CHEMO-HYDRODYNAMIC PATTERNS AND INSTABILITIES IN GIANT HYDROTHERMAL ORE SYSTEMS

by

Qiangqiang Liu
MS. in Computer Application Technology

THE UNIVERSITY OF WESTERN AUSTRALIA

This thesis is presented for the degree of
Doctor of Philosophy
of
The University of Western Australia

Petroleum Engineering
School of Mechanical and Chemical Engineering

July 2015
ABSTRACT

Although a large volume of research on the formation of giant ore deposits exists in the literature, two fundamental questions remain unanswered: 1). what leads to the highly localized and irregular patterns of mineral distribution? 2). why is there such a huge concentration difference of minerals between ore bodies and their crustal surroundings? The traditional way of describing such mineralizing systems is on a case-by-case basis and the linear equilibrium theory is applied which assumes only one final system state. Such an approach fails to explain most of the important characteristics of mineralising systems such as the existence of large spatial gradients in chemical potentials, paragenetic sequences and zoned mineral assemblages at all spatial scales.

Instead of concentrating on one particular ore body or one specific mineral type, this research is concerned with the general physical and chemical processes involved in the genesis of giant ore bodies. In linear systems, the principle of superposition holds whereas in nonlinear systems, completely different changes in system behaviour can take place when the controlling parameters pass some critical values. In this research, nonlinear methods and non-equilibrium approaches are adopted to study the chemo-hydrodynamic patterns generated by the coupled nonlinear reaction-diffusion-advection process in open hydrothermal mineralising systems. Open mineralising systems, can exhibit a variety of system behaviours which are different from closed systems. Different chemical reactions have been studied under steady and chaotic flow regimes. The traditional studies of mineralization assume uniform residence time for mineral components, which is only the case in steady flow regimes. Chaotic flow will lead to the fractal distribution of residence time; therefore, it will give rise to new system behaviours different from those in steady
flow. Numerical simulations have also been performed to investigate the complex interactions between chemical reaction, fluid/heat flow and diffusion at the ore body and grain scale in porous media.

This study provides some insight into the irregularity and variability that characterises large hydrothermal systems in the crust of the Earth. Major findings are summarized as follows:

1. The pattern formation process of autocatalytic reaction is investigated in the presence of both steady and chaotic porous media flow during dissolution and precipitation. Chemical reactant A is modelled to dissolve from the matrix space into the pore space where the \( A+2B \rightarrow 3B \) autocatalytic reaction takes place. Reaction B can precipitate into product P at some rate in the pore space saturated with solutions. Linear stability analysis has been performed to analyse the impact of uniform flow on the spatial and temporal distribution of chemical product. Results show that the presence of fluid flow can introduce extra instability into reaction-diffusion systems. Perturbations around trivial uniform steady states decay in an oscillatory way. The frequency of the oscillations is determined by flow velocity and the wavenumber of the perturbation. Nonlinear simulation has been carried out to study the complex patterns for three different flow cases, namely, constant horizontal, time-dependent horizontal and chaotic flow.

2. The patterns and instabilities of miscible reactive fronts are investigated numerically in homogeneous hydrothermal porous media where reactant A displaces reactant B of different temperature and viscosity, generating product C in the interface between fluid A and B. On the one hand, fluid flow can transport chemical components and heat into the open flow chemical reactor. On the other
hand, the flow field itself can be affected by fluid viscosity which is dependent on temperature and chemical components. The feedback process gives rise to complicated reactive and thermal fronts. Nonlinear simulation has been carried out to investigate the nonlinear dynamics of this fully coupled process that generates “finger-like” patterns. Parametric studies have been used to investigate the influence of controlling parameters on the averaged temperature and concentration field, the length of mixing area and the total amount of chemical product. Results show that this chemo-hydrodynamic pattern of chemical fronts is highly dependent on the thermal mobility ratio, the solute mobility ratio, the Lewis number, the thermal lag coefficient, and the Damkohler number.

3. Two-dimensional discrete and continuous computational modelling has been conducted to study fracture scale diffusion and chaotic advection in hydrothermal mineralising systems. Chaotic advection can be introduced by the periodicity of a side channel flow. Particle tracing method is used to answer two of the most important questions about mineralisation: 1). what can lead to the fractal distribution of minerals? 2). where are the most likely places for mineral particles to concentrate? The numerical results show that the concentration of minerals in the chaotic regions of the flow is rapidly homogenised whereas heterogeneous concentration gradients can be maintained between chaotic regions and flow pathways because of the existence of open flow within the system.

4. Autocatalytic and bimolecular reactions are coupled into the chaotic advection and diffusion processes. Case studies have been carried out to study the impact of advection and chemical kinetics. The results show that both chemical kinetics and chaotic advection induced by periodic side-channel flow have strong impacts on the
spatiotemporal dynamics of concentration distribution. The bi-stable case shows that the final state of the system is strongly dependent on the product of the volumetric flow rate and species concentration. Stronger perturbations will propagate through the system while smaller perturbations die out.
ACKNOWLEDGEMENTS

I would like to express my sincere thanks to my supervisor, Professor Jishan Liu, who not only offered the opportunity to commence my PhD study in the University of Western Australia but also gave me patient and valuable guidance and support through the period of PhD candidature.

I would like to thank Professor Bruce Hobbs and Professor Alison Ord for providing the scholarship for this research. I thank them for their enthusiasm, dedication and patience for this research. They provided valuable suggestions and insightful advice which is crucial to the completion of this research.

I am very grateful to Dr. Daniel Lester who offered me the opportunity to visit CSIRO and had fruitful discussion with me. His assistance is much appreciated.

This research is funded by the grant “Multiscale Dynamics of Ore Body Formation” which was awarded by Australian Research Council to the Centre for Exploration Targeting (CET), School of Earth and Environment, the University of Western Australia. The financial support from the University of Western Australia in the form of the Scholarship for International Research Fees and UIS living allowance is also gratefully acknowledged.

I would also like to acknowledge the administrative and technical support from the school of Mechanical and Chemical Engineering. Many thanks go out to all who had discussions during the course of this study in the research group: Dr. Jianguo Wang, Dr. Zhongwei Chen, Dr. Hongyan Qu and Mr. Yan Peng. I am grateful to Mr. Paul Spargo and Mr. Hubert Day for their time and effort to proofread this thesis and improve my English.

Finally I would most like to thank my family. I am eternally grateful to my wife, Dr. Chunxiao Bao, for her constant love and encouragement. Thanks also go to my son, Anthony Liu, for the happiness and joy he brought to us.
TABLE OF CONTENTS

ABSTRACT ....................................................................................................................... 3
ACKNOWLEDGEMENTS ............................................................................................... 7
TABLE OF CONTENTS ................................................................................................. 9
LIST OF FIGURES ......................................................................................................... 13
LIST OF TABLES ........................................................................................................... 21
CHAPTER 1
INTRODUCTION ........................................................................................................... 23
  1.1 Background ...................................................................................................... 23
  1.2 Research contents ......................................................................................... 24
  1.3 Research objectives ...................................................................................... 33
  1.4 Thesis organization ...................................................................................... 34
CHAPTER 2
MODELLING OF PATTERN FORMATION IN DISSOLUTION AND PRECIPITATION OF OPEN POROUS MEDIA ................................................................. 37
  2.1 Introduction .................................................................................................... 37
  2.2 Gray-Scott model in the presence of flow .................................................... 41
  2.3 Linear stability analysis ................................................................................ 43
    2.3.1 Stability analysis for trivial steady states ............................................ 45
    2.3.2 Stability analysis for other uniform steady states ............................ 45
  2.4 Nonlinear simulation ..................................................................................... 48
    2.4.1 Constant horizontal flow .................................................................... 50
    2.4.2 Time-dependent horizontal flow ......................................................... 53
    2.4.3 Chaotic flow ....................................................................................... 54
  2.5 Conclusion .................................................................................................... 58
CHAPTER 3
NON-LINEAR INTERACTIONS OF DYNAMIC REACTIVE INTERFACES IN HYDROTHERMAL MINERALISING PROCESSES ............................................. 61
  3.1 Introduction .................................................................................................... 61
  3.2 Mathematical model ...................................................................................... 66
3.2.1 Physical problem.................................................................................. 66
3.2.2 Governing equations.............................................................................. 67
3.3 Result analysis................................................................................................... 74
  3.3.1 Role of mobility ratio................................................................. 76
  3.3.2 Role of thermal lag coefficient.................................................. 76
  3.3.3 Role of Lewis number................................................................. 77
  3.3.4 Role of Damkohler number......................................................... 78
3.4 Parametric study............................................................................................. 79
  3.4.1 Averaged temperature and concentration ........................................... 80
  3.4.2 Mixing area......................................................................................... 82
  3.4.3 Total amount of chemical product.................................................. 87
3.5 Conclusion...................................................................................................... 88

CHAPTER 4
MODELLING OF CHAOTIC ADVECTION OF MINERAL PARTICLES
INDUCED BY PERIODIC OPEN FLOW................................................................. 91
  4.1 Introduction................................................................................................. 91
  4.2 Model system............................................................................................. 96
    4.2.1 Scale analysis.............................................................................. 98
    4.2.2 Continuous model and discrete models........................................ 100
  4.3 Chaotic advection analysis.......................................................................... 101
    4.3.1 Particle trajectories................................................................. 102
    4.3.2 Fractal patterns............................................................................ 106
    4.3.3 Stroboscopical map................................................................. 107
    4.3.4 Residence time distribution.................................................... 110
    4.3.5 Poincare section................................................................. 114
    4.3.6 Escape rate.................................................................................. 116
  4.4 Case studies................................................................................................ 116
    4.4.1 Case study 1............................................................................. 117
    4.4.2 Case study 2............................................................................. 119
  4.5 Conclusion................................................................................................... 121

CHAPTER 5
MODELLING OF FRACTURE-SCALE CHEMICAL REACTION AND CHAOTIC
ADVECTION INDUCED BY PERIODIC FLOW.................................................. 123
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>123</td>
</tr>
<tr>
<td>5.2</td>
<td>Model system</td>
<td>127</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Governing equations</td>
<td>128</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Scale analysis</td>
<td>130</td>
</tr>
<tr>
<td>5.3</td>
<td>Case studies</td>
<td>131</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Steady flow and chaotic flow</td>
<td>131</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Chemical reactions with different reaction rate</td>
<td>140</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Multi-stability</td>
<td>142</td>
</tr>
<tr>
<td>5.3.4</td>
<td>A+B-&gt;C type of reaction</td>
<td>145</td>
</tr>
<tr>
<td>5.4</td>
<td>Conclusion</td>
<td>150</td>
</tr>
<tr>
<td><strong>CHAPTER 6</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>Main findings</td>
<td>153</td>
</tr>
<tr>
<td>6.2</td>
<td>Implications for mineral exploration</td>
<td>154</td>
</tr>
<tr>
<td>6.3</td>
<td>Recommendations for future work</td>
<td>156</td>
</tr>
<tr>
<td><strong>APPENDICES</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Appendix 1</td>
<td>Fracture-scale flow</td>
<td>159</td>
</tr>
<tr>
<td><strong>REFERENCES</strong></td>
<td></td>
<td>163</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 1-1 KCGM super pit in Kalgoorlie, Australia. The pit is over 0.6 km deep, 3.6 km long and 1.6 km wide which produced more than 50 million ounces of gold. (Cited from http://www.kalgoorlietourism.com/KCGM-Super-Pit) .................................................. 24

Figure 1-2 Different scenarios for nullclines of pure reaction in the Oregonator model (Cross and Hohenberg, 1993). The differences in the behaviour of this system depend on the magnitude of perturbations and the slope of the $g = 0$ nullcline relative to that of the $f = 0$ nullcline at the point of intersections of the two nullclines. .................................................. 26

Figure 1-3 Three types of travelling wave: pulse, front, train. ................................................. 27

Figure 1-4 Mass balance of reaction-diffusion-advection process ........................................... 27

Figure 1-5 System behaviour for reactions coupled with flow (Ord et al., 2012). ............... 28

Figure 1-6 Five possible stationary state loci patterns in the reaction-diffusion process of time-independent flow (Gray and Scott, 1990). The vertical axis is the extent of the reaction whilst the horizontal axis is the residence time. ....................................................... 29

Figure 1-7 Fluid element is deformed by 2D time-dependent laminar flow (Welander, 1955). ....................................................................................................................................... 30

Figure 1-8 Conceptual model of an open flow hydrothermal system (Ord et al., 2012). ... 31

Figure 2-1 Groups of patterns found by Pearson (Pearson, 1993) ........................................ 38

Figure 2-2 Phase diagram of the Gray-Scott model (Ueyama, 1999) ............................... 39

Figure 2-3 Phase portrait of the Gray-Scott model (Nishiura and Ueyama, 1999) .......... 40

Figure 2-4 Schematic diagram of porous media ................................................................. 42

Figure 2-5 Pattern formed by different $F$ and $k$
Figure 2-6 Evolution of spot multiplication for different scenarios in Table 2-1

Figure 2-7 Time evolution of stripe-like pattern for different scenarios from Table 2-2

Figure 2-8 Concentration variation for point (0, 0.2). It oscillates before becoming time-independent.

Figure 2-9 Pattern comparison between constant flow (A1-A4) and time-dependent flows of different frequencies $\omega_1$ (B1-B4) and $\omega_2$ (C1-C4) at time 400, 800, 1200, 1600.

Figure 2-10 Chaotic flow traced out by particle with side entry flow.

Figure 2-11 Pattern profile for different flow velocity v1 (A), v2 (B), v3 (C) at dimensionless time 500(1), 1000(2), 2000(3), 4000(4).

Figure 2-12 Contour plots for different flow velocity v1 and v3 at time 4000.

Figure 2-13 Pattern comparison between different flow frequency at t = 500, 1000, 2000, 4000.

Figure 2-14 Disappearance of a spot in the chaotic flow at different time t = 200, 240, 280, 320.

Figure 3-1 Tectonically-driven groundwater flow (Garven and Raffensperger, 1997).

Figure 3-2 Effect of temperature on viscosity (Barnes, 1997).

Figure 3-3 System configuration.

Figure 3-4 Profile of concentration and flow field of reactant A at t = 450 with $\lambda = 0.5, R_A = 2, R_T = 2, Le = Da = 1$.

Figure 3-5 Temperature field shows a thermal lag effect at t = 450 with the same parameters as in Figure 3-4.
Figure 3-6 3D concentration field of product C at $t = 450$ with $\lambda = 0.5, R_A = 2, R_T = 2, Le = Da = 1$…………………………………………………………………………….75

Figure 3-7 Profile of concentration field of reactant A at $t = 400$ with $R_A = 2, Le = Da = \lambda = 1$: a) $R_T = -2$; b) $R_T = 0$; c) $R_T = 1$; d) $R_T = 2$……………………………………………………………………76

Figure 3-8 Concentration field contrast at $t = 400$ with $R_A = 2, R_T = 2, Le = Da = 1$: a) $\lambda = 1$; b) $\lambda = 0.5$…………………………………………………………………………………………77

Figure 3-9 Temperature field contrast at $t = 400$: a) $\lambda = 1$; b) $\lambda = 0.5$ with $R_A = 2, R_T = 2, Le = Da = 1$…………………………………………………………………………….77

Figure 3-10 Concentration field contrast at $t = 450$ with $R_A = 2, R_T = 2, \lambda = Da = 1$: a) $Le = 10$; b) $Le = 1$…………………………………………………………………………………………78

Figure 3-11 Temperature distribution at $t = 450$ with $R_A = 2, R_T = 2, \lambda = Da = 1$: a) $Le = 10$; b) $Le = 1$…………………………………………………………………………………………78

Figure 3-12 Profile of concentration field of reactant A at $t = 400$ with $R_A = 2, R_T = -2, Le = \lambda = 1$: a) reactive case with $Da = 1$; b) nonreactive case with $Da = 0$…………..79

Figure 3-13 Profile of concentration field of reactant A at $t = 250$ with $R_A = 2, R_T = 2, Le = \lambda = 1$: a) $Da = 0.5$; b) $Da = 1$…………………………………………………………………………….79

Figure 3-14 Profile of transversely averaged concentration of reactant A at different time with $R_A = 2, R_T = 2, Le = 2, \lambda = 0.75, Da = 1$……………………………………………………………………………………………80

Figure 3-15 Profile of transversely averaged temperature $T$ at different time with $R_A = 2, R_T = 2, Le = 2, \lambda = 0.75, Da = 1$…………………………………………………………………………………………………………81

Figure 3-16 Profile of transversely averaged concentration of the product C at different time with $R_A = 2, R_T = 2, Le = 2, \lambda = 0.75, Da = 1$……………………………………………………………………………………………81

Figure 3-17 Thermal and fluid fronts with $\lambda = 0.5$ and 0.25 (dashed lines) with $R_A = 2, R_T = 2, Le = 1, Da = 1$……………………………………………………………………………………………82

Figure 3-18 Concept of reverse and forward reacting area length……………………………..82
Figure 3-19 Total reacting area length $L$ with different $\lambda$: case 1 $\lambda = 0.75$; case 2 $\lambda = 0.5$; The other parameters are: $R_A = 2, R_T = 2, Le = Da = 1$………………..83

Figure 3-20 Reverse reacting area length $L_-$ with different $\lambda$: case 1 $\lambda = 0.75$; case 2 $\lambda = 0.5$; The other parameters are: $R_A = 2, R_T = 2, Le = Da = 1$………………..83

Figure 3-21 Forward reacting area length $L_+$ with different $\lambda$: case 1 $\lambda = 0.75$; case 2 $\lambda = 0.5$; The other parameters are: $R_A = 2, R_T = 2, Le = Da = 1$……………….84

Figure 3-22 Total reacting area length $L$ with different $R_T$: case 3 $R_T = -2$; case 4 $R_T = 2$; case 5 $R_T = 1$; case 6 $R_T = 0$. The other parameters are: $R_A = 2, \lambda = Le = Da = 1$……………………………………………………………………………………..84

Figure 3-23 Reverse reacting area length $L_-$ with different $R_T$: case 3 $R_T = -2$; case 4 $R_T = 2$; case 5 $R_T = 1$; case 6 $R_T = 0$. The other parameters are: $R_A = 2, \lambda = Le = Da = 1$…………………………………………………………………………………………….85

Figure 3-24 Forward reacting area length $L_+$ with different $R_T$: case 3 $R_T = -2$; case 4 $R_T = 2$; case 5 $R_T = 1$; case 6 $R_T = 0$. The other parameters are: $R_A = 2, \lambda = Le = Da = 1$……………………………………………………………………………………..85

Figure 3-25 Reverse reacting area length $L_-$ with different $Da$: case 3 $Da = 1$; case 7 $Da = 0$. The other parameters are: $R_A = 2, R_T = -2, \lambda = Le = 1$…………………86

Figure 3-26 Forward reacting area length $L_+$ with different $Da$: case 3 $Da = 1$; case 7 $Da = 0$. The other parameters are: $R_A = 2, R_T = -2, \lambda = Le = 1$…………………87

Figure 3-27 Evolution of overall amount of product C for the above 6 cases……………..88

Figure 4-1 Core from Tropicana deposit, Western Australia. The gold grade is 6.24 g/tonne. The image is approximately 15 cm long………………………………………………………………………………..91

Figure 4-2 Illustration of an open flow. (b) Schematic depiction of the stable ($Ws$) and unstable ($Wu$) manifolds in an open flow. The gray bands are neighborhoods of $Ws$ and $Wu$. R1 and R2 indicate regions where initial conditions are chosen.(de Moura, 2011) ....94

Figure 4-3 Schematic of a fluid element undergoing stretching, folding ……………………..95
Figure 4-4 Arrow plot of velocity field (blue) and streamline (red) of $\vec{V}_1(a)$ and $\vec{V}_2(b)$..97

Figure 4-5 Regimes of laminar and turbulent flow defined in log(permeability)-log(pore size) by the Peclet number, Pe(Lester et al., 2012) .................................................................99

Figure 4-6 Reconstructed 3D plot of the vertical (a) and horizontal (b) velocity field .....101

Figure 4-7 Trajectories plots for particles distributed along the line $x = 0.3$, $x = 1.2$, and $x = 1.4$ after $t = 40$. The arrows point to the location of the side channel ......................103

Figure 4-8 Trajectories of particles distributed evenly along a horizontal line of different height at $t = 40$, the arrows point to the location of the side channel. .....................105

Figure 4-9 Particle distribution at $t=0$ (black line), 8(green), 12(purple), 16(blue) by using 10,000 particles with the same parameter of A, B and T in Table 4-1 .........................107

Figure 4-10 Initial location of 10,000 particles. .................................................................108

Figure 4-11 Stroboscopic map plot of particles distribution at $t=T$, 2T, 3T, 4T, 5T. The arrows point to the location of side channel. .................................................................109

Figure 4-12 Residence time distribution for initial line at $x=0.3$, $x=1.1$ and $x=1.3$. .......111

Figure 4-13 Comparison of residence time for vertical line $y=0$ to $y=1$ (above) and $y=0.5$ to $y=0.7$(bottom). Both cases use 10, 000 particles. .................................................................113

Figure 4-14 Residence time distribution over the whole domain .......................................114

Figure 4-15 Contour of the above residence time distribution ...........................................114

Figure 4-16 Poincare section for particles listed in Table 4-2 ...........................................115

Figure 4-17 Trajectories for particles listed in Table 4-2 by $t=40$. .....................................115

Figure 4-18 Total number of particles in the domain (red line). The blue line plots the curve characterised by escape rate $\kappa$. .........................................................116

Figure 4-19 Concentration distribution for case 1 at $t=10$ and 30. ...............................117

Figure 4-20 Concentration distribution for case 2 at $t=10$ and 30. ...............................118
Figure 4-21 Concentration distribution for case 3 at $t = 4$ and 10, respectively .......... 118

Figure 4-22 Total amount of mineral left at different times for cases 1, 2, 3 .................. 119

Figure 4-23 Spatial-temporal distribution of concentration for case 1 at time 5, 10, 20, 40. ............................................................................................................................................ 120

Figure 4-24 Spatial-temporal distribution of concentration for case 2 at time 5, 10, 20, 40. ............................................................................................................................................ 120

Figure 4-25 Comparison for case 1 and case 2 .............................................................. 121

Figure 4-26 Comparison of flux at the right boundary for case 1 and case 2 ............... 121

Figure 5-1 Pattern induced by flow in rock due to chaotic advection. Photo copy-right by Roberto Weinberg, school of geoscience, Monash University, Australia,  
http://users.monash.edu.au/~weinberg/Pages/disharmonic_folds/irreg_folds_tng/50pct/DS C03825.jpg ......................................................................................................................... 125

Figure 5-2 Atmospheric scale advection coupled with chemical reaction. Concentration field of Hydrogen Chloride (in parts per billion (ppb)) above the South Pole at about 18 km altitude on September 24, 2002.(Groß et al., 2005) ................................................................. 126

Figure 5-3 Velocity profile at $t = 34T$ with $A = 10, B = 15, \omega = \pi/2$ .................... 128

Figure 5-4 Initial perturbation with $(x_0, y_0) = (0.2, 0.2), \alpha = 200$, blue colour corresponding to $C=0$, red corresponding to $C=1$ .................................................................................................................... 132

Figure 5-5 Contour plot of concentration field for chaotic flow (left column) and steady flow (right column) at $t=1, 2, 4, 6, 8, 30$ .............................................................................................................. 134

Figure 5-6 Production curve from $t=0$ to $t=20$ .......................................................... 135

Figure 5-7 Evolvement of perturbation for steady flow ............................................. 136

Figure 5-8 Evolvement of perturbation for chaotic flow at $t = 10$, $t = 20$ and $t = 30$. .... 137

Figure 5-9 Spatiotemporal evolution of perturbation initially located at (0.2, 0.2) and (0.2, 0.5) at dimensionless time $t = 0, 5, 10$ .............................................................................................................. 138
Figure 5-10 Reaction rate k=0.1 case at t=0, 1, 5 ................................................................. 139

Figure 5-11 Reaction rate k=0.3 case at t=10, 20, 30 .......................................................... 140

Figure 5-12 Distribution of reactant B for k = 0 (left column) and k = 0.5 (right column) cases at t=5, 10, 20, 30 .................................................................................................................. 141

Figure 5-13 Production for different reaction rate ................................................................. 142

Figure 5-14 Concentration profile for bi-stable reaction at t=5, 10, 20, 40. The threshold $\alpha = 0.8$, the concentration of the inlet of the side channel is 0.6 ................. 143

Figure 5-15 Concentration profile for bi-stable reaction at t=5, 10, 20, 40. The threshold $\alpha = 0.4$, the concentration of the inlet of the side channel is 0.9 .............. 144

Figure 5-16 Concentration distribution of reactant A at t=0.5, 3, 10, 20. ......................... 145

Figure 5-17 Contour plot of distribution of product C at t=0.5, 3, 10, 20. ......................... 146

Figure 5-18 Contour plot for product C with different reaction rate k=0.1, 1, 10 at t=30.147

Figure 5-19 Production curve for reactions with different reaction rate ......................... 148

Figure 5-20 Comparison of production distribution for steady flow (left column) and chaotic flow (right column) at t = 5, 10, 20, 40 ................................................................. 149

Figure 5-21 Production curve for steady flow and chaotic flow ................................. 150
LIST OF TABLES

Table 2-1 Scenarios of different times and velocities. ..............................................50
Table 2-2 Scenarios of different times and velocities............................................. 51
Table 2-3 Scenarios of different times and velocities for chaotic flow case ............ 55
Table 3-1 Different cases with different parameter values.................................87
Table 4-1 Parameter settings used in discrete chaotic advection simulation..........102
Table 4-2 Points used to obtain the Poincare section........................................115
Table 5-1 Parameter settings used in case study 1..............................................133
CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The origin of giant ore bodies represents one of the most challenging intellectual problems in geoscience. Whatever the processes of formation are, they produce at least a $10^3$ to $10^5$ times enhancement of economic metals above crustal background levels. Some fundamental questions regarding mineralization of ore bodies rich in Au, Ag, Pb, Zn, Cu, U, and Fe remain unknown: what are the processes involved in the local concentration of mineral aggregates deep inside the Earth, leading to the enrichment of economically valuable resources? What leads to the highly irregular pattern of distribution of ore deposits? How are the processes of heat transport, fluid flow and chemical reaction coupled to each other? A generally accepted assumption now is that the transport of minerals, presumably hydrothermal, must be associated with fluid flow through fractures within rocks that a hydrologist may consider hardly permeable, over time intervals that are relatively short geologically.

This thesis concerns an analysis and computational modelling of some of the fundamental processes that result in the development of large mineralised systems in the Earth’s crust. The discovery rate for large new mineral deposits in Australia and worldwide has diminished dramatically in the past two decades. This study is aimed at gaining a better understanding of these processes to assist in greater success rates for the discovery and development of the less obvious mineral deposits in Australia. Despite the apparent importance of geochemistry, fluid flow, and diffusion for mineralisation, this coupled process remains poorly understood. This research uses a non-equilibrium approach to study the reaction-diffusion-advection process in hydrothermal mineralising systems. It is of fundamental importance in not only guiding future exploration strategies but enables better evaluation of the content of a deposit prior to the commencement of mining. The outcomes
of this study will enhance the scientific understanding of any mineral exploration target area and serve to increase the probability of discovery of significant deposits.

Figure 1-1 KCGM super pit in Kalgoorlie, Australia. The pit is over 0.6 km deep, 3.6 km long and 1.6 km wide which produced more than 50 million ounces of gold. (Cited from http://www.kalgoorlietourism.com/KCGM-Super-Pit).

1.2 RESEARCH CONTENTS

In terms of the distribution patterns of hydrothermal ore deposits, the following observations have been made in the geological literature:

1. Many hydrothermal deposits are associated, both in space and in time, with faulting. Ore deposits are often highly localized within the crust, occupying only parts of major faults and shear zones (Alt-Epping and Zhao, 2010).

2. Ore deposits require large volumes of fluid flow to provide the necessary volume of precipitated metals with low solubilities in aqueous fluids (Barnes, 1997).

3. Fractal distribution patterns of mineralogy are observed both inside and outside the ore body. The alteration envelope is commonly very large (tens of cubic kilometres or larger) compared to the mineralised parts of the system (Raines, 2008, Agterberg et al., 1993, Ford and Blenkinsop, 2008).

4. Fluid mixing is probably the dominant ore-forming process. One example is the Olympic Dam Cu-U-Au deposit (Haynes et al., 1995). One fluid (oxidised) meets another fluid (reduced) and mixing takes place at the interface. Fluid mixing in this context is envisaged. The plumbing systems responsible for such mixing are
commonly difficult to define. Such a process is very inefficient and part of the applications of this thesis is the analysis of some efficient modes of mixing.

5. Grades of ore deposits are not uniformly distributed and the variance in metal values changes radically between individual sites and from place to place along a vein. This also is the case at the microscopic scale (Henley and Berger, 2000).

This research provides a new approach for geoscience to study the dynamics of ore-forming systems. Many models of hydrothermal mineralising system adopt the assumption of local equilibrium which assumes only one stationary equilibrium state (Ord et al., 2012). This assumption is only valid for closed linear systems in which far-from-equilibrium conditions can only exist during an initial transient period. Open and nonlinear systems exhibit much more complex system behaviours. The biggest difference between linear system and nonlinear system lies on whether the change of controlling parameters crossing a critical point can cause the system to re-organize itself into a completely new state. When systems are driven sufficiently far away from equilibrium, three different types of spatiotemporal patterns could arise within the characteristic wave vector and frequency of the instabilities (Cross and Hohenberg, 1993): Type I systems are stationary in time and periodic in space; type IIIo are periodic in time and uniform in space; type Io systems are periodic in both space and time. Gray and Scott showed that if the controlling parameters lie outside the closed region of the Hopf bifurcation points, the spatially uniform stationary state is stable. If the controlling parameters lie within the closed region, the stationary state is unstable and spatial oscillations exist (Gray and Scott, 1990). Figure 1-2 shows various possibilities for null-clines of the “well-mixed” Oregonator model. The term “well-mixed” means the effect of diffusion could be neglected. Symbols $u_1$ and $u_2$ represent the concentration of different chemical components. This model shows a variety of nonlinear behaviours: small amplitude oscillations, large amplitude relaxation oscillations, multistabilities, and excitable behaviours.
Figure 1-2 Oscillatory and excitable behaviours for nullclines of pure reaction in the Oregonator model (Cross and Hohenberg, 1993). The differences in the behaviour of this system depend on the magnitude of perturbations and the slope of the $g = 0$ nullcline relative to that of the $f = 0$ nullcline at the point of intersections of the two nullclines.

The coupling between diffusion and chemical kinetics can give rise to time-independent chemical patterns such as the Turing pattern and time-dependent patterns such as propagating fronts, target patterns, spiral waves, etc.. Figure 1-3 shows three types of travelling waves in reaction-diffusion systems. Those propagating pulse solutions can travel through the system without attenuation, generating spatial and temporal distribution patterns (Cross and Hohenberg, 1993, Gray and Scott, 1990).
Figure 1-3 Three types of travelling wave: pulse, front, train.

Different from closed systems in which there is no exchange of matter or energy, open systems can have continuous inflow of fresh chemical ingredients. Based on the mass-balance law, the rate of change of product can be given by:

\[
\text{Net rate of change of product} = \text{Rate of inflow} - \text{Rate of outflow} + \text{Rate of reaction} + \text{Rate of addition by diffusion}
\]

Figure 1-4 Mass balance of reaction-diffusion-advection process.

Reaction and diffusion processes in open flow system can exhibit a variety of system behaviours dependent on the characterising residence time, and the extent of reaction. The complex dynamic behaviours include multiple stationary states, spatiotemporal periodic oscillations, aperiodic oscillations, the growth of travelling waves and spatial structures (Epstein, 1984). Long residence time corresponds to lower flow rate while a short residence time corresponds to higher flow rate. Figure 1-5 shows that chemical reactions could be ignited by the inflow of fresh reactant at a lower flow rate and quenched by a higher flow rate. If the residence time is long enough, the equilibrium state which corresponds to complete reaction could be approached. However, when the flow rate is
high, the system has low extent of reaction because chemical components are advected out of the domain before fully reacted. Depending on constraints such as residence time and the extent of reaction, systems can have multiple stationary states, which are represented by an unstable branch and a stable branch between the ignition, and extinction flow rates in Figure 1-5. In Figure 1-5, the extent of reaction is defined by:

\[ \xi = \frac{a_0 - a}{a_0} \]  

(1.1)

where \( a_0 \) and \( a \) are the initial and current concentration of reactant. \( \xi \) varies from zero at the start of a reaction to one at completion. The possible stationary-state patterns include unique, isola, mushroom, single hysteresis loop, and hysteresis loop plus isola as shown in Figure 1-6.

Figure 1-5 System behaviour for reactions coupled with flow (Ord et al., 2012).
Open flow systems can generally be categorized into two groups: time-dependent and time-independent. In homogeneous porous media, time-independent flow means that the residence time for each fluid particle is uniform and the shape of a fluid element is not changed. Most flows in nature are time-dependent. The assumption of uniform residence time does not hold for time-dependent flow. Time-dependent flow can result in “chaotic advection”, which means fluid elements flow in an unpredictable manner and small changes of initial conditions lead to totally different system behaviour (Aref, 2002, Aref, 1990, Khakhar et al., 1986, Moura et al., 2012, Tél et al., 2005). This mechanism is referred to as Lagrangian turbulence which is different from the turbulence in a normal fluid dynamics sense (Eulerian turbulence) (Tél et al., 2005). Because of the existence of a chaotic saddle and its associated stable and unstable manifolds, some fluid particles may undergo long excursions before being transported out of the domain. The most exceptional fluid particles, which locate exactly on the chaotic saddle, stay in the domain forever. When the fluid element moves, its shape becomes highly irregular. Time-dependent flow can continuously stretch, fold and re-orient a fluid element, generating highly irregular distribution patterns as shown in Figure 1-7. Because of this process, the distribution of residence time becomes fractal. This mechanism can give rise to patterns and dynamics fundamentally different from those in the time-independent flow case.

Figure 1-6 Five possible stationary state loci patterns in the reaction-diffusion process of time-independent flow (Gray and Scott, 1990). The vertical axis is the extent of the reaction whilst the horizontal axis is the residence time.
Figure 1-7 Fluid element is deformed by 2D time-dependent laminar flow (Welander, 1955).

In this study, hydrothermal mineralising systems are regarded as open flow chemical reactors held far-from-equilibrium. The reaction-diffusion-advection system involves many factors: fluid flow, heat generation and transfer, species transport and chemical reaction (including dissolution and precipitation). The mineralising systems are subject to constant non-equilibrium external conditions. Therefore, macroscopic spatial structures in steady states could be formed. A closed chemical system ultimately must come to equilibrium. Non-equilibrium phenomena occur either as a transient process or in response to some external chemical perturbation. However, in open systems, the states of non-equilibrium can be maintained indefinitely so long as the relevant reactant and energy supply is continuously fed to the system. As pointed out by Cross and Hohenberg, because the system is not near equilibrium, there is no a priori reason to suppose there exists a Gibbs ensemble or a free energy functional whose minima yield the patterns obtained under given external conditions (Cross and Hohenberg, 1993). The term “open” refers to a system where both mass and heat can enter and leave the system in a constrained manner. From a mathematical point of view, it means that the assumption of translational invariance and of a statistical steady state, is no longer valid in such systems. The concepts of chemical engineering can be applied to the formation of giant ore bodies.
In this thesis, we are interested in two different types of chemical reactions, in particular: autocatalytic reactions and bimolecular reactions. The reaction scheme of an autocatalytic reaction is represented by A+B→2B or A+2B→3B. Reactant B can convert reactant A into B. B is the reactant as well as the product of this type of chemical reaction. The rate equations for autocatalytic reactions are fundamentally nonlinear. This type of reaction leads to “infection-like” or “explosion-like” processes in which a small amount of stable phase B can completely convert the unstable phase A into product B. The patterns of this reaction are fronts propagating at some velocity with relatively sharp boundaries (Neufeld et al., 2002). When autocatalytic reactions are coupled with other reactions, the chemical systems can exhibit multiple steady states, hysteresis, periodic oscillations or chaos (Tél et al., 2005). An example of autocatalytic reaction in mineralising process is as follows (Anderson and Garven, 1987):

\[ H_2O + CO_2 \rightarrow HCO_3^- + H^+ \]

\[ ZnFe(CO_3)_2 + 4H^+ \leftrightarrow Fe^{2+} + Zn^{2+} + 2CO_2 + 2H_2O \]

\[ Zn^{2+} + H_2S \rightarrow 2H^+ + ZnS \]

\[ Fe^{2+} + H_2S \rightarrow 2H^+ + FeS \]
A positive feedback is triggered by the generation of \( H^+ \) by the flux of \( CO_2 \). Then \( Fe^{2+} \) and \( Zn^{2+} \) are further generated. Reaction of \( Fe^{2+} \) and \( Zn^{2+} \) with \( H_2S \) generates even more \( H^+ \). The autocatalytic chemical reaction may be regarded as an ingredient so as to explain the huge difference of mineral concentrations between ores and its surroundings. Another type of chemical reaction considered in this thesis is bimolecular which is caused by a collision between two reactants. Its scheme is represented by \( A+B\rightarrow C \). The rate of a bimolecular reaction between the reactant A and B is expressed by Equation 1.2:

\[
R = k(T)[A][B] \tag{1.2}
\]

where \( k \) is the reaction’s rate constant which is dependent on temperature. \([A]\) and \([B]\) are the reactants’ concentrations. Different from the autocatalytic reaction, both components A and B are needed to keep the reaction going on indefinitely.

The main purpose of this study is to model geochemical reactions associated with the mineralizing process, including fluid flow, heat generation and transfer and mass diffusion. From a chemical engineering point of view, the mixing of two or more fluids from completely different sources, plays an important role in chemical reactions. “Well mixed” chemical systems may exhibit a range of dynamics including steady, multi-stable, oscillatory and chaotic behaviour. However, unlike the stirring vessel from the chemical engineering area, fluid flow in porous media can only generate imperfect mixing. We extend these concepts to the case where reactants are not well mixed. The heterogeneous spatial distributions can significantly influence both physical and chemical phenomena in hydrothermal systems, which in turn impacts on mineral deposition. Two distinct mechanisms are regarded to result in dramatically enhanced mixing for chemical reactions and fluid flows in porous media: First, gradients in physical parameters such as chemical potential, fluid density and surface tension generate flow instabilities that propagate the reaction front. Secondly, so-called chaotic advection, a behaviour in which fluid particles follow chaotic trajectories, arises inherently from Stokes flow in open porous networks as a result of the complexity of the pore geometry. We refer the first one as “fingering” and the second one as “chaotic advection” or “chaotic mixing”. Both fingering and chaotic advection can significantly enhance mineralisation rates. Such interactions between chemical reaction and fluid advection generate mineral deposits with fractal spatial signatures similar to those observed in the field (Lester et al., 2012).
The interactions between fluid flow, temperature and chemical reaction are complex. On the one hand, in the presence of fluid pressure gradients or buoyancy forces and temperature gradients, convective fluid flow can be triggered and play an important role in efficiently mixing reactive fluids containing metal species in solution (Nield and Bejan, 1992, Zhao et al., 2008). On the other hand, chemical reactions in the porous medium can interact with hydrodynamic instabilities and influence the stability as well as the nonlinear spatiotemporal dynamics of the system (Ortoleva et al., 1987b). A combination of structural geology, nonlinear chemical dynamics and fluid mechanics is needed to perform the modelling of ore body mineralization. Structural geology defines the geometry and characteristics of the matrix. Fault and/or fracture zones typically exhibit hydraulic properties that are different from the surrounding rocks. Sometimes the horizontal and vertical extension of a fault/fracture zone can be in the order of several kilometres (Alt-Epping and Zhao, 2010). Geochemistry specifies the nature of the coupled reactions that can occur in the upper crust of the Earth and in general these coupled reactions are of a nonlinear nature.

Two types of numerical modelling are applied to different scenarios to investigate the fully coupled processes of chemical reaction, fluid flow, diffusion and thermal effects. Continuous modelling techniques are used to explore the pattern formation process in dissolution and precipitation process, non-linear interactions of dynamic reactive interfaces, and the transport of mineral particles at the fracture scale. Discrete modelling techniques are applied to examine the chaotic motion of mineral particles subject to periodic fluid flow. This thesis is only focused on the understanding of physical and chemical mechanisms behind giant ore body formation and mineralization in permeable rocks. We stress here that we are not concerned with specific process within any particular ore deposits. Therefore, general types of geochemical reactions such as the autocatalytic reaction A+B->2B (or A+2B->3B) and the bi-molecular reaction A+B->C are adopted. We are trying to gain some understanding in a quantitative rather than qualitative way by using different simulations.

1.3 RESEARCH OBJECTIVES

The primary goals of this research are:
1. to explore the origin of the characteristics of mineralised hydrothermal systems within a non-equilibrium framework in which mineral diffusion, fluid flow and chemical reactions are fully coupled and to probe the complex interactions of this coupled reaction-diffusion-advection process in the presence of temperature.

2. to integrate multi-discipline modelling spanning geology, geodynamics, chemical engineering and fluid dynamics in order to obtain a better understanding of the formation mechanisms of ore deposits from micro-scales to regional-scales.

3. to simulate the possible distribution of chemo-hydrodynamic patterns during dissolution and precipitation processes.

4. to investigate the possible mechanisms which are responsible for the creation of large local depositions and the fractal distribution of the minerals and link these mechanisms with observed spatiotemporal signatures of mineral deposition.

5. to identify critical parameters which produce the successful mineralising systems and provide useful diagnostic criteria for exploration geologists.

1.4 THESIS ORGANIZATION

This thesis consists of six chapters. Chapter 2 to chapter 5 are written in manuscript style, and are prepared to be published as journal articles. The five chapters following this introductory chapter are arranged as follows:

Chapter 2: modelling of pattern formation in dissolution and precipitation of open porous media flow

Chapter 2 simulates the formation of chemo-hydrodynamic patterns formed in the mineralising processes which involve both dissolution and precipitation in the presence of open flow. Hydrothermal mineralising porous medium is treated as an open flow reactor. The porous medium where the mineralising process takes place is initially saturated with fluid. The reactant A of the associated chemical reaction can be continuously supplied into the fluid by dissolution from the matrix. An autocatalytic chemical reaction A+2B->3B takes place in the fluid space and B can precipitate into product of P at some decay rate. At the same time, the fluid in the porous media is advected by an open flow. The extended
Gray-Scott model is used to simulate the localized structures which are analogous to those observed in the field. Then the dynamical behaviour of the chemical system is determined by the bifurcation controlling parameters: supply rate of reactant A and decay rate of B and fluid velocity. Both linear stability analysis and nonlinear simulation have been carried out to investigate the impact of flow on the distribution patterns of mineral deposits. Hydro-chemical patterns such as spot multiplication, stripe, travelling fronts and pulses, as well as spatiotemporal chaos are successfully simulated.

Chapter 3: non-linear interactions of dynamic reactive interfaces in hydrothermal mineralising processes

Chapter 3 numerically investigates the patterns and non-linear dynamics of miscible viscous fingering by using an A+B->C type of reaction in chemically reactive porous media. Reactive transport modelling has been adopted to investigate the complex interactions when a fluid containing reactant A displaces another fluid containing reactant B of different temperature. The distribution of chemical components and heat is affected by the flow field while the flow field can be in turn affected by fluid mobility caused by the difference of chemical components and temperature. A complex feedback process sets in. Chapter 3 studies the effects of the solute and thermal mobility ratio, the thermal lag coefficient, the Lewis number, and the Damkohler number on the distribution patterns and chemical production in ore-forming systems.

Chapter 4: modelling of chaotic advection of mineral particles induced by periodic open flow

Chapter 4 presents two-dimensional discrete and continuous computational modelling to study the fracture-scale diffusion and chaotic advection processes in hydrothermal mineralising systems. Chaotic advection is triggered by the periodicity of fluid flow. Different non-linear tools have been used to characterise the transport process of mineral particles.

Chapter 5: modelling of fracture-scale chemical reaction and chaotic advection induced by periodic flow
Chapter 5 couples chemical reaction into the fracture-scale diffusion and chaotic advection processes presented in chapter 4. The impact of steady flow and chaotic flow on chemical reaction is investigated. Different chemical schemes such as an autocatalytic reaction with multi-stability and the A+B→C type of reaction are simulated.

Chapter 6 summarizes the main findings of this research and suggests the perspectives for future studies.
CHAPTER 2

MODELLING OF PATTERN FORMATION IN DISSOLUTION AND PRECIPITATION OF OPEN POROUS MEDIA

2.1 INTRODUCTION

One of the most important issues involved in the understanding of giant ore deposit formation processes is the emergence of spatial patterns in the presence of porous media flow. The apparently irregular pattern of distribution of minerals such as gold, uranium, copper, zinc and lead, etc. in mineralising hydrothermal systems has attracted extensive research efforts (Carlson, 1991, Hou et al., 2006, Mao et al., 2008, Jefferson et al., 2007).

Those spatial distribution of mineral deposits are proved to be fractal (Raines, 2008, Agterberg et al., 1993, Ford and Blenkinsop, 2008). Reaction and diffusion of chemical species are thought to be two fundamental mechanisms behind the processes that lead to the fractal patterns of different mineral deposits (Maini et al., 1997, Cross and Hohenberg, 1993). The interplay of chemical reaction and diffusion causes the homogeneous state of the system to become unstable and gives rise to the spontaneous formation of spatially heterogeneous structures (Turing, 1952, Rovinsky and Menzinger, 1992). Diffusion was traditionally regarded as a homogenizing mechanism because it can disperse any perturbation in the system. However, the result from Turing (Turing, 1952) shows that diffusion can cause instability within a chemical system, leading to spatial patterns.

Another reaction-diffusion system which attracted extensive research efforts is the Gray-Scott model (Gray and Scott, 1985, Pearson, 1993, Mazin et al., 1996, Rasmussen et al., 1996, Ueyama, 1999, Wei, 2001, McGough and Riley, 2004, Wei and Winter, 2008, Wang et al., 2011, Gray and Scott, 1983, Gray and Scott, 1984). It simulates the cubic autocatalytic chemical reaction $A + 2B \rightarrow 3B$ as well as the decay of reactant B to product P. Its governing equations are of the following form:
\[
\frac{du}{dt} = D_u \Delta u - uv^2 + F(1 - u) \quad (2.1)
\]

\[
\frac{dv}{dt} = D_v \Delta v + uv^2 - (F + k)v \quad (2.2)
\]

where \( u \) is the dimensionless reactant concentration of A and \( v \) is the dimensionless concentration of catalyst, B. \( D_u \) and \( D_v \) are the diffusivities of the chemicals A and B. \( F \) denotes the rate at which reactant A is fed and \( k \) is the rate constant which equals the rate at which B is converted to an inert product.

Wei and Winter mathematically proved the existence and stability of single and multiple spots patterns for the Gray-Scott system in a two-dimensional domain which is far from spatial homogeneity (Wei, 2001, Wei and Winter, 2003). Pearson found that the two dimensional Gray-Scott model can generate very complex patterns depending on the controlling parameters \( F \) and \( k \) (Pearson, 1993). Those irregular spatiotemporal patterns can be generally categorized into 12 groups as shown in Figure 2-1. The resulting patterns include global Turing structures, stable localized structures, interacting fronts, travelling waves, mixed Turing-Hopf modes and spatiotemporal chaos.

![Figure 2-1 Groups of patterns found by Pearson (Pearson, 1993).](image)

By setting the diffusivities \( D_u \) and \( D_v \) to zero, the local dynamics of the “reduced” Gray-Scott model can be investigated (McGough and Riley, 2004, Malchow and Petrovskii,
2002). The system has up to three steady states. As shown in Figure 2-2, below the saddle node line, the system has only one trivial homogeneous steady state

\[ E_0 = (u_0, v_0) = (1,0) \]  \hspace{1cm} (2.3)

which is always stable. Whereas above the saddle node line where

\[ \Delta_1 = 1 - \frac{4(F + k)^2}{F} > 0 \]  \hspace{1cm} (2.4)

the system has two nontrivial steady states \( E_1 = (u_1, v_1) \) and \( E_2 = (u_2, v_2) \)

\[ E_1 = (u_1, v_1) = \left( \frac{1 + \sqrt{\Delta_1}}{2}, \frac{F(1 - \sqrt{\Delta_1})}{2(F + k)} \right) \]  \hspace{1cm} (2.5)

\[ E_2 = (u_2, v_2) = \left( \frac{1 - \sqrt{\Delta_1}}{2}, \frac{F(1 + \sqrt{\Delta_1})}{2(F + k)} \right) \]  \hspace{1cm} (2.6)

Figure 2-2 Phase diagram of the Gray-Scott model (Ueyama, 1999).

The linear stability analysis indicates that the state \( E_1 \) is a saddle point which is always unstable (McGough and Riley, 2004) while the state \( E_2 \) loses its stability via a Hopf bifurcation from a stable state to an unstable state. When \( k \) is large, the system has only one trivial steady state. All trajectories approach the trivial state \( E_0 = (u_0, v_0) \). Inside the
region bounded by the solid line in Figure 2-2, there are three equilibrium points. Above the dotted line and below the upper solid line, the system is bi-stable. The saddle-node bifurcation line and Hopf bifurcation line collide with each other at \((k_c, F_c) = (\frac{1}{16}, \frac{1}{16})\).

When \(k\) decreases for a fixed \(F < F_c\), two unstable equilibria appear via a saddle-node bifurcation, then one of these changes from an unstable node to an unstable focus as shown in Figure 2-3 and eventually recovers its stability via Hopf bifurcation. The Hopf bifurcation is of subcritical type when \(F > F^* \approx 0.0116\), and the resulting periodic orbits are unstable as shown in Figure 2-3.

![Figure 2-3](image)

Figure 2-3 Phase portrait of the Gray-Scott model (Nishiura and Ueyama, 1999).

The presence of a flow can significantly affect the resulting patterns generated from reaction-diffusion processes (Yochelis and Sheintuch, 2009, Nakagaki et al., 1999, Zhao et al., 2000b, Kuznetsov et al., 1997, Kuptsov et al., 2005). Zhao et al. (Zhao et al., 2000a) mathematically proved the existence of non-uniform solutions for the steady-state problem and used the finite element method to simulate the patterns formed in the Brusselator type of non-equilibrium chemical reaction in a fluid-saturated medium with the presence of flow. Both constant horizontal and convective flows were considered. The conclusion shows that the fluid flow has a profound effect on the formation of ore patterns in a fluid-
saturated porous medium. If a localized initial perturbation gives rise to growing amplitudes at all fixed points in space, this fluid instability is called an absolute one. If the growing perturbation drifts in such a way that observation at a fixed point asymptotically shows an amplitude that decays towards zero, this is known as a convective instability (Chomaz, 1992, Kuznetsov et al., 1997). Results show that Hopf and Turing instabilities can be either absolute or convective, depending on bifurcation controlling parameters (Kuznetsov et al., 1997).

The goal of this chapter is to simulate the formation of mineral patterns in the dissolution and precipitation processes by using the Gray-Scott model with the presence of uniform and chaotic flow. To the best of our knowledge, few studies have been performed to investigate the pattern formation of mineral deposit distribution. We believe it will shed some light on the understanding of the distribution of metals within giant ore deposits. The outline of this paper is as follows. In section 2.2 we model the dissolution and precipitation process by using the extended Gray-Scott model which couples uniform flow and chaotic flow. In section 2.3 we perform the linear stability analysis for the uniform flow case. In section 2.4 nonlinear simulations are carried out to investigate how the flow can affect the distribution of mineral product. The paper concludes with a summary of our findings in section 2.5.

### 2.2 GRAY-SCOTT MODEL IN THE PRESENCE OF FLOW

Following the same method as Mazin et al. (Mazin et al., 1996), we model the following chemical reactions in porous media:

\[
\begin{align*}
A + 2B & \rightarrow 3B \\
B & \rightarrow P
\end{align*}
\]

Chemical reactant A can be transformed into product B. B is the catalyst as well as the product of this reaction which is called autocatalytic. If A is continuously fed into the system, the concentration of B will become larger. Therefore the system will exhibit “self-enhancing” behaviour which is constrained by the second reaction represented by the precipitation or decay of B into the product of P.
We assume that the porous medium is saturated with water, then chemical reactant A can be released from the matrix space into the pore space because of dissolution. The feeding rate is as follows:

\[ D(a) = F(1 - a) \]  \hspace{1cm} (2.9)

\( F \) is a constant characterising the supplement rate of reactant A. We also assume the precipitation rate of B is

\[ P(b) = -(F + k)b \]  \hspace{1cm} (2.10)

The chemical kinetics for the cubic autocatalytic chemical reaction is

\[ R = ab^2 \]  \hspace{1cm} (2.11)

Because of the decay process, the sum of concentration of A and B are no longer conserved. Hence, we obtain a system involving two independent concentrations \( a \) and \( b \).

Taking fluid flow and diffusion into consideration, the final reaction-diffusion-advection equations are

\[ \frac{da}{dt} + \bar{u} \cdot \nabla a = D_a \Delta a - ab^2 + F(1 - a) \]  \hspace{1cm} (2.12)
\[
\frac{db}{dt} + \bar{u} \cdot \nabla b = D_b \Delta b + ab^2 - (F + k)b
\]  

(2.13)

\(\bar{u}\) is the flow field. \(D_a\) and \(D_b\) are the diffusivity of A and B, respectively.

### 2.3 LINEAR STABILITY ANALYSIS

For the above reaction-diffusion-advection system, our interest is the stability of its steady states. We can introduce some small perturbations around the steady states into the system. When the system is subject to these perturbations, a transient response of this system will take place. If such perturbations decay with time, then the corresponding steady state is regarded as stable. However, if any small perturbation grows with time, the corresponding steady state is unstable. The nonlinear system will evolve from one steady state to another steady state.

Assume the steady state of the above nonlinear system is \((A_{ss}, B_{ss})\) and the small perturbation is \((A', B')\), then if we substitute into Equations 2.12-2.13 and drop the higher order perturbation, the resulting linear stability equations governing small perturbations are

\[
\frac{dA'}{dt} + \bar{u} \cdot \nabla A' = D_a \Delta A' - 2A_{ss}B_{ss}B' - A'B_{ss}^2 - FA' 
\]  

(2.14)

\[
\frac{dB'}{dt} + \bar{u} \cdot \nabla B' = D_b \Delta B' + 2A_{ss}B_{ss}B' + A'B_{ss}^2 - (F + k)B' 
\]  

(2.15)

\(A'\) and \(B'\) represent small fluctuations in the steady states \(A_{ss}\) and \(B_{ss}\).

We can “freeze” time by applying quasi-steady-state approximation theory which assumes that the growth rate of the perturbations will be much faster than the rate of change of the base state (Tan and Homsy, 1986).

\[
A' = \alpha(x, t_0)e^{\sigma(t_0)t} 
\]  

(2.16)

\[
B' = \beta(x, t_0)e^{\sigma(t_0)t} 
\]  

(2.17)
Then we can obtain

\[ D_a \Delta \alpha - \bar{u} \cdot \nabla \alpha - (B_{ss}^2 + F + \sigma(t_0)) \alpha - 2A_{ss}B_{ss} \beta = 0 \]  
\[(2.18)\]

\[ D_b \Delta \beta - \bar{u} \cdot \nabla \beta + B_{ss}^2 \alpha + (2A_{ss}B_{ss} - F - k - \sigma(t_0)) \beta = 0 \]  
\[(2.19)\]

We can decompose the perturbation into Fourier components and seek the solutions of the form

\[ \alpha = \Phi \exp(i\theta x) \]  
\[(2.20)\]

\[ \beta = \Psi \exp(i\theta x) \]  
\[(2.21)\]

\(\theta\) is the wavenumber of the perturbation. \(\theta = 0\) corresponds to a spatially uniform mode while \(\theta > 0\) corresponds to a spatially non-uniform mode. \(\sigma\) is the corresponding growth rate for each wavenumber. If the real part of \(\sigma\) is positive, from a mathematical perspective, the perturbation will become larger and larger. The system is unstable and the associated stationary state is unstable as a result.

Substituting Equations 2.20 and 2.21 into Equations 2.14 and 2.15, we have

\[ M \begin{pmatrix} \Phi \\ \Psi \end{pmatrix} = \sigma \begin{pmatrix} \Phi \\ \Psi \end{pmatrix} \]  
\[(2.22)\]

where

\[ M = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \]  
\[(2.23)\]

and

\[ m_{11} = -\theta^2D_a - u\theta i - B_{ss}^2 - F \]  
\[(2.24)\]

\[ m_{12} = -2(F + k) \]  
\[(2.25)\]
2.3.1 Stability analysis for trivial steady states

The nonlinear system with governing equations 2.12 and 2.13 has one uniform stationary state $A_{ss} = 1, B_{ss} = 0$. Substitute the value of $A_{ss}$ and $B_{ss}$ into Equations 2.24-2.27, we can have

$$m_{11} = -\theta^2 D_a - u\theta i - F$$

(2.28)

$$m_{12} = 0$$

(2.29)

$$m_{21} = 0$$

(2.30)

$$m_{22} = -\theta^2 D_b - u\theta i - F - k$$

(2.31)

The two eigenvalues of matrix $M$ are

$$\sigma_1 = m_{11}$$

(2.32)

$$\sigma_2 = m_{22}$$

(2.33)

We conclude that this uniform steady state is stable for any flow rate $u$ because both of the real parts of eigenvalue, $\text{Re}(\sigma_1)$ and $\text{Re}(\sigma_2)$, are negative. The difference introduced by flow is that the steady state is absolutely stable for the no-flow case, which means any perturbation decays exponentially while the steady state is convectively stable for the flow case, which means any perturbation decays in an oscillatory way. The frequency of the oscillation is determined by the product of flow velocity $u$ and wavenumber $\theta$.

2.3.2 Stability analysis for other uniform steady states

For other uniform steady states, the eigenvalue $\sigma$ is determined by
\[ \det(M - \sigma I) = \sigma^2 + m(\theta)\sigma + h(\theta) = 0 \quad (2.34) \]

where

\[ m(\theta) = -(m_{11} + m_{22}) = \theta^2(D_a + D_b) + 2u\theta i + B_{ss}^2 - k \quad (2.35) \]

and

\[
\begin{align*}
    h(\theta) &= m_{11}m_{22} - m_{12}m_{21} \\
    &= (D_a \theta^2 + u\theta i + B_{ss}^2 + F)(D_b \theta^2 + u\theta i - F - k) + 2(F + k)B_{ss}^2 \quad (2.36)
\end{align*}
\]

Both \( m(\theta) \) and \( h(\theta) \) are complex numbers. The solution for Equation 2.34 is not necessarily conjugate.

Assume that

\[ m(\theta) = A(\theta) + iB(\theta) \quad (2.37) \]
\[ h(\theta) = C(\theta) + iD(\theta) \quad (2.38) \]

Expressions \( A(\theta), B(\theta), C(\theta) \) and \( D(\theta) \) have the following forms:

\[ A(\theta) = \theta^2(D_a + D_b) + B_{ss}^2 - k \quad (2.39) \]
\[ B(\theta) = 2u\theta \quad (2.40) \]
\[
C(\theta) = D_aD_b\theta^4 + (\langle B_{ss}^2 + F \rangle D_b - (F + k)D_a - u^2)\theta^2 + (F + k)(B_{ss}^2 - F) \quad (2.41)
\]
\[ D(\theta) = u\theta^3(D_a + D_b) - ku\theta + u\theta B_{ss}^2 = u\theta A(\theta) \quad (2.42) \]

If the system is stable without diffusion, the inequality \(-B_{ss}^2 + k < 0\) applies. Since \( \theta^2(D_a + D_b) > 0 \), we have \( A(\theta) > 0 \). Because \( u \) and \( \theta \) are positive, therefore, \( B(\theta) \) and \( D(\theta) \) are positive.
Because the following equation holds

\[ \Delta_1 = A(\theta)B(\theta) - 2D(\theta) = 0 \]  \hspace{1cm} (2.43)

so the real parts of eigenvalue are

\[ \text{Re}(\sigma) = -\frac{1}{2} (A(\theta) \pm |\Delta_2|^{1/2}) \]  \hspace{1cm} (2.44)

which is bounded by

\[ \Delta_2 = 4C(\theta) + B(\theta)^2 - A(\theta)^2 \geq 0 \]  \hspace{1cm} (2.45)

For the two eigenvalues in Equation 2.44, one of them is guaranteed to have negative real part shown as follows:

\[ \text{Re}(\sigma) = -\frac{1}{2} (A(\theta) + |\Delta_2|^{1/2}) < 0 \]  \hspace{1cm} (2.46)

For any real positive wave number \( \theta \), if the other eigenvalue also has a negative real part (shown in Equation 2.47), then the steady state is stable. Otherwise, the corresponding steady state is a saddle point.

\[ \text{Re}(\sigma) = -\frac{1}{2} (A(\theta) - |\Delta_2|^{1/2}) \]  \hspace{1cm} (2.47)

which reduces to

\[ H(\theta^2) = (D_a^2 + D_b^2)\theta^4 + 2(D_a(B_{ss}^2 + F) - D_b(F + k))\theta^2 \]

\[ + 2(F + k)(B_{ss}^2 - F) + (B_{ss}^2 - k)^2 \]  \hspace{1cm} (2.48)

Assume

\[ \Delta_3 = D_a(B_{ss}^2 + F) - D_b(F + k) \]  \hspace{1cm} (2.49)
\[ \Delta_4 = 2(F + k)(B_{ss}^2 - F) + (B_{ss}^2 - k)^2 \]  

We have

\[ \min(H(\theta^2)) > 0 \quad \text{if} \quad \Delta_3 \leq 0 \]  

\[ \Delta_4 > 0 \quad \text{if} \quad \Delta_3 > 0 \]  

which is

\[ (D_a^2 + D_b^2) \Delta_4 > \Delta_3^2 \quad \text{if} \quad \Delta_3 \leq 0 \]  

\[ \Delta_4 > 0 \quad \text{if} \quad \Delta_3 > 0 \]  

### 2.4 NONLINEAR SIMULATION

Depending on different control parameters \( F \) and \( k \), the Gray-Scott model can exhibit a variety of dynamical behaviours. The right spatially uniform purple area corresponds to the trivial state of \( a = 1 \) while the left blue area represents \( a \approx 0.2 \). In the intermediate green and yellow area as shown in Figure 2-5, patterns such as stripe, multiple-dot, standing or travelling waves have been observed because of Hopf and Turing bifurcations (Pearson, 1993). Between the homogeneous “blue” and “red” states, those patterns were generally categorized into 12 different groups by Pearson as shown in Figure 2-1.
In this section, we perform nonlinear numerical simulation to investigate the effect of porous media flow on the formation of the patterns caused by the dissolution-precipitation process. Three different flow regimes are considered in the nonlinear simulation. The first is horizontal uniform fluid flow. The second is time-dependent horizontal flow and the third is chaotic flow. The size of the dimensionless system for the first and second horizontal flow case are $2.5 \times 2.5$ while the geometry for the chaotic flow case is a main channel of size $3 \times 1$ in which the flow is manipulated by a smaller side channel at an angle. We apply insulation conditions for the upper and lower boundaries and Neumann boundary conditions for the right and left boundaries, respectively. Initially, the entire system is divided into two parts. The smaller square located symmetrically at the centre has a size of $0.2 \times 0.2$ and has an initial state of $(a = 0.5, b = 0.25)$. Outside of this square, the system is placed in the trivial state of $(a = 1, b = 0)$. For the nonlinear simulation, we choose the dimensionless constant diffusivities of A and B as $D_a = 2e^{-5}$ and $D_b = 1e^{-5}$. The Gray-Scott model has been investigated by numerous researchers from different disciplines. Rather than focusing on the scale of time, this thesis extends the original model to simulate the vast complexity of mineral patterns during dissolution/precipitation in porous media.

As can be seen from Figure 4-5, porous media flow spans an enormously large range. In chapter 2, the diffusivity scale is at around $e^{-5} \text{ m}^2/\text{s}$ and the flow velocity scale is at around $e^{-4}\text{m/s}$. The domain size is 2.5 km. It takes around $e^8\text{s}$ for a mineral particle to be transported from one side of domain to the other. In a more realistic scenario, the porous media flow is around $e^{-8}\text{m/s}$, which means the time scale is around $e^{12}\text{s}$.
2.4.1 Constant horizontal flow

In study case 1, we set $k = 0.06$ and $F = 0.024$, respectively. As shown in Figure 2-5, we expect a multiple-spot pattern. In order to investigate the impact of horizontal flow, we use three flows flowing from left side to right side with a velocity of $v_1 = 0$, $v_2 = 1\times10^{-4}$, $v_3 = 5\times10^{-4}$ at different dimensionless times as shown in Table 2-1.

Table 2-1 Scenarios of different times and velocities for case study 1

<table>
<thead>
<tr>
<th>dimensionless velocity</th>
<th>dimensionless time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>v1</td>
<td>A1</td>
</tr>
<tr>
<td>v2</td>
<td>B1</td>
</tr>
<tr>
<td>v3</td>
<td>C1</td>
</tr>
</tbody>
</table>

Depending on the parameters, we can obtain the so-called “self-replicating” patterns which means that the spot may self-replicate in a self-sustaining fashion and develop into a variety of time-dependent or time-independent asymptotic states (Wei and Winter, 2003). For the non-flow case, the spots increase in number until they fill the whole domain. As the spots become further apart, they begin to elongate in the direction perpendicular to their motion. When they are stretched to a critical size, the gradient is no longer sufficient to maintain the centre in the blue state, so the centre decays to red, leaving two blue spots (Pearson, 1993). These spots generally maintain the symmetry of the pattern. However, this symmetry is broken by the constant horizontal flow. In Figure 2-6 B1-B4, C1-C4, we can see that in the downstream direction, the effect of replication is suppressed. As these spots grow parallel to the flow direction, they are further stretched by the flow, making it easier to split into two. We can clearly see this effect from Figure 2-6 C4, which has a higher flow velocity.
In study case 2, we change the value of $k$ and $F$ to 0.056 and 0.028, respectively. A stripe-like pattern is expected for the non-flow case. Similar to study case 1, we assume three flows flowing from the left side to the right side with the same constant horizontal velocity as case 1.

Table 2-2 Scenarios of different times and velocities for case study 2

<table>
<thead>
<tr>
<th>dimensionless velocity</th>
<th>dimensionless time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400</td>
</tr>
<tr>
<td>$v_1$</td>
<td>A1</td>
</tr>
<tr>
<td>$v_2$</td>
<td>B1</td>
</tr>
<tr>
<td>$v_3$</td>
<td>C1</td>
</tr>
</tbody>
</table>

The final state of the stripe-like pattern is time-independent. It consists mainly of stripes but there exist localized unstriped regions. We can see the spatiotemporal evolution of the concentration of reactant $A$ at point $(0, 0.2)$ of the velocity of $v_1$ as shown in Figure 2-8. Clearly, there exists a moving reaction front propagating radially outward without the
presence of horizontal flow in Figure 2-7 A1-A4. The symmetry is broken by horizontal constant flow as shown in Figure 2-7 B1-B4 and C1-C4. The localized regions are squeezed on the upstream direction while stretched on the downstream direction.

![Figure 2-7 Time evolution of stripe-like pattern for different scenarios from Table 2-2.](image)

Figure 2-7 Time evolution of stripe-like pattern for different scenarios from Table 2-2.
2.4.2 Time-dependent horizontal flow

The parameters of study case 3 are similar to those in study case 2 only with the difference that a time-dependent horizontal flow is adopted. The velocity is assumed as follows

\[ V = A \sin(\omega t) + B \] (2.55)

with \( A = 2 \times 10^{-4} \), \( B = 5 \times 10^{-4} \) and frequencies \( \omega_1 = 2 \pi \times 0.01 \) and \( \omega_2 = 2 \pi \times 0.05 \).
Figure 2-9 Pattern comparison between constant flow (A1-A4) and time-dependent flows of different frequencies $\omega_1$ (B1-B4) and $\omega_2$ (C1-C4) at time 400, 800, 1200, 1600.

By comparing Figure 2-9 A1-A4 with Figure 2-9 B1-B4 and Figure 2-9 C1-C4, we can conclude that not only the time-dependence but also the frequency of flow can dramatically change the pattern profile.

2.4.3 Chaotic flow

In this section, we apply our simulation to a more realistic geoscience scenario. The geometry for the model is shown in Figure 2-10. This geometry is similar to that proposed for many unconformity-related uranium deposits (Raffensperger and Garven, 1995a, Raffensperger and Garven, 1995b, Schaub et al., 2003, Jefferson et al., 2007, De Veslud et al., 2009, Cui et al., 2012a, Cui et al., 2012b). The horizontal constant porous media flow is manipulated by a time-dependent side fracture-flow with higher magnitude. The system configuration and flow velocity field can be found in detail in Appendix 1. We obtain a complex time-dependent flow field which can generate chaotic mixing effects. At $t = 5000$, we can see that an isolated region is traced out by the particles illustrated by red dots. Those isolated regions are potentially important from a mineralization point of view.
as the geochemical reaction can be pinned there for a longer time, giving minerals sufficient time to dissolve, react and precipitate. The tracing particles would be transported out of the domain if only steady flow exists.

![Image](image1)

Figure 2-10 Chaotic flow traced out by particle with side entry flow.

We are interested in what kind of effects the chaotic fluid flow can exert on the spatiotemporal evolution of mineral distribution for the far-from-equilibrium chemical reaction. In particular, we investigate the role of flow velocity and frequency on the distribution of minerals. The study cases are listed in Table 2-3.

Table 2-3 Scenarios of different times and velocities for chaotic flow case

<table>
<thead>
<tr>
<th>dimensionless velocity</th>
<th>dimensionless time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>v1</td>
<td>A1</td>
</tr>
<tr>
<td>v2 = 5*v1</td>
<td>B1</td>
</tr>
<tr>
<td>v3 = 10*v1</td>
<td>C1</td>
</tr>
</tbody>
</table>

As can be seen from Figure 2-11, higher velocity flow can confine the spreading of minerals to an isolated region whereas for lower flow velocity, the chemical reactive front can overcome the vortex boundary generated by chaotic flow and spread to the whole domain. The radially growing pattern is strongly suppressed. The shapes of the spots are more irregular as shown in Figure 2-11.
Figure 2-11 Pattern profile for different flow velocity $v_1$ (A), $v_2$ (B), $v_3$ (C) at dimensionless time 500 (1), 1000 (2), 2000 (3), 4000(4).

Figure 2-12 Contour plots for different flow velocity $v_1$ and $v_3$ at time 4000.
In order to investigate the frequency effect, we maintain the flow velocity constant at $v_2$ and raise the frequency from $\omega_0 = 2 \times \pi/100$ to by a factor of four $\omega_1 = 4 \times \omega_0$ and plot the distribution of reactant A at time 500, 1000, 2000, 4000, respectively. As illustrated in Figure 2-13, more spots are generated when the frequency is increased.

![Image 1](image1.png)
![Image 2](image2.png)
![Image 3](image3.png)
![Image 4](image4.png)

Figure 2-13 Pattern comparison between different flow frequency at $t = 500, 1000, 2000, 4000$.

Another interesting phenomenon is the disappearance of spots in a chaotic flow regime. In the no-flow or constant horizontal flow cases, when one spot is generated by self-replicating, it will never vanish. However, it will “die” in the chaotic flow regime as illustrated by Figure 2-14. The disappearance or replication of a spot is dependent on the lateral diffusive and advective flux of reactant A into it. Due to the chaotic convective effects of porous media flow, the concentration gradient can no longer be maintained, causing the disappearance of spots. In general, the growth rate is diminished.
2.5 CONCLUSION

In summary, the formation and distribution of patterns in the dissolution and precipitation process has been modelled, with the presence of flow in porous media by using the extended Gray-Scott model. Linear stability analysis was performed to see how the flow affects the stability of steady states. The results show that fluid flow can introduce extra instability into the reaction-diffusion system. When there is no flow, any perturbation around the trivial steady state will decay exponentially. For the flow case, it will decay in an oscillatory way with decreasing amplitude. The frequency of the decaying oscillation is determined by the product of flow velocity and a wavenumber of the perturbation. The question of linear stability analysis for spatially non-uniform steady states is still open.

Furthermore, numerical nonlinear simulations were carried out to see the formation processes of different patterns under different flow scenarios. Depending on the controlling parameters, a variety of spatiotemporal patterns characterising the mineralising processes can be generated. Both spot and stripe patterns have been simulated with the presence of flow. For the constant horizontal flow case, the propagation of both spot-replication and of stripes is suppressed downstream of the flow. For the time-dependent flow, the frequency of the flow can strongly affect the distribution of chemical concentration. For the chaotic flow case, higher flow rates can curb the propagation of chemical fronts, making the chemo-hydrodynamic pattern occupy less space. Higher frequencies of flow can result in patterns with a larger number of spots. It can be concluded that both the geometry and the

![Figure 2-14 Disappearance of a spot in the chaotic flow at different time t = 200, 240, 280, 320.](image-url)
porous media flow have profound effects on the pattern selection process for the non-equilibrium dissolution-precipitation system in a fluid-saturated porous medium.
CHAPTER 3

NON-LINEAR INTERACTIONS OF DYNAMIC REACTIVE INTERFACES IN HYDROTHERMAL MINERALISING PROCESSES

3.1 INTRODUCTION

The transport of solutes and heat through porous media and modification of porous media by reactive fluids has become an important area of research in the mineralization process of Earth science. Giant hydrothermal ore systems can be regarded as chemical reaction vessels held far from equilibrium by the influx of heat and mass (Ord et al., 2012). Heat and fluid flow can keep the ore-forming system active, otherwise, the system could be quenched and only evolve to the equilibrium steady state, leading probably to a failed mineralised system. The formation of giant hydrothermal ore bodies is a metasomatic process whereby the influx of heat and of large volumes of mineral-rich fluids results in chemical reactions both within the fluids, and between the fluids and the rock mass (Lester et al., 2012, Ord et al., 2012). Aqueous solutions and heat that flow through a porous rock and interact with its mineral components establish a moving fluid front as well as a thermal front in the rock (Ortoleva et al., 1987a). Formation of ore deposits requires high fluid/rock ratios, a focussing system, and a suitable depositional site in terms of high porosity (intrinsic, mechanical and chemical) and permeability, and an appropriate chemistry (Marshall and Gilligan, 1987). Fyfe proposes that wherever large volumes of mineral rich fluid flow through soil, sediment or rock, the potential exists to form ore deposits. His analysis of liquid-state mobilization as a major ore-forming process, particularly during metamorphism and deformation, is most compelling (Fyfe et al., 1958, Fyfe et al., 1976, Kerrich et al., 1977). Relatively rapid, large-scale fluid circulation is likely during metamorphism, and geologist have been discussing possible consequences of this for mass and heat transport (Etheridge et al., 1983).

When temperature, fluid flow and chemical reactions are coupled, the interaction is complex. The most important mechanisms involving mass and heat transport are advection,
molecular diffusion, and chemical reaction. Chemical reaction can not only change the physical properties of the porous medium, such as porosity and permeability, through dissolution or precipitation, but also alter properties such as the density and viscosity of fluids in porous media. Therefore, there exists a feedback between chemistry and hydrodynamics. Law pointed out that the evolution of giant hydrothermal systems may be a progression through many exothermic-endothermic transitions in the same way as efficiently combusting or explosive systems do (Law, 2006, Ord et al., 2012). Endothermic-dominated reactions could result in a slight decrease in temperature with an attendant increase in both the viscosity and density of the fluid in the system thus initiating brecciation (Lester et al., 2012, Ord et al., 2012). Thermal instability may take place because of the heat generated by chemical reactions and/or exchanged between rocks and fluids in mineralising systems.

The spatiotemporal dynamics resulting from the interplay between hydrodynamics and chemical reaction can be rather complex because a number of effects such as viscosity or density variations, surface tension or heat effects may come into play. As soon as a denser fluid lies on top of a lighter one in the gravity field, a hydrodynamic instability known as a Rayleigh-Taylor instability will occur. The so-called Rayleigh-Saffman instability refers to an instability occurring when a fluid of high mobility displaces a fluid of low mobility (Saffman et al., 1958). There is a vast literature studying viscous fingering which is a hydrodynamic instability that occurs when a less viscous fluid tends to penetrate and finger through a more viscous fluid in nonreactive and isothermal systems (Saffman et al., 1958, Wooding, 1969, Homsey, 1987). Tan & Homsy (Tan and Homsy, 1986) carried out the first analyses of the linear stability of a fluid front with miscible properties under quasi-steady state approximation which assumes the growth rate of disturbances to be much faster than the rate of change of the base state. They also found that transverse dispersion stabilizes
disturbances with a wavenumber greater than a certain value and existence of the most “dangerous” wavenumber which has the biggest growth rate for fixed mobility ratio. Tan and Homsy (Tan and Homsy, 1988) also performed nonlinear simulations for viscous fingering for miscible displacement using the Fourier spectral method. They simulated phenomena in the nonlinear regime such as spreading, shielding and merging and explained the mechanism of tip-splitting for the first time. The effect of dispersion on the instability of miscible displacement in rectilinear porous media was studied by Yortsos and Zeybek (Yortsos and Zeybek, 1988). They found that the dependence of the dispersion coefficient on flow rate induced a destabilizing contribution at short wavelengths, which was different from the stabilization commonly associated with isotropic dispersion. Manickam et al. (Manickam and Homsy, 1993) studied viscous fingering using a non-monotonic viscosity-concentration profile. Under this assumption, diffusion could have a destabilizing effect on the hydrodynamic instability instead of the normally expected stabilizing one. In the nonlinear simulation, a new phenomenon of “reverse” fingering was found. Because of the non-monotonic concentration-viscosity relation, there could be an instability followed downstream by a potentially stable region, or vice versa. If the stable region is on the downstream side, it has the potential to act as a barrier to the growth of viscous fingers, thereby the displaced fluid fingers move through the displacing fluid more rapidly than vice versa (Manickam and Homsy, 1994). The role of permeability heterogeneity (Tan and Homsy, 1992, De Wit and Homsy, 1997a, De Wit and Homsy, 1997b), high Peclet number (Islam and Azaiez, 2007) and anisotropic dispersion (Zimmerman and Homsy, 1991) were also investigated without considering chemical reaction and temperature effects.

The coupling between viscous fingering and chemical reaction has been investigated both experimentally and theoretically (Homsy, 1999, De Wit and Homsy, 1999, Nagatsu et al., 2008, Nagatsu et al., 2007, Nagatsu et al., 2009, Nagatsu and De Wit, 2011, Fernandez and Homsy, 2003). Not only can chemical species be passively transported by fluid flows, but also chemistries can modify dynamic flow properties such as density or viscosity, therefore fluid flow itself can be changed. A feedback between chemistry and hydrodynamics occurs in the reaction-diffusion-convection (RDC) process (Chadam et al., 1986). De Wit and Homsy (Homsy, 1999) found that chemistry can not only strongly enhance tip-splitting but also change the overall aspect of the hydrodynamic pattern. The characteristic length
scale is smaller and the number of fingers is larger, indicating that chemistry increases instability within the displacement process. They also found that the mixing length of the reactive front grows convectively at a higher rate than the nonreactive counterpart. Damkohler number, Da, is the ratio of the dispersive time scale to the chemical time scale. Hence, when Da is small, dispersion will dominate kinetics. The general influence of larger Da is to produce sharper fronts, more vigorous tip-splitting and more rapid formation of droplets.

Recently, an A+B→C type of chemical reaction coupled with viscous fingering has been investigated (Nagatsu and De Wit, 2011, Gérard and De Wit, 2009, Hejazi et al., 2010, Hejazi and Azaiez, 2010). The A+B→C chemical reaction takes place when a reactive solution of A displaces a solution of B of different viscosity. It produces C at the interface. Podgorski et al. have performed an experiment where both the reactants A and B have the same viscosity while the product C is more viscous (Podgorski et al., 2007). The interesting observation was that the viscous fingering pattern is different depending whether reactant A is injected into reactant B or vice versa. The author attributed it to the double diffusive effect. Gerard and De Wit numerically simulated the phenomenon described by Podgorski et al. (Gérard and De Wit, 2009). Hejazi et al. (Hejazi and Azaiez, 2010, Hejazi et al., 2010) performed linear stability analysis as well as non-linear simulations for the A+B→C type of reaction in the RDC process in which the viscosity of the solution is a function of all species concentrations. Their results showed that the flow is always unstable if the initial front between the displacing reactant A and displaced reactant B is unstable. However, the initially stable front could be destabilized by chemical reaction.

When a fluid flows through a porous media already saturated with a native fluid of different temperature and composition, a fluid front and a thermal front may develop (Pritchard, 2004). The thermal front normally travels more slowly than the fluid front, since the fluid front advances through the pore space only while heat is transported through the whole porous medium (Phillips, 1991). As an intruding fluid moves through a porous matrix, the fluid may become under-saturated or supersaturated as a result of changes in temperature and pressure, leading to dissolution or precipitation reactions which act to restore the system to equilibrium (Phillips, 1991, Jupp and Woods, 2003). Across both fronts, viscous fingering may arise because of viscosity differences due to compositional and thermal gradients. At the same time, one can expect that both fronts are coupled
because each front is affected by the perturbations induced by the instability on the other front. Viscosity contrast induced by concentration or temperature differences, thermal lag effect and the diffusive ratio between composition and heat are regarded as the three most important factors influencing the viscous fingering instability (Pritchard, 2004, Jupp and Woods, 2003, Pritchard, 2009, Kalliadasis et al., 2004, Islam and Azaiez, 2010a, Islam and Azaiez, 2010b). One can expect a non-monotonic viscosity profile if there are both thermal and compositional differences. However, such a profile differs from that studied by Manickam and Homsy (Manickam and Homsy, 1993, Manickam and Homsy, 1994) in the different rate that the thermal and fluid properties diffuse and are advected. If the thermal lag coefficient is increased, the fingering dynamics become more strongly coupled. Pritchard (Pritchard, 2004) found that the effect of the thermal front is only to modify slightly the stability of the fingering dynamics. An unstable thermal front can enhance the growth rate of an already unstable mass front while a stable one can reduce the growth rate. If either change promotes fingering, then an instability is likely to develop, although its rate of growth may be modified significantly by the coupling. Islam et al. (Islam and Azaiez, 2010a) found that an increase in thermal mobility ratio, $\beta_T$, is shown to enhance the instability for fixed solute mobility ratio, $\beta_C$, Lewis number and thermal lag coefficient whereas for fixed $\beta_T$ and $\beta_C$, a decrease in the thermal lag coefficient and/or an increase in the Lewis number always decrease the instability.

![Figure 3-2 Effect of temperature on the viscosity of pure water (Barnes, 1997).](image)

Compared to its isothermal counterpart, non-isothermal reaction-diffusion-convection processes have received relatively little attention. The focus in this chapter is to study the interaction between viscously driven instabilities, temperature and chemical reaction in the
transport process of heat and mass for an A+B->C type of chemical reaction in porous media. The objective is to investigate to what extent heat and chemical reaction can affect the viscous fingering and the nonlinear development of the flow, in terms of the mixing length and the yield of chemical reaction.

This chapter is organized as follows: In section 3.2, the basic equations and the scaling are established. Then the nonlinear simulation is performed in section 3.3. In section 3.4, parametric studies are carried out under different scenarios. The conclusions are drawn in section 3.5. The author stresses that the aim of this chapter is not to exhaust every possible effect in the coupled processes of temperature, fluid flow and chemical reaction. A few assumptions were adopted in order to make the simulation possible. For example, Dufour effect, where a temperature gradient leads to mass transport, can be safely neglected as chemical reactions are neither exothermic nor endothermic.

3.2 MATHEMATICAL MODEL

3.2.1 Physical problem

The length and width of the considered porous medium are $L_x$ and $L_y$ as shown in Figure 3-3. The porous medium is treated as a continuum which is initially saturated with fluid B of viscosity $\mu_2$ and temperature $T_2$. Then fluid containing reactant A of viscosity $\mu_1$ and temperature $T_1$ flows through the porous medium from the left-hand side with a uniform velocity $U$ and reacts with fluid B. A new product C is generated in the interface between fluid A and B. This calculation assumes that all fluids are incompressible and fully miscible. The flow is taking place in a homogeneous medium of constant porosity $\phi$ and permeability $\kappa$. The direction of the flow is along the x-axis while the y-axis is parallel to the initial plane of the interface.
3.2.2 Governing equations

The flow is governed by the equations for conservation of mass, conservation of momentum in the form of Darcy’s law, and the reaction-diffusion-convection (RDC) mass and energy balance equations.

\[
\nabla \cdot \mathbf{u} = 0 \quad (3.1)
\]

\[
\nabla p = -\frac{\mu}{\kappa} \mathbf{u} \quad (3.2)
\]

\[
\phi \frac{\partial A}{\partial t} + \mathbf{u} \cdot \nabla A = \phi D_A \nabla^2 A - \phi^2 K_{AB} \quad (3.3)
\]

\[
\phi \frac{\partial B}{\partial t} + \mathbf{u} \cdot \nabla B = \phi D_B \nabla^2 B - \phi^2 K_{AB} \quad (3.4)
\]

\[
\phi \frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = \phi D_C \nabla^2 C + \phi^2 K_{AB} \quad (3.5)
\]

\[
(\rho C)_m \frac{\partial T}{\partial t} + \rho_l C_p \mathbf{u} \cdot \nabla T = (\phi D_t + (1 - \phi) D_s) \nabla^2 T \quad (3.6)
\]
u is the Darcy velocity, \( p \) the fluid pressure, \( \mu \) the viscosity, \( \kappa \) the medium permeability which is a constant in this model, and \( \phi \) the porosity. The concentration of the two reactants and the product are denoted by \( A, B, \) and \( C \), respectively, while \( D_{A,B,C} \) are their corresponding diffusion coefficients. It will be assumed that all species involved have the same diffusion coefficient \( D \) for the sake of simplicity. \( D_s, D_f \) are Fourier’s thermal conductivity of the pore matrix and fluid, respectively. The effective volumetric heat capacity for the porous medium \( (\rho C)_m \) is based on mixture theory:

\[
(\rho C)_m = [\phi \rho_f C_{pf} + (1 - \phi)\rho_s C_{ps}]
\]

(3.7)

where \( C_{ps}, C_{pf} \) are the specific heat for solid phase and fluids while \( \rho_s \) and \( \rho_f \) are the densities of the solid and the fluid, respectively.

\( T \) is the equilibrium temperature. \( D_T \) is the thermal conductivity for the solid-water mixture defined as:

\[
D_T = (\phi D_f + (1 - \phi)D_s)/\rho_mC_{pm}
\]

(3.8)

Equation 3.6 represents the conservation of thermal energy in the whole of the porous medium, including the fluid and solid phase under the following assumptions:

1. The medium is isotropic and radiation effects, viscous dissipation, and the work done by pressure changes are negligible.

2. The medium is under local thermal equilibrium which means the difference in temperature between the fluid and solid phase is negligible and ignored (Nield and Bejan, 1992, Kaviany, 2001).

3. The model assumes that heat conduction in the solid and fluid phases takes place in parallel so that there is no net heat transfer from one phase to the other.

For the sake of simplicity, this model assumes that the viscosity of the fluid is only a function of the local concentration of reactant \( A(x, y, t) \) and temperature \( T(x, y, t) \). It also assumes that the viscosity of the mixed fluid varies exponentially with the concentration of
A and temperature T so that the following dependence of viscosity on concentration and temperature is adopted:

\[ \mu(A, T) = \mu_1 \exp(R_A(1 - \frac{A}{A_0}) + R_T(1 - \frac{T - T_2}{T_1 - T_2})) \]  \hspace{1cm} (3.9)

where \( A_0 \) is the initial concentration of reactant A and \( R_A \) is the log-mobility ratio in an isothermal miscible displacement at temperature \( T_0 \) defined as

\[ R_A = \ln \left( \frac{\mu(0, T_0)}{\mu(1, T_0)} \right) \ln \left( \frac{\mu_2}{\mu_1} \right) \]  \hspace{1cm} (3.10)

while \( R_T \) represents the log-mobility ratio of the viscosity \( \frac{\mu(1, T_2)}{\mu(1, T_1)} \) in a thermal displacement involving a single fluid defined as:

\[ R_T = \ln \left( \frac{\mu(1, T_2)}{\mu(1, T_1)} \right) \ln \left( \frac{\mu_2}{\mu_1} \right) \]  \hspace{1cm} (3.11)

In isothermal cases, \( R_A > 0 \), corresponds to a fluid of a less viscosity displacing one of a greater viscosity, fingering will occur between the interface of fluid A and C. whereas \( R_A < 0 \), corresponds to a stable displacement. In single fluid cases, \( R_T > 0 \), corresponds to a fluid of higher temperature displacing the same fluid at a lower temperature, and vice versa.

Since the fluids are injected with a constant velocity \( U \), we switch to a reference frame moving with \( U/\phi \) taking \( x' = x - (U/\phi) t \) and \( u' = u - (U/\phi) e_x \) where \( e_x \) is the unit vector along direction x. The governing equations are then as follows:

\[ \nabla \cdot u' = 0 \]  \hspace{1cm} (3.12)

\[ \nabla p = -\frac{\mu(A, T)}{\kappa} (u' + (U/\phi)e_x) \]  \hspace{1cm} (3.13)
\[ \phi \frac{\partial A}{\partial t} + u' \cdot \nabla A = \phi D \nabla^2 A - \phi^2 KAB \]  
(3.14)

\[ \phi \frac{\partial B}{\partial t} + u' \cdot \nabla B = \phi D \nabla^2 B - \phi^2 KAB \]  
(3.15)

\[ \phi \frac{\partial C}{\partial t} + u' \cdot \nabla C = \phi D \nabla^2 C + \phi^2 KAB \]  
(3.16)

\[ \frac{\partial T}{\partial t} + \frac{\lambda}{\phi} u' \cdot \nabla T = \phi D_T \nabla^2 T \]  
(3.17)

The above equations model the propagation of two fronts, one associated with temperature and will be referred as the thermal front, while the other corresponds to mass transport and will be named as the fluid front. To reduce the complexity of modelling, the simulated chemical reaction is neither exothermic nor endothermic. This is to say that the chemical reaction rate coefficient \( K \) is independent on temperature. This chapter concentrates more on the transport of heat and its effect on viscosity, rather than the generation and/or absorption of heat caused by chemical reaction. The parameter \( \lambda \) is referred to as the thermal-lag coefficient, representing the ratio of the speed of the thermal front to that of the fluid front (Pritchard, 2004, Islam and Azizie, 2010a):

\[ \lambda = \frac{\phi \rho f C_p f}{(\rho C)_m} \]  
(3.18)

There are two characteristic velocities, \( U/\phi \) and \( \lambda U/\phi \), associated with the mass and temperature transport. The former is the velocity of the flow in interstitial space.

The equations are made dimensionless by the characteristic velocity \( U/\phi \), hydrodynamic time \( \tau_h = D\phi^2/U^2 \), and length \( L = D\phi/U \). The constant permeability \( \kappa \) is incorporated in the expression for the velocity by treating \( \mu/\kappa \) as \( \mu \). The viscosity and pressure are scaled with \( \mu_1 \) and \( \mu_1 D\phi \). The temperature is scaled as:

\[ T' = (T - T_2)/(T_1 - T_2) \]  
(3.19)
We further introduce the definition of Lewis number as well as Damkohler number:

\[
Le = \frac{D_r / D}{Pe_A / Pe_T} = \frac{Pe_A}{Pe_T} \quad (3.20)
\]

\[
Da = \phi^2 DKA_0 / U^2 \quad (3.21)
\]

Lewis number \( Le \) is the ratio between the diffusion coefficients of the reactant \( A \) and heat. \( Pe_A \) and \( Pe_T \) are the solutal and thermal Peclet numbers. The Damkohler number \( Da \) corresponds to the ratio between the hydrodynamic time \( \tau_h \) and the chemical time

\[
\tau_A = 1 / \phi KA_0 \quad (3.22)
\]

The following dimensionless equations are obtained:

\[
\nabla \cdot u = 0 \quad (3.23)
\]

\[
\nabla p = -\mu (u + e_x) \quad (3.24)
\]

\[
\frac{\partial A}{\partial t} + u \cdot \nabla A = \nabla^2 A - DaAB \quad (3.25)
\]

\[
\frac{\partial B}{\partial t} + u \cdot \nabla B = \nabla^2 B - DaAB \quad (3.26)
\]

\[
\phi \frac{\partial C}{\partial t} + u \cdot \nabla C = \nabla^2 C + DaAB \quad (3.27)
\]

\[
\frac{\partial T}{\partial t} + \lambda u \cdot \nabla T = Le \nabla^2 T \quad (3.28)
\]

In order to complete the model, it is assumed that viscosity is dependent on the concentration of \( A \) and temperature:

\[
\mu(A, T) = \exp(R_A (1 - A) + R_T (1 - T)) \quad (3.29)
\]
Taking the curl of the flow equation and introducing the streamfunction \( \psi(x,y) \) defined by
\[ u = \frac{\partial \psi}{\partial y} \quad \text{and} \quad v = -\frac{\partial \psi}{\partial x}, \]
we have the following equations in terms of vorticity \( \omega \):
\[
\omega = \left( \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right) = -\nabla^2 \psi
\]
\[
= -R_A \left[ \frac{\partial \psi}{\partial x} \frac{\partial A}{\partial x} + \frac{\partial \psi}{\partial y} \frac{\partial A}{\partial y} \right] + R_T \left[ \frac{\partial \psi}{\partial x} \frac{\partial T}{\partial x} + \frac{\partial T}{\partial y} \frac{\partial \psi}{\partial y} \right] \tag{3.31}
\]
\[
\frac{\partial A}{\partial t} + \frac{\partial \psi}{\partial y} \frac{\partial A}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial A}{\partial y} = \nabla^2 A - DaAB \tag{3.32}
\]
\[
\frac{\partial B}{\partial t} + \frac{\partial \psi}{\partial y} \frac{\partial B}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial B}{\partial y} = \nabla^2 B - DaAB \tag{3.33}
\]
\[
\frac{\partial C}{\partial t} + \frac{\partial \psi}{\partial y} \frac{\partial C}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial C}{\partial y} = \nabla^2 C + DaAB \tag{3.34}
\]
\[
\frac{\partial T}{\partial t} + (\lambda - 1) \frac{\partial T}{\partial x} + \lambda \frac{\partial \psi}{\partial y} \frac{\partial T}{\partial x} - \lambda \frac{\partial \psi}{\partial x} \frac{\partial T}{\partial y} = Le\nabla^2 T \tag{3.35}
\]

The vorticity equation shows that the vorticity \( \omega(x,y,t) \) is generated by concentration and temperature gradients which are not parallel to the local velocity vector.

### 3.2.2.1 Initial and boundary conditions

Equations 3.31-3.35 form a closed set that can be solved for the concentration and velocity fields. The initial conditions used for this simulation are as follows:

\[
A(x,y) = \begin{cases} 
1, & 0 \leq x \leq Pe/2 \\
0, & Pe/2 < x \leq Pe 
\end{cases} \tag{3.36}
\]

\[
B(x,y) = \begin{cases} 
0, & 0 \leq x \leq Pe/2 \\
1, & Pe/2 < x \leq 1000 
\end{cases} \tag{3.37}
\]

There is no chemical product at first, so the concentration for C equals zero.
The dimensionless initial temperature distribution is

\[ T(x, y) = \begin{cases} 
1, & 0 \leq x \leq \text{Pe}/2 \\
0, & \text{Pe}/2 < x \leq \text{Pe} 
\end{cases} \]  

As we consider a constant linear velocity \( U \) corresponding to a zero velocity relative to the translating frame, the streamfunction has been set at zero everywhere.

\[ \varphi(x, y) = 0 \]  

In terms of boundary conditions, Tan (Tan and Homsy, 1988), De Wit (De Wit and Homsy, 1999) and Hejazi (Hejazi and Azaiez, 2010) used a periodic boundary condition which is convenient for the spectral method. Periodic boundary conditions are used to approximate an infinite system by a small unit cell. When the fluid and/or heat passes through one side of the unit cell, it re-enters from the opposite side with the same velocity. In our model, insulation conditions for the upper and lower boundaries are used, which simply means there is no flux of chemical species or heat. The stream-wise direction boundary conditions in dimensionless form are:

Left boundary

\[ u = 0, v = 0, A = 1, \text{Convective flux for } B, C, T = 1 \]  

Right boundary

\[ u = 0, v = 0, B = 1, \text{Convective flux for } A, C, \text{ and } T \]  

The solution of the model (Equations 3.31-3.35 ) with the initial (Equations 3.36-3.40 ) and boundary conditions (Equations 3.41-3.42 ) yields the temporal development of the spatial distribution of the concentration of A, B, and C, the temperature T and fluid velocity.
3.2.2.2 Numerical methods and validation

To numerically solve Equations 3.31-3.35, the finite element method has been used to solve the multi-physical equations using COMSOL multiphysics. To validate our result, we first simulated a non-reactive case \( D_a = 0 \) in which reactant A displaces reactant B without the generation of product C. Furthermore, we verified the isothermal case \( R_T = 0 \) with a solutal mobility ratio \( R_A = -2 \). This corresponds to a more viscous fluid displacing a less viscous one, so there is no fingering at the fluid interface. Then we consider the case \( R_A = 3 \) which results in an unstable displacement. We found that the time evolution of the viscous fingers and the associated nonlinear interactions are similar to the results presented by Tan and Homsy (Tan and Homsy, 1988) and Islam et al. (Islam and Azaiez, 2010b). However, they are not necessarily the same because the boundary conditions used in those papers are periodic. Periodic boundary condition is convenient for spectral computational methods and is used to approximate an infinite system. The evolution of the fingering pattern is robust with refinement of both time and spatial steps.

3.3 RESULTS AND ANALYSIS

All the results presented in this section are obtained for a cell of aspect ratio \( A = 2 \), a solute Peclet number \( \text{Pe} = 500 \). Different solutal mobility ratio \( R_A \), thermal mobility ratio \( R_T \), thermal lag coefficient \( \lambda \), Lewis number \( \text{Le} \) and Damkohler number are analysed under different scenarios. This chapter investigates qualitatively the roles of \( R_A, R_T, \lambda, \text{Le} \) and \( \text{Da} \) in influencing the concentration and temperature fields. A non-reactive and isothermal displacement with \( R_A = 2 \) was taken as the reference. It simply means a less viscous fluid A displacing a more viscous fluid B as investigated by Tan and Homsy (Tan and Homsy, 1988). As expected, nonlinear phenomena such as shielding, spreading and merging were observed. “Shielding” refers to the effect that a finger slightly ahead of its neighbours quickly outruns them and shields them from further growth. Tip-splitting was not observed in this simulation. That is probably because the Peclet number is below a critical value, as discussed by De Wit and Homsy (Homsy, 1999, Homsy, 1987). Interestingly, at the late stage, almost isolated tips cut by reverse flow are observed as shown in Figure 3-4. It was found that when one finger penetrates into another fluid, it creates an enhanced flow channel for the downstream fluid.
Figure 3-4 Profile of concentration and flow field of reactant A at $t = 450$ with $\lambda = 0.5, R_A = 2, R_T = 2, Le = Da = 1$ (arrow represents the flow velocity).

Figure 3-5 Temperature field shows a thermal lag effect at $t = 450$ with the same parameters as in Figure 3-4.

Figure 3-6 3D concentration field of product C at $t = 450$ with $\lambda = 0.5, R_A = 2, R_T = 2, Le = Da = 1$. 
By comparing Figure 3-4 and Figure 3-5, we can clearly see that the thermal front lags behind the solute front with the thermal lag coefficient less than one. Figure 3-6 shows the location where has the highest concentration of product C in the solute front. Its distribution pattern is finger-like because of the effect of viscous instability.

3.3.1 Role of mobility ratio

As the solute mobility ratio \( R_A \) increases, a larger instability growth rate as well as an elongated mixing length was observed, consistent with the conclusion of the linear stability analysis drawn by Tan (Tan and Homsy, 1986). If the pressure drop between the left and right boundaries are the same, the displacing fluid A, with a higher mobility ratio will penetrate further than that of a displacing fluid of lower mobility ratio. If both \( R_A \) and \( R_T \) are positive, the solutal and thermal effects are collaborative. If \( R_A > 0 \) and \( R_T < 0 \), that is fluid A with lower temperature displaces fluid B with higher temperature, the solutal and thermal effects are competing. We fix \( R_A = 2 \), and vary \( R_T \) with values -2, 0, 1, 2 at the dimensionless time \( t = 400 \) to see the difference in the fluid front as shown in Figure 3-7.

![Figure 3-7 Profile of concentration field of reactant A at t = 400](image)

with \( R_A = 2 \), \( Le = Da = \lambda = 1 \): a) \( R_T = -2 \); b) \( R_T = 0 \); c) \( R_T = 1 \); d) \( R_T = 2 \).

3.3.2 Role of thermal lag coefficient
Thermal lag coefficient $\lambda$ is a parameter to assess the coupling of reactant A and heat. As can be observed from Figure 3-8 and Figure 3-9, the closer $\lambda$ approaches 1, the tighter the coupling of solute and heat effect. When $\lambda < 1$, a separate thermal reaction front propagates downstream of the fluid front. When both $R_A$ and $R_T$ are positive, the concentration and heat effect are collaborative. The instability is enhanced (Islam and Azaiez, 2010a). The closer $\lambda$ approaches 1, the greater the instability.

Figure 3-8 Concentration field contrast at $t = 400$ with $R_A = 2, R_T = 2, Le = Da = 1$: 
\begin{enumerate}
  \item $\lambda = 1$; 
  \item $\lambda = 0.5$.
\end{enumerate}

Figure 3-9 Temperature field contrast at $t = 400$: 
\begin{enumerate}
  \item $\lambda = 1$; 
  \item $\lambda = 0.5$ with $R_A = 2, R_T = 2, Le = Da = 1$.
\end{enumerate}

### 3.3.3 Role of Lewis number

Diffusion plays a dominant role in a flow regime with lower Peclet number. Based on different Peclet numbers, three different flow regimes have been identified. They are diffusion dominated when $Pe < 1,000$; convection dominated one when $Pe > 3,000$, and a transition flow when $1,000 < Pe < 3,000$. It was pointed out that the higher the Peclet
number, the more easily tip splitting occurs and there exists a critical Peclet number under which tip-splitting does not occur at a fixed mobility ratio (Islam and Azaiez, 2010a).

Transverse dispersion is regarded as having a stabilizing effect on the fingering instability, leading to a cut-off wavenumber (Tan and Homsy, 1986, Yortsos and Zeybek, 1988). Any disturbance with a wavenumber larger than the cut-off one will be damped out. Heat normally diffuses much faster than the chemical species, leading to the Lewis number $Le \gg 1$. The viscosity of the fluids is influenced by a slow-diffusing reactant A and a fast-diffusing heat. As can be seen from Figure 3-10 and Figure 3-11, there is a greater instability for both the solute and temperature fronts with a lower $Le$.

![Figure 3-10](image)

Figure 3-10 Concentration field contrast at $t = 450$ with $R_A = 2, R_T = 2, \lambda = Da = 1$: 

a) $Le = 10$; b) $Le = 1$.

![Figure 3-11](image)

Figure 3-11 Temperature distribution at $t = 450$ with $R_A = 2, R_T = 2, \lambda = Da = 1$: 

a) $Le = 10$; b) $Le = 1$.

### 3.3.4 Role of Damkohler number

Chemical reaction could be the origin of the hydrodynamic instability. Figure 3-12 shows that the fingering instability can be triggered by chemical reaction alone.
Figure 3-12 Profile of concentration field of reactant A at $t = 400$ with $R_A = 2, R_T = -2, Le = \lambda = 1$: a) reactive case with $Da = 1$; b) nonreactive case with $Da = 0$.

Damkohler number, $Da$, is defined as the ratio between the characteristic time of fluid motions and that of the chemical reaction. If the chemical reaction is dominant in the dynamics, which means a very small chemical time, $Da$ is correspondingly large. For faster reactions which correspond to a larger $Da$, the effect of shielding is suppressed (Nagatsu and De Wit, 2011). From Figure 3-13, we can see that the width of each finger in Figure 3-13 (a) is generally larger than that in Figure 3-13 (b) which has $Da = 1$. For higher $Da$, we expect a narrower reacting area.

Figure 3-13 Profile of concentration field of reactant A at $t = 250$ with $R_A = 2, R_T = 2, Le = \lambda = 1$: a) $Da = 0.5$; b) $Da = 1$.

3.4 PARAMETRIC STUDY

This section performs a quantitative analysis of the reaction-diffusion-advection process for the distribution patterns of reactant A, product C and temperature T in the fronts. First, concentration of reactant A, product C and temperature T will be transversely averaged in terms of different $R_A, R_T, \lambda, Le$ and $Da$ to find out how those parameters affect the
concentration and temperature distribution in the evolution of the mass and heat transport process. Second, the length of relative contact area is of particular interest from the point of view of hydrothermal systems and mineralising processes since it enhances reaction rates. Lastly, the variation of the overall amount of chemical product C is estimated and the characteristics of the fingering patterns in terms of mixing length, the total amount of product C as well as average concentrations of A, B, and C are investigated.

3.4.1 Averaged temperature and concentration

The definition of transversely averaged temperature and concentration of A and C is as follows:

$$\langle S(x,t) \rangle = \frac{1}{Pe} \int_0^{Pe} S(x,y,t) dy$$  \hspace{1cm} (3.43)

$Pe$ stands for the width of the domain. $S$ could be temperature $T$ or concentration of $A$ or $C$. Figure 3-14 illustrates the evolution of transversely averaged concentration of reactant $A$. As time evolves, the gradient of concentration $A$ becomes less and less steep and the distribution curve becomes increasingly complex. The same trend can be observed from the temperature curve in Figure 3-15.

![Figure 3-14 Profile of transversely averaged concentration of reactant A at different time](image)

Figure 3-14 Profile of transversely averaged concentration of reactant A at different time with $R_A = 2$, $R_T = 2$, $Le = 2$, $\lambda = 0.75$, $Da = 1$. 

 experimented.
Figure 3-15 Profile of transversely averaged temperature $T$ at different time with $R_A = 2$, $R_T = 2$, $Le = 2$, $\lambda = 0.75$, $Da = 1$.

Figure 3-16 plots the transversely averaged concentration distribution of product $C$. Product $C$ can only be generated within the interface of reactant $A$ and $B$. The patterns of production curve are highly nonlinear because of the penetration of fingering as shown in Figure 3-16.

Figure 3-16 Profile of transversely averaged concentration of the product $C$ at different time with $R_A = 2$, $R_T = 2$, $Le = 2$, $\lambda = 0.75$, $Da = 1$.

Figure 3-17 shows the thermal and solute fronts for thermal lag coefficient $\lambda = 0.5$ and 0.25 at $t = 200$, respectively. Higher thermal lag coefficient minimise the distance between the fluid front and the thermal front.
3.4.2 Mixing area

The mixing area is defined as area of the contacting interface between two species involved in the displacement. In this model, there are two classes of mixing area: one is driven by heat and the second is driven by chemical composition of reactant A or product C. In this chapter, we use the contour of concentration of reactant A to define the reverse reacting area length $L_-$ and the forward reacting area length $L_+$. The whole reacting length $L$ is the sum of $L_-$ and $L_+$ at dimensionless time $t = 300$ as shown in Figure 3-18.

Figure 3-18 Concept of reverse and forward reacting area length.

Figure 3-17 Thermal and fluid fronts with $\lambda = 0.5$ and 0.25 (dashed lines) with $R_A = 2$, $R_T = 2$, $Le = 1$, $Da = 1$. 

Length

Figure 3-17 Thermal and fluid fronts with $\lambda = 0.5$ and 0.25 (dashed lines) with $R_A = 2$, $R_T = 2$, $Le = 1$, $Da = 1$. 

Length

0 200 400 600 800 1000

0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1

Fluid Front 1
Thermal Front 1
Fluid Front 2
Thermal Front 2

$\langle A(x, 300) \rangle$

Length

$\langle T(x, 200) \rangle$

and $\langle A(x, 200) \rangle$
Following the methodology of Nagatsu and De Wit (Nagatsu and De Wit, 2011), the previously defined transversely averaged concentration of reactant A is used to determine the reverse reacting area length $L_-$ as the distance between the position $x_1$ along x where $\langle A(x_1, t_0) \rangle = 0.99$ and the position $x = Pe/2$ while the forward reacting area length $L_+$ as the distance between $x = Pe/2$ and the position where $\langle A(x_2, t_0) \rangle = 0.01$. The dimensionless time interval is 100. The overall reacting area length then is then defined as:

$$L = L_+ + L_-$$  \hfill (3.44)

Figure 3-19 Total reacting area length L with different $\lambda$: case 1 $\lambda = 0.75$; case 2 $\lambda = 0.5$;
The other parameters are: $R_A = 2, R_T = 2, Le = Da = 1$.

Figure 3-20 Reverse reacting area length $L_-$ with different $\lambda$: case 1 $\lambda = 0.75$; case 2 $\lambda = 0.5$; The other parameters are: $R_A = 2, R_T = 2, Le = Da = 1$. 
Figure 3-21 Forward reacting area length $L_+$ with different $\lambda$: case 1 $\lambda = 0.75$; case 2 $\lambda = 0.5$; The other parameters are: $R_A = 2, R_T = 2, Le = Da = 1$.

From the above three graphs we can see that an increase of the thermal lag coefficient $\lambda$ leads to larger reacting area. The effect on the reverse reacting area length is insignificant while the forward reacting area is dramatically affected.

Figure 3-22 Total reacting area length $L$ with different $R_T$: case 3 $R_T = -2$; case 4 $R_T = 2$; case 5 $R_T = 1$; case 6 $R_T = 0$.

The other parameters are: $R_A = 2, \lambda = Le = Da = 1$. 
The other parameters are: $R_A = 2, \lambda = L_e = D_a = 1$.

If the chemical reaction is extremely rapid, it corresponds to an infinite $D_a$. Reactant A and B cannot coexist. A new product C will be generated as soon as reactant A and B are
brought into contact. The finger-like intrusion pattern between A and B is sharper. For a moderate Da, the reactants A and B and the product C can coexist. We compare case 3 with its nonreactive counterpart Da = 0 which is a stable displacement. For a stable case, the enlargement of contact area is only caused by the mechanism of diffusion and the total mixing area length can be calculated analytically as $L = 2\sqrt{Dt}$. We can see that the reverse contact area lengths are almost the same as shown in Figure 3-25 while the forward contact area length for reactive case is dramatically smaller than the nonreactive counterpart as shown in Figure 3-26.

Figure 3-25 Reverse reacting area length $L_-$ with different Da: case 3 Da = 1; case 7 Da = 0. The other parameters are: $R_A = 2, R_T = -2, \lambda = L_e = 1$. 

3.4.3 Total amount of chemical product

The overall chemical component yielded by the displacement is calculated using the following definition.

\[
\langle C(t) \rangle = \int_0^{Pe'} \int_0^{Pe} C(x, y, t) dy \, dx \tag{3.45}
\]

Table 3-1 Different cases with different parameter values

<table>
<thead>
<tr>
<th>Case No.</th>
<th>( R_A )</th>
<th>( R_T )</th>
<th>( \lambda )</th>
<th>( Le )</th>
<th>( Da )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>-2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>2</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 3-27 Evolution of overall amount of product C for the above 6 cases. Table 3-1 lists 6 cases of different controlling parameters $R_A$, $R_T$, $\lambda$, Le and Da. Figure 3-27 shows the production curve for the above 6 cases. The overall amount of chemical product C increases monotonically with time. At early times, diffusive effects are dominant and the rate of production is independent of the species mobility ratios. In the late time regime, the flow instability plays a more important role and enhances mixing between reactants, which results in a larger rate of production. Case 3 has the highest production rate because it has a larger $R_A$, $R_T$, $\lambda$, and Da. Comparing case 3 and case 4, we can see that a larger Da will lead to higher production curve. Comparing case 3 with case 5, we can obtain the conclusion that a higher thermal lag coefficient can lead to a higher production curve. A higher thermal lag coefficient simply corresponds to a tighter coupling between the thermal front and the solute front. Because both $R_A$ and $R_T$ are positive, the effects of solute and heat on fingering are collaborative. Therefore, tighter coupling is favourable for the generation of product. In case 1 where the effects of solute and heat on fingering are competing, the enlargement of contact reacting area is suppressed, therefore, it has the lowest production among all 6 cases.

3.5 CONCLUSION

The objective of this chapter is to simulate the nonlinear reaction-diffusion-convection process involving the A+B->C type of geochemical reaction in hydrothermal porous media. The highly nonlinear character of the underlying dynamics leads to complex
spatiotemporal evolution of concentration and temperature patterns. The viscosity may change across each front so that a fingering instability may develop on either front. In this model, the viscosity of the fluids is assumed to be dependent only on the concentration of reactant A and temperature. The effects of solute and thermal mobility ratio, $R_A$ and $R_T$, the Lewis number $Le$ and the Damköhler number $Da$ on the distribution of temperature and concentration, the size of reacting area and the overall amount of the chemical product $C$ are investigated under different scenarios.

The solute and thermal mobility ratios play the most important role on finger structures, the size of the reacting contact area and the efficiency of the chemical reaction. The less viscous fluid will penetrate farther into the more viscous fluid if the mobility ratio is higher. Therefore, the finger structure becomes more complex and the reacting contact area is dramatically enlarged, generating more chemical product $C$.

The coupling of solute and thermal fronts is characterised by the thermal lag coefficient. Because heat is transported through the complete domain rather than the pore space alone, the thermal lag coefficient has a value less than 1. It was found that when both the solute and thermal mobility ratios are positive, the fingering instability is enhanced by a larger thermal lag coefficient, leading to complex concentration and temperature distribution and larger reacting area, therefore, the production of the chemical reaction will be enhanced.

Chemical reactions always increase the destabilization of the system. It could be the only origin of the hydrodynamic instability, compared with its nonreactive counterpart. Higher Damköhler number suppresses the shielding effect of fingering, making the front sharper. Higher $Da$ also leads to shorter reacting contact area length. The difference mainly comes from the forward reacting area length.

Diffusion plays a dominant role in underground fluid flow, especially for the flow with low Peclet number. Overall, diffusion has stabilizing effect on fingering. High $Le$ number represents that heat diffuses faster than solute so that any disturbance caused by temperature difference vanishes more rapidly.

The high level conclusion from this study is that fingering can have a dramatic effect on the efficiency of the chemical system with enhancements in production of the reaction product of close to an order of magnitude (Figure 3-27). Such enhancements are associated
with greater complexity in the spatial distribution of the product. Such a result is consistent with what is observed in mineral deposits so that higher concentrations of metals are associated with more irregular spatial patterns.
CHAPTER 4

MODELLING OF CHAOTIC ADEVENTION OF MINERAL PARTICLES INDUCED BY PERIODIC OPEN FLOW

4.1 INTRODUCTION

Some fundamental questions in terms of mineralization of ore bodies rich in Au, Ag, Pb, Zn, Cu, U, Mo and Fe remain unknown: what are the processes for the local concentration of mineral aggregates deep inside the Earth, leading to the accumulation of economically valuable resources? Mineral associations in the Olympic Dam Cu-U-Au-Ag deposit display complex overlapping and indistinct boundaries (Haynes et al., 1995). What could be the possible reason that leads to the apparently irregular pattern of distribution of orogenic lode-gold deposits? Another important issue regarding the characteristics of ore bodies is that grades are not uniformly distributed and the relative proportions of the ore minerals are not consistent as shown in Figure 4-1. The variance in metal values changes radically between individual sample sites and from place to place along a vein. At the microscopic scale, mineralogical compositions vary widely within deposits (Henley and Berger, 2000). Concentrations of gold are larger than 10,000 times above background levels at specific sites in Earth’s crust. The existence of such huge spatial grade differences is a challenging question in geoscience.

Figure 4-1 Core from Tropicana deposit, Western Australia. The gold grade is 6.24 g/tonne. The image is approximately 15 cm long.
Mixing of different fluids plays an important role in ore-forming processes in hydrothermal systems. Numerical modelling shows that fluid mixing was probably the dominant ore-forming process in the Olympic Dam Cu-U-Au deposit (Haynes et al., 1995). Mixing is intimately connected with turbulence, earth and natural sciences, and various branches of engineering (Sakuyama, 1984, Ottino, 1990, Wiggins and Ottino, 2004, Moura et al., 2012, Jha et al., 2011, Henzler, 2000, Bringer et al., 2004). When discussing mixing behaviour of a flow, turbulent and laminar flows have to be treated separately. In turbulent flows, the velocity field of the fluid behaves chaotically and mixing occurs in a chaotic manner. However, underground porous media flow is more likely to be laminar, where the velocity field behaves in a non-chaotic manner. As have been pointed out, it is difficult to mix two fluids in a porous medium where the geometry involves two flows that meet and streamlines are parallel to each other. In this situation, mixing can only be achieved by diffusion across the interface between the flows. Although fluid mixing is regarded as an important ingredient in the formation of giant hydrothermal ore bodies, it remains poorly understood. Aref applied the theory of dynamical systems to mixing (Aref, 1984, Aref, 1990). Since then, a variety of conceptual and experimental studies have enhanced on understanding of mixing and of mixing rates. Based on its complex nature, mixing problems have been investigated traditionally on a case-by-case basis. There is no single measure for the quantification of mixing. It is also important to distinguish clearly between the mixing measure and the process producing the mixing. Wiggins and Ottino used dynamic system theory to investigate chaotic mixing and laid the mathematical foundations of chaotic mixing (Wiggins and Ottino, 2004). In that paper, they addressed two fundamental questions: 1). how does one quantitatively evaluate the quality of mixing? 2). what are the necessary and sufficient conditions that lead to the best mixing?

From the mineralization point of view, mixing of different mineralising species in porous media can be categorized into two different mechanisms: diffusion and fluid advection. Diffusion alone is proved inefficient for large-scale transport which is observed in geophysical flow since the diffusivity of mineral components is generally an extremely small number. Moving fluids, however, can greatly enhance mixing through chaotic advection.

Chaotic advection simply means advected particles undergo chaotic motion. Chaotic mixing in this thesis refers to flows which are laminar in an Eulerian framework but
chaotic in a Lagrangian framework. Thus the phenomenon is often referred to as Lagrangian chaos (Ottino, 1989, Ottino, 1990, Ottino, 1994, Wiggins and Ottino, 2004). The effect of chaotic advection on the transient mixing of impurities has been explored theoretically and numerically. Chaotic advection can be categorized into two types: closed flow system and open flow system. Some important studies addressing chaotic advection in closed systems which has led to a better understanding of the problem of mixing and stirring are those by Aref (Aref, 1984) who investigated the blinking-vortex flow which was the first two-dimensional, time-periodic flow studied in the context of chaos and Hamiltonian mechanics. Cavity-flow and journal-bearing flow are widely used to gain some insight into the behaviour of chaotic systems (Ottino et al., 1988). Tel and his co-workers also used the blinking vortex-sink system in which two sinks opened alternately to investigate the chaotic scattering process and the fractality induced by chaotic advection (Péntek et al., 1999, Toroczkai et al., 1998, Tél et al., 2000, Karolyi and Tél, 1997). Khakhar et al. investigated the tendril-whorl flow (Khakhar et al., 1986). Daitche and Tel investigated the dynamics of N moving point vortices and found that the degree of chaos decreases monotonically with time (Daitche and Tél, 2009).

For those closed systems, there exist a complicated set of non-escaping orbits which never escape to the asymptotic regions, either in the past \((t->-\infty)\) or in the future \((t->\infty)\). These orbits make up a set which has a fractal structure in phase-space. This invariant set of non-escaping orbits is called the chaotic saddle. The chaotic saddle dominates the associating process of chaotic mixing. Two important invariant sets associated with the chaotic saddle are its stable and unstable manifolds. The stable manifold is defined as the set of initial conditions in phase space such that their corresponding orbits approach asymptotically the chaotic saddle, as the discrete forward time \(n->+\infty\). Particles moving along the stable manifold, enter the mixing region and stay there forever. The unstable manifold refers to the set of phase-space points whose orbits approach the chaotic saddle asymptotically as the discrete backward time \(n->-\infty\). The unstable manifold is the set of points along which points lying infinitesimally close to the chaotic saddle will eventually escape from it in the course of time. The concept of stable and unstable manifolds are shown by a schematic depiction in Figure 4-2 (b).

The unstable manifold can be directly observed experimentally. By considering initially a droplet of particles, corresponding to a set of initial conditions which overlap the stable
manifold, as time goes on the particles get advected to the mixing region. Those particles which last a long time there without escaping fall very close to the chaotic saddle, and when they finally leave, they trace out the unstable manifold. In short, once the bulk of the particles has escaped, the remaining ones, with longer lifetimes in the mixing region, are concentrated around a fractal set, namely the unstable manifold. Periodic orbits provide a backbone of the chaotic advection process in the sense that the particle might remain close to a periodic orbit for a while, then leaves it and comes to the vicinity of another one, and so on. The motion can be considered as a random walk among periodic orbits (Ziemniak et al., 1994).

![Diagram](image)

Figure 4-2 (a) Illustration of an open flow. (b) Schematic depiction of the stable ($W_s$) and unstable ($W_u$) manifolds in an open flow. The gray bands are neighborhoods of $W_s$ and $W_u$.

$R_1$ and $R_2$ indicate regions where initial conditions are chosen (de Moura, 2011).

Chaotic advection stretches and folds the fluid volume to give rise to an exponential decrease in the striation thickness. Figure 4-3 shows schematically how the striation thickness decreases through a series of stretching, folding, and reorientating events in the baker’s transformation. In reality, the motion generated by the chaotic flow is normally far more complex than the baker’s transformation.
In contrast to investigations restricted to flows in closed regions, an increasing number of researchers have investigated chaotic advection in open systems characterized by the existence of a net current. In other words, the fluid is moving from an upstream region towards a downstream region and the velocity field in the far upstream and downstream regions is normally uniform but non-stationary in a bounded region. Open systems differ from closed ones in the following aspects: 1) there is no way for fluid particles to travel out of the domain for closed systems; therefore, a Poincare section is sufficient to obtain the chaotic regions or transport barriers and islands over a long period of time. However, tracing particles could be transported out of the domain fairly rapidly unless they locate exactly on the stable manifold or in the very near neighbourhood of the stable manifold. 2) in the long run, there is only one homogeneous state of concentration in closed systems while heterogeneous states with very high concentration gradients can be maintained in open systems. The examples for closed system are blinking vortex flow, journal bearing flow and cavity flow while the typical open flow example is the so-called von Karman flow (Jung et al., 1993, Ziemniak et al., 1994, Toroczkai et al., 1998). In this chapter, open flow is used to perform the simulations.

Hydrothermal ore forming systems should be considered as open flow chemical reactors held far from equilibrium by the supply of energy and mass (Lester et al., 2012). From the chemical engineering point of view, the mineralising components have to be mixed before the mineralisation process takes place. If there is laminar flow and no perturbations, it is incredibly difficult to get anything to react. However, the mechanism of chaotic advection can significantly enhance mixing and hence metal/sulphide deposition. This chapter only

Figure 4-3 Schematic of a fluid element undergoing stretching, folding and reorientation (Bringer et al., 2004).
concerns how the mineralising components are transported by chaotic advection and diffusion. Chapter 5 will couple chemical reaction into the mineralising open system.

The chapter is organized as follows: in section 4.2 we perform both continuous and discrete studies for fracture scale flow systems where the main channel is connected with a side channel. Scale analysis is also performed in this section. In Section 4.3, we use different nonlinear tools to quantitatively investigate how the chaotic advection can affect the spatial and temporal distribution of individual mineral particles. In section 4.4, the diffusion-advection equation is used to characterize the evolution of concentration of mineral particles. A conclusion is drawn in section 4.5.

4.2 MODEL SYSTEM

The equation for 2D transport of minerals by advection and diffusion is

\[
\frac{\partial c}{\partial t} + \vec{v} \cdot \nabla c = D \Delta c \tag{4.1}
\]

where \(c\) is the concentration of transported minerals. \(\vec{v}\) is the velocity field and \(D\) is the diffusivity. The geometry of the system is shown in Figure App.1. The main straight rectangular fluid channel is 3 m in width and 1 m in height and at \(x = 1\) m the main channel is connected with a side channel at an angle of 30°. The side channel is 0.1 m in width and 0.5 m in length. The inlets of this system are the left boundary and bottom side channel while the outlet is the right boundary. Most models use an explicit flow velocity field. In this chapter, we obtain our velocity field \(\vec{V}\) numerically by applying Stokes equation for the main and side channels in our system. The flows in the main and side channels are steady Stokes flows represented by \(\vec{V}_1\) and \(\vec{V}_2\), respectively. Both \(\vec{V}_1\) and \(\vec{V}_2\) are two-dimensional stationary flows. Their streamfunctions \(\phi\) do not depend on time and the particle trajectories coincide with the streamlines which are the level sets of streamfunctions \(\phi = \text{constant}\). Because the streamfunction is time-independent, it would be impossible for a particle to enter a vortex from outside or to leave it from inside.
In order to have chaotic advection, we can introduce a time factor

$$f(t) = A \sin(\omega t) + B$$ (4.2)

Both $\mathbf{V}_1$ and $\mathbf{V}_2$ are within the Stokes flow regimes; therefore, the superposition principle holds. The flow in the fracture can be obtained in the following form:

$$\mathbf{V} = \mathbf{V}_1 + f(t) \mathbf{V}_2$$ (4.3)

Where $\mathbf{V} = (u_x, u_y)$ is the velocity vector for the whole domain. The flow is specified by the parameters $A$, $B$ and $\omega$. The period of this flow is

$$T = \frac{2\pi}{\omega}$$ (4.4)
The reason we use time-periodic flow is that it can induce chaotic advection even though the flow velocity field is relatively simple. Based on dynamic system theory, Lagrangian trajectories are determined by a dynamical system which can be chaotic if it has enough degrees of freedom ($\geq 3$). Therefore, unsteady 2D flows and steady 3D flows can give rise to chaotic advection. Chaotic advection does not necessarily mean the flow velocity field is chaotic. A very simple two dimensional flow is sufficient to generate chaotic motion of fluid particles. Such a system can provide some useful insight into the behaviour of the chaotic system. Furthermore, the specific feature of passive advection in a two-dimensional time dependent flow is that the phase space of the particle dynamics coincides then with the configuration space. Passively advected particles mean that the particles do not change the velocity field, because they are very small, and they move along with the same velocity as the surrounding fluid which means that the inertia effect is ignored. The phase space structures thus become observable by the naked eye. Incompressibility of the flow implies phase volume conservation. If the flow becomes non-steady, then streamlines can cross at successive times but not at any particular instant. When the velocity field is time-dependent, the positions of vortices change relative to the particles and the particles can travel from one vortex to another. We emphasize here that the reason we construct this particular flow is because of its simplicity. As long as the flow trajectories are non-integrable or chaotic, the flow can introduce chaotic advection to the system.

4.2.1 Scale analysis

An important dimensionless number to characterize the relative importance of advective and diffusive process is the Peclet number. Its definition is as follows:

$$Pe = \frac{Lv}{D}$$  \hspace{1cm} (4.5)

where $L$ and $v$ respectively are the characteristic length and fluid velocity scales of the system. $D$ is the molecular diffusivity of mineral species. As Lester et al. (Lester et al., 2012) pointed out, when $Pe < 1$, the diffusion plays a dominate role. When $Pe > 100$, advection becomes dominant. When $Pe$ is in the range of 1 to 100, both advection and diffusion play an equivalently important role.
The main rectangular fluid channel has a size of 3 metre in width and 1 meter in height and the side channel is 0.1 meter high. The maximum velocity is in the range of $10^{-7}$ m\(s^{-1}\). The typical range of diffusivity $D$ is of magnitude $10^{-8}$ m\(^2\)s\(^{-1}\). Therefore, the advective time scale

$$t = \frac{L}{v}$$ (4.6)

is around $10^7$ s and the diffusive time scale

$$t = \frac{L^2}{D}$$ (4.7)

is around $10^9$ s.

The dimensionless Peclet number

$$Pe = \frac{Lv}{D}$$ (4.8)

is in the range of 10 which is within the chaotic mixing regime.
Because of diffusion, any small but finite diffusivity would impose a cut-off of the smallest spatial scale. This effectively guarantees that a chaotic zone occupies finite volume for the purpose of passive scalar transport. The characteristic diffusion time $\frac{L^2}{D}$ is much longer than the Lyapunov time of the flow. As the fluid moves, the region containing the impurity is strongly deformed, the length of its boundary grows exponentially and diffusion becomes efficient. The key to understanding chaotic mixing is the characterization of the deformation of fluid elements. The process is one of stretching, which increases the length of the interface, and folding, which constrains the fluid element to fill a finite region of space. These geometric processes are often studied in simple mathematical models such as the baker’s or horseshoe maps. For the advection-diffusion problem, fluid is stretched and thinned up to the Batchelor scale $w_B = \sqrt{D/\lambda}$. At this length scale, fluctuations of concentration decay because of the effect of advection and diffusion.

### 4.2.2 Continuous model and discrete models

In this chapter, two distinct simulations are carried out. The continuous model is concerned with the spatial-temporal evolution of the concentration for minerals. Case studies are performed in Section 4.4. Particle tracing methods are used to investigate how the mineral species are advected by the chaotic flow. One thing we should emphasize is, as pointed out by Metcalfe, a fluid particle is not one molecule of the fluid. Fluid particles can be any size but their volume is usually taken to be much smaller than the length scale of the geometry of the flow or domain (Metcalfe, 2010).

For known streamfunction cases, the equations of motion for a passively advected particle in the (x, y) plane can be worked out straightforwardly because they are the derivatives of the streamfunction. The dynamics for the Lagrangian motion are

\[
\dot{x} = u_x \equiv \frac{\partial \phi(x, y, t)}{\partial y} \tag{4.9}
\]

\[
\dot{y} = u_y \equiv -\frac{\partial \phi(x, y, t)}{\partial x} \tag{4.10}
\]
where $u_x$ and $u_y$ are the two components of the velocity field, respectively. $\varphi$ is the streamfunction. One can immediately notice that the pair of equations above has a Hamiltonian structure, with the variable $x$ playing the role of position, $y$ playing the role of conjugate momentum, and the stream function $\varphi(x,y,t)$ being the Hamiltonian. Thus, we identify the dynamics of a passively advected particle in a planar incompressible flow with a one-degree-of-freedom Hamiltonian system. The phase space of this Hamiltonian system coincides with the physical plane in which the flow occurs. As a consequence, the phase-space structures of this dynamical system are directly visible. The most popular way of visualising a flow field is in terms of its streamlines. However, streaklines are more convenient in understanding some of the fundamental mechanics of mixing since very simple streamlines can sometimes produce very complicated streaklines.

Because we compute the steady Stokes flows $\mathbf{V}_1$ and $\mathbf{V}_2$ numerically, we can only export the flow velocity for specific grid points. The grid size we use is $60 \times 40$. Then we import those grid data into Mathematica and interpolate those grid data using the built-in function `ListInterpolation` in order to get the $u_x$ and $u_y$ over the whole domain. The reconstructed velocity field is shown in Figure 4-6.

![Figure 4-6](image)

Figure 4-6 Reconstructed 3D plot of the vertical (a) and horizontal (b) velocity field.

### 4.3 Chaotic Advection Analysis

In this part, we use particle tracing methods to investigate the role of chaotic advection on the transport of mineral particles in the hydrothermal porous media. The mineral particles are assumed to take on the velocity of the surrounding flow very rapidly which means the inertial effect can be neglected. We can thus assume that at each instant the velocity of the advected particles is the same as that of the fluid at the same position. Several nonlinear
dynamics tools are used to characterize the chaotic advection process induced by the periodic side channel flow.

### 4.3.1 Particle trajectories

100 particles are placed to be evenly distributed along the three different dimensionless lines located at $x = 0.3$, $x = 1.2$ and $x = 1.4$, respectively. Those three lines correspond to lines before, in the middle and after the place where the side channel is connected. We record the trajectories of all points from dimensionless time $t = 0$ to $t = 40$ as shown in Figure 4-7. The parameters which are used to trace the trajectories are listed in Table 4-1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time step</td>
<td>$\Delta t$</td>
<td>0.1</td>
</tr>
<tr>
<td>Run time</td>
<td>$T_{\text{total}}$</td>
<td>40</td>
</tr>
<tr>
<td>Amplitude of the periodic flow</td>
<td>$A$</td>
<td>20</td>
</tr>
<tr>
<td>Adjusting parameter of the periodic flow</td>
<td>$B$</td>
<td>30</td>
</tr>
<tr>
<td>Frequency</td>
<td>$\omega$</td>
<td>$\pi/2$</td>
</tr>
<tr>
<td>Period</td>
<td>$T$</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 4-1 Parameter settings used in discrete chaotic advection simulation
Figure 4-7 Trajectory plots for particles distributed along the line $x = 0.3$, $x = 1.2$, and $x = 1.4$ after $t = 40$. The arrows point to the location of the side channel.

From Figure 4-7, we can see that after $t = 40$, the motion of those particles becomes totally unpredictable. Even though those particles are initially distributed evenly and every step of the motion is deterministic, after 10 periods, the locations are totally different. The trajectories diverge from each other rapidly. The typically exponential growth of the distance between initially close particles is a unique sign of the chaotic tracer motion, although the flow itself is fairly simple and strictly periodic. Particle trajectories can be of different types. Some of them are directly transported out of the domain. Particles near the surface of the domain are advected very slowly. Some particles are trapped by the two vortices shown in the dark red region and stay there for a long time, leaving a complicated,
chaotic motion. We note that complicated particle trajectories occur in spite of the fact that
the streamlines are smooth. Chaotic regions are revealed as disordered clouds of points
(Muzzio and Liu, 1996). From Figure 4-7, two chaotic regions can be observed: one is in
front of the side channel and the other locates behind it. Particles located outside of chaotic
regions are simply transported out of the domain directly. However, some particles travel a
long distance, moving from one place to another in the chaotic region before they are
eventually washed away by the open flow. Theoretically, if one particle is initially located
on the stable manifold of the chaotic saddle, it will stay in the domain forever. However,
because the stable manifold of the chaotic saddle has zero measure, the chance of one
particle locating exactly on the stable manifold is zero. What is more likely is for particles
to locate in the neighbourhood of the stable manifold. Those particles will stay in the
chaotic region for a longer time before they are transported out of the chaotic region via
unstable manifolds.

From a mineralisation point of view, those chaotic regions have profound impacts on the
transport process of mineral particles since they are the places where particles stay longer
times, have more chance to “meet” other particles and to react and precipitate.

The flow in the hydrothermal system is non-hyperbolic, that is, it has regular islands
existing in the chaotic saddle. Non-hyperbolic flows contain regular islands or KAM tori
which do not exchange material with the surrounding fluid through separation via
kinematic barriers. These islands act as barriers to transport, where mineral particles can
only be exchanged with the surrounding areas via diffusion (Lester et al., 2012). A direct
consequence of the island is the phenomenon known as stickiness: in non-hyperbolic flows,
many trajectories spend extremely long times inside Contori, leading to very long typical
escape times compared to hyperbolic dynamics (Moura et al., 2012).

An island can be observed as the region devoid of points within the chaotic region.
Interestingly, even though it is located in the chaotic region, no particles can actually reach
it. It acts as an obstacle to the fluid flow. Particles with long residence time can travel
arbitrarily close to the surface of the white holes in Figure 4-7 but they will never be able
to touch them or enter them. The play the role of a basic periodic orbit of marginal stability.
In this respect, it is similar to a KAM surface. The boundary of the latter is, however, a
complicated fractal structure. From a chemical engineering point of view, good mixing can
be achieved in the chaotic regions while flow pathways and KAM islands lead to bad mixing. So it is more desirable to have larger chaotic regions and smaller pathways and KAM islands.

Particles are placed to be distributed evenly with the dimensionless distance interval of $\Delta x = 5e^{-3}$ from $x = 1$ to $x = 1.2$ at the fixed height of $y_0$. The location of $y_0$ is changed and then the trajectories of each particle are plotted as shown in Figure 4-8.

Figure 4-8 Trajectories of particles distributed evenly along a horizontal line of different height at $t = 40$, the arrows point to the location of the side channel.

For $y_0 = 0.1$, 0.2, 0.7, 0.9 cases, particles are advected by the flow velocity out of the domain. For the $y_0 = 0.3$, 0.4, 0.5, 0.6 cases, because of the effect of the chaotic saddle, some particles stay in the interaction zone for a much longer time and travel in a much larger space. This is particularly the situation for the $y_0 = 0.5$ case, with only a small proportion of particles having left the interaction regions. Fluid particles no longer follow
the streamlines of the flow which is the case for steady flow; instead, they follow the chaotic streaklines which are fractal.

### 4.3.2 Fractal patterns

Fractals are scale-invariant geometric objects; any piece of a fractal, appropriately magnified, resembles the whole, at least statistically. Such geometric figures are characterized by a dimension which, unlike that of a familiar Euclidean figure, is generally not an integer. Many physical processes have been shown to produce phenomena that, even though not scale-invariant in an absolute mathematical sense, are self-similar over a very wide range of scales (Sommerer and Ott, 1993). Although physical fractal spatial patterns are frequently observed, a quantitative connection between the measured numerical value of the fractal dimension and the underlying physics of the process has largely been lacking (Sommerer and Ott, 1993). Chaotic advection produces highly ordered structures in stirred fluids. The fluids are folded and stretched and these generated filaments are themselves stretched and folded, generating a fractal structure. The distance between the chemical species that are involved in reactions is drastically reduced and therefore the reaction rate is singularly enhanced. The evolution of a fluid particle line originally locates vertically at x = 0.3 is shown in Figure 4-9. The black line represents the initial position of tracing particles. The positions of those particles are presented at t = 8 (green), t = 12 (purple) and t = 16 (blue). When the fluid line is stretched and folded, clearly, a fractal pattern is traced out.

From a mathematical point of view, the advection dynamics can be regarded as a stroboscopic map $M$, which connects the position of the advected particle at time $t_0$ to that at time $t_0 + \Delta t$ ($\Delta t$ is the time step for the computation):

$$ (x_{n+1}, y_{n+1}) = M_{t_0}(x_n, y_n) $$

Since the flow is incompressible, $M_{t_0}$ is an area-preserving diffeomorphism. If we keep applying this diffeomorphism to the advected particle line iteratively, we would get a fractal pattern eventually.
Figure 4-9 Particle distribution at $t = 0$ (black line), 8 (green), 12 (purple), 16 (blue) by using 10,000 particles with the same parameter of $A$, $B$ and $T$ in Table 4-1.

Chaotic flows can reorientate and bend material elements in a natural way. Stretching and folding can generate complex spatiotemporal structures. Short-time deformation is dominated by stretching, whereas folding occurs only after fluid elements are prolonged. The relative strength of the two processes depends strongly on space and time. Folding dominated regions are initially isolated, but later grow to fill space.

There are two places in which the fluid line is stretched and folded. One is in the vortex near the side channel and the other is in the left-upper region. These places are important to the mineralisation process because chemical reactions are enormously enhanced by mixing which brings the chemical components into intimate contact along lines or surfaces. From a geological point of view, when mineral particles are transported through the domain, most particles are advected out of the domain by an open flow. Some particles will be trapped in the domain. The questions are where they would stay and what the spatial distribution pattern would be. The analysis above probably is the answer to those two questions. When mineralising particles flow past the reaction site, they would distribute in a fractal way. However, the reaction site itself stays still. Therefore, the grade of minerals in those regions is significantly larger than outside those regions. The fractal distribution of the reaction sites renders mineral precipitation in such systems also to be fractally distributed, as can be observed from Figure 4-9.

4.3.3 Stroboscopic map
Since the velocity field is periodic, it is convenient to monitor the particle motion on a stroboscopic map obtained by recording the position of particles after integer multiples of T only. We use $100 \times 100$ points with the dimensionless interval of 0.03 in the x direction and 0.01 in the y direction to trace out the stroboscopic map over the whole domain. The total simulation time is 20 which is 5 periods. Figure 4-10 shows the initial position of those 10,000 particles.

![Figure 4-10 Initial location of 10,000 particles.](image)

In this section, we choose the starting time at $t = 0$. After each period $T = 4$, we take a snapshot of the distribution of those particles. From Figure 4-11, we can clearly see the location of the interaction zones. The particles are advected by the flow, concentrate along the unstable manifolds and leave the system eventually via the unstable manifolds. If there is no chaotic flow, the particles in the domain would have been transported out of the domain in a more rapid manner. The chaotic advection generates a chaotic saddle which is the invariant set of non-escaping orbits in the interaction region. This chaotic saddle can induce profound effects on the transport of mineral particles in the domain.
Figure 4-11 Stroboscopic map plot of particles distribution at t = T, 2T, 3T, 4T, 5T. The arrows point to the location of side channel.
4.3.4 Residence time distribution

An alternative approach to analysing the dynamics of an open flow is the study of residence time of particles in the chaotic region. This approach has been widely used both theoretically and experimentally (Castelain et al., 1997, Castelain et al., 2000, Vikhansky, 2008, Bošković and Loebbecke, 2008). The residence time of the initial position is defined as the time it takes for particles to cross the right boundary of the domain. For the flow described above, the residence time is studied for different initial positions. Following the same logic, three vertical lines are chosen, which are located before, in the middle and after the side channel, respectively. 10,000 particles are used to obtain the distribution of residence time. The flow parameters A, B and T are the same as in Table 4-1. The total time for this computation is 100 which is 25 periods. By depicting the residence time as a function of the y position, clearly a fractal structure is found for each vertical line.
Figure 4-12 Residence time distribution for initial line at $x = 0.3$, $x = 1.1$ and $x = 1.3$.

10,000 particles which initially are distributed evenly have been used to trace out the fractal patterns.
The stable manifold has in general zero area, more precisely, zero Lesbegue measure, which means that the probability that a randomly chosen point in phase space belongs to the stable manifold is zero. Thus, almost all particles will leave the interaction region some finite time after entering it, and only a set of particles having zero measure do not leave the domain. In spite of this, the stable manifold has a great influence on the global dynamics of the system. Particles starting from points close to it will spend a longer time in the interaction zone before escaping, and these long-lived trajectories are responsible for the sensitivity of the dynamics to initial conditions.

From Figure 4-12, it can be seen that the curve can generally be categorized into two types: the lower and smooth parts and the higher parts with spikes. The former are particles initially located in the flow pathways. They are simply flushed by the flow in a regular manner; therefore, they have smaller residence time. The more interesting are those with spikes which exhibit a fractal pattern. A fractal structure of the residence times indicates that particles with initial conditions close to each other show a structurally different trajectory which causes the jumps in the residence time as shown in Figure 4-12. This indicates a strong dependence on initial conditions, which means the underlying dynamics are chaotic.

From the x = 0.3 case, it can be seen that from y = 0 to y = 1, particles experience chaotic motion. We choose a smaller segment from y = 0.5 to y = 0.7. We also use 10,000 distributed evenly to see the distribution of residence time for this smaller segment. Self-similar phenomenon can be shown by the comparison of residence time for line y = 0 to y = 1 and line from y = 0.5 to y = 0.7 in Figure 4-13 (bottom). Notice that the computation time is limited to 100 which is the reason there is cut-off residence time.
Figure 4-13 Comparison of residence time for vertical line $y = 0$ to $y = 1$ (above) and $y = 0.5$ to $y = 0.7$ (bottom). Both cases use 10,000 particles.

We use the same configuration as described in Section 4.3.3 to trace out the residence time for the 10,000 particles over the whole domain. Figure 4-14 shows the resulting distribution and Figure 4-15 is the plot of the contour of residence time distribution. The total simulation time is 100 and the time interval is 0.1. So the longest time one particle can stay is 100. From Figure 4-14, we clearly can see the flow pathway which is the lower part while in Figure 4-15, it corresponds to the dark purple part. Note that Figure 4-14 and Figure 4-15 have opposite directions horizontally. From Figure 4-14, we can also see some lines at the left side of the domain. It shows how many periods the system has undergone. From Figure 4-14 and Figure 4-15, we can see that two regions are apparently higher than the surrounding regions. They are the chaotic region where chaotic mixing occurs.
Figure 4-14 Residence time distribution over the whole domain.

Figure 4-15 Contour of the above residence time distribution. The arrows point to the location of the side channel.

4.3.5 Poincare section

The asymptotic-in-time topology of flows can be examined by means of a Poincare section. Poincare sections plot the locations of a small number of fluid particles after every period of the flow. For our two-dimensional time dependent flow, the dimension for the phase space is 3 (2D geometry plus time). By using Poincare section, we can reduce the phase dimension by 1. In our simulation, we use 10 particles to obtain the Poincare section. The coordinates are listed in Table 4-2.
Table 4-2 Coordinates of points used to obtain the Poincare section

<table>
<thead>
<tr>
<th>x</th>
<th>0.3</th>
<th>0.3</th>
<th>0.3</th>
<th>0.3</th>
<th>1.1</th>
<th>1.1</th>
<th>1.3</th>
<th>1.3</th>
<th>1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>y</td>
<td>0.5</td>
<td>0.65</td>
<td>0.75</td>
<td>0.9</td>
<td>0.15</td>
<td>0.3</td>
<td>0.46</td>
<td>0.02</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
</tbody>
</table>

Trajectories for the selected particles are supposed to be followed for hundreds or thousands of periods to obtain the asymptotic time advection behaviour. However, unlike the close flow case, there exists an open current in our system. Unless carefully selected, most particles will leave the domain very soon. The existence of open current limited the computing time for our simulation. The Poincare section of 10 periods is shown in Figure 4-16.

**Figure 4-16** Poincare section for particles listed in Table 4-2.

Good mixing is achieved in the chaotic region.

**Figure 4-17** Trajectories for particles listed in Table 4-2 by $t = 40$.

Only four points stay in the domain (represented by red dots).

On the Poincare section of a two-dimensional time-periodic flow, integrable trajectories lie on topological circles which are called regular components. They are the flow pathway of the system. The non-integrable or chaotic trajectories fill a finite area called irregular components.

---

115
component. Only chaotic regions, occupy a finite volume, which is required for good mixing. Periodic trajectories locate in the irregular component. In our numerical computations we did not find periodic trajectories. The reasons we evaluate are probably that the chaotic saddle has zero measure, which means the chance of the particles to be distributed exactly on its stable manifold is zero.

4.3.6 Escape rate

The chaotic saddle has zero measure so that the probability for tracing particles to distribute on the chaotic saddle is zero. Therefore, almost all the particles will eventually leave the interaction zone sooner or later. We record the number \( \mathcal{N}(t) \) of particles that have not escaped the region up to time \( t \). Another important characteristic quantity associated with this process is the escape rate \( \kappa \) defined as

\[
\mathcal{N}(t) = \mathcal{N}(0)e^{-\kappa t}
\]  

(4.12)

Where \( \mathcal{N}(0) \) is the initial particle number, 10000 in our case.

In Figure 4-18, the red line represents the total particle number and the blue line represents the estimated particle number with \( \kappa = 1.15e^{-2} \).

![Figure 4-18](image)

Figure 4-18 Total number of particles in the domain (red line). The blue line plots the curve characterised by escape rate \( \kappa \).

4.4 CASE STUDIES
The analysis of chaotic advection in section 4.3 is in the absence of additional transport mechanism of molecular diffusion. In this part, we investigate the complex interplay of chaotic advection and diffusion. As can be seen from section 4.2, both diffusion and advection play an equivalently important role for the transport of mineralising chemical reactants when the Peclet number is within the range of 1-100. By using the advection-diffusion equation, we can investigate how the concentration scalar $c$ in the fracture space evolves. The dimensionless form of the advection-diffusion equation is as follows:

$$\frac{\partial c}{\partial t} + \vec{v} \cdot \nabla c = \frac{1}{Pe} \Delta c$$  \hspace{1cm} (4.13)

Two different study cases are performed to show how the distribution of mineral particles is affected by the combined processes of chaotic advection and diffusion.

### 4.4.1 Case study 1

In this case study, the domain is initially saturated with a mineral component with the dimensionless concentration of 1 (represented by the red colour). We assume the right boundary is always open. We can have 3 different cases: case 1) open the left boundary in the main channel; case 2) open the bottom boundary in the bottom side channel; case 3) open both boundaries simultaneously. For all the three cases, we assume that the flux from the inlet is zero. We want to see how the concentration field evolves with time. For case 1, we can clearly see a linear displacement of concentration field induced by horizontal velocity in Figure 4-19.

![Figure 4-19 Concentration distribution for case 1 at t = 10 and 30.](image)

For case 2, as shown in Figure 4-20, the rectangular domain is generally divided into two parts by the side channel flow. The left part becomes “trapped” whereas most of the right part is washed away by the side channel flow.
For case 3, as shown in Figure 4-21, we see a much more rapid replacement process with both inlets open. At time equals 10, most of the minerals have been transported out of the domain.

The total amount of minerals at time $t_0$ can be expressed as follows:

$$ C = \int \int c(x, y, t_0) dx dy $$

(4.14)
Figure 4-22 shows how the total amount of minerals changes with time for the above 3 cases.

![Figure 4-22 Total amount of mineral left at different times for cases 1, 2, 3.](image)

**4.4.2 Case study 2**

In this part, the domain initially has zero concentration of mineral components. For case 1, the boundary at the bottom is open with constant concentration \( c = 1 \) and the boundary at the left is open with constant concentration \( c = 0 \). For case 2, the boundary at the bottom is open with constant concentration \( c = 0 \) and the boundary at the left is open with constant concentration \( c = 1 \).

We are interested in the spatial-temporal evolution of concentration field. Figure 4-23 shows the spatial-temporal distribution of concentration for case 1 at \( t \) equals 5, 10, 20, and 40. We can see that the chaotic region near the side channel becomes homogeneous very soon while other parts have a very low concentration because of the existence of open currents. In closed domains, the zero-flux conditions guarantee that finite amounts of reacting species eventually are driven to a homogeneous equilibrium state. However, as can be seen from Figure 4-23, the continual flux of reactants in open systems can indefinitely sustain spatial and temporal patterns and hence concentration is maintained as a stationary pattern.
Figure 4-23 Spatial-temporal distribution of concentration for case 1 at time 5, 10, 20, 40.

Figure 4-24 shows the spatial-temporal distribution of concentration for case 2 at $t = 5$, 10, 20, and 40, respectively. We can see that the chaotic region in the left-upper of the domain is difficult to sweep downstream by the horizontal flow. However, its concentration becomes larger and larger because of the effect of diffusion.

Figure 4-25 shows the comparison of the total amount of minerals for the above two cases. From Figure 4-25 we can see that after $t = 40$, the integral of the concentration field oscillates around a constant value which means that the system reaches a steady state. This is also confirmed by Figure 4-26 which plots the flux at the outlet of this domain.
The flux at the right outlet can be defined as follows:

\[ (-D \nabla c + c \bar{u}) \cdot \bar{n} \]  \hspace{0.3cm} (4.15)

where \( \bar{n} \) is the unit vector normal to the boundary.

From Figure 4-26 we can conclude that the flux at the right boundary is strongly affected by the flow. The frequency of the flux is synchronized by the frequency of the side channel flow.

4.5 CONCLUSION

In this chapter, we have learned that chaotic advection can be induced at the fracture scale where the main flow channel is connected with a periodic side flow channel. Fluid mixing is undoubtedly an important aspect of the mineralising process. We have found that the
impact of chaotic advection on mixing is profound in the open flow system. Efficient fluid mixing is very difficult to achieve if the flow is steady in porous media. Chaotic advection can dramatically enhance mixing which is desirable for chemical reactions. By using a large number of tracing particles, we found that the whole open system domain is divided into different regions: regions are flow pathways where particles are swept away very rapidly; regions where tracing particles can stay a longer time, and regions where particles can never enter into, which are KAM islands within the chaotic region. Two specific chaotic regions have been identified by the Poincare section method. These two chaotic regions are places where tracing particles can concentrate and the distribution pattern for these tracing particles is fractal.

From the continuous model, we can conclude that highly heterogeneous spatial distributions of concentration are generated by coupled chaotic advection and diffusion in the open flow system. A strong concentration gradient can be maintained between chaotic regions and flow pathways. Within a chaotic region, concentration becomes homogeneous rapidly due to diffusion. With the introduction of chaotic advection, the concentration becomes difficult to sweep downstream by the open flow. In some places, the concentration decays very slowly. Those fixed spatial sites are important for the mineralising process since they are where mineral reactions are localised and ore bodies are likely to form.

The ultimate goal in performing modelling on a hydrothermal system is to solve the inverse problem of gaining insight into the nonlinear dynamical processes responsible for the mineralisation from limited field observations. From the modelling of this chapter, we can see that mechanisms of chaotic advection and diffusion can bring the chemical components into intimate contact along fractal chaotic regions. It gives one possible answer to the question of how mineral reactants are mixed before they can react with each other. The corresponding mineralisation process would be enormously accelerated by those two mechanisms.
CHAPTER 5

MODELLING OF FRACTURE-SCALE CHEMICAL REACTION AND CHAOTIC ADECTION INDUCED BY PERIODIC FLOW

5.1 INTRODUCTION

The traditional approach to do mineralization simulation is to assume that chemical equilibrium has been established in the hydraulic-chemical systems. However, as pointed out by Zhao et al. (Zhao et al., 2007), the overall pattern of mineralization in these systems results from intimate interactions between advection, diffusion and/or dispersion and chemical reaction and chemical equilibrium may never be attained in these systems. The relative importance of individual processes cannot be fully assessed without considering them in the context of the other dynamic processes. Integrated approaches have to be carried out to investigate the complex interplay of material flow, transport, and chemical reaction at multiple spatial and temporal scales.

In well-mixed chemical systems, nonlinear phenomena such as chemical oscillations, and solitary and travelling waves can be generated in reaction-diffusion systems with multiple equilibria (Gray and Scott, 1990, Kuramoto, 2003, Neufeld, 2001, Horváth et al., 1993, Scott, 1994). Numerical simulations found that the application of a laminar shear flow to an autocatalytic reaction front can lead to an enhanced rate of reaction (Allen et al., 1996). More complicated spatiotemporal patterns can be generated by steady shear flows in excitable media (Biktashev et al., 1998, Biktashev et al., 1999b, Biktashev et al., 1999a). It was found that the waves of excitation may be broken by the flow motion (Biktashev et al., 1998). For quadratic (A+B->2B) and cubic (A+2B->3B) autocatalytic reactions, it was found that travelling wave fronts of uniform speed and constant profile can be generated (Gray and Scott, 1990). When a localized perturbation exceeds the excitation threshold in a motionless medium, solitary waves can be generated which in two dimensions propagate in the form of an expanding circular ring (Neufeld, 2001). In an open flow system with
chemical reactions coupled with diffusion, the governing equation is described (Scott, 1994) as follows:

$$\frac{\partial c(r, t)}{\partial t} = Dc(r, t) + R(c, b) + \frac{c_0 - c}{\tau} \quad (5.1)$$

$\tau$ is the residence time and $\frac{c_0 - c}{\tau}$ is called the feeding term. This equation adopts the assumption of homogeneous state. That is, at a specific time, the system only has one homogeneous concentration and the residence times for all of the chemical components are equal.

However, most hydrothermal systems in the real world are imperfectly mixed systems. Chaotic mixing produces complex structures that appear to be a collection of different size filaments filling chaotic regions. The two controlling mechanisms of the convective mixing processes, stretching and folding, occur simultaneously at different rates in each portion of the flow, creating complex patterns (Szalai et al., 2003). As time evolves, the interplay of stretching, diffusion, and reaction creates heterogeneous patterns, with regions of high and low product concentration. There are regions of low stretching where the interface between reactants grows approximately linearly in time, and the local reaction rate is less than that in regions of high stretching. These qualitative differences show that the product distribution is substantially affected by the flow pattern.

If the laminar flow field is unsteady, chaotic advection will be triggered by the time-dependent flow which means the fluid particles will follow chaotic trajectories. Chaotic advection acts as a deformation that stretches and folds fluid elements generating a filamental structure. Concentration fields along the stretching direction of filaments are quickly homogenized while strong concentration gradients along the contracting direction can be maintained. Neufeld et al. (Neufeld et al., 2002) developed a 1D model to investigate the interplay between chaotic advection, diffusion and chemical reaction and found that there exists a critical Da number under which chemical reaction can be completely extinguished by advection. Another important consequence of chaotic advection is the exponential separation of nearby fluid elements, that is in contrast to two-dimensional steady flows where advection is non-chaotic and the separation of fluid particles increases only linearly in time.
Figure 5-1 Pattern induced by flow in rock due to chaotic advection. Photo copyright by Roberto Weinberg, school of geoscience, Monash University, Australia, http://users.monash.edu.au/~weinberg/Pages/disharmonic_folds/irreg_folds_tng/50pct/DS_C03825.jpg.

Chaotic advection is normally coupled with non-equilibrium chemical reactions. In studying active flows, it is of particular importance to relate the dynamics of the reactive system to the underlying advection dynamics of the flow (Tél et al., 2005). The stretching and folding of fluids caused by chaotic advection can significantly enhance mixing of different chemical species; therefore, the chemical reaction rates can be dramatically enhanced as the consequence of the chaotic mixing. Metcalfe and Ottino (Metcalfe and Ottino, 1994) chose eccentric cylinder flow to illustrate the effect of chaotic flow on the propagation and evolution of patterns produced by competing autocatalytic processes in a closed system. Grooß et al. used a chemical Lagrangian model to investigate how chemical ozone depletion is affected by chaotic advection in atmospheric scale (Grooß et al., 2005). Figure 5-2 shows that the pattern of the chemical reactant distribution (HCl production) has filamentary structures (Grooß et al., 2005).
Chaotic advection coupled with chemical reaction generally can be categorized into two types: closed systems and open systems. Simple closed flow such as cavity flow or journal bearing flow can generate complex mixing patterns (Muzzio and Liu, 1996). In contrast to investigations restricted to flows in closed regions, an increasing number of researchers consider two dimensional “open” flows in which the velocity field in the far upstream and downstream regions is uniform but non-stationary in a bounded region (Toroczkai et al., 1998, Neufeld, 2001, Neufeld et al., 2002, Tél et al., 2005). Hydrothermal systems are “open” in the sense that fresh fluid and chemical reactants can flow into the reaction site and leave the system in a later time. Different from closed systems where only equilibrium states can be expected, open systems can maintain far-from-equilibrium states indefinitely. The chemical activities are strongly affected by the chaotic saddle and its associated stable and unstable manifolds generated by chaotic advection.

A wide range of chemical reactions are relevant to mineralization in hydrothermal systems, including autocatalytic reactions, multi-stable reactions, competitive reactions and reactions representative of excitable media involving catalysis and inhibition (Lester et al.,

Figure 5-2 Atmospheric scale advection coupled with chemical reaction. Concentration field of Hydrogen Chloride (in parts per billion (ppb)) above the South Pole at about 18 km altitude on September 24, 2002 (Groß et al., 2005).
In terms of the chemical reaction for the deposition of gold, the following set of reactions have been suggested by Henley and Berger (Henley and Berger, 2000):

\[
Fe^{2+}(aq) + H_2S \rightarrow FeS + 2H^+
\]

\[
FeS + H_2S \rightarrow FeS_2 + 2H
\]

\[
Au^+ + H \rightarrow Au + H^+
\]

The deposition site stays fixed in space while the fluid passes by and precipitates gold and pyrites so long as the \(Fe^{2+}\) in solution and \(H_2S\) are supplied.

In this chapter, we couple chemical reaction for the ore-forming system considered in chapter 4 in which fluid in the main channel is manipulated by time-dependent flow in the side channel. One mineralisation example is the uranium deposits in Athabasca Basin in Canada (Jefferson et al., 2007). Several numerical simulations have been carried out to investigate the role of fluid flow, geochemistry, deformation, and solute and heat transport in the formation of unconformity-type uranium ore deposits (Raffensperger and Garven, 1995a, Raffensperger and Garven, 1995b, Schaub et al., 2003, Yang et al., 2006, Zhang et al., 2006, Jefferson et al., 2007, De Veslud et al., 2009, Cui et al., 2012a, Cui et al., 2012b, Poulet et al., 2012, Mercadier et al., 2013, Clowes et al., 2010). We are in particular interested in how the advection dynamics affect the distribution of product and total reaction productivity. When chemical solutes are continually fed into the mineralising sites, non-homogeneity of spatial concentration distributions can be maintained indefinitely under the condition of chaotic advection and the pattern of the minerals distribution would be fractal which is consistent with the observation from fields. In section 5.2, we describe the model used for the reaction dynamics and for the flow and perform scale analysis for the reaction-diffusion-advection process. Then, in section 5.3, analysis is carried out to investigate the effect of chaotic advection and chemical kinetics on the chemo-hydrodynamic pattern of product and reaction productivity. This chapter ends with a conclusion in section 5.4.

5.2 MODEL SYSTEM
The system configuration is the same as that in chapter 4 detailed in the Appendix. The original flow in the main channel is parabolic and steady, and then it is manipulated by a periodic side channel flow with an angle. Therefore the overall flow profile is time dependent and chaotic advection can be generated. In this chapter, we assume that the mineral particles are “active” which means that they are subject to chemical reactions but do not modify the underlying flow. This is clearly different from chapter 3 in which concentration variation can affect the viscosity of the flow and change the flow velocity field. This one-way coupling can dramatically simplify our simulation because the flow field is independent of both the species concentrations and reaction dynamics. Figure 5-3 shows the arrow plot of the velocity at $t = \frac{3}{4}T$ with the flow parameters $A = 10, B = 15, \omega = \frac{\pi}{2}$.

![Figure 5-3 Velocity profile at $t = \frac{3}{4}T$ with $A = 10, B = 15, \omega = \frac{\pi}{2}$](image)

5.2.1 Governing equations

The spatial-temporal dynamics of the field are governed by the reaction-diffusion-advection equations.

$$\frac{\partial}{\partial t} C_i + u \cdot \nabla C_i = D \Delta C_i + R_i(C_1, C_2, ..., C_N; k_1, k_2, ..., k_N)$$  (5.2)
where $R_i$ describes the reaction rate between the different components, $k_i$ represent the reaction rate coefficients characterizing the speed of the chemical interactions and $D$ is the diffusivity which is assumed the same for all components.

The dimensionless form of Equation 5.2 is as follows

$$\frac{\partial}{\partial t} C_i + u \cdot \nabla C_i = Pe^{-1} \Delta C_i + DaR_i \quad (5.3)$$

Different kinds of chemical reactions have different rate equations. In chemical kinetics, the following expression is adopted to link the rate of a reaction to the concentration of each reactant:

$$R = k(T)[A]^n[B]^m \quad (5.4)$$

Therefore, the units of the rate constant depend on the global order of reaction. For order $(n + m)$, the rate coefficient has units of $mol^{1-(m+n)} \cdot L^{-(m+n)-1} \cdot s^{-1}$ if concentration is measured in units of $mol \cdot L^{-1}$.

5.2.1.1 Autocatalytic chemical reaction

For the chemical kinetics, we consider $A+B\rightarrow 2B$ type of chemical reaction. In this type of reaction, $B$ is the catalyst as well as the product. The reaction rate for this type of reaction is assumed as follows:

$$R = kC_A C_B \quad (5.5)$$

Because the total number of molecules of $A$ and $B$ is conserved, we can introduce another variable

$$C \equiv \frac{C_B}{C_A + C_B} \quad (5.6)$$

representing the proportion of component $B$. The final governing equation in terms of $C$ is
\[ R = kC(1 - C) \]  

Equation 5.7 has two steady states: \( C = 0 \) which is unstable and \( C = 1 \) which is stable. Another form of chemical kinetics is a multi-stable system which has several stable steady states. The simplest example of a multi-stable system is the so-called bi-stable system which has two stable steady states. Its reaction equation is

\[ R = kC(C - \alpha)(1 - C), \quad 0 < \alpha < 1 \]  

\( C = 0 \) and \( C = 1 \) are the two stable steady states while \( c = \alpha \) is the unstable steady state. Perturbations smaller than \( \alpha \) die out, whereas bigger ones exceeding the threshold, grow until reaching the upper limit \( C = 1 \). The autocatalytic reaction \( A+B -> 2B \) represents a simplified model of a wide range of reactive dynamics, including many relevant to mineral precipitations such as autocatalytic redox reactions and thermo-catalytic reactions.

### 5.2.1.2 A + B -> C type of reaction

The A + B -> C reaction is also considered in which the collision of two molecules A and B generates a new one C. The rate expression shows that the reaction rate is directly associated with the concentration of reactant A and B:

\[ R = kC_A C_B \]  

#### 5.2.2 Scale analysis

The most two important dimensionless numbers characterising the advection-diffusion-reaction process are Damkohler number, \( Da \), and Peclet number, \( Pe \). The definition of Damkohler number \( Da \) and Peclet number \( Pe \) is:

\[ Da \equiv \frac{kL}{U} \]  

\[ Pe \equiv \frac{LU}{D} \]
The Damkohler number Da characterizes the ratio between the advective and the chemical time scales. Large Da corresponds to slow advection or equivalently fast chemical reactions. The Peclet number Pe is a measure of the relative strength of advective and diffusive transport. Normally, the diffusivity is a very small number which means the Peclet number is large, corresponding to advection dominated processes.

The following dimensionless process is adopted in the modelling of grain-scale mineralization processes:

\[ x \rightarrow \frac{x}{L}, t \rightarrow \frac{tU}{L}, u \rightarrow \frac{u}{U}, k_i \rightarrow \frac{k_i}{k_1}, R_i \rightarrow \frac{R_i}{k_1} \]  

(5.12)

where L and U are the characteristic length-scale and velocity of the flow.

As discussed in section 5.2.1, the modelling geometry size is in the range of 1m, while the maximum velocity is in the range of $10^{-7}$ ms$^{-1}$. The typical range of diffusivity $D$ is of magnitude $10^{-8}$ m$^2$s$^{-1}$. The magnitude of chemical rate constant can span a fairly large range. In our simulation, we use $k$ from $10^{-6} \text{mol}^{1-(m+n)} \cdot L^{(m+n)-1} \cdot s^{-1}$ to $10^{-8} \text{mol}^{1-(m+n)} \cdot L^{(m+n)-1} \cdot s^{-1}$ which gives us the Da number spanning from 0.1 to 10. As to the other dimensionless values, they are the same as that which are described in chapter 4.

### 5.3 CASE STUDIES

In the following part, we perform 4 case studies of different scenarios to investigate the impact of chaotic advection, diffusion and chemical reaction on the fracture scale mineralization process.

#### 5.3.1 Steady flow and chaotic flow

In this case study, we compare the impact of steady flow and chaotic flow on the autocatalytic chemical reaction $A+B \rightarrow 2B$. The governing equation is as follows:

\[ \frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = D \Delta C + kC(1 - C) \]  

(5.13)
where $C$ represents the proportion of component B. For autocatalytic chemical reaction $A+B\rightarrow 2B$. Essentially reactant $A$ is converted into product $B$. The total amount of chemicals $A$ and $B$ is conserved. The changing part is the proportion of chemical $B$ (or $A$) to the total amount of $A$ and $B$ as depicted by Equation 5.6. Instead of considering concentration of $B$, equation is used in this thesis to describe the proportion which varies from 0 to 1. The gradient of $C$ resembles the gradient of concentration of $B$. $u$ is the flow velocity field. Following the same methodology from chapter 4, we can obtain a time-dependent flow field:

$$V = V_1 + f(t)V_2$$  \hspace{1cm} (5.14)$$

where the definition of the time factor is

$$f(t) = A\sin(\omega t) + B$$  \hspace{1cm} (5.15)$$

We compare this time-dependent flow with its time-independent counterpart $V'$:

$$V' = V_1 + (A + B)V_2$$  \hspace{1cm} (5.16)$$

The initial state is $C = 0$, corresponding to component $A$ alone. This unstable state is subject to a localized Gaussian perturbation of this form:

$$C(x, y, t = 0) = e^{\frac{(x-x_0)^2+(y-y_0)^2}{\alpha}}$$  \hspace{1cm} (5.17)$$

Figure 5-4 Initial perturbation with $(x_0, y_0) = (0.2, 0.2)$, $\alpha = 200$ (blue colour corresponding to $C = 0$, red corresponding to $C = 1$).
The left and bottom inlets have constant concentration $C = 0$ boundary conditions while the right outlet has convective flux boundary condition. Other boundaries have insulated boundaries.

Table 5-1 Parameter settings used in case study 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domain size</td>
<td></td>
<td>$3 \times 1$</td>
</tr>
<tr>
<td>Peclet number</td>
<td>$Pe$</td>
<td>$1 \times 10^2$</td>
</tr>
<tr>
<td>Reaction rate coefficient</td>
<td>$k$</td>
<td>1</td>
</tr>
<tr>
<td>Initial location</td>
<td>$x_0$</td>
<td>0.2</td>
</tr>
<tr>
<td>Initial location</td>
<td>$y_0$</td>
<td>0.2</td>
</tr>
<tr>
<td>Gaussian parameter</td>
<td>$\alpha$</td>
<td>200</td>
</tr>
<tr>
<td>Time step</td>
<td>$\Delta t$</td>
<td>0.1</td>
</tr>
<tr>
<td>Run time</td>
<td>$T_{total}$</td>
<td>40</td>
</tr>
<tr>
<td>Amplitude of the periodic flow</td>
<td>$A$</td>
<td>10</td>
</tr>
<tr>
<td>Adjusting parameter of the periodic flow</td>
<td>$B$</td>
<td>15</td>
</tr>
<tr>
<td>Frequency</td>
<td>$\omega$</td>
<td>$\pi/2$</td>
</tr>
<tr>
<td>Period</td>
<td>$T$</td>
<td>4</td>
</tr>
</tbody>
</table>

The spatiotemporal evolution of the chemical perturbation is plotted in Figure 5-5 at different times for steady flow and chaotic flow in the right and left columns, respectively. At dimensionless time $t = 1$, it can be seen that the symmetric pattern is stretched by the parabolic flow in the main channel. At later time, the concentration field is stretched and folded by the chaotic side channel flow. At $t = 30$, the majority of the domain is occupied by component B represented by red colour.
Figure 5-5 Contour plot of concentration field for chaotic flow (left column) and steady flow (right column) at dimensionless $t = 1, 2, 4, 6, 8, 30$ (blue colour corresponding to $C = 0$, red corresponding to $C = 1$).
Fluid flow is an important mechanism for transporting mineralising chemical components from one location into another. Fluid flow can also determine the positions where different chemical components may meet and mix and hence where chemical reactions take place. From Figure 5-5, we can see that the chemical patterns are strongly influenced by fluid flow. The right column is for the steady flow case $V'$ which is stronger than the left column chaotic flow. As can be clearly seen at dimensionless $t = 4$, the perturbation has been spread by the stronger steady flow and occupy a larger space. However, after just two periods, the chaotic flow occupies more space than the steady flow.

At each time $t_0$, there is a concentration field of $C(x,y,t_0)$. If integrates the concentration field all over the whole domain, the total product can be obtained. The total production of the chemical reaction at time $t_0$ can be expressed as

$$C_{production} = \int \int C(x, y, t_0) dx dy \quad (5.18)$$

Figure 5-6 shows the total production for steady and chaotic flow cases from dimensionless time 0 to 20. The production curve for the steady flow case evolves all the way to a constant while the production curve for the chaotic flow case oscillates around another constant value. The frequency is synchronized with that of the chaotic flow. By dimensionless time $t = 20$, steady states have been achieved for both cases.

![Figure 5-6 Production curve from dimensionless t = 0 to t = 20.](image)
Steady flow and chaotic flow cases are contrasted for perturbations initially centred at point \((x = 2.5, y = 0.5)\). From Figure 5-7, one can see that the perturbation diminishes because of the effect of diffusion at dimensionless \(t = 0.5\) and the perturbation has been transported out of the domain by dimensionless \(t = 1\).

Figure 5-7 Evolution of perturbation for steady flow at \(t = 0\), \(t = 0.5\) and \(t = 1\) (blue colour corresponding to \(C = 0\), red corresponding to \(C = 1\)).

Figure 5-8 plots the transport process for chaotic flow case at \(t = 10\), \(t = 20\), and \(t = 30\). It can be seen that at \(t = 30\), the chaotic regions are traced out, represented by the dark red colour.
Another phenomenon is that the final concentration profile is insensitive to the initial location of the perturbation for chaotic flow as long as it overlaps with the stable manifold of the chaotic flow. Figure 5-9 plots how the perturbation, initially located at different places, evolves with time. The centre of the initial perturbation in the left column is located at point (x = 0.2, y = 0.2) while the centre of the right column is located at point (x = 0.2, y = 0.5). It can be seen that after t = 10, the distribution of concentration becomes almost the same.
Figure 5-9 Spatiotemporal evolution of perturbation initially located at (0.2, 0.2) and (0.2, 0.5) at dimensionless time $t = 0, 5, 10$ (blue colour corresponding to $C = 0$, red corresponding to $C = 1$).

For chaotic flow, the effect of reaction rate $k$ on the distribution of concentration $c$ is investigated for $k = 0.1$ and $k = 0.3$. The case $k = 0.1$ corresponds to a very slow reaction. As shown in Figure 5-10, the perturbation initially centred at point $(x = 0.2, y = 0.5)$ is completely expelled out of the domain.
In Figure 5-11, with $k = 0.3$, it can be seen that the chemical reaction is unable to occupy regions where the flow rate is high. However, in chaotic regions where the flow rate is low, chemical reactions become localised. From the mineralization point of view, those chaotic regions are the most likely sites for the mineralising reactants to precipitate.
5.3.2 Chemical reactions with different reaction rate

In this case study, we investigate how chemical kinetics affect the distribution of chemical components and the time dependence of product growth for our model. The fluid in the main channel is assumed to contain chemical reactant A while the fluid in the side channel contains chemical reactant B. The chemical reaction is the autocatalytic chemical reaction \( A + B \rightarrow 2B \) with different reaction rate \( k = 0, 0.1, 0.5 \) and 1. All the other parameters are the same as listed in table 5-2.

Figure 5-12 plots the chemical pattern generated for chemical reaction rate \( k = 0 \) (which corresponds to no reaction) and \( k = 0.5 \), respectively. No chemical reaction takes place for the \( k = 0 \) case, therefore, a concentration gradient is formed in the chaotic regions where
the side channel is connected. While for the $k = 0.5$ case, the concentration becomes homogeneous rapidly in the chaotic regions.

Figure 5-12 Distribution of reactant B for $k = 0$ (left column) and $k = 0.5$ (right column) cases at dimensionless time $t = 5, 10, 20, 30$ (blue colour corresponding to $C = 0$, red corresponding to $C = 1$).
Figure 5-13 is the production curve for different reaction rates $k = 0$, 0.1, 0.5, and 1. As shown in Figure 5-13, a higher production is obtained for a higher reaction rate. At $t = 20$, the production curve becomes flat for all the cases which means dynamic steady states have been reached.

5.3.3 Multi-stability

The bi-stable system is the simplest model for multi-stability. Equation 5.8 has two stable steady states $C = 0$ and $C = 1$, separated by one unstable steady state $C = \alpha$. It has two attraction basins. For any perturbation having concentration $c$ within the range of $0 < C < \alpha$, the concentration will be attracted to the stable steady state $C = 0$. If $\alpha < C < 1$, the concentration will be attracted to the other stable steady state $C = 1$. This means that stronger perturbations will propagate through the system, whereas smaller ones die out.

In this study, we assume the fluid in the main channel has a concentration of $C = 0$. The periodic side channel continuously feeds the main channel with reactant of concentration $C_0$ which can be smaller or larger than the threshold $\alpha$. 
Figure 5-14 Concentration profile for the bi-stable reaction at $t = 5, 10, 20, 40$. The threshold $\alpha = 0.8$, the concentration of the inlet of the side channel is 0.6 (blue colour corresponding to $C = 0$, red corresponding to $C = 1$).

In figure 5-14, the concentration can only evolve to the stable steady state $C = 0$ because the feeding concentration of the side channel is smaller than the threshold.

The more interesting case is when the inlet of the side channel has a supplying concentration $C_0$ which is larger than the threshold $\alpha$. In the following case, the threshold $\alpha$ and the supplying concentration $C_0$ are set to 0.4 and 0.9, respectively. The evolution of the concentration field is shown in Figure 5-15. Before dimensionless time $t = 20$, the inlet has a higher concentration than the other places of the domain. When at the time $t = 40$, the chaotic region has a higher concentration than the inlet. The concentration in the chaotic region is attracted to the other steady state $c = 1$. 
Figure 5-15 Concentration profile for bi-stable reaction at $t = 5, 10, 20, 40$. The threshold $\alpha = 0.4$, the concentration of the inlet of the side channel is 0.9 (blue colour corresponding to $C = 0$, red corresponding to $C = 1$).

The chemical reaction has two stable and one unstable fixed points. As shown in Figure 1-2, a larger perturbation from one fixed point may lead to dynamics with a final state at the other fixed point, although each fixed point is stable to small perturbations. At first, the chemical reactant is transported into the interaction region by the fluid flow. The advection increases the average concentration of chemical reactant in the interaction region. The average concentration in the interaction region is smaller than the threshold, therefore, the chemical reaction suppresses the growth of concentration. The flow is competing with diffusion and reaction. Because of strong advection, the concentration keeps increasing. When the average concentration is between the region $\alpha < C_{avg} < C_0$, the chemical reaction can enhance the growth of concentration, so the advection and chemical reactions are competing with diffusion. When the average concentration increases above the supplying concentration $C_0$, the advection has a diluting effect on the growth of concentration. The chemical reaction is competing with advection and diffusion. The state selection is defined by the net flow rate (the product of the volumetric flow rate and species concentration) and by the nature of the volumetric flow system during fluid mixing. The net flow rate depends on the permeability and so slight local fluctuations in permeability can result in entirely different modes of chemical behaviour including little or no reaction, steady reaction at high yield and oscillatory and chaotic behaviour at both high
and low yield. Such strong dependence on local conditions also is apparent in spatial patterning (Lester et al., 2012).

5.3.4 **A+B→C type of reaction**

Study cases 1 and 2 in chapter 4 are concerned with one fluid mixing with itself subject to the chaotic advection induced by the periodic side channel flow. In this part, we simulate two fluids mixed with each other subject to the same chaotic advection. The fluid in the main channel is referred as fluid A while the fluid in the side channel is fluid B. Both fluids will mix in the interaction zone transported by the periodic flow. We also assume that an A+B→C chemical reaction takes place between the interface of fluid A and fluid B. In order to simplify the process, we set the diffusivity for A and B the same for both species. The dimensionless reaction rate constant $k$ is set to 1.

![Figure 5-16 Concentration distribution of reactant A at t = 0.5, 3, 10, 20 (blue colour corresponding to C = 0, red corresponding to C = 1).](image)

Figure 5-16 displays the concentration distribution of reactant A at different times. Initially, the whole domain is saturated with reactant A, with dimensionless concentration $C_A = 1$ represented by dark red colour. Then another flow containing reactant B with dimensionless concentration $C_B = 1$ (represented by dark blue) comes into play via the side channel. Chaotic advection induced by the side channel flow can stretch the fluid while diffusion and reaction can increase the width of filaments. As time evolves, the
homogeneous concentration of A becomes highly complex caused by chaotic advection and diffusion.

Chaos has a strong impact on the dynamics of the reactive system. A high concentration of the product develops throughout the chaotic region. This occurs because C forms predominantly at the interface between A and B, and hence the amount of C at a given location depends on the local efficiency of the mixing process. In the chaotic region, the interface between A and B grows exponentially fast and intimate mixing is achieved in a short time, facilitating rapid reaction.

Figure 5-17 Contour plot of distribution of product C at t = 0.5, 3, 10, 20 (blue colour corresponding to C = 0, red corresponding to C = 1).

Figure 5-17 plots the distribution of product C at different times. As can be seen from Equation 5.9, the chemical reaction can only take place where neither $C_A$ nor $C_B$ equals zero which means that product C can only be generated in the interface of fluid A and B. As displayed by Figure 5-17 at t = 10, the distribution of product C is strongly affected by the periodic chaotic flow, generating complex spatial patterns.

The impact of chemical kinetics on the product distribution pattern is investigated by varying the chemical reaction rate constant, $k = 0.1$, $k = 1$ and $k = 10$. A larger chemical reaction rate corresponds to more rapid chemical reaction which means it takes less time to generate product C when reactant A and B coexist; therefore, the interface between A and B would be sharper. From Figure 5-18, a clearer interface between A and B can be observed at higher reaction rate $k$. 
Figure 5-18 Contour plot for product C with different reaction rate $k = 0.1, 1, 10$ at $t = 30$
(blue colour corresponding to $C = 0$, red corresponding to $C = 1$).

Figure 5-19 shows the production curve for reactions with different reaction rate constants $k = 0.1, 1, 10$. The macroscopic equations describing the active process reach a steady state synchronized with the temporal behaviour of the background flow. A slower chemical reaction corresponds to equally stronger advection. Even though reactants A and B are mixed by the chaotic flow and diffusion, they never have time to form product C before they are transported out of the domain. Figure 5-19 displays the nonlinear dependence of production on reaction rate $k$. At the late stage, the production curve shows that a descending trend means part of the product is transported out of the domain.
The steady flow has the form of

\[ V' = V_1 + (A + B)V_2 \]  \hspace{1cm} (5.19)

while the chaotic flow adopts the following time factor \( f(t) \):

\[ f(t) = A\sin(\omega t) + B \]  \hspace{1cm} (5.20)

From the above definition, we can see that the steady flow is stronger than the chaotic flow. Figure 5-20 illustrates the comparison regarding the distribution of product for steady flow and chaotic flow. The distribution of product C for the steady flow case differs entirely from the one in chaotic flow.
Figure 5-20 Comparison of production distribution for steady flow (left column) and chaotic flow (right column) at t = 5, 10, 20, 40 (blue colour corresponding to C = 0, red corresponding to C = 1).

Figure 5-21 displays the production curve for steady and chaotic flow. For the chaotic flow case, we can clearly see that at the late time, the production is synchronized by the chaotic flow. Even though the steady flow is stronger, it produces a lower amount of product C. The result suggests that the presence of chaotic advection in hydrothermal system has a significant impact upon the qualitative nature of the chemical reactions which lead to mineral depositions.
5.4 CONCLUSION

The dynamics of the autocatalytic chemical reaction $A+B\rightarrow 2B$ and bimolecular reaction $A+B\rightarrow C$ have been investigated in a fracture scale two-dimensional periodic flow by solving numerically the reaction-diffusion-advection equations. Four case studies have been performed in which the concentration of reactants and product displayed considerable spatial heterogeneity. Case study 1 compares the impact of steady flow and chaotic flow on the propagation of concentration perturbations for the $A+B\rightarrow 2B$ “infection-like” chemical reaction. Chaotic flow has an important impact on the evolution of the perturbation. For steady flow, if the initial perturbation is located at the right of the vortex, it is completely expelled out of the domain. However, for the chaotic flow case, the perturbation is pinned in the domain. The associated chemical reaction stays forever in the domain. It is also found that the long term system behaviour is insensitive to the initial location of perturbations so long as the perturbation overlaps with the stable manifolds of the chaotic flow. If the chemical reaction rate constant is low, the perturbation will be swept away from the domain because of the strong net current. Chemical reactions cannot be maintained for a slow reaction rate constant in the hydrodynamic systems.

The results in case study 2 show the spatial-temporal pattern of concentration $B$ is strongly dependent on the chemical reaction rate constant $k$. The production curve is nonlinear, but
the general trend is that a higher chemical reaction rate will lead to a higher chemical production. In multi-stable chemical reactions, there exist several attraction basins. In case study 3, the simplest bi-stable case is used to illustrate how the state selection is defined by concentration flux which is the product of the volumetric flow rate and species concentration. When average concentration is smaller than the unstable threshold, it evolves towards the stable state $c = 0$. When average concentration is larger than the unstable threshold, it evolves towards the other stable state $c = 1$.

Case study 4 shows the spatial-temporal distribution of product C when the flow in the side channel having reactant B penetrates the fluid in the main channel with reactant A. Chemical product can only be generated in the interface between fluid A and fluid B. Results show that higher reaction rate constant $k$ leads to larger production and sharper interfaces between reactants and product. The contrast between steady flow and chaotic flow suggests that chaotic advection plays a more important role upon the mineralising chemical reaction.

These 4 case studies involve a wide range of chemical reactions in hydrothermal mineralising systems. The results in this chapter suggest that the presence of chaotic advection in fracture-scale hydrothermal systems has a significant impact on the qualitative nature of the chemical reactions which lead to mineral depositions. The nature of chaotic advection can alter the stability and speciation of non-equilibrium reactions relevant to hydrothermal systems. From the above modelling, the conclusion can be drawn that the mineralization process is not only dependent on fluid flow, but also on diffusion and chemical reactions. It might shed some light on the possible nature of mineralization at the fracture scale, which is believed to generate some new practices for mineral exploration.
CHAPTER 6

CLOSING REMARKS

6.1 MAIN FINDINGS

This focus of this thesis is on the chemo-hydrodynamic patterns and instabilities in the formation of giant hydrothermal ore systems. The major contributions and findings made in this study are summarized below.

Chapter 2 models the formation of distribution patterns in the dissolution and precipitation processes in the presence of an open flow in a porous medium. Linear stability analysis shows that flow can introduce new instability into the chemical system, changing the steady state from stable node to stable focus. The following non-linear simulation shows that constant horizontal, time-dependent horizontal, and chaotic flow can generate a variety of spatiotemporal patterns, characterizing the mineralising processes in non-equilibrium dissolution-precipitation systems.

In chapter 3, fluid flow, temperature, chemical reaction and diffusion are fully coupled to quantitatively investigate the impact of various controlling parameters on the mineral distribution pattern and production. The complex underlying dynamics are characterized by solute and thermal mobility ratios, \( R_A \) and \( R_T \), the Lewis number \( Le \), the thermal lag coefficient \( \lambda \), and the Damkohler number \( Da \). The results show that solute and thermal mobility ratios play a determining role in the spatiotemporal evolution of concentration and temperature. The coupling of solute and thermal fronts is characterized by a thermal lag coefficient. A higher thermal lag coefficient corresponds to a tighter coupling. A higher Damkohler number suppresses the shielding effect of fingering, leading to a sharper front. A higher Lewis number means that heat diffuses faster than the chemical solute so that viscosity difference caused by temperature rapidly diminishes.

Chapter 4 considers the impact of grain-scale chaotic advection and diffusion on fluid mixing. The results show that periodic side-channel flow can lead to enhanced mixing and
the particle tracing method shows the location of chaotic regions induced by chaotic advection. Particles representing chemical species concentrate and spend a longer time in the chaotic regions which we propose to be one answer to the cause of fractal distributions of minerals and also to explain why there exist huge grade differences in ore bodies.

In chapter 5, different chemical reactions are coupled to the chaotic advection and diffusion processes described in chapter 4. Four studies have been performed where the concentration of reactants and product display considerable spatial heterogeneity. Chaotic flow has a more important role on the propagation of perturbations than steady flow. Results also show that an increased chemical reaction rate can lead to higher chemical production and the state selection is determined by the concentration flux in a bi-stable chemical reaction.

6.2 IMPLICATIONS FOR MINERAL EXPLORATION

It is widely proposed that many large hydrothermal mineral deposits occur at the boundary between one set of host rocks that were saturated with oxidised fluids and another set that were saturated with reduced fluids (Haynes et al., 1995). The former are recognised by the presence of alteration minerals such as haematite or sericite whereas the latter are recognised by the presence of alteration minerals such as pyrrhotite or iron rich chlorite.

Hence a common exploration procedure is to map these boundaries using magnetic and/or infra-red reflectance data and then use some other criterion to narrow down the target area before expensive drilling commences.

This study provides a new model for narrowing down the targeting area and so builds upon existing procedures. The important result from this study is that fluid mixing is most efficiently carried out by some form of chaotic advection and so a first step in any narrowing down strategy should be to look for geometries and/or unsteady time dependent processes that would enable chaotic advection of the oxidised and reduced fluids. A typical geometry would be a complicated three dimensional network of fractures. This gives some insight into a common observation that mineralisation typically occurs in highly damaged parts of the crust. However it is not just the degree of damage that is important. This study indicates that the detail of the three dimensional network is the important factor. The unsteady time dependent processes may be reflected in complicated, overprinting patterns
of vein or breccia formation. Again such situations are common in large mineral systems but this study provides an understanding of why unsteady flow systems are important.

Secondly this study shows that high mineral concentrations are likely to form in a chaotic saddle where fluid flow is held captive for large periods of time relative to the lifetime of the system. This increases the time for mineral reactions to take place at a single locality whilst continuously supplying new nutrient rich fluids to the site. Thus the geometry needs to be such that mineral precipitation is sustained and self-enhancing at a localised position and recognition of the geometry that enables the chaotic saddle to be spatially localised over long periods of time is a key criterion. The situation is enhanced if the chemical reactions taking place are autocatalytic, exothermal or comprise a networked system of exothermic and endothermic reactions. Then chaotic mixing greatly enhances the yield of the reactants. Having completed this study it is reasonably straightforward to undertake modelling of stream-lines for simplified geometries of the system of interest in order to investigate such geometries. The vast amount of study already directed to the development and evolution of Lagrangian chaos in mixing fluid systems provides insight as well.

Important here are also the details of the flow system that may enable one to understand the geometry of the chaotic system better. Such details may include the recognition of KAM islands which would be represented by regions of anomalously low mineral concentrations and mineralisation associated with unstable manifolds which means that mineralisation is likely to be transported out of the system resulting in dispersed mineralisation possibly over a wide area.

Thus one might picture a mineralising system as composed of four parts. The first part comprises regions where the flow remains laminar in a Lagrangian framework so that the existence of significant mineralisation is unlikely since any reaction products will be swept downstream by the flow with relatively poor mixing and little chemical reaction. Nevertheless such regions are likely to have higher than background concentrations of minerals. A second part corresponds to the KAM islands where mineralisation never occurred and concentrations are near background. A third corresponds to the unstable manifolds where mineralisation is dispersed and in fact is in the process of leaving the system. Failed or relatively disseminated mineralisation may be preserved in such regions. The fourth are regions on the chaotic saddle where the flow pattern is characterised by
processes that enable mineral bearing fluids (already mixed) to spend considerable time thus allowing extended opportunities for mineral reaction and precipitation processes to occur.

A third result of this study is that the chaotic mixing process produces a fractal distribution of mineralisation. This arises from the continuous stretching and folding of fluid volume elements during the mixing process so that the mineralising reactions play out on fractal template that comprises the chaotic saddle. Some insight into the nature of such fractal geometries is indicated in this thesis but much more work is required. One can see however from this work that the development of KAM islands together with the fractal nature of the chemically reacting template will lead to the kind of irregularity that is commonly observed in hydrothermal mineral deposits. Recognition of such processes and the incorporation of such knowledge into procedures for estimating mineral grades can dramatically increase the accuracy of mineral grade estimates, a problem that at present is a major cause of economic failure of mining operations.

6.3 RECOMMENDATIONS FOR FUTURE WORK

Other aspects of hydrothermal mineralising systems might be worth further investigation. Substantially more research efforts are necessary in the future as outlined as follows:

1. In the above chapters, all the simulations have been done in two dimensions. Three-dimensional flows may have additional transport mechanisms. For example, two-dimensional steady flow cannot generate chaotic advection while three-dimensional steady flow can. The complex geometry inherent in open porous networks can cause fluid splitting and recombination and chaotic advection can occur in three-dimensional domains even though the flow is time-independent. This mechanism can also significantly enhance the reaction rate of mineralisation (Lester et al., 2012). Some three-dimensional models have been performed regarding the formation processes of Proterozoic unconformity-associated uranium deposits (De Veslud et al., 2009, Clowes et al., 2010, Schaub et al., 2003).

2. So far, we have considered the effects of fluid flow, diffusion and chemical reaction. Deformation also plays an important role in the mineralising process. One
scenario is that the ore body can be treated as elastic or plastic continuum. If such a continuum subject to shortening or extension, plastic deformation could induce changes in porosity and hence permeability. Such effects need to be coupled with the processes discussed in this thesis and would certainly change the evolution of concentration of product. Deformation can also induce fluid flow in porous media (Oliver, 1996, Ord and Oliver, 1997, Cox, 1999, Jiang et al., 1997, Zhao et al., 2000b, Poulet et al., 2012, Cui et al., 2012b). Deformation undoubtedly impacts on fluid flow and determines flow directions and rates.

3. In this study, permeability is assumed as a constant. Relatively small local changes in permeability can lead to fluid focusing. Therefore, rocks with a higher permeability could be highly mineralised and have exceptionally high grades while rocks with low permeability are highly unlikely to be mineralized. Permeability can also be affected by mineral deposition and temperature. Mineral deposition can progressively reduce the permeability of a hydrothermal system (Henley and Berger, 2000). Porous media usually is sensitive to temperature. The evolution of permeability during mineralization and the effect of temperature should be considered in any future study.

4. The reaction dynamics used in this research are relatively simple. The investigation of more realistic reactions is important. Other more complex kinetics such as competitive-consecutive reactions and networked reactions should also be considered to obtain realistic results. Competitive-consecutive reactions are the simplest model system where a loss of yield is caused by over-reaction, i.e. the product of the desired reaction is consumed in an unwanted subsequent reaction with one of the initial reactants. Both reactions are irreversible, once the by-product is generated, it causes a permanent loss of efficiency. Multiple reaction schemes simply mean several reactions take place simultaneously and each reaction generates different products (Muzzio and Liu, 1996). The different proportion of minerals in the paragenesis of ore deposits may be attributed to the competitive behaviour in networked chemical reaction. The effect of the reversibility of chemical reaction within mineralising fluids should also be considered.
5. Thermal feedbacks on the reaction rate should be considered in the future research. In chapter 3, in order to reduce the complexity of the simulation, the chemical reaction constant $K$ is assumed to be independent of temperature. In reality, higher temperature can lead to higher reaction constant; Therefore, more complex spatial and temporal instabilities are expected to occur if the effect of thermal feedback is coupled (Poulet et al., 2012, Yang et al., 2006, Raffensperger and Garven, 1995a).
APPENDICES

APPENDIX 1 FRACTURE-SCALE FLOW

In this thesis, the system configuration used is a horizontal main flow channel connected with a side channel at an angle. Following the same methodology as developed by Trefry et al. (2012) and Kim and co-workers (2007), we use the Stokes equation to obtain the flow field, subject to non-slip conditions at the geometry boundaries. For an incompressible Newtonian fluid, the Stokes equations for pure fluid flow are as follows:

\[ \mu \nabla^2 u - \nabla p = 0 \]  
(1)

Fluid flows are also constrained by the mass conservation law. The continuity equation for the fluid density \( \rho \) is

\[ \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0 \]  
(2)

For a constant density fluid, Equation 2 becomes the following:

\[ \nabla \cdot u = 0 \]  
(3)

which is also known as the incompressibility condition. \( \mu \) is the dynamic viscosity, \( p \) is the fluid pressure.

The geometry of the system is shown in Figure App.1. The main straight rectangular fluid channel is 3 m in width and 1 m in height and at \( x = 1 \) m the main channel is connected with a side channel at an angle of 30°. The side channel is 0.1 m in width and 0.5 m in length. The inlets of this system are the left boundary and bottom side channel while the outlet is the right boundary. For other boundaries, we apply no-slip boundary conditions. First, we block the inlet of the side channel and apply a parabolic horizontal velocity field with the maximum velocity at the centre equal to \( v_{\text{max1}} \) for the left boundary of the main
channel. Then we obtain the flow velocity field shown as Figure App.1. We use V1 to represent the flow field of this case.

Figure App.1. Geometry of the flow system and V1 profile with $v_{\text{max}} = 1.3 \times 10^{-7}$ m/s.

Second, we block the inlet of the main channel in the left boundary and open the bottom inlet of the side channel. We also apply a parabolic velocity boundary condition for the boundary at the bottom with the maximum velocity of $v_{\text{max}2}$. The flow velocity profile is shown in Figure App.2 represented by V2.

Figure App.2. V2 profile with $v_{\text{max}2} = v_{\text{max}1}$ for simplicity purpose.

The velocity of the fluid is sufficiently small and both V1 and V2 are within the Stokes flow regimes; therefore, the principle of superposition holds (Lester et al., 2012). Both V1 and V2 are steady flows. In order to generate a chaotic flow, periodicity is introduced to the flow of the side channel by timing V2 with a time factor

$$f(t) = Asin(\omega t) + B$$

(4)
Then the flow in the whole domain becomes time-dependent. It is represented by:

\[ V = V_1 + f(t)V_2 \]  

(5)

As can be seen from the above equation, the flow is characterized by three parameters A, B and frequency \( \omega \). The period of this time dependent flow is

\[ T = \frac{2\pi}{\omega} \]  

(6)

Streamlines are the level sets of the streamfunction. Along streamlines, the streamfunction \( \phi \) is constant. The tangent along a streamline is the vector velocity at that point, and the level sets of streamfunction \( \phi \) are lines tangent to the velocity at any fixed instant of time.

Figure App.3 plots the instantaneous arrow of the velocity field and streamlines of the periodic flow with \( T = 4 \). The time-dependence causes streamlines to cross at successive times. The pattern of the flow field changes with time; therefore, the flow field is not integrable. Streamlines of the flow at one instant of time cross the streamlines of the flow at a subsequent instant of time which means “passive” tracing particles will follow chaotic trajectories during the advection process. The word “passive” means that tracing particles have no effect on the flow field. As can be observed from Figure App.3, this flow generates two vortices which are called the interaction zones. The chaotic regions are of importance in solute transport processes from a chaotic advection point view (Tél et al., 2005). In both the far upstream and far downstream direction, the streamlines are nearly parallel which means that the direction of the flow is horizontal and the passive particles will move downstream along the straight lines.
Figure App.3 Arrow of velocity and streamline plot at $t = 0$, $(1/4)T$, $(2/4)T$, $(3/4)T$.

The period of this flow is 4. Flow parameters $A$ and $B$ are 20, 30, respectively.
REFERENCES


