-MINERAL**

** 'Calcite' **This is the volume fraction of each mineral in the model**

0.047  **Volumefraction is fraction of bulk volume, not of grain volume**

**-------------------------------------NUMERICAL METHOD-----------------**

**The following numerical settings were used**

*NUMERICAL*

*MAXSTEPS 399999

*NORM  *PRESS 5000

*NORM  *SATUR 0.05

*ITERMIN 2

*ITERMAX 200

*AIM OFF

**-------------------------------------WELL DATA------------------------**

*RUN

*DATE 2006 1 1

**Minimum and maximum timestep sizes (in days)**

*DTMIN 1.0E-14

*DTMAX 0.10

*DTWELL 0.0000000001

*WELL 1 'INJ-1' **This is an injector on a constant rate constraint**

*INJECTOR 1

*INCOMP  *AQUEOUS

**SEE COMMENTS AT END OF FILE ABOUT INJECTED FLUID COMPOSITION**

** 'C7-16' 'PLM' 'H+' 'Ca++' 'Na+' 'Cl-' 'CO3--' 'tracer' 'HCO3-' 'H2CO3' 'OH-'

0.0  1.3437E-5  0.1  1E-60  0.5  0.5  1E-60  0.0  1E-60  1E-60  1E-13

**Should have used Cl- of 0.6, but polymer concentrations selected to work with 0.5
**NOTES ABOUT INJECTED FLUID COMPOSITION**

**Cases were run to model pH-sensitive polymer viscosity increases *in situ* and to model injection of high-viscosity fluid.

**In cases where pH-sensitive polymer was injected:**

- Initial reservoir water composition of spent pH=1 HCl was used (has pH of 5.39)
- Injected fluid composition contained polymer, 0.1 molality HCl
- Zero molalities were replaced with 1E-60 to prevent run crashes when running cases
- for the given calcite reservoir mineralogy the following polymer concentrations give the following viscosities
- when the acid-polymer mixture reaches equilibrium with the reservoir at pH=5.39
- 3.44E-6 polymer concentration gives final viscosity of 10-cp
- 8.051E-6 polymer concentration gives final viscosity of 100-cp
- 1.3437E-5 polymer concentration gives final viscosity of 1000-cp

**In cases where high-viscosity fluid (polymer) was injected:**

- Initial reservoir water composition was used
- "PLM' 'H+' 'Ca++' 'Na+' 'Cl-' 'CO3--' 'tracer'
- 0.0 5.84269E-11 9.24104E-5 0.5 0.5 4.11414E-5 0.0
- Injection well was set to inject the same fluid (along with associated secondary species) along with polymer
- The following polymer concentrations gave the following polymer viscosities
- 2.669E-6 polymer concentration gives final viscosity of 10-cp
- 6.251E-6 polymer concentration gives final viscosity of 100-cp
- 1.0434E-5 polymer concentration gives final viscosity of 1000-cp
Appendix 3: GEM-GHG INPUT FILE FOR COREFLOOD HISTORY MATCH SIMULATION

**NOTE: see Appendix 2 for annotations to describe input keywords

*FILENAMES *OUTPUT *SRFOUT *RESTARTOUT *INDEXOUT *MAINRESULTSOUT
*TITLE1 'Coreflood simulation of HCl coreflood #2'
*TITLE2 'Linear 1D Model'
*INUNIT *SI
*RESULTFILE *SR2

*OUTSRF *GRID *Z 'C1' *SW *DENW *VISW *DENG *TEMP *KRW *VELOCRC *PRES
*MOLALITY 'CO2'
*MOLALITY 'PLM'
*MOLALITY 'H+'
*MOLALITY 'Ca++'
*MOLALITY 'Na+'
*MOLALITY 'Cl-'
*MOLALITY 'Al+++'
*MOLALITY 'OH-
*MOLALITY 'H2O'
*MOLALITY 'CO3--'
*MOLALITY 'H2CO3'
*MOLALITY 'K+'
*MOLALITY 'HCO3-'
*MOLALITY 'Al(OH)4-'
*MOLALITY 'H4SiO4'

*MINERAL 'Kaolinit'
*MINERAL 'Calcite'
*MINERAL 'Quartz'
*MINERAL 'Kfeld'

*WSRF *WELL *TIME **output data each time given below in input file
*WSRF *GRID *TIME
*WPRN *GRID *TIME
*DIM *MDIMPL 100

-------------------------------------RESERVOIR & GRID DATA------------
*GRID *CART 50 1 1
*DI *CON 4.54E-3
*DJ *CON 0.022067
*DK *CON 0.022067
*KDIR *DOWN
*DEPTH 1 1 1 100
*POR *CON 0.177
*PERMI 50*5.6 **made perms smaller to increase delta P
*PERMJ 50*5.6
*PERMK *CON 0.0
*CPOR 4.5E-7
*PRPOR 101.325

-------------------------------------FLUID PROPERTY DATA--------------
**used full 7 pseudocomponent hydrocarbon model. This was not necessary for history matching exercise
*MODEL *PR
*NC 7 7
*TRES 25 **Temperature, degrees C
*COMPNAMES
 'CO2' 'C1' 'C2-3' 'C4-6' 'C7-16' 'C17-29' 'C30+
*PCRIT 7.2799000E+01 4.5400000E+01 4.4932000E+01 3.3238000E+01 2.0676400E+01
1.5675000E+01 1.5636000E+01
*VCrit 0.093444255 0.098415289 0.175488026 0.3093708 0.58957324
1.117086139 2.17211936
*TCRIT 303.89132 166.668 338.33604 466.11484 611.116 777.784
972.23
*AC 2.2500000E-01 8.0000000E-03 1.2600000E-01 2.4390000E-01 6.3860000E-01
1.0002000E+00 1.2810000E+00
*MW 4.4010000E+01 1.6043000E+01 3.6013000E+01 7.0520300E+01 1.4718200E+02
3.0147620E+02 5.6280500E+02
*HCFLAG 0 0 0 0 0 0 0
*BIN
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  0.05 0
  0.09 0 0
  0.09 0 0 0
  0.09 0 0 0 0

*VSHIFT 0.14 -0.15400 -0.009 -0.041 0.064 0.1792 0.3005
*PCHOR 49 71 135 231.6201 439.1472 788.2221 1112.4612
*VISCOR  *MODPEDERSEN
*VISCOEFF 1.3040000E-04 2.3030000E+00 7.3780000E-03 1.8470000E+00 5.1730000E-01

*OMEGA 4.5723553E-01 0.34962 4.5723553E-01 4.5723553E-01
4.5723553E-01 4.5723553E-01 4.5723553E-01
*OMEGAB 7.7796074E-02 0.06803 7.7796074E-02 7.7796074E-02
7.7796074E-02 7.7796074E-02 7.7796074E-02

*DER-CHEM-EQUIL  *ANALYTICAL
*DER-REACT-RATE  *ANALYTICAL
*PERM-VS-POR 0
*ACTIVITY-MODEL  *IDEAL
*AQUEOUS-DENSITY  *LINEAR
*VISW 1
*AQFILL  *OFF
**NC-AQUEOUS** 13
** The polymer must be defined as the first aqueous component.
*COMPNAME-AQUEOUS
  'PLM' 'H+' 'Ca++' 'K+' 'Na+' 'Al+++' 'Cl-' 'H4SiO4' 'HCO3-' 'Al(OH)4-' 'H2CO3'
  'OH-' 
*MW-AQUEOUS
  1500000 1.00794 40.078 39.0983 22.98977 26.98154 35.453 60.0092 96.11486 61.01714
  95.0109 62.02508 17.00734 
*ION-SIZE-AQUEOUS
  0 9 6 3 4 9 3 4.5 0 4.5 4 0 3.5 
*CHARGE-AQUEOUS
  0 1 2 1 1 3 -1 -2 0 -1 -1 0 -1 
*NC-MINERAL 4
*COMPNAME-MINERAL
  'Calcite' 'Kaolinit' 'Kfeld' 'Quartz'
**Calcite is CaCO3(s)
**Kaolinite is Al2Si2O5(OH)4(s)
**K-feldspar is KAlSi3O8(s)
**Quartz is SiO2(s)
*MW-MINERAL
**Calcite Kaolinite Kfeldspar Quartz
  100.0869 258.1616 278.33 60.0843 
*MASSDENSITY-MINERAL
  2710 2410.0 2600.0 2650.0 
*N-CHEM-EQUIL 4
*N-RATE-REACT 4
**RXN 1 HCO3-' = 'H+' + 'CO3--'
*STOICHIOMETRY
  0 0 0 0 0 0 0 0 0 -1 0 0
  0 0 0 0 0 0 0 0 0 0 0 0
  0 0 0 0 
*LOG-CHEM-EQUIL-CONST
  10.329 
**RXN 2 Al+++' + 4 'H2O' = Al(OH)4-' + 4 'H+'
*STOICHIOMETRY
  0 0 0 0 0 0 0 -4 0 4 0 0
  0 -1 0 0 0 0 1 0 0 0 0 0
  0 0 
*LOG-CHEM-EQUIL-CONST
  -22.7 
**RXN 3 H2CO3' = 2 'H+' + 'CO3-' 
*STOICHIOMETRY
  0 0 0 0 0 0 0 0 0 -2 0 0
  0 0 0 -1 0 0 0 1 0 0 0 0
  0 0 
*LOG-CHEM-EQUIL-CONST
  16.6
**RXN 4**  \( \text{H}_2\text{O}' = '\text{H}^+ + '\text{OH}.' \)

*STOICHIOMETRY

\[
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0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
\]

*LOG-CHEM-EQUIL-CONST

-14

**RXN 5:** 'Calcite' = 'Ca++' + 'CO3--'

*STOICHIOMETRY

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0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{array}
\]

*REEACTIVE-SURFACE-AREA 470.0 **based on 4.7% composition

*ACTIVATION-ENERGY 41870.0

*LOG-CHEM-EQUIL-CONST

-8.42

*LOG-TST-RATE-CONSTANT -3.37

*REF-TEMP-RATE-CONST 25.0

**RXN 6:** 'Kaolinite + 6 'H+' = 2 'Al+++ + 2 'H4SiO4' + 'H2O'

*STOICHIOMETRY

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*LOG-CHEM-EQUIL-CONST

7.435

*REEACTIVE-SURFACE-AREA 50000 **based on 5% composition

*ACTIVATION-ENERGY 62760.0

*LOG-TST-RATE-CONSTANT -7.5

*REF-TEMP-RATE-CONST 25.0

**RXN 7:** 'K-feldspar + 8 'H2O' = K+ + Al(OH)4- + 3 'H4SiO4'

*STOICHIOMETRY

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\begin{array}{ccccccccccccc}
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0 & 0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 1 & 0 & 0 \\
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*LOG-CHEM-EQUIL-CONST

-20.573

*REEACTIVE-SURFACE-AREA 300 **based on 3% composition

*ACTIVATION-ENERGY 67830.0

*LOG-TST-RATE-CONSTANT -6.28

*REF-TEMP-RATE-CONST 25.0

**RXN 8:** 'Quartz + 2 'H2O' = 'H4SiO4'

*STOICHIOMETRY

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*LOG-CHEM-EQUIL-CONST

191
*LOG-CHEM-EQUIL-CONST
-3.98
*REACTIVE-SURFACE-AREA  6960.0 **based on 69.6% composition
*ACTIVATION-ENERGY     87500.0
*LOG-TST-RATE-CONSTANT -6.52
*REF-TEMP-RATE-CONST   25.0

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*PHASEID *CRIT
*CW  4.35E-7
*REFPW  101.325
*OGW_FLASH *NO_H2OVAP
*DERIVATIVE_METHOD *NUMERALL

** Activate the Huh, Choi and Sharma (SPE 96914) polymer solution viscosity model
*PLM-VISCOSITY *HCS
** Polymer specific volume in cm3/g
*PLM-SPCVOL 0.714286
**Polymer dissociation constant
*PLM-DISCST 4.46684E-05
**Polymer average molecular weight. This value will overwrite the molecular weight of
**the polymer entered as the first entry with *MW-AQUEOUS
*PLM-MW 1.5E+06
**Polymer average molecular weight
*PLM-CLMW 8.0E+04
**Polymer-solvent interaction parameter
*PLM-INTPAR 0.2
**Polymer volume fraction in the relaxed state
*PLM-VOLFR 0.2
**Polymer specific empirical constant "a"
*PLM-PARA 0.146349970294204
**Polymer specific empirical constant "b"
*PLM-PARB 1.16589153642437
**Empirical constant k''
*PLM-SCST 0.4
**Polymer limiting viscosity at high shear limit
*PLM-VISINF 1.0
**Alpha appears to be assumed to be 2 in the model
**Five polymer empirical constants
*PLM-PARE1 -0.038
*PLM-PARE2 0.032
*PLM-PARE3 0.000
*PLM-PARE4 0.0000001
*PLM-PARE5 5.842

*---------------------------------------------------------------ROCK FLUID DATA-------------------------
*ROCKFLUID

*RPT **not relevant to model since only water phase was present in coreflood
**kro = ((1-Sw-0.2)/(1-0.2-0.2))²
**kro = ((1-Sw-0.2)/(1-0.2-0.2))²

*SWT
0.20000000 0.00000000 1.00000000
0.21250000 0.00043403 0.95876736
0.22500000 0.00173611 0.91840278
0.23750000 0.00390625 0.87890625
0.25000000 0.00694444 0.84027778
0.26250000 0.01085069 0.80251736
0.27500000 0.01562500 0.76562500
0.28750000 0.02126736 0.72960069
0.30000000 0.02777778 0.69444444
0.31250000 0.03515625 0.66015625
0.32500000 0.04340278 0.62673611
0.33750000 0.05251736 0.59418403
0.35000000 0.06250000 0.56250000
0.36250000 0.07335069 0.53168403
0.37500000 0.08506944 0.50173611
0.38750000 0.09765625 0.47265625
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**-----------------------------INITIAL RESERVOIR CONDITION------**

*INITIAL
*SEPARATOR 101.325 15.56
*VERTICAL *OFF
*PRES *CON 101.325
*SW *CON 0.99999 **Include some hydrocarbon for model stability
*ZGLOBAL *CON
  0.0192 0.0693 0.1742 0.1944 0.3138 0.1549 0.0742

*VOLUMEFRACTION-MINERAL **Don't include secondary species

**'PLM' 'H+' 'Ca++' 'K+' 'Na+' 'Al+++' 'Cl-' 'CO3--' 'H4SiO4'
  0.0 5.84269E-11 9.24104E-5 1.36808E-4 0.5 9.9389E-24 0.5 4.11414E-5 0.000104713

*NUMERICAL
*CONVERGE *MAXRES 1.0E-8
*SDEGREE *GAUSS
*NORTH 50
*PRECC 1E-8
*MAXSTEPS 399999

**-------------------------------WELL DATA-------------------------------**

*RUN
*DATE 2006 1 1
  *DTMIN 1.0E-16
  *DTMAX 0.00005
  *DTWELL 0.00000000001
  *AIMSET *CON 3 **This sets implicit calculations

**Define Wells

*WELL 1 'INJ-1' **This well injects 3wt% NaCl brine with pH=7 into the core
  *INJECTOR 1
  *INCOMP *AQUEOUS

**CO2' 'C1 'C2-3' 'C4-6' 'C7-16' 'C17-29' 'C30+' 'PLM' 'H+' 'Ca++' 'K+' 'Na+' 'Al+++' 'Cl-
 'CO3--' 'H4SiO4' 'HCO3-' 'Al(OH)4-' 'H2CO3' 'OH-
 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1E-7 0.0 0.0 0.5 0.0 0.0 0.0 0.0 0.0 0.0 0.0
 0.0 0.0 1E-7
  *OPERATE *MAX *STW 2.88E-3 **This rate is 1 cc/minute
  *OPERATE *MAX *BHP 200000.0 *CONT *REPEAT

*GEOMETRY *K 0.001 0.5 1 0.0
*PERF *GEO 1
  1 1 1 100.0

*WELL 2 'INJ-2' **This well injects pH=1 HCl acid into the core
  *INJECTOR 2
  *INCOMP *AQUEOUS

**CO2' 'C1 'C2-3' 'C4-6' 'C7-16' 'C17-29' 'C30+' 'PLM' 'H+' 'Ca++' 'K+' 'Na+' 'Al+++' 'Cl-
 'CO3--' 'H4SiO4' 'HCO3-' 'Al(OH)4-' 'H2CO3' 'OH-
 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 1E-1 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0
 0.0 1E-13
  *OPERATE *MAX *STW 2.88E-3 **This rate is 1 cc/minute
  *OPERATE *MAX *BHP 200000.0 *CONT *REPEAT

*GEOMETRY *K 0.001 0.5 1 0.0
*PERF *GEO 2
  1 1 1 100.0

*WELL 3 'PROD-3' **Producer on BHP constraint
  *PRODUCER 3
  *OPERATE *MIN *BHP 101.325

*GEOMETRY *K 0.001 0.5 1 0.0
*PERF *GEO 3
  50 1 1 100.0

*SHUTIN 'INJ-2' **start with acid injection well off

**The following times selected to print data to file after each pore volume of fluid was injected
*TIME 0.00679
*TIME 0.01359
*TIME 0.02038
*TIME 0.02717
*TIME 0.03397
*TIME 0.04076
*TIME 0.04755
*TIME 0.05435
*TIME 0.06114
*TIME 0.06794
*TIME 0.07473  *OPEN 'INJ-2' *SHUTIN 'INJ-1' **Stops brine injection, starts pH=1 acid injection
*TIME 0.09511
**Not all times included in this file to save space
*TIME 2.03805
*STOP
Appendix 4: CALCULATION OF FRACTIONAL FLOW
ALLOCATION OF HIGH-VISCOSITY FLUID INTO A MULTIPLE-
LAYER LINEAR GEOMETRY FLOOD WITHOUT CROSSFLOW

Analytical Equations for Fluid Displacement in a Single Layer Linear Reservoir

The flow rate of injected fluid into a single layer linear reservoir depends on the
viscosities of the injected fluid and the fluid initially in a reservoir when a constant
pressure drop is assumed across the layer. An equation for the flow rate of the injection
rate is derived for a linear reservoir given the following assumptions:

1) Piston like fluid displacement of the initial reservoir fluid by the injected fluid
2) Ignore residual fluid saturations, relative permeability effects, adsorption and
   inaccessible pore volume
3) Length x is the distance from the injection well to the front of fluid 2 (x = 0 at time 0)
4) Assume consistent units for all variables
5) Incompressible fluids (flow rate into reservoir equals flow rate out of reservoir)

The variables in the derivation are: \( \Delta P \) is total pressure drop across reservoir, \( L \) is the
length of the reservoir, \( \Delta P_1 \) and \( \Delta P_2 \) are the pressure drops across the reservoir filled with
the initial reservoir fluid and the injected fluid, respectively. \( q \) is the resultant fluid flow
rate into the reservoir, \( \phi \) is the porosity of the zone, \( k \) is the permeability of the zone, \( A \)
is the cross-sectional area of the reservoir, \( \mu_{\text{inj}} \) is the viscosity of the injected fluid, \( \mu_{\text{res}} \) is
the viscosity of the fluid initially present in the reservoir, and \( t \) is time. \( \Delta P \) is assumed constant with respect to time for the following one layer derivation.

\[
\frac{q}{\mu_{\text{inj}}} \cdot (L-x) = \frac{kA(L-x)}{kA} \quad (A4-1)
\]

Define the pressure drop across the zone filled with the initial reservoir fluid using Darcy’s law:

\[
\Delta P_1 = \frac{q \mu_{\text{res}} (L-x)}{kA} \quad (A4-1)
\]

Express flow rate \( q \) as function of \( \Delta P \) (which is constant) only:

\[
q = kA(\Delta P - \Delta P_1) = \frac{kA(\Delta P - q \mu_{\text{res}} (L-x))}{\mu_{\text{inj}} x} \quad (A4-2)
\]

Rearranging formula yields:

\[
q = kA \Delta P \left[ \frac{\mu_{\text{inj}} x}{\mu_{\text{inj}} x + \mu_{\text{res}} (L-x)} \right] = \frac{kA \Delta P}{\mu_{\text{inj}} x + \mu_{\text{res}} (L-x)} \quad (A4-3)
\]

Solve for the interstitial velocity of the injected fluid front:

\[
\frac{dx}{dt} = \frac{q}{\phi A} = \frac{kA \Delta P}{\mu_{\text{inj}} x + \mu_{\text{res}} (L-x)} = \frac{k \Delta P}{\phi \mu_{\text{inj}} x + \mu_{\text{res}} (L-x)} \quad (A4-4)
\]

Rearrange, put in integral form:
\[
\int k\Delta P \, dt = \int \phi \left[ (\mu_{\text{inj}} - \mu_{\text{res}}) x + \mu_{\text{res}} L \right] dx
\]  \hspace{1cm} (A4-5)

Solve R.H.S. integral and rearrange into a quadratic equation

\[
k\int \Delta P \, dt = \phi \left( \frac{\mu_{\text{inj}} - \mu_{\text{res}}}{2} \right) x^2 + \phi \mu_{\text{res}} L x \Rightarrow \left( \frac{\mu_{\text{inj}} - \mu_{\text{res}}}{2} \right) x^2 + \mu_{\text{res}} L x - \frac{k}{\phi} \int \Delta P \, dt = 0 \hspace{1cm} (A4-6)
\]

Note that the \( \int \Delta P \, dt \) integral can be easily solved when \( \Delta P \) is assumed to be constant, however, this has not been done to maintain the equation in a form that can be converted to a more general form later on for Equation A4-9 for a multiple-layer linear system.

Use the quadratic equation to solve for \( x \) which is the position of the injected fluid front. Keep only the positive solution since it is physically real.

\[
x = \frac{-\mu_{\text{res}} L \pm \sqrt{(\mu_{\text{res}} L)^2 + 2(\mu_{\text{inj}} - \mu_{\text{res}}) \left( \frac{k}{\phi} \int \Delta P \, dt \right)}}{\mu_{\text{inj}} - \mu_{\text{res}}} \hspace{1cm} (A4-7)
\]

Take the derivative of \( x \) with respect to time then solve for rate \( q \) again

\[
q = \left( \frac{dx}{dt} \right) \phi A = \left( \frac{k\Delta P \phi A}{\phi \sqrt{(\mu_{\text{res}} L)^2 + 2(\mu_{\text{inj}} - \mu_{\text{res}}) \left( \frac{k}{\phi} \int \Delta P \, dt \right)}} \right) = \left( \frac{k\Delta P A}{\sqrt{(\mu_{\text{res}} L)^2 + 2(\mu_{\text{inj}} - \mu_{\text{res}}) \left( \frac{k}{\phi} \int \Delta P \, dt \right)}} \right)
\]  \hspace{1cm} (A4-8)

Convert Single Layer Rate Equation into Multiple-Layer Fractional Flow Equation

The fractional flow allocation of injected fluid into each layer of a multiple-layer linear reservoir system (assuming parallel layers as shown in Figure 6-1) can be calculated using Equation A4-8. Combination of Equation A4-8 with the fractional flow equation
(Equation 6-1) gives equation 6-4 when the width of the layers is assumed to be equal for all layers and there is no crossflow between layers.

\[
\frac{q_i}{\sum_{i=1}^{n} q_i} = \frac{k_i h_i}{\sqrt{(\mu_{res} L)^2 + 2(\mu_{inj} - \mu_{res}) \frac{k_i}{\phi_i} \int \Delta P dt}} \quad (A4-9)
\]

This equation is only valid before the injected fluid (fluid 2) breaks through to the producing well in any of the layers.

Equation A4-9 has been derived for the constant reservoir \( \Delta P \) case assuming a similar pressure drop across all the parallel linear layers. Interestingly, this equation holds for a multiple-layer linear reservoir that has a constant total injected fluid rate into the injection well. For this equation to be valid for the constant injection rate case the reservoir pressure drop across all the layers must be equal at any given time, but the reservoir pressure drop may change over time. Reznik et al. (1983) discuss the equivalence between the constant injection rate (CIR) case and the constant reservoir pressure drop cases by defining “process time” (same as \( t \) above). The \( \Delta P \) and the \( t \) terms in the \( \int \Delta P dt \) integral vary between the two cases, but the integral \( \int \Delta P dt \) varies identically for both cases as only a function of the volume of fluid injected into the linear reservoir system at
all times before any of the injected fluid breaks through to the production well in any of the layers.
Appendix 5: SPREADSHEET CALCULATIONS TO SOLVE FOR FLUID FRONT POSITIONS IN A MULTIPLE-LAYER LINEAR GEOMETRY FLOOD

**Purpose:** Calculate the injected fluid front positions, $x_i$, in each layer of a multiple-layer linear system. The swept reservoir volume can be calculated as a function of the volume of fluid injected using the fluid front locations.

**Assumptions:**
- Consistent units, used SI
- Constant flow rate into layered system = Q
- Newtonian fluid rheology, Darcy flow in layers
- Piston-like displacement of fluid fronts in each layer
- Single phase flow behavior (no relative permeability or residual saturations)
- Pressure drop across all the linear layers in parallel is the same at any time although $\Delta P$ varies with time
- $n$ layers in system (used 2 for polymer/water system, used 3 for pH-sensitive polymer slug calculations)
- Common width, $w$, and length, $L$, for all layers

The following procedure is used to calculate the swept volume of each layer

1) Require initial injected fluid front positions, $x_i$ (usually zero), and reservoir properties ($k$, $h$, porosity) for each layer

2) Define effective viscosity-length term for each layer $i$

Use Equation A5-1 for high-viscosity fluid displacing reservoir fluid. Use Equation A5-2 for water displacing a pH-sensitive polymer slug that is displacing reservoir fluid

$$EVL_i = \mu_{inj} x_{i,inj} + \mu_{res} (L - x_{i,inj})$$  \hspace{1cm} (A5-1)

$$EVL_i = \mu_{waterflood} x_{i,waterflood} + \mu_{pHsenspolymer} (x_{i,pHsenspolymer} - x_{i,waterflood}) + \mu_{res} (L - x_{i,pHsenspolymer})$$ \hspace{1cm} (A5-2)

3) Calculate $\Delta P$ required to inject additional fluid into the system at rate $Q$ at the current time
\[ \Delta P = \frac{Q \prod_{i=1}^{n} [EVL_i]}{\sum_{i=1}^{n} \left( k_i h_i w_i \prod_{i=1}^{n} [EVL_i] \right)} \]  

(A5-3)

4) If desired the fractional flow into each layer, layer \( i \), in the system for the current time step

\[ f_i = \frac{q_i}{Q} = \frac{k_i h_i w_i \Delta P}{Q(EVL_i)} \]  

(A5-4)

5) Calculate the volume injected (in pore volumes) at the current time, \( \text{time} \)

\[ t_D = \frac{Q \cdot \text{time}}{L w \sum_{i=1}^{n} h_i \phi_i} \]  

(A5-5)

6) Update \( x_i \) for each fluid front (\( x_{i,\text{waterflood}} \), \( x_{i,\text{pHsenspolymer}} \) and/or \( x_{i,\text{inj}} \)) in each layer for the next time step

\[ x_{i,\text{new}} = x_{i,\text{old}} + \frac{Q f_i \Delta t}{w_i h_i \phi_i} \]  

(A5-6)

if \( x_{i,\text{new}} > L \) then \( x_{i,\text{new}} = L \)

7) Increment \( \text{time} \) variable by \( \Delta t \). Smaller time step sizes give better results

8) Repeat procedure starting at step 1 using the new \( x_i \) values from step 6

Comments: The analytical calculations from Appendix 4 have been found by the author to closely agree with those using this spreadsheet method at times before any injected fluid breaks through to the end of any of the layers. Such a comparison was made using small \( \Delta t \) values for the spreadsheet calculations and for cases where high-viscosity fluid displaced low-viscosity fluid. Use of the “if” statement in step 6 of this method allows the spreadsheet calculations to be valid after the injected fluid breaks through to the production well end of the reservoir.

Note: Sorbie and Mackay (2005) describe linear and radial spreadsheet calculations similar to these.
NOMENCLATURE

English Symbols

a  Empirical constant
a  Acid proton concentration
a  Activity of species in solution
Â  Reactive surface area at time zero
Â  Reactive surface area of reactant mineral per unit bulk volume of porous medium
A  Species name
b  Empirical constant
c  Rock or fluid compressibility
C_i Concentration of species i
E  Activation energy for reaction
e1 Empirical parameter 1
e2 Empirical parameter 2
e3 Empirical parameter 3
e4 Empirical parameter 4
e5 Empirical parameter 5
h  Height of reservoir zone
I  Ionic strength of solution
i  Index for species type (usually a subscript)
k  Permeability
K  Dispersion coefficient
K_a Polymer dissociation constant
k  Index for species number in GEM manual
k  Rate constant of mineral reaction
k’’  Empirical constant
Keq Equilibrium constant of a reaction for a given temperature
L  Length of medium
m_i Molar Concentration of ionic species
M_c Average molecular weight of polymer between crosslinks
M_n Average Polymer Molecular Weight
P  Pressure
n  Carreau equation empirical parameter
N  Number of moles of mineral per grid block volume
N_{Da} Damköhler number for acid-matrix chemical reaction
n  Number of species in simulation
pH pH of solution
Q  Equilibrium swelling volume
q  Fluid flow rate
Q  Ion activity product of a reaction
R  Number of mineral reactions in simulation
R  Radius

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rate of transfer or reaction-rate
\( R \) Reaction-rate
\( R \) Universal gas constant (8.314 J/(mol K))
\( S \) Saturation
\( T \) Temperature
\( t \) Time
\( u \) Darcy velocity
\( V \) Solvent (water) molar volume
\( w \) Width of reservoir
\( z \) Ion valence factor (charge)

Greek Symbols

\( \lambda \) Carreau equation empirical parameter
\( \gamma_{\text{eff}} \) Effective polymer shear rate in cell
\( \eta \) Polymer intrinsic viscosity
\( \eta_0 \) Polymer solution viscosity in the zero-shear-limit
\( \eta_0 \) Polymer solution viscosity in the zero-shear-limit
\( \eta_\infty \) Polymer viscosity at infinite shear rate,
\( \nu_{2,r} \) Polymer volume fraction in relaxed state,
\( \chi \) Polymer-solvent interaction parameter
\( \phi \) Porosity
\( \eta_s \) Solvent viscosity
\( \mu \) Viscosity
\( \xi \) Exponent parameter in reaction equation
\( \beta \) Mineral in simulation
\( \xi_{\beta} \) Exponent parameter in reaction equation
\( \nu \) Polymer specific volume
\( \nu \) Stoichiometric coefficient in chemical reaction equation
\( \rho \) Density of mineral

Subscripts

\( w \) Water
\( \beta \) Subscript indicating a mineral in GEM equations
\( 0 \) Indicates property at initial condition
\( i \) Species index
REFERENCES


