Numerical studies of reactive polymer flows in porous materials

Honggao Liu
Louisiana State University and Agricultural and Mechanical College

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_dissertations

Part of the Chemical Engineering Commons

Recommended Citation
https://digitalcommons.lsu.edu/gradschool_dissertations/1065

This Dissertation is brought to you for free and open access by the Graduate School at LSU Digital Commons. It has been accepted for inclusion in LSU Doctoral Dissertations by an authorized graduate school editor of LSU Digital Commons. For more information, please contact gradetd@lsu.edu.
NUMERICAL STUDIES OF REACTIVE POLYMER FLOWS IN POROUS MATERIALS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by

Honggao Liu
B.S., Xi’an Jiaotong University, 1994
M.S., Tianjin University, 1997
M.S., Louisiana State University, 2001
December 2002
ACKNOWLEDGEMENTS

I would like to gratefully acknowledge my major advisor Dr. Karsten Thompson, who provided me with relentless assistance, helpful guidance, and suggestions. It would have been impossible for me to finish this work without his great patience and full support.

I want to give my thanks to the Department of Chemical Engineering at Louisiana State University for providing me with financial support during my dissertation study. Also, I want to give my appreciation to all of my dissertation committee members for their time and support.

I would like to thank my fellow students, Gang Guo, Guangli Liu, Le Yan and Matthew Balhoff. Also, I would like to thank numerous people in the lab and Department who provided valuable assistance.

Last but not least, I would like to thank my family and friends who helped and supported me to finish.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS ........................................................................................................ ii

LIST OF TABLES .................................................................................................................. vi

LIST OF FIGURES ................................................................................................................ vii

ABSTRACT ........................................................................................................................ xi

CHAPTER 1 INTRODUCTION ................................................................................................ 1

CHAPTER 2 BACKGROUND AND LITERATURE REVIEW .............................................. 8
  2.1 Multiphase Flow in Porous Media ............................................................................ 8
    2.1.1 Darcy’s Law .................................................................................................... 9
    2.1.2 Relative Permeability and Capillary Pressure .............................................. 11
    2.1.3 Miscible and Immiscible Fluid Displacement ............................................ 15
  2.2 Viscous Instabilities of Flow in Porous Media .................................................... 18
    2.2.1 Viscous Fingering ....................................................................................... 18
    2.2.2 Effect of Heterogeneity ............................................................................. 20
    2.2.3 Effect of Chemical Reaction .................................................................... 22
  2.3 Flows of Reactive Polymers through Porous Materials ..................................... 25
    2.3.1 Viscous Instabilities of Reactive Polymer Flows in Porous Media .......... 26
    2.3.2 Oilfield Polymer-Gel Treatments ............................................................... 28
  2.4 Reservoir Simulation ............................................................................................. 34
  2.5 Modeling Reactive Polymer Flows in Porous Media ........................................... 36
    2.5.1 Modeling Flow in Porous Media ............................................................... 37
    2.5.2 Modeling Reactive Transport in Porous Media ........................................ 38
  2.6 Additional Mathematical Background .................................................................. 39
    2.6.1 Method of Moments ................................................................................... 39
    2.6.2 Residence Time Distribution and Holdback ............................................. 41

CHAPTER 3 MODEL FORMULATION .............................................................................. 44
  3.1 Governing Equations ............................................................................................. 44
    3.1.1 Overall Conservation Equation ................................................................... 44
    3.1.2 Molecular Weight Distribution ................................................................. 45
    3.1.3 Gelation Reaction Kinetics ......................................................................... 45
  3.2 Constitutive and Auxiliary Equations .................................................................... 47
  3.3 Geostatistical Permeability Model ....................................................................... 49
  3.4 Numerical Solution ................................................................................................ 50
    3.4.1 Updating Pressure and Fluid-Phase Saturation ....................................... 51
    3.4.2 Transport of Mobile-Phase Polymer ........................................................... 52
    3.4.3 Polymer Reaction ....................................................................................... 53
    3.4.4 Updating Parameters .................................................................................. 53
  3.5 Numerical Example ............................................................................................... 55
**CHAPTER 4 PARAMETER SENSITIVITY AND MODEL LIMITATIONS**

- 4.1 Form of the Molecular Weight Distribution
- 4.2 Discretization of the Distribution
- 4.3 Mobile Polymer Transport
- 4.4 Timestep Size

**CHAPTER 5 SIMULATION OF POLYMER AND CROSSLINKER SOLUTION DISPLACING WATER**

- 5.1 Injection of Polymer/Crosslinker Solutions without Gelation
  - 5.1.1 Residence Time Distribution for Transient Flows
  - 5.1.2 Instantaneous Residence Time Distributions
  - 5.1.3 Effects of Parameters on Steady-State Viscous Fingering
  - 5.1.4 Mechanistic Explanation of the Critical Damkohler Number
- 5.2 Injection of Polymer/Crosslinker Solutions with Gelation
  - 5.2.1 Effect of Gelation on Steady-State Fingering
  - 5.2.2 Effects of Other Parameters on Steady-State Fingering
  - 5.2.3 Effect of Gelation on Breakthrough Residence Time Distributions
  - 5.2.4 Gel Placement

**CHAPTER 6 SIMULATION OF CROSSLINKER DISPLACING POLYMER**

- 6.1 Standard Viscous Fingering
  - 6.1.1 The General Phenomena of Viscous Fingering
  - 6.1.2 Variation of the Mobility Ratio
  - 6.1.3 Variation of the Peclet Number
  - 6.1.4 Heterogeneous Systems
  - 6.1.5 Layered Systems
- 6.2 Nonlinear Fingering in the Presence of Crosslinking Reactions
  - 6.2.1 Variation of the Damkohler Numbers
  - 6.2.2 Reactive Stabilization
  - 6.2.3 Mechanisms of Finger Growth with Crosslinking Reactions
- 6.3 Nonlinear Fingering in the Presence of Gelation
  - 6.3.1 Effect of Gelation
  - 6.3.2 Gelation Stabilization
  - 6.3.3 Heterogeneous Systems
  - 6.3.4 Layered Systems

**CHAPTER 7 CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS**

- 7.1 Summary of the Conclusions
  - 7.1.1 Numerical Model
  - 7.1.2 Polymer and Crosslinker Solutions Displacing Water
  - 7.1.3 Crosslinker Solution Displacing Polymer
- 7.2 Future Research Directions
  - 7.2.1 Model Improvements and 3D Reactive Polymer Flow Simulation
  - 7.2.2 Coorflow Experiments
  - 7.2.3 Pore-Scale Modeling
# LIST OF TABLES

Table 3.1  The polydispersities of polymer in gridblocks (10,10) and (10,30) at various times……………………………………………………………….58

Table 4.1  Effect of the number of fractions on MWD discretization error………………62

Table 4.2  Effect of upper mass cutoff on MWD discretization error ……………………63

Table 4.3  Comparison of trapezoid area approximation versus spline interpolation…… 63
LIST OF FIGURES

Figure 1.1 Structure of the Project.................................................................6

Figure 3.1 Spatial map of the absolute permeability distribution..............................55

Figure 3.2 Concentration distribution of polymer components at gridblock (10, 10) at various times.................................................................56

Figure 3.3 Concentration distribution of polymer components at gridblock (10, 30) at various times.................................................................57

Figure 3.4 Concentration distribution of polymer components at time=1226s in different gridblocks.................................................................58

Figure 4.1 Two log-normal distributions..........................................................60

Figure 4.2 Distribution of the mixed log-normal distributions..................................61

Figure 4.3 The pre- and post-transport concentration distributions and the log-normal distribution using moments of the post-transport curve........65

Figure 4.4 The post transport concentration distribution and the optimized log-normal distribution.................................................................66

Figure 4.5 Change in polydispersity versus reaction coefficient for a fixed reaction time.................................................................69

Figure 4.6 Minimum Damkohler number versus number of fractions at $X_0=1.67 \times 10^{-4}$ mol/cm$^3$.................................................................69

Figure 5.1 Spatial maps of the absolute permeability distributions: (a) Layered; (b) Heterogeneous.................................................................71

Figure 5.2 The breakthrough residence time distributions at different Damkohler numbers: (a) $Da=0$; (b) $Da=1.0$; (c) $Da=2.0$; (d) $Da=3.0$; (e) $Da=4.0$; (f) $Da=5.0$; (g) $Da=6.0$.................................................................73

Figure 5.3 The holdback of the breakthrough RTD at different Damkohler numbers....74

Figure 5.4 The mean residence time of the breakthrough RTD at different Damkohler numbers.................................................................75

Figure 5.5 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=0.7, 3.1, 6.6, and 9.1 from left to right when $Pe=625$ at (a) $Da=1.0$; (b) $Da=2.0$; (c) $Da=4.0$.................................................................76
Figure 5.6  The instantaneous holdback versus PV injected at different Damkohler numbers at $Pe=625.0$ in a layered domain of $\gamma=2.0$...............................78

Figure 5.7  The instantaneous holdback versus PV injected at different Damkohler numbers at $Pe=625.0$ in a layered domain of $\gamma=1.1$...............................78

Figure 5.8  The instantaneous holdback versus PV injected at different Damkohler numbers at $Pe=625.0$ in a heterogeneous domain.................................79

Figure 5.9  The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=0.7, 3.6, 5.1, and 9.1 from left to right in the heterogeneous domain ($Pe=625$) at (a) $Da=1.0$; (b) $Da=2.0$; (c) $Da=4.0$.................................................................80

Figure 5.10 The instantaneous holdback versus PV injected at different Damkohler numbers at $Pe=31250$ in a heterogeneous domain.............................81

Figure 5.11 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=0.7, 3.1, 6.6, and 9.1 from left to right when $Pe=31250$ at (a) $Da=1.0$; (b) $Da=2.0$; (c) $Da=4.0$......................82

Figure 5.12 The instantaneous holdback vs. PV plot at $\gamma=2.0$ (layered) and $Pe=312500$...83

Figure 5.13 The instantaneous holdback vs. PV injected at different Damkohler numbers at $Pe=625.0$ in a layered domain with $\gamma=2.0$.................................83

Figure 5.14 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV = 4.6, 5.6, 6.6, and 9.1 when $Pe = 625$ at $Da = 2$ if PV<4.0, $Da=4$ if PV>4.0.................................84

Figure 5.15 The instantaneous holdback versus PV injected at different Damkohler numbers in the presence of gelation at $Pe=625.0$ in the layered domain with $\gamma=2.0$.................................................................87

Figure 5.16 Comparison of the development of the velocity profile (the color corresponds to the magnitude of velocity) without (top row) and with (bottom row) gelation at (a) $Da=2.0$; (b) $Da=4.0$.........................88

Figure 5.17 The instantaneous holdback versus PV injected at different Damkohler numbers in the presence of gelation (a) at $\gamma=2.0$ (layered) and $Pe=31250$; (b) at $\gamma=1.1$ (layered) and $Pe=625.0$; (c) at $\gamma=2.0$ (heterogeneous) and $Pe=625.0$.................................................................91

Figure 5.18 Comparison of the holdback of the breakthrough RTD with and without gelation at different Damkohler numbers.................................92
Figure 5.19 Gel saturation distributions at different Damkohler numbers......................... 94

Figure 6.1 Standard viscous fingering for $M=100$ and $Pe=1000$ at $t=480$, 720, and 960s (the color corresponds to the magnitude of crosslinker concentration)..................................................................................................................97

Figure 6.2 Spatial maps of the absolute permeability distribution ($\sigma=0.001$). (a) heterogeneous; (b) layered.................................................................98

Figure 6.3 Comparison of viscous fingering for different values of $M$ increasing from top to bottom from 1 to 50. Columns (a), (b), and (c) correspond respectively to $t=480$, 720, and 960s (the color corresponds to the magnitude of crosslinker concentration).................................................................................................99

Figure 6.4 Comparison of viscous fingering for different values of $Pe$ increasing from top to bottom at $Pe=150$, 312.5, 625, 1250, 2500, 5000, and $\infty$. Columns (a), (b), and (c) correspond respectively to $t=360$, 600, and 840s (the color corresponds to the magnitude of crosslinker concentration).............101

Figure 6.5 Relationship between the number of fingers and Peclet number...................... 102

Figure 6.6 Comparison of viscous fingering for different values of $\sigma$: 0.01, 0.1, and 1.0 from top to bottom. Columns (a), (b), (c), and (d) correspond to $t=240$, 480, 720, and 960s (the color corresponds to the magnitude of crosslinker concentration).................................................................................104

Figure 6.7 Comparison of viscous fingering for different values of permeability contrast of 1.1, 2.0, and 4.0 from top to bottom. Columns (a), (b), (c), and (d) correspond respectively to $t=240$, 480, 720, and 960s (the color corresponds to the magnitude of crosslinker concentration).............105

Figure 6.8 Experiments comparing unreactive viscous fingering (left) and reactive viscous fingering (right) when 0.15 PV fluid is injected.................................106

Figure 6.9 Comparison of fingering for $Da=2.0$, 6.0 and 10.0 from top to bottom. Columns (a), (b), and (c) correspond respectively to $t=360$, 480, and 600s (the color corresponds to the magnitude of crosslinker concentration)........107

Figure 6.10 Comparison of polymer $M_w$, concentration and viscosity distributions for $Da=2.0$, 6.0 and 10.0 from left to right at $t=480$s. (a) polymer $M_w$; (b) concentration; (c) viscosity.................................................................108
Figure 6.11 Comparison of fingering at time $t=600s$. (a) $Da=10.0$ with higher initial polymer concentration; (b) $Da=15.0$; (c) $Da=10.0$ but the polymer solution’s viscosity is a function of polymer concentration at first order; (d) $Da=10.0$ at lower Peclet number (the color corresponds to the magnitude of crosslinker concentration)……………………………….110

Figure 6.12 Comparison of fingering for $Da = 2.0, 6.0$ and $10.0$ from left to right at time $t=840s$. (a) no gel formation; (b) gel formation (the color corresponds to the magnitude of crosslinker concentration)…………………………..114

Figure 6.13 Comparison of viscosity distributions for $Da = 2.0, 6.0$ and $10.0$ from left to right at $t=840s$. (a) no gel formation; (b) gel formation (the color corresponds to the magnitude of polymer solution viscosity)………………..115

Figure 6.14 Gel saturation distributions for $Da = 2.0, 6.0$ and $10.0$ from left to right at time $t=840s$………………………………………………………………...116

Figure 6.15 Crosslinker concentration at PV=0.3, 0.5, 0.7, and 0.9 from left to right (a) $Da=15$ and $Pe=1250$; (b) $Da=10$ and $Pe=312.5$ (the color corresponds to the magnitude of crosslinker concentration)………………..117

Figure 6.16 Comparison of fingering for $Da = 0.0, 2.0, 6.0$ and $10.0$ from left to right at 0.8 PV injected in domains of (a) $\gamma=0.1$; (b) $\gamma=1.0$ (the color corresponds to the magnitude of crosslinker concentration)…………………………..119

Figure 6.17 Comparison of velocity fingering for $Da = 0.0, 2.0, 6.0$ and $10.0$ from left to right at 0.8 PV injected in layered systems with (a) $\gamma=1.1$; (b) $\gamma=2.0$; (c) $\gamma=4.0$ (the color corresponds to the magnitude velocity)…….. 120

Figure 6.18 Distributions in layered systems with $\gamma=1.1, 2.0, and 4.0$ from left to right for $Da=10.0$ at 1.2 PV injected. (a) Crosslinker concentration; (b)Velocity; (c) Gel placement……………………………………………………….121

Figure B.1 The instantaneous holdback versus PV injected at different timestep sizes at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=0.………………..152$

Figure B.2 The instantaneous holdback versus PV injected at different grid resolutions at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=0.………………..152$

Figure B.3 The instantaneous holdback versus PV injected at different timestep sizes at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=2.………………..153$

Figure B.4 The instantaneous holdback versus PV injected at different grid resolutions at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=2.………………..153
ABSTRACT

This dissertation presents a new numerical model of reactive polymer flow in heterogeneous porous media. A moment representation of the log-normal polymer molecular weight distribution is used to model polymer as a multi-component species. Three leading moments are used to simulate the polymer transport and reaction processes in a two-dimensional porous medium. A new operator splitting technique that allows the moment equations for polymerization to be incorporated into a finite-difference transport model is developed. The novelty of this approach is the use of two different dependent variables (for the transport versus reaction parts of the problem). It is significant from a physical standpoint because previous techniques did not allow us to observe the full evolution of polymer molecular weights in space and time.

In this dissertation, two types of flows are examined. The first is the injection of a polymerizing fluid into a heterogeneous material containing low viscosity fluid (e.g., air or water). Simulations show that, depending on the Damkohler number, preferential loss of material permeability can occur in either low or high permeability regions. Because this effect dictates subsequent flow patterns, this result suggests that front stability can be controlled through proper design of the flow dynamics versus reaction dynamics. The formation of steady viscous fingers was observed, which is a fundamentally different phenomenon than previously observed transient viscous finger fingering formed during displacements. It is affected by the competition between reaction and convection, which allows the behavior to be correlated with the Damkohler number. A critical Damkohler number exists, above which steady-state conditions are not observed. The critical Damkohler number is affected by the Peclet number and permeability field. The second type of simulation is the injection of polymerizing fluids
under conditions that lead to viscous instabilities. Results show the Damköhler number again to be a critical parameter. In both cases, the scale and structure of the material heterogeneities have a significant effect on the resulting flow. These research results provide important information for various polymer processing applications.
CHAPTER 1

INTRODUCTION

Porous media are made up of pore spaces and a solid matrix. The pore spaces are typically connected, which allows transport processes such as fluid flow, and mass and heat transfer to take place inside. Fluid flow and transport in porous media are important parts of many engineering processes such as chromatography, reactor design, environmental remediation, petroleum recovery, catalysis, ion exchange, etc. The structure of porous media is usually very complex so it is customary to model porous media by ignoring the micro-mechanical details within the pores and instead work with the volume-averaged laws that treat a porous medium as a macroscopically uniform continuum. At this scale, porous media are described by parameters such as permeability and dispersion coefficients.

The flows of reactive polymers through porous media are of interest to engineers because of practical applications such as the manufacture of composite materials, the hydraulic fracturing of oil wells, gel treatments in oil recovery, and types of polymer processing. During the manufacture of certain composite materials, polymeric fluids are injected into porous media and allowed to react in situ (Greenkorn, 1983; Svensson et al., 1998). Hydraulic fracturing is widely used to increase production from petroleum wells, and crosslinking polymers are used in this process (Economides and Nolte, 1989; Powell et al., 1999; Coveney et al., 2000; Romero et al., 2000). In gel treatments, polymerizing fluids are injected into reservoirs, and gels that are formed in situ plug higher-permeability zones and divert the injected fluids to less-permeable zones where oil is trapped, resulting in increased oil recovery (Liang et al., 1992, 1995, 1997; Thompson and Fogler, 1997; Seright et al., 1998; Thompson and Kwon, 1998; McCool et al., 2000). Some thermoplastic polymers and resins are being
used to impregnate softwood or dense fiber networks for fiber-reinforced composites (Kim et al., 1991; Kazi et al., 1997). How the reactive polymers move through the porous matrix is essential to these applications.

A number of previous studies have focused on reactive polymer flow through porous materials; however, viscous instabilities in polymerizing flows have not received much attention, although experiments have shown both destabilizing and stabilizing effects associated with reaction (Losure et al., 1996; Thompson and Kwon, 1998). These phenomena have been examined using both linear stability analysis (Satyadev et al., 2000) and numerical modeling (Thompson and Kwon, 1998).

Losure (1996) studied instabilities that occur during reactive resin molding and showed that the scale of fingers would determine the mechanical performance of the molded part. Large viscous instabilities can lead to significant defects in molded parts of the preforms. Thompson and Kwon (1998) performed experiments in a visual flow cell and performed numerical simulations to study fundamental changes in viscous fingering due to polymer-crosslinker reactions. They showed the existence of unstable regimes caused by fingering as well as stabilizing phenomena associated with the crosslinking reaction. Three regimes were observed in numerical simulations (depending on reaction rate): viscous fingering at slow reaction rates, a stabilized regime at moderate reaction rates, and reactive fingering at high reaction rates.

Satyadev et al. (2000) studied instabilities during the impregnation of fibrous preforms by reactive resins (for the fabrication of composite materials). They showed that reactions can induce a flow instability, but can also stabilize the front, depending on the coupling of flow and reaction dynamics. They define stable and unstable flow regimes and explain how the
competition in reaction rates across a disturbance dictates whether the reaction will stabilize the disturbance.

While the studies mentioned above address transport and reaction at the continuum scale, microscale structure can have important effects. Examples that share dynamic similarities with the proposed work include the formation of nonuniform nutrient fronts during the growth of bacteria and biopolymers (Dillon and Fauci, 2000) and the nonuniform propagation of combustion fronts due to microscale heterogeneity (Varma et al., 2001). Additionally, a number of previous investigations have examined how crosslinked polymers affect permeability and relative permeability for oilfield applications (Dawe and Zhang, 1994; Liang et al., 1992, 1995; Thompson and Fogler, 1997; Hild and Wackowski, 1999; McCool et al., 2000).

Understanding and modeling these reactive flows is difficult because of the complexity of the coupling that occurs between transport, changes in fluid properties due to reaction, and heterogeneity in the materials. Traditional reactive-polymer-flow models treat the polymer as a single-component species (Woods et al., 1991; Gao et al., 1993; Todd et al., 1993; De et al., 1998; Thompson and Kwon, 1998; Rajesh and Bhagat 1999). However, most polymers of interest are polydisperse, and the transport properties of lower and higher molecular weight species are known to be different. Furthermore, the single species kinetic models used in these flow models are too simple to represent the polymerization process well. In order to effectively model polymer transport and gelation in porous materials, it is important to address effects associated with polydispersity and evolution of the molecular weight distribution due to crosslinking reactions. The polydispersity effects have been addressed by Brown and Sorbie (1989) for modeling the transport of xanthan polymer; they used 26
discrete molecular weight fractions for which a set of 26 convection-dispersion equations were solved. For that case, however, no reaction occurred, so the polydispersity remained constant. If there are in-situ gelation reactions, the distribution of molecular weight can rapidly change and can span orders of magnitude. The problem with modeling flow and reaction for the reactive case is that a very large number of dependent variables would be needed to accurately describe the system. This approach is not tractable in large heterogeneous domains.

An alternative approach for modeling polymer reactions is to use the polymer molecular weight distribution (MWD), which can be described by moments of that distribution. Depending on the form of the MWD, the first three moments may contain sufficient information about the distribution to model the dynamics of the chemical reaction. This approach has successfully been used to model polymerization kinetics in batch, semibatch, and continuous reactors (Zabisky et al., 1992; Doston et al., 1996; Dube et al., 1997). However, it has not been used for modeling reactive polymer flow in porous materials.

In this work, we develop a new computational modeling technique in which the traditional dependent variables in the conservation equations (i.e., species concentrations) are replaced with moments of the polymer molecular weight distribution to model reactive polymer flows in heterogeneous porous media. We use a moment representation of the log-normal polymer molecular weight distribution to model polymer as a multi-component species. Three leading moments of the polymer MWD are used to simulate the polymer transport and reaction processes in a two-dimensional porous medium. The 2D, two-phase polymer flow model is based on a mass-transport equation for multi-component species. It is coupled with kinetic models of the crosslinking process by using an operator splitting scheme.
This approach allows for the efficient modeling of polymerization reactions in which orders-of-magnitude polymer molecular weight changes can occur during flow. We discuss the sensitivity of various parameters and constitutive equations, some of which require further research.

Using the new model, we address two important issues that remain poorly understood in the context of reactive polymers flows.

1. Viscous instabilities due to crosslinking reaction and gelation. Previous studies that address the viscous instabilities due to reaction, have been focused on transient behavior rather than steady state.

2. Effects caused by heterogeneity. Heterogeneity is an important factor affecting dynamics and can induce flow instabilities. Although some of the research relates to nonuniform materials (Binetruy et al., 1998; Lappan et al., 1997; Sorbie and Seright, 1992), the heterogeneities were very specific to the problems (for instance, a layered material or low-permeability annulus). As such, heterogeneity was not treated as a phenomenological parameter in the system. More importantly, studies have not been made in which heterogeneity is a dynamic parameter that is affected by the reaction process itself.

In our work, we consider the flow of reactive polymers through heterogeneous materials and investigate the effects of the in-situ crosslinking reactions on the stability of liquid flows. We examine two types of flows. One is the injection of a polymerizing fluid into a heterogeneous material containing low viscosity fluid such as water, the other is the injection of crosslinker into polymer under conditions that lead to viscous instabilities. Results show that the flow behavior and stability are strong functions of the Damkohler number, Peclet number, the mobility ratio, and the structure and scale of the heterogeneity. We discuss the
formation of steady viscous fingers, which arise from a viscous instability but represent a fundamentally new and different phenomenon than transient viscous fingers formed during displacements. The steady process is affected by the competition between reaction and convection, which allows their behavior to be correlated with the Damkohler number. A critical Damkohler number exists, above which steady-state conditions are not readily achieved, and which is affected by the Peclet number and permeability field.

![Flow Chart](image)

**Figure 1.1 Structure of the Project**

The research is outlined in Figure 1.1, and the remainder of this dissertation is organized as follows. Chapter 2 gives a background and literature review. Chapter 3 describes the method that was developed for solving the governing equations of reactive polymer flows in porous media. Chapter 4 analyzes the sensitivity of parameters and describes the limitations
of the model. Chapter 5 describes numerical simulations of a polymerizing fluid displacing water. Chapter 6 describes the unstable flow of crosslinker displacing polymer. Finally, Chapter 7 summarizes the conclusions and proposes the future research directions.
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Multiphase Flow in Porous Media

Ideally, physical descriptions of multiphase flow in porous media should be based on fundamental principles. It is theoretically possible to treat the problems of multiphase flow in porous media by starting at the pore scale and solving the Navier-Stokes equations (together with the equations of state of the fluids and the equations of continuity) over the medium with certain boundary conditions. However, this process is impractical, especially for the problem of multiphase flow. Hence, direct solution of the Navier-Stokes equations is generally reserved for highly theoretical studies, in which cases special computational methods such as the lattice-Boltzmann method (Chen et al., 1991; Chen et al., 1995) or approximate methods such as network modeling (Blunt and King, 1991; Blunt, 1997) are used. In an attempt to circumvent the fundamental difficulties, and in response to practical needs, an empirical macroscopic description of multiphase flow in porous media has been developed. Darcy's law, an empirical surrogate for momentum conservation based on data obtained from experimental studies of one-dimensional single-phase flow (Darcy, 1856), is used for the calculation of fluid flow through porous media. It relates the macroscopic flux of a fluid to the pressure gradient by a proportionality factor called absolute permeability. Permeability is a measure of the ability of porous media to conduct flow and is determined by the geometry of the pore network. Oftentimes, fluid flow in porous media involves more than one fluid. In this case, the ability of each fluid to flow is reduced by the presence of other fluid(s). Darcy's law has been extended to such cases using the concept of relative permeability, which is the apparent permeability of a fluid at a given saturation. (Saturation is the volume fraction of the pore...
space occupied by a particular phase.) Since 1856, Darcy’s relation has been changed by allowing the original constant coefficient to be a spatially dependent tensor, and nonlinear function of fluid and medium properties, particularly of the quantities of these phases in the flow system.

### 2.1.1 Darcy’s Law

Darcy’s law is a very good empirical equation describing flow of liquid and gas in the continuum representation of a porous medium. In 1856, Henry Darcy carried out experiments on the flow of water through a packed sand column. Darcy’s experiments demonstrated that the flow rate of water through the porous media, $Q$, is proportional to both the head loss between the ends of the cylinder, $h_2 - h_1$, and the cross-sectional area $A$, and is inversely proportional to the packed length, $l$:

$$Q = -KA \frac{h_2 - h_1}{l}$$  \hspace{1cm} (2-1)

where $K$ is the hydraulic conductivity, which is a function of the porous medium and fluid properties ($K = \frac{k \rho g}{\mu}$, $k$ is the absolute permeability of porous media, $g$ is the magnitude of the gravitational acceleration, and $\rho$ and $\mu$ are the density and viscosity). Analogously to Darcy’s law, the following equations have been written for two-phase flow in porous media under steady-state conditions (Dullen, 1992).

$$Q_i = -\frac{k_i A \Delta p_i}{\mu_i l}, \hspace{1cm} i = 1, 2$$  \hspace{1cm} (2-2)

where $Q_i$ is the volumetric flow rate, $\Delta p_i$ is the pressure drop, $\mu_i$ is the viscosity, and $k_i$ is the effective permeability or phase permeability of the porous medium, all written respect to fluid $i$. It is customary to introduce relative permeability $k_{ri} = k_i / k$. Relative permeability, which
accounts for the reduction of permeability to a phase when it does not fully occupy the porous medium, is the ratio of the effective permeability of a fluid to the absolute permeability of the porous medium. Hence the relative permeability of a phase is usually taken to be unity when the phase fully occupies the medium and is zero when its occupied volume fraction is sufficiently low; this saturation is called the irreducible or residual saturation. This extension of Darcy’s law was first suggested by Muskat and coworkers (Muskat and Meres, 1936; Muskat et al., 1937). In 1982, Marle further generalized Darcy’s law by assuming that it applies at all points in the porous media and also in non-steady flow (Marle, 1982):

\[
\mathbf{u}_i = -\frac{1}{\mu_i} \mathbf{K}_i \cdot \nabla p_i \quad i = 1, 2
\]  

(2-3)

where \(\mathbf{u}_i\) is the Darcy velocity of phase \(i\); \(\mathbf{K}_i\) is the permeability dyadic for phase \(i\), \(\mathbf{K}_i = \mathbf{K} \cdot \mathbf{K}_r\), \(\mathbf{K}\) is the (purely morphologic) permeability tensor, and \(\mathbf{K}_r\) is the relative permeability tensor. Gravity effects may be incorporated by replacing the preceding pressure-gradient term by \(\nabla p_i - \rho g\). In isotropic cases, these tensorial relations degenerate into simpler scalar relations, as the permeability tensors are generally taken to be isotropic.

Darcy’s law is the well-known equation for describing fluid flow in porous media. Darcy’s law assumes the porous medium to be a continuum material where flow or other transport properties such as permeability or dispersion coefficients can be derived from averaging the pore-level transport over an appropriate representative elementary volume. The microscale properties of the medium are conveniently buried in the permeability. The validity of Darcy’s law requires that the pore size be much smaller than other characteristic dimensions governing the flow field. Darcy’s law represents a balance between viscous forces
and the pressure gradient. Inertial effects are neglected and hence Darcy’s law holds only for sufficiently low velocities.

2.1.2 Relative Permeability and Capillary Pressure

Relative permeability and capillary pressure are commonly used to predict rates of multiphase fluid flow in porous media, and therefore, are important properties in the design of petroleum recovery processes and the prediction of groundwater flow. Values of relative permeability obtained from drainage (displacement by the nonwetting phase or reduction of wetting phase saturation) are different from those for imbibition (displacement by the wetting phase or increase in wetting phase saturation) at the same saturation. This phenomenon is called hysteresis. The relative permeability is not only a function of saturation but also depends on the displacement history. Relative permeability hysteresis is usually more prominent in the nonwetting phase than in the wetting phase. To understand the origins of relative permeability hysteresis, Jerauld et al. (1990) conceptualized the geometric structure of a phase in porous media in terms of three fractions: a flowing fraction, a nonflowing fraction and an isolated fraction. Although the isolated and immobile connected fractions contribute to the measurement of saturation, they won’t contribute to the relative permeability. Therefore, for a single value of saturation, more than one value of relative permeability could result depending on how the fluid partitions itself among the mobile, immobile, and isolated fractions.

Capillary pressure is the equilibrium pressure difference between the non-wetting and wetting phase:

\[ p_{c}^{eq} = p_{nw} - p_{w} \]  \hspace{1cm} (2-4)
Where $nw$ and $w$ label the non-wetting and wetting phases respectively. To begin to formulate a theoretical framework for incorporation of capillary pressure into models of multiphase flow, it is important to account for capillary forces. The capillary pressure is actually a property of the interface between the fluids. It depends on the interfacial tension $\sigma$ between the fluids and the principal radii of curvature of the surface, $r_1$ and $r_2$, as shown by the Young-Laplace equation:

$$p_c = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \quad (2-5)$$

The capillary pressure depends on the geometry of the interface at any particular instant in time, whether the interface is dynamically deforming or has arrived at a stable equilibrium shape. At equilibrium, the capillary pressure can be obtained by equation (2-4). Equations (2-4) and (2-5) provide useful descriptions of the capillary pressure from a microscale perspective. Equation (2-4) can be invoked and used as a definition of macroscale equilibrium capillary pressure; however, equation (2-5) is not appropriate for a macroscale definition because the definition is in terms of microscale interfacial properties. In porous medium flow, dynamics are usually assumed to be slow enough that the interface shape adjusts relatively rapidly to changes in pressure in the adjacent phase. Equation (2-4) is often considered to apply even for non-equilibrium systems. In general multiphase flow in porous media, the capillary pressure exhibits hysteretic behavior. An initial, small increase in capillary pressure may result in little or no change in the saturation because the capillary pressure must exceed a certain value, known as the entry pressure, to displace the wetting fluid. When the capillary pressure reaches the entry pressure, the nonwetting fluid will penetrate the porous medium, which is initially saturated by a wetting fluid. As the pressure difference is further increased,
the saturation will eventually decrease to the irreducible saturation (which can’t be reduced because the wetting fluid that remains is disconnected from the wetting fluid and thus is immobile). If, starting at this initial condition, the pressure difference in the porous medium is reduced, the wetting-phase saturation will increase to some maximum value, which cannot be increased further because the nonwetting phase is now trapped.

Relative permeability and capillary pressure are important parameters for quantifying multiphase flow in porous media. Determination of relative permeability and capillary pressure from experimental data has received a great deal of attention in the past. Relative permeability is usually determined from flow experiments performed on core samples. The most direct methods to measure relative permeability are steady-state methods (Honarpour and Mahmood, 1988). Steady-state methods include the Hassler, single-sample dynamic, stationary phase, Penn State, and modified Penn State methods (Honarpour et al., 1986; Rose, 1987). Each experimental run generates just one point on the relative permeability vs. saturation curve. The experiment has to be repeated at different flow-rate fraction to determine the entire curve, and the steady-state method is thus very time-consuming.

Relative permeabilities can be measured from displacement experiments, and this technique is referred to as the unsteady-state method. A core is initially saturated with a single-phase fluid, and this fluid is then displaced by injecting other phases into the core. Welge (1952) proposed a method to calculate the ratio of the relative permeability for the two-phase-flow case and Efros (1956) was the first to compute individual relative permeabilities from displacement experiments. Johnson et al. (1959) presented a calculation procedure in a more rigorous manner, and this method is usually referred to as the Johnson-Bossler-Naumann (JBN) method. The JBN method is based on the Buckley-Leverett theory of
multiphase flow in porous media (Buckley and Leverett, 1942). The main assumption in this theory is that capillary pressure can be neglected. To suppress capillary-pressure effects, they performed displacement experiments at high flow rates, and thus the relative permeabilities could not be determined for a substantial range of saturation. Helset et al. (1998) presented a method to interpret displacement experiments with capillary pressure included using in-situ measurements of saturation and phase pressure. The experiments can be performed at low flow rates and the relative permeabilities can be determined for all saturations.

In the past decade, relative permeability and capillary pressure properties have also been calculated by pore-scale modeling. Pore-scale modeling of porous media is used to describe the flow and transport processes on the scale of individual pores. One of the main purposes of pore-scale models is to predict macroscopic properties from the underlying microscopic structure and pore-scale physics. The macroscopic properties can be determined by averaging the pore-scale solution over a large volume. A number of pore-level models have been developed in the past and they vary with respect to dimensionality and details of the pore-level mechanisms used. Of these, network modeling is the most common technique for studying multiphase flow and transport in porous media. Network modeling, in which the pore space is represented as a lattice of connected sites, effectively includes the effects of interconnectivity and pore-scale heterogeneity. Its simplicity allows for the simulation of many thousands of pores, although this same simplicity has traditionally forced significant compromises in regard to the topologic description. In recent years, models have become more sophisticated and have been used to provide insight into a variety of different phenomena, such as relative permeability and capillary pressure hysteresis, the perturbative effects of viscous and buoyancy forces, the behavior of mixed-wet media, three phase flow, and so on (Blunt, 1997).
2.1.3 Miscible and Immiscible Fluid Displacement

In a miscible displacement process, a fluid is displaced in a porous medium by another fluid that is miscible with the first fluid. Miscible displacement in porous media plays a prominent role in many engineering and science fields, such as oil recovery in petroleum engineering, contamination of ground water by waste products disposed underground, movement of minerals in the soil, and recovery of spent liquors in pulping process. Miscible displacement in a heterogeneous medium can be severely affected by channeling, which refers to the bypassing of resident fluid by displacing fluid that preferentially passes through the channels in a heterogeneous porous medium. In oil recovery, profile modification techniques have been developed to suppress channeling of the displacing fluid by reduction of its mobility in channels during miscible displacement in heterogeneous media. Profile modification can be achieved using polymer floods, gel treatments, the flow of emulsions, and placement of foamed gels in the heterogeneous media (Willhite and Dominguez, 1977; Lake, 1989; Brown and Sorbie, 1989; Sorbie, 1991; Mennella et al., 1998; Zaitoun et al., 1998; McCool et al, 1991; Liang et al., 1992, 1995, 1997; Thompson and Kwon, 1998; Nisson et al, 1998; Hofinan et al., 1991; Miller and Fogler, 1995). In pulping process, the formation of a macroscopic precipitate, which is from the reaction between an anionic polymer in the resident phase and a cationic polymer in the displacing phase, has been exploited to suppress channeling and improve the performance of miscible displacement in a heterogeneous porous medium (Li and Pelton, 1992; De et al., 1997, 1998; Lappen et al., 1997).

In miscible displacement there is no capillary effect, but there is dispersive mixing between the two fluids, which can play an analogous role. Under certain conditions, the effect of dispersion is slight as compared with the advance rate of the displacing fluid even at
relatively low flow rates. Under these conditions, there is a sharp front between the displacing and the displaced fluids.

An immiscible displacement is a transient process where one fluid displaces another fluid from a porous medium with no mixing at the interface. In the petroleum industry, there are two basic terms to describe immiscible displacement: drainage and imbibition. The two processes occur by different mechanisms and usually result in completely different pressure and saturation profiles. These differences occur because, in a confined geometry, the contact angles cause a curvature of the fluid interface and thus a capillary pressure difference between the two phases; the direction and magnitude of this pressure difference depends on the interface geometry. In the event that the wetting fluid invades, the capillary pressure difference creates a driving force such that the invading fluid spontaneously imbibes until it is balanced by hydrostatic pressure. For drainage, the pressure at an invading interface must rise above the pressure in the adjacent displaced fluid by an amount that allows the interface to deform to the curvature of the local pore.

Dynamic saturation during a displacement process, and/or the final average saturation that is left behind after displacement, are important parameters. Saturation is an important parameter in many processes, either directly or because of its effect on other quantities. Saturation is affected by how uniformly a displacement front moves through the medium and the amount of displaced fluid that becomes trapped behind the front. The displacement pattern depends on the morphology of the medium, mobility ratio, wettability, and the balance between capillary and viscous forces. For any one medium and a specific fluid pair, the capillary and viscous forces alone dictate the displacement. These can be combined into the dimensionless capillary number:
\[ N_{Ca} = \frac{u \mu}{\sigma} \]  

The capillary number is essentially the ratio of viscous to capillary forces and has been successful in qualitatively characterizing displacement patterns, especially drainage. During a drainage process, the macroscopic advance of the displacement front occurs by a series of pore-level invasions, each of which occurs when the local capillary pressure overcomes the forces needed to deform the interface into a pore. Hence, at low capillary numbers, a single-pore invasion occurs only when the applied inlet pressure is sufficient. At low capillary numbers, local hydrodynamics do not affect invasion, and this mechanism creates a tortuous path known as capillary fingering that is defined by the local pore morphology. In contrast, the viscous forces present in high-capillary-number displacements are capable of creating significant capillary pressure differences behind the front. Hence, small pores can be invaded shortly after the front has passed. The macroscopic pattern approaches plug flow for high capillary numbers because all pores are invaded within a small distance of the advancing front. Imbibition fronts advance very differently than drainage fronts for three reasons. First, pore-scale advances occur most quickly in small pores, where the capillary pressures are highest. Second, wetting fluid can be drawn through some pores without displacing the non-wetting fluid because of flow in crevices and pendular rings. Finally, non-wetting fluid can become trapped behind the front by pore-scale snap-off mechanisms or by the splitting and rejoining of advancing fingers. This trapping phenomenon is particularly important because trapped non-wetting phase is hydraulically isolated and represents a zero-permeability fraction of the phase. Mobilization of these ganglia occurs only under fairly large surface stress, and the only other mechanism by which the trapped phase can be transported is by dissolution into the wetting phase (Thompson and Fogler, 1997).
When two immiscible fluids are injected simultaneously through a porous medium, they tend to flow in separate channels and maintain their identities, however, for two miscible fluids no such phenomenon is observed. Displacement in the case of immiscible fluids is generally not complete, but a fluid can be displaced completely from a pore by another fluid that is miscible with it. Thus in the case of miscible displacement there is no residual saturation. In immiscible displacement process, neglecting capillarity results in the prediction of a sharp front between the displacing and the displaced fluids when the flow rate is relatively high. At low flow rates, the capillarity causes a smearing of the saturation profile. There are major differences between miscible and immiscible displacements. The most important is that saturation effects are involved in immiscible multiphase flow processes.

2.2 Viscous Instabilities of Flow in Porous Media

2.2.1 Viscous Fingering

The descriptions of miscible and immiscible displacements given above implicitly assumed equal viscosity between the displacing and the displaced fluids. If the viscosity of the displacing fluid is greater than that of the displaced fluid, the displacement will differ only slightly from the equal viscosity case (for relatively homogeneous domains). In the reverse case, however, instability may set in, resulting in viscous fingering.

Viscous fingering during flow in a porous medium is the result of displacing a more viscous fluid by a less viscous one. Instead of a stable, uniform displacement front, an uneven, fingered front occurs. These viscous fingers propagate rapidly, causing early breakthrough and poor sweep efficiency. Viscous fingering is usually caused by perturbations at the displacement front that then continue to grow because of the instability of the process. The severity of the fingering is determined by the mobility ratio of the fluids.
Viscous fingering in porous media is one that continues to receive attention in a wide variety of fields, including secondary and tertiary oil recovery, fixed bed regeneration in chemical processing, hydrology, and filtration, and the literature is diverse. We cannot provide an exhaustive review, and many important areas of research are omitted in our discussion. Hill (1952) firstly observed the phenomenon of viscous fingering, or uneven fluid displacement, in the solvent-flushing of packed beds and filters. Viscous fingering occurs under conditions in which the mobility (medium permeability / fluid viscosity) is larger upstream than downstream. Homsy (1987) provides an extensive review of the viscous fingering phenomenon. For immiscible displacement, interfacial tension can damp out fingers of smaller widths than a critical size, and the stability of advancing front depends on the mobility ratio, the Darcy velocity and the capillary number (Saffman and Taylor, 1958; Chouke et al., 1959). For miscible displacement, dispersion can smear fingers of smaller widths than a critical size, even though interfacial tension is absent from the displacement process. The stability depends on the mobility ratio, the Peclet number and time (Slobod and Thomas, 1963; Tan and Homsy, 1986). There have been significant advances in the understanding of viscous instabilities in homogeneous media. For viscous fingering in homogeneous media, there is an intrinsic scale of fingering set by the speed of the displacement, the viscosity ratio, and the level of dispersion. Dynamical processes such as tip splitting and shielding and their underlying physical mechanisms are now well understood from a conceptual perspective, and can be quantified in some cases.

In order to understand the basic mechanism of the viscous instability, the following simple arguments are made (Homsy, 1987). Consider a displacement in a porous medium with a constant permeability $K$. The flow typically involves the displacement of a fluid of viscosity
\( \mu_1 \) and density \( \rho_1 \) by a second of viscosity \( \mu_2 \) and density \( \rho_2 \). In miscible cases without reaction, only forces associated with viscosity and gravity are considered here. (If the viscosity gradient is due to differences in solute concentration, the molecular diffusion and mechanical dispersion of the solute must be also considered.) For simplicity, a one-dimensional flow can be written using Darcy’s law as \( \frac{dp}{dx} = -\frac{\mu u_c}{K} + \rho g \). Considering a sharp interface or zone where density, viscosity, and solute concentration all change rapidly, the pressure force on the displaced fluid as a result of a virtual displacement \( \Delta x \) of the interface from its simple convected location is \( \dot{p} = (p_2 - p_1) = [(\mu_1 - \mu_2)u_c/K + (\rho_2 - \rho_1)g]\Delta x \). If the net pressure \( \dot{p} \) is positive, any small displacement will be amplified, then viscous instability can be induced. Therefore, the unfavorable density and/or viscosity ratios and flow direction can conspire to render the displacement unstable.

### 2.2.2 Effect of Heterogeneity

Heterogeneity has long been recognized as an important factor affecting the flow of fluids in porous media. The term heterogeneity refers to situations in which variations in the microstructure of the porous media lead to corresponding variations in the macroscopic flow resistance, as expressed in the permeability. For instance, for a porous medium with uniform permeability except for a high permeability layer, there will be preferential flow in the high permeability streak and the heterogeneity will cause early breakthrough and reduced sweep efficiency. If the injected fluid has lower viscosity than the fluid initially in place, preferential flow in the high-permeability streak will be enhanced, and fingers may form in both the high- and low-permeability zones. Brock and Orr (1991) performed flow visualization experiments and numerical simulations to investigate the effects of viscous fingering and permeability...
heterogeneity in three types of heterogeneous media, the two-layer and streak models with permeability correlation lengths equal to the flow length and the checkered model with a correlation length equal to 1/8 of the flow length. In the two-layer and checkered models, the flow was determined largely by the permeability field, with some viscous fingering superimposed. Instead, the flow in the streak model was dominated by the permeability distribution, and the spreading and splitting of viscous fingering was suppressed by the permeability contrast at the edges of high permeability layer. The fingering patterns developed along the same streamline followed during flow at unit mobility ratio. The fingering patterns were dictated not only by the permeability contrast, but also by the permeability distribution.

Heterogeneity interferes with both the onset and the development of the instability, while most studies have focused on the effect of permeability heterogeneity on the fully developed instability. Waggoner et al (1992) classified fully developed patterns in three regimes, viscous fingering, dispersion, and channeling, depending on the values of mobility ratio, the variance and correlation length of the heterogeneity. According to this classification, viscous fingering is the unstable regime when the variance and the correlation length of heterogeneity are small. Araktingi and Orr (1993) studied viscous fingering in heterogeneous porous media and presented analogous ideas. In these studies, numerical simulations were used and heterogeneity was modeled as a stationary spatially correlated random field. The interplay between heterogeneity and fully developed viscous instability has also been addressed analytically (Welty and Gelhar, 1991; Lenormand and Wang, 1995).

A number of previous studies have considered the effect of heterogeneity on the stability of displacement front. De Wit and Homsy (1997) provided a stability analysis of miscible displacement in periodic heterogeneous porous media. They presented an argument that
unstable wavelengths are amplified when the wavelengths are in resonance with the heterogeneity, the effect being larger at higher mobility ratio and when the heterogeneity is transverse to the direction of displacement in a layered system. The fingering regime of layered systems can be completely disrupted by modest levels of heterogeneity, leading to a channeling regime. However, in the checkerboard cases, the channeling regime can in turn be disrupted by the axial dependence of the heterogeneity, which stimulates tip splitting and a return to complex nonlinear finger dynamics. Shariati and Yortsos (2001) studied the stability of miscible displacements across stratified porous media, where the heterogeneity was along the direction of displacement. They found that heterogeneity enhances or reduces the instability depending on whether permeability increases or decreases in the direction of displacement. For a fluid with a non-monotonic viscosity profile, the flow becomes unstable if the permeability increase in the direction of displacement is sufficiently large even though the end-point viscosity ratio is smaller than unity. Conversely, a sufficiently large permeability decrease in the direction of displacement can stabilize the displacement. Chen and Neuman (1996) studied numerically the stability of immiscible displacements in porous media where the displacement is in a direction perpendicular to the layers, and investigated the linear evolution of instabilities of a wetting front.

2.2.3 Effect of Chemical Reaction

The effects of reaction on viscous instabilities have been examined in relation to various application areas, including chromatographic separation (Dickson et al., 1997; Shalliker et al., 1999), fixed bed regeneration fluid (Tan and Homsy, 1988; Zimmerman and Homsy, 1991), reactions at boundaries and interfaces (Carey et al., 1996; Vasquez, 1997, Eckert and Grahn, 1999; Bockmann and Muller, 2000), and reactive infiltration (Chadham et al. 1988; Chadham
et al., 1991; Xin et al., 1993; Crompton and Grindrod, 1996; Renard et al., 1998; De Wit and Homsy, 1999a, b). In chromatography, the viscosity of the solution being separated is a function of concentration and hence of the degree of adsorption of different components of the mixture. Experimental and simulation results have shown that preferential adsorption of the more viscous components leads to a viscous instability, and therefore long tails in the elution profiles (Dickson et al., 1997; Shalliker et al., 1999). In most fixed bed regeneration cases, the chemistry is considered slow relative to any physical processes, leading to a class of problems in which all physical properties are sharply divided regions of the fluid (Tan and Homsy, 1988; Zimmerman and Homsy, 1992).

Most research work on reactions at boundaries and interfaces has focused on the onset of buoyancy driven instabilities of the Rayleigh-Benard-type. The chemical reaction provides the source of the density gradient, leading to bounded convection rolls and a weak distortion of the interface, rather than the large scale fingering patterns (Carey et al., 1996; Vasquez, 1997, Ewckert and Grahn, 1999). Bockmann and Muller (2000) studied the density-driven instability of an autocatalytic reaction front in a narrow cell, and showed that the system instability depends on wave number.

In reactive infiltration, the injected fluids react with the solid matrix material, leading to chemical dissolution and an increase in porosity. The dissolution of porous media leads to an increase in the mobility of the fluid in those regions. The resulting convection of reactant through these higher mobility regions results in further dissolution and positive feedback, leading to viscous instability. Linear and nonlinear analyses have been performed to provide an understanding of the coupling between the viscously and reaction driven instabilities (Chadham et al. 1988; Crompton and Grindrod, 1996). Chadham et al. (1991), Xin et al.
(1993) and Renard et al. (1998) discussed the infiltration of water into a porous material under conditions where solubilization can affect the material’s porosity as well as the fluid viscosity. They showed the existence of unstable regimes caused by fingering as well as stabilizing phenomena associated with the diffusion of dissolved solute into the fingers. De Wit and Homsy (1999a, b) showed unusual behavior (e.g., droplets breaking from the tips of viscous fingers) in the presence of certain types of chemical reaction. They explained the phenomenon mechanistically in terms of the source of vorticity in the flows.

Nagatsu and Ueda (2001) performed viscous fingering experiments, showing differences in behavior based on the location of the reaction zone (inside or outside of the displacing fingers). De Wit (2001) analyzed the effects of reactions on the hydrodynamical fingering instability for miscible systems and found that the stability towards density fingering of chemical interfaces crucially depends upon the width and the speed of the front.

The effects of chemical reactions are more difficult to generalize, because of the variety of physical-property changes that they can induce. The most commonly studied effects are associated with small density and viscosity changes, for instance those arising from dissolution, precipitation, autocatalytic reactions, etc. (Carey and Morris, 1996; Eckert and Grahn, 1999; Bockmann and Muller, 2000; De Wit, 2001; Chadam et al., 1991). More dramatic effects can be observed in reactive flows that produce large changes in fluid or material properties. De Wit and Homsy (1999) examined the general problem in which fluid viscosity is a function of reactant/product species, showing that reactive coupling can lead to unique behavior such as the detachment (followed by propagation) of finger tips. Dissolution can lead to substantial changes in mobility ratio via the permeability term rather than
viscosity. In particular, for completely soluble media, wormholes form, which are of interest in carbonate acidizing (Daccord, 1987; Hoefner and Fogler, 1988; Nilson, 1990).

Both heterogeneity and chemical reactions can provide additional coupling that affects fingering behavior, and this interaction has been the subject of more recent research. Results show that heterogeneity can dictate the location for finger growth (Tan and Homsy, 1992) and can promote instability by introducing vorticity earlier in a displacement sequence than would occur in homogeneous media (Chen and Meiburg 1998). The coupling is particularly strong for stratified heterogeneities because of the possibility for resonance between the natural fingering wavelength and the scale of the stratification (De Wit and Homsy, 1997).

2.3 Flows of Reactive Polymers through Porous Materials

Reactive polymer flows through porous materials are of interest to engineers because of practical applications such as polymer-gel treatment in oil recovery, hydraulic fracturing of oil wells, frontal polymerization in porous medium reactors, the manufacture of composite materials, and certain types of polymer processing. In polymer-gel treatments, a polymer solution with crosslinker is injected into high permeability areas in the reservoir, and gels that are formed in situ plug higher permeability zones and divert the injected fluids to less permeable zones where oil is trapped, resulting in increased oil recovery (Gao et al., 1993; Dawe and Zhang, 1994; Liang et al., 1992, 1995, 1997; Thompson and Fogler, 1997; Seright et al., 1998; Thompson and Kwon, 1998; Hild and Wackowski, 1999; Raje et al., 1999; El-Hadidi et al., 2000; McCool et al., 2000). Hydraulic fracturing is widely used to increase production from petroleum wells, and crosslinking polymers are used in this process (Economides and Nolte, 1989; Powell et al., 1999; Coveney et al., 2000; Romero et al., 2000). In frontal polymerization, the polymerization reaction converts monomers into polymer in a
localized reaction zone that propagates through a porous medium reactor (Pojman et al., 1998; Volpert et al., 1998). During the manufacture of certain composite materials, polymeric fluids are injected into porous medium and allowed to react in situ (Greenkorn, 1983; Svensson et al., 1998). Some thermoplastic polymers and resins are being used to impregnate softwood or dense fiber networks for fiber-reinforced composites (Kim et al., 1991; Kazi et al., 1997). How the reactive polymers move through the porous matrix is essential to these applications.

2.3.1 Viscous Instabilities of Reactive Polymer Flows in Porous Media

A number of previous studies have focused on reactive polymer flow through porous materials; however, viscous instabilities in polymerizing flows have not received much attention, although experiments have shown both destabilizing and stabilizing effects associated with reaction (Losure, 1994; Losure et al., 1996; Thompson and Kwon, 1998). These phenomena have been examined using both linear stability analysis (Satyadev et al., 2000) and numerical modeling (Thompson and Kwon, 1998).

Losure (1994) performed mold-filling experiments with a polymerizing mixture of resin in a rectangular fiber preform containing a random glass mat, and observed finger-like structures in miscible displacement of the reacting resin. Losure et al. (1996) studied the instabilities during reactive resin molding and showed that the scale of fingers would determine the mechanical, performance of the molded part. Large viscous instabilities could lead to significant defects in molded parts made from the preforms.

Thompson and Kwon (1998) performed experiments in a visual flow cell and performed numerical simulations to study fundamental changes in viscous fingering due to polymer-crosslinker reactions. They showed the existence of unstable regimes caused by fingering as well as stabilizing phenomena associated with the crosslinking reaction. In the numerical
simulations, three regimes were observed (depending on reaction rate): viscous fingering at slow reaction rates, a stabilized regime at moderate reaction rates, and reactive fingering at high reaction rates.

Satyadev et al. (2000) studied instabilities during the impregnation of fibrous performs by reactive resins (for the fabrication of composite materials). They show that the changes in fluid viscosity caused by the reaction can induce a flow instability, but can also stabilize the front, depending on the coupling of flow and reaction dynamics. They define stable and unstable flow regimes and explain how the competition in reaction rates across a disturbance dictates whether the reaction will stabilize the disturbance. Numerous other investigations illustrate the detrimental effects of nonuniform impregnation during materials processing (Batch et al., 1996; Bickerton and Advani, 1997; Binetruy et al., 1998; Chawla et al., 1998; Einset, 1996; Mahale et al., 1992; Rice et al., 1994; Scheu et al., 2001; Patel et al., 1995).

Volper et al. (1998) studied reactive polymer flows in the context of frontal polymerization. The focus was on planar reaction fronts that have no instabilities associated with mobility ratio or heterogeneity. However, using a linear stability analysis, they defined conditions under which flow and reaction coupling leads to temporal flow instabilities, which can cause a reaction front to be displaced from reactor. In frontal polymerization, the polymerization converts monomers into polymer in a localized reaction zone that propagates. Viscosity and/or density gradients in the reaction zone may lead to viscous fingering that affect the front shape and velocity (Pojman et al., 1998).

In the area of pulp processing, Li and Pelton (1992) suggested the use of precipitation polymer reaction to suppress channeling in a heterogeneous packed bed. It is thought that the stabilizing effects observed under these conditions arise from better mixing of reactants in the
central high-permeability zones (caused by increased rates of transport due to dispersion, concentration gradients, and/or pressure gradients) (De et al., 1997; De et al., 1998; Lappan et al., 1997).

Lindner et al. (2000) investigated viscous instabilities for a polymer gel and a foam in a rectangular Hele-Shaw cell. The results for the gel showed a yield-stress-dominated fingering regime where very branched fingers formed at low velocities, and a viscous regime where only a single stable finger was observed at high velocities. For the foam, however, no such crossover was observed due to the absence of an apparent yield stress (because the foam slips at the wall).

While the studies mentioned above address transport and reaction at the continuum scale, microscale structure can have important effects. Examples that share dynamic similarities with the proposed work include the formation of nonuniform nutrient fronts during the growth of bacteria and biopolymers (Dillon and Fauci, 2000) (which in turn causes heterogeneous growth patterns) and the nonuniform propagation of combustion fronts due to microscale heterogeneity (Varma et al., 2001).

Additionally, a number of previous investigations, which are reviewed in next section, have examined how crosslinked polymers affect permeability and relative permeability in the oilfield. However, these latter efforts have focused on steady-state multiphase flow rather than transient flows and reaction dynamics.

2.3.2 Oilfield Polymer-Gel Treatments

A potentially important application of reactive polymer flow in porous media is fluid diversion treatments using polymer gels in oil recovery. Polymer-gel treatments can be an effective method to alter permeability and improve production. The goal of polymer-gel
treatments is to plug higher-permeability zones and divert drive water to the less permeable zones of the reservoir. The polymer-gel treatment technique can control water productivity and enhance oil recovery.

2.3.2.1 Controlling Water in Producing Operations

A common problem in the oil field is that water bypasses lower permeability zones containing mobile oil when it is injected into heterogeneous and fractured formations. This bypassing seriously reduces oil recovery and causes early water breakthrough at oil production wells. Excess water production increases the produced fluid head in the wellbore and creates extra backpressure on the formation.

In the United States, each year more than 20 billion barrels of water are produced in the oilfield operations (Seight et al., 1998). Hence, tremendous economic pressure exists to reduce water production without significantly decreasing hydrocarbon production. Reduced water production can result in enhanced oil recovery efficiency in addition to lower oil-production costs. A significant reduction of water production also positively impacts the environment. However, reducing high water production while maintaining or even enhancing oil recovery is a major technical challenge.

A proposed method to reduce water production is with profile modification or fluid diversion technology using polymers and gels. Some gels can selectively block fractures and high-permeability zones. Some polymer gels also reduce the water effective permeability significantly more than the oil permeability (at least in the laboratory) (Seright et al., 1998; Liang et al., 1992, 1995, 1997; Needham et al., 1974; Avery and Wells, 1998; Sandiford and Graham, 1973; Scheider and Owens, 1982; Sparlin, 1976; White et al., 1973; Zaitourn and Kohler, 1991, 1998; Seright, 1995, 1996; Dawe and Zhang, 1994; Seright and Martin 1992;
Zaitoun et al., 1998; Mennelia et al., 1998; Nilsson et al., 1998; Zheng et al., 1998; Barreau et al., 1997). We use the terminology of Liang et al. (1992, 1995), disproportionate permeability reduction (DPR), to describe this selectivity phenomenon. This unique property is the basis for using polymer gels as water control agents in production wells (especially when a gel treatment is performed in the near-wellbore region of production wells without zone isolation, to protect the oil-bearing zones).

2.3.2.2 Reduction of Water and Oil Permeabilities Using Gels

Results from the literature have shown that many polymers and gels exhibit disproportionate permeability reduction under certain conditions. Many researchers examined the possible mechanisms for this disproportionate permeability reduction. Although the mechanisms for this phenomenon are not yet fully understood, many interesting leads have been generated. Several physical processes have been proposed to explain the selective action of the polymers and gels. The possible explanations for DPR included lubrication effects, gravity effects, wettability effects, gel swelling and shrinking, pathway segregation, oil and water passing through the gel by different mechanisms, a balance between capillary forces and gel elasticity, wall effects, or a gel-droplet model, among others. Despite the large amount of research on DPR gels, their effectiveness is questioned by many producers and researchers, and there is hesitation to implement the techniques because the loss of absolute permeability and/or increase in water saturation may damage the oil-phase permeability of treated zones.

A review of disproportionate permeability reduction is provided in this section because the current model can be applied to oilfield applications to understand how gelation and/or polymer reaction affect production. Liang et al. (1992) performed core-flood experiments to test whether the DPR was sensitive to core orientation and flow direction and found that
Gravity effects are unlikely to provide a valid explanation for DPR. They used two oils with different viscosities to investigate the lubrication effect in a strongly water-wet core and suggested that the DPR is not caused by lubrication effect. Zaitoun and Kohler (1998) found that hydrophilic polymer adsorbed on the pore wall may enhance the water wettability of rock and thus modify the relative permeability. Seright et al. (1998) recently conducted oil/water experiments in a strongly oil-wet core to study the wettability effect. However, the wettability effects on DPR remain in question. In the past, researchers commonly thought that DPR was caused by gel swelling in the presence of water and shrinking in the presence of oil because of gel affinity towards water and repulsion to oil. Liang et al. (1992, 1995) demonstrated that gel shrinking and swelling effects are not responsible for the DPR because gel hydration water has no affinity towards oil and thus cannot be expelled by osmotic force. Zaitoun et al. (1991, 1998) studied DPR using a nonionic polyacrylamide (HPAM) polymer and proposed a wall effect mechanism. However, the results reported by Seright et al. (1995, 1996, 1997) that water-based gel reduced the permeability to water much more than that to oil in an oil-wet core do not support this theory because no water-wet surfaces were available for oil-wet polymer to anchor. Also, the wall-effect model could not explain the DPR from oil-based gel in strongly water-wet cores. Using micromodel experiments, Dawe and Zhang (1994) showed that the injected oil flowed into the center of the pore channels and the oil droplets broke the gel lenses during flow. After viewing these results, Seright et al. (1998) questioned whether the balance between capillary forces and gel elasticity might contribute to the DPR. The findings of Liang et al. (1997) in a small glass conduit support this theory. However, a similar experiment in a Berea sandstone does not support this capillary-elastic-force balance theory.
The most probable theory is that put forth by Liang et al. (1992, 1995, 1997) among others, which suggests the DPR is associated with the different flow pathways for the two liquid phases. On a microscopic scale, aqueous gellants follow water pathways more than oil pathways because of their hydrophilic character. If water-based gellants follow the water pathways, most of the water pathways would be blocked by gels while the oil pathways could remain open after gelation. Therefore, water-based gels can reduce permeability to water more than to oil. Using the same logic, if oil-based gelants follow primarily the oil pathways, most of the oil pathways would be blocked by gels while the water pathways could still be open after gel treatment. Their previous work showed that water-based gel reduced permeability to water much more than that to oil, and oil-based gel reduced permeability to oil much more than to water. If this theory is correct, DPR should be enhanced by simultaneously injecting water with oil-based gelant or oil with water-based gelant. Further studies (Liang, et al., 1997) showed that simultaneous injection of water with oil-based gel enhanced the DPR; however, the simultaneous injection of oil with water-based gel did not enhance the DPR.

The main reason that good laboratory results are viewed skeptically is that changes in reservoir saturation could easily negate any added benefit of DPR. Nilsson et al. (1998) suggested that the water/oil ratio used by Seright et al. is too high to change the water saturation, which is still close to end point saturation in his experiments. They argued for the segregated pathway mechanism but stated that the fractional flow must be chosen to significantly change the saturation in the core during placement. Zaitoun et al. (1998) maintained that segregated water-oil pathways may be important at intermediate fractional flow values. The weakness of this theory to explain the DPR lies on the fact DPR occurs not only at intermediate fractional flow values, but at end points. At the end-point situations, the
gelant will sweep away the fluids including oil, and gel can form in channels where oil otherwise would flow. Even if segregated fluid pathways exists, the gel should also block the natural oil pathways. Thompson and Fogler (1997) also argued for segregated pathways. However, they suggested that gels could change the medium’s morphology, and the pathways where oil would flow might be disrupted if the water fractional flow after a gel treatment is nonzero. The redistribution of fluids will reduce oil permeability. Also, they suggested that the gel could reduce the connectivity of the medium and cause a large percentage of isolated or dead-end ganglia in the oil phase. In short, the mechanisms by which fluid distribution and multiphase flow are affected by gels are still unclear.

2.3.2.3 Influence of Polymer Gels on Capillary Pressure

Most studies have focused on relative permeability modification but a few studies have considered the effect of polymers and gels on the capillary pressure (Barrufet and Ali, 1994). Barreau et al. (1997) performed unsteady-state core experiments at low flow rate to measure the capillary pressure after injection of water-soluble polymer. They measured directly the capillary pressure along the core using semipermeable membranes at pressure taps. For the water-wet core, the capillary pressure remained positive but increased dramatically after polymer adsorption. For the oil-wet core, the capillary pressure curve moved from negative to positive values. They concluded that polymer has little effect on the interfacial tension and the capillary pressure variation was attributed to the reduction of pore and throat size and the changes in core wettability after polymer adsorption. Zaitoun et al. (1998) studied two-phase flow modification by polymer adsorption using core experiments. They obtained similar results concerning the adsorbed polymer effect on capillary pressure as Barreau’s. It is commonly thought that the capillary pressure will increase due to gel treatment, but no
experiments or modeling have been performed to investigate the effect of gels on capillary pressure to the author’s knowledge.

2.4 Reservoir Simulation

The understanding, prediction, and history matching of reservoir performance during production and optimization of oil recovery are based on reservoir simulations. In typical reservoir simulation models, the reservoirs are represented by a large number of gridblocks. Effective reservoir rock properties such as permeability, porosity, and fluid saturations must be known in these gridblocks. The assignment of representative values of these properties to the blocks is critically significant in reservoir simulation. Reservoir characterization is a process for quantitatively assigning reservoir properties, and recognizing geological information and uncertainties in spatial variability (Stone and Garder, 1961). Geostatistics provides the tools to integrate the available information in a unified and consistent framework and to generate multiple realizations that can account for the uncertainty and spatial variability of the key reservoir parameters. Geostatistics emerged with the work of Krige in the early 1950’s and was introduced to the petroleum industry in the 1970’s (Lake and Carrol, 1986). Important reservoir characteristics include the structural outline of reservoir formation, the petrophysical characteristics of reservoir matrix, and the fluid properties and saturations. All these parameters are functions of spatial position, and thus the reservoir characteristics should be represented by multivariate spatial variables. In reality, a multivariate spatial stochastic model is required to represent the reservoir characteristics. Omre and Tjelmeland (1996) gave a detailed description of the stochastic reservoir characterization approach. Damsleth et al. (1997) reviewed the use of geostatistics in reservoir characterization.
Two types of reservoir simulation for isothermal reservoirs are widely used in the petroleum industry: black oil simulators and compositional simulators. The black oil model characterizes the reservoir fluid simply by a pseudo-gas and a pseudo-oil component with a simple pressure-dependent solubility of gas in the oil phase. The black oil models are used to study recovery techniques in the reservoir for which the fluid properties can be considered as a function of pressure and saturation. For some processes where the fluid properties are also dependent on composition, a compositional model which characterizes the reservoir fluid with more than two hydrocarbon components is required. The major difficulty in compositional simulators is how to efficiently predict the PVT behavior of the reservoir fluid, which is typically a complex hydrocarbon mixture. Malachowski et al. (1990) presented a compositional reservoir model, in which they used the Redlich-Kwong equation of state, and particularly discussed vectorization of the phase equilibrium and fluid properties. Other similar generalized compositional procedures have also been presented by Young et al. (1983), and Wang and Stenby (1994). Coat et al. (1998) developed a numerical model, which incorporated black oil and compositional capabilities and used an implicit pressure, explicit saturation/concentration (IMPES) method, for simulating three-dimensional, three-phase flow in heterogeneous, single-porosity reservoirs. IMPES is an implicit pressure, explicit saturation method independently conceived by Stone et al. (1961). Their method has been widely used in black oil simulation.

Streamline methods have been developed as a valuable alternative to traditional finite difference methods for large, heterogeneous, multiphase simulations (Peddibhotla et al., 1997; Thiele et al., 1997). The key feature of streamline simulators is that fluid transport occurs on a streamline grid rather than between the discrete gridblocks. Since the early works of Muskat
(1934, 1948) and Higgins et al. (1962), many streamline and streamtube simulators have been
developed to model convective displacements in heterogeneous media. This method has
allowed for solution of fine-scale models on the order of $10^6$ gridblocks, thus reducing the
need for significant scale up. The streamline method is appropriate for large, heterogeneous,
multiwell reservoir flow problems that are convectively dominated, and thus is suitable for
only a limited number of reservoirs (Thiele et al., 1997).

Reservoir and flow simulations using too-coarsely-scaled models are not representative,
while simulations using fined-scaled models are quite costly computationally. In practice,
multiphase fluid-flow reservoir simulations are limited to large-scale gridblocks because of
prohibitive computational costs of very fine-scale grid simulations, despite great
developments in computational speed. With currently available computers, most oil
companies cannot afford reservoir simulations using more than $10^5$ gridblocks. Therefore, the
average gridblock size used to simulate reservoirs is on the order of 100m areally and about 1
to 10m vertically (Barker and Thibeau, 1997). Each coarse gridblock represents a rather large
part of a reservoir and thus is heterogeneous. Upscaling is needed to bridge the gap between a
fine-scale description and a coarse-gridblock simulation. Values for permeability, porosity,
and other flow functions on the coarse simulation grid are obtained from the results of core
experiments or empirical means, along with some proper upscaling.

2.5 Modeling Reactive Polymer Flows in Porous Media

Understanding reactive flows is difficult because of the complexity of the coupling that
occurs between transport, changes in fluid properties due to reaction, and heterogeneity in the
materials. Numerical modeling affords a number of advantages over experimental studies such
as the ability to analyze the concentrations of each chemical components, follow the evolution
of pressure contours over time, and quickly vary parameters such as injection rate, reaction rate, diffusion coefficient, and permeability distribution. The tradeoff, of course, is that many approximations are inherent to the models of flow, transport, and reaction.

2.5.1 Modeling Flow in Porous Media

The modeling of flow in porous media is required in a number of chemical engineering processes. A continuum representation of porous media is typically used in which the conservation equations are combined with the necessary constitutive equations for transport. The fluid properties and flow parameters are continuous functions of position and time and correspond to local volume averages. The continuum approach eliminates the necessity of knowing the detailed microscopic geometry, but can preclude fundamental analyses of certain problems.

The flow of two fluid phases (wetting and non-wetting) can be described by the continuity equation and Darcy’s equation for each fluid phase as:

\[
\frac{\partial (\phi \rho_a S_a)}{\partial t} = -\nabla \cdot (\rho_a u_a) \tag{2-7}
\]

\[
u_a = -\frac{k_{ra} K}{\mu_a} \cdot (\nabla p_a - \rho_a g) \tag{2-8}
\]

where \( \phi \) is porosity, the subscript \( a \) indicates the various phases in the system. Here we assume \( a \) takes the values \( w \) and \( nw \) (wetting and non-wetting). The relative permeabilities are strong functions of pore structure and saturation, and can also depend on saturation history, capillary number, and viscosity ratio (Marle, 1982; Jerauld and Salter 1990; Dullien, 1992; Muccino et al., 1998). The saturations of the fluid phases are related by \( \sum S_a = 1 \), and the
pressures of different fluid phases are related by the capillary pressure \( p_c (S_\alpha) = p_{nw} (S_\alpha) - p_w (S_\alpha) \).

2.5.2 Modeling of Reactive Transport in Porous Media

The modeling of reactive transport in porous media is challenging because of the dynamic coupling that can occur between flow, reaction, and pore structure. The general convection-dispersion-reaction equations for multicomponent systems can be written for each phase \( \alpha \) as

\[
\frac{\partial (\phi SC_i)}{\partial t} = -\nabla \cdot (u C_i) + \nabla \cdot (\phi D \nabla C_i) + \phi SR_i
\]  

(2-9)

where the subscript \( i \) denotes a solute species (or in our case a discrete range of polymer molecular weights). Normally, the partial differential equations for transport without the reaction term are solved by Eulerian methods, for example finite difference or finite element methods; a grid or mesh is constructed representing the spatial domain, and then concentrations are updated by stepping through time. Using block-centered finite difference schemes, one assumes that a property at the node is representative of the entire cell. In finite element modeling, one typically assigns nodal values of properties, assuming appropriate basic functions within the elements.

An accurate solution of Equation (2-9) requires that the reaction and transport terms be coupled at some level because they affect each other. Several methods have been proposed to solve the coupled set of equations. Conceptually, the most straightforward way is referred to as a global implicit method (Oran and Boris, 1987; Steel and Lasaga, 1994), in which one solves the governing equations including both reaction and transport terms simultaneously. The major drawback of this method is the computational requirement, especially for large multi-component systems.
Alternatively, operator-splitting techniques have been used to decouple the reaction and transport calculations. In the classic time-splitting approach (referred to as the sequential non-iterative approach (SNIA)), one advances time by sequentially updating the fluid transport and then the reaction terms (which use the newly transported concentrations) (Xu et al., 1999; Walter et al., 1994; Valocchi and Malmstead, 1992). This approach can be written as

\[
\frac{(C_i^* - C_i^n)}{t^{n+1} - t^n} = L(C_i)^n
\]

(2-10)

\[
\frac{(C_i^{n+1} - C_i^*)}{t^{n+1} - t^n} = R_i^{n+1}
\]

(2-11)

where \( L \) is the spatial operator. The sequential iteration approach (SIA), where iteration is performed between the reaction and transport calculations, has been suggested to reduce the operator splitting errors (Yeh and Tripathi, 1989). However, this approach can be numerically unstable (Engesgaard and Kipp, 1992) and adds greatly to the computational requirements.

2.6 Additional Mathematical Background

2.6.1 Method of Moments

In most polymeric fluids, polymer chain length is a distribution, which we denote by \( [P_i] \) \((i = 1, \infty)\), the molar concentration of species of length \( i \). The polymer chain length distribution can be described by moments \( \mu_j \) (Dotson et al., 1996)

\[
\mu_j = \sum_{i=1}^{\infty} i^j [P_i]
\]

(2-12)

Two useful indicators of the properties of the polymer are the weight- and number-average degree of polymerization denoted by \( ADP_w \) and \( ADP_n \).

\[
ADP_w = \frac{\mu_2}{\mu_1}, \quad ADP_n = \frac{\mu_1}{\mu_0}
\]

(2-13)
A single parameter commonly used to describe the breadth of the polymer chain length
distribution is the polydispersity $I_p$

$$I_p = \frac{ADP_w}{ADP_n}$$  \hspace{1cm} (2-14)

The molecular weight distribution $C_i = [P_i]m_i$ is an alternative expression of the
polymer’s composition. Molar masses are usually written with respect to the monomer’s
molecular weight (i.e. $m_i = im_m$). A departure from this approximation is due to chain ends
and branch points. Two common descriptors of the polymer MWD are the number- and
weight-average molecular weights, $M_n$ and $M_w$

$$M_n = \frac{\sum_{i=1}^\infty C_i}{\sum_{i=1}^\infty C_i / m_i}, \quad M_w = \frac{\sum_{i=1}^\infty m_i C_i}{\sum_{i=1}^\infty C_i}$$  \hspace{1cm} (2-15)

Therefore,

$$M_n = m_m ADP_n = m_m \frac{\mu_1}{\mu_0}, \quad M_w = m_m ADP_w = m_m \frac{\mu_2}{\mu_1}$$  \hspace{1cm} (2-16)

$$I_p = \frac{ADP_w}{ADP_n} = \frac{M_w}{M_n}$$  \hspace{1cm} (2-17)

The method of moments is a useful technique to account for polymer chain length or
molecular weight distribution. We assume that distributions that have a finite number of equal
lower moments are, for practical purposes, similar. Hence, in cases where we do not know a
distribution function explicitly, we can approximate the distribution by finding another known
function that has the same lower order moments. In practical applications, this approximation usually turns out to be remarkably good (Dotson et al., 1996; Kendall et al., 1994).

### 2.6.2 Residence Time Distribution and Holdback

The tracer-determined residence time distribution has been utilized in the analysis of many types of flow systems such as underground reservoirs, chemical reactors and biological systems. The external residence time distribution $E(t)$ was defined by Danckwerts (1953) as follows:

$$E(t)dt = \text{the fraction of molecules in the exit stream with residence time between } t \text{ and } t + dt.$$  

If a pulse of tracer injected in the inlet stream follows the same paths as the fluid, then $E(t)$ is calculated using the following expression by assuming that all of the injected tracer eventually reaches the outlet stream:

$$E(t) = \frac{C(t)}{\int_{0}^{\infty} C(t)dt}$$

(2-18)

where $C(t)$ is the concentration-time response measured in the outlet stream. For multiphase flow in porous materials, many systems have complex internal flow fields resulting from large-scale flow heterogeneities such as channeling and slow-moving flow regions.

In the literature, the terminology used to describe flow distributions is quite diverse, with the same words meaning different things depending on the context or the author. In our work, the terms stagnancy and bypassing denote a type of flow maldistribution in which preferential flow paths conduct a significant portion of fluid rapidly through the system, while the other portions travel quite slowly. Sluggish-flow zone is used to denote a flow zone that conducts fluid, but at a rate much slower than the mean. This phenomenon is also referred to as relative
**stagnancy.** Danckwerts (1953) defined the holdback $\chi$ as the fraction of the internal contents of age (since entering the vessel) greater than $\tau$.

$$\chi = \frac{1}{\tau} \int F(t) dt$$

(2-19)

where $\tau$ is the mean residence time ($\tau = V/Q = \int^\infty \tau E(t) dt$) and $F(t)$ is the outlet response of the system to a unit step change in tracer concentration ($F(t)$ is also called external cumulative residence time distribution). The holdback $\chi$ is a parameter to describe the extent of relative stagnancy in vessels with large-scale flow heterogeneities. Robinson and Tester (1986) showed that the holdback is the difference between the flow fraction of fluid of residence time less than $\tau$ and the volume fraction of the internal flow paths through which that fluid flows. Higher values of $\chi$ correspond to a greater tendency of fluid toward bypassing. The holdback $\chi$ can be explained as a parameter describing either relative stagnancy or bypassing since these are relative terms that refer to a single type of flow maldistribution. The residence time distribution curves are not unique for a given value of $\chi$, since no single-parameter model can describe an RTD exactly. They are simply tools for describing the general features of a system with a certain degree of bypassing. In reaction engineering, quantifying this effect is important because increased holdback increases the tendency of fluid to short-circuit, thereby lowering the conversion. This is similar to the effect caused by an increasing dispersion coefficient (or decreased Peclet number). The bypassing increases the tendency for unreacted reactant to be transmitted through the domain.

In our work, the holdback is used as a natural single parameter for estimating the relative stagnancy and bypassing of reactive polymer flow in porous materials. To compute its value, tracer particles are injected into the domain over the entire left side of the computational
domain at the beginning of a simulation. The total number of particles injected is usually 10,000 and the number of particles is distributed in each gridblock over the left side of domain according to the flux into those gridblocks at the beginning time. The particles follow the same paths as the injected polymer and/or crosslinker solution. Each particle moves in the $x$ and $y$ directions according to the instantaneous velocity and timestep of the model. The positions of tracer particles are updated during each timestep until they flow out of the domain. The residence time of each particle can be obtained when it reaches the exit of the system, from which the residence time distribution of the tracer particles can be established and the holdback can be calculated.
CHAPTER 3
MODEL FORMULATION

We are interested in understanding how polymer transport in porous media is affected by in-situ crosslinking reactions. Conceptually we address this problem by solving a system of equations given by (2-9), for $i=1,N$, where $N$ is the total number of solute species including crosslinker, all discrete ranges of polymer weights, and any other components that may be present in the flow. Because the molecular weight distribution changes over orders of magnitude, the number of molecular weight ranges required to accurately model the dynamics would make many real problems intractable. Hence, the approach presented below is to describe the current state of the fluid and its reaction using moments of the molecular weight distribution. The distribution is discretized into finite ranges only during the transport step in the algorithm.

In this formulation, we make the following assumptions. First, the polymer is a dilute, aqueous-phase solution (representing guar, for instance, which is used in hydraulic fracturing applications). Second, the molecular-weight distribution of polymer is a log-normal distribution. Third, we assume that the crosslinking reaction proceeds by a stepwise polymerization mechanism.

3.1 Governing Equations

3.1.1 Overall Conservation Equation

Assuming that all the chemical species are transported by the aqueous phase (wetting phase) only, the mass conservation equations can be written as

$$\frac{\partial(\phi \rho S_u C_i)}{\partial t} + \nabla \cdot (\phi \rho S_u \nabla C_i) - \nabla \cdot (\rho C_i u) + \phi \rho S_u R_i = \frac{\partial}{\partial t}[\rho_r (1-\phi) C_i]$$ (3-1)
where \( C_i \) is mass concentration of component \( i \) \((i = 1, 2, \ldots, N)\), and \( C_{ir} \) is the mass concentration of component \( i \) adsorbed on porous medium surface. The left-hand side describes the time rate of change of solute and adsorbed species respectively. The three terms on the right-hand side of the equation describe dispersion, convection, and reaction respectively.

### 3.1.2 Molecular Weight Distribution

Many types of polymer solutions can be described using a log-normal distribution of molecular weight (Biesenberger and Sebastian, 1983; Zabisky et al., 1992). In this work, we use the empirical form of the Wesslau distribution (Rodriguez, 1983), which defines a log-normal molecular-weight-fraction distribution, \( C(m) \), as

\[
C(m) = \frac{1}{\sqrt{\pi}} \frac{1}{m} \exp\left\{-\left[\left(\ln(m/m_0)\right)^2 / \gamma^2\right]\right\}
\]

(3-2)

with \( \gamma^2 = (\ln(I_p))^2 \), \( m_0 = [M_w \cdot M_n]^{-\frac{1}{2}} \), \( I_p = M_w / M_n \).

### 3.1.3 Gelation Reaction Kinetics

A simple polymer and crosslinker gelation model is used for the kinetics. Crosslinking of the polymer is described using the following uptake and crosslinking sequence, where \( P_n = \) polymer, and \( X = \) crosslinker:

\[
P_i + X \stackrel{k_1}{\rightarrow} P_i-X
\]

\[
P_{i-k}X + P_k \stackrel{k}{\rightarrow} P_{i-k}X-P_k \approx P_{i+k}
\]

Writing molar concentration balances on each component involved in the reactions we obtain the following set of coupled differential equations:
\[ \frac{d[X]}{dt} = -k_i [X] \sum_{i=1}^\infty [P_i] \]

\[ \frac{d[P_i]}{dt} = -k_i[X][P_i] + k_i \sum_{i=1}^{i-1} ([P_{i-k}][P_{k}X]) + k_i \sum_{k=1}^{i-1} ([P_{i-k}][P_kX]) - k_i[P_i] \sum_{k=1}^\infty [P_kX] \]

\[ \frac{d[P_iX]}{dt} = k_i[I][P_i] - k_i[P_iX] \sum_{k=1}^\infty [P_k] \]

(3-4)

We assume that \( \frac{d[P_iX]}{dt} = 0 \) and let \( \tau = \int_0^t k_i[X]dt \), which gives:

\[ \frac{d[X]}{d\tau} = -\sum_{k=1}^\infty [P_k] \]

\[ \frac{d[P_i]}{d\tau} = -2[P_i] + \frac{2}{\sum_{i=1}^{i-1} ([P_{i-k}][P_k])} \sum_{k=1}^{i-1} [P_k] \]

(3-5)

This set of differential equations cannot be solved analytically. However, applying the method of moments (Doston et al., 1996), one obtains:

\[ \frac{d\mu_0}{dt} = 0 \]

\[ \frac{d\mu_1}{dt} = 2k_i\mu_1[X] \]

\[ \frac{d\mu_2}{dt} = k_i[X](2\mu_2 + \frac{4\mu^2_1}{\mu_0}) \]

\[ \frac{d[X]}{dt} = -k_i[X]\mu_0 \]

(3-6)

Because we have used a simple model, factors such as termination, cyclization, and branching are not accounted for. However, other kinetic models, if more appropriate, can be substituted into the same numerical framework.
3.2 Constitutive and Auxiliary Equations

To solve the governing transport equations, some additional relationships are required such as capillary pressure, relative permeability, polymer intrinsic viscosity, adsorption coefficient, etc. Since the focus of the current work is modeling the dynamics of flow and reaction we have used generalized auxiliary equations, which can be changed for specific situations as information is available. The general equations are given below.

**Capillary pressure:**

\[ P_c = P_d \left( \frac{1}{S_r} \right)^\lambda \quad (P_c \geq P_d) \quad (3-7) \]

where \(P_d\) is the displacement pressure, \(S_r = \frac{S_w - S_e}{1 - S_r}\), \(S_e\) is the residual aqueous phase saturation, and \(\lambda\) is a pore size distribution index. Equation (3-7) is the Brooks-Corey capillary pressure curve (Brooks and Corey, 1964).

**Relative permeability:**

The relative permeabilities to the nonwetting and wetting phase are specified by Brooks and Corey (1964).

\[ k_{rmw} = (1 - S_e)^{(2 + \lambda / \lambda)} \]
\[ k_{rw} = S_e^{[(2 + \lambda / \lambda)]} \quad (3-8) \]

**Polymer intrinsic viscosity:**

\[ [\eta] = K' M_w^\beta \quad (3-9) \]

The relationship between the intrinsic viscosity and the molecular weight is given by the Mark-Houwink equation (Sorbie, 1991). Values of the coefficient, \(K'\), can vary by a
considerable amount but are typically in the range $3 \times 10^{-5}$-$700 \times 10^{-5}$, and the range of $\beta$ values is usually $[0.5, 1]$. These values give $[\eta]$ in units of cm$^3$/g.

*Polymer solution viscosity:*

The polymer solution viscosity $\mu_p$ is related to the intrinsic viscosity $[\eta]$ and the polymer concentration $C_p$ as follows:

$$\mu_p = \mu_s \left( C_p [\eta] + k_H [\eta]^2 C_p^2 - 1 \right)$$  \hspace{1cm} (3-10)

where $\mu_s$ is the solvent viscosity; $k_H$ is the Huggins constant, which typically has the value 0.3-0.5 (Rodriguez, 1983).

*Mixed viscosity:*

The mixed viscosity of the aqueous phase is calculated using a quarter-power mixing rule (Koval, 1963)

$$\mu_m = \frac{1}{\left( \frac{f_p}{\eta_p^{1/2}} + \frac{f_c}{\mu_c^{1/2}} \right)^2}$$  \hspace{1cm} (3-11)

where $f_p$ and $f_c$ are volume fraction of polymer solution and crosslinker.

*Mixed density:*

We assume volume conservation during mixing so that the aqueous phase mixed density is given as

$$\rho_m = f_p \rho_p + f_c \rho_c$$  \hspace{1cm} (3-12)

*Adsorption coefficient:*

$$C_{IV} = \frac{k_1 C_i}{1 + k_2 C_i}$$  \hspace{1cm} (3-13)

The adsorption for chemical components follows the Langmuir equation. Irreversible adsorption is assumed for polymer, crosslinker, and gel.
**Polymer velocity enhancement:**

Many observations have confirmed that polymer molecules are transported through the porous media faster than the inert species (Dawson and Lantz, 1972; Willhite and Dominguez, 1977). The physical causes of this phenomenon are inaccessible pore volume and/or surface exclusion. In this paper, the specific mechanism is not proposed, but the velocity enhancement can be incorporated in the model using

\[ \phi = f\phi_0 \]

(3-14)

where \( f \) is a function of the molecular weight of the polymer species (Sorbie, 1991). Pore-scale modeling will likely help to determine the functionality of Equation (3-14).

**3.3 Geostatistical Permeability Model**

The numerical solution is obtained for two-dimensional rectangular domains. Permeability maps are generated using a geostatistical model that allows one to specify average permeability and its standard deviation, as well as the correlation lengths in the \( x \) and \( y \) directions. A complete description permeability distribution in a 2D domain consists of an array containing permeabilities of every node point (cell or gridblock). It is needed for the reactive polymer flow simulator. The permeability map is initialized by the input parameters, which dictate the physical properties of the simulated domain. The input parameters are the mean permeability, the standard deviation, the number of nodes in each dimension, and the correlation lengths for permeability (set to zero for an uncorrelated permeability). In this computer-simulated domain, we include spatial correlation in permeability. This may be reasonable when nonrandom microscale heterogeneity exists from a depositional or a weathering process. For example, a layered structure may result from small-scale cross-bedding, or clusters may be associated with macropore or soil aggregates. The spatial
correlation is very important because the permeability and relative permeability depends strongly on pore structure. In this computer-simulated model, we assume that the permeability is correlated using Kriging, which is a statistical estimation technique (see the Appendix A for details of the Kriging technique used in this model).

In our geostatistical permeability model, we assign a few randomly selected locations with permeabilities from a normal distribution in the domain. Using the ordinary Kriging technique, permeabilities of the other cells in the domain are assigned from the known values. Each gridblock permeability is determined by 10 known permeabilities of the nodes that are nearest the estimated node. The advantages of this type of algorithm are the following: (1) It is numerically stable. (2) It works for arbitrary size distributions. (3) It is easy to include a spatial correlation in permeability.

3.4 Numerical Solution

The spatial domains generated using the geostatistical model are discretized into a number of finite difference gridblocks that remain fixed for the course of a simulation. Dependent variables in the numerical algorithm include pressure(s), fluid-phase saturations, gel saturation, and species concentrations (in the aqueous phase only in the current work). Although conceptually each polymer molecular weight is viewed as a different solute species, only the three moments of the molecular weight distribution are carried through the simulation for computational reasons. Concentrations of any other species (i.e., crosslinker and any other solute species or reactants present) are kept track of separately from the polymer weight distribution.
The transient solution is obtained by advancing the dependent variables in discrete
timesteps. In each timestep, the dependent variables and parameters are updated in the
following sequence:

1. Pressure field and fluid-phase saturations;
2. Species concentrations (due to solute transport);
3. Molecular weight distribution and gel-phase saturation (due to reaction);
4. Other dependent parameters.

The specific numerical procedures associated with each of these steps are given below:

### 3.4.1 Updating Pressure and Fluid-Phase Saturation

Substitution of Darcy’s law for multiphase flow into the continuity equation gives the
following equation in two dimensions:

\[
\frac{\partial}{\partial x} \left( \frac{K_{ra}}{\mu_a} \left( \frac{\partial p_a}{\partial x} - \rho_a g_x \right) \right) + \frac{\partial}{\partial y} \left( \frac{K_{ra}}{\mu_a} \left( \frac{\partial p_a}{\partial y} - \rho_a g_y \right) \right) = \phi \frac{\partial S_a}{\partial t} \tag{3-15}
\]

By writing equation (3-15) in finite difference form and using the auxiliary equations
\[S_w + S_{nw} = 1\] and \[p_c = p_{nw} - p_w,\] a set of coupled equations for pressure in each gridblock is obtained.

This system is solved using a Biconjugate gradient method (Van Der Vorst, 1992). Once
pressure is known, the wetting-phase saturation in each gridblock can be updated explicitly
using the finite-difference version of equation (3-15), which takes the form

\[
(S_w)_l^{n+1} = \frac{\Delta t}{\phi(\Delta x)^2} \left( K \frac{k_{rw}}{\mu_w} \right)^n \left( (p_w)_{l+1,j}^{n+1} - (p_w)_{l,j}^{n+1} - \rho_w g_x \right) + \frac{\Delta t}{\phi(\Delta y)^2} \left( K \frac{k_{rw}}{\mu_w} \right)^n \left( (p_w)_{l,j+1}^{n+1} - (p_w)_{l,j}^{n+1} - \rho_w g_y \right) + \frac{\Delta t}{\phi(\Delta y)^2} \left( K \frac{k_{rw}}{\mu_w} \right)^n \left( (p_w)_{l,j-1}^{n+1} - (p_w)_{l,j}^{n+1} - \rho_w g_y \right) \tag{3-16}
\]
Non-wetting phase saturation is updated using $S_{nw} = 1 - S_w$.

### 3.4.2 Transport of Mobile-Phase Polymer

For two-dimensions, the solute transport equation (for polymer components and crosslinker) can be written as

$$
\frac{\partial (\phi S_w C_i)}{\partial t} + \frac{\partial}{\partial x} \left( D\phi S_w \frac{\partial C_i}{\partial x} \right) + \frac{\partial}{\partial y} \left( D\phi S_w \frac{\partial C_i}{\partial y} \right) - u_x \frac{\partial C_i}{\partial x} - u_y \frac{\partial C_i}{\partial y} = 0
$$

(3-17)

Because the coefficients in this equation are applied to solute species rather than moments of the distribution, we must convert the moments into concentrations of polymer components. Numerically, the polymer is discretized into finite molecular weight fractions, each of which is treated as a different component. Convection and dispersion of these discrete fractions are modeled using an explicit finite-difference version of equation (3-17). The result is a new discretized distribution of species in each gridblock, which is transformed back into moments of a log-normal distribution.

Two numerical issues arise in this procedure. The first is that the log-normal equation (3-2) cannot be integrated analytically to calculate the concentration of each polymer fraction. This problem is addressed by using spline interpolation. An interpolation function is obtained that approximates the original distribution, and concentrations of polymer components are calculated by integrating the interpolated function. These concentrations, along with the concentration of crosslinker, are used as the initial conditions for the transport equation (3-17).

Second, the new distribution (after transport) does not necessarily conform to a log-normal distribution because of mixing. We approximate the new distribution by calculating the new moments, and then performing a minimization procedure to ensure that the mass of crosslinked polymer is conserved. This procedure is discussed more in section 4.3. The new
moments (which reflect polymer transport during the current timestep) are used as initial values in the subsequent reaction step.

### 3.4.3 Polymer Reaction

To model reaction, each gridblock is treated as a perfectly mixed batch reactor. The set of reaction equations (3-6) is solved once per gridblock per timestep using a fourth-order Runge-Kutta method. The initial conditions for equations (3-6) are the moments calculated at the end of the solute transport step. Completion of this reaction step changes the molecular weight distribution. This new distribution is used to determine the amount of gel (i.e., immobile crosslinked polymer) in each gridblock, and the saturation of the gel phase is changed accordingly (see below).

### 3.4.4 Updating Parameters

Since the transport and reaction steps are solved explicitly, parameters must be updated before beginning a new timestep. The most difficult issue to contend with is determining how in-situ crosslinking affects the morphology of the porous medium, specifically for cases where gel formation occurs. (The formation of gel has a dramatic impact on hydraulic conductivity (Liang, Sun, and Seright, 1992, 1995).)

From a mathematical standpoint (i.e., in the context of equation (3-1)), two options appear viable for quantifying morphologic changes caused by crosslinking. One option is to adjust the medium’s porosity to account for volume that has become inaccessible due to gel formation, and then to use an empirical equation to update permeability. The second option is to account for this inaccessibility in the phase-saturation terms. We choose the latter option, so that the value of porosity reflects the original porous medium only. This approach
introduces a third phase consisting of immobile polymer, and permeability changes are accounted for by Equation (3-8).

Calculation of the immobile-phase saturation is not straightforward because the volume of pore space to be occupied by newly formed gel cannot be directly inferred from the known parameters. Consider a low-concentration polymer in one gridblock versus a high-concentration polymer in another, both of which become fully crosslinked during a timestep. It is likely that both will cause significant loss of available porosity (and thus permeability), but at the same time it is known that polymer concentration has a significant effect on this process (Liang, Sun, and Seright, 1992, 1995). Because these issues will require more research (including experiments and a pore-scale analysis of the problem), a constant gel density is assumed so that the saturation change (mobile to immobile phase) in a gridblock is proportional to the mass of polymer that becomes crosslinked. All parameters such as mixed viscosity, mixed density, relative permeability etc., are based on the mobile polymer fraction. However, moments are calculated based on the total aqueous phase volume since both polymer and gel participate in the polymerization reaction.

Finally, an equally or more complicated issue is the relative permeability changes that accompany gelation. Relative permeability is very sensitive to pore-space morphology (Thompson and Fogler, 1997). Hence, one would expect the function $k_r(S)$ to change due to gelation. Again, because of the complexity of this problem and its dependence on pore-scale processes, no general constitutive equations are available. Hence, we assume a constant relative permeability function as given by equations (3-8) (It should be noted that because aqueous relative permeability is very strong function of phase saturation, the formation of gel
does induce drastic reductions in fluid conductivity, even with the relatively simplistic approach used here).

3.5 Numerical Example

An example is presented to demonstrate the model in a heterogeneous material. The simulation was performed on a domain of 50×50 gridblocks, the physical size of which is 3m×3m. The permeability map of the heterogeneous domain is shown in Figure 3.1. The highest and lowest permeabilities are 2.195 Darcy and 0.2556 Darcy respectively.

![Spatial map of the absolute permeability distribution.](image)

Initially the material is saturated with water. Polymer solution was injected at constant flow rate into this domain over the entire left side. Polymer 1 (\( M_w = 1.63 \times 10^6 \), \( I_{p1} = 1.43 \) with a concentration \( 2.5 \times 10^{-3} \) g/cm³) was injected until 1.0 pore volumes (PV) of fluid were
displaced. (The filtration of polymer is neglected here, although it can easily be accounted for in the same way as the velocity enhancement)

![Graph](image)

**Figure 3.2 Concentration distribution of polymer components at gridblock (10, 10) at various times.**

In this simulation, the first three moments of the polymer MWD, the total polymer concentration, and the concentration of crosslinker were monitored. The moments were converted into concentrations over 500 discrete ranges in the transport step. The simulation was run at a Damkohler number of 4.0 using an average timestep of 6.1s. The polymer concentration distributions in gridblocks (10,10) and (10,30) at different times are shown in Figures 3.2 and 3.3, respectively. Gridblock (10,30) is located in a high-permeability region (see Figure 3.1) while gridblock (10, 10) is in a low-permeability region.
By comparing Figures 3.2 and 3.3, it is noted that polymer in the high-permeability region has a higher concentration and is more polydisperse at early times. This is a transient effect. At long times, the polymer MWD in the lower-permeability region becomes much broader because of the longer residence times for fluids flowing here. The polydispersities of polymer in gridblocks (10,10) and (10,30) at different times are given in Table 3.1. In Figure 3.4, the polymer concentration distributions in gridblocks (10,10), (10,30), (30,10), and (30,30) at the same time ($t = 1226s = 1.0$ PV) are also shown.
Table 3.1. The polydispersities of polymer in gridblocks (10,10) and (10,30) at various times

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Gridblock (10,10)</th>
<th>Gridblock (10,30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>1.4593</td>
<td>1.5203</td>
</tr>
<tr>
<td>176</td>
<td>1.5924</td>
<td>1.7675</td>
</tr>
<tr>
<td>365</td>
<td>2.0873</td>
<td>2.0925</td>
</tr>
<tr>
<td>416</td>
<td>2.1527</td>
<td>2.1226</td>
</tr>
<tr>
<td>1038</td>
<td>3.1881</td>
<td>2.2972</td>
</tr>
<tr>
<td>1226</td>
<td>3.2621</td>
<td>2.3434</td>
</tr>
</tbody>
</table>

Figure 3.4 Concentration distribution of polymer components at time=1226s in different gridblocks.
CHAPTER 4

PARAMETER SENSITIVITY AND MODEL LIMITATIONS

To effectively model reactive polymer flow in porous media, it is important to understand the sensitivity of various parameters in the model. Of primary concern is what type of molecular weight distribution should be chosen to best represent the polymer because the form of the molecular weight distribution determines the range of application for the model. Additionally, the resolution for discretization of the distribution can affect accuracy. Mixing of fluids alters the shape of the distributions, and forcing these new distributions to conform to simple functions introduces error. Finally, timestep size affects accuracy in a way unique to this algorithm.

4.1 Form of the Molecular Weight Distribution

One of the most important limitations of this modeling technique is how well a given mathematical distribution can represent a true polymer weight distribution. This issue is especially significant if mixing of different compositions occurs so as to create distributions with anomalies such as multiple peaks. Four polymer molecular weight distributions frequently encountered in practice are Wesslau log-normal, Lansing log-normal, Poisson, and Most probable distributions (Biesenberger and Sebastian, 1983). In our work, we use a log-normal molecular weight distribution, which is the empirical form of the Wesslau distribution. This choice can easily be modified if a more appropriate polymer molecular weight distribution is available for a specific polymer.

In our model, we assume that the polymer MWD remains log-normal during the transport processes. This restriction imposes limitations on the amount of mixing that can occur from different regions in the porous media because the mixed distributions may not be log-normal.
As an extreme example, consider two distributions \( M_w = 1.63 \times 10^6, \ I_p = 1.43; \)
\[ M_w = 1.63 \times 10^7, \ I_p = 2.43 \] shown in Figure 4.1, which are mixed in volume fractions
\( f_1 = 0.2, \ f_2 = 0.8. \) The mixed distribution is shown in Figure 4.2. For comparison, the first
three moments of the true distribution were calculated and used in the log-normal distribution,
which is also shown in Figure 4.2. Clearly the mixed distribution cannot be described using a
log-normal equation, and if a practical case exhibits this type of mixing, additional
considerations will have to be made in the modeling approach.

![Figure 4.1 Two log-normal distributions.](image)

To partially investigate this mixing effect during flow, we have sequentially injected
different log-normal MWDs into heterogeneous domains. Some
of these domains were specifically designed to induce downstream mixing of two different distributions. These tests were run without reaction so that the distributions could remain in their discretized form and therefore conform to any possible MWD. For the scenarios tested, the mixed MWDs inside the domain conformed well to log-normal distributions. It is more difficult to assess how this effect will exhibit itself when reaction occurs, and this is a subject for future research.

![Figure 4.2 Distribution of the mixed log-normal distributions.](image)

**Figure 4.2 Distribution of the mixed log-normal distributions.**

### 4.2 Discretization of the Distribution

To model the transport step, it is necessary to discretize the polymer MWD, converting the moments into concentrations of polymer components. Each component represents a range of polymer molecular weights. A number of practical points must be considered regarding the
discretization. The number of components must be sufficient to represent the MWD adequately, but this number must not be impractically large from a computational standpoint. We must also choose a suitable upper mass cutoff for the discretized distribution. This upper limit is critical because the high-molecular-weight components in the tail have a large effect on the higher-order moments.

To determine how to best discretize the whole distribution, tests were performed to investigate the following four parameters: (1) number of fractions; (2) upper mass cutoff; (3) method of discretization; (4) method to calculate concentrations. In each test, we discretized various log-normal distributions using three known moments, and then recalculated the moments. The midpoint of each discrete range is taken to represent the entire fraction, and the properties of that fraction are calculated using this value of molecular weight. By comparing the new moments with the old ones, factors such as the required number of fractions, length of the tail, discretization method, and method to recalculate the moments were determined.

Table 4.1 Effect of the number of fractions on MWD discretization error

<table>
<thead>
<tr>
<th>#of fractions</th>
<th>Weight Average Molecular</th>
<th>Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_w^{cal}$</td>
<td>$I_p^{cal}$</td>
</tr>
<tr>
<td></td>
<td>$\left(\frac{</td>
<td>M_w^{cal} - M_w</td>
</tr>
<tr>
<td>50</td>
<td>1651758</td>
<td>1.477958</td>
</tr>
<tr>
<td>100</td>
<td>1631175</td>
<td>0.0721</td>
</tr>
<tr>
<td>200</td>
<td>1629934</td>
<td>0.00406</td>
</tr>
<tr>
<td>500</td>
<td>1629998</td>
<td>0.000113</td>
</tr>
<tr>
<td>1000</td>
<td>1629998</td>
<td>0.000119</td>
</tr>
<tr>
<td>2000</td>
<td>1629998</td>
<td>0.000119</td>
</tr>
</tbody>
</table>

Consider the log-normal distribution of Polymer 1 ($M_w = 1.63 \times 10^6$, $I_p = 1.43$). The upper mass cutoff for the discretized distribution is taken to be $20M_w (3.26 \times 10^7)$ (at the cutoff, the mass concentration is $7.7901 \times 10^{15}$ g/cm$^3$). The recalculated parameters using
different numbers of discretization fractions are given in Table 4.1, where $M_w^{\text{cal}}$ and $I_p^{\text{cal}}$ are the recalculated values, after discretization was performed. Clearly, it is desirable to use fewer discretizations from the standpoint of computational efficiency. The appropriate choice depends on the acceptable level of error relative to changes in the reaction step, as discussed in Section 4.4.

To find a suitable upper mass cutoff for the discretized distribution, several numerical experiments were performed using 500 fractions. Results are given in Table 4.2, from which 20M$_w$ was selected for our runs.

### Table 4.2 Effect of upper mass cutoff on MWD discretization error

<table>
<thead>
<tr>
<th>$M_{\text{cut}}$</th>
<th>$C(M_{\text{cut}})$</th>
<th>Weight Average Molecular Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M_w^{\text{cal}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$M_w^{\text{cal}} - M_w$</td>
</tr>
<tr>
<td>10M$_w$</td>
<td>3.738552×$10^{-12}$</td>
<td>1629711</td>
</tr>
<tr>
<td>20M$_w$</td>
<td>7.790111×$10^{-15}$</td>
<td>1629998</td>
</tr>
<tr>
<td>30M$_w$</td>
<td>1.129093×$10^{-16}$</td>
<td>1630000</td>
</tr>
<tr>
<td>50M$_w$</td>
<td>2.830950×$10^{-19}$</td>
<td>1629935</td>
</tr>
<tr>
<td>80M$_w$</td>
<td>6.013136×$10^{-22}$</td>
<td>1629883</td>
</tr>
</tbody>
</table>

A log discretization method was also tested (as opposed to equal size discretizations above) with 500 fractions and 20M$_w$ as the upper mass cutoff. However, this approach did not improve the numerical performance.

### Table 4.3 Comparison of trapezoid area approximation versus spline interpolation

<table>
<thead>
<tr>
<th>Method</th>
<th>Weight Average Molecular Polydispersity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_w^{\text{cal}}$</td>
</tr>
<tr>
<td></td>
<td>$M_w^{\text{cal}} - M_w$</td>
</tr>
<tr>
<td>Spline Interpolation</td>
<td>1629999</td>
</tr>
<tr>
<td>Trapezoid Approximation</td>
<td>1630081</td>
</tr>
</tbody>
</table>

The discretization process itself can be a source of error. Each discrete concentration is the product of the total polymer concentration and the fraction of the total area (under the
curve) found in that range. Since the log-normal Equation (3-2) cannot be integrated analytically, an approximation must be used. A simple trapezoid rule produced significant error. Hence, a spline is fit to the log-normal distribution. The polynomial approximating function is then integrated to determine the mass concentrations in each range. Table 4.3 shows the comparison between the trapezoid and spline interpolation approaches.

4.3 Mobile Polymer Transport

During the species transport step, only the mobile fraction of the molecular weight distribution is allowed to flow, while the highest-molecular-weight species are considered to be part of the gel phase. For this reason, in addition to changes in the MWD due to mixing, the post transport distribution often has a small discontinuity at the cutoff weight for the mobile-phase.

This behavior causes a number of problems. First, the new distribution is usually not log-normal. Hence, a simple recalculation of the moments from the discretized molecular weights will compromise the shape of the true distribution. Second, parameters calculated from the new log-normal distribution will contain errors associated with this compromised shape. Of these parameters, the mass of immobile phase polymer is of most concern because of its strong effect on the overall transport process. Clearly, the mass of immobile phase polymer should remain constant during the transport calculations of a timestep. However, the use of the compromised distribution usually causes an apparent increase in the mass of immobile polymer. Figure 4.3 shows an example for a representative gridblock undergoing transport. It contains the pre-transport distribution, the post-transport distribution, and the log-normal distribution calculated directly from the discretized distribution. In this example, the apparent change in the mass of immobile phase due to this approximation was 67.7%.
Figure 4.3 The pre- and post-transport concentration distributions and the log-normal distribution using moments of the post-transport curve.

We have investigated a number of techniques for minimizing this conversion error. The approach that appears to be most effective is to calculate new moments from the discretized distribution as initial values, and then to perform an optimization procedure to search for an optimal log-normal distribution to best approximate the new distribution after transport. This optimization minimizes the least-squares error in the difference between true post-transport concentrations (i.e., discretized concentrations) and the concentrations found from the log-normal equation. The optimization is performed using a variable metric method (BFGS scheme) to find an optimal log-normal distribution. Figure 4.4 shows the results of this optimization.
Figure 4.4 The post transport concentration distribution and the optimized log-normal distribution.

4.4 Timestep Size

Timestep size plays a unique role in this model because of differing effects in the transport versus reaction parts of the algorithm. If the timestep is large, the normal truncation errors associated with the finite difference method become significant. If it is small, repeated discretizations are required, which causes cumulative error in the distribution.

Clearly, to minimize cumulative discretization error, the model should be operated using large timesteps. However, there is a maximum allowable timestep dictated by the finite difference approximation. Our approach is to operate near the maximum timestep allowed by the finite difference constraint. Whether this size is sufficiently large depends on how much
the polymer molecular weight distribution changes in a given timestep due to reaction versus the error accumulation caused by the MWD discretization. Problems are expected in cases where the reaction is very slow because the discretization error may overwhelm the changes in reactant compositions, even at the maximum timestep.

Considering these factors separately, it can be seen that either a low flowrate or rapid reaction rate will provide some flexibility in choosing the timestep size. A low flowrate allows for longer timesteps according to the finite difference criterion, which in turn reduces the relative effect of the MWD discretization error. Similarly, a rapid reaction rate means that, even with short timesteps, the MWD discretization error is small relative to changes due to reaction. Considering these factors together, we expect problems to arise in low-Damkohler-number flow regimes, where reaction rates are slow and/or convective transport is rapid.

The Damkohler number is defined as the product of $k_{i}$ (from Equation (3-6)), the injected crosslinker concentration $[X]_{0}$, and the average resident time $\tau$:

$$Da = k_{i}[X]_{0} \frac{l}{u} = k_{i}[X]_{0} \tau$$

(4-1)

where $l$ is the characteristic length and $u$ is the superficial velocity in the domain. Of interest is a critical value of the Damkohler number ($Da_{\text{min}}$), below which discretization error will make the model inoperable.

To define the critical $Da_{\text{min}}$, we need the minimum acceptable timestep that MWD discretization will allow. The minimum timestep is determined by comparing $R_{M_{w}}$ and $R_{I_{p}}$ (the error of $M_{w}$ and $I_{p}$ due to discretization) to $\Delta M_{w}$ and $\Delta I_{p}$ (the changes of $M_{w}$ and $I_{p}$ due to reaction). These parameters are used because the weight-average molecular weight
\( M_w \) and polydispersity \( I_p \) define the polymer MWD. It is found that \( \frac{\Delta I_p}{R_{I_p}} \) is always smaller than \( \frac{\Delta M_w}{R_{I_p}} \); we arbitrarily define \( \frac{\Delta I_p}{R_{I_p}} = 1 \) as the critical benchmark. The minimum Damkohler number \( Da_{\text{min}} \) is where the minimum timestep governed by reaction rate and discretization level is equal to the maximum timestep limited by transport. That is, the minimum Damkohler number is the critical point at which the discretization error completely overwhelms the change in polymer molecular weight distribution due to reaction. Clearly, one would want to operate away from this critical value as it is defined because it represents numerical errors equal in magnitude to changes caused by reaction. The critical \( Da_{\text{min}} \) is almost constant at a given discretization level because \( \Delta I_p \) is nearly linear with \( k_I \) (see Figure 4.5) and \( R_{I_p} \) is constant (In Figure 4.5, the number of fractions, the upper cutoff point and discretization method are fixed).

Considering all of these factors together, \( Da_{\text{min}} \) is a function that depends on the MWD discretization. Because cumulative discretization error can be reduced by increasing the number of fractions, the minimum Damkohler number \( Da_{\text{min}} \) can be controlled effectively in the numerical scheme. Figure 4.6 shows this effect.
Figure 4.5 Change in polydispersity versus reaction coefficient for a fixed reaction time.

Figure 4.6 Minimum Damköhler number versus number of fractions at $[X]_0 = 1.67 \times 10^{-4}$ mol/cm$^3$. 
CHAPTER 5
SIMULATION OF POLYMER AND CROSSLINKER SOLUTION DISPLACING WATER

Numerical simulations are important to help understand how the dynamics of polymer flow are affected by in-situ crosslinking reactions. Numerical modeling can be used to easily vary parameters such as injection rate, reaction rate, and permeability distribution, thus providing the ability to quickly analyze the stability of reactive polymer flows in heterogeneous materials.

In this work, reactive polymer flow is studied using a two-dimensional numerical simulation of nonlinear, transient injection processes. The simulations were performed on domains of 50 x 50 gridblocks generated using a geostatistical model. The permeability maps of the layered and heterogeneous domains are shown in Figure 5.1. The permeability ratio (the highest to the lowest) in Figure 5.1(b) is 2.0 \( \gamma = \frac{k_{\text{max}}}{k_{\text{min}}} = 2.0 \). The triple-zone domain (Figure 5.1(a)) is created by simply scaling the permeability by a set amount for a specified section of the domain, in which the local heterogeneity is retained. In this layered system, the layers are parallel to the main flow direction.

Initially the material is saturated with water. Polymer and crosslinker solutions are injected at constant flow rate into this domain over the entire left side. No-flow boundaries are imposed along the upper and bottom sides of the domain. The transient solution is obtained by advancing the dependent variables of the model in discrete timesteps. During each timestep, the dependent variables and parameters are updated. The residence time distribution of a passive tracer is obtained numerically by injecting particles into the flow field at the entrance
of the system. The outlet histogram representing this RTD can be established by counting the number of particles reaching the exit of the system in a given residence time interval.

5.1 Injection of Polymer/Crosslinker Solutions without Gelation

Two types of numerical RTD experiments are conducted in this study. First, we examine the residence time distributions during transient reactive polymer flows at different Damkohler numbers. The Damkohler number is defined as the product of the polymerization reaction constant $k_r$, the injected crosslinker concentration $[X]_0$ and the average residence time $\tau$ ($Da = k_r[X]_0 \frac{l}{u} = k_r[X]_0 \tau$, where $l$ is the characteristic length and $u$ is the superficial velocity in the domain). It represents the rate of chemical reaction relative to the rate of transport. Second, we conduct an extensive series of numerical experiments in which we examine instantaneous residence time distributions (see below), under conditions of varying Damkohler number ($Da$), Peclet number ($Pe$), and heterogeneity. The Peclet number ($Pe = \frac{ul}{D}$, where $D$ is the dispersion coefficient) is varied by controlling the polymer dispersion coefficient. In general, the dispersion coefficient between fluids in the porous
media comes from two terms—molecular diffusion and mechanical mixing. The former term is usually a constant, while the latter depends on the displacing velocity and has different values in different directions, so that the dispersion coefficient becomes a tensor. For simplicity, the dispersion coefficient is constant in the $x$ and $y$ directions in this study. From a numerical standpoint, the two dimensionless parameters ($Da$ and $Pe$) are independently controlled by varying $k_i$ and $D$ respectively. The heterogeneity is varied by controlling the permeability ratio and spatial correlation in permeability.

### 5.1.1 Residence Time Distribution for Transient Flows

During RTD simulations, tracer particles are injected into the domain over the entire left side (along with polymer and crosslinker) from the beginning of the simulation. The total number of particles injected is 10,000, and the number of particles is distributed in each gridblock over the left side of the domain according to the flux into that respective inlet gridblock at the beginning time. The particles follow the same paths as the polymer and crosslinker solution. Each particle moves a corresponding distance in the $x$ and $y$ directions as calculated by the instantaneous velocity and the timestep of the model. The positions of tracer particles are followed during a simulation and are updated during each timestep until they flow out of the domain. The residence time of each particle can be obtained when it reaches the exit of the system, and then the residence time distribution of the tracer particles can be established.

Initially, numerical experiments were performed on a layered domain of $\gamma=2$ (which is shown in Figure 5.1(a)) at $Pe=625$ for different Damkohler number. The external RTD, which provides one measure of the displacement pattern, can be examined as a function of the
reaction rate. The breakthrough residence time distributions at different Damkohler numbers are shown in Figure 5.2.

For the unreactive case ($Da = 0$), the breakthrough residence time distribution contains two peaks, whose breakthrough times differ by a factor of approximately 1.35. This value is less than $\gamma$ because the overstable displacement helps prevent the front in the low-conductivity
region from lagging. As the Damkohler number is increased, the feedback between reaction and flow changes the flow pattern. For $Da=1$, the peaks in the breakthrough RTD are closer together slightly, compared to the unreactive case. At $Da=2$, however, the breakthrough peaks are spread widely apart. The ratio of breakthrough times for the two peaks increases up to a maximum (among the set of values tested) of approximately 1.8 for $Da = 2$. This spreading apart of the peaks is caused by increased polymerization in the lower conductivity regions (due to longer residence times), so that the material heterogeneity is amplified by the fluid properties.

![Graph showing holdback of breakthrough RTD](image)

**Figure 5.3 The holdback of the breakthrough RTD at different Damkohler numbers**

The most interesting observation is that as the Damkohler number is increased beyond a value of two, the peaks again grow closer, which suggests a more complex behavior than the positive feedback described above. At $Da \approx 6$, the external residence time distribution no longer contains two distinct peaks; it is a significantly broader distribution, centered near the average residence time $\tau$. Surprisingly, the results (Figure 5.2) show that as the Damkohler number is increased, the peaks in the breakthrough residence time distributions first become closer together, but then are very far apart at $Da=2$, and grow closer at $Da=3$ and higher.

The holdback and mean residence time of injected tracers are shown in Figures 5.3 and 5.4. At $Da=2$, the polymer solution has the greatest tendency towards bypassing since the
holdback and mean residence time are the largest. This observation, along with separation in
the RTD peaks, suggests that an interesting phenomenon occurs near the point $Da=2$. 

![Figure 5.4 The mean residence time of the breakthrough RTD at different Damköhler numbers](image)

Figure 5.4 The mean residence time of the breakthrough RTD at different Damköhler numbers

To better understand the critical behavior, we examined the displacements visually by
plotting the velocity profiles in the domain at different Damköhler numbers. The images in
the Figure 5.5(a), (b), and (c) show the development of the velocity profile at $Da=1$, $Da=2$,
and $Da=4$. The color corresponds to the magnitude of velocity, which is the most effective
way to visualize the presence of the viscous fingers under these conditions. These images
indicate that a steady flow pattern develops at approximately 4 PV for $Da=1$ and $Da=2$. At
$Da=3$ and higher, however, no steady state is achieved, even at long times.

The significance of the steady-state behavior at $Da=1$ and $Da=2$ is that the flow contains
a strong viscous instability. This is in marked contrast to previously studied viscous fingering,
which is limited to transient displacement processes. Evidence of the viscous contribution to
the flow comes from examining the velocity profiles in the domain. At steady state, the ratio
of average velocity between the two layers is 6.9 for $Da=1$ and 13.9 for $Da=2$. The velocity
ratio between the two layers shows that the flow pattern is responding in large part to the
viscous instability rather than the permeability ratio (which would give a velocity ratio 2).
Therefore, steady viscous fingers, which represent a fundamentally different phenomenon than transient viscous fingers formed during displacement, have formed at $Da=1$ and $Da=2$.

![Figure 5.5 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=0.7, 3.1, 6.6, and 9.1 from left to right when $Pe=625$ at (a) $Da=1.0$; (b) $Da=2.0$; (c) $Da=4.0$.](image)

The mechanism behind the steady-state process can be conceptualized easily: Assume that fresh polymerizing fluid is continuously injected into a finite porous medium so that downstream fluid will attain a higher viscosity than the injected fluid. If both the viscosity gradient in the direction of flow (Loggia et al., 1999) and the Peclet number are sufficiently high, then a disturbance in the velocity field will remain unstable, growing into a viscous finger. The polymerization reaction provides positive feedback to the process because (at any given length from the inlet) the more rapidly moving fluid inside the finger will be characterized by a shorter residence time than fluid outside the finger, and therefore will exhibit a lower average molecular weight and apparent viscosity. The unique aspect of this
behavior is the ability to form a stationary finger (i.e., a spatially nonuniform viscosity field that is invariant with time), which is not possible during miscible displacement in a finite domain because higher viscosity fluid will ultimately be displaced.

To better quantify the approach to steady state, we define the instantaneous holdback, \( \gamma^I \), which is obtained by freezing the transient velocity profile at a point in time, then calculating the holdback by applying a pulse tracer as if the velocity profile represented a steady-state field. Results shown below are presented as instantaneous holdback versus time, which provides a very good measure of the degree of fingering and whether the flow is tending toward a steady-state viscous instability.

5.1.2 Instantaneous Residence Time Distributions

The instantaneous residence time distribution is obtained numerically by injecting particles into the entrance of the system for a current solution to the flow field. The methodology is the same as what was described above, except that the residence time of each particle in the system is calculated using the instantaneous flow velocity in each gridblock (where the instantaneous velocity map is simply a solution for velocity at the current timestep). Each particle is translated one gridblock distance in the \( x \) direction at a time. The distance each particle travels in the \( y \) direction can be calculated from the instantaneous velocity in the \( y \) direction, and the time needed to move one gridblock distance in the \( x \) direction. The instantaneous residence time distribution can be established from the number of particles reaching the exit of the system in a given residence time interval. After obtaining the instantaneous residence time distribution, the instantaneous holdback can be calculated according to Equation (2-19), thus providing an estimate of the relative stagnancy and bypassing for the current conditions.
Values of the instantaneous holdback were obtained for the same numerical experiments discussed above (the layered domain of $\gamma=2$ at $Pe=625.0$), and are plotted in Figure 5.6. For $Da=1$ and $Da=2$, a steady flow pattern develops at approximately 4 PV. Furthermore, the final value of the instantaneous holdback increases with increasing Damkohler number, as qualitative arguments might suggest. At $Da=4$, however, significantly different behavior occurs. Most significantly, no steady-state flow pattern develops, even at long times, which confirms the visual observations from Figure 5.5. The results in Figures 5.5-5.6 show that there exists a critical Damkohler number, above which a steady flow pattern can no longer develop.
The instantaneous holdback, plotted in Figure 5.6, provides a more complete temporal analysis than $E(t)$ alone. Without reaction, the instantaneous holdback $\chi'(t)$ decreases during the first pore volume of polymer injected (because of the overstable displacement). Subsequently, it rises to a steady state value of $\chi = 0.17$ (this value also depends on the respective thicknesses of the layers), reflecting the 2:1 permeability field ($\chi$ is equivalent to $\chi'$ at steady state). Plateau values of $\chi'$ are also obtained for moderate reaction rates ($Da = 1$ or 2), but at significantly higher values. These larger holdbacks are associated with the formation of steady-state viscous fingers by the mechanism given above. For $Da = 2$, the value $\chi = 0.48$ demonstrates that the flow maldistribution caused by $\gamma$ is significantly enhanced by the viscous instability. As with $E(t)$, anomalous behavior is observed for $Da > 2$, for which a steady-state value of holdback cannot be achieved, as evidenced by the oscillating values of $\chi'$ for $Da = 4$ (the unsteady behavior is caused by a physical process rather than a numerical instability. See the Appendix B for details of the numerical stability analysis).

Figure 5.8 The instantaneous holdback versus PV injected at different Damkohler numbers at $Pe=625.0$ in a heterogeneous domain.

It would make sense that there is something special about $Da=2$ for the case of $\gamma=2$: first, because the characteristic length in the Damkohler number is the domain length, $Da=1$ should have special significance regarding the extent of reaction within the domain; second when $\gamma=2$
and $Da=2$, the flow in the high-permeability streak is really behaving as $Da=1$. To test this hypothesis, simulations were performed in a layered domain with $\gamma = 1.1$ (with the same Peclet number as before). The instantaneous holdback versus pore volume is shown in Figure 5.7, which supports the above hypothesis since a steady flow pattern develops at $Da=1$, but does not develop at $Da=2$ and higher.

Figure 5.9 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=0.7, 3.6, 5.1, and 9.1 from left to right in the heterogeneous domain ($Pe=625$) at (a) $Da=1.0$; (b) $Da=2.0$; (c) $Da=4.0$.

Since we argue that the fundamental mechanism governing these flows is a viscous instability (rather than the permeability streak), we should observe analogous behavior in the heterogeneous domain (Figure 5.1(b)). Figure 5.8 shows the instantaneous holdback versus PV at different Damkohler numbers, and the images in Figure 5.9 show the development of the velocity profile in the heterogeneous domain. A steady flow pattern does not develop at $Da=2$ and $Da=4$, even at long times. However, the flow is steady at $Da=1$ after about 5 PV is injected.
5.1.3 Effects of Parameters on Steady-State Viscous Fingering

To study the effect of dispersion on reactive polymer flow in the layered domain, numerical simulations were performed at large Peclet numbers. However, there exists an upper Peclet-number limit since the finite difference method is used in the model. This limit occurs in the range over which numerical dispersion becomes larger than physical dispersion. To minimize numerical dispersion, the gridblock Peclet number (which is the ratio of the convective to diffusive terms in one gridblock) should be (ideally) less than two (Pinder and Gray 1977). In practice, the theoretical $Pe$ limit is often relaxed outside the area of interest (Spitz and Moreno 1996). Because we are examining qualitative behavior, we have relaxed this criterion somewhat, and will look for the point at which the RTD does not change. To determine this upper $Pe$ limit, a series of simulations of unreactive viscous fingering displacements were performed in the Figure 5.1(b) domain at $Pe=312.5, 1250, 3125, 6250, 31250, 312500, 3125000, 31250000, and infinity$. By analyzing the RTDs, we find that the RTDs become narrower as $Pe$ increases, and they no longer change at $Pe=312500$ and higher. Therefore, the maximum $Pe$ is defined to be near this value.

![Figure 5.10](image.png)

**Figure 5.10** The instantaneous holdback versus PV injected at different Damkohler numbers at $Pe=31250$ in a heterogeneous domain.
Reactive polymer flow in the layered domain is simulated at a high Peclet number of 31250 to investigate the dispersion effect. The holdback vs. PV plot is shown in Figure 5.10, and the images in Figure 5.11 show the development of the velocity profile. These results confirm that a steady flow pattern develops at $Da=1$, but the steady viscous finger can no longer form at $Da=2$ and higher. Additionally, a steady flow pattern does not develop even at $Da=1$ when the Peclet number is increased to 312500, which is shown in Figure 5.12.

![Image](image1)

(a)

![Image](image2)

(b)

![Image](image3)

(c)

Figure 5.11 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=0.7, 3.1, 6.6, and 9.1 from left to right when $Pe=31250$ at (a) $Da=1.0$; (b) $Da=2.0$; (c) $Da=4.0$.

These results show that, as the Peclet number is increased, the critical Damkohler number for steady flow decreases. At lower Peclet numbers, there is increased diffusive/dispersive mixing at the interface between the finger and the slower moving fluid. Large fingers form in the high permeability region, and are wide enough so that they are not destroyed by reaction. At high Peclet numbers however, the diffusion does not damp out growth of the thinner
fingers, while between the fingers very high viscosity fluid forms. Over a longer timescale (than the displacement), diffusion of this very high viscosity fluid into the thin finger, ultimately destroys the finger.

![Figure 5.12](image1.png)

**Figure 5.12** The instantaneous holdback vs. PV plot at $\gamma=2.0$ (layered) and Pe=312500

![Figure 5.13](image2.png)

**Figure 5.13** The instantaneous holdback vs. PV injected at different Damkohler numbers at Pe=625.0 in a layered domain with $\gamma=2.0$.

The strong correlated heterogeneity in the layered domain helps induce a finger through the middle of the domain, and this simple geometry is helpful in elucidating the fundamental dynamics. However, analogous behavior is observed in the random domain, as indicated in Figure 5.8. Decreasing the heterogeneity factor $\gamma$ also leads to lower values of the critical Damkohler number for steady flow, as indicated by Figures 5.6 and 5.7, the reason being a
smaller degree of heterogeneity-induced flow maldistribution (i.e., the flow maldistribution is helpful to the development of steady viscous fingers).

Figure 5.14 The development of the velocity profile (the color corresponds to the magnitude of velocity) at PV=4.6, 5.6, 6.6, and 9.1 when Pe=625 at Da=2 if PV<4.0, Da=4 if PV>4.0.

The critical Damkohler number for steady flow also depends on the initial condition. The unsteady Da=4 flow shown in Figure 5.5(c) and 5.6, reaches a steady state if the initial condition is a strong existing finger (e.g., the Da=2 steady finger) rather than a flat injection front. In Figures 5.13 and 5.14, the steady-state finger from the Da=2 case is suddenly exposed to an increased reaction rate corresponding to Da=4.

5.1.4 Mechanistic Explanation of the Critical Damkohler Number

Analyzing the instantaneous holdback in Figures 5.6-5.8 and Figure 5.10 shows that once the Damkohler number reaches a critical value, a steady viscous finger can no longer form, because even the short residence times in the finger are too long to prevent a large degree of polymerization. The ability to attain a steady-state viscous finger depends on the system’s response to a sequence of events, starting with a disturbance that decreases the velocity inside a current finger. Assuming a constant overall injection rate, a number of events can occur that will decrease the velocity inside the primary finger: the formation of a new finger at another location (Figure 5.9(b)), splitting of the current finger (Figure 5.11(b)), bulging of the finger (Figure 5.11) due to pressure gradients normal to the flow, etc.. Each of these events can increase the residence time in the current finger, leading in turn to various forms of high-
viscosity inclusions in the finger due to an increase in the extent of reaction. Inclusions that have been observed include isolated pockets in the center of a finger, wedges between a splitting tip, or higher-viscosity contours that back into the domain from the fingers’ right-hand side. At low values of \( Da \), convection is strong and the high-viscosity inclusion is diluted by fresh polymer from the inlet, or swept to the outlet, which preserves the steady-state finger (Figure 5.9 (a)). However, at high values of \( Da \), the rate of viscosity increase exceeds the dilution rate, and the disturbance to the finger grows, in turn leading to continued transient behavior. Good examples are shown in Figure 5.9(b) and Figure 5.10(b), in which the fingers are stopped, either pushed elsewhere or allowed to reform elsewhere. A critical Damkohler number \( Da^* \) is defined as the largest Damkohler number for which steady state fingering is achieved. Above this point, the velocity field remains unsteady, continually changing with time.

We conclude that the onset of this long-time unsteady regime can be caused by at least four factors: increasing the Damkohler number; increasing the Peclet number; decreasing the permeability distribution; decreasing the correlation length for permeability in the direction of flow. Three important parameters affect the critical Damkohler number. Increasing the Peclet number decreases the critical Damkohler number, which is in part due to the thinning of fingers, making them more susceptible to viscous disturbances. Higher Peclet numbers also correspond to slower diffusive mixing between the fluids of different viscosity, and therefore a greater likelihood that transient high-viscosity pockets can persist. Decreasing the heterogeneity factor \( \gamma \) also leads to lower values of the critical Damkohler number, the reason being smaller heterogeneity-induced flow maldistribution, which can lead to the formation of steady viscous fingers. Finally, it should be noted that the critical Damkohler number depends
on the initial condition. The unsteady $Da = 4$ flow reaches a steady state if it is begun with the $Da = 2$ steady finger rather than a flat injection front.

5.2 Injection of Polymer/Crosslinker Solutions with Gelation

In the above, we have studied the effect of a crosslinking reaction on polymer and crosslinker flows in porous media, under conditions where no gel formation occurs. In this section, we study how the dynamics of reactive polymer flow are affected by in-situ gelation, which is expected to have a significant effect because of its influence on the microscopic flow structure, and therefore the permeability and/or relative permeability.

In the numerical model, gel is allowed to form when the polymer weight-average molecular weight reaches the prescribed gel point. During reaction, the weight-average molecular weight of polymer grows rapidly as the crosslinking reaction proceeds. If there is gelation, the crosslinking reaction not only affects the viscosity of polymer solution but the medium’s morphology. Numerically, this morphologic change is accounted for using the phase saturation term (which reflects the volume that has become inaccessible to flow due to gel formation).

Gel is an insoluble polymer network that can be formed under certain crosslinking reaction conditions. The gel point is generally defined as the point where the weight-average molecular weight becomes infinite. In this type of modeling, this criterion is not appropriate, and therefore, a maximum molecular weight that is effectively infinite is assigned arbitrarily. Fortunately, the weight average molecular weight grows very rapidly with increasing crosslinking density at the gel point, so that the practical gel point is not particularly sensitive to the gel cutoff point chosen. In our model, we arbitrarily state a gel cutoff point of $M_w$ equal to $1.63 \times 10^9$ (where the weight average molecular weight of initial polymer is $1.63 \times 10^6$).
5.2.1 Effect of Gelation on Steady-State Fingering

Numerical experiments were performed on the layered domain with $\gamma=2$ (shown in Figure 5.1(a)) at $Pe=625.0$ for different Damkohler numbers. Initially there is no gel in the domain and both the average molecular weight and the polydispersity increase as the polymer and crosslinker flow in the system. When the set gel point is reached within a gridblock, the gel saturation begins to increase. Instantaneous residence time distributions are obtained by injecting particles into the flow field at the entrance of the system, as described in Section 5.1.2.

![Figure 5.15 The instantaneous holdback versus PV injected at different Damkohler numbers in the presence of gelation at $Pe=625.0$ in the layered domain with $\gamma=2.0$.](image)

When gelation occurs, the major difference is that the critical Damkohler number $Da^*$ for steady-state viscous fingering is lower. The instantaneous holdback versus pore volume injected at different Damkohler numbers are shown in Figure 5.15. The results after 5 PV injected for $Da=4$ and after 9.1 PV injected for $Da=2$ are not shown in Figure 5.15, because simulations cannot run longer for large Damkohler number cases. Specially, at these points the gel saturation in certain gridblocks can increase to a value 1.0. If a number of gridblocks reach this condition, the simulation breaks down. In contrast to the higher-$Da$ cases, the
instantaneous holdback at $Da=1$ with and without gelation are exactly the same, since there is no gel formed by 20 PV injected.

Figure 5.16 Comparison of the development of the velocity profile (the color corresponds to the magnitude of velocity) without (top row) and with (bottom row) gelation at (a) $Da=2.0$; (b) $Da=4.0$.

The instantaneous holdbacks at $Da=2$ with and without gelation begin to differ at 1.1 PV, showing that the gel is initially formed at approximately 1.1 PV. For $Da=4$, the gel forms at 0.7 PV, earlier than that for $Da=2$. The images in Figure 5.16 show the development of the velocity profiles in the domain at Damkohler number equal to 2.0 and 4.0. Figure 5.16 shows
the differences in flow patterns for cases with and without gelation at $Da=2$ and $Da=4$. At $Da=2$, a steady-state viscous finger develops for the case without gelation, but can no longer form under conditions in which gel formation occurs. At $Da=4$, steady-state fingering does not develop in either case, but the flow patterns are distinctly different. In Figure 5.16, the flow patterns are similar at early times but different at later times, showing that the gelation can have large effects on the flow after significant gel formation occurs.

The reason for such distinct differences in the critical Damköhler number and flow patterns when gelation occurs is because the gel formation is irreversible. If gel is not allowed to form, the reaction changes the flow pattern by changing the aqueous phase viscosity only. When gelation occurs, gel forms within the domain, and the gel saturation increases. At the same time, the crosslinking reaction changes the flow velocity through changes in the aqueous phase viscosity and relative permeability (which is strong function of phase saturation and therefore decreases as gel phase saturation increases). The formation of gel induces drastic reductions in fluid conductivity, thus the polymer solutions are slowed down in the gel formation region and are pushed into other regions. The molecular weight averages and polydispersity of polymer will decrease in the downstream of the gel formation region because gel will not flow and only the low-molecular-weight fraction of polymer flows in. At later stages of injection, gel can form in other regions and new fingers will form at other locations. The irreversible gel formation causes new fingers to continue to form, and therefore the steady-state viscous fingering will no longer occur.

**5.2.2 Effects of Other Parameters on Steady-State Fingering**

Reactive polymer flow in the layered domain is simulated at a higher Peclet number of 31250 to investigate the effect of dispersion if there is gelation. The holdback vs. PV plot
shown in Figure 5.17(a), shows that a steady viscous finger can no longer form at \( Da=1 \) and higher. Therefore, the critical Damköhler number also decreases for cases with gel formation at high Peclet numbers. The instantaneous holdbacks at \( Da=1 \) with and without gelation are different beginning at 0.9 PV, showing that gel is initially formed at that time. As Damköhler number increases, gel forms earlier. The instantaneous holdback begins to differ at 0.7 PV for \( Da=2 \) and at 0.5 PV for \( Da=4 \).

As the Peclet number is increased, gel forms at earlier times for the same Damköhler number. This effect is caused by the decreased diffusive/dispersive mixing at the interface between the faster and the slower moving fluid, which causes large differences in polymer concentration and weight-average molecular weight between the fast and the slow flow regions. In turn, the polymer solutions in the low-flow zones exhibit longer residence times. These longer times for crosslinking to occur cause the polymer weight-average molecular weight to increase more quickly in the low-flow regions. Therefore, at higher Peclet numbers, the polymer weight-average molecular weight will reach the set gel point earlier.

Simulations were performed on a layered domain of \( \gamma=1.1 \) with \( Pe=625.0 \) at different Damköhler number. The instantaneous holdback versus pore volumes is shown in Figure 5.17(b), in which a steady flow pattern develops at \( Da=1 \) since there is no gel formed by 20 PV injected, but does not develop at \( Da=2 \) and higher.

In contrast to the no-gelation case, when gel forms in the domain, there is nothing special about \( Da=2 \) for the case of \( \gamma=2 \) (demonstrated by the lack of a steady flow pattern developing at \( Da=2 \) for the case of \( \gamma=2 \)). The numerical experiments were also performed on a random heterogeneous domain (Figure 5.1(b)). Figure 5.17(c) shows the instantaneous holdback
versus PV at different Damkohler numbers. A steady flow pattern does not develop at \( Da = 1 \) and higher, even at long times.

![Graph (a)](image1)

![Graph (b)](image2)

![Graph (c)](image3)

**Figure 5.17** The instantaneous holdback versus PV injected at different Damkohler numbers in the presence of gelation (a) at \( \gamma = 2.0 \) (layered) and \( Pe = 31250 \); (b) at \( \gamma = 1.1 \) (layered) and \( Pe = 625.0 \); (c) at \( \gamma = 2.0 \) (heterogeneous) and \( Pe = 625.0 \).
5.2.3 Effect of Gelation on Breakthrough Residence Time Distributions

The breakthrough residence time distributions are of interest in certain research areas because this information can be applied to applications such as the manufacture of composite materials, polymer processing, and polymer-gel treatments in oil recovery. The breakthrough residence time distributions for cases with gelation are obtained numerically by using the same particle-tracking model described in the Section 5.1.1. The breakthrough RTD at $Da=1$ with and without gelation are exactly the same as those shown in Figures 5.2(b), since no gel forms by the time that all tracer particles have exited the domain. At $Da=2$ and higher, gel does form during the initial transient, and the breakthrough RTDs are not the same as those in Figure 5.2, though the differences are only slight. (At $Da=1$, the peaks in the breakthrough RTD are closer together compared to the unreactive case. At $Da=2$, the breakthrough peaks are again spread widely. Also, at $Da=3$ and higher, the peaks move closer together).

![Figure 5.18 Comparison of the holdback of the breakthrough RTD with and without gelation at different Damkohler numbers.](image)

The mean residence times and breakthrough pore volumes are very close (with and without gelation) even at large Damkohler numbers. However, the holdbacks are different as
shown by Figure 5.18. Specifically, the holdbacks are smaller, showing less bypassing if there is gelation.

5.2.4 Gel Placement

Information about where polymer gels form in porous media is very important in the application of gel treatments for profile modification in oil recovery. Figure 5.19 shows the time evolution of the gel saturation at different Damkohler numbers in the layered domain with \( \gamma = 2 \). The results show that the gel placement is governed by both the Damkohler number and permeability distribution. At low Damkohler numbers (\( Da = 2 \)), gel initially forms in the low-permeability zone. However, at high Damkohler numbers (\( Da = 6 \)), gel forms in the high-permeability layer first, and continues to form here. This gel formation can divert flow to lower permeability zones, which is the goal of profile modification. At long times the gel also forms in low permeability layers, which suggests halting injection at a critical time. At moderate Damkohler numbers (\( Da = 4 \)), gelation occurs in the high-permeability layer first, but is followed by significant gel formation in the low-permeability layers over the long run. Therefore, the Damkohler number (as well as the permeability distribution and injection time) is an important factor to control the effectiveness of gel treatments in layered domains.

The mechanisms for this observed behavior are fairly straightforward. At low Damkohler numbers, the residence time of the polymer solution in the low-permeability layers is long, as is the reaction time. This longer reaction time causes the average molecular weight to increase more significantly in the low-permeability layer. The higher molecular weight polymer, of course, has a higher viscosity, which in turn causes slower flow in low permeability layer. This feedback causes gelation to occur earlier in the low-permeability layer. Finally, the formation of gel can induce drastic reductions in fluid conductivity, further contributing to the
effect. Under the proper conditions, residence times in the high-permeability zone may be sufficiently short to prevent gelation in these finite-domain conditions.

(a) Gel saturation distribution for $\text{Da}=2$ at injected $\text{PV}=2.6, 3.6, \text{ and } 4.6$

(b) Gel saturation distribution for $\text{Da}=4$ at injected $\text{PV}=1.1, 2.1, \text{ and } 3.1$

(c) Gel saturation distribution for $\text{Da}=6$ at injected $\text{PV}=0.7, 1.1, \text{ and } 2.1$

Figure 5.19 Gel saturation distributions at different Damkohler numbers.

At high Damkohler numbers, the reaction rate is high and the reaction causes the average polymer molecular weight to increase very rapidly. At the beginning of the displacement, polymer and crosslinker mainly flow in high-permeability layer due to the high conductivity. The average polymer molecular weight increases quickly in this region due to fast crosslinking reaction, and reaches the gel point in a short time. Therefore, gel forms in the high-permeability layer first. The formation of gel reduces fluid conductivity in this layer, thus diverting fluid to the lower-permeability region. This behavior will continue
temporarily, though gelation ultimately occurs in the low-permeability layers due to the speed of reaction.

Finally, at moderate Damkohler numbers, gelation occurs later than at high $Da$ but earlier than at low $Da$. The polymer molecular weights reach the gel point first in high permeability region but only small amounts of gel form since the reaction is not sufficiently fast. These small amounts of gel cause faster flow, thus requiring more time to reach gel point in neighboring regions of the high-permeability layer. On the other hand, the reaction time is long enough to cause a significant amount of gel to form in the low-permeability layer.

We conclude by emphasizing that the critical Damkohler number $Da^*$ decreases if gelation occurs, for the simple reason that gel formation is irreversible. The onset of the long-time unsteady regime can be caused by at least five factors: increasing gel formation; increasing the Damkohler number; increasing the Peclet number; decreasing the permeability distribution; decreasing the correlation length for permeability in the direction of flow. The unsteady viscous fingers appear at different locations due to gelation at high Damkohler numbers. And, the Damkohler number is an important factor affecting gel placement (which in a practical sense affects the effectiveness of gel treatments).
CHAPTER 6

SIMULATION OF CROSSLINKER DISPLACING POLYMER

Generally, the viscosity of polymer is greater than that of crosslinker. Therefore, displacing a more viscous polymer by a less viscous crosslinker will result in viscous fingering. The term viscous fingering refers to the onset and evolution of instabilities that occur during the displacement of fluids in porous materials. The viscous instabilities are important in a wide variety of applications including hydrocarbon recovery, water production and treatment, fixed bed regeneration in chemical processing, soil stabilization, filtration, hydrology, and purification in various laboratory and industrial processes.

Of particular interest in the present work is the occurrence of fingering in systems where crosslinking reactions take place. When crosslinker is injected into a porous medium filled with a polymer solution, the crosslinker may react with polymer in situ. The polymerization reaction will change greatly the polymer solution’s viscosity, which affects the viscous instabilities during flow through porous media. If there is gelation, the formed gel can change the flow pattern by altering the saturation and relative permeability. In this chapter, we will study the effect of the crosslinking reaction (polymerization via crosslinker reaction) on the viscous instabilities when crosslinker displaces polymer, and investigate the interaction between viscously driven instabilities and the reactive-diffusive-convective transport of crosslinker through polymer. The mobility contrast occurs because of the viscosity dependence on concentration and weight-average molecular weight. Using numerical simulation, we analyze the extent that chemical reactions affect the characteristics of viscous fingers in the nonlinear regime.
6.1 Standard Viscous Fingering

In the absence of chemical reactions, when a less viscous fluid displaces a more viscous fluid, the displacement front is unstable and develops fingers. We refer to such behavior (in the absence of chemical reactions) as standard viscous fingering. Before detailing the effect of crosslinking reactions on fingering, we first recall the properties of nonlinear fingering in the absence of reactive coupling, and introduce quantities useful in characterizing the nonlinear dynamical regimes.

6.1.1 The General Phenomena of Viscous Fingering

As an example of viscous fingering behavior, Figure 6.1 shows the time evolution of standard viscous fingering obtained by direct numerical simulation in the absence of reactions. The simulation was performed on a domain of 50×50 gridblocks. The permeability maps of the domains are shown in Figure 6.2(a). The permeability ratio \( \gamma \) is 1.0043 (the standard deviation of permeability \( \sigma = 0.001 \)). Initially the material is saturated with polymer. Crosslinker solution is injected at constant flow rate into this domain over the entire left side. The mobility ratio \( M \) of polymer to crosslinker is 100 and the Peclet number is 1000. As seen in Figure 6.1, an uneven, fingered front occurs instead of a stable, uniform displacement front. These viscous fingers propagate rapidly, causing an early breakthrough of the injected fluid.

Figure 6.1 Standard viscous fingering for \( M=100 \) and \( Pe=1000 \) at \( t=480, 720, \) and 960s (the color corresponds to the magnitude of crosslinker concentration).
6.1.2 Variation of the Mobility Ratio

A large number of simulations have been conducted in which the relevant parameters were varied. We first consider the cases of miscible displacement without reactions varying the mobility ratio at $Pe=1000$. We have run simulations in the domain shown in Figure 6.2(a) with permeability ratio $\gamma=1.0043$ for three different values of the mobility ratio, i.e., $M=1, 10, 50$. Figure 6.3 shows the time evolution of the injected-fluid concentration as contour plots.

The effects of mobility ratio on viscous fingering are well-known (Homsy, 1987; Brock and Orr, 1991). Simulations performed for three different values of the mobility ratio here are used to verify the model and to confirm that these phenomena occur, prior to discussing the effects of crosslinking reaction. A comparison of viscous fingering for different values of mobility ratio from 1 to 100, as shown in Figures 6.1 and 6.3, shows that the displacement pattern depends most strongly on the mobility ratio.

If the viscosities of the two fluids (polymer and crosslinker) are identical (the mobility ratio equals one), the flow resistance is simply a function of the permeability. (For consistency in this chapter, we will refer to the injected fluid as *crosslinker* regardless of whether reaction is occurring or not.) Hence, the rate at which the displacement front propagates through the medium is proportional to the macroscopic permeability. The contour
lines are evenly spaced since the permeability distribution is almost homogeneous. For an unfavorable-mobility-ratio displacement (viscosity of the displaced fluid is higher), viscous fingering occurs, but the rate of finger propagation increases as the mobility ratio increases. The viscous fingers cause early breakthrough (and poor sweep efficiency in the context of petroleum production). The severity of the fingering is determined by the mobility ratio of the fluids. The viscous fingering occurs earlier when the mobility ratio is higher. Breakthrough also occurs earlier in the higher mobility ratio cases.

![Figure 6.3 Comparison of viscous fingering for different values of M increasing from top to bottom from 1 to 50. Columns (a), (b), and (c) correspond respectively to t=480, 720, and 960s (the color corresponds to the magnitude of crosslinker concentration).](image)

6.1.3 Variation of the Peclet Number

Keeping the mobility ratio equal to 100 and the crosslinking reaction coefficient equal to zero, we have run simulations in the same domain for eight different values of the Peclet number, i.e., $Pe=150, 312.5, 625, 1250, 2500, 5000, 10000, 20000,$ and $\infty$, some examples of which are shown in Figure 6.4.
As shown in Figure 6.4, the Peclet number $Pe$ determines the number of fingers present across the domain perpendicular to flow. The dispersion has a tendency to continuously coarsen the length scales of the fingering pattern (De Wit and Homsy, 1997b). For smaller Peclet numbers, the merging and fading tend to decrease the number of fingers. The Peclet number is primarily responsible for determining the preferred wavelength of the fingers. Larger Peclet numbers (corresponding to small transverse dispersion) lead to an increase in the growth rate and a shift to the smaller fingers, while small Peclet numbers stabilize the displacement at all length scales. Dispersion acts to spread the mobility profile, thereby causing a shift to longer wavelength fingers.

In the current study, the reason for performing nonreactive simulations over a series of $Pe$ values is to determine the point at which numerical dispersion becomes significant and/or what point the fingers become close to the width of a gridblock. At this limiting value of $Pe$, it is impossible to obtain higher resolution using the current grid resolution.

If there is no dispersion, viscous fingering may occur on all scales, with growth rates that increase with decreasing scale. When scales are decreased to some point at which the continuum hypothesis is no longer valid, a pore-level description would be necessary. Therefore, the nature of viscous fingering at very high Peclet number may be more conveniently described in non-continuum terms (Homsy, 1987). In numerical simulations using the finite-different method, there exists an upper limit for $Pe$ at which numerical dispersion is larger than physical dispersion. To ensure numerical stability and minimize numerical dispersion, the Peclet number should be not greater than this maximum $Pe$. This limit can be seen in Figure 6.3 as the point at which the number of fingers become independent of $Pe$ as $Pe \to \infty$. 
Figure 6.4 Comparison of viscous fingering for different values of $Pe$ increasing from top to bottom at $Pe=150, 312.5, 625, 1250, 2500, 5000, \text{ and } \infty$. Columns (a), (b), and (c) correspond respectively to $t=360, 600, \text{ and } 840s$ (the color corresponds to the magnitude of crosslinker concentration).
The viscous fingers developing with a certain Peclet number on a given domain feature \( m \) fingers, where \( m \) is related to \( Pe \) as \( Pe = k' \cdot m \), and where \( k' \) is a constant (De Wit and Homsy, 1997b). The relationship between number of fingers and Peclet number in our simulations is shown in Figure 6.5. This figure shows that at lower values of \( Pe \), the number of fingers is nearly linearly related to the Peclet number as predicted by De Wit and Homsy (1997b). The upper limit (at which the number of fingers becomes independent of Peclet number and the fingers are the width of a gridblock) is taken to be \( Pe \approx 5000 \).

6.1.4 Heterogeneous Systems

It is generally recognized that permeability interacts with viscously driven instabilities in a significant way. In natural media, permeability is usually taken to be a random stationary function of space with a given variance and correlation statistics to describe the heterogeneities. It is well known that the nature of heterogeneous fingering depends on two physical mechanisms leading to flow instabilities: viscous fingering due to unfavorable viscosity ratios and preferential flow paths due to the variance of the permeability (Brock and
Orr, 1991; Tan and Homsy, 1992; De Wit and Homsy, 1997). To examine the effects of heterogeneities, the latter authors performed experiments and numerical simulations in a random checkerboard system. All of these studies help general understanding fingering in heterogeneous media.

We now consider the effect of heterogeneity by increasing the standard deviation of permeability \( \sigma \). These simulations are run using the random heterogeneous domain shown in Figure 6.2(a) with fixed correlation statistics but with different variances. We take three values of \( \sigma = 0.01, 0.1, \) and 1.0, together with \( Pe = 1250 \). Figure 6.6 shows the time evolution of finger dynamics at times \( t = 240, 480, 720, \) and 960s for different values of \( \sigma \). It is clear that the heterogeneities do have a significant effect on the nonlinear fingering. Merging, shielding, fading, and spreading phenomena become more pronounced as the heterogeneity increases. The location and pattern of fingering are strongly influenced by the permeability distribution. The simulation results indicate an increase in the degree of instability as a result of increasing heterogeneities. Two unstable regimes are observed (depending on the level of heterogeneity): viscous fingering occurs in homogeneous or slightly heterogeneous domains, while channeling occurs when the variance of the permeability becomes high (the flow tends to follow the more permeable path, leading to a channeling regime). Heterogeneities can modify the growth rates of disturbances and stimulate the flow instabilities. Nonlinear fingering in heterogeneous media is a result of the coupling effect of the intrinsic scale of viscous fingering and those of the heterogeneity. A number of previous studies have considered the effect of heterogeneity on the viscous fingering (see Section 2.2.2). These results helped validate the underlying physics in the current model before reactive cases were studied.
6.1.5 Layered Systems

The situation is now examined in which the permeability field is layered. The triple-zone domain is created simply by scaling the permeability by a set amount for a specified section of the domain, in which the local heterogeneity is retained (see Figure 6.2(b)). In this layered system, the layers are parallel to the main flow direction. The simulations are run at conditions of $M = 100$ and $Pe = 1250$ for three layered systems with permeability contrasts between the layers equal to 1.1, 2.0, and 4.0.

The time evolution plots for standard viscous fingering for three layered systems are shown in Figure 6.7. It is clear that the flow enters the high permeability layer preferentially. By 0.1 pore volumes injected, two main fingers have formed at the interface between two permeability layers, with little fluid penetrating the low permeability layer. The reason fingers are initiated at these locations is small perturbations caused by the numerical approximation to
the pressure gradient. Though the location of finger growth is somewhat artificial due to this phenomenon, the rapid finger growth is characteristic of a high-mobility displacement.

At the permeability interface, the permeabilities change suddenly leading to perturbations at the displacement front. The net pressure $\delta p \ (\delta p = [(\mu_i - \mu_2) u_x / K] \delta x$) is positive and large, since the mobility ratio $M \ (M = \mu_i / \mu_2$) of polymer to crosslinker is 100. For layered systems, the fingering regime can be disrupted by modest levels of heterogeneity within the layers, leading to a channeling regime, in which flow enters the high permeability layer preferentially. For a system having a permeability contrast of 1.1, there is no viscous finger formed in the center of the high permeability layer. However, viscous fingering occurs within the high permeability layer as the permeability contrast is increased.

Figure 6.7 Comparison of viscous fingering for different values of permeability contrast of 1.1, 2.0, and 4.0 from top to bottom. Columns (a), (b), (c), and (d) correspond respectively to $t=240, 480, 720$, and 960s (the color corresponds to the magnitude of crosslinker concentration).
6.2 Nonlinear Fingering in the Presence of Crosslinking Reactions

In the current work, of particular interest is the occurrence of fingering in systems where crosslinking reactions take place. When crosslinker is injected into a porous medium filled with a polymer solution, the crosslinker reacts with polymer in situ. The in-situ crosslinking reactions often cause changes in material or fluid properties. These effects in turn affect flow through porous media, thereby causing a distinct coupling between the reaction dynamics and the flow dynamics. Reactive displacements of polymer by crosslinker can exhibit very interesting behavior because of the coupling effect. An example is shown on Figure 6.8 in which a low-viscosity water and crosslinker solution is injected into a visual cell saturated with a higher-viscosity polymer solution (Thompson and Kwon, 1998). The two images were recorded under identical conditions and times, except that the crosslinking reaction occurred in the right frame. In this case, the crosslinking reaction clearly has a stabilizing effect on the displacement front.

In the current research, a numerical simulation study is performed to investigate how the dynamics of viscous fingering is affected by crosslinking reactions. The focus is on the study of the interaction between viscously driven instabilities and the reactive-diffusive-convective transport of reactive polymer and crosslinker.

Figure 6.8 Experiments comparing unreactive viscous fingering (left) and reactive viscous fingering (right) when 0.15 PV fluid is injected (taken from Thompson and Kwon, 1998)
6.2.1 Variation of the Damkohler Numbers

Initially the material is saturated with polymer, whose viscosity is 100.0 cp. Crosslinker solution with viscosity 1.0 cp is injected at constant flow rate into the heterogeneous domain shown in Figure 6.2(a) where $\sigma=0.001$. The simulations are run at a series of Damkohler number equaling 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0. No gel formation is allowed for these simulations, and the Peclet number is 1250. Figure 6.9 shows the finger dynamics at three of these different Damkohler numbers: $Da=2.0$, 6.0, and 10.0.

![Figure 6.9 Comparison of fingering for $Da = 2.0$, 6.0 and 10.0 from top to bottom. Columns (a), (b), and (c) correspond respectively to $t=360$, 480, and 600s (the color corresponds to the magnitude of crosslinker concentration).](image)

The crosslinking reaction leads to an increasing viscosity along the flow direction, and high viscosity within the fingers should slow down the fingering. However, in Figure 6.9, we have not seen a stabilizing effect from crosslinking reaction as observed experimentally by
Thompson and Kwon (1998). Also, we have not observed increased stability as the reaction rate increases, as shown by the large fingers that remain for cases of $Da=2.0$, $6.0$, and $10.0$.

(a) The color corresponds to the magnitude of polymer $M_w$

(b) The color corresponds to the magnitude of polymer concentration

(c) The color corresponds to the magnitude of polymer solution viscosity

Figure 6.10 Comparison of polymer $M_w$, concentration and viscosity distributions for $Da = 2.0$, $6.0$ and $10.0$ from left to right at $t=480s$. (a) polymer $M_w$; (b) concentration; (c) viscosity.

The reason for the behavior in the model is that the viscosity in the large fingers behind their tips is not high enough to damp out these fingers. The polymer solution viscosity is a function of polymer concentration and polymer intrinsic viscosity as shown in Equation 3-10, where the intrinsic viscosity is a function of the weight average molecular weight ($M_w$) of polymer. Therefore, there are two parameters that determine the viscosity of polymer solution: one is the polymer concentration, the other is $M_w$. The larger the polymer concentration and molecular weight, the higher the viscosity of the polymer solution will be.
The weight average molecular weight increases due to reaction, but the overall polymer concentration decreases because of dilution with the displacing crosslinker solution.

Figure 6.10 shows the polymer $M_w$, concentration and viscosity distributions for $Da = 2.0$, 6.0 and 10.0 from left to right at time $t=480s$. Clearly, the polymer $M_w$ in the fingers is higher than that of the displaced fluid; however, the polymer concentration is very low in the fingers due to its displacement by crosslinker solution. These low polymer concentrations due to dilution lead to the low viscosity in the fingers, which in turn prevents any significant stabilizing effect.

6.2.2 Reactive Stabilization

The above results indicate that, to stabilize the displacement process, the fluid in the viscous fingers must attain a higher viscosity during displacement. Numerically, there are four mechanisms that will lead to increased fluid viscosity within the fingers: (1) increasing the polymer concentration; (2) increasing the reaction rate to obtain higher $M_w$; (3) decreasing the concentration effect on the viscosity by changing the functionality of polymer viscosity; (4) increasing dispersion to increase the mixing between the surrounding high-viscosity polymer and the finger. Four simulations were run in comparison with the $Da=10.0$ base case to check whether reaction can contribute to flow stabilization in the displacement process:

1. $Da=10.0$ with a higher initial polymer concentration;
2. $Da=15.0$, but otherwise similar conditions;
3. $Da=10.0$, but a first-order functionality (instead of second order) is used for the polymer solution’s viscosity;
4. $Da=10.0$, but at a lower Peclet number (equal to 312.5).
Figure 6.11 Comparison of fingering at time $t=600s$. (a) $Da=10.0$ with higher initial polymer concentration; (b) $Da=15.0$; (c) $Da=10.0$ but the polymer solution’s viscosity is a function of polymer concentration at first order; (d) $Da=10.0$ at lower Peclet number (the color corresponds to the magnitude of crosslinker concentration).

All of these simulations were run at a mobility ratio $M$ equal to 100. For higher initial polymer concentration, the value of the coefficient $K’$ in the Mark-Houwink equation (3-9) is decreased to keep the viscosity of initial polymer the same, and thus $M=100$. Figure 6.11(a) shows the fingering for $Da=10$ at $t=600s$ for the case where the initial polymer concentration is 1000 times larger than the base case (Figure 6.9(b)). Comparing the fingering in the third row in Figure 6.9(b) at $Da=10$ with Figure 6.11(a), we can see that increasing the initial polymer concentration cannot stabilize the displacement process even if the concentration is increased by three orders of magnitude. The reason for this behavior can be inferred from Equation (3-10), which shows the viscosity of the polymer solution to be a second-order function of concentration and intrinsic viscosity. To keep the same displacement mobility ratio, the polymer concentration was increased while the intrinsic viscosity was decreased accordingly by reducing the coefficient in the intrinsic viscosity equation. Therefore, increasing the initial polymer concentration cannot increase the fluid viscosity in the fingers due to the corresponding decrease in intrinsic viscosity, though it can increase the polymer concentration.

The viscous fingering at $Da=15$ when crosslinker displaces polymer is shown in Figure 6.11(b), indicating that some fingers are indeed damped due to reaction. This effect shows
that at very high Damkohler numbers, it may be possible to stabilize the displacement process to some extent and provides some guidance about how to adjust the compositions of reactants.

If the concentration effect is reduced as in case three, the high Damkohler number makes the displacement significantly more stable as shown in Figure 6.11(c). The reason is that the reaction has a greater effect on increasing the viscosity where fluids mix (since the contribution of concentration to the viscosity is reduced, thus reducing the effects of dilution). Thus, the fingers propagating through this region will be slowed down. In practice, polymers that have small concentration effect on the viscosity would be chosen to stabilize the flow process. Though this parameter is probably difficult to control as a design parameter, it should be noted that the equation used in the model (i.e., Equation 3-10) is highly general, and therefore may not represent well the behavior of any one specific fluid/fluid combination.

Finally, as we discussed in section 6.1.3, the Peclet number has important effect on the fingering pattern, as dispersion has a tendency to continuously coarsen the length scales of the viscous fingers. Increasing dispersion can increase the mixing between the surrounding high-viscosity polymer and low-viscosity polymer in the fingers. The low Peclet number makes the displacement significantly more stable as shown in Figure 6.11(d) since dispersion can help to smear fingers.

### 6.2.3 Mechanisms of Finger Growth with Crosslinking Reactions

A comparison of fingering for the no-reaction case and the reactive case in which other parameters are the same (as shown in Figures 6.4 (fourth row) and 6.9), shows that both cases are very unstable, but the numbers of fingers are different and the fingers occur in different places. As the reaction rate increases, the fingering occurs earlier and the differences between large and small fingers become more pronounced. At larger Damkohler number, the
breakthrough occurs earlier. The reason appears to be that the crosslinking reaction leads an increasing viscosity along the flow direction (particularly behind the advancing liquid front). At larger Damkohler numbers, the viscosity gradient becomes larger. The larger unfavorable viscosity gradient causes larger viscous instability in the miscible displacement process.

Despite the absence of stabilization in general, comparison of the $Da=2$ versus $Da=10$ cases shows a specific phenomenon of interest: note that the largest finger for the $Da=2$ case (near the bottom of the domain) also begins as a large disturbance for the $Da=10$ case, but ultimately is completely suppressed by the reaction. At the high reaction rate ($Da=10$), a high-viscosity wall is formed quickly behind the displacing front. Most of the fingers that are able to pass through the high-viscosity wall will continue to grow because the viscosities in the fingers are low. (In fact, they will grow more quickly because the high-viscosity wall prevents significant movement of the bulk injected front.) The smaller fingers, which did not pass through the high-viscosity wall, are not able to grow. However, the fastest finger in the $Da=2$ case is thin and very close to another smaller finger, which represents a special case. At $Da=10$, this finger is squeezed and slowed down by the high-viscosity wall due to high reaction rate. It appears that this finger’s small width led to its elimination by diffusion and reaction.

6.3 Nonlinear Fingering in the Presence of Gelation

In the above section, we studied the effect of a crosslinking reaction on the displacement of polymer by crosslinker in porous media, but assuming there was no gel formed during the crosslinking process. In this next section, gel formation is allowed to occur when the polymer weight-average molecular weight becomes large enough due to reaction to reach the set gel point. If there is gel formation, the crosslinking reaction not only affects the viscosity of
polymer solution but also the phase saturation terms. The purpose of this section is to study how the dynamics of crosslinker flow in polymer are affected by in-situ gelation.

The crosslinking reaction can significantly increase a polymer solution’s viscosity, which then affects the viscous instabilities of flow through porous media as discussed in Section 6.2. When gel formation occurs, gel becomes a third phase, while the aqueous-phase saturation is decreased. An assumption is made that the gel remains where it is formed and will not flow any more. The gel can greatly change the resulting flow patterns by affecting the saturation and relative permeability. Relative permeability is very sensitive to pore-space morphology and is expected to change due to gelation. However, because of the complexity of this problem and its dependence on pore-scale processes, no general constitutive equations are available. Hence, we assume a constant relative permeability function as given by equations (3-8). The reduction in fluid conductivity due to the formation of gel is accounted for in the phase saturation term.

6.3.1 Effect of Gelation

The numerical experiments are performed on the domain shown in Figure 6.2(a) where \( \sigma = 0.001 \) at \( Pe = 1250 \) for different Damkohler numbers. Initially the material is saturated with polymer whose viscosity is 100.0 cp, and there is no gel in the domain. The average polymer molecular weight grows and the polydispersity increases as the crosslinker is injected in the system over the entire left side. When the prescribed gel point is reached in the simulations, gel begins to form and the gel-phase saturation (in the respective gridblock) begins to increase.

To see the effects of gelation on the flow, we compare fingering in the presence of gelation with cases where no gelation occurred (i.e., Figures 6.12(a) and (b)).
be no effects at the lower Damkohler number (see the left column). However, there are observable differences at very high $Da$ (see the right column). As the Damkohler number increases, the flow patterns become increasingly affected by the formation of gel (the amount of which, of course, increases with increasing $Da$). At higher Damkohler numbers (see the center and right columns), the fingers in the bottom of domain are damped out for the case without gelation (the center and right figures in Figure 6.12(a)), but they grow continuously in the gelation case (the center and right figures in Figure 6.12(b)).

![Comparison of fingering for $Da = 2.0$, $6.0$ and $10.0$ from left to right at time $t=840s$. (a) no gel formation; (b) gel formation (the color corresponds to the magnitude of crosslinker concentration).](image)

If there is no gel formation, the reaction causes instability at earlier times, and as the reaction proceeds, the viscous fingers can be somewhat stabilized by reaction, especially at large Damkohler numbers. However, for cases with gel formation, the largest fingers remain dominant, but small fingers are shielded. At high $Da$ late in injection, the number of fingers decreases, and only several main fingers are left. The injected crosslinker continually flows
into these large fingers, and the viscous fingers are not diverted to other regions of the domain.

For the injection of crosslinker into polymer without gelation, the reaction changes the flow pattern by changing the aqueous-phase viscosity only. The crosslinking reaction causes the average polymer molecular weight continually to grow faster in the slower flow zone where the polymer concentration decreases slower due to dilution with crosslinker. In this slow flow zone, the higher molecular weight and larger polymer concentration induce higher polymer-solution viscosity. This high viscosity slows down the flow and damps out the fingers.

For injection of crosslinker into polymer with gelation, the crosslinking reaction alters the flow velocity by changing both the aqueous-phase viscosity and relative permeability (the latter of which is a function of phase saturation, and decreases as gel-phase saturation increases). The high-molecular-weight tail is treated as gel once the polymer weight-average

---

**Figure 6.13 Comparison of viscosity distributions for $Da = 2.0, 6.0$ and $10.0$ from left to right at $t=840s$. (a) no gel formation; (b) gel formation (the color corresponds to the magnitude of polymer solution viscosity).**
molecular weight becomes large enough to reach the prescribed gel point. If gel forms, gel is not part of the MWD of the mobile part of the polymer, but becomes a third phase and will not flow into next gridblock. The interesting effect is thus that the weight-average molecular weight of mobile polymer will be reduced, and the viscosity of mobile polymer therefore is smaller than in the non-gelled case, all else being equivalent.

Figure 6.13 compares the viscosity distributions for $Da = 2.0, 6.0$ and $10.0$ at $t=840s$ between no-gel cases and the gel cases. The viscosities of the displacing front in the no-gel cases are larger than those at the same locations in cases where gel formed. The very high viscosities in the bottom regions of the domain for $Da=6$ and $Da=10$ in the no-gel cases cause the fingers to slow down, and finally lead to a damping effect. When gel forms, the viscosity of flowing polymer in the bottom regions is not high enough to damp out the fingers because the high-molecular-weight tail of the distribution becomes gel. It should be noted that the reduction in polymer solution conductivity due to the formation of gel is accounted for in the phase saturation term, but at 0.7 pore-volume injected, the fluid conductivity reduction due to the formation of gel is not significant.

![Figure 6.14 Gel saturation distributions for $Da = 2.0, 6.0$ and $10.0$ from left to right at time $t=840s$](image)

The gel saturation distributions in the system for different Damkohler numbers are shown in Figure 6.14. The maximum gel saturations are about 0.2%, 11%, 41% respectively. Figure 6.14 shows that gel is always formed in locations where the fingers begin to occur, and
gelation always damps out the small fingers at high Damkohler numbers, since a reasonable amount of gel is formed in front of the small fingers. There is no gel formed in the large fingers because of the short residence time and lower polymer concentration due to dilution with crosslinker.

6.3.2 Gelation Stabilization

In the no-gel cases discussed in section 6.2.2, we presented four mechanisms for increasing the fluid viscosity in the fingers to stabilize the displacement process. In practice, increasing the reaction rate and dispersion are two of the more realistic ways that this might occur. With gel formation, the stabilization mechanism is similar to the reactive no-gelation case, since the reaction in both cases can reduce the flow conductivity by increasing polymer weight-average molecular weight. We have run two simulations to check if increasing the reaction rate and dispersion can increase the flow stabilization in the displacement process. One simulation is at higher reaction rate with $Da=15.0$, the other simulation is at $Da=10.0$ but at a Peclet number equal to 312.5. These two simulations are run at a mobility ratio $M$ equal to 100.

![Figure 6.15](image)

Figure 6.15 Crosslinker concentration at PV=0.3, 0.5, 0.7, and 0.9 from left to right (a) $Da=15$ and $Pe=1250$; (b) $Da=10$ and $Pe=312.5$ (the color corresponds to the magnitude of crosslinker concentration).
Viscous fingering at $Da=15$ (when crosslinker displaces polymer) is shown in Figure 6.15(a), in which some fingers are damped and the number of fingers decreases. The fastest finger at 0.3 PV injected is slowed down and damped out at long times. The two small fingers at the bottom of the domain at earlier times become one big finger at 0.9 PV injected.

Figure 6.15(b) shows the time evolution of crosslinker fingering at $Da=10$ and $Pe=312.5$. The flow process is significantly more stable compared to that of higher Peclet number cases, and the fastest finger is slowed down. The reason for this behavior is simply that increasing dispersion and/or diffusion can increase the mixing between the polymer in the fingers and surrounding polymer, and can smear the fingers together, thus stabilizing the displacement process.

6.3.3 Heterogeneous Systems

We now study the effect if all else is equivalent, but the heterogeneity is increased by increasing the standard deviation of the permeability $\sigma$. Simulations were run in domains of $\sigma=0.1$, and 1.0 at a series of Damkohler numbers of 2.0, 6.0, and 10.0, together with $Pe=1250$. At early injection times, the differences in the reaction effect for different Damkohler numbers are not obvious, because the short reaction time does not cause much change in the polymer viscosity, and does not lead to gel formation. However, at late injection times, the crosslinking reaction changes the flow patterns significantly, especially at higher Damkohler number and with larger heterogeneity.

Figure 6.16 shows the fingering at different Damkohler numbers in domains of $\sigma=0.1$ and 1.0 when 0.8 PV has been injected. The numbers, locations, and flow patterns of fingers are substantially different for the no-reaction case versus the reactive case. Large fingers become damped and small fingers become large at $Da=10$, however, large fingers remain dominant at
At low Damkohler numbers, the growth of fingers occurs faster than reaction can damp them out. At high Damkohler numbers, on the other hand, the crosslinking reaction is faster than the rate at which the fingers would grow; this enables damping of these large fingers. The faster reaction can also eliminate small fingers by a reactive-stabilization mechanism.

![Figure 6.16 Comparison of fingering for Da = 0.0, 2.0, 6.0 and 10.0 from left to right at 0.8 PV injected in domains of (a) \( \sigma = 0.1 \); (b) \( \sigma = 1.0 \) (the color corresponds to the magnitude of crosslinker concentration).](image)

The heterogeneity and the crosslinking reaction are both important factors affecting the viscous instabilities. Heterogeneity can enhance the viscous instabilities. However, the crosslinking reaction has two different effects. The reaction causes the adverse viscosity gradient, which leads to viscous fingering. On the other hand, the reaction can also stabilize the flow process by damping out the fingers when the reaction rate is faster than the rate at which the fingers would grow. For reactive polymer flow in heterogeneous porous media, the effects of heterogeneity and reaction are coupled together.

### 6.3.4 Layered Systems

If the permeability field is now layered, we run simulations to see the effects of layered heterogeneity and crosslinking reaction on the instabilities. The simulations are run at different Damkohler numbers with conditions that \( M = 100 \) and \( Pe = 1250 \) for three layered...
systems with permeability contrasts between the layers equal to 1.1, 2.0, and 4.0. In this layered system, the layers are parallel to the main flow direction. The flow enters the high permeability layer preferentially at the beginning of injection. By 0.1 pore volumes injected, two main fingers have formed at the interface between two permeability layers with little fluid penetrating the low permeability layer, similar to the case where there is no reaction.

The viscous fingering for $Da = 0.0, 2.0, 6.0$ and 10.0, at 0.8 PV injected are shown in Figure 6.17. In the domain with $\gamma=1.1$, no viscous fingering forms in the high and low permeability layers except the main viscous fingers formed at the beginning for $Da=0.0, 2.0$, and 6.0. However, at $Da=10$, the two main fingers become thinner and several other fingers occur in the high and low permeability layers. It appears that the fast reaction can thin the large fingers and divert viscous fingers to other regions of the domain. At lower Damkohler
numbers, the reaction causes the dimensions of the two main fingers to become larger than if there is no reaction.

(a) The color corresponds to the magnitude of crosslinker concentration

(b) The color corresponds to the magnitude of velocity

(c) The color corresponds to the magnitude of gel saturation

Figure 6.18 Distributions in layered systems with $\gamma=1.1$, 2.0, and 4.0 from left to right for $Da=10.0$ at 1.2 PV injected. (a) Crosslinker concentration; (b) Velocity; (c) Gel placement.

Viscous fingering occurs in the high-permeability layers in domains with $\gamma=2$, and $\gamma=4$ under conditions where there is no reaction. However, no fingers except the two main fingers in the high permeability layer are observed at $Da=2.0$ and 6.0. At $Da=10.0$ in a domain with $\gamma=2.0$, the reaction causes the two main fingers to become larger at early times, and to become thinner at late injection times. However, at $Da=10.0$ in the domain with $\gamma=4.0$, the reaction causes more fingering (and different structures) to occur in high permeability layer. The
reaction-driven fingering is unstable and changes instantly; some fingers are damped out and
some new fingers occur.

In the domain with $\gamma=4.0$, little fluid is diverted into low permeability layers, even at high
Damkohler number, though the two main fingers are slowed down and more fingers occur in
the high-permeability layer. However, a significant amount of fluid is diverted into the low-
permeability layer for the $\gamma=1.1$ case. The reaction profile modification is likely for the low
and moderate permeability contrast.

To better understand the effect of gelation on viscous fingering in layered domains, we
focus our studies on these cases where significant gel forms (e.g., at $Da=10$). Figure 6.18
shows the simulation results of $Da=10.0$ at late injection times in the layered domains. Figure
6.18(a) and (b) show that as the permeability contrast increases, more of the injected fluid
flows through the high-permeability layer, and less is diverted into the low-permeability layer.
Figure 6.18(c) shows the gel-placement distributions for the different domains. A large
amount of gel forms in the places where the two main fingers flow. In the $\gamma=1.1$ domain, most
of the gel forms in the low-permeability region, near the interface of the two layers and in the
displacing front in the low-permeability layer. However, for the $\gamma=4.0$ domain, most of the gel
forms in the high-permeability region. Finally, in the $\gamma=2.0$ domain, gel forms in both the low-
and high-permeability layers. (Refer to Section 5.2.4 for explanation of gel placement in
layered domains.)
CHAPTER 7

CONCLUSIONS AND FUTURE RESEARCH DIRECTIONS

7.1 Summary of the Conclusions

7.1.1 Numerical Model

The mathematical modeling of reactive polymer flow in porous media is important for a number of engineering processes. Numerical modeling helps us to understand how the dynamics of reactive polymer flow are affected by in-situ reaction.

In this work, a mathematical model for two-phase, reactive polymer flow was developed. The polydispersity effects of the polymer have been addressed using three leading moments to represent the polymer MWD. From a numerical standpoint, this is significant because only a few finite moments are needed to describe polymer transport and reaction (rather than a very large number of polymer species). Yet, order-of-magnitude changes in molecular weight are accounted for accurately.

The mass-transport equations for multi-component species coupled with kinetic models of the gelation process are solved using an operator splitting scheme, in which the gridblock conditions are updated according to both flux and reaction in that order. Within each gridblock, the kinetic model is that of a batch-reactor.

The polymer molecular weight distribution is chosen to be log-normal and is forced to remain log-normal during the transport and reaction processes. Discretization of the MWD for the transport step is very important to the accuracy of the model. The suitable number of fractions and upper mass cutoff for the discretized distribution have been determined. A spline interpolation method is used to reduce the discretization error, and an optimization
procedure is used to find the best approximation to the polymer concentration profile after transport and mixing.

Crosslinking of the polymer can lead to gel formation, which is known to have a significant effect on permeability. This effect is accounted for by separately defining immobile and mobile polymer phases, and using the mobile-phase saturation in the relative permeability function.

It is shown that the discretization error (of the MWD) may overwhelm changes in composition if the reaction is slow and/or the timesteps are short. To quantify this behavior, we define a minimum Damkohler number $Da_{\text{min}}$, below which the model is not effective. The minimum Damkohler number can be adjusted by controlling the number of fractions used to discretize the MWD during transport.

### 7.1.2 Polymer and Crosslinker Solutions Displacing Water

Polymer and crosslinker solutions displacing water in heterogeneous porous media has been simulated using the new model under conditions where there is no gel formation. The tracer-determined RTD (which is obtained numerically by injecting particles into the flow field at the entrance of the system) has been used in the analysis of reactive polymer flow systems. The holdback (calculated from the RTD to quantify relative stagnancy and bypassing) is used as a natural single parameter for estimating the degree of fingering of reactive polymer flow through porous materials.

During numerical simulation of the displacement processes, we have observed the formation of steady viscous fingers in reactive polymer flows. This is in marked contrast to previously studied viscous fingering, which is limited to transient displacement processes. Steady viscous fingers represent a fundamentally different phenomenon than transient viscous
fingers formed during displacement. The formation of steady viscous fingers is affected by the competition between reaction and convection, which allows their behavior to be correlated with the Damkohler number. A critical Damkohler number $Da^*$ exists, above which a steady-state flow is not observed.

The critical Damkohler number $Da^*$ (defined as the largest Damkohler number for which steady state fingering is achieved) is affected by three important parameters. Increasing the Peclet number decreases the critical Damkohler number, which is in part due to the thinning of fingers, making them more susceptible to viscous disturbances. Higher Peclet numbers also correspond to slower diffusive mixing between the fluids of different viscosities, and therefore a greater likelihood that transient high-viscosity pockets can persist. Decreasing the heterogeneity factor $\gamma$ also leads to lower values of the critical Damkohler number, the reason being that smaller heterogeneity-induced flow maldistribution can prevent the strong disturbances needed to initiate the steady viscous fingers. Finally, it should be noted that the critical Damkohler number depends on the initial condition.

Polymer and crosslinker solutions displacing water under conditions that allowed for gelation were simulated in layered and random heterogeneous porous media. If there is gel formation, it not only affects the viscosity of polymer solution but the medium’s morphology, which can be accounted for in the phase saturation terms via the relative permeability.

The critical Damkohler number $Da^*$ for steady-state viscous fingering decreases if gel forms during flow. The flow patterns are significantly different in comparison to no-gelation conditions. The simple reasons are that gel formation is irreversible and the gel itself does not flow. The onset of the long-time unsteady regime can be caused by at least five factors: increasing gel formation; increasing the Damkohler number; increasing the Peclet number;
decreasing the permeability distribution; decreasing the correlation length for permeability in the direction of flow. We have also observed that there is less bypassing if gelation occurs.

The Damkohler number is an important factor affecting gel placement (which in a practical sense affects the effectiveness of oilfield gel treatments). The gel placement is governed by both the Damkohler number and permeability distribution. At low Damkohler numbers, gel initially forms in low-permeability zones. However, at high Damkohler numbers, gel forms in the high-permeability layer first, and continues to form here. This gel formation can divert flow to lower permeability zones, which is the goal of profile modification. At long times, the gel also forms in low-permeability layers, which suggests halting injection at a critical time. At moderate Damkohler numbers, gelation occurs in the high-permeability layer first, but is followed by significant gel formation in the low-permeability layers at longer times. These results are very important with regard to the application of gel treatments for profile modification in oil recovery.

### 7.1.3 Crosslinker Solution Displacing Polymer

Crosslinker solution displacing polymer was studied in layered and random heterogeneous porous media. In the absence of chemical reactions, the displacement front is unstable and develops fingers because less viscous crosslinker displaces more viscous polymer. A large number of simulations were conducted to verify that the model reproduced well-known viscous fingering phenomena, prior to investigating the effects of crosslinking reaction.

In the presence of reactions when crosslinker displaces polymer, the numbers of fingers are different and the fingers occur in different places compared to the non-reactive case. In
certain cases, the fastest propagating fingers are damped at very high Damkohler number by the high viscosity caused by rapid reaction in the region.

We have not observed that the crosslinking reaction has a general stabilizing effect on the displacement front in our simulations. However, we presented three mechanisms that will lead to increased stability. At very high Damkohler numbers, it may be possible to stabilize the displacement process to some extent, which provides some guidance about how to adjust the compositions of reactants. Numerically, if the concentration effect is reduced, the fast reaction can make the displacement significantly more stable. At low Peclet number, the crosslinking reaction can stabilize the displacement process significantly.

If there is gel formation, the flow patterns becomes different as compared to no-gelation conditions. As the Damkohler number increases, the number of fingers is fewer, and the dimensions of the largest fingers increase. Increasing the reaction rate and dispersion (and/or diffusion) can be used in practice to obtain more stable displacement when crosslinker displaces polymer in porous media under conditions where there is gel formation.

The heterogeneity and the crosslinking reaction are both important factors affecting the viscous instabilities. We have observed large instabilities in the presence of chemical reaction in heterogeneous domains due to the coupled effects of these two factors. We have also found that the displacement process is stabilized slightly at high Damkohler numbers due to reactive stabilization.

For layered systems, rapid gelation can damp out the largest fingers and divert viscous fingers to other regions of the domain. The small fingers occurring in the high permeability layer for non-reactive cases can be eliminated by the reactive coupling mechanism at low and moderate reaction rates. However, at high Damkohler numbers, the gelation causes more
fingering in high permeability layer, in which the reaction driven instabilities are different from the pure viscous fingering in the non-reactive case. The reaction-driven fingering is unstable and changes instantly; some fingers are damped out and some new fingers occur.

7.2 Future Research Directions

7.2.1 Model Improvements and 3D Reactive Polymer Flow Simulation

In this work, we developed a new operator splitting technique that allows the moment equations for polymerization to be incorporated into a finite-difference transport model. This new model allows us to address successfully the polydispersity effects of the polymer and to observe the full evolution of polymer molecular weights in space and time. However, certain limitations of the numerical model do exist.

In-situ gelation is expected to have a significant effect on flow because of its influence on the microscopic flow structure. Numerically, this effect enters through the permeability and/or relative permeability. In the model, this morphologic change is accounted for using the phase saturation term (which reflects the volume that has become inaccessible to flow due to gel formation). For relative permeability, no general constitutive equation is available (because of the complexity of this problem and its dependence on pore-scale processes). Therefore, we assume a constant relative permeability function (equation 3-8). This approach allows the lower viscosity solution to remain flowing in regions where gel has formed, but this premise may not be true for a real polymer, which means the numerical code may not reproduce the real physics well in certain cases. The effect of gelation on the properties of porous media such as absolute permeability and porosity should be studied using coreflood experiments (refer to Section 7.2.2), and the new information should be incorporated into the model. Additionally, a good constitutive equation for relative permeability should be generated using
pore-scale modeling and upscaling, (refer to Section 7.2.3) to be incorporated into the current model to better reproduce the effects of gel treatments.

A second numerical problem is the formation of fingers that occurs at distinct permeability interfaces under viscous fingering conditions. The origin of the fingers at these locations is small perturbations caused by the numerical approximation to the pressure gradient. We do not believe this represents a physical phenomenon, although a large finger was formed close to the permeability interface in an experimental study by Brock and Orr (1991) in a two layered system. However, the experimental fingers were more diffuse at their tips. We have performed an extensive analysis of this numerical phenomenon, and believe that the two large fingers are caused by numerical approximation (using the finite-difference method). The use of flux limiters improves the situation, but does not eliminate the problem. Hence, further work is needed to improve the model in this regard.

This model did not reproduce the stabilizing effect on the displacement front as observed experimentally by Thompson and Kwon (1998). Although the model has considered many fundamental effects, we must conclude that there are additional physics missing from the model, or that are insufficiently considered. A careful analysis of the experimental work and the model should be performed.

In this work, our study is limited to two-dimensions. To quantitatively represent reactive polymer flows in real porous media, a three-dimensional model is desirable. Using the algorithm developed in Chapter 3, there are no restrictions that prevent 3D modeling, except for the straightforward computational issues which accompany any increases in dimensionality for numerical simulation.
The mathematical formulation of the 3D model (which has been developed) is the same as that of the 2D model described in Chapter 3. Analogous finite-difference discretization techniques are used to approximate the system of conservation laws for three-dimensional flow. A grid or mesh representing the 3D spatial domain contains parallelepipeds or cubes instead of rectangles or squares in the 2D discretization. The mass-transport equations for multi-component species coupled with kinetic models of the gelation process are again solved using an operator splitting scheme, in which the gridblock conditions are updated according to both flux and reaction in that order. In this 3D model, Equations (3-15) to (3-17) are extended to three dimensions.

The new 3D model should be used to help understand how reactive polymer flow is affected by in-situ gelation in three-dimensional porous media, which are created using a 3D geostatistical model based on the 2D geostatistical model described in Chapter 3. One possibility for using the 3D modeling is to test whether DPR gels can reduce water production without significant harm to the overall permeability, and to test at a simple level whether it can reproduce effects of gel treatments observed in coreflood experiments. Subsequently, this will enable testing of various reservoir conditions to study the effects of gel treatments on oil recovery in typical but simple reservoirs.

7.2.2 Coorfflood Experiments

Coreflood experiments can be used to determine the changes in two-phase flow properties in porous media induced by polymer gels. The question of how the two-phase flow properties such as relative permeability or saturation will be changed after gel treatments, and what effects the gel treatments have on the properties of porous media, are expected to be answered by coreflood experiments.
In general, there are two different coreflood configurations. One is a linear-flow configuration, the other is a center-tap configuration. The center-tap configuration is more representative of production geometry, but less reliable experimentally. The linear-flow configuration is more conventional and appropriate for fundamental mechanistic studies.

An existing linear-flow configuration coreflood apparatus can be used for future experiments. The cores are mounted in a high-pressure Hassler cell, along which pressure is monitored at various axial positions by pressure taps and transducers. The pressure transducers are connected to a computer data acquisition system. Brine and oil are injected into the cell by two piston pumps separately. Therefore, oil and brine volumetric flow rates are set independently and thus the fluid saturation can be varied by changing the injection flow rates. Two tracer loops, which are used for the steady-state injection of oil-phase and aqueous phase tracers, are placed immediately preceding the coreflood cell inlet. The dead volumes, between the tracer loop and core inlet, and between the core outlet and the collection system, can be measured and are accounted for in the residence time distribution analysis to determine flowing saturation. Two electrical taps installed in the cell inlet and outlet are used to measure the cell electrical resistance. It is hoped that the true wetting-phase saturation can be measured using this electrical resistivity technique.

The presence of gels in the porous matrix may induce a significant amount of either isolated or dead-end fractions of the nonwetting phase (oil phase or aqueous phase according to water- or oil-based core). Tracer experiments performed at known saturation demonstrate that the isolated or dead-end fractions do not contribute to holdup. The volume obtained using oil-phase tracers can be utilized to calculate the flowing (mobile) volume of the oil-phase. Assuming negligible trapping or dead-end fractions in the wetting phase, we similarly can
determine the total water saturation under all conditions using aqueous-phase tracers. Knowing these two values and the total pore space, we can calculate the volume of isolated or dead-end oil phase. Combining the results of the electrical resistivity measurement and tracer analysis, we can determine the volume of trapped aqueous phase and thus we can calculate the true total water saturation without ignoring the trapping or dead-end fractions in aqueous phase.

Relative permeability is the main means of quantifying the effect of gel on two-phase flow and transport in porous media. The relative permeability of a given phase is not only saturation dependent but also both path- and history-dependent. From a mechanistic point of view, we want to compare the relative permeabilities before and after gel treatment at the same saturation. Varying the oil and water fractional flow, we will set up the relation between the relative permeability to oil and to water and the water saturation in the core and test whether the DPR occurs at different fractional flow values, especially at end points. Also, we can obtain the relative permeability curves before and after gel treatment.

7.2.3 Pore-Scale Modeling

The domains on which simulations were performed were created using a geostatistical model in this work. Improved mechanistic understanding can be obtained from pore-scale modeling.

The objective of pore-scale modeling is to determine how pore-scale properties of porous media influence its macroscopic flow and transport properties, and thereby to predict the macroscopic properties and to improve the understanding of multiphase flow in porous media. Pore-scale models capture micron-scale resolution, which in many processes such as reservoir water control using gel treatments, can have a large effect on macroscopic phenomena. Flow
properties (such as relative permeability and capillary pressure), ultimately depend on pore-space morphology (Thompson and Fogler, 1997). A constitutive equation for relative permeability can be generated using pore-scale modeling. Therefore, the desire to understand underlying fundamentals drives the need for modeling at the pore level. Network modeling is an effective means of incorporating pore-scale heterogeneity into flow models of porous media.

Various three-dimensional network models for flow in porous media have been developed in our group. The model best suited for this work includes both a complete description of the porous media and a fundamental description of pore-scale multiphase-fluid-flow mechanics. In the model, the porous medium is created by a computer algorithm that simulates the correlated, non-overlapping packing of spheres into a periodic specified volume. A Delaunay tessellation is used to map the bed into a network in the manner described by Bryant et al. (1993). The resulting tetrahedrons are used to set up the network fluid conservation equations, but all microscopic fluid transport equations are solved by examining the locally bounding spheres. Using this methodology, the heterogeneity is introduced into the structure of the packed bed rather than by randomly assigning size distributions onto the network itself.

The model can be used to develop a conceptual model of in-situ gelation by combining transport equations for various chemical species with models of gelation kinetics and gel placement. Polymer-solution viscosity can be correlated with polymer concentration and crosslinker density in a similar manner to the continuum model. The permeability and relative permeability reduction caused by gels can be modeled using the basic flow equations in the network model. The changes in pore and throat volumes caused by gels should be also
considered, as gelation kinetics result in an evolving size distribution of pregel clusters leading to the formation of a gel. Ideally, the pore-scale model of the gel treatment process would be expected to predict the relative permeability, capillary pressure, and other flow properties after gel treatment in the porous media, and this information could be used in the continuum model. Pore-scale modeling can also be used to test mechanisms of fluid transport in the presence of crosslinked polymers, and whether the behavior agrees with the experiments.
REFERENCES


APPENDIX A: KRIGING TECHNIQUE

Kriging is a basic statistical estimation technique, which is named after its originator D. Krige (1951). The statistical point of view is that every point in the field and each random variable has a probability density function (PDF). For measured points, the PDF consists of a single value, however, the PDF has a nonzero variance and can take on an arbitrary shape for the unknown points. Considering a three-dimensional field, we look for an estimator of the property \( Z^* \) at an unmeasured location that is based on the \( Z_i, i=1,..., I \) known values.

\[
Z^* = \sum_{i=1}^{I} \lambda_i Z_i
\]  

Equation A.1 is the Kriging estimator, which is linear in the \( Z_i \). If we can determine the \( \lambda_i \), which are the Kriging weights, we can calculate \( Z^* \). Statistical estimation techniques are best linear unbiased estimators. “Best” means that the estimators have been arrived at through some kind of minimization of variance. “Linear” means that the estimator is a linear combination of known values. “Unbiased” means that the expectation of the estimator will return to the true value. To determine the Kriging weights, We define and minimize the simple Kriging (SK) variance (Jensen et al. 1997):

\[
\sigma_{SK}^2 = E[(Z - Z^*)^2]
\]  

where \( Z^* \) is the estimator of \( Z \) at a single point, and \( \sigma_{SK}^2 \) is the variance of the distribution at the point being estimated. Substituting equation A.1 into equation A.2 and rearranging it, we obtain:

\[
\sigma_{SK}^2 = \sigma_o^2 - 2 \sum_{i=1}^{I} \lambda_i \sigma_{oi}^2 + \sum_{j=1}^{I} \sum_{i=1}^{I} \lambda_j \lambda_i \sigma_{ij}^2
\]  

A.3
where \( \sigma_o^2 = \text{Var}(Z) \), \( \sigma_{oi}^2 = \text{Cov}(Z_i, Z) \), and \( \sigma_{ij}^2 = \text{Cov}(Z_i, Z_j) \) are known quantities. If the weights are independent, the minimal simple Kriging variance will occur when

\[
\frac{\partial \sigma_{SK}^2}{\partial \lambda_j} = 0 \quad \text{for } j = 1, 2, \ldots, I \tag{A.4}
\]

Performing the differentiations of equation A.3, we obtain the following equations:

\[
\sum_{i=1}^{I} \sigma_{ij}^2 \lambda_i = \sigma_{ij}^2 \quad j = 1, \ldots, I \tag{A.5}
\]

Unfortunately, the \( Z^* \) obtained from simple Kriging are biased, since \( \text{SK} \) is not constrained to estimate the true mean at unsampled locations. The \( \text{SK} \) bias can be determined as

\[
b^*_Z = E(Z^*) - E(Z) = E\left( \sum_{i=1}^{I} \lambda_i Z_i \right) - E(Z) = \sum_{i=1}^{I} \lambda_i E(Z_i) - E(Z) = \left( \sum_{i=1}^{I} (\lambda_i - 1) \right) E(Z) \tag{A.6}
\]

Therefore, the bias can be removed by constraining the \( \lambda_i \) to sum to 1. Now we use the Lagrange multiplier technique to minimize the Kriging variance subject to the statistical constraint \( \sum_{i=1}^{I} \lambda_i = 1 \), and obtain the objective function:

\[
L(\lambda_1, \ldots, \lambda_I, \mu) = \sigma_o^2 - 2 \sum_{i=1}^{I} \lambda_i \sigma_{oi}^2 + \sum_{j=1}^{I} \sum_{i=1}^{I} \lambda_i \lambda_j \sigma_{ij}^2 + 2 \mu \left[ \sum_{i=1}^{I} (\lambda_i - 1) \right] \tag{A.7}
\]

where \( \mu \) is the Lagrange multiplier and the factor 2 in the last term is for mathematical simplicity. Minimizing the above objective function in the usual way, we obtain the following equations for Ordinary Kriging.

\[
\sum_{i=1}^{I} \lambda_i \sigma_{ij}^2 = \sigma_{ij}^2 + \mu \quad j = 1, \ldots, I \tag{A.8}
\]

In matrix form, equation A.8 can be written as follows:
In our computer-simulated permeability domain, we initialize randomly a few permeabilities from a normal distribution in the domain. Using the above ordinary Kriging technique, we can estimate the permeabilities of the other nodes in the domain from the known values. Each node permeability is determined by 10 known permeabilities of nodes which are the nearest from the estimated node (I=10). We assume the semivariance is a function of separation distance only, there is a simple relation between the autocovariance and the semivariance:

\[
\text{Cov}(Z_i, Z_j) = \text{Cov}(h) = \text{Cov}(0) - \gamma(h)
\]

where \(h\) is the separation distance between point \(i\) and \(j\). We use a model of the semivariance (Jensen et al. 1997):

\[
\gamma(h) = \begin{cases} 
\sigma^2 & \text{for } h > \lambda_R \\
\sigma^2 - \sigma_0^2 - \frac{3}{2} \left( \frac{h}{\lambda_R} \right) - \frac{1}{2} \left( \frac{h}{\lambda_R} \right)^3 + \sigma_0^2 & \text{for } h \leq \lambda_R
\end{cases}
\]

where \(\sigma^2\) is the sill that should approximate the sample variance, \(\sigma_0^2\) is the nugget which is an inferred quantity, and \(\lambda_R\) is the range which is the extent of the autocorrelation.
APPENDIX B: NUMERICAL STABILITY

The finite-difference approach to solving the flow and transport is used in the current model. The finite-different model discretizes space and time in intervals. All values such as pressures, saturations, and concentrations are represented as nodal values. Hence, discretization, averaging, and solution procedures invoke numerical errors.

The stability (or instability) of a numerical model is of considerable importance. Instability is the result of a feedback process in which errors grow as each succeeding step is taken to obtain the solution. The growth of numerical errors is always exponential and oscillatory (Spitz and Moreno 1996). Stability is a necessary and sufficient condition for convergence. Convergence implies stability, however, convergence does not imply convergence to the correct solution. Therefore, consistency must be tested before an approximate solution is accepted.

Generally, the numerical errors can be controlled by the time and space discretization. To address the numerical stability of this model, timestep size and grid resolution were considered. Numerical experiments were performed on a two-layered domain of \( n=2 \) at \( Pe=625 \) at different timestep sizes and grid resolutions. In this layered system, the permeability is homogeneous in each layer, and the layers are parallel to the main flow direction. Initially the domain is saturated with water. Polymer and crosslinker solutions are injected at constant flow rate into this domain over the entire left side. No-flow boundaries are imposed along the upper and bottom sides of the domain. The transient solution is obtained by advancing the dependent variables of the model in discrete timesteps. The instantaneous residence time distribution is obtained numerically by injecting particles into the entrance of
the system for a current solution to the flow field. The methodology is the same as what was described in Section 5.1.2.

![Figure B.1](image1.png)

**Figure B.1** The instantaneous holdback versus PV injected at different timestep sizes at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=0$

![Figure B.2](image2.png)

**Figure B.2** The instantaneous holdback versus PV injected at different grid resolutions at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=0$

For the unreactive case ($Da = 0$), Figures B.1 and B.2 show the instantaneous holdback versus pore volume at different timestep sizes and grid resolutions. Without reaction, the instantaneous holdback $\chi$ decreases during the first pore volume of polymer injected (because of the overstable displacement). Subsequently, it rises to a steady state value of $\chi = 0.1666$. 
(this value also depends on the respective thicknesses of the layers), reflecting the 2:1 permeability field ($\chi$ is equivalent to $\chi^l$ at steady state). Figures B.1 and B.2 show that the instantaneous holdbacks at different timestep sizes and different grid resolutions are nearly the same and converge to a steady state value at long times. These two figures show the convergence and consistency of instantaneous holdback at different time and space discretizations, which suggests the numerical stability of the model.

Figure B.3 The instantaneous holdback versus PV injected at different timestep sizes at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=2$

Figure B.4 The instantaneous holdback versus PV injected at different grid resolutions at $Pe=625.0$ in a layered domain of $\gamma=2.0$ when $Da=2$
If injected polymer and crosslinker react in situ, however, the feedback between reaction and flow changes the numerical stability. The instantaneous holdbacks at different timestep sizes and different grid resolutions are not close to each other and do not converge even at long times. At $Da=2$, for example, the instantaneous holdbacks versus pore volumes at different timestep sizes and grid resolutions are shown in Figures B.3 and B.4, respectively. The flow patterns for different timesteps and grid resolutions are similar though the values of instantaneous holdbacks are different.

We have examined this numerical phenomenon, and believe that this instability is caused by the numerical approximation of reaction. Too large of a timestep results in difficulty in reaching a mass-conserving solution, and numerical instability. Conversely, as the timestep is decreased, the repeated discretizations (and additional timesteps) to obtain the solution cause cumulative error in the distribution and additional numerical errors in the process. The cumulative discretization error and other numerical errors counteract the effect of reaction, which causes a decrease in the “apparent” Damkohler number. Consequently, it is not possible to show convergence with decreasing timestep size.

Further work is needed to improve the model in this regard. However, the behavior described in the body of the thesis is still believed to be qualitatively correct because the formation of steady viscous fingers have been observed when the Damkohler numbers are smaller than a critical Damkohler number $Da^*$ at different timestep sizes. Above this $Da^*$, an unsteady-state flow has been observed over a large range of timestep sizes, and the reasons for this behavior are consistent with qualitative arguments concerning the physics of the flow.
VITA

Mr. Honggao Liu was born in 1972 in People’s Republic of China. He entered college in 1990 and finished his undergraduate studies in the Department of Chemical Engineering at Xi’an Jiaotong University in 1994. In 1997, he obtained his master of science degree in organic chemical technology at the Chemical Engineering Department of Tianjin University, P. R. China. He then came to Louisiana State University to pursue his doctoral degree in chemical engineering. In 2001, he obtained a second master’s degree in chemical engineering at LSU. In December 2002, he will receive the degree of Doctor of Philosophy in chemical engineering at LSU.