## UNIVERSITY OF CAMBRIDGE

BP INSTITUTE DEPARTMENT OF EARTH SCIENCES

# Precipitation and Dissolution Reactions in Porous Media

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A dissertation submitted for the degree of Master of Philosophy in Quantitative Modelling of Industrial and Environmental Fluid Flow

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### DECLARATION

I hereby declare that my thesis is not substantially the same as any that I have submitted for a degree or diploma or other qualification at any other University. I further state that no part of my thesis has already been or is being concurrently submitted for any such degree, diploma or qualification.

I hereby declare that my thesis does not exceed the limit of length prescribed in the Special Regulations of the MPhil examination for which I am a candidate. The length of my thesis is 14,500 words.

Signed



Andrew French.

Cambridge, 29<sup>th</sup> July 2002.

To my parents

*Est unusquisque faber ipsae suae fortuna* - Appius Claudius Caecus

## Contents

1	List	of variables and definitions	1
	1.1	Fixed physical and geometrical quantities	1
		1.1.1 Physical data specific to sodium chloride	2
		1.1.2 Physical data specific to sodium sulphate	2
	1.2	Input parameters with typical values (Sodium Chloride)	3
	1.3	Variables with dimensions	3
	1.4	Dimensionless variables	4
<b>2</b>	Intr	roduction	<b>5</b>
3	Phy	sical analysis of system: The Sharp Front Model	8
	3.1	Depletion, Thermal and Fluid reaction fronts (for linear porous media)	9
		3.1.1 Depletion front leads thermal front	10
		3.1.2 Depletion front lags thermal front	11
	3.2	Derivation of fluid and thermal front lengths for linear and axisymmetric	
		media	16
		3.2.1 Linear porous media	16
		3.2.2 Axisymmetric porous media	20
	3.3	Summary of formulae for reaction front lengths	21
		3.3.1 Linear porous media	21
		3.3.2 Axisymmetric porous media	21
4	App	oles and baskets: A numerical analogy	22
<b>5</b>	Exp	perimental analysis	30
	5.1	Schematic of laboratory setup	31
	5.2	Calculation of input parameters from easily measurable quantities and	
		physical data	32
	5.3	Calculation of important experimental timescales	34
	5.4	Experimental methodology and observations	36
		5.4.1 Sodium Chloride experiments	36
		5.4.2 Sodium sulphate experiments	41
	5.5	Experimental results and comparison to 'sharp front' predictions	42

6 Salinity and Precipitation Field Equations			51
	6.1	Derivation of field equations from conservation laws	51
		6.1.1 Temperature equation	51
		6.1.2 Salt conservation equation	54
	6.2	Solution of the temperature equation	55
		6.2.1 Case 1: neglect heat diffusion $Q \gg \frac{2\kappa\pi w}{Q}$	56
		6.2.2 Case 2: include heat diffusion $Q \sim \frac{2\kappa\pi w}{\Theta}$	58
	6.3	Solution of the salt conservation equation	61
		6.3.1 Case 1: neglect heat diffusion $Q \gg \frac{2\kappa\pi w}{Q}$	62
		6.3.2 Case 2: include heat diffusion $Q \sim \frac{2\kappa\pi w}{Q}$	67
	6.4	Summary of solutions to conservation equations	71
		6.4.1 Case 1: ignore heat diffusion $Q \gg \frac{2\kappa \pi w}{\Theta}$	71
		6.4.2 Case 2: include heat diffusion $Q \sim \frac{2\kappa\pi w}{\Theta}$	72
	6.5	Field equation solutions (neglecting heat diffusion) computed for a real	
		experimental system	72
		6.5.1 Sodium sulphate salt, $t_r = 100$ s $\dots \dots \dots \dots \dots \dots \dots$	73
		6.5.2 Sodium sulphate salt, $t_r = 0.06$ s	75
		6.5.3 Sodium chloride salt, $t_r = 0.06$ s $\dots \dots \dots \dots \dots \dots$	75
7	Cor	nclusion	87
	7.1	Outline of achievements and proposals for further study	87
	7.2	Acknowledgements	89
٨	The	Soffman Taylor Instability in paraus modia	02
A	THE	samnan rayior mistability in porous media	92
В	Ten ura	perature variation of Sodium Chloride and Sodium Sulphate sat tion solubility	,- 100

## List of Figures

2.1	Injection of undersaturated (fresh in this example) fluid into an axisymmetric porous medium containing solid reactive species, inert matrix and saturated fluid	7
3.1	Stepwise jump in salinity from $c_2$ to $c_1$ over the range of length scale $\begin{bmatrix} a & b \end{bmatrix}$	0
3.2	Snapshot of axisymmetric salinity and precipitation fields in the sharp front approximation. The shaded areas indicate salt lost or gained. If one scales the axes by $\phi$ and $(1 - \phi)\nu$ respectively, the volume of revolution of the shaded areas will be equivalent since salt is conserved. In this particular case $c_f > c_{ei}$ and the depletion front leads the thermal	9
<u></u>	front.	12
3.3	Snapshot of salinity and precipitation fields in sharp front model. In this case $c_f < c_{ei}$ and the depletion front leads the thermal front	13
3.4	Snapshot of salinity and precipitation fields in sharp front model. In	
	this case $c_f > c_{ei}$ and the depletion front lags the thermal front	17
3.5	Snapshot of salinity and precipitation fields in sharp front model. In this case $c_f < c_{ei}$ and the depletion front leads the thermal front. In	
20	addition $c_i > c_f$	18
3.0	Snapshot of samily and precipitation fields in sharp front model. In this case $c_f > c_{ei}$ and the depletion front leads the thermal front	19
4.1	Illustration of <i>Apples</i> model. A simplified version of the apple eating law is used - only one apple can be consumed between whistles. (i.e. in time interval $\Delta t$ ). Persons have a red hue when saturated with (five) apples. After twelve time intervals one can see the development of a	
	depletion front as the first few baskets become empty	23
4.2	$B = 12 \ c_i = 0 \ c_{ei} = 5 \ c_f = 10 \ F = 0.2.$ Single depletion front	25
4.3	$B = 12 \ c_i = 0 \ c_{ei} = 5 \ c_f = 10 \ F = 0.7$ . Double front structure	26
4.4 4 5	$B = 12 c_i = 0  c_{ei} = 10  c_f = 0  F = 0.2  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  \dots  $	21 20
4.0 4.6	$D = 12 c_i = 0 c_{ei} = 10 c_f = 0 F = 0.7 \dots \dots$	28 20
<del>1</del> .0	$D = 12 c_l = 1 c_{el} = 10 c_f = 0 1 = 0.1 \dots \dots \dots \dots \dots$	29
5.1	Experimental setup	32

Photograph of a depletion front in a sodium chloride plus 0.5 mm bal- lotini bead pack. The depleted region is artificially coloured for clarity.	97
Photograph of a fluid front in a sodium chloride plus 0.5 mm ballotini bead pack. The front marks the interface between fresh water (coloured with red food dye) and saturated sodium chloride solution.	38
Outflow mass flowrate plotted against experimental running time.	40 40
Test for power law time dependance of flowrate	41
theoretical predictions though less so for the depletion front Reaction front length predictions for a linear porous medium containing	43
sodium sulphate solids and saturated solution	44
imental (sodium chloride) system.	45
imental (sodium sulphate) system.	46
Snapshot of salinity and precipitation fields precicted by the linear (sodium chloride) sharp front model. Offset refers to the difference between the actual bead pack height and $H = 11$ cm. All previous	
graphs have been corrected for this systematic error	47
front structure compared to sodium chloride	48
Snapshot of salinity and precipitation fields predicted by the axisymmetric (sodium sulphate) sharp front model	49 50
Volume element V of medium containing Tempertaure field $T(r, t)$ and	00
Darcy velocity field $\mathbf{u}(r,t)$	52
velocity field $\mathbf{u}(r,t)$	$54 \\ 77$
Axisymmetric Saturation field for Sodium Chloride satt. $t_r = 0.06$ s. Axisymmetric Precipitation field for Sodium Chloride salt. $t_r = 0.06$ s.	78
diffusion is ignored	79
diffusion is <i>not</i> ignored.	80
Axisymmetric Salinity field for Sodium Sulphate salt. $t_r = 100$ s Axisymmetric Salinity field for Sodium Sulphate salt. $t_r = 0.06$ s Axisymmetric Precipitation field for Sodium Sulphate salt. $t_r = 100$ s.	81 82 83
	Photograph of a depletion front in a sodium chloride plus 0.5 mm ballotini bead pack. The depleted region is artificially coloured for clarity. Note non linearity of front

6.10 6.11	Axisymmetric Precipitation field for Sodium Sulphate salt. $t_r = 0.06$ s.	84
0.11	diffusion is ignored	85
6.12	Axisymmetric Saturation Salinity field for Sodium Sulphate salt. Heat diffusion is <i>not</i> ignored.	86
A 1	The Coffman Taylor instability despites a mitarian for the month of	00
A.1	perturbations to the interface of two incompressible fluids with defined	
	densities and viscosities, each existing in a porous solid matrix with	
	known permeabilities and porosities. Here cartesian geometry is studied.	93
A.2	Illustration of the Saffman Taylor instability at an initially circular in-	
	terface	95
B.1	Saturation solubility of sodium chloride as a function of temperature.	101
B.2	Saturation solubility of sodium sulphate as a function of temperature.	102

v

#### Abstract

The injection of a fluid containing a dissolved reactive species into a porous formation consisting of an inert matrix, a precipitate of reactive species and a saturated solution of the reactive species is investigated. A *fluid front* will initially propagate through the medium marking a sharp interface between the injected and formation fluids. If the injectate is undersaturated a dissolution reaction will occur upstream of the fluid front leading to a growing region depleted of precipitate. The interface between this and the newly saturated fluid shall be defined as the *depletion front*. If injectate and formation initially differ in temperature a third *thermal front* shall propagate through the porous medium at a rate necessarily slower than the fluid front since heat must flow through both solid and fluid volumetric fractions. If the kinetics of reaction are sufficiently fast a 'sharp front' model can be used to desribe the concentration and precipitation fields. Mass and mass flux balances shall be used to derive analytic expressions for the fluid, thermal and depletion front lengths in axisymmetric and linear media. A condition will be derived to select whether the depletion front will lead or lag the thermal front. In the latter case a double front structure is predicted since two different saturations are possible either side of the thermal front. An initial experimental study with a linear porous medium consisting of 0.5 mm glass beads and sodium chloride salt is presented and compared with the predictions of the sharp front model.

A more extensive theoretical analysis involving the solution of the appropriate continuity equations is presented for constant flowrate injection into an axisymmetric medium. Analytic solutions are derived for the concentration and precipitation fields when all diffusive processes are ignored and a long time asymptotic series is presented when heat diffusion is included. In addition to these elements a novel (discrete) numerical metaphor of the system is described and encoded with the MATLAB language. The results of these computer simulations seem to compare well with the theoretical predictions of the sharp front model.

## Chapter 1

## List of variables and definitions

## 1.1 Fixed physical and geometrical quantities

l	Length of linear porous medium	24	$\mathrm{cm}$
w	Width of porous medium	4.2	$\mathbf{cm}$
H	Depth of porous medium	11	$\mathrm{cm}$
$w_{ins}$	Width of insulating material	5	$\mathrm{cm}$
$w_{glass}$	Thickness of glass tank walls	0.5	$\mathrm{cm}$
$l_s$	Length of fluid region	36	$\mathrm{cm}$
$w_{bead}$	Mean diameter of glass beads	510	$\mu { m m}$
R	Radius of axisymmetric porous medium	20	$\mathrm{cm}$
$ ho_w$	Density of water	0.998	$\rm g cm^{-3}$
$\rho_{glass}$	Density of glass	2.6	$\rm g cm^{-3}$
$\rho_{ins}$	Density of insulating material	0.032	$\rm g cm^{-3}$
$C_w$	Specific heat capacity of water	4.182	$\mathrm{JK}^{-1}\mathrm{g}^{-1}$
$C_{glass}$	Specific heat capacity of glass	0.84	$\mathrm{JK}^{-1}\mathrm{g}^{-1}$
$C_{ins}$	Specific heat capacity of insulating material	1.38	$\rm JK^{-1}g^{-1}$
$\kappa_w$	Thermal diffusivity of water	$1.44 \text{ x} 10^{-3}$	$\rm cm^2 s^{-1}$
$\kappa_{ins}$	Thermal diffusivity of insulating material	$6.25 \ \mathrm{x10^{-3}}$	$\rm cm^2 s^{-1}$
$\kappa_{glass}$	Thermal diffusivity of glass	$4.12 \text{ x} 10^{-3}$	$\rm cm^2 s^{-1}$

### 1.1.1 Physical data specific to sodium chloride

$\rho_{salt}$	Density of pure solid salt	2.170	$\rm g cm^{-3}$
$ ho_{fluid}$	Average density of fluid region in formation	1.23	$\rm g cm^{-3}$
$\rho_{solid}$	Average density of solid region in formation	2.46	$\rm g cm^{-3}$
$C_{salt}$	Specific heat capacity of solid salt	0.86	$\mathrm{JK}^{-1}\mathrm{g}^{-1}$
$C_{fluid}$	Average fluid region specific heat capacity	1.74	$\mathrm{JK}^{-1}\mathrm{g}^{-1}$
$C_{solid}$	Average solid region specific heat capacity	0.85	$\mathrm{JK}^{-1}\mathrm{g}^{-1}$
$\kappa_{salt}$	Thermal diffusivity of solid salt	$9.70 \ \mathrm{x10^{-3}}$	${\rm cm}^2 {\rm s}^{-1}$
$\kappa_{solid}$	Average thermal diffusivity of solid region	$5.7 \ \mathrm{x10^{-3}}$	$\rm cm^2 s^{-1}$
$\kappa_{fluid}$	Average thermal diffusivity of fluid region	$7.5 \ \mathrm{x10^{-3}}$	$\rm cm^2 s^{-1}$
D	Salt bulk diffusion constant (in water)	$1.611 \ \mathrm{x10^{-5}}$	$\rm cm^2 s^{-1}$
$M_{salt}$	Molar mass of salt	58.443	$\mathrm{gmol}^{-1}$
ν	Stoichiometric ratio of precipitate to solute	1	

#### 1.1.2 Physical data specific to sodium sulphate

$\rho_{salt}$	Density of pure solid salt	1.46	$\rm g cm^{-3}$
$\rho_{fluid}$	Average density of fluid region in formation	1.74	$\rm g cm^{-3}$
$\rho_{solid}$	Average density of solid region in formation	2.12	$\rm g cm^{-3}$
$C_{salt}$	Specific heat capacity of solid salt	1.82	$\rm JK^{-1}g^{-1}$
$C_{fluid}$	Average fluid region specific heat capacity	2.95	$\rm JK^{-1}g^{-1}$
$C_{solid}$	Average solid region specific heat capacity	1.12	$\mathrm{JK}^{-1}\mathrm{g}^{-1}$
$\kappa_{salt}$	Thermal diffusivity of solid salt	$3.01 \text{ x} 10^{-3}$	$\rm cm^2 s^{-1}$
$\kappa_{solid}$	Average thermal diffusivity of solid region	$3.8 \text{ x} 10^{-3}$	$\rm cm^2 s^{-1}$
$\kappa_{fluid}$	Average thermal diffusivity of fluid region	$2.3 \text{ x} 10^{-3}$	$\rm cm^2 s^{-1}$
D	Salt bulk diffusion constant (in water)	$1.230 \text{ x} 10^{-5}$	$\rm cm^2 s^{-1}$
$M_{salt}$	Molar mass of salt	142.04	$\mathrm{gmol}^{-1}$
ν	Stoichiometric ratio of precipitate to solute	1	

## 1.2 Input parameters with typical values (Sodium Chloride)

$c_i$	Injectate 'salinity' (dissolved mass density)	0	$\rm g cm^{-3}$
$c_f$	Porous medium or 'formation' initial salinity	0.325	$\rm g cm^{-3}$
$s_f$	Formation solid salt density or 'precipitation'	0.54	$\rm g cm^{-3}$
$c_{ei}$	Saturation salinity of injectate	0.323	$\rm g cm^{-3}$
$T_i$	Injectate temperature	5	$^{\mathrm{o}}\mathrm{C}$
$T_f$	Formation temperature	24	$^{\mathrm{o}}\mathrm{C}$
Q	Volumetric flowrate (variable)	$\sim 0.3$	${\rm cm}^3{\rm s}^{-1}$
$\phi$	Porosity of porous medium	$\sim 0.5$	
k	Permeability of porous medium	${\sim}6~{\rm x}10^{-10}$	$\mathrm{m}^2$
$t_r$	Salt reaction time constant	0.06	s
h	Head driving flow	2	$\mathrm{cm}$
$m_{salt}$	Mass of salt initially in porous medium	$\sim 420$	g
$\Re_V$	<u>Saturated salt solution volume</u> Solvent (Water) volume	1.1	
$\Re_{GS}$	Mass ratio of glass beads to solid salt	2.5	

### 1.3 Variables with dimensions

r	Radial coordinate	$\mathrm{cm}$
t	Time	$\mathbf{S}$
$t_{cool}$	Cooling timescale	$\mathbf{S}$
$t_{flush}$	Fluid flush timescale	S
$t_{therm}$	Heat flush timescale	S
$t_{sd}$	Salt diffusion timescale	S
$t_{hd}$	Heat diffusion timescale	$\mathbf{S}$
c	Formation salinity	$\rm g cm^{-3}$
$c_e$	Formation saturation salinity	$\rm g cm^{-3}$
s	Formation precipitation	$\rm g cm^{-3}$
s'	Formation precipitation upstream of thermal front	$\rm g cm^{-3}$
$L_F$	Length of fluid front	$\mathrm{cm}$
$L_T$	Length of thermal front	$\mathrm{cm}$
$L_D$	Length of depletion front	$\mathrm{cm}$
T	Temperature field	$^{\mathrm{o}}\mathrm{C}$
$T_{ext}$	Fixed external temperature	$^{\mathrm{o}}\mathrm{C}$
u	Darcy velocity field	${\rm cm s^{-1}}$

### 1.4 Dimensionless variables

λ	Radial coordinate	$\frac{r}{R}$
au	Temporal coordinate	$\frac{t}{t_r}$
$\chi$	Salinity variable	$\frac{c-c_i}{c_f-c_i}$
$\chi_e$	Saturation salinity variable	$\frac{c_e - c_i}{c_f - c_i}$
$\psi$	Precipitation variable	$\frac{s}{s_f}$
lpha	Extent that reactive species are advected	$\frac{Qt_r}{2\pi wR^2}$
$\beta_T$	Extent of thermal diffusion	$\frac{\kappa t_r}{R^2}$
$\beta_c$	Extent of salt diffusion	$\frac{Dt_r}{R^2}$
$\theta$	Ratio of reaction induced to initial precipitation	$\frac{\phi(c_f - c_i)}{\nu(1 - \phi)s_f}$
ω	Saturation salinity variable at injector	$rac{c_{ei}-c_i}{c_f-c_i}$
Θ	Thermal parameter 'Big theta'	$\frac{\rho_{fluid}C_{fluid}}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$
$\kappa$	Thermal diffusivity parameter	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$
$\kappa$ $F$	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup>	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$
κ F	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup> 'Big omega' if $\phi \Theta < \left(1 + \frac{1}{\theta}\right)^{-1}$	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$ $2\alpha\Theta\left\{1 - \frac{1}{\phi\Theta}\left(1 + \frac{1}{\theta}\right)^{-1}\right\}$
κ F Ω	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup> 'Big omega' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Big omega' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$ $2\alpha\Theta\left\{1 - \frac{1}{\phi\Theta}\left(1 + \frac{1}{\theta}\right)^{-1}\right\}$ $2\alpha\Theta\left\{1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right\}$
κ F Ω Ω	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup> 'Big omega' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Big omega' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$ $2\alpha\Theta\left\{1 - \frac{1}{\phi\Theta}\left(1 + \frac{1}{\theta}\right)^{-1}\right\}$ $2\alpha\Theta\left\{1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right\}$ $\frac{\phi(\theta+1)}{2\alpha}$
κ F Ω Ω Υ	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup> 'Big omega' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Big omega' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$ $2\alpha\Theta\left\{1 - \frac{1}{\phi\Theta}\left(1 + \frac{1}{\theta}\right)^{-1}\right\}$ $2\alpha\Theta\left\{1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right\}$ $\frac{\phi(\theta+1)}{2\alpha}$ $\frac{\phi}{2\alpha}\left\{1 + \frac{\theta(\omega + \phi\Theta - 1)}{\phi\Theta}\right\}$
κ F Ω Ω Υ Υ	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup> 'Big omega' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Big omega' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$ Advection to thermal diffusivity ratio	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$ $2\alpha\Theta\left\{1 - \frac{1}{\phi\Theta}\left(1 + \frac{1}{\theta}\right)^{-1}\right\}$ $2\alpha\Theta\left\{1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right\}$ $\frac{\phi(\theta+1)}{2\alpha}$ $\frac{\phi}{2\alpha}\left\{1 + \frac{\theta(\omega + \phi\Theta - 1)}{\phi\Theta}\right\}$ $\frac{\Theta\alpha}{2\beta_{T}}$
κ F Ω Ω Υ Υ Φ f	Thermal diffusivity parameter Ratio of thermal to fluid front distances <sup>1</sup> 'Big omega' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Big omega' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta < (1 + \frac{1}{\theta})^{-1}$ 'Upsilon' if $\phi \Theta > (1 + \frac{1}{\theta})^{-1}$ Advection to thermal diffusivity ratio Extent of precipitation	$\frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$ $\phi\Theta$ $2\alpha\Theta\left\{1 - \frac{1}{\phi\Theta}\left(1 + \frac{1}{\theta}\right)^{-1}\right\}$ $2\alpha\Theta\left\{1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right\}$ $\frac{\phi(\theta+1)}{2\alpha}$ $\frac{\phi}{2\alpha}\left\{1 + \frac{\theta(\omega + \phi\Theta - 1)}{\phi\Theta}\right\}$ $\frac{\Theta\alpha}{2\beta_T}$ $\frac{s_f - s'}{s_f}$

## Chapter 2

## Introduction

This study is motivated by the industrial problem of scale deposition in oil reservoirs. In many hydrocarbon bearing formations, barium and calcium ions are found to be dissolved in the mobile pore fluid. Seawater is often pumped into such systems with the aim of displacing oil towards a well. Sulphate ions within the seawater react with the barium or calcium species to form a precipitate. The barium sulphate variety is highly insoluble in water and thus injection of seawater can induce solid deposition in the formation. This will reduce the porosity (the connected volume fraction occupied by mobile fluid) and can significantly effect the flow field within the reservoir, ultimately impacting on overall well performance. Qualitatively, a reduction in porosity can have a significant effect on the permeability<sup>1</sup>, the ratio of the volumetric flux per unit area multiplied by fluid viscosity to the applied pressure gradient. Hence for a given pressure applied to a reservoir, formation precipitation can noticeably reduce flowrate and thus reduce the rate of oil recovery. The transfer of heat from formation to cooler injectate with also modify this process as the saturation solubility of prograde salts like Barium Sulphate increases with temperature. To combat the effects of scale deposition may oil companies cease production at regular intervals and inject chemical inhibitors. The cost of such a strategy is high and hence there is much desire to understand the fundamental controls and dynamics of precipitation induced by injected fluid.

To contribute to the current understanding of these and other physically similar systems such as geothermal reservoirs and limestone Dolomites<sup>2</sup>, a simple generic model is described here in addition to a preliminary experimental study. The model

<sup>&</sup>lt;sup>1</sup>Permeability k is known to vary strongly with porosity  $\phi$ . A well known empirical relationship for structures consisting of packed spheres of diameter D is the Karman Cozeny equation  $k(\phi, D) = \frac{D^2 \phi^3}{180(1-\phi)^2} \Rightarrow \frac{\Delta k}{k} \sim \frac{3-\phi}{\phi(1-\phi)} \Delta \phi$ . For a change in porosity of 10% from 0.5, the resultant change in permeability is ~ 100%.

 $<sup>^{2}</sup>$ Limestone can transform to Dolomite when magnesium rich seawater percolates through a formation previously flooded with fresh water.

#### 2. Introduction

considers injection of a fluid of known temperature  $T_i$  into a homogeneous porous formation of, in general, a different temperature  $T_f$ . The formation shall initially contain volume fraction  $\phi$  of mobile fluid saturated with a dissolved reactive salt. The remainder will be composed of a defined proportion of inert porous solid and solid salt. Thermodynamic equilibrium is assumed prior to injection. The injected fluid shall in general be undersaturated with dissolved reactive salt. In the first instance the injected fluid will simply displace the saturated formation liquid and the interface between them shall be defined as the *Fluid Front*. Upstream of this a dissolution reaction will occur between the injected fluid and the solid salt with the goal of saturating the injectate, eventually leaving a region depleted of solid salt growing from the source. The boundary of this region shall be defined as the Depletion Front. The degree of saturation (and hence the amount of dissolution) will depend on the local temperature. If injectate and formation are isothermal this will be fixed<sup>3</sup>. In the more general case a Thermal Front will propagate through the medium marking the interface between downstream formation temperature  $T_f$  and injectate temperature  $T_i$ . The effect of this will be to dynamically change the dissolution reaction endpoint and in some cases induce precipitation instead.

The system has been investigated in four ways. Firstly, salt mass and salt mass flux balance calculations have been used to predict the extent of the two (or three) reaction fronts, the resultant changes in salinity and precipitation and selection criteria to predict the ordering of thermal and depletion fronts<sup>4</sup> in linear and axisymmetric media. This will be referred to as the *Sharp Front Model*. In addition an asymptotic/similarity solution method has been employed to solve the set of partial differential equations which govern the flow. (Heat advection diffusion, salt advection plus reactions, an equation of state for salt saturation vs temperature and fluid continuity). Analytic solutions for constant flowrate injection into an axisymmetric medium are derived for flowrate regimes such that heat and salt diffusion can be ignored and a long time asymptotic series is presented for the intermediate regime where although salt diffusion can still be ignored, heat diffusion cannot. The effect of the latter is to broaden the thermal front.

To balance this theoretical approach a novel percolation-type MATLAB code has been developed to visualize the problem via a numerical analogy (which seems to match the mass balance predictions) and a series of experiments with a linear porous media (consisting of glass beads and sodium chloride salt) has been conducted to test the fluid and depletion front predictions of the Sharp Front Model.

 $<sup>^{3}</sup>$ Note we ignore changes of saturation solubility with pressure. If large pressure gradients are also present in addition to changes in temperature one will have to modify the models desribed here.

<sup>&</sup>lt;sup>4</sup> If the latter leads, one does not see the former.

#### 2. Introduction

This thesis is primarily based on current research at the BP Institute in Cambridge, UK by Woods and Jupp [4] (thermal and depletion fronts in linear media) and the published work of Phillips [7]. The experimental results presented form part of an ongoing laboratory based study at the BP Institute. The results of Bell and Shaw-Champion [10] are referred to in the text and possible future experiments to highlight thermally driven reactions are described in the conclusion of this report.



Figure 2.1: Injection of undersaturated (fresh in this example) fluid into an axisymmetric porous medium containing solid reactive species, inert matrix and saturated fluid.

## Chapter 3

## Physical analysis of system: The Sharp Front Model

Before the salinity, precipitation and temperature fields are solved via detailed mathematical analysis it will be informative to predict, using simple physical arguments, the range of possible solutions and the selection criteria for such.

If conditions are such for Saffman Taylor type instabilities to be suppressed<sup>1</sup>, injection of fluid into a cylindrical formation should result in the propagation of reaction fronts radially through the medium. i.e. the salinity, precipitation and temperature field should follow 's shaped' curves between the unreacted formation downstream to the injectate upstream. Let us simplify this situation further by ignoring diffusive processes and reaction kinetics and thus consider stepwise jumps in our field solutions. In this case a simple transformation relates the axisymmetric solutions to those for a linear geometry. [4]

Consider a stepwise jump in salinity as illustrated in Figure 3.1. The amount of salt contained within our porous medium over the length scale range [a, b] is:

- Axisymmetric geometry  $(c_1 c_2)\pi(b^2 a^2)w^{-2}$
- Linear geometry  $(c_1 c_2)(b a)lw^{-3}$

When comparing 'shaded regions' one matches the absolute areas in the linear case. To convert to axisymmetric solutions, where annuli are equated, transform all linear length scales to radii by squaring.

<sup>&</sup>lt;sup>1</sup>See appendix.

 $<sup>^{2}</sup>w$  is the height of the cylindrical bead pack.

 $<sup>^{3}</sup>lw$  is the cross sectional area of a rectangular bead pack used for linear geometry.



Figure 3.1: Stepwise jump in salinity from  $c_2$  to  $c_1$  over the range of length scale [a, b].

i.e. For a single reaction front, one can show that for linear geometry the depletion front  $L_D$  is related to the fluid front  $L_F$  by the equation<sup>4</sup>:

$$L_D = \left(1 + \frac{1}{\theta}\right)^{-1} L_F \tag{3.1}$$

For axisymmetric geometry the corresponding result is found using  $L \longrightarrow L^2$ 

i.e.

$$L_D = \left(1 + \frac{1}{\theta}\right)^{-\frac{1}{2}} L_F \tag{3.2}$$

In the analysis below we will discuss a *linear* medium because of its geometrical simplicity. The above transformation will then be used to derive corresponding results for axisymmetric geometry. All figures will refer to the axisymmetric geometry.

### 3.1 Depletion, Thermal and Fluid reaction fronts (for linear porous media)

If one ignores the reaction of the injected fluid with solid reactant amongst the porous medium, injected fluid will simply displace fluid already present. If diffusion is also ignored then a sharp front will mark the boundary between injected and downstream regions. We will define this to be the *fluid front*. In addition, heat transfer from injected to downstream fluid will, in a similar manner, result in a *thermal front*. Unlike

<sup>&</sup>lt;sup>4</sup>These equations are given merely to illustrate the lengthscale transformation between linear and axisymmetric geometries. All equations will be properly derived below.

the fluid, heat will flow through the entire medium rather than simply through fraction  $\phi$  occupied by mobile fluid. This extra 'inertia' prevents the thermal front from ever travelling faster than the fluid front.

A thermal front implies a boundary across which is a jump in saturation salinity. Ahead of this boundary a disequilibrium of dissolved salt drives reactions which may result in dissolution or precipitation<sup>5</sup>. If undersaturated fluid is injected the finite amount of solid salt initially mixed with the porous medium will cause an additional *depletion front* to propagate. At the inlet, undersaturated injected fluid will dissolve a portion of solid salt already present in the medium before being advected downstream. This process will occur continuously until, at the inlet, no solid salt remains. From this point in time onwards injected fluid will remain at the injection salinity as there is no solid salt to dissolve. From the injected fluid's perspective the inlet (the separation point between injected fluid and potentially reactive species) has now moved slightly downstream and thus the process repeats as this *depleted* region propagates through the entire medium.

Unlike the fluid front, which must travel fastest, the ordering of thermal and depletion front velocities is dependent on the initial properties of the medium and the injected fluid. Two regimes are apparent.

- 1. Depletion front leads thermal front. In this case no reactions can occur since no solid salt is available downstream of the thermal front.
- 2. Depletion front lags thermal front. In this case precipitation or dissolution will occur in the intermediate region between the thermal and depletion fronts, leading to a double front structure.

Let us consider cases (1) and (2) separately. Define fluid front, thermal front and depletion fronts to be marked by lengths  $L_F, L_T$  and  $L_D$ . Define the ratio between thermal and fluid fronts to be

$$F = \frac{L_T}{L_F} \qquad \qquad ; \quad F < 1$$

#### 3.1.1 Depletion front leads thermal front

 $L_D$  can be determined as a fraction of  $L_F$  by considering the balance of salt mass dissolved into solution to salt mass removed from medium. We shall include a parameter  $\nu$  to take into account more general stoichiometries of dissolution, precipitation reactions. (1 mole solute  $\leftrightarrow \nu$  moles of solid). For sodium chloride this is unity.

<sup>&</sup>lt;sup>5</sup>Note the fluid front travels faster than the thermal signal so thermally driven reactions occur when saturated fluid crosses the thermal front and then becomes either undersaturated or oversaturated.

Referring to Figure 3.2 one can balance salt by equating the shaded areas scaled by  $\phi$  or  $\nu(1-\phi)$  for salinity and precipitation respectively.

$$\nu(1-\phi)L_D s_f = \phi(L_F - L_D)(c_f - c_i)$$
(3.3)

$$\Rightarrow \frac{\phi(c_f - c_i)}{\nu(1 - \phi)s_f} (L_F - L_D) = L_D \tag{3.4}$$

Define

$$\theta = \frac{\phi(c_f - c_i)}{\nu(1 - \phi)s_f} \tag{3.5}$$

Hence

$$L_D(1+\theta) = \theta L_F \tag{3.6}$$

 $\Rightarrow$ 

$$L_D = \left(1 + \frac{1}{\theta}\right)^{-1} L_F \tag{3.7}$$

Now for the depletion front to lead the thermal front  $L_D > FL_F$ . Using (3.7) this criterion becomes:

Depletion front leads thermal front

$$F < \frac{1}{1 + \frac{1}{\theta}} \tag{3.8}$$

#### 3.1.2 Depletion front lags thermal front

In this case salt mass balance is insufficient to fully solve the problem as one does not know the change in precipitation s (from  $s_f$  to s') in the thermally reactive region. The missing equation is the conservation of salt mass *flux* across the thermal front. Referring to Figure 3.4 we can write down these conservation laws simultaneously and solve for  $L_D$  and s'.

Salt mass conservation (match shaded areas)

$$\nu(1-\phi)L_D s_f + \nu(1-\phi)(FL_F - L_D)(s_f - s') = \phi(L_F - FL_F)(c_f - c_i) + \phi(FL_F - L_D)(c_{ei} - c_i)$$
(3.9)

Define

$$f = \frac{s_f - s'}{s_f} \tag{3.10}$$



 $\theta = \frac{\phi(c_f - c_i)}{v(1 - \phi)s_f}$ 

Figure 3.2: Snapshot of axisymmetric salinity and precipitation fields in the sharp front approximation. The shaded areas indicate salt lost or gained. If one scales the axes by  $\phi$  and  $(1 - \phi)\nu$  respectively, the volume of revolution of the shaded areas will be equivalent since salt is conserved. In this particular case  $c_f > c_{ei}$  and the depletion front leads the thermal front.



Figure 3.3: Snapshot of salinity and precipitation fields in sharp front model. In this case  $c_f < c_{ei}$  and the depletion front leads the thermal front.

and

$$\omega = \frac{c_{ei} - c_i}{c_f - c_i} \tag{3.11}$$

 $\Rightarrow$ 

$$L_D + (FL_F - L_D)f = \theta(1 - F)L_F + \theta\omega(FL_F - L_D)$$
(3.12)

$$L_D = \left(\frac{\theta(1-F) + \theta\omega F - fF}{1 - f + \theta\omega}\right) L_F$$
(3.13)

Now for the depletion front to lag the thermal front  $L_D < FL_F$ . Using (3.13) this criterion becomes:

Depletion front lags thermal front

$$F > \frac{1}{1 + \frac{1}{\theta}} \tag{3.14}$$

Conserving salt mass flux at the thermal front we find<sup>6</sup>: (using shorthand  $\dot{L} \equiv \frac{dL}{dt}$ and assuming F is a constant)

$$\underbrace{\phi(c_f - c_i)(\dot{L}_F - \dot{L}_T)}_{\text{salt flux if no reactions}} = \underbrace{\phi(c_{ei} - c_i)(\dot{L}_F - \dot{L}_T)}_{\text{dissolved salt flux}} + \underbrace{\nu(1 - \phi)(s_f - s')\dot{L}_T}_{\text{precipitative flux}}$$
(3.15)

$$\Rightarrow$$

$$f = \frac{\theta(1-F)(1-\omega)}{F} \tag{3.16}$$

Hence

$$s' = \left(1 - \frac{\theta(1-F)(1-\omega)}{F}\right)s_f \tag{3.17}$$

Substitution of this result into (3.13) yields an expression for the depletion front length in terms of known parameters.

$$L_D = \left(\frac{F\theta\omega}{F + \theta(\omega + F - 1)}\right)L_F \tag{3.18}$$

Note precipitation will occur between the thermal and depletion fronts if  $s' > s_f$ . Using the formula above and noting 0 < F < 1, one finds that for precipitation to occur  $\theta(1-\omega) < 0$ 

<sup>&</sup>lt;sup>6</sup>Note that the dissolved salt, and hence the salinity field moves at velocity  $\dot{L}_F$  relative to the porous medium, whereas the precipitation is static. Hence the  $\dot{L}_F - \dot{L}_T$  terms.

 $\Rightarrow$ 

$$c_{ei} > c_f \tag{3.19}$$

This result may at first glance appear counter intuitive. Assuming a prograde salt solution, (where saturation solubility increases with temperature) injection of hot solution into a cold formation will result in precipitation, despite a zone of greater salinity between the thermal and depletion fronts. To explain this let us track a fluid parcel as it enters the medium. Initially the parcel has salinity  $c_i$  and desires to dissolve enough solid salt to reach saturation  $c_{ei}$ . The parcel initially travels through a depleted zone and remains at salinity  $c_i$  until it reaches the depletion front. From this point onwards it rapidly dissolves salt and reaches saturation. (Infinitely rapidly in the sharp front approximation). The effect of this is to increase the length of the depleted region. The fluid parcel will eventually overtake the thermal front. Beyond this the saturation decreases from  $c_{ei}$  to  $c_f$  and hence the fluid parcel now at salinity  $c_{ei}$  will have to precipitate salt.

A critical value of  $c_{ei}$ ,  $c_{ei}^*$  will reduce s' to zero. This occurs when  $\frac{\theta(1-F)(1-\omega)}{F} = 1 \Rightarrow \omega = 1 - \frac{F}{(1-F)\theta}$ . Hence

$$c_{ei}^* = c_f - \frac{(1-\phi)vs_f F}{\phi(1-F)}$$
(3.20)

 $c_{ei}$  must be greater than zero and hence this definition is only valid if  $c_f > \frac{(1-\phi)vs_f F}{\phi(1-F)}$ . A problem now arises if  $c_{ei} < c_{ei}^*$  since it is unphysical to have a negative precipitation. The only possible solution is a transformation to a single front system, i.e. with the depletion front now leading the thermal front. This transformation is justified theoretically by applying the condition that the fluid front must always lead the depletion front. Using (3.18) this criterion becomes

$$1 > \frac{F\theta\omega}{F + \theta(\omega + F - 1)} \tag{3.21}$$

 $\Rightarrow$ 

$$F + \theta(\omega + F - 1) > F\theta\omega$$
  

$$\omega\theta(1 - F) > \theta(1 - F) - F$$
  

$$\omega > 1 - \frac{F}{(1 - F)\theta}$$

Hence a negative s' for  $c_{ei} < c_{ei}^*$  cannot occur without contradicting the fact that the fluid front must exceed the depletion front. We can deduce from this that the double front assumption (which allowed us to derive the above expression for the depletion front) is invalid and hence only the single front model is appropriate for  $c_{ei} < c_{ei}^*$ .

### 3.2 Derivation of fluid and thermal front lengths for linear and axisymmetric media

#### 3.2.1 Linear porous media

If fluid is injected at volumetric flowrate Q into a rectangular medium of porosity  $\phi$ , cross sectional area wl and has migrated a distance  $L_F$  in time t

$$Qt = \phi L_F wl \tag{3.22}$$

 $\Rightarrow$ 

$$L_F = \frac{Qt}{\phi wl} \tag{3.23}$$

A similar balance can be written down for the heat injected into the medium up to distance  $L_T$ .

$$\rho_{fluid}C_{fluid}Qt = \left\{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)\right\}L_Fwl$$
(3.24)

 $\Rightarrow$ 

$$L_T = \frac{\Theta Qt}{wl} \tag{3.25}$$

where

$$\Theta = \frac{\rho_{fluid} C_{fluid}}{\rho_{fluid} C_{fluid} \phi + \rho_{solid} C_{solid} (1 - \phi)}$$
(3.26)

Hence for linear media

$$F = \frac{L_T}{L_F} = \Theta\phi \tag{3.27}$$

Note  $\Theta \phi$  can be written as

$$\Theta\phi = \frac{1}{1 + \frac{\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi}}$$
(3.28)

Since  $\frac{\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi}$  cannot be negative  $(0 < \phi < 1)$  this demonstrates that

$$0 < F < 1$$
 (3.29)



Figure 3.4: Snapshot of salinity and precipitation fields in sharp front model. In this case  $c_f > c_{ei}$  and the depletion front lags the thermal front.



Figure 3.5: Snapshot of salinity and precipitation fields in sharp front model. In this case  $c_f < c_{ei}$  and the depletion front leads the thermal front. In addition  $c_i > c_f$ .





Figure 3.6: Snapshot of salinity and precipitation fields in sharp front model. In this case  $c_f > c_{ei}$  and the depletion front leads the thermal front.

#### 3.2.2 Axisymmetric porous media

If fluid is injected at volumetric flowrate Q into a cylindrical medium of porosity  $\phi$ and depth w and this fluid has migrated a radial distance  $L_F$  in time t

$$Qt = \phi \pi w L_F^2 \tag{3.30}$$

 $\Rightarrow$ 

$$L_F = \left(\frac{Qt}{\phi\pi w}\right)^{\frac{1}{2}} \tag{3.31}$$

Repeating the same argument for the injection of heat we find

$$L_T = \left(\frac{\Theta Qt}{\pi w}\right)^{\frac{1}{2}} \tag{3.32}$$

Hence for axisymmetric media

$$F = \left(\frac{L_T}{L_F}\right)^2 = \Theta\phi \tag{3.33}$$

(Note our definition of F incorporates the  $L \to L^2$  transform converting between linear and axisymmetric coordinates).

Using  $F = \Theta \phi$  we can express the criterion for the thermal front to lead the depletion front (valid in both geometries) as

$$F > \frac{1}{1 + \frac{1}{\theta}} \tag{3.34}$$

 $\Rightarrow$ 

$$\frac{vs_f}{c_f - c_i} > \frac{\rho_{solid}C_{solid}}{\rho_{fluid}C_{fluid}} \tag{3.35}$$

### 3.3 Summary of formulae for reaction front lengths

#### 3.3.1 Linear porous media

$$L_F = \frac{Qt}{\phi wl} \tag{3.36}$$

$$L_T = \frac{\Theta Qt}{wl} \tag{3.37}$$

$$F = \Theta\phi \tag{3.38}$$

depletion front leads thermal front,  $F < \frac{1}{1 + \frac{1}{\theta}}$ 

$$L_D = \left(1 + \frac{1}{\theta}\right)^{-1} L_F \tag{3.39}$$

depletion front lags thermal front,  $F>\frac{1}{1+\frac{1}{\theta}}$ 

$$L_D = \left(\frac{F\theta\omega}{F + \theta(\omega + F - 1)}\right)L_F \tag{3.40}$$

#### 3.3.2 Axisymmetric porous media

$$L_F = \left(\frac{Qt}{\phi\pi w}\right)^{\frac{1}{2}} \tag{3.41}$$

$$L_T = \left(\frac{\Theta Qt}{\pi w}\right)^{\frac{1}{2}} \tag{3.42}$$

$$F = \Theta\phi \tag{3.43}$$

depletion front leads thermal front,  $F < \frac{1}{1+\frac{1}{\theta}}$ 

$$L_D = \left(1 + \frac{1}{\theta}\right)^{-\frac{1}{2}} L_F \tag{3.44}$$

depletion front lags thermal front,  $F>\frac{1}{1+\frac{1}{\theta}}$ 

$$L_D = \left(\frac{F\theta\omega}{F + \theta(\omega + F - 1)}\right)^{\frac{1}{2}} L_F \tag{3.45}$$

## Chapter 4

## Apples and baskets: A numerical analogy

A quasi-discrete model of precipitation/dissolution reactions caused by injection of undersaturated saline into a initially saturated linear porous medium.

Model is as follows. Consider an infinite line of baskets, each containing B apples. (c.f. precipitation  $s_f$  of saturated medium). Each basket has beside it a person whose sole aim in life is to eat apples. Every person has a maximum apple capacity of  $c_e$  apples and initially each person along the line has this number contained within their ample stomachs. A whistle is blown every  $\Delta t$  seconds and the line of people shifts along one basket. Between then and the next whistle they are allowed to eat up to N apples until they have reached their limit of  $c_e$ . N is proportional to the difference between the current person apple content and their maximum capacity and the number of apples in the basket. The first basket is presented with a hungry person, initially with  $c_i < c_e$  apples in his or her stomach. Hence between the first and second whistle he/she consumes apples from the first basket. After the second whistle another hungry person is introduced to the first basket (now containing less than B apples) while the previously hungry person eats more apples from the second basket, if he/she is not already full. In addition to this a 'chinese whisper of hunger change' travels along the line at fraction F of the speed of line movement. (F < 1). Upstream of this shock the apple capacity  $c_e$  is changed from  $c_f$  to  $c_{ei}$ . Persons may discover that their apple content exceeds their maximum apple capacity. In this case they 'put back' apples into their local basket according to the same law as for apple eating. A MATLAB program creates a basket and person array representing the first M baskets and a simulation is run according to the rules above. A graph of apple number is plotted as a function of basket number for both arrays each time the whistle



Figure 4.1: Illustration of *Apples* model. A simplified version of the apple eating law is used - only one apple can be consumed between whistles. (i.e. in time interval  $\Delta t$ ). Persons have a red hue when saturated with (five) apples. After twelve time intervals one can see the development of a depletion front as the first few baskets become empty.

is blown. Sequentially numbered BMP files of these graphs are created for animated GIF creation. The model is described as quasi-discrete because although time step between motions of the person line is fixed and non zero, the number of apples that can be eaten/regurgitated between whistles need not be integer.

Persons are the analogue of fluid moving through a (linear) porous medium whereas apples in baskets model the solid salt deposits. The front of line progression is analogous to the fluid front and the 'hunger change chinese whisper' analogous to the thermal signal. A depletion front is common to both systems.

One should expect the linear sharp front analysis above to predict the basket number of line, hunger change and depletion fronts. Since the apples model has no analogue of porosity and apples eaten have the same numerical currency as apples in baskets, stoichiometry v and porosity  $\phi$  will be set to 1 and 0.5 respectively. Equations for the basket number positions of line, hunger change and depletion fronts in the apples model after n blows of the whistle are thus:

$$L_F = n\Delta t \tag{4.1}$$

$$L_T = Fn\Delta t \tag{4.2}$$

$$\theta = \frac{c_f - c_i}{B} \tag{4.3}$$

$$\omega = \frac{c_{ei} - c_i}{c_f - c_i} \tag{4.4}$$

depletion front leads hunger change front,  $F < \frac{1}{1+\frac{1}{\theta}}$ 

$$L_D = \left(1 + \frac{1}{\theta}\right)^{-1} L_F \tag{4.5}$$

depletion front lags hunger change front,  $F > \frac{1}{1+\frac{1}{4}}$ 

$$L_D = \left(\frac{F\theta\omega}{F + \theta(\omega + F - 1)}\right)L_F \tag{4.6}$$

The final images of five different scenarios are illustrated below. The curves of person and basket apple content (plotted against basket number) are generated by the MATLAB code and are shown with indicators predicted by the theory above.

Black asterisk	$\star$	Line ('fluid') front
Green asterisk	$\star$	Hunger change ('thermal') front
Red asterisk	$\star$	Depletion front
Green line		Basket content downstream of depletion front (c.f. $s'$ )

Theory seems to match the numerical results rather well, though some additional observations are worth recording.

- In the region between hunger change and depletion fronts, the apples in baskets curve is somewhat noisy.
- The fronts themselves have a continuous structure. Note diffusive processes are *not* modelled.



Figure 4.2: B = 12  $c_i = 0$   $c_{ei} = 5$   $c_f = 10$  F = 0.2. Single depletion front.



Figure 4.3: B = 12  $c_i = 0$   $c_{ei} = 5$   $c_f = 10$  F = 0.7. Double front structure.



Figure 4.4:  $B = 12 c_i = 0 c_{ei} = 10 c_f = 5 F = 0.2$


Figure 4.5:  $B = 12 c_i = 0 c_{ei} = 10 c_f = 5 F = 0.7$ 



Figure 4.6: B = 12  $c_i = 7$   $c_{ei} = 10$   $c_f = 5$  F = 0.7

## Chapter 5

## Experimental analysis

The theory (for linear porous media) derived above will be tested in the laboratory. Only a preliminary study will be described here. It is hoped that future work in this area can expand upon the experiments described below and employ a cylindrical rather than rectangular tank.

The experimental setup will be described below and its known physical properties used to predict the whereabouts of fluid, thermal and depletion fronts, plus the degree of precipitation if the injected fluid is of a different temperature to the formation. The timescale for the reaction fronts to propagate through the formation will be compared to those for diffusion and temperature equilibration with the surroundings. For the theory to be applicable the latter two must far exceed the former.

At the time of writing a substantial series of isothermal<sup>1</sup> experiments using sodium chloride salt has been performed, culminating in three repeated runs. The processed results are described below and compared with the sharp front model. An initial investigation using sodium sulphate and differing injectate and formation temperatures has also been conducted.<sup>2</sup> The methodology and observed problems of the current iteration of this experiment will be discussed.<sup>3</sup> The practical knowledge acquired in the running of both sodium chloride and sodium sulphate tests is planned to be used in the design of new experiments in a radial geometry to hopefully compare directly to the axisymmetric theory that forms the bulk of this thesis. Preliminary details of these plans will be discussed in the Conclusion.

<sup>&</sup>lt;sup>1</sup>i.e. the injected fluid is the same temperature as the formation - hence no thermal fronts.

<sup>&</sup>lt;sup>2</sup>The significant change (> 10%) in saturation solubility of sodium sulphate over a 10-20 degree temperature deviation from laboratory conditions allows for changes in salinity or precipitation upstream of the thermal front to be observed. The changes for sodium chloride are some two orders of magnitude less. See Appendix for the temperature variation of saturation solubility for solutions of both salts.

<sup>&</sup>lt;sup>3</sup>With the current system the medium appears to coalese into impermeable aggregates of salt and beads soon after the injection of cold fresh water. These arrest the propagation of the fluid front.

### 5.1 Schematic of laboratory setup

- The porous medium consists of a 11 cm deep homogenous cuboid of 425-600  $\mu$ m glass beads and solid salt with rectangular cross section 24 x 4.2 cm<sup>2</sup>. This sits on a 2.5 cm deep layer of 1.5 mm beads and this in turn on a 2 cm layer of 3 mm beads. The entire bead pack rests on a plastic drain raised 4 cm above the base of the tank. Fluid can pass through the bead pack and through the drain whereas the solid salt is prevented from falling through the drain's holes by the additional layers of glass beads.
- Horizontal lines every 1 cm are marked on the exterior of the tank. Images of the bead pack are recorded via a digital camera at regular intervals. The guidelines allow front lengths to be discerned from the images.
- Fluid will pass from the drain into a large purely fluid filled region of length  $l_s = 36$  cm. This is connected to a beaker atop a mass balance via a siphon and a constant head is maintained between this and the porous region to drive a flow through the system. The porous region is topped up from a large reservoir of unsalty injectate (coloured red with food dye) forming a perpetual layer 4.5 cm deep above the glass beads. The reservoir (a large tank with a tap at the base) is raised on a jack above the injectate fluid layer and fluid flow is controlled via a screw clamp. The author found this method of inflow preferable to a second siphon based 'constant head machine' controlled by the raising of the reservoir (to compensate for the reduction of fluid height due to outflow) via a jack.
- A serial port connection between the mass balance and a computer automatically records the mass of fluid displaced from the system. If the salt content of this fluid is also recorded (and thus the total density deducible), the time derivative of mass/density will yield a continuous log of the volumetric flowrate through the system.
- An array of thermocouples embedded vertically in the bead pack are also connected via serial link to a computer. If uniformity in cross section is assumed, these should give an indication of the extent of the thermal front.
- Single or arrays of needles can be inserted into the medium and used to record the fluid salt content by extracting small samples and recording a Brix measurement with a digital refractometer.
- The experiment is contained within a 5 mm thick glass tank surrounded by Dow Floormate 200X insulating material to reduce heat transfer with the surround-



All tank dimensions are INTERNAL. Tank contains a 0.5cm thick glass wall and sits on a 10.4cm deep layer of Dow Floormate 200-X insulating material.



ings. The reservoir is enclosed in a sarcophagus of such material and the tank enclosed by several removable panels to allow photographs to be taken at regular intervals. The inlet pipe is surrounded by foam padding to achieve a similar effect.

## 5.2 Calculation of input parameters from easily measurable quantities and physical data

Let porous medium contain mass  $m_{salt}$  salt and mass  $m_{salt} \Re_{GS}$  of glass beads of diameter  $w_{bead}$ . If salt and glass specific heat capacities are  $C_{salt}$  and  $C_{glass}$  respectively then the average formation solid region specific heat capacity is

$$C_{solid} = \frac{C_{salt} + \Re_{GS} C_{glass}}{1 + \Re_{GS}} \tag{5.1}$$

A similar average can be defined for the solid region thermal diffusivity.

$$\kappa_{solid} = \frac{\kappa_{salt} + \Re_{GS}\kappa_{glass}}{1 + \Re_{GS}} \tag{5.2}$$

If the tank interior has volume lwH and solid region occupies volumetric fraction  $1 - \phi$ , the average solid density is

$$\rho_{solid} = \frac{m_{salt}(1 + \Re_{GS})}{(1 - \phi)lwH}$$
(5.3)

whereas the formation solid salt density, or 'precipitation' is

$$s_f = \frac{m_{salt}}{(1-\phi)lwH} \tag{5.4}$$

Initially, the porous medium contains volumetric fraction  $\phi$  of saturated salt solution at temperature  $T_f$ . The ratio of salt mass to water mass  $\Re_{SW}$  in this solution can be found from the solubility S, the fraction of salt mass to total solution mass.

$$\Re_{SW} = \frac{S}{1-S} \tag{5.5}$$

The solubilities of sodium chloride and sodium sulphate are known empirical functions of temperature. (Variation with pressure is neglected). These are given in the Appendix. If the ratio  $\Re_V$  of saturated salt solution volume to volume of water used is known in addition to the density of water, one can calculate the density  $\rho_{fluid}$  of the saturated solution and salinity  $c_f$ , the initial mass per unit volume of salt dissolved in fluid region<sup>4</sup>.

$$\rho_{fluid} = \frac{\rho_w (1 + \Re_{SW})}{\Re_V} \tag{5.6}$$

$$c_f = \frac{\rho_w \Re_{SW}}{\Re_V} \tag{5.7}$$

In an analogous manner to above one can compute averages for the specific heat capacity and thermal diffusivity of the fluid region of the porous medium.

$$C_{fluid} = \frac{C_{salt} + \Re_{SW} C_w}{1 + \Re_{SW}} \tag{5.8}$$

$$\kappa_{fluid} = \frac{\kappa_{salt} + \Re_{SW} \kappa_w}{1 + \Re_{SW}} \tag{5.9}$$

 ${}^{4}\rho_{fluid} = \frac{\text{salt mass + water mass}}{\text{fluid volume}}. \text{ Now } \Re_{V} = \frac{\text{fluid volume}}{\text{water volume}} \text{ and } \Re_{SW} = \frac{\text{salt mass}}{\text{water mass}}. \text{ Hence}$  $\rho_{fluid} = \frac{(1+\Re_{SW})}{\Re_{V}} \frac{\text{water mass}}{\text{water volume}} = \frac{\rho_{w}(1+\Re_{SW})}{\Re_{V}}$ 

Lastly, the medium porosity  $\phi$  can be estimated from known parameters.

$$\underbrace{(1-\phi)wlH}_{\text{solid volume}} = \underbrace{\frac{m_{salt}}{\rho_{salt}}}_{\text{salt volume}} + \underbrace{\frac{m_{salt}\Re_{GS}}{\rho_{glass}}}_{\text{glass volume}}$$
(5.10)

 $\Rightarrow$ 

$$\phi = 1 - \left(\frac{1}{\rho_{salt}} + \frac{\Re_{GS}}{\rho_{glass}}\right) \frac{m_{salt}}{wlH}$$
(5.11)

Note this very likely to be an overestimate since  $\phi$  corresponds to the connected porosity rather than simply than 1 - solid volume fraction.

### 5.3 Calculation of important experimental timescales

For practical purposes it is important to know the approximate running time of an experiment and how this compares to the timescales associated with neglected effects such as heat loss though the walls of the tank and diffusion of salt and heat.

If fluid is injected at volumetric flowrate Q into the porous medium with volume wlH and porosity  $\phi$ , the time for injected fluid to flush though the medium is

$$t_{flush} = \frac{\phi w l H}{Q} \tag{5.12}$$

If the injected fluid is of a different temperature to the formation, heat will propagate through the entire medium after a time  $t_{therm}$ .

$$\rho_{fluid}C_{fluid}Qt_{therm} = \left\{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)\right\}wlH$$
(5.13)

 $\Rightarrow$ 

$$t_{therm} = \frac{1}{\Theta} \frac{w l H}{Q} \tag{5.14}$$

where

$$\Theta = \frac{\rho_{fluid} C_{fluid}}{\rho_{fluid} C_{fluid} \phi + \rho_{solid} C_{solid} (1 - \phi)}$$
(5.15)

One can show that the typical timescale for a diffusive processes is proportional to the square of the diffused distance. (For example, a random walk mechanism in discrete systems). Hence we can define timescales for thermal and salt diffusion along the depth H of our experiment. D and  $\kappa$  are the respective bulk diffusion constants<sup>5</sup>.

 $<sup>^5\,{\</sup>rm The}$  bulk thermal diffusivity is given by

 $<sup>\</sup>kappa = \frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}.$  A derivation of this is given on page (52)

$$t_{sd} = \frac{H^2}{D} \tag{5.16}$$

$$t_{td} = \frac{H^2}{\kappa} \tag{5.17}$$

Finally, one must consider a heating or cooling timescale if injected fluid is of a different temperature to that of the formation initially.

If heat is transported only by conduction (diffusion) from a volume V of density  $\rho$ , heat capacity C and thermal diffusivity  $\kappa$  at temperature T(t) to ambient surroundings at temperature  $T_{ext}$  through bounding surface S; conservation of heat yields (if one assumed *Fourier's law* for heat conduction)

$$-\frac{\partial}{\partial t} \int_{V} \rho C T dV = \int_{S} \kappa \rho C (-\nabla T) \cdot d\mathbf{S}$$
(5.18)

If the volume is a slab of homogenous material of thickness  $\delta$  and cross sectional area A (where  $\sqrt{A} \gg \delta$ ) we can approximate the above by a simple ordinary differential equation for T(t). (Only considering conduction through one surface).

$$\rho CA\delta \frac{dT}{dt} = \frac{\kappa \rho CA(T_{ext} - T)}{\delta}$$
(5.19)

 $\Rightarrow$ 

$$\int_{T_0}^T \frac{dT'}{T_{ext} - T'} = \frac{\kappa}{\delta^2} t \tag{5.20}$$

 $\Rightarrow$ 

$$T(t) = T_{ext} - (T_{ext} - T_0)e^{-\frac{\kappa t}{\delta^2}}$$
(5.21)

Hence we can define a cooling timescale

$$t_{cool} = \frac{\delta^2}{\kappa} \tag{5.22}$$

We can calculate this by averaging over the entire volume of our experimental apparatus, including tank walls and insulation.

$$t_{cool} = \left(\frac{w_{glass}^2}{\kappa_{glass}}\right) \left(\frac{V_{glass}}{V_{total}}\right) + \left(\frac{w^2}{\kappa_{fluid}}\right) \left(\frac{\phi w l H}{V_{total}}\right) +$$
(5.23)

$$\left(\frac{w^2}{\kappa_{solid}}\right) \left(\frac{(1-\phi)wlH}{V_{total}}\right) + \left(\frac{w_{ins}^2}{\kappa_{ins}}\right) \left(\frac{V_{ins}}{V_{total}}\right)$$
(5.24)

Assuming glass and insulation are uniform in thickness, the experiment has a lid consisting purely of insulating material and ignoring losses through the base of the tank (it sits on a three-ply layer of insulation) the glass and insulation volumes are

$$V_{glass} = \underbrace{2(l+l_s+2w_{glass})Hw_{glass}}_{\text{long walls}} + \underbrace{2wHw_{glass}}_{\text{side walls}}$$
(5.25)

$$V_{ins} = \underbrace{2(l+l_s+2w_{glass}+2w_{ins})Hw_{ins}}_{lows,model} + \underbrace{2(w+2w_{glass})Hw_{ins}}_{cids,model}$$
(5.26)

$$+\underbrace{(l+l_s+2w_{glass}+2w_{ins})(w+2w_{ins}+2w_{glass})w_{ins}}_{\text{lid}}$$
(5.27)

The total volume is given by

$$V_{total} = wlH + V_{glass} + V_{ins} \tag{5.28}$$

### 5.4 Experimental methodology and observations

### 5.4.1 Sodium Chloride experiments

- Preparation of a homogenous salt plus bead pack required the mixing of two different sized grains. To minimize inevitable stratification the smallest size of ballotini was chosen (0.5 mm). The medium was laid down in approximately 1 cm thick layers, each containing 40 g of salt and 100 g of ballotini mixed dry in a beaker and then poured into the tank already filled with saturated solution. Each layer was carefully mixed with the previous in an attempt to homogenize the boundaries. This was only partially successful as interfacial regions with slightly different salt to bead ratios were often observed to form as the experiment was set up and run.<sup>6</sup> These interfaces were observed to act as higher permeability channels as the dyed injected fluid propagated sideways rather that purely downwards. This, in conjunction with the disrupting effect of the thermocouple array, could have played a part in the perturbation of the fluid and depletion fronts. (See illustration below).
- The siphon at the outlet was connected to a shallow bath hollowed out of plastic with a 'plughole' positioned over a large beaker placed on a mass balance. The

 $<sup>^{6}</sup>$  The entire process took several hours. An entire run took a full day to complete and clean up. The tank was emptied using a siphon with a rigid nossel that could be used to suck up ballotini. The latter were collected in a fine sive and dried in an oven overnight. The three grades (3 mm 1.5 mm and 0.5 mm) were separated dry the following day using three grades of sieve.



Figure 5.2: Photograph of a depletion front in a sodium chloride plus 0.5 mm ballotini bead pack. The depleted region is artificially coloured for clarity. Note non linearity of front.



Figure 5.3: Photograph of a fluid front in a sodium chloride plus 0.5 mm ballotini bead pack. The front marks the interface between fresh water (coloured with red food dye) and saturated sodium chloride solution.

siphon, bath and fastenings connected to a retort stand were placed on a platform that could be raised or lowered to fix the system fluid head. The separation of mass balance and reception beaker to the siphon meant any leakages could be kept clear and the reception beaker could be changed when full without disrupting the system.

- Pre injection, the level of saturated solution in both regions of the tank was left to equilibrate at the height of the fluid bath. The 4.5 cm fluid layer above the bead pack was then topped up with injectate by this amount minus the desired head . On reflection I think a better procedure would have been to lower the height of the fluid bath (from an initial height that gives a 4.5 cm layer above the bead pack) to create the desired head and top up loss of fluid on the bead pack side of the experiment with injectate. This removes the need for an initially high injectate flowrate to perform the ~ 2.5 cm top up. On a few occasions this jet of fluid (compared to a drip) disrupted the upper surface of the bead pack and behaved initially as a point rather than distributed source.
- As salt was depleted from the bead pack the medium was observed to compact by an amount commensurate with the volume fraction of salt dissolved. If the ballotini : solid salt ratio  $\Re_{GS}$  is high enough for depletion of salt to not result in a structural collapse one would expect a *linear* decay of volumetric flowrate through the system as the pressure loss across the bead pack is diminished<sup>7</sup>. Unfortunately this scenario gives rise to such a small contrast change between the depleted and undepleted regions that a tracking of the depletion from from time lapse photographs becomes impossible. (This was discovered experimentally with  $\Re_{GS} = 10$ , hence the reduction to 2.5). With continuous compaction one might expect an *exponential* decay of flowrate. The gradient of mass balance readings with time yields a recording of mass flowrate against time. It was observed that the density of outflow fluid changed little over the experimental timescale (from saturation) and thus by dividing by the fluid density one can arrive at a graph of instantaneous flowrate during the experiment. The results (as illustrated below) we clearly non-linear and plots of  $\ln Q$ , t and  $\ln Q$ ,  $\ln Q$  were compared to assess whether an exponential or power law was more appropriate. In all cases the former gave a better  $\chi^2$  fit to the data.

<sup>&</sup>lt;sup>7</sup>We are qualitatively invoking Darcy's Law which states a proportionality between the volumetric flowrate per unit area and the imposed pressure gradient.



Figure 5.4: Outflow mass flowrate plotted against experimental running time.



Figure 5.5: Test for exponential time dependance of flowrate.



Figure 5.6: Test for power law time dependance of flowrate.

#### 5.4.2 Sodium sulphate experiments

• The methodology for these preliminary tests was identical in concept to those for Sodium Chloride except for the encasing of the experiment in insulation material and a change in injectate temperature. The latter was achieved by placing the reservoir tank in a fridge overnight. Although the injectate and formation temperatures deviated little over the  $\sim$  seventy minutes running time (indicating satisfactory performance of the insulation strategy) it was observed that the actual injection temperature was 14°C compared to a steady reservoir temperature of  $7^{\circ}$ C. More surprising was the subtle positive deviation in temperature,  $(\sim 2^{\circ}C)$  between the formation and tank fluid and the laboratory, despite the saturated solution being left to equilibrate overnight before being poured into the medium. Assuming the sodium sulphate solution to be super-saturated, a possible explanation of this effect could be a growth of crystals via an 'Otswold Ripening' mechanism<sup>8</sup>. This would produce heat due to the reduction in surface energy of crystals present in solution as they coalecse. This would also offer an explanation for the solidification of much of the bead pack which arrested the propagation of the fluid front.

<sup>&</sup>lt;sup>8</sup>Where larger crystals nucleate and feed on smaller ones present in a super-saturated solution.

## 5.5 Experimental results and comparison to 'sharp front' predictions

For each data set, an analytical form of the volumetric flowrate is defined to be

$$\frac{Q}{\rm cm^3 s^{-1}} = \frac{1}{\rho_{fluid}} e^{q_0} \exp\left(q_1 \frac{t}{60 \ \rm s}\right)$$
(5.29)

with the parameters  $q_0$  and  $q_1$  obtained from a linear fit  $y = q_0 + q_1 x$  to a graph of  $y = \ln(\text{mass flowrate/gs}^{-1})$  against x = time/minutes.

In the derivation of the sharp front model above a constant flowrate Q is assumed which gives rise to a fluid front length  $L_F = \frac{Qt}{\phi wl}$ . However, unlike in the solution of the conservation equations for salinity and precipitation fields<sup>9</sup>, there is no restriction on the time variance of Q in the sharp front model since all mass and mass flux balance computations refer to an arbitrary time snapshot. Hence if we redefine the thermal and fluid front lengths to be

$$L_F = \frac{1}{\phi w l} \int^t Q(t') dt'$$
(5.30)

$$L_T = \frac{\Theta}{wl} \int^t Q(t')dt'$$
 (5.31)

we can use the empirical form of Q above in our predictions for the reaction front lengths and changes in salinity and precipitation upstream of the fluid front.

For sodium chloride experiments, observed reaction front lengths are compared with theory in figure 5.7. Predicted reaction front lengths for axisymmetric media are also presented for an otherwise identical system plus a parallel series of graphs for sodium sulphate. In addition, two snapshots of predicted salinity and precipitation fields assuming an initial formation temperature of  $24.5^{\circ}$ C and injectate temperature of  $5^{\circ}$ C are shown, comparing sodium chloride and sodium sulphate. In these latter figures the differences between the properties of both salts is most apparent.

Good agreement is seen between observed and predicted lengths of the fluid front in figure 5.7. A less than impressive correlation is seen for the depletion front. The difficulty in recording an accurate position of the front could perhaps contribute to this discrepancy. A moving average was taken of this quite perturbed interface. Although

<sup>&</sup>lt;sup>9</sup>See next chapter.



Figure 5.7: Plot of experimentally determined reaction front lengths against theoretical predictions. A medium with 10:4 mass ratio of 0.5 mm glass ballotini and solid sodium chloride was used. The entire system was held at 24°C and thus data for the thermal reaction front was not collected. There is good agreement between fluid front measurements and theoretical predictions though less so for the depletion front.

not really justified by only three sets of data, one might expect a large set of repeated measurements to form a triangle of data about the theoretical curve. i.e. one expects the predicted trend to be the mean of data that becomes increasingly more inaccurate as one approaches the end of the bead pack. Here it becomes difficult to discern where the depletion front ends as the most downstream of the depleted areas will have reached the drain at the base of the bead pack.



Figure 5.8: Reaction front length predictions for a linear porous medium containing sodium sulphate solids and saturated solution.



Figure 5.9: Plot of reaction front lengths for an axisymmetric variant of the experimental (sodium chloride) system.



Figure 5.10: Plot of reaction front lengths for an axisymmetric variant of the experimental (sodium sulphate) system.



Figure 5.11: Snapshot of salinity and precipitation fields precicted by the linear (sodium chloride) sharp front model. *Offset* refers to the difference between the actual bead pack height and H = 11 cm. All previous graphs have been corrected for this systematic error.



Figure 5.12: Snapshot of salinity and precipitation fields predicted by the linear (sodium sulphate) sharp front model. Note a much more obvious double front structure compared to sodium chloride.



Figure 5.13: Snapshot of salinity and precipitation fields predicted by the axisymmetric (sodium chloride) sharp front model.



Salinity snapshot fot L  $_{\rm F}$ =R, axisymmetric porous media

Figure 5.14: Snapshot of salinity and precipitation fields predicted by the axisymmetric (sodium sulphate) sharp front model.

## Chapter 6

# Salinity and Precipitation Field Equations

### 6.1 Derivation of field equations from conservation laws

### 6.1.1 Temperature equation

Consider a volume element V of a porous medium containing average fraction  $\phi$  (connected porosity) of mobile fluid. Define **u** to be a field of the volumetric flowrate per unit vector area (the Darcy velocity) and consider averages of parameters that characterize the thermal properties of V. (Specific heat capacity C, thermal diffusivity  $\kappa$ , density  $\rho$ ). Let us only consider the variation with temperature of these parameters and thus compute their average over the temperature range of interest - in our case s.t.  $T_i, T_f \in T$ . One can balance the rate of change of heat contained within V with advective and diffusive transport processes to form a differential equation for the Temperature field T. Fourier's law shall be used to model thermal diffusion. i.e. the diffusive heat flux is proportional to the temperature gradient.

$$\frac{\partial}{\partial t} \int_{V} \left\{ \rho_{fluid} C_{fluid} \phi + \rho_{solid} C_{solid} (1 - \phi) \right\} T dV =$$

$$- \int_{S} \rho_{fluid} C_{fluid} T \mathbf{u} \cdot d\mathbf{S}$$

$$- \int_{V} - \left\{ \kappa_{fluid} \rho_{fluid} C_{fluid} \phi + \kappa_{solid} \rho_{solid} C_{solid} (1 - \phi) \right\} \nabla T \cdot d\mathbf{S}$$
(6.1)

Applying the divergence theorem  $\int_{S} \mathbf{f} \cdot d\mathbf{S} = \int_{V} \nabla \cdot \mathbf{f} dV$  and equating integrands we can write (6.1) in differential form.



Figure 6.1: Volume element V of medium containing Tempertaure field T(r, t) and Darcy velocity field  $\mathbf{u}(r, t)$ .

$$\frac{\partial T}{\partial t} + \Theta \nabla \cdot (\mathbf{u}T) = \kappa \nabla^2 T \tag{6.2}$$

where

$$\Theta = \frac{\rho_{fluid} C_{fluid}}{\rho_{fluid} C_{fluid} \phi + \rho_{solid} C_{solid} (1 - \phi)}$$
(6.3)

and

$$\kappa = \frac{\kappa_{fluid}\rho_{fluid}C_{fluid}\phi + \kappa_{solid}\rho_{solid}C_{solid}(1-\phi)}{\rho_{fluid}C_{fluid}\phi + \rho_{solid}C_{solid}(1-\phi)}$$
(6.4)

Now continuity of fluid implies

$$\frac{\partial}{\partial t} \int_{V} \rho_{fluid} dV = -\int_{S} \rho_{fluid} \mathbf{u} \cdot d\mathbf{S} = -\int_{V} \nabla \cdot (\rho_{fluid} \mathbf{u}) dV \tag{6.5}$$

Since we have asserted  $\rho_{fluid}$  is an average quantity and therefore constant, continuity of fluid implies

$$\nabla \cdot \mathbf{u} = 0 \tag{6.6}$$

We can use this result to simplify (6.2) since we can now write  $\nabla \cdot (\mathbf{u}T) = \mathbf{u} \cdot \nabla T + T(\nabla \cdot \mathbf{u}) = \mathbf{u} \cdot \nabla T$ .

$$\frac{\partial T}{\partial t} + \Theta \mathbf{u} \cdot \nabla T = \kappa \nabla^2 T \tag{6.7}$$

Our medium of interest, of which volume element V is a subset, is deemed to be two dimensional and axisymmetric. If we use a plane polar coordinate system centred on the line of axisymmetry, all fields are spatially only dependant on the absolute distance r from the coordinate origin. They will in general also have a dependence on time variable t. Since we are injecting fluid at 90° to the plane of our medium at the origin, we can assume it to spread in a purely radial manner. Hence if  $\hat{\mathbf{r}}$  is the unit displacement vector from the origin we can write  $\mathbf{u}(r,t) = u(r,t)\hat{\mathbf{r}}$ . This assumption will break down if some mechanism causes the Darcy velocity field to acquire angular components. Medium anisotropy could cause such an effect, (this could be glossed over in our definition of thermal parameters as temperature averages) as could an instability such as the Saffman Taylor variety. The latter of these is described in the Appendix and both this and other possible effects shall be ignored in the following discussion.

If we define the Temperature field T = T(r,t) and therefore can write  $\nabla T = \hat{\mathbf{r}} \frac{\partial T}{\partial r}$  and  $\nabla^2 T = \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right)$ , we can reduce (6.7) to a partial differential equation in variables r and t.

$$\frac{\partial T}{\partial t} + \Theta u \frac{\partial T}{\partial r} = \kappa \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right)$$
(6.8)

Since fluid continuity implies  $\nabla \cdot \mathbf{u} = 0$  and  $\mathbf{u}(r,t) = u(r,t)\hat{\mathbf{r}}$  we find u(r,t) obeys the equation

$$\frac{1}{r}\frac{\partial}{\partial r}(ru) = 0 \tag{6.9}$$

By inspection we see that the solution to this equation is  $u(r,t) = \frac{const(t)}{r}$ . Since we assert the fluid to be incompressible, for all radii and times

$$Q = 2\pi r w u(r, t) \tag{6.10}$$

where w is the width of the spreading fluid,<sup>1</sup> i.e. the depth of the porous cylinder confining the flow in the case of our experimental system.

 $\Rightarrow$ 

$$ru(r,t) = \frac{Q}{2\pi w} \Rightarrow const = \frac{Q}{2\pi w}$$
 (6.11)

Hence the Darcy velocity field for our system is

<sup>&</sup>lt;sup>1</sup>Note this implicitly assumes a steady state, i.e. significantly upstream of the fluid front. Since Q is time invariant this steady state should asymptotically be approached.



Figure 6.2: Volume element V of medium containing Salinity field c(r, t) and Darcy velocity field  $\mathbf{u}(r, t)$ .

$$u(r,t) = \frac{Q}{2\pi w} \frac{1}{r} \tag{6.12}$$

and the equation for Temperature field T(r, t) is

$$\frac{\partial T}{\partial t} + \Theta \frac{Q}{2\pi w} \frac{1}{r} \frac{\partial T}{\partial r} - \kappa \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) = 0$$
(6.13)

### 6.1.2 Salt conservation equation

A similar approach utilized in the previous section will be employed to derive the equation of (aqueous) salt conservation, i.e. a partial differential equation for salinity field c(r, t).

Again considering a volume V of the porous medium (with mobile fluid fraction  $\phi$ ) we find to conserve salt:

$$\frac{\partial}{\partial t} \int_{V} \phi c dV = -\int_{S} c \mathbf{u} \cdot d\mathbf{S} - D \int_{V} -\nabla c \cdot d\mathbf{S} + \phi \int_{V} Q_{c} dV \qquad (6.14)$$

D is the diffusion constant and  $Q_c$  is the rate of salt dissolution per unit volume. We shall adopt a reaction law as described by Phillips in [7].

$$Q_c = \frac{1}{t_r} (c_e - c) \frac{s}{s_f}$$
(6.15)

 $t_r$  is the reaction time constant,  $s_f$  is the initial 'formation' (bead pack in our case) precipitation and  $c_e$  is the equilibrium salinity, assumed to be a function of Temperature only. Let us assume a linear variation.

$$c_e(T) = c_e^* \left( a_0 + a_1 \frac{T}{T^*} \right)$$
 (6.16)

 $T^*$  is some reference temperature,  $c_e^* = c_e(T^*)$  and  $a_0$ ,  $a_1$  are dimensionless constants. Applying the divergence theorem to (6.14), using  $\nabla \cdot \mathbf{u} = 0$  to write  $\nabla \cdot (\mathbf{u}c) = \mathbf{u} \cdot \nabla c + c(\nabla \cdot \mathbf{u}) = \mathbf{u} \cdot \nabla c$ , equating integrands and substituting equation (6.12) for the Darcy velocity; we arrive at a partial differential equation for salinity c(r, t).

$$\frac{\partial c}{\partial t} + \frac{1}{\phi} \frac{Q}{2\pi w} \frac{1}{r} \frac{\partial c}{\partial r} - \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) = \frac{1}{t_r} \left( c_e - c \right) \frac{s}{s_f} \tag{6.17}$$

A change  $\delta c$  in fluid salinity leads, by mass balance, to a change in precipitation of  $\delta s = -\frac{\phi}{(1-\phi)v}\delta c$  where v is the stoichiometric ratio of dissolved reactive species to solid reactant. For the dissolution of salt v will be unity, though since these results are designed to cover generalized dissolution/precipitation reactions, (where the reactant may change in chemical species) it shall be included for the rest of this document and only be set to unity in the specific discussion of sodium chloride and sodium sulphate. Now  $\delta c/\delta t = Q_c$ . Hence:

$$\frac{\partial s}{\partial t} = -\frac{\phi}{(1-\phi)v} \frac{1}{t_r} (c_e - c) \frac{s}{s_f}$$
(6.18)

### 6.2 Solution of the temperature equation

Writing as a differential operator on field T, the temperature equation is:

$$\left(\frac{\partial}{\partial t} + \Theta \frac{Q}{2\pi w} \frac{1}{r} \frac{\partial}{\partial r} - \kappa \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r}\right) T = 0$$
(6.19)

with thermal constants  $\Theta$  and  $\kappa$  defined on page 52. In equation (6.16) we asserted the equilibrium salinity to vary linearly with temperature. Since the operator of (6.19) is also linear, the linearity of equilibrium salinity temperature variation implies:

$$\frac{\partial c_e}{\partial t} + \Theta \frac{Q}{\pi r_0} \frac{1}{r} \frac{\partial c_e}{\partial r} - \kappa \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c_e}{\partial r} \right) = 0$$
(6.20)

Let us remove dimensional quantities from (6.20) by defining the following variable scalings.

$$au = \frac{t}{t_r}$$
  $\lambda = \frac{r}{R}$   $\chi_e = \frac{c_e - c_i}{c_f - c_i}$ 

Recall  $c_i$  is the salinity of injected fluid (either saturated - i.e. at equilibrium, or undersaturated) and  $c_f$  is the initial (equilibrium) salinity of the formation. (In our case a cylindrical bead pack). Substituting for t, r, and  $c_e$  in (6.20) we find:

$$\frac{\partial \chi_e}{\partial \tau} + \Theta \alpha \frac{1}{\lambda} \frac{\partial \chi_e}{\partial \lambda} - \beta_T \frac{1}{\lambda} \frac{\partial}{\partial \lambda} \left( \lambda \frac{\partial \chi_e}{\partial \lambda} \right) = 0$$
(6.21)

where

$$\alpha = \frac{Qt_r}{2\pi w R^2} \tag{6.22}$$

and

$$\beta_T = \frac{\kappa t_r}{R^2} \tag{6.23}$$

We now have a dimensionless equation for  $\chi_e(\lambda, \tau)$  controlled by pure numbers  $\Theta \alpha$ and  $\beta_T$  which parameterize transport mechanisms advection and diffusion respectively. The relative magnitudes of these numbers lead us naturally to two solution regimes governed by flowrate Q.

• Ignore heat diffusion  $\beta_T \ll \Theta \alpha \Rightarrow Q \gg \frac{2\kappa \pi w}{\Theta}$ • Don't ignore heat diffusion  $\beta_T \sim \Theta \alpha \Rightarrow Q \sim \frac{2\kappa \pi w}{\Theta}$ 

### 6.2.1 Case 1: neglect heat diffusion $Q \gg \frac{2\kappa\pi w}{\Theta}$

Our aim is to find a special variable  $\eta(\lambda, \tau)$  that transforms (6.21) into an ordinary differential equation in  $\eta$ . This should greatly ease the solution method. A crude model of a radially spreading injected fluid of constant depth w and radius r equates the cylindrical volume  $\pi r^2 w$  to the fluid volume injected Qt. i.e.  $r^2(t) = \frac{Qt}{\pi w}$ . This tells us the natural relationship between the powers of variables r and t. Hence we should intuitively chose a variable of the form

$$\eta = \lambda^2 + \sigma\tau \tag{6.24}$$

where  $\sigma$  is a constant. Since we have a two variable system let define another variable  $\mu = \tau$  to complete a functional equivalence

$$\chi'_e(\eta,\mu) = \chi_e(\lambda,\tau) \tag{6.25}$$

Using the chain rule

$$\frac{\partial \chi'_e}{\partial \tau} = \frac{\partial \chi'_e}{\partial \eta} \frac{\partial \eta}{\partial \tau} + \frac{\partial \chi'_e}{\partial \mu} \frac{\partial \mu}{\partial \tau} = \sigma \frac{\partial \chi'_e}{\partial \eta} + \frac{\partial \chi'_e}{\partial \mu}$$
(6.26)

$$\frac{\partial \chi'_e}{\partial \lambda} = \frac{\partial \chi'_e}{\partial \eta} \frac{\partial \eta}{\partial \lambda} + \frac{\partial \chi'_e}{\partial \mu} \frac{\partial \mu}{\partial \lambda} = 2\lambda \frac{\partial \chi'_e}{\partial \eta}$$
(6.27)

Hence if the diffusion term is ignored (6.21) becomes:

$$(\sigma + 2\Theta\alpha)\frac{\partial\chi'_e}{\partial\eta} + \frac{\partial\chi'_e}{\partial\mu} = 0$$
(6.28)

If we set  $\sigma = -2\Theta\alpha$  then  $\frac{\partial \chi'_e}{\partial \mu} = 0 \Rightarrow \chi'_e = \chi'_e(\eta)$ . Since  $\chi'_e = \chi_e$  this implies any function of the form  $\chi_e(\lambda, \tau) = \chi_e(\lambda^2 - 2\Theta\alpha\tau)$  will be a solution of (6.21) where heat diffusion is ignored. Let us make the choice of a *step function* that satisfies the initial (IC) and boundary (BC) conditions on  $\chi_e$ .

• IC 
$$c_e(r, t = 0) = c_f, r \ge 0 \Rightarrow \chi_e(\lambda, \tau = 0) = 1, \lambda \ge 0$$

• BC 
$$c_e(r=0,t) = c_{ei}, t > 0 \Rightarrow \chi_e(\lambda = 0, \tau) = \omega, \tau > 0$$

where  $c_{ei} = c_e^* \left( a_0 + a_1 \frac{T_i}{T^*} \right)$  and  $\omega = \frac{c_{ei} - c_i}{c_f - c_i}$ .

Hence set  $\chi_e(\lambda, \tau)$  to be:

$$\chi_e(\lambda,\tau) = \begin{cases} 1 & \eta \ge 0\\ \omega & \eta < 0 \end{cases}$$
(6.29)

where

$$\eta = \lambda^2 - 2\Theta\alpha\tau \tag{6.30}$$

The temperature field for flowrates such that heat diffusion can be ignored therefore takes the form:

$$T(r,t) = \begin{cases} \left(\frac{c_f}{c_e^*} - a_0\right) \frac{T^*}{a_1} & \frac{r^2}{R^2} - \frac{2\Theta\alpha t}{t_r} \ge 0\\ \left(\frac{\omega(c_f - c_i) + c_i}{c_e^*} - a_0\right) \frac{T^*}{a_1} & \frac{r^2}{R^2} - \frac{2\Theta\alpha t}{t_r} < 0 \end{cases}$$
(6.31)

Note that when  $\eta = 0$ ,  $r = \left(\frac{\Theta Qt}{\pi w}\right)^{\frac{1}{2}}$ . Note this describes the radius of the thermal front in the sharp front model described previously. We can therefore interpret the  $\eta > 0$  region as being 'downstream of the thermal signal.' This has a literal significance in the absence of heat diffusion since we have asserted a sharp front formalism for the solution to the heat conservation equation.

## 6.2.2 Case 2: include heat diffusion $Q \sim \frac{2\kappa\pi w}{\Theta}$

When the diffusion term is included the variable  $\eta = \lambda^2 - 2\Theta\alpha\tau$  is insufficient to transform the equation for the equilibrium salinity field (6.21) into an ordinary differential equation in  $\eta$ . This is clear from the presence of  $\lambda(\eta \text{ AND } \tau)$  amongst the  $\frac{\partial}{\partial\lambda} \left(\lambda \frac{\partial}{\partial\lambda}\right)$ operator. Let us instead consider the modification:

$$\eta = \frac{\lambda^2 - 2\Theta\alpha\tau}{\epsilon\tau^n} \tag{6.32}$$

where  $\epsilon$  and n are constants. Note for positive  $n, \eta$  becomes singular as  $\tau \to 0$ . If we consider only  $\tau \gg 0$  asymptotic solutions then we can be unconcerned about this fact.

Let us assert a functional equivalence

$$\chi'_e(\eta) = \chi(\lambda, \tau) \tag{6.33}$$

We can use the chain rule to express  $\lambda$  and  $\tau$  partial derivatives in terms of total derivatives by  $\eta$ .

$$\frac{\partial \chi'_e}{\partial \tau} = \frac{\partial \eta}{\partial \tau} \frac{d \chi'_e}{d\eta} = -\left(\frac{2\Theta\alpha}{\epsilon}\tau^{-n} + \eta n\tau^{-1}\right) \frac{d\chi'_e}{d\eta}$$
(6.34)

$$\frac{\partial \chi'_e}{\partial \lambda} = \frac{\partial \eta}{\partial \lambda} \frac{d \chi'_e}{d\eta} = \frac{2\lambda}{\epsilon} \tau^{-n} \frac{d \chi'_e}{d\eta}$$
(6.35)

$$\frac{\partial^2 \chi'_e}{\partial \lambda^2} = \frac{\partial}{\partial \lambda} \left( \frac{2\lambda}{\epsilon} \tau^{-n} \frac{d\chi'_e}{d\eta} \right) = \frac{2}{\epsilon} \tau^{-n} \frac{d\chi'_e}{d\eta} + \frac{2\lambda}{\epsilon} \tau^{-n} \frac{\partial \eta}{\partial \lambda} \frac{d^2 \chi'_e}{d\eta^2} = \frac{2}{\epsilon} \tau^{-n} \frac{d\chi'_e}{d\eta} + \frac{4\lambda^2}{\epsilon^2} \tau^{-2n} \frac{d^2 \chi'_e}{d\eta^2}$$
(6.36)

Substitution of these results into (6.21) yields, (dropping primes for brevity and noting  $\frac{1}{\lambda} \frac{\partial}{\partial \lambda} \left( \lambda \frac{\partial \chi_e}{\partial \lambda} \right) = \frac{\partial^2 \chi_e}{\partial \lambda^2} + \frac{1}{\lambda} \frac{\partial \chi_e}{\partial \lambda}$ ) yields:

$$-\left(\frac{2\Theta\alpha}{\epsilon}\tau^{-n} + \eta n\tau^{-1}\right)\frac{d\chi_e}{d\eta} + \frac{2\Theta\alpha}{\epsilon}\tau^{-n}\frac{d\chi_e}{d\eta} - \beta_T\left(\frac{2}{\epsilon}\tau^{-n}\frac{d\chi_e}{d\eta} + \frac{4\lambda^2}{\epsilon^2}\tau^{-2n}\frac{d^2\chi_e}{d\eta^2} + \frac{2}{\epsilon}\tau^{-n}\frac{d\chi_e}{d\eta}\right) = 0$$
(6.37)

$$\Rightarrow \left(-\frac{2\Theta\alpha}{\epsilon}\tau^{-n} - \eta n\tau^{-1} + \frac{2\Theta\alpha}{\epsilon}\tau^{-n} - \frac{4\beta_T}{\epsilon}\tau^{-n}\right)\frac{d\chi_e}{d\eta} - \frac{4\beta_T\left(\epsilon\tau^n\eta + 2\Theta\alpha\tau\right)}{\epsilon^2}\tau^{-2n}\frac{d^2\chi_e}{d\eta^2} = 0$$

$$\tag{6.38}$$

$$\Rightarrow -\left(\eta n\tau^{2n-1} + \frac{4\beta_T}{\epsilon}\tau^n\right)\frac{d\chi_e}{d\eta} - \frac{4\beta_T\left(\epsilon\tau^n\eta + 2\Theta\alpha\tau\right)}{\epsilon^2}\frac{d^2\chi_e}{d\eta^2} = 0 \tag{6.39}$$

Letting:  $\epsilon = 4\beta_T$  :

$$\Rightarrow \frac{d^2 \chi_e}{d\eta^2} + \frac{4\beta_T \left(\eta n \tau^{n-1} + 1\right)}{\left(4\beta_T \eta + 2\Theta\alpha\tau^{1-n}\right)} \frac{d\chi_e}{d\eta} = 0 \tag{6.40}$$

We can eliminate  $\tau$ , and thus create an ordinary differential equation for  $\chi_e(\eta)$  if n = 1. Setting n to unity and defining

$$\Phi = \frac{\Theta \alpha}{2\beta_T} \tag{6.41}$$

we arrive at

$$\frac{d^2\chi_e}{d\eta^2} + \frac{\eta+1}{\eta+\Phi}\frac{d\chi_e}{d\eta} = 0 \tag{6.42}$$

where

$$\eta = \frac{\lambda^2 - 2\Theta\alpha\tau}{4\tau\beta_T} \tag{6.43}$$

To solve (6.42) define

$$z(\eta) = \frac{d\chi_e}{d\eta} \tag{6.44}$$

(6.42) then becomes a *separable* first order ordinary differential equation.

$$\frac{dz}{d\eta} + \frac{\eta + 1}{\eta + \Phi} z = 0 \tag{6.45}$$

$$\Rightarrow \frac{dz}{z} = -\frac{\eta + 1}{\eta + \Phi} d\eta \tag{6.46}$$

Noting the standard integral  $\int \frac{\eta+1}{\eta+\Phi} d\eta = \eta + (1-\Phi) \ln(\eta+\Phi) + const$ 

$$\Rightarrow \ln z = -\eta - (1 - \Phi) \ln(\eta + \Phi) + const \tag{6.47}$$

$$\Rightarrow z(\eta) = Be^{-\eta}(\eta + \Phi)^{\Phi - 1} \tag{6.48}$$

where B is a constant.

Hence

$$\chi_e(\eta) = B \int^{\eta} e^{-\varepsilon} (\varepsilon + \Phi)^{\Phi - 1} d\varepsilon$$
(6.49)

In terms of  $\eta,$  the boundary condition for  $\chi_e$  (see page 57 ) can be written as

- BC1  $\chi_e(\eta \to \infty) = 1$  (This replaces the Initial Condition, invalid if one considers  $\tau \gg 0$  solutions)
- BC2  $\chi_e(\eta = -\Phi) = \omega$

We can write (6.49) as a definite integral to incorporate BC2 and then apply BC1 to determine the constant B.

$$\chi_e(\eta) - \omega = B \int_{-\Phi}^{\eta} e^{-\varepsilon} (\varepsilon + \Phi)^{\Phi - 1} d\varepsilon$$
(6.50)

Define  $\zeta = \varepsilon + \Phi$ 

$$\Rightarrow \chi_e(\eta) - \omega = B e^{\Phi} \int_0^{\eta + \Phi} e^{-\zeta} \zeta^{\Phi - 1} d\zeta$$
(6.51)

Special functions  $\Gamma(a)$  (gamma function) and  $\gamma(x, a)$  (lower-incomplete gamma function) are defined

$$\Gamma(a) = \int_0^\infty e^{-\zeta} \zeta^{a-1} d\zeta \tag{6.52}$$

$$\gamma(x,a) = \frac{1}{\Gamma(a)} \int_0^x e^{-\zeta} \zeta^{a-1} d\zeta$$
(6.53)

Hence

$$\chi_e(\eta) - \omega = Be^{\Phi} \Gamma(\Phi) \gamma(\eta + \Phi, \Phi)$$
(6.54)

Applying the BC  $\chi_e(\eta \to \infty) = 1$  and noting  $\lim_{x\to\infty} \gamma(x,a) = 1$  we can rearrange the above to find B.

$$B = \frac{1 - \omega}{e^{\Phi} \Gamma(\Phi)} \tag{6.55}$$

We now have an analytical solution to the unapproximated equation for  $\chi_e(\lambda, \tau)$ , i.e. inclusive of advection and diffusion of heat.

$$\chi_e(\lambda,\tau) = \omega + (1-\omega)\gamma(\eta + \Phi, \Phi) \tag{6.56}$$

where

$$\eta = \frac{\lambda^2 - 2\Theta\alpha\tau}{4\tau\beta_T} \tag{6.57}$$

The equilibrium salinity field can be found from the scaling relation  $c_e = (c_f - c_i)\chi_e + c_i$  and the temperature field from the (rearranged) equation of state  $T = \frac{T^*}{a_1} \left(\frac{c_e}{c_e^*} - a_0\right)$ .

### 6.3 Solution of the salt conservation equation

As shown above, conservation of salt yields the following coupled partial differential equations for salinity field c(r, t) and precipitation field s(r, t).

$$\frac{\partial c}{\partial t} + \frac{1}{\phi} \frac{Q}{2\pi w} \frac{1}{r} \frac{\partial c}{\partial r} - \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) = \frac{1}{t_r} \left( c_e - c \right) \frac{s}{s_f}$$
(6.58)

$$\frac{\partial s}{\partial t} = -\frac{\phi}{(1-\phi)v} \frac{1}{t_r} (c_e - c) \frac{s}{s_f}$$
(6.59)

Let us remove dimensional quantities from (6.21) and (6.59) by defining the following variable scalings.

$$\tau = \frac{t}{t_r} \qquad \lambda = \frac{r}{R} \qquad \chi_e = \frac{c_e - c_i}{c_f - c_i} \qquad \chi = \frac{c - c_i}{c_f - c_i} \qquad \psi = \frac{s}{s_f}$$

Substitution of these relations yields:

$$\frac{\partial \chi}{\partial \tau} + \frac{\alpha}{\phi} \frac{1}{\lambda} \frac{\partial \chi}{\partial \lambda} - \beta_c \frac{1}{\lambda} \frac{\partial}{\partial \lambda} \left( \lambda \frac{\partial \chi}{\partial \lambda} \right) = (\chi_e - \chi) \psi$$
(6.60)

$$\frac{\partial \psi}{\partial \tau} = -\theta(\chi_e - \chi)\psi \tag{6.61}$$

where

$$\beta_c = \frac{Dt_r}{R^2} \tag{6.62}$$

$$\theta = \frac{\phi(c_f - c_i)}{v(1 - \phi)s_f} \tag{6.63}$$

and (as defined previously)

$$\alpha = \frac{Qt_r}{2\pi w R^2} \tag{6.64}$$

To ignore diffusion of salt  $\beta_c \ll \frac{\alpha}{\phi}$ .  $\Rightarrow Q \gg 2D\pi w\phi$ . Flowrates of order  $2D\pi w\phi$ are typically much less than the critical values below which heat diffusion cannot be ignored.  $(Q \sim \frac{2\kappa\pi w}{\Theta})$ . Hence to incorporate diffusion of heat and salt, one requires extremely low flowrates, for NaCl solutions,  $\leq 3 \times 10^{-5} \text{ cm}^3 \text{s}^{-1}$ . We shall ignore this lower limit and therefore ignore the diffusion of salt for the remainder of of our discussion. Hence the salt conservation equations reduce to:

$$\frac{\partial \chi}{\partial \tau} + \frac{\alpha}{\phi} \frac{1}{\lambda} \frac{\partial \chi}{\partial \lambda} = (\chi_e - \chi) \psi \tag{6.65}$$

$$\frac{\partial \psi}{\partial \tau} = -\theta(\chi_e - \chi)\psi \tag{6.66}$$

We shall now consider the two solution regimes of the Temperature equation. i.e. where flowrates are such that heat diffusion must be incorporated or can be ignored as a negligible effect.

## 6.3.1 Case 1: neglect heat diffusion $Q \gg \frac{2\kappa\pi w}{\Theta}$

Equation (6.29) gives the scaled equilibrium salinity  $\chi_e$  as:

$$\chi_e(\lambda,\tau) = \begin{cases} 1 & \eta \ge 0\\ \omega & \eta < 0 \end{cases}$$
(6.67)

with variable  $\eta$  defined as

$$\eta = \lambda^2 - 2\Theta\alpha\tau \tag{6.68}$$

Let us define an additional variable  $\mu = \tau$  to allow us to make the following functional equivalences:

$$\chi'(\eta,\mu) = \chi(\lambda,\tau) \tag{6.69}$$

$$\psi'(\eta,\mu) = \psi(\lambda,\tau) \tag{6.70}$$

Using the chain rule

$$\frac{\partial \chi'}{\partial \tau} = \frac{\partial \chi'}{\partial \eta} \frac{\partial \eta}{\partial \tau} + \frac{\partial \chi'}{\partial \mu} \frac{\partial \mu}{\partial \tau} = -2\Theta \alpha \frac{\partial \chi'}{\partial \eta} + \frac{\partial \chi'}{\partial \mu}$$
(6.71)

$$\frac{\partial \chi'}{\partial \lambda} = \frac{\partial \chi'}{\partial \eta} \frac{\partial \eta}{\partial \lambda} + \frac{\partial \chi'}{\partial \mu} \frac{\partial \mu}{\partial \lambda} = 2\lambda \frac{\partial \chi'}{\partial \eta}$$
(6.72)

$$\frac{\partial \psi'}{\partial \tau} = \frac{\partial \psi'}{\partial \eta} \frac{\partial \eta}{\partial \tau} + \frac{\partial \psi'}{\partial \mu} \frac{\partial \mu}{\partial \tau} = -2\Theta \alpha \frac{\partial \psi'}{\partial \eta} + \frac{\partial \psi'}{\partial \mu}$$
(6.73)

(6.65) and (6.66) now become:

$$2\alpha \left(\frac{1}{\phi} - \Theta\right) \frac{\partial \chi'}{\partial \eta} + \frac{\partial \chi'}{\partial \mu} = (\chi_e - \chi) \psi$$
(6.74)

$$\frac{2\Theta\alpha}{\theta}\frac{\partial\psi'}{\partial\eta} - \frac{1}{\theta}\frac{\partial\psi'}{\partial\mu} = (\chi_e - \chi)\psi \tag{6.75}$$

Let us now define a special variable  $\eta^* = \eta^*(\eta, \mu)$  and functions  $\chi^*(\eta^*)$  and  $\psi^*(\eta^*)$ such that

$$\chi^*(\eta^*) = \chi'(\eta, \mu)$$
 (6.76)

$$\psi^*(\eta^*) = \psi'(\eta, \mu)$$
 (6.77)

Define

$$\eta^*(\eta,\mu) = \eta + \Omega\mu \tag{6.78}$$

The chain rule then yields
$$\frac{\partial \chi^*}{\partial \eta} = \frac{d\chi^*}{d\eta^*} \frac{\partial \eta^*}{\partial \eta} = \frac{d\chi^*}{d\eta^*}$$
(6.79)

$$\frac{\partial \chi^*}{\partial \mu} = \frac{d\chi^*}{d\eta^*} \frac{\partial \eta^*}{\partial \mu} = \Omega \frac{d\chi^*}{d\eta^*} \tag{6.80}$$

$$\frac{\partial \psi^*}{\partial \eta} = \frac{d\psi^*}{d\eta^*} \frac{\partial \eta^*}{\partial \eta} = \frac{d\psi^*}{d\eta^*}$$
(6.81)

$$\frac{\partial \psi^*}{\partial \mu} = \frac{d\psi^*}{d\eta^*} \frac{\partial \eta^*}{\partial \mu} = \Omega \frac{d\psi^*}{d\eta^*} \tag{6.82}$$

Hence (6.74) and (6.75) become

$$\left(\frac{2\alpha}{\phi} - 2\alpha\Theta + \Omega\right)\frac{d\chi^*}{d\eta^*} = (\chi_e - \chi^*)\psi^* \tag{6.83}$$

$$\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right)\frac{d\psi^*}{d\eta^*} = (\chi_e - \chi^*)\psi^* \tag{6.84}$$

Motivated by the results of the sharp front model, one expects two classes of solutions to emerge from the equations above. We expect a single sharp transition from  $\chi = 0$  to  $\chi = 1$  in the case where the 'depletion front leads the thermal front' and a double front structure for the converse in which one expects an intermediate region where  $\chi \sim \omega$  and  $\psi \sim 1 - \frac{\theta(1-\phi\Theta)(1-\omega)}{\phi\Theta}$ . The mathematical encoding of these scenarios is related to the sign of parameter  $\Omega$ . If one regards the variable  $\eta$  as a 'space-like' coordinate (and  $\mu$  as a time coordinate) then our solutions are waveforms moving along the one dimensional space of  $\eta$  at velocity  $\Omega$ . (In the direction of decreasing  $\eta$ ). In the case of a purely depletive front, the waveform propagates in the positive  $\eta$  direction from the source at  $\eta = -2\alpha\Theta$ . i.e.  $\Omega < 0$ . In the case of a double front system the waveform propagates in the opposite direction from the 'thermal front' at  $\eta = 0$ . i.e.  $\Omega > 0$ .

Motivated by the above discussion plus the analysis of Phillips [7] and Hinch and Bhatt [2] we will postulate the following solution set:

$$\psi'(\eta,\mu) = \frac{\psi_0(\eta)}{1+e^{-\Upsilon(\eta+\Omega\mu)}} \tag{6.85}$$

$$\chi'(\eta,\mu) = \frac{\chi_e(\eta)}{1+e^{-\Upsilon(\eta+\Omega\mu)}}$$
(6.86)

where

$$\psi_0(\eta) = \begin{cases} 1 & \eta \ge 0\\ 1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta} & \eta < 0 \end{cases}$$
(6.87)

In the 'far away from the source' limit  $\eta \to \infty$ , one expects  $\chi, \psi \to 1$ .Both postulated solutions have this property.

One would expect in the limit  $\tau \gg 0$  the depletion front to maintain its structure as it propagates along the  $\lambda^2$  coordinate. (This behavior was observed in the Apples numerical experiment). Hence at the depletion front  $\lambda = \lambda_D$  we expect the value of  $\psi$ and  $\chi$  to remain constant  $\forall \tau$ . This can only occur if  $\eta_D^* = \eta_D + \Omega \mu = 0 \quad \forall \tau$ .

For a single front system, the sharp front model gives the dimensionless depletion front radius as

$$\lambda_D = \left(1 + \frac{1}{\theta}\right)^{-\frac{1}{2}} \sqrt{\frac{2\alpha\tau}{\phi}} \tag{6.88}$$

Hence 'stationary front' condition  $\eta_D^* = 0$  implies

$$\left(1+\frac{1}{\theta}\right)^{-1}\frac{2\alpha\tau}{\phi} - 2\alpha\Theta\tau + \Omega\tau = 0 \tag{6.89}$$

This is true  $\forall \tau$  if

$$\Omega = 2\alpha\Theta \left\{ 1 - \frac{1}{\phi\Theta} \left( 1 + \frac{1}{\theta} \right)^{-1} \right\}$$
(6.90)

For the double front system

$$\lambda_D = \left(\frac{\phi\Theta\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right)^{\frac{1}{2}}\sqrt{\frac{2\alpha\tau}{\phi}}$$
(6.91)

Using the same argument as above an equivalent equation for  $\Omega$  can be derived

$$\Omega = 2\alpha\Theta\left\{1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)}\right\}$$
(6.92)

Substitution of these results into the single, double front criteria yield the following:

Single front system  $\Omega < 0$ 

$$\phi\Theta < \left(1 + \frac{1}{\theta}\right)^{-1} \tag{6.93}$$

Double front system  $\Omega > 0$ 

$$\phi\Theta > \left(1 + \frac{1}{\theta}\right)^{-1} \tag{6.94}$$

These results exactly match the conclusions of the sharp front model.

To complete the analysis let us substitute our postulated solutions into (6.84) to compute  $\Upsilon$ . Let us evaluate these separately at  $\eta^* = 0$  for single and double front cases as one might expect them to differ.

Case (I): single front. At  $\eta^* = 0$ ,  $\psi_0 = 1$ ,  $\chi_e = 1$ 

$$\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right)\frac{d}{d\eta^*}\left(\frac{1}{1 + e^{-\Upsilon\eta^*}}\right) = \left(1 - \frac{1}{1 + e^{-\Upsilon\eta^*}}\right)\frac{1}{1 + e^{-\Upsilon\eta^*}} \tag{6.95}$$

$$\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right)\frac{\Upsilon e^{-\Upsilon\eta^*}}{\left(1 + e^{-\Upsilon\eta^*}\right)^2} = \left(1 - \frac{1}{1 + e^{-\Upsilon\eta^*}}\right)\frac{1}{1 + e^{-\Upsilon\eta^*}} \tag{6.96}$$

At  $\eta^*=0$ 

$$\Upsilon\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right) = 1 \tag{6.97}$$

 $\Rightarrow$ 

 $\Rightarrow$ 

$$\Upsilon = \left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right)^{-1} \tag{6.98}$$

Using the expression for (sing front)  $\Omega$  derived above

$$\Upsilon = \frac{\phi(\theta+1)}{2\alpha} \tag{6.99}$$

Case (II): double front. At  $\eta^* = 0, \psi_0 = 1 - \frac{\theta(1-\phi\Theta)(1-\omega)}{\phi\Theta}, \chi_e = \omega$ 

$$\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right) \frac{d}{d\eta^*} \left(\frac{1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta}}{1 + e^{-\Upsilon\eta^*}}\right) = \left(\omega - \frac{\omega}{1 + e^{-\Upsilon\eta^*}}\right) \frac{1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta}}{1 + e^{-\Upsilon\eta^*}} \quad (6.100)$$

$$\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right) \frac{\Upsilon \left(1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta}\right) e^{-\Upsilon \eta^*}}{(1 + e^{-\Upsilon \eta^*})^2}$$
$$= \omega \left(1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta}\right) (1 - \frac{1}{1 + e^{-\Upsilon \eta^*}}) \frac{1}{1 + e^{-\Upsilon \eta^*}}$$
(6.101)

At  $\eta^* = 0$ 

 $\Rightarrow$ 

$$\Upsilon\left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right)\left(1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta}\right) = \omega\left(1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta}\right) \quad (6.102)$$

$$\Upsilon = \omega \left(\frac{2\Theta\alpha}{\theta} - \frac{\Omega}{\theta}\right)^{-1} \tag{6.103}$$

Using the expression for (double front)  $\Omega$  derived above

$$\Upsilon = \frac{\phi}{2\alpha} \left\{ 1 + \frac{\theta(\omega + \phi\Theta - 1)}{\phi\Theta} \right\}$$
(6.104)

We can use the formulae for  $\Upsilon$  to estimate the salt reaction time constant  $t_r$ . Preliminary experiments conducted by Bell and Shaw-Champion [10] showed depletion fronts in Sodium Chloride plus glass ballotini bead packs to have widths<sup>2</sup>  $\delta R \sim 10$ mm. The width of a sigmoid function of the form  $y(x) = \frac{1}{1 + \exp(-\Upsilon x)}$  is  $\sim \frac{3}{\Upsilon}$ . (Setting  $x = \frac{3}{\Upsilon}$  yields  $y \approx 0.95$ ). Since  $\psi, \chi$  both have this form (with  $x \propto \frac{r^2}{R^2}$ ) we can relate  $\Upsilon$ to the experimental width above. <sup>3</sup>

$$\frac{3}{\Upsilon} \sim \left(\frac{\delta R}{R}\right)^2 \tag{6.105}$$

From above  $\Upsilon \sim \frac{\phi}{2\alpha}$  and  $\alpha = \frac{Qt_r}{2\pi w R^2}$ . Hence

$$t_r \sim \frac{\pi w \phi}{3Q} \left(\delta R\right)^2 \tag{6.106}$$

Using  $Q \sim 0.3 \text{ cm}^3 \text{s}^{-1}$ ,  $\phi \sim 0.4$  and  $w = 4.2 \text{ cm} \Rightarrow t_r \sim 0.06 \text{ s}$ .

### 6.3.2 Case 2: include heat diffusion $Q \sim \frac{2\kappa\pi w}{\Theta}$

Equation (6.56) gives the scaled equilibrium salinity  $\chi_e$  as:

$$\chi_e(\eta) = \omega + (1 - \omega)\gamma(\eta + \Phi, \Phi) \tag{6.107}$$

with variable  $\eta$  defined as

 $<sup>^2</sup>$  'Width' is defined as the distance between the centre of the depletion front and where the curve is within 95% of its downstream value.

 $<sup>^{3}</sup>$  This is all very approximate - the experiments performed by Bell and Shaw-Champion were with linear not axisymmetric media.

$$\eta = \frac{\lambda^2 - 2\Theta\alpha\tau}{4\tau\beta_T} \tag{6.108}$$

This definition allows us to write partial derivatives  $\frac{\partial}{\partial \lambda}$  and  $\frac{\partial}{\partial \tau}$  in terms of total derivatives  $\frac{d}{d\eta}$ , recalling definition  $\Phi = \frac{\Theta \alpha}{2\beta_T}$ .

$$\frac{\partial}{\partial \tau} = \frac{\partial \eta}{\partial \tau} \frac{d}{d\eta} = -\frac{(\Phi + \eta)}{\tau} \frac{d}{d\eta}$$
(6.109)

$$\frac{\partial}{\partial \lambda} = \frac{\partial \eta}{\partial \lambda} \frac{d}{d\eta} = \frac{\Phi \lambda}{\Theta \alpha \tau} \frac{d}{d\eta}$$
(6.110)

(6.65) and (6.66) now become:

$$\left(-\Phi - \eta + \frac{\Phi}{\phi\Theta}\right)\frac{1}{\tau}\frac{d\chi}{d\eta} = (\chi_e - \chi)\psi$$
(6.111)

$$\frac{(\Phi+\eta)}{\theta}\frac{1}{\tau}\frac{d\psi}{d\eta} = (\chi_e - \chi)\psi \tag{6.112}$$

Define  $A = \frac{1}{\phi \Theta} - 1$  to simplify the  $\chi$  equation slightly

$$(A\Phi - \eta)\frac{1}{\tau}\frac{d\chi}{d\eta} = (\chi_e - \chi)\psi$$
(6.113)

The presence of  $\tau$  in these equations means they cannot be solved in the same manner as for the 'ignore heat diffusion' case. We shall instead investigate the  $\tau \gg$ 0 asymptotic limit and postulate a series solution for  $\chi, \psi$  of the form

$$\chi(\eta,\tau) = \sum_{n=0}^{\infty} \frac{f_n(\eta)}{\tau^n}$$
(6.114)

$$\psi(\eta,\tau) = \sum_{n=0}^{\infty} \frac{g_n(\eta)}{\tau^n}$$
(6.115)

with the definition

$$f_0(\eta) = \chi_e(\eta) \tag{6.116}$$

Substitution of these series expansions into (6.113) and (6.112) yields:

$$-\frac{A\Phi - \eta}{\tau} \left( f_0' + \frac{f_1'}{\tau} + \frac{f_2'}{\tau^2} \dots \right) = \left( g_0 + \frac{g_1}{\tau} + \frac{g_2}{\tau^2} \dots \right) \left( \frac{f_1}{\tau} + \frac{f_2}{\tau^2} \dots \right)$$
(6.117)

$$-\frac{\Phi+\eta}{\theta\tau}\left(g_0'+\frac{g_1'}{\tau}+\frac{g_2'}{\tau^2}\dots\right) = \left(g_0+\frac{g_1}{\tau}+\frac{g_2}{\tau^2}\dots\right)\left(\frac{f_1}{\tau}+\frac{f_2}{\tau^2}\dots\right)$$
(6.118)

We can match coefficients of  $\{\tau^{-n}\}$  to generate the following series of ordinary differential equations for the sets of functions  $\{f_n(\eta)\}, \{g_n(\eta)\}$ .

Up to n = 2:

$$\tau^{-1}$$
 :  $-\frac{\Phi+\eta}{\theta}g'_0 = g_0 f_1$  (6.119)

$$\tau^{-1} : - (A\Phi - \eta)f'_0 = g_0 f_1 \tag{6.120}$$

$$\tau^{-2} : \qquad -\frac{\Phi+\eta}{\theta}g_1' = g_1f_1 + g_0f_2 \tag{6.121}$$

$$\tau^{-2}$$
 :  $-(A\Phi - \eta)f_1' = g_1f_1 + g_0f_2$  (6.122)

Since  $f_0(\eta)$  is known we can divide the first two equations and integrate to find  $g_0(\eta)$ . Note from the boundary conditions  $\psi(\eta = 0) = 1$  so we can write  $g_0(\eta)$  as a definite integral.

$$g_0(\eta) = 1 + \int_0^{\eta} \frac{\theta(A\Phi - \xi)}{\Phi + \xi} f'_0(\xi) d\xi$$
 (6.123)

This result can then be used to find  $f_1$  courtesy of the second equation.

$$f_1(\eta) = \frac{-(A\Phi - \eta)f'_0(\eta)}{g_0(\eta)}$$
(6.124)

This solution method is simple to extend to general n. Comparing coefficients of  $\tau^{-(n+1)}$ :

$$\tau^{-(n+1)} : \qquad -\frac{\Phi+\eta}{\theta}g'_n = \sum_{i=0}^n g_i f_{n-i+1} \tag{6.125}$$

$$\tau^{-(n+1)}$$
 :  $-(A\Phi - \eta)f'_n = \sum_{i=0}^n g_i f_{n-i+1}$  (6.126)

Assuming one knows the set of solutions up to  $f_n$  and  $g_{n-1}$ ; one can find the next solutions in the series,  $f_{n+1}, g_n$ , by the formulae

$$g_n(\eta) = 1 + \int_0^{\eta} \frac{\theta(A\Phi - \xi)}{\Phi + \xi} f'_n(\xi) d\xi$$
 (6.127)

$$f_{n+1}(\eta) = \frac{-(A\Phi - \eta)f'_n(\eta) - \sum_{i=1}^n g_i(\eta)f_{n-i+1}(\eta)}{g_0(\eta)}$$
(6.128)

Let us use these results to compute the terms  $g_0(\eta)$  and  $f_1(\eta)$ .

$$f_0(\eta) = \chi_e(\eta) = \omega + (1 - \omega)\gamma(\eta + \Phi, \Phi)$$
(6.129)

 $\Rightarrow$ 

$$f_0'(\eta) = \frac{1-\omega}{\Gamma(\Phi)} e^{-(\eta+\Phi)} (\eta+\Phi)^{\Phi-1}$$
(6.130)

$$\Rightarrow$$

$$g_0(\eta) = 1 + \frac{\theta(1-\omega)}{\Gamma(\Phi)} \int_0^\eta \frac{(A\Phi - \xi)}{\Phi + \xi} e^{-(\xi+\Phi)} (\xi+\Phi)^{\Phi-1} d\xi$$
(6.131)

 $\Rightarrow$ 

 $\Rightarrow$ 

$$g_0(\eta) = 1 + \frac{\theta(1-\omega)}{\Gamma(\Phi)} \left\{ (A\Phi - \eta) \int_0^{\eta} e^{-(\xi+\Phi)} (\xi+\Phi)^{\Phi-2} d\xi + \int_0^{\eta} \int_0^{\zeta} e^{-(\xi+\Phi)} (\xi+\Phi)^{\Phi-2} d\xi d\zeta \right\}$$
(6.132)

Define the 'second order lower incomplete gamma function'

$$\gamma^{(2)}(x,a) = \frac{1}{\Gamma(a)} \int_0^x \int_0^\zeta e^{-\xi} \xi^{a-1} d\xi d\zeta$$
 (6.133)

$$g_0(\eta) = 1 + \frac{\theta(1-\omega)\Gamma(\Phi-1)}{\Gamma(\Phi)} \left\{ (A\Phi - \eta)\gamma(\eta + \Phi, \Phi - 1) + \gamma^{(2)}(\eta + \Phi, \Phi - 1) \right\}$$
(6.134)

Now  $f_1(\eta) = \frac{-(A\Phi - \eta)f'_0(\eta)}{g_0(\eta)}$   $\Rightarrow$  $f_1(\eta) = \frac{(\eta - A\Phi)e^{-(\eta + \Phi)}(\eta + \Phi)^{\Phi - 1}}{\frac{\Gamma(\Phi)}{1 - \omega} + \theta\Gamma(\Phi - 1)\left\{(A\Phi - \xi)\gamma(\eta + \Phi, \Phi - 1) + \gamma^{(2)}(\eta + \Phi, \Phi - 1)\right\}}$  (6.135)

### 6.4 Summary of solutions to conservation equations

## 6.4.1 Case 1: ignore heat diffusion $Q \gg \frac{2\kappa \pi w}{\Theta}$

$$\eta = \lambda^2 - 2\Theta\alpha\tau \tag{6.136}$$

$$\chi_e(\lambda,\tau) = \begin{cases} 1 & \eta \ge 0\\ \omega & \eta < 0 \end{cases}$$
(6.137)

$$\psi_0(\eta) = \begin{cases} 1 & \eta \ge 0\\ 1 - \frac{\theta(1 - \phi\Theta)(1 - \omega)}{\phi\Theta} & \eta < 0 \end{cases}$$
(6.138)

$$\psi(\lambda,\tau) = \frac{\psi_0(\eta)}{1 + e^{-\Upsilon(\eta + \Omega\tau)}}$$
(6.139)

$$\chi(\lambda,\tau) = \frac{\chi_e(\eta)}{1 + e^{-\Upsilon(\eta + \Omega\tau)}}$$
(6.140)

Depletion front leads thermal front  $\Omega < 0 \Rightarrow \phi \Theta < \left(1 + \frac{1}{\theta}\right)^{-1}$ 

$$\Omega = 2\alpha\Theta \left\{ 1 - \frac{1}{\phi\Theta} \left( 1 + \frac{1}{\theta} \right)^{-1} \right\}$$
(6.141)

$$\Upsilon = \frac{\phi(\theta+1)}{2\alpha} \tag{6.142}$$

Depletion front lags thermal front  $\Omega > 0 \Rightarrow \phi \Theta > \left(1 + \frac{1}{\theta}\right)^{-1}$ 

$$\Omega = 2\alpha\Theta \left\{ 1 - \frac{\theta\omega}{\phi\Theta + \theta(\omega + \phi\Theta - 1)} \right\}$$
(6.143)

$$\Upsilon = \frac{\phi}{2\alpha} \left\{ 1 + \frac{\theta(\omega + \phi\Theta - 1)}{\phi\Theta} \right\}$$
(6.144)

## **6.4.2** Case 2: include heat diffusion $Q \sim \frac{2\kappa \pi w}{\Theta}$

$$\eta = \frac{\lambda^2 - 2\Theta\alpha\tau}{4\tau\beta_T} \tag{6.145}$$

$$\chi_e(\eta) = \omega + (1 - \omega)\gamma(\eta + \Phi, \Phi)$$
(6.146)

$$\chi(\eta,\tau) = \sum_{n=0}^{\infty} \frac{f_n(\eta)}{\tau^n}$$
(6.147)

$$\psi(\eta,\tau) = \sum_{n=0}^{\infty} \frac{g_n(\eta)}{\tau^n}$$
(6.148)

$$f_0(\eta) = \chi_e(\eta) \tag{6.149}$$

$$A = \frac{1}{\phi \Theta} - 1 \qquad \Phi = \frac{\Theta \alpha}{2\beta_T} \tag{6.150}$$

$$g_n(\eta) = 1 + \int_0^{\eta} \frac{\theta(A\Phi - \xi)}{\Phi + \xi} f'_n(\xi) d\xi$$
 (6.151)

$$f_{n+1}(\eta) = \frac{-(A\Phi - \eta)f'_n(\eta) - \sum_{i=1}^n g_i(\eta)f_{n-i+1}(\eta)}{g_0(\eta)}$$
(6.152)

$$g_0(\eta) = 1 + \frac{\theta(1-\omega)\Gamma(\Phi-1)}{\Gamma(\Phi)} \left\{ (A\Phi - \eta)\gamma(\eta + \Phi, \Phi - 1) + \gamma^{(2)}(\eta + \Phi, \Phi - 1) \right\}$$
(6.153)

$$f_1(\eta) = \frac{(\eta - A\Phi)e^{-(\eta + \Phi)}(\eta + \Phi)^{\Phi - 1}}{\frac{\Gamma(\Phi)}{1 - \omega} + \theta\Gamma(\Phi - 1)\left\{(A\Phi - \xi)\gamma(\eta + \Phi, \Phi - 1) + \gamma^{(2)}(\eta + \Phi, \Phi - 1)\right\}}$$
(6.154)

## 6.5 Field equation solutions (neglecting heat diffusion) computed for a real experimental system

The salinity, precipitation and equilibrium salinity fields for an axisymmetric porous medium have been computed using the MATLAB code SRIPM. (Salt Reactions In Porous Media). The medium has identical physical characteristics to the linear case described above in the Experimental Analysis section, except that a cylindrical geometry is used (Radius R = 20 cm, width w = 4.2 cm). Graphical solutions are presented for sodium chloride and sodium sulphate salts.

In both cases  $\phi \Theta > (1 + \frac{1}{\theta})^{-1} \Rightarrow$  the thermal front leads the depletion front. However, because the saturation solubility of sodium chloride varies ~ 0.2% compared to ~ 10% for sodium sulphate, the double front structure is only clearly observed for the latter. On page 67 the salt reaction time constant  $t_r$  was estimated to be ~ 0.06 s. For both species of salt this yields sharp fronts and the predictions of the sharp front model (as illustrated above via coloured asterisks) fit to very good accuracy. To demonstrate the effect of increasing  $t_r$  (from 0.06 to 100 s) an additional series of plots have been computed for sodium sulphate salt. Qualitatively, the result is a broadening of the depletion front about a mid point given by the sharp front model depletion front length. The thermal front remains sharp because the equation for the temperature field contains no salt reaction term (with an associated  $t_r$ ). If heat diffusion were to be included one would expect this front to broaden also<sup>4</sup>.

Below is a summary of input and output parameters of the SRIPM code.

#### 6.5.1 Sodium sulphate salt, $t_r = 100$ s

$24 \mathrm{~cm}$
$4.2~\mathrm{cm}$
$11 \mathrm{~cm}$
$5~{\rm cm}$
$0.5~\mathrm{cm}$
$36~{ m cm}$
$0.051~{\rm cm}$
$20~{\rm cm}$
1
$0.998 \text{ gcm}^{-3}$
$2.6 \ \mathrm{g cm^{-3}}$
$0.032~{\rm g cm^{-3}}$
$1.46~{\rm g cm^{-3}}$

<sup>&</sup>lt;sup>4</sup>The asymptotic solutions for the salinity and precipitation fields when heat diffusion is included are not plotted because of a lack of numerical code to plot succesive integrals of the gamma function. However, the saturation salinity fields are plotted, recalling the assumption of a linear relation between saturation salinity and temperature.

Specific heat capacity $C_w$ of water	$4.182 \ \mathrm{JK^{-1}g^{-1}}$
Specific heat capacity $C_{glass}$ of glass	$0.84 \ \mathrm{JK^{-1}g^{-1}}$
Specific heat capacity $C_{ins}$ of insulation	$1.38 \ \mathrm{JK^{-1}g^{-1}}$
Specific heat capacity $C_{salt}$ of solid salt	$1.82 \ \mathrm{JK^{-1}g^{-1}}$
Thermal diffusivity $\kappa_w$ of water	$0.00144 \text{ cm}^2 \text{s}^{-1}$
Thermal diffusivity $\kappa_{ins}$ of insulation	$0.00625 \ {\rm cm}^2 {\rm s}^{-1}$
Thermal diffusivity $\kappa_{glass}$ of glass	$0.00412 \ {\rm cm}^2 {\rm s}^{-1}$
Thermal diffusivity $\kappa_{salt}$ of solid salt	$0.00301 \ {\rm cm}^2 {\rm s}^{-1}$
Salt bulk diffusion constant $D$	$1.23 \text{ x} 10^{-5} \text{ cm}^2 \text{s}^{-1}$
Molar mass $M_{salt}$ of salt	$142.04 \text{ gmol}^{-1}$
Injectate temperature $T_i$	$5^{\mathrm{o}}\mathrm{C}$
Initial formation temperature $T_f$	$24.5^{\mathrm{o}}\mathrm{C}$
Mean volumetric flow rate through system ${\cal Q}$	$0.22453 \text{ cm}^3 \text{s}^{-1}$
Porosity $\phi$ of porous medium	0.29
Mass of salt $m_{salt}$ initially in medium	420 g
Head $h$ driving flow	$2~{ m cm}$
Mass ratio $R_{GS}$ of glass beads to salt	2.5
Saturated solution volume/solvent volume $R_V$	1.1
Weight fraction of salt in injected fluid	0
Salt reaction time constant $t_r$	100 s
Sat. salt weight fraction of initial formation fluid	0.91792
Sat. salt weight fraction of injected fluid	0.14468
Initial formation salinity $c_f$	$0.8328 \text{ gcm}^{-3}$
Saturation salinity $c_{ei}$ of injectate	$0.13126 \text{ gcm}^{-3}$
Injectate salinity $c_i$	$0 \text{ gcm}^{-3}$
Initial solid salt density $s_f$	$0.60736 \ {\rm g cm}^{-3}$
Initial formation fluid density $\kappa_{fluid}$	$1.7401 \ {\rm g cm^{-3}}$
Initial formation solid density $\kappa_{solid}$	$2.1258 \text{ gcm}^{-3}$
Formation fluid specific heat capacity $C_{fluid}$	$2.9505 \ \mathrm{JK^{-1}g^{-1}}$
Formation fluid thermal diffusivity $\kappa_{fluid}$	$0.0022586~{\rm cm^2 s^{-1}}$

Formation solid specific heat capacity $C_{solid}$	$1.12 \ \mathrm{JK^{-1}g^{-1}}$
Formation solid thermal diffusivity $\kappa_{solid}$	$0.0038029~{\rm cm}^2{\rm s}^{-1}$
Karman-Cozeny permeability $k$	$6.5769 \ \mathrm{x10^{-11}} \ \mathrm{m^2}$
Volume $V_{glass}$ of glass used in walls on tank	$631.8~{\rm cm}^3$
Volume $V_{ins}$ of insulation used around tank	$12711.2 \ {\rm cm}^3$
Total volume $V_{total}$ of experiment	$14310.68 \ {\rm cm}^3$
Averaged thermal diffusivity parameter $\kappa$	0.0030883
Averaged thermal parameter $\Theta$	1.6213
Extent of reactive species advection $\alpha$	0.0021271
Extent of thermal diffusion $\beta_T$	0.00077208
Extent of salt diffusion $\beta_c$	$3.075 \text{ x} 10^{-6}$
Reaction parameter $\theta$	0.54759
Injector saturation salinity variable $\omega$	0.15761
Ratio of thermal to fluid front lengths $F$	0.4627
Upsilon $\Upsilon$	36.9397
Big omega $\Omega$	0.004561
Advection to thermal diffusion ratio $\Phi$	2.2334
Fluid flush time $t_{flush}$	1229 s
Thermal flush time $t_{therm}$	$2658 \mathrm{\ s}$
Salt diffusion time $t_{sd}$	$7492682 \ s$
Heat diffusion time $t_{hd}$	29841 s
Cooling time $t_{cool}$	$3930 \mathrm{\ s}$

### **6.5.2** Sodium sulphate salt, $t_r = 0.06$ s

Only differences to the above are shown.

Salt reaction time constant $t_r$	0.06 s
Extent of reactive species advection $\alpha$	$1.2763 \ {\rm x10^{-6}}$
Extent of thermal diffusion $\beta_T$	$4.6325 \ \mathrm{x10^{-7}}$
Extent of salt diffusion $\beta_c$	$1.845 \text{ x} 10^{-9}$
Upsilon $\Upsilon$	61566.2347
Big omega $\Omega$	$2.7366 \ \mathrm{x10^{-6}}$
Advection to thermal diffusion ratio $\Phi$	2.2334

### 6.5.3 Sodium chloride salt, $t_r = 0.06 \text{ s}$

Again, only differences to the above are shown.

Specific heat capacity $C_{salt}$ of solid salt	$0.86 \ \mathrm{JK}^{-1}\mathrm{g}^{-1}$
Density $\rho_{salt}$ of pure solid salt	$2.17 \text{ gcm}^{-3}$
Thermal diffusivity $\kappa_{salt}$ of solid salt	$0.0097 \text{ cm}^2 \text{s}^{-1}$
Salt bulk diffusion constant $D$	$1.611~{\rm x}10^{-5}~{\rm cm}^{2}{\rm s}^{-1}$
Molar mass $M_{salt}$ of salt	$58.443 \text{ gmol}^{-1}$
Mean volumetric flow rate through system ${\cal Q}$	$0.31763 \text{ cm}^3 \text{s}^{-1}$
Porosity $\phi$ of porous medium	0.38
	0.00
Salt reaction time constant $t_r$	0.06 s
Sat. salt weight fraction of initial formation fluid	0.35968
Sat. salt weight fraction of injected fluid	0.35658
Initial formation salinity $c_f$	$0.32633 \text{ gcm}^{-3}$
Saturation salinity $c_{ei}$ of injectate	$0.32351 \text{ gcm}^{-3}$
Injectate salinity $c_i$	$0 \text{ gcm}^{-3}$
Initial solid salt density $s_f$	$0.70305 \ {\rm g cm^{-3}}$
Initial formation fluid density $\kappa_{fluid}$	$1.2336 \ {\rm g cm}^{-3}$
Initial formation solid density $\kappa_{solid}$	$2.4607 \text{ gcm}^{-3}$
Formation fluid specific heat capacity $C_{fluid}$	$1.7388 \ \mathrm{JK}^{-1}\mathrm{g}^{-1}$
Formation fluid thermal diffusivity $\kappa_{fluid}$	$0.007515 \text{ cm}^2 \text{s}^{-1}$
Formation solid specific heat capacity $C_{solid}$	$0.84571 \ \mathrm{JK^{-1}g^{-1}}$
Formation solid thermal diffusivity $\kappa_{solid}$	$0.0057143 \ {\rm cm}^2 {\rm s}^{-1}$
Karman-Cozeny permeability $k$	$2.1243 \ \mathrm{x10^{-10}} \ \mathrm{m^2}$
Averaged thermal diffusivity parameter $\kappa$	0.0064162
Averaged thermal parameter $\Theta$	1.0187
Extent of reactive species advection $\alpha$	$1.8054 \text{ x} 10^{-6}$
Extent of thermal diffusion $\beta_T$	$9.6243 \text{ x} 10^{-7}$
Extent of salt diffusion $\beta_c$	$2.4165 \text{ x} 10^{-9}$
Reaction parameter $\theta$	0.2877
Injector saturation salinity variable $\omega$	0.99138
Ratio of thermal to fluid front lengths $F$	0.38982
Upsilon $\Upsilon$	135785.6997
Big omega $\Omega$	$1.578 \text{ x} 10^{-6}$
Advection to thermal diffusion ratio $\Phi$	0.95554



Surface plot of formation salinity, ignoring heat diffusion

Figure 6.3: Axisymmetric Salinity field for Sodium Chloride salt.  $t_r = 0.06$  s.

Fluid flush time $t_{flush}$	$1165~{\rm s}$
Thermal flush time $t_{therm}$	$2990~{\rm s}$
Salt diffusion time $t_{sd}$	$5720670~\mathrm{s}$
Heat diffusion time $t_{hd}$	$14363~{\rm s}$
Cooling time $t_{cool}$	$3745~{\rm s}$



Figure 6.4: Axisymmetric Precipitation field for Sodium Chloride salt.  $t_r = 0.06$  s.



Surface plot of saturation salinity, ignoring heat diffusion

Figure 6.5: Axisymmetric Saturation Salinity field for Sodium Chloride salt. Heat diffusion is ignored.



Surface plot of saturation salinity, inclusive of heat diffusion

Figure 6.6: Axisymmetric Saturation Salinity field for Sodium Chloride salt. Heat diffusion is not ignored.



Surface plot of formation salinity, ignoring heat diffusion

Figure 6.7: Axisymmetric Salinity field for Sodium Sulphate salt.  $t_r = 100$  s.



Surface plot of formation salinity, ignoring heat diffusion

Figure 6.8: Axisymmetric Salinity field for Sodium Sulphate salt.  $t_r = 0.06$  s.



Figure 6.9: Axisymmetric Precipitation field for Sodium Sulphate salt.  $t_r = 100$  s.



Surface plot of formation precipitation, ignoring heat diffusion

Figure 6.10: Axisymmetric Precipitation field for Sodium Sulphate salt.  $t_r = 0.06$  s.



Surface plot of saturation salinity, ignoring heat diffusion

Figure 6.11: Axisymmetric Saturation Salinity field for Sodium Sulphate salt. Heat diffusion is ignored.



Surface plot of saturation salinity, inclusive of heat diffusion

Figure 6.12: Axisymmetric Saturation Salinity field for Sodium Sulphate salt. Heat diffusion is not ignored.

## Chapter 7

## Conclusion

To conclude I will comment under three headings. Firstly I will outline what has been achieved and then make an assessment of the success of the models presented by comparison to experimental results. In mind of this analysis I will voice my own suggestions for future study, both in theoretical and practical terms. Finally I will thank those who have supported the project over the past year

# 7.1 Outline of achievements and proposals for further study

- A sharp front model has been derived for linear and axisymmetric media. Conditions that select between a single front (depletion front leads thermal front) and a double front (thermal front leads depletion front) solution are given. Equations for the lengths of all fronts are presented in addition to the degree of dissolution between the thermal and depletion fronts.
- Conservation of heat, total mass and salt mass have been used to derive a system of partial differential equations for the salinity, equilibrium salinity and precipitation fields for axisymmetric geometry and a constant injection flowrate.<sup>1</sup> In all cases salt diffusion has been neglected implying a lower bound to applicable flowrates of  $2D\pi w\phi$ . For sodium chloride  $D \sim 1.611 \ge 10^{-5} \text{ cm}^2 \text{s}^{-1}$ . If

<sup>&</sup>lt;sup>1</sup>As discussed in the the section concerning the processing of experimental data, the sharp front model is valid for flowrates that vary with time. Unfortunately, closed (i.e non series) analytic solutions to the corresponding continuum model can only be found for constant flowrates. One can show this by seeking solution functions in terms of a variable  $\eta = \lambda^a \tau^b$  and defining a power law flowrate  $Q = Q_0 \tau^c$ . Substitution into the governing partial differential equations only yields ordinary differential equations in  $\eta$  when c = 0.

#### 7. Conclusion

the injection length scale is ~ 10 cm and porosity ~ 0.5, flowrates must exceed ~ 3 x  $10^{-5}$  cm<sup>3</sup>s<sup>-1</sup>. Long time asymptotic solutions have been derived for  $2D\pi w\phi \ll Q \sim \frac{2\kappa\pi w}{\Theta}$  and analytic solutions for  $Q \gg \frac{2\kappa\pi w}{\Theta}$ , i.e. when heat and salt diffusion are both neglected. The latter yields the same double/single front selection criterion as the sharp front model and indeed approaches the sharp front solutions in the limit of the reaction time parameter  $t_r \to 0$ . (i.e. an infinitely fast reaction rate). Note for the experimental system adopted in this study,  $\frac{2\kappa\pi w}{\Theta} \sim 5 \times 10^{-2} \text{ cm}^3 \text{s}^{-1}$  an order of magnitude less than the average flowrate Q used. (~ 0.2 cm<sup>3</sup>s<sup>-1</sup>).

- The numerical analogy of 'Apples and Baskets' encoded in MATLAB appears to confirm the predictions of the sharp front model and seems to serve its purpose and an educational aid in the understanding of the physical processes that generate depletion and thermal fronts. The idea could readily be extended to a greater multiplicity of 'chinese whispers' (i.e. fronts that fix a species saturation) or indeed more than one mobile species. For example, baskets could contain apples and *oranges* and people could have eating laws that depend on the amounts of both in the baskets and in their stomachs. This would have a direct application in the energy industry where acid or gas is often injected to stimulate reservoir performance. A greater complexity could be introduced to take into account of reactions between dissolved or precipitated species.
- Many difficulties were encountered in the running of experiments designed to contradict or verify the theory presented. The current design proved adequate for achieving results of fluid and depletion fronts using sodium chloride. However, as indicated by a very preliminary study with sodium sulphate, the setup may not be the most appropriate method of investigating thermal fronts. Also, the rectangular nature of the current equipment meant no direct comparison with the mostly axisymmetric theory could be made. An experiment based on a thin cylindrical Hele Shaw cell using sodium sulphate salt would be the most logical step forward. This could be oriented horizontally to reduce the possibility of gravity driven Saffman-Taylor instability and fluid would be injected centrally from a raised source. A double front system resulting in a near depletion of salt upstream of the thermal front would be desirable for visual purposes. This could be achieved by having an injectate significantly colder that the formation. However, as shown on page 16, as the injectate temperature is lowered, although the precipitation s' tends to zero, the separation between depletion and thermal fronts also reduces. When s' is zero the double front structure is lost and a single front system remains. An informative series of experiments could involve

#### 7. Conclusion

such a system with increasingly lower injectate temperature until the doublesingle front transition is observed. For a sodium sulphate system initially at a lab temperature of  $24.5^{\circ}$ C we can calculate the initial precipitation required to cause a transition at  $10^{\circ}$ C.

$$c_{ei}^*(T = 10^{\circ}C) = 0.2030 \text{ gcm}^{-3}$$
 (7.1)

$$c_f(T = 24.5^{\circ}C) = 0.8328 \text{ gcm}^{-3}$$
 (7.2)

Using  $c_{ei}^* = c_f - \frac{(1-\phi)vs_fF}{\phi(1-F)}$  and  $F = \phi\Theta$  $\Rightarrow$   $s_f^* = \frac{(c_f - c_{ei}^*)(1-\phi\Theta)}{(1-\phi)v\Theta}$ (7.3)

 $\Rightarrow$ 

$$s_f^* = 0.29 \text{ gcm}^{-3}$$
 (7.4)

For a Hele Shaw cell of porosity  $\phi = 1 - \left(\frac{1}{\rho_{salt}} + \frac{\Re_{GS}}{\rho_{glass}}\right) \frac{m_{salt}}{\pi R^2 w}$ , radius R = 20 cm and depth w = 4.2 cm, this implies a salt mass

$$m_{salt} = s_f^* (1 - \phi) \pi R^2 w \tag{7.5}$$

$$1 = s_f^* \left( \frac{1}{\rho_{salt}} + \frac{\Re_{GS}}{\rho_{glass}} \right) \tag{7.6}$$

 $\Rightarrow$ 

 $\Rightarrow$ 

$$\Re_{GS} = \frac{\rho_{glass}}{s_f^*} - \frac{\rho_{glass}}{\rho_{salt}}$$
(7.7)

$$= 7.1$$
 (7.8)

 $(\rho_{glass} = 2.6 \text{ gcm}^{-3}, \ \rho_{salt} = 1.46 \text{ gcm}^{-3}).$ 

In summary, the ballotini to salt ratio at the transition between double and single front systems (given a desired transition temperature and thus injectate saturation salinity) is given by

$$\Re_{GS} = \frac{\rho_{glass}(1-\phi)v\Theta}{(c_f - c_{ei}^*)(1-\phi\Theta)} - \frac{\rho_{glass}}{\rho_{salt}}$$
(7.9)

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<sup>&</sup>lt;sup>2</sup>Under consideration for publication

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## Appendix A

# The Saffman Taylor Instability in porous media

Consider a time and space varying perturbation  $\varepsilon(x,t)$  to a (previously) sharp interface between fluid regions 1 and 2 as illustrated in figure (A.1)

$$\varepsilon(x,t) = ae^{inx+\sigma t}f(z) \tag{A.1}$$

where a = real positive constant and n is the (dimensionless) wavenumber of the perturbation,  $\frac{2\pi}{\lambda}$ .

Aim to determine  $\sigma$  in terms of Darcy velocity **u**; porosities  $\phi_1, \phi_2$ ; permeabilities  $k_1, k_2$ ; viscosities  $\eta_1, \eta_2$ ; fluid densities  $\rho_1, \rho_2$  and gravitational field strength g. If  $\sigma > 0 \Rightarrow$  perturbation will grow with time and thus interface will be unstable.

Define Darcy velocity field in perturbed region to be  $\mathbf{u} = \overline{u}\hat{\mathbf{z}} + u_x\hat{\mathbf{x}} + u_z\hat{\mathbf{z}}$ . Let  $u_z \approx \phi \frac{\partial \varepsilon}{\partial t} \Rightarrow$ 

$$u_z = \phi \sigma a e^{inx + \sigma t} f(z) \tag{A.2}$$

In each region one assumes  $\nabla \rho$  and  $\frac{\partial \rho}{\partial t} = 0$ . Hence by continuity of fluid

$$\nabla \cdot \mathbf{u} = 0 \Rightarrow \frac{\partial u_x}{\partial x} + \frac{\partial u_z}{\partial z} = 0$$
 (A.3)

Substitution of (A.2) into this result and integrating wrt x expression for  $u_x$  gives

$$u_x = \frac{-f'(z)\phi\sigma a e^{inx+\sigma t}}{in} + \alpha(z,t)$$
(A.4)



Figure A.1: The Saffman Taylor instability desribes a criterion for the growth of perturbations to the interface of two incompressible fluids with defined densities and viscosities, each existing in a porous solid matrix with known permeabilities and porosities. Here cartesian geometry is studied.

where  $\alpha(z,t)$  is the constant of integration.

Darcy's Law relates the transport velocity  $\mathbf{u}$  to the pressure field p

$$\mathbf{u} = -\frac{k}{\eta} (\nabla p - pg\widehat{\mathbf{z}}) \Rightarrow u_x = -\frac{k}{\eta} \frac{\partial p}{\partial x}$$
(A.5)

For the x component

$$\frac{\partial p}{\partial x} = -\frac{\eta}{k} \left\{ \alpha(z,t) + \frac{-f'(z)\phi\sigma a e^{inx+\sigma t}}{in} \right\}$$
(A.6)

One may expect p to be oscillatory in x so set  $\alpha(z, t) = 0$  to prevent any  $\alpha x$  terms.  $\Rightarrow$ 

$$p(x, z, t) = \frac{-f'(z)\eta\phi\sigma a e^{inx+\sigma t}}{kn^2} + \beta(z, t)$$
(A.7)

Inserting this result into Darcy's law yields the following result for the z component

$$-\frac{\eta}{k}\left\{\overline{u} + \phi\sigma a e^{inx+\sigma t} f(z)\right\} + \rho g = \frac{-f''(z)\eta\phi\sigma a e^{inx+\sigma t}}{kn^2} + \frac{\partial\beta(z,t)}{\partial z}$$
(A.8)

Since this must be true  $\forall x$  we can compare coefficients of  $e^{inx}$  to find an ordinary differential equation for f(z)

$$f(z) = \frac{f''(z)}{n^2} \tag{A.9}$$

Let  $f(z) = e^{\xi z}$ .<sup>1</sup> Substitution into the above yields  $\frac{\xi^2}{n^2} = 1 \Rightarrow \xi = \pm n$ . Hence

$$f(z) = Ae^{\pm nz} \tag{A.10}$$

Substitution of this result into the z component of Darcy's law yields an equation for p in terms of known quantities. (Absorbing the constant A into a)

$$\frac{\partial p}{\partial z} = -\frac{\eta}{k} \left\{ \overline{u} + \phi \sigma a e^{inx \pm nz + \sigma t} \right\} + \rho g \tag{A.11}$$

 $\Rightarrow$ 

$$p = -\frac{\eta}{k} \left\{ \overline{uz} \pm \frac{\phi \sigma a}{n} e^{inx \pm nz + \sigma t} \right\} + \rho gz + p^*(x, t)$$
(A.12)

In regions 1 and 2 we expect perturbations to decay far away from the interface. i.e.

$$\begin{cases} \lim_{z \to +\infty} \varepsilon = 0 & \text{region } 2\\ \lim_{z \to -\infty} \varepsilon = 0 & \text{region } 1 \end{cases}$$
(A.13)

Hence fix sign of  $\xi$  accordingly in each region to solve for the pressure field

$$p = \begin{cases} -\frac{\eta_1}{k_1} \left\{ \overline{uz} + \frac{\phi_1 \sigma a}{n} e^{inx + nz + \sigma t} \right\} + \rho_1 gz + p_1^*(x, t) & z < \varepsilon \\ -\frac{\eta_2}{k_2} \left\{ \overline{uz} - \frac{\phi_2 \sigma a}{n} e^{inx - nz + \sigma t} \right\} + \rho_2 gz + p_2^*(x, t) & z > \varepsilon \end{cases}$$
(A.14)

These expressions must be equivalent at  $z = \varepsilon$  if surface tension is ignored

$$(\rho_1 - \rho_2) g\varepsilon + \overline{u}\varepsilon \left(\frac{\eta_2}{k_2} - \frac{\eta_1}{k_1}\right) + p_1^*(x, t) - p_2^*(x, t) - \frac{\sigma a}{n} e^{inx + \sigma t} \left(\frac{\phi_1 \eta_1}{k_1} e^{n\varepsilon} + \frac{\phi_2 \eta_2}{k_2} e^{-n\varepsilon}\right) = 0$$
(A.15)

If at t = 0 perturbations are small  $\Rightarrow \varepsilon \ll \lambda$ . Since  $\lambda = \frac{2\pi}{n} \Rightarrow n\varepsilon \ll 2\pi \Rightarrow n\varepsilon \ll 1$ . Hence by Taylor expansion of  $e^{\pm n\varepsilon}$ 

$$e^{\pm n\varepsilon} = 1 \pm n\varepsilon + \dots \approx 1 \tag{A.16}$$

<sup>&</sup>lt;sup>1</sup>Let one constant of integration be absorbed into a. Consider different values for A depending on the sign of  $\xi$  to incorporate the second constant.



Figure A.2: Illustration of the Saffman Taylor instability at an initially circular interface.

Applying this and differentiating wrt  $\varepsilon$  we find

$$(\rho_1 - \rho_2)g + \overline{u}\left(\frac{\eta_2}{k_2} - \frac{\eta_1}{k_1}\right) - \frac{\sigma a}{n}e^{inx}\left(\frac{\phi_1\eta_1}{k_1} + \frac{\phi_2\eta_2}{k_2}\right) = 0$$
(A.17)

At x = 0 (A.17) becomes

$$\left(\rho_1 - \rho_2\right)g + \overline{u}\left(\frac{\eta_2}{k_2} - \frac{\eta_1}{k_1}\right) = \left(\frac{\eta_1\phi_1}{k_1} + \frac{\eta_2\phi_2}{k_2}\right)\frac{\sigma a}{n} \tag{A.18}$$

The sign of  $\sigma$  is fixed by the sign of the LHS since the RHS coefficients of  $\sigma$  must all be positive for a real physical system.

Hence interface is unstable, i.e.  $\sigma > 0$  if

$$\overline{u} > \frac{(\rho_2 - \rho_1) g}{\frac{\eta_2}{k_2} - \frac{\eta_1}{k_1}}$$
(A.19)

A conceptually identically analysis can be applied to axisymmetric geometry. In this case consider a perturbation  $\varepsilon(r, \theta)$  to a circular interface between regions 1 and 2 as illustrated in figure (A.2).

$$\varepsilon(r,\theta) = ae^{in\theta + \sigma t}f(r) \tag{A.20}$$

If L is the radius of the unperturbed interface then the (dimensionless) wavenumber n is defined to be

$$n = \frac{2\pi L}{\lambda} \tag{A.21}$$

Let us define a Darcy velocity field in the local vicinity of the perturbed interface. As before  $\overline{u}$  is defined to be the (purely radial in this case) velocity of the unperturbed interface.

$$\mathbf{u} = \overline{u}\widehat{\mathbf{r}} + u_{\theta}\widehat{\boldsymbol{\theta}} + u_{r}\widehat{\mathbf{r}}$$
(A.22)

Let  $u_r \approx \phi \frac{\partial \varepsilon}{\partial t} \Rightarrow u_r = \phi a \sigma e^{in\theta + \sigma t} f(r)$ . Continuity of fluid implies  $\nabla \cdot \mathbf{u} = 0$ .  $\Rightarrow \qquad \qquad \frac{1}{r} \frac{\partial}{\partial r} (r u_r) + \frac{1}{r} \frac{\partial u_{\theta}}{\partial \theta} = 0 \qquad (A.23)$ 

Hence  $\frac{\partial u_{\theta}}{\partial \theta} = -\frac{\partial}{\partial r}(ru_r)$ . Substituting the expression for  $u_r$  above and integrating yields an expression for  $u_{\theta}$ .

$$\frac{\partial u_{\theta}}{\partial \theta} = -\phi a\sigma e^{in\theta + \sigma t} \left\{ rf'(r) + f(r) \right\}$$
(A.24)

 $\Rightarrow$ 

$$u_{\theta} = -\frac{\phi a \sigma e^{in\theta + \sigma t}}{in} \left\{ rf'(r) + f(r) \right\} + \alpha(r, t)$$
(A.25)

Let us consider a horizontal medium, i.e. where the gravitational potential is constant  $\forall r, \theta$ . In this case Darcy's Law becomes  $\mathbf{u} = -\frac{k}{\eta}\nabla p$ . Evaluating the angular and radial components we find

$$u_{\theta} = -\frac{k}{\eta} \frac{1}{r} \frac{\partial p}{\partial \theta} \tag{A.26}$$

$$\overline{u} + u_r = -\frac{k}{\eta} \frac{\partial p}{\partial r} \tag{A.27}$$

Substitution of  $u_{\theta}$  in the first of these equations and integrating yields an expression for the pressure field p.

$$p = -\frac{\eta\phi a\sigma e^{in\theta+\sigma t}}{n^2k} \left\{ r^2 f'(r) + rf(r) \right\} + \alpha(r,t)\theta + \beta(r,t)$$
(A.28)

To prevent p from being multivalued as  $\theta$  is varied from  $0 \to 2\pi$  the integration constant  $\alpha(r,t) = 0$ . Substituting this formula for  $\frac{\partial p}{\partial r}$  into the radial component of Darcy's law yields (also substituting for  $u_r$ )

$$-\frac{\eta}{k}\left\{\overline{u} + \phi a\sigma e^{in\theta + \sigma t}f(r)\right\} = -\frac{\eta\phi a\sigma e^{in\theta + \sigma t}}{n^2k}\left\{r^2 f''(r) + 3rf'(r) + f(r)\right\} + \frac{\partial\beta(r,t)}{\partial r}$$
(A.29)

$$r^{2}f'' + 3rf' + f(1 - n^{2}) = 0$$
(A.30)

To solve let us define f in terms of a new variable v.

$$f = vr \tag{A.31}$$

 $\Rightarrow$ 

$$f' = v + rv' \tag{A.32}$$

$$f'' = 2v' + rv'' (A.33)$$

Substituting these results yields

$$r^{2}(2v' + rv'') + 3r(v + rv') + rv(1 - n^{2}) = 0$$
(A.34)

 $\Rightarrow$ 

$$r^{3}v'' + 5r^{2}v' + (3 - n^{2})rv = 0$$
(A.35)

Let define an additional variable **z** 

$$z = \ln r \tag{A.36}$$

 $\Rightarrow$ 

$$\frac{dz}{dr} = \frac{1}{r} \tag{A.37}$$

$$v' = \frac{dv}{dz}\frac{dz}{dr} = \frac{1}{r}\frac{dv}{dz}$$
(A.38)

$$v'' = \frac{d}{dz} \left(\frac{dv}{dr}\right) \frac{dz}{dr} = \frac{d}{dz} \left(\frac{1}{r}\frac{dv}{dz}\right) \frac{dz}{dr}$$
(A.39)

$$= \frac{1}{r} \left\{ \frac{1}{r} \frac{d^2 v}{dz^2} - \frac{1}{r^2} \frac{dr}{dz} \frac{dv}{dz} \right\}$$
(A.40)

$$= \frac{1}{r^2} \left\{ \frac{d^2 v}{dz^2} - \frac{dv}{dz} \right\}$$
(A.41)

Hence  $r^3v'' + 5r^2v' + (3 - n^2)rv = 0$  transforms to (note elimination of variable r)

$$\frac{d^2v}{dz^2} - \frac{dv}{dz} + 5\frac{dv}{dz} + (3 - n^2)v = 0$$
 (A.42)

 $\Rightarrow$ 

$$\frac{d^2v}{dz^2} + 4\frac{dv}{dz} + (3-n^2)v = 0 \tag{A.43}$$

Substitution of a prototype solution of the form  $v = e^{\xi z}$  yields

$$\xi^2 + 4\xi + 3 - n^2 = 0 \tag{A.44}$$

 $\Rightarrow$ 

$$\xi = -2 \pm \sqrt{1+n^2} \tag{A.45}$$

Hence a general solution for v(z) takes the form

$$v(z) = Ae^{\left(-2+\sqrt{1+n^2}\right)z} + Be^{\left(-2-\sqrt{1+n^2}\right)z}$$
(A.46)

Now  $v = \frac{f}{r}$  and  $z = \ln r$ , hence

$$f(r) = Ar^{-1+\sqrt{1+n^2}} + Br^{-1-\sqrt{1+n^2}}$$
(A.47)

Integration of the radial component of Darcy's Law yields the simplest expression of the pressure field

$$p = -\frac{\eta}{k} \left\{ \overline{u}r + \phi a\sigma e^{in\theta + \sigma t} \int^{r} f(r')dr' \right\}$$
(A.48)

 $\Rightarrow$ 

$$p = -\frac{\eta}{k} \left\{ \overline{u}r + \frac{\phi a\sigma e^{in\theta + \sigma t}}{\sqrt{1+n^2}} \left( Ar^{\sqrt{1+n^2}} - Br^{-\sqrt{1+n^2}} \right) \right\} + p^*$$
(A.49)

where  $p^*$  is the constant of integration. In order for p perturbations to decay far away from the interface in both regions; in region 1  $(r < L + \varepsilon)$ : B = 0 and in region 2  $(r > L + \varepsilon)$ : A = 0. Absorbing the remaining constant into a we arrive at a complete solution for the pressure field

$$p = \begin{cases} -\frac{\eta_1}{k_1} \left\{ \overline{u}r + \frac{\phi a\sigma e^{in\theta + \sigma t}}{\sqrt{1+n^2}} r^{\sqrt{1+n^2}} \right\} + p_1^* & r < L + \varepsilon \\ -\frac{\eta_2}{k_2} \left\{ \overline{u}r - \frac{\phi a\sigma e^{in\theta + \sigma t}}{\sqrt{1+n^2}} r^{-\sqrt{1+n^2}} \right\} + p_2^* & r > L + \varepsilon \end{cases}$$
(A.50)

These two expressions must be equivalent at the interface  $r = L + \varepsilon$ . Making this equivalence we find

$$0 = -\frac{\eta_1}{k_1} \left\{ \overline{u}(L+\varepsilon) + \frac{\phi a \sigma e^{in\theta + \sigma t}}{\sqrt{1+n^2}} (L+\varepsilon)^{\sqrt{1+n^2}} \right\} + p_1^*$$
(A.51)

$$-p_2^* + \frac{\eta_2}{k_2} \left\{ \overline{u}(L+\varepsilon) - \frac{\phi a \sigma e^{inb+\sigma t}}{\sqrt{1+n^2}} (L+\varepsilon)^{-\sqrt{1+n^2}} \right\}$$
(A.52)

If perturbations  $\varepsilon$  are initially small<sup>2</sup>, i.e.  $\varepsilon \ll L$  one can approximate the  $(L + \varepsilon)^{\pm \sqrt{1+n^2}}$  terms binomially

$$(L+\varepsilon)^{\sqrt{1+n^2}} = L^{\sqrt{1+n^2}} \left(1 + \frac{\varepsilon}{L}\right)^{\sqrt{1+n^2}} \approx L^{\sqrt{1+n^2}} \left\{1 + \frac{\varepsilon}{L}\sqrt{1+n^2}\right\} \approx L^{\sqrt{1+n^2}}$$
(A.53)

$$(L+\varepsilon)^{-\sqrt{1+n^2}} = L^{-\sqrt{1+n^2}} \left(1 + \frac{\varepsilon}{L}\right)^{-\sqrt{1+n^2}} \approx L^{-\sqrt{1+n^2}} \left\{1 - \frac{\varepsilon}{L}\sqrt{1+n^2}\right\} \approx L^{-\sqrt{1+n^2}}$$
(A.54)

Applying this and differentiating the above expression wrt to  $\varepsilon$  yields (at  $\theta, t = 0$ )

$$\sigma = \overline{u} \left(\frac{\eta_2}{k_2} - \frac{\eta_1}{k_1}\right) \left(\frac{\eta_1}{k_1} L^{\sqrt{1+n^2}} + \frac{\eta_2}{k_2} L^{-\sqrt{1+n^2}}\right)^{-1} \frac{\sqrt{1+n^2}}{\phi a}$$
(A.55)

Since  $\left(\frac{\eta_1}{k_1}L^{\sqrt{1+n^2}} + \frac{\eta_2}{k_2}L^{-\sqrt{1+n^2}}\right)^{-1}\frac{\sqrt{1+n^2}}{\phi a}$  must be > 0 for a real physical system, the sign of  $\sigma$  is fixed by the sign of  $\frac{\eta_2}{k_2} - \frac{\eta_1}{k_1}$ .

Hence for instability

$$\frac{\eta_2}{k_2} > \frac{\eta_1}{k_1}$$
 (A.56)

which agrees with the more general condition derived for linear geometry when the effect of gravity is also included.

Note these results agree with those presented by Phillips in [8] (pp 164) if one changes the sign of  $\overline{u}$ . In his analysis the unperturbed interface is defined to move in the opposite direction of the gravitational field.

<sup>&</sup>lt;sup>2</sup>The jist of the entire analysis is to assert a small perturbation and calculate conditions for that perturbation to grow (by the sign of  $\sigma$ ). The aim is not to solve for the exact shape of the interface.
## Appendix B

## Temperature variation of Sodium Chloride and Sodium Sulphate saturation solubility

Solubility is defined as the mass of salt dissolved divided by the total mass of solution.



Figure B.1: Saturation solubility of sodium chloride as a function of temperature.



Figure B.2: Saturation solubility of sodium sulphate as a function of temperature.