Self-Potential during multiphase flow in complex porous media

A thesis submitted for the degree of

Doctor of Philosophy of Imperial College London

Jiazuo Zhang

January 2017

Department of Earth Science and Engineering

Imperial College London

SW7 2AZ London, United Kingdom
DECLARATION OF ORIGINALITY

I certify that all contents in this thesis are my own work and that all references have been cited to the best of my knowledge in line with the guidance of Imperial College London, whether published or unpublished, except with full and proper acknowledgement.
COPYRIGHT DECLARATION

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.
Abstract

The rock pore space in many subsurface settings is saturated with water and one or more immiscible fluid phases; examples include non-aqueous-phase liquids (NAPLs) in contaminated aquifers, supercritical CO$_2$ during sequestration in deep saline aquifers, the vadose zone, and hydrocarbon reservoirs. Self-potential (SP) methods have been proposed to monitor multiphase flow in such settings. However, to properly interpret and model these data requires an understanding of the saturation dependence of the streaming potential.

This study presents a methodology to determine the saturation dependence of the streaming potential coupling coefficient and streaming current charge density in unsteady-state drainage and imbibition experiments and applies the method to published experimental data. Unsteady-state experiments do not yield representative values of coupling coefficient and streaming current density (or other transport properties such as relative permeability and electrical conductivity) at partial saturation because water saturation within the sample is not uniform. An interpretation method is required to determine the saturation dependence of coupling coefficient and streaming current density within a representative elementary volume with uniform saturation. The method makes no assumptions about the pore-space geometry.

We also applied pore network models that can capture the distribution of fluids and electrical charge in real complex porous media to investigate and quantify streaming potential signals during multiphase flow at the pore level. The network modelling results were tested against the interpreted data and experimental data of Estaillades carbonate and St. Bees sandstone, which provided reliable pore-scale explanations of the experimental observations. The results presented here can be used to help interpret SP measurements obtained in partially-saturated subsurface settings.
List of conferences and publications

Poster presentation on ‘Relationship between streaming potential and water saturation during drainage and imbibition in sandstones’ on American Geophysics Union conference, San Francisco, 2013.

Poster presentation on ‘Streaming potential dependence on water saturation during drainage and imbibition’ on American Geophysics Union conference, San Francisco, 2014.

# Contents

DECLARATION OF ORIGINALITY ............................................................................................................. 2
COPYRIGHT DECLARATION ..................................................................................................................... 3
Abstract.................................................................................................................................................. 4
List of Figures ....................................................................................................................................... 8
List of Tables ......................................................................................................................................... 14
ACKNOWLEDGEMENTS .......................................................................................................................... 19

Chapter 1 Introduction ............................................................................................................................. 20

Chapter 2: Spontaneous Potentials ........................................................................................................ 23
  2.1 Definition and origin of Spontaneous Potentials ........................................................................... 23
  2.2 Applications of SP measurements ................................................................................................. 27
  2.3 Mathematical description of flow ................................................................................................... 29
    2.3.1 Transport of flow ....................................................................................................................... 30
    2.3.2 Transport of electrical charge ................................................................................................... 31
  2.4 Electrical coupling terms ................................................................................................................. 34
    2.4.1 Streaming coupling coefficient ................................................................................................. 34
    2.4.2 Electrochemical coupling coefficient ......................................................................................... 42
    2.4.3 Thermoelectric coupling coefficient .......................................................................................... 46

Chapter 3 Streaming potential during drainage and imbibition .......................................................... 47
  3.1 Introduction .................................................................................................................................... 47
  3.2 Methodology .................................................................................................................................... 48
    3.2.1 Parameter optimization during drainage .................................................................................... 51
    3.2.2 Parameter optimization during imbibition ............................................................................... 57
  3.3 Results ........................................................................................................................................... 57
    3.3.1 Drainage optimization ............................................................................................................... 57
    3.3.2 Imbibition optimization ............................................................................................................. 63
    3.3.3 Interpretation of optimization results ......................................................................................... 67
  3.4 Discussion ....................................................................................................................................... 73
    3.4.1 Saturation-dependence of the streaming current charge density .............................................. 73
    3.4.2 Comparison of our model for $Q_r$ against previous studies .................................................... 75
    3.4.3 Application of the relative streaming current charge model to predict the relative streaming potential coupling coefficient .................................................................................................................. 77
    3.4.4 Implications for subsurface flow monitoring using the SP and SE methods ......................... 79
List of Figures

Figure 2.1: (a) Schematic of electrical double layer in water at contact with negatively-charged solid. (b) Detailed illustration of the corresponding interfaces and electric potentials. These are modified from Hunter [1981b]. .......................................................... 24

Figure 2.2: Schematic showing the origin of the (a) EK potential, (b) EC potential and TE potential. The electrical double layer is shown in a highly simplified form [Jackson et al., 2012b]. ......................................................................................... 27

Figure 2.3: Numerical results from a heterogeneous-reservoir model with a single high-permeability layer of thickness of 15m [Jackson et al., 2012b]. (a) through (c) present 2-D cross sections of water saturation at different times. (d) through (f) present the corresponding potentials recorded along the well. .................................................................................. 28

Figure 2.4: (a, b) Experimental studies of the saturation dependence of the relative streaming potential coupling coefficient during drainage: (a) [1] data from Guichet et al. [2003]; [2-1], [2-2] data Revil and Cerepi [2004] for samples E39 and E3, respectively; [3-1] data from Revil et al. [2007] with extrapolated $C(S_w=1)$, [3-2] data from Revil et al. [2007] with $C_r$ calculated using $C(S_w=1)$ reported by Revil and Cerepi [2004]; [4-1], [4-2] data from Vinogradov and Jackson [2011] for samples Stainton and St. Bees respectively. (b) shows the relative coupling coefficient obtained by Allègre et al. [2010] between their electrodes 6 and 7 in experiment #1. .......................................................... 37

Figure 2.5: (a) Flow velocity (solid line) and excess counter-charge within a capillary, invoking the thin (short dashes) and thick (long dashes) double layer assumption and a constant excess surface charge density. (b) Calculation of the steaming current [Jackson, 2010]. ......................................................................................... 42

Figure 2.6: Measured voltage against water saturation obtained by McCall [1970] by partially draining sandstone core plugs by paraffin injection. The symbol labels refer to the sample descriptions reported by Ortiz et al. [1973]. ......................................................................................... 44

Figure 2.7: The relative EC coupling coefficient $C_{rEC}$ is chosen to match the experimental data of McCall [1970]. The symbol labels refer to the sample descriptions reported by Ortiz et al. [1973] [Jackson, 2010]. ......................................................................................... 45

Figure 3.1: Schematic of the 1-D numerical models used to interpret hydraulic and electrical properties measured experimentally: (a) Hydraulic model during drainage. Dashed arrows represent flow within the hydraulic model. Black bold lines represent no flow boundaries. (b)
Electrical model during both drainage and imbibition to interpret the measured apparent electrical conductivity and coupling coefficient. (c) Hydraulic model during imbibition, in which the inlet flowline was modified by connecting to the base of the core sample.

Figure 3.2: Flowchart showing the three optimization steps during drainage/imbibition: the hydraulic optimization, the electrical conductivity optimization and the electrokinetic optimization.

Figure 3.3: Objective function values in hydraulic ($f_1$), electrical conductivity ($f_2$) and electrokinetic ($f_3$) optimizations: (a, c, e) objective function values from St. Bees (solid points) and Stainton samples (hollow points) during drainage; (b, d, f) objective function values in St. Bees (solid points) and Stainton samples (hollow points) during imbibition. Case number corresponds to the 8 sets of optimized parameters obtained in the hydraulic optimization during drainage. We selected two initial conditions for imbibition from the ensemble obtained at the end of the drainage optimization (one showing monotonic behavior of $C_r$ denoted M, and the other showing non-monotonic behavior denoted NM). The error bars shown in (e, f) represent the spread in $f_3$ that yield a similar quality of match after the electrokinetic optimization.

Figure 3.4: Typical results from the hydraulic optimization during drainage showing simulated (lines) and observed (points) data ($f_1$=4.01 and 9.58 for St. Bees and Stainton respectively): (a, b): pressure difference across the Stainton and St. Bees samples respectively; (c, d) cumulative water production from the Stainton and St. Bees samples respectively; (e, f) water fractional flow at the outlet of the Stainton and St. Bees samples. Error bars denote the typical experimental error.

Figure 3.5: Typical results from the electrical conductivity optimization during drainage for Stainton ($f_2$=0.89*10^{-3})(a, c) and St. Bees ($f_2$=1.3*10^{-3}) (b, d) during drainage: (a, b) selected optimization results using Archie’s law ($a_2 = 0$); (c, d) selected optimization results using modified Archie’s law with non-zero $a_2$. The error bar denotes the typical experimental error.

Figure 3.6: Typical results from the electrokinetic optimization during drainage for (a) Stainton ($f_3$=0.045) and (b) St. Bees ($f_3$=0.068). The error bar denotes the typical experimental error.

Figure 3.7: Typical results from the hydraulic optimization during imbibition showing simulated (lines) and observed (points) data ($f_1$=3.48 and 5.01 for St. Bees and Stainton respectively): (a, b): pressure difference across the Stainton and St. Bees samples respectively; (c, d) cumulative water production from the Stainton and St. Bees samples respectively; (e, f)
water fractional flow at the outlet of the Stainton and St. Bees samples. Error bars denote the
typical experimental error ................................................................. 65

Figure 3.8: Typical results from the electrical conductivity optimization during imbibition for
Stainton \( (f_2=0.31 \times 10^{-3}) \) (a, c) and St. Bees \( (f_2=0.63 \times 10^{-3}) \) (b, d) during drainage: (a, b)
selected optimization results using Archie’s law \( (a_2 = 0) \); (c, d) selected optimization results
using modified Archie’s law with non-zero \( a_2 \). The error bar denotes the typical experimental
error ........................................................................................................... 66

Figure 3.9: Typical results from the electrokinetic optimization during imbibition for (a)
Stainton \( (f_3=0.027) \) and (b) St. Bees \( (f_3=0.085) \). The error bar denotes the typical
experimental error .................................................................................. 67

Figure 3.10: Summary results from the hydraulic optimization showing simulated (solid and
dot-dash lines) data and variations (dash lines): (a, c): relative permeability and capillary
pressure of the Stainton sample during drainage and imbibition respectively, and (e)
represents the comparison of relative permeability during drainage and imbibition; (b, d)
relative permeability and capillary pressure of the St. Bees sample during drainage and
imbibition respectively, and (f) represent the comparison of relative permeability during
drainage and imbibition. ........................................................................... 69

Figure 3.11: Summary results from the electrical conductivity optimization showing
simulated (solid lines) data and variations (dashed lines). (a, b): relative electrical
conductivity of the Stainton sample during drainage and imbibition respectively; (c, d)
relative electrical conductivity of the St. Bees sample during drainage and imbibition
respectively. .................................................................................................. 70

Figure 3.12: Summary results from the electrokinetic optimization showing simulated (solid
lines) coupling coefficient and variations (dash lines): (a, b): relative coupling coefficient for
the Stainton sample during drainage and imbibition respectively; (c, d) relative coupling
coefficient for the St. Bees sample during drainage and imbibition respectively. .............. 71

Figure 3.13: Relative streaming charge density as a function of normalized water saturation
for Stainton (solid shaded area) and St. Bees (textured shaded area) during drainage (black)
and imbibition (grey); the curves are given by our power law model for the relative streaming
charge density (equation 3.10) to fit the mean value of the optimized variations in each core
and displacement \( (R^2=0.99999 \text{ in all cases}) \). Fitting parameters \( p, q, r \) are summarized in
Table 3.4. ........................................................................................................ 74

Figure 3.14: Predicted variation of streaming charge density with water saturation compared
against other published models: solid and long dash lines are predicted using equation (3.10)
and the values of \( p, q \) and \( r \) reported in Table 5. The dotted line represents the model of Revil et al. [2007]. Models of Jougnot et al. [2012] for Stainton and St.Bees are also presented using (a) WR and (b) RP approaches.

Figure 3.15: Predicted behavior of the relative streaming potential coupling coefficient using our model of the relative streaming charge (equation 3.11) in conjunction with a simple Corey model of relative permeability (\( \alpha \) and \( \beta \) over range 2-5) and a simple Archie model for electrical conductivity (\( n \) over range 1.5-3.5). Dash lines represent the ranges of the predicted coupling coefficients; solid lines are three selected examples (a) Example_1 represents \( \alpha=4 \) and \( n=2.875 \), Example_2 represents \( \alpha=4.4 \) and \( n=3 \) and Example_3 represents \( \alpha=5 \) and \( n=3 \) during drainage, and (b) Example_1 represents \( \alpha=3 \) and \( n=2.75 \), Example_2 represents \( \alpha=3 \) and \( n=2.5 \) and Example_3 represents \( \alpha=3.3 \) and \( n=2.25 \) during imbibition.

Figure 4.1: Representations of the pore space of sandstone samples [Øren et al., 1998]: (a) Three-dimensional image of a sandstone; (b) a topologically equivalent network representation.

Figure 4.2: Comparison between experimental and predicted relative permeability for reservoir sandstone. (a) The Larger pores become preferentially oil wet. (b) The smaller pores become preferentially oil wet. (c) The oil wet pores are spatially correlated [Valvatne and Blunt, 2004].

Figure 4.3: Simulated bulk electrical resistivity and experimental data from Binley et al. [2002] as a function of water saturation [Dalla et al., 2004]. The solid line shows Archie’s equation with \( n=1.13 \).

Figure 4.4: Streaming potential between two pores: pore body \( i \), throat and pore body \( j \).

Figure 4.5: (a) Cross-sectional view of water in a water-wet pore; (b) cross-sectional view of a single corner in a triangular pore. \( L_{wr} \) represent the total water-rock interface in a single corner; \( \beta \) is the half contact angle; \( a_i \) is the contacting interface on one side of the corner; \( L_{ow} \) is the oil-water interface; \( r_{ow} \) is the corresponding inscribed radius of the oil-water interface.

Figure 4.6: Possible fluid configurations modified from Valvatne and Blunt [2004] and Jackson et al. [2016] (a) Initially strongly water-wet pore only filled with water; (b) After primary drainage, the part of pore in contact with oil may be altered to oil-wet, which is highlighted by bold lines \( b \); (c) During imbibition, the pore can be completely filled with water again, but part of it can retain altered wettability; (d) Oil may become sandwiched between water in the corner and the centre. Figure d shows postulated wettability of water-rock and oil-water interfaces in polygons saturated with water and oil. Oil may have a
negatively charged oil-brine interface or a positively charged interface as shown respectively.

Figure 4.7: A) Entire scan of St. Bees sandstone with dimension of 2000\(^3\). B) Sub-volume image with dimension of 1000\(^3\). C) The sub-volume image after applying non-local mean filter. D) The red area represents pores and blue area represents grains. E) Segmented image.

Figure 4.8: Predicted relative permeability for water-wet Berea sandstones in oil-water displacements during drainage and imbibition (lines) compared to experimental data by Oak [1990] (circles).

Figure 4.9 (a, b): Capillary pressure and resistivity index as functions of water saturation during drainage and imbibition in water-wet Berea network model.

Figure 4.10: Relative coupling coefficient during drainage and imbibition in the water-wet Berea pore network, respectively.

Figure 4.11: (a) Predicted relative streaming current charge density during drainage and imbibition in the water-wet Berea network; (b) A comparison of predicted relative streaming charge density from the inversion and pore network modelling approaches.

Figure 4.12: (a) Zeta potential as a function of Amott water wetting index for each of the four oils tested (B-E) using the Estaillades samples saturated with formation brine and residual oil saturation. Empty circles represent aging in the absence of water (‘oil-only’), empty squares represent aged samples in the presence of water, filled square represents non-aged sample and the diamond symbol represents the water-only sample; (b) Zeta potential as a function of water wetting index using the Estaillades pore network model. Empty squares represent model prediction after drainage to different initial water saturations; empty circles represent predictions of dry models (no initial water present).

Figure 4.13: Relative permeability, capillary pressure, resistivity index and relative coupling coefficient as functions of water saturation during drainage and oil wet imbibition in the Estaillades pore network with the more positive zeta potential at oil-wet water-rock and oil-water interfaces (22 mV). The initial water saturation (\(S_{wir}\)) is 0.35 for imbibition and no surface conductivity is included. The corresponding wettability index is 0.090668 as shown in Table 4.4.

Figure 4.14: Relative permeability, capillary pressure, resistivity index and relative coupling coefficient as functions of water saturation during drainage and oil wet imbibition in the Estaillades pore network with the more negative zeta potential at oil-wet water-rock and oil-water interfaces (-2.4 mV). The initial water saturation (\(S_{wir}\)) is 0.42 for imbibition and no
surface conductivity is included. The corresponding wettability index is 0.059769 as shown in Table 4.4.

Figure 4.15: (a, b) comparisons of relative permeability interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition, respectively; (c, d) comparison of resistivity index interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition respectively. Measured apparent resistivity index across the core samples are represented by stars for reference.

Figure 4.16: (a) comparisons of relative coupling coefficient interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition, respectively; (b) comparison of relative streaming charge density model that interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition respectively.
List of Tables

Table 2.1 Summary of published relationships for the saturation dependence of the relative coupling coefficient. ........................................................................................................................................39
Table 3.1 Optimized values of fitting parameters during drainage shown in Figure 3.4-3.6. 59
Table 3.2 Optimized values of fitting parameters shown in Figure 3.7-3.9 during imbibition. ........................................................................................................................................64
Table 3.4 Values of fitting parameters \((p, q, r)\) of relative streaming charge density functions with water saturation for Stainton and St. Bees during drainage and imbibition. ...............75
Table 4.1: Properties of the Berea pore network .................................................................................................................................109
Table 4.2: Fluid properties applied in pore network modelling ...........................................................................................................109
Table 4.3: Properties of the Estaillades pore network and the Estaillades core sample that was used by Jackson et al. [2016]......................................................................................................................................117
Table 4.4. Summary of pore network modelling values to match the experimental initial water saturation, wettability index and measured zeta potential in carbonates ..............121
Table 4.5: Properties of St. Bees predicted by pore network modelling (PNM) and measured in experiments [Vinogradov and Jackson, 2011]. .....................................................................................................126
Nomenclature

\( q \)  Darcy velocity  \( \text{m} \cdot \text{s}^{-1} \)

\( P \)  Pressure potential  \( \text{Pa} \)

\( \mu \)  Viscosity  \( \text{Pa} \cdot \text{s} \)

\( g \)  Gravitational acceleration vector  \( \text{m} \cdot \text{s}^{-2} \)

\( \rho \)  Fluid density  \( \text{kg} \cdot \text{m}^{-3} \)

\( p \)  Fluid phase \( p \)  —

\( K \)  Absolute permeability of porous media  \( \text{m}^2 \)

\( K_{rwe} \)  Water endpoint relative permeability  \( \text{m}^2 \)

\( K_{roe} \)  Oil endpoint relative permeability  \( \text{m}^2 \)

\( k_{rw} \)  Relative permeability of water  —

\( k_{ro} \)  Relative permeability of oil  —

\( S_{wr} \)  Irreducible water saturation  —

\( S_{nwr} \)  Residual non wetting phase saturation  —

\( S_w \)  Water saturation  —

\( S_{wn} \)  Normalized water saturation  —

\( I \)  Electrical current  \( \text{A} \cdot \text{m}^{-2} \)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_s$</td>
<td>Streaming current</td>
<td>A·m$^{-2}$</td>
</tr>
<tr>
<td>$h$</td>
<td>Heat current</td>
<td>J·m$^{-2}$</td>
</tr>
<tr>
<td>$v$</td>
<td>Mass current</td>
<td>g·m$^{-2}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Electrical conductivity</td>
<td>S·m$^{-1}$</td>
</tr>
<tr>
<td>$\sigma_r$</td>
<td>Relative electrical conductivity</td>
<td>—</td>
</tr>
<tr>
<td>$\sigma_s$</td>
<td>Surface electrical conductivity</td>
<td>S·m$^{-1}$</td>
</tr>
<tr>
<td>$L_{EK}$</td>
<td>Electrokinetic coupling term</td>
<td>—</td>
</tr>
<tr>
<td>$L_{TE}$</td>
<td>Thermoelectric coupling term</td>
<td>—</td>
</tr>
<tr>
<td>$L_{EC}$</td>
<td>Electrochemical coupling term</td>
<td>—</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
<td>m$^2$·s$^{-1}$</td>
</tr>
<tr>
<td>$U$</td>
<td>Voltage potential</td>
<td>V</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>°C/°F</td>
</tr>
<tr>
<td>$C_f$</td>
<td>Fluid salinity</td>
<td>g·L$^{-1}$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity</td>
<td>—</td>
</tr>
<tr>
<td>$F$</td>
<td>Formation factor</td>
<td>—</td>
</tr>
<tr>
<td>$C_{EK}$</td>
<td>Electrokinetic coupling coefficient</td>
<td>—</td>
</tr>
<tr>
<td>$C_{TE}$</td>
<td>Thermoelectric coupling coefficient</td>
<td>—</td>
</tr>
<tr>
<td>$C_{EC}$</td>
<td>Electrochemical coupling coefficient</td>
<td>—</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>$C_r$</td>
<td>Relative coupling coefficient</td>
<td>—</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>Streaming charge density</td>
<td>C·m⁻³</td>
</tr>
<tr>
<td>$Q_v$</td>
<td>Excess charge density per unit pore volume</td>
<td>C·m⁻³</td>
</tr>
<tr>
<td>$Q_{rs}$</td>
<td>Relative streaming charge density</td>
<td>—</td>
</tr>
<tr>
<td>$V_{EC}$</td>
<td>Electrochemical potential</td>
<td>V</td>
</tr>
<tr>
<td>$V_E$</td>
<td>Exclusion potential</td>
<td>V</td>
</tr>
<tr>
<td>$V_D$</td>
<td>Diffusion potential</td>
<td>V</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Capillary pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$P_{ce}$</td>
<td>Capillary entry pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Total liquid volume produced</td>
<td>L</td>
</tr>
<tr>
<td>$F_w$</td>
<td>Water fractional flow at the outlet</td>
<td>—</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Experimental uncertainty</td>
<td>—</td>
</tr>
<tr>
<td>$f$</td>
<td>Objective function</td>
<td>—</td>
</tr>
<tr>
<td>$g_p$</td>
<td>Fluid conductance</td>
<td>—</td>
</tr>
<tr>
<td>$L_{ij}$</td>
<td>Length between two pores</td>
<td>m</td>
</tr>
<tr>
<td>$A$</td>
<td>Cross-sectional area</td>
<td>m²</td>
</tr>
<tr>
<td>$G$</td>
<td>Shape factor</td>
<td>—</td>
</tr>
<tr>
<td>$L$</td>
<td>Length of model</td>
<td>m</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>$R$</td>
<td>Electrical resistivity</td>
<td>$\Omega \cdot m$</td>
</tr>
<tr>
<td>$RI$</td>
<td>Resistivity index</td>
<td>$-$</td>
</tr>
<tr>
<td>$M$</td>
<td>Streaming coupling term</td>
<td>$S$</td>
</tr>
<tr>
<td>$S$</td>
<td>Electrical conductance</td>
<td>$S$</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Electrical permittivity</td>
<td>$F \cdot m^{-1}$</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Zeta potential</td>
<td>$mV$</td>
</tr>
<tr>
<td>$P_r$</td>
<td>Perimeter of interfaces</td>
<td>$cm$</td>
</tr>
<tr>
<td>$r$</td>
<td>Pore radius</td>
<td>$cm$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Half corner angle</td>
<td>$^\circ$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
<td>$^\circ$</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Water-rock contacting length in one side</td>
<td>$cm$</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

First of all, I would like to thank my dearest parents who provided both financial and spiritual support during my study. While doing a PhD programme was challenging, my family has also experienced some significant difficulties throughout the years. However, they have provided continuous support and numerous loves under all circumstances. Completing a PhD programme would not be possible without their generous help, and I realized what the real meaning of the family, responsibility and love is.

Secondly, I would express my gratitude to my supervisor, Professor Matthew Jackson, who gave me the valuable opportunity to pursue a PhD from one of the world’s top universities. He is one of the most brilliant people I have met in my life and extremely responsible and considerate for every PhD student he has. Without his support and guidance I would not be able to achieve the result.

I would also like to thank Dr Jan Vinogradov who has been a Post Doc at Imperial. Without his support and kindly patient, I was not able to survive in the first two years of my PhD. Thanks to everyone in our group who have assisted me in various ways throughout the four years of studying.

Last but not least, thanks to all my friends whose friendship I truly value, for not only supporting and encouraging me throughout my study, but also for making my five years in London a memorable experience.
Chapter 1 Introduction

Spontaneous potentials (SP) arise from a separation of electrical charge in response to gradients in pressure, chemical composition or temperature. When a fluid is subjected to a pressure gradient that causes it to flow relative to the mineral surface, some of the excess ions will be transported with the flow. The electrical potential required to maintain electrical neutrality is known as the electrokinetic (EK) or streaming potential. Concentration and temperature gradients result in charge separation because of the differing mobility of ions. Similarly, charge separation is balanced by a conduction current at steady state, which gives rise to the electrochemical (EC) or thermoelectric potential (TE). The total SP anomalies are composed of the electrokinetic, electrochemical and thermoelectric potentials.

The pore space in many subsurface settings is saturated with water and another immiscible fluid phase; examples include non-aqueous-phase liquids (NAPLs) in contaminated aquifers, the vadose zone, saline aquifers during CO₂ sequestration, and hydrocarbon reservoirs. Use of the self-potential (SP) and seismo-electric (SE) method has been proposed to monitor flow in such settings [e.g. Antraygues and Aubert, 1993; Doussan et al., 2002; Darnet and Marquis, 2004; Moore et al., 2004; Jackson et al., 2005; Linde et al., 2007; Kulessa et al., 2012; J Saunders et al., 2012,b; Talebian et al., 2013; Warden et al., 2013; Revil et al., 2014; Jougnot et al., 2015]. SP measurements offer several advantageous for monitoring of subsurface flow and transport processes compared to other geophysical methods, because they are arise directly from the flow or transport phenomena of interest. Recent research has demonstrated that SP signals are obviously detectable ahead of the source, which demonstrated a great capability to characterize and monitor multiphase flow in the subsurface settings [e.g. Gulamali et al., 2011; Jackson et al., 2012b]. Moreover, Jackson and
Vinogradov [2012a] suggested another potential application that SP anomalies can be used to characterize the wetting state of porous media.

The results to date are promising, but the SP signals generated in a porous media saturated with more than one fluid phase are still poorly understood. Limited experimental data have been collected [Ortiz et al., 1973; Jouniaux and Pozzi, 1995; Guichet et al., 2003; Moore et al., 2004; Linde et al., 2007; Revil et al., 2007; Allègre et al., 2010; Vinogradov and Jackson, 2011]. Most of experiments focused on streaming potential and presented contrasting and inconsistent behaviours in different systems that cannot be used to describe the general streaming behaviour during multiphase flow. Only one study conducted by Ortiz et al. [1973] describes the behaviour of EC potential during multiphase flow, while there is no published paper dealing with multiphase TE potential. Moreover, present numerical models are not able to explain the pore-level distribution of fluid and electrical charge in complex geologic porous media, because most numerical models were established at continuum scale that paid no attention to pores or pore structure [Wurmstich and Morgan, 1994; Darnet et al., 2004; Linde et al., 2007; Revil et al., 2007]. Only Jackson [2010] attempted to describe multiphase streaming potentials at the pore level, but the capillary tube model built by him is a topologic simple model that cannot capture the pore-level distribution of fluids and charge in real geological porous media.

The aim of this study is to focus on the streaming potential behaviour and to investigate and quantify saturation dependence of streaming potential in complex porous media by two approaches: (i) interpreting experimental measurements of the streaming potential during drainage and imbibition in sandstone plugs, to provide an understanding of the saturation dependence of streaming potential at the continuum level; (ii) using network models that can capture the distribution of fluids and electrical charge in real complex porous media to investigate and quantify streaming potential signals during multiphase flow at the pore level.
The network modelling results will be tested against the interpreted data and experimental data of Estaillades carbonate and St. Bees sandstone, to provide reasonable support and explanation to the experimental observations at pore-scale.
Chapter 2: Spontaneous Potentials

This chapter begins with an introduction of the definition and origins of spontaneous potentials, followed by a brief review of various applications of SP measurements. Since the aim of this project is to investigate and quantify streaming potential signals during multiphase flow at the continuum and pore scales, the second part of this chapter will discuss previous experimental and numerical studies of the streaming potential, and highlight the importance of further study.

2.1 Definition and origin of Spontaneous Potentials

SP anomalies are generated to maintain overall electroneutrality when gradients in pressure, composition or temperature result in a separation of electrical charge [Corwin and Hoover, 1979; Revil, 1999]. The voltages generated by such flows are, respectively, referred to as electrokinetic (streaming) (EK), thermoelectric (TE), and electrochemical (EC) potentials.

In porous media (such as fully or partially saturated soil and rocks), charge separation occurs at the solid-fluid interface due to a host of chemical interactions between an electrolyte such as brine and the mineral surface. The solid surfaces become electrically charged and create an electrostatic field that will affect the ions in the bulk of water as shown in Figure 2.1 (a). The electrical ions that adsorbed to the solid surface because of chemical interactions composed the Helmholtz layer or the Stern layer, while the second layer is composed of ions loosely associated with each other and the surface via the Coulomb force, electrically screening the Helmholtz layer. The second layer is termed as the diffusive layer [Hunter, 1981b]. This arrangement of charge including the Stern layer and the diffuse layer at the solid/liquid interface is known as the electrical double layer [Hunter, 1988]. The electric potential on the external boundary of the Helmholtz layer versus the bulk electrolyte is known as Helmholtz...
potential as shown. More importantly, the diffusive layer or the part of diffusive layer can move under the influence of tangential stress. We termed the electric potential at the diffuse layer as electrokinetic or zeta potential (denoted as $\zeta$ in Figure 2.1b).

Figure 2.1: (a) Schematic of electrical double layer in water at contact with negatively-charged solid. (b) Detailed illustration of the corresponding interfaces and electric potentials. These are modified from Hunter [1981b].

Specifically, when a fluid is subjected to a pressure gradient that causes it to flow relative to the mineral surfaces, some of the excess counter-ions in the fluid adjacent to mineral surfaces will be transported with the flow (denoted in Figure 2.2a by the arrows), which gives rise to a
streaming current. To balance this streaming current, conduction current is established to maintain overall electroneutrality. The electrical potential required to maintain this conduction current is known as the electrokinetic (EK) or streaming potential.

It has been long investigated that the concentrations of ions at the water/air interface are markedly different from those in fluids [e.g. Kamieński, 1959; Dynarowicz and Paluch, 1992; Davies, 2012; Manciu and Ruckenstein, 2012]. The electrical double layer at the air/water interfaces is generated spontaneously due to reorientation of the dipoles of water molecules and adsorption of hydroxyl ions. This air-water interface electric double layer is not considered in the study of streaming potential because there is no sufficient amount in aqueous phase to accumulate essential density of electrical charges [Birdi, 2015]. However, there will be a much denser packed adsorption monolayer of ionized surfactants if air bubbles are formed within fluids. In this case, the zeta potential of air-water interface plays a significant role [Birdi, 2015]. In this study, we only consider fluid-fluid displacement, so air-water electrical double layer is not included.

Variations in the chemical composition of the electrolyte result in concentration gradients where ions with contrasting mobility may migrate down at differing rates (denoted in Figure 2.2b by the length of the arrows). For example, the mobility of sodium ions at 25°C is around 70% that of chloride ions [Braun and Weingärtner, 1985]. This effect results in a charge separation, which is countered by the EC potential to maintain electroneutrality [Revil, 1999]. If the mineral surface of the porous media is not charged, the EC potential comes solely from the liquid junction or diffusion potential caused by the contrasting mobility [Ortiz et al., 1973]. However, the presence of the electric double layer leads to a membrane or exclusion potential, which means some of the co-ions in the electrolyte are excluded from the pore space while a net excess of counter-charge migrates down the concentration gradient. Therefore, in the porous media EC potential is attributable to the sum of the diffusion and
membrane potentials; the relative contribution depends on the thickness of the electrical double layer relative to the pore radius and the mobility contrast between ionic species.

The TE potential has a similar origin to the EC potential (Figure 2.2b). Variations in flow temperature result in a temperature gradients down which different ionic species may also migrate at different rates. The differing mobility of the ions and exclusion of co-ions from the pore space again results in charge separation, which is countered by the TE potential to maintain electroneutrality [Revil, 1999].

The total SP is the sum of the streaming, electrochemical and thermoelectric potentials.
Figure 2.2: Schematic showing the origin of the (a) EK potential, (b) EC potential and TE potential. The electrical double layer is shown in a highly simplified form [Jackson et al., 2012b].

2.2 Applications of SP measurements

Measurements of SP have long been applied in various subsurface settings including geothermal systems, active volcanoes, contaminant aquifers, carbon dioxide sequestration and hydrocarbon recovery [Ishido and Mizutani, 1981; Antraygues and Aubert, 1993; Guichet et al., 2003; Darnet et al., 2004; Moore et al., 2004; Maineult et al., 2006; Maineult et al., 2008; Jackson et al., 2012b; Jackson and Vinogradov, 2012a].

In geothermal systems, the measurements of SP signals were suggested as early as 1979 when Corwin and Hoover [1979] observed that SP signals caused by hydrothermal activities ranged from 50 mV to more than 2V. Then more researchers reported significant SP signals could be observed ahead of eruptive episodes, which made it possible to define the hydrothermal systems and outline their extension using SP measurements [Ishido and
Mizutani, 1981; Finizola et al., 2002; Maineult et al., 2006]. In vadose zones, the SP response to rainfall infiltration and evaporation in the unsaturated soil indicated an application of SP measurements to characterize contaminant fluxes for water resource management [Darnet et al., 2004]. Moore et al. [2004] conducted displacement experiments during drainage in five intact sandstone samples, and demonstrated detectable SP signals in response to carbon dioxide injection. In tectonically active areas, SP anomalies originate from the fluid motions between reservoirs observed prior to earthquakes ranging from several minutes to a few hours [Park et al., 1993].

Figure 2.3: Numerical results from a heterogeneous-reservoir model with a single high-permeability layer of thickness of 15m [Jackson et al., 2012b]. (a) through (c) present 2-D cross sections of water saturation at different times. (d) through (f) present the corresponding potentials recorded along the well.
Recent numerical simulation results demonstrate that measurements of SP using permanently installed downhole or surface electrodes could be used to monitor subsurface flow in hydrocarbon reservoirs during waterflooding [Gulamali et al., 2011; Vinogradov and Jackson, 2011; Jackson et al., 2012b]. Figure 2.3 shows the numerical results from a 3-D reservoir model, in which SP signals is obviously higher the noise level around 0.1 mV when the waterfront is still 50 meters away. Moreover, the position and distribution of waterfronts are also clearly reflected by the shape of SP signal curves at different times. Recently, a new potential application of SP signals was suggested by Jackson and Vinogradov [2012a] who suggested measurements of streaming potential could be used to quantify the wetting state of core samples, and determine if and how changes in surface charge and the wetting state of rocks are responsible for improved oil recovery during low salinity waterflooding [Jackson and Vinogradov, 2012a].

Various applications of SP measurements show the importance of further investigation and development in this area. However, due to the complex structure of real geologic porous media, it becomes more difficult to understand SP anomalies during multiphase flow than single phase flow in subsurface settings. Multiphase flow will be discussed in the following section.

### 2.3 Mathematical description of flow

This section starts with a macroscopic description of flow and an introduction to the important transport properties, followed by a mathematical description of the transport of electrical charge during multiphase flow.
2.3.1 Transport of flow

The macroscopic equations used to describe multiphase flow in porous media are generalizations of Darcy’s law of single-phase flow in porous media that assume to apply at all points in the porous medium, even in unsteady-state flow [Dullien, 1992]:

\[ q_p = -\frac{k_{rp}}{\mu_p} (\nabla P_p - \rho_p g), \quad (p = 1, 2, 3, \ldots) \quad (2.1) \]

A relative permeability \( k_{rp} = k_p/K \) is defined for each phase in terms of the phase permeability \( k_p \) and the total permeability \( K \) of the porous media. The relative permeability is determined by the pore structure of the porous media, the hydraulic coupling between phases and the interfacial tension of flows [Dullien, 1992].

Various mathematical models of relative permeability have been developed. Dullien [1992] classified them into four categories: capillary models, statistical models, empirical models and network models. Since capillary models do not include the interconnected nature of the pores, they cannot give us a realistic description of multiphase flow phenomena. Statistical models have the same disadvantages as capillary models. In order to improve the results of capillary and statistical models, empiricism can be resorted to. At present, the most accurate model of relative permeability is network models that take the interconnectedness of the pore structure and microscopic flow mechanisms into account at the pore level. Network modelling approaches will be used in the second part of this project when we try to investigate and quantify the streaming potential behavior during multiphase flow at the pore level. However, when it is necessary to describe the relative permeability at the continuum level, basic empirical models are normally used. Here we introduce two simplified empirical models of relative permeability, which are important in the continuum approach to investigate the behaviour of SP signals:
• **Corey-type:** an often used model of the saturation dependence of relative permeability is the Corey-type correlations (equation 2.3 (a, b)) [Brooks and Corey, 1964]. A normalized water saturation can be defined:

\[ S_{wn} = \frac{S_w - S_{wir}}{1 - S_{wir} - S_{nwr}} \]  

\[ \text{ ....... (2.2) \]  

And relative permeability of oil and water can be expressed as:

\[ k_{rw} = K_{rwe} s_{wn}^{n_w} \]  

\[ \text{ ....... (2.3a) \]  

\[ k_{ro} = K_{roe} (1 - S_{wn})^{n_o} \]  

\[ \text{ ....... (2.3b) \]  

This type of correlations will be applied in chapter 3 to interpret obtained experimental data.

• **LET-type:** the Corey approximation has two shared degrees of freedom for \( S_{nwr} \), \( S_{wir} \) to adjust the end points, and two independent degrees of freedom for \( K_{roe} \), \( K_{rwe} \), \( n_w \), and \( n_o \) to accommodate the shape of the relative permeability. The LET-correlation adds more independent degrees of freedom in order to accommodate the shape of measured relative permeability curves [Lomeland et al., 2005]:

\[ K_{rwr} = \frac{K_{rwe} s_{wn}^{L_w}}{S_{wn} + E_w (1 - S_{wn}) T_w} \]  

\[ \text{ ....... (2.4a) \]  

\[ K_{ro} = \frac{(1 - S_{wn})^{L_o}}{(1 - S_{wn})^{L_o} + E_o S_{wn} T_o} \]  

\[ \text{ ....... (2.4b) \]  

where \( L, E \) and \( T \) are empirical parameters.

**2.3.2 Transport of electrical charge**

The charge polarisation mechanisms that have been proposed to explain SP anomalies are associated with streaming, electrochemical and thermoelectric effects as discussed in Section 2.1. This electrodynamic problem is coupled to the hydrodynamic problem. Previous
experiments [Guichet et al., 2003; Moore et al., 2004] and numerical models [Wurmstich and Morgan, 1994; Linde et al., 2007; Revil et al., 2007] at the continuum level have only considered the case of porous media saturated with water and a nonpolar, non-wetting phase such as air, in which case water is the only phase that is assumed to contribute to the electric current. Most experimental and numerical descriptions of the SP are based on this assumption. Although few numerical simulations described the transport of charges including the contributions of non-wetting phases [Saunders et al., 2008], the nature of the SP is still unclear when water is not the wetting phase, or other phases contribute to the streaming current. The transport of electrical charge, mass, heat and species can then be expressed in a general constitutive equation with [Revil, 1999]:

\[
\begin{pmatrix}
I \\
q_w \\
h \\
v
\end{pmatrix} = -
\begin{pmatrix}
\sigma_w(S_w) & \frac{L_{EK}(S_w)}{k_{rw}(S_w)} & L_{TE}(S_w) & L_{EC}(S_w) \\
L_{EK}(S_w) & \frac{k_{rw}(S_w)}{\mu_w} & 0 & 0 \\
L_{TE}(S_w) & 0 & k(S_w) & 0 \\
L_{EC}(S_w) & 0 & 0 & D(S_w)
\end{pmatrix}
\begin{pmatrix}
\nabla U \\
\nabla T \\
\nabla C_f
\end{pmatrix}
\]

(2.5)

The on-diagonal terms in the right matrix are Ohm’s law, Darcy’s law, Fourier’s law, and Fick’s law, respectively. The nonzero off-diagonal terms describe the coupling terms between constitutive equations that are generated because of charge separation. If we take a closer look at the transport of electric charge as below

\[
I = -\sigma_s \nabla U + \sum L_{EK}\nabla(P_w - \rho_w g z) + \sum L_{TE}\nabla T + \sum L_{EC}\nabla C_f 
\]

(2.6)

A key problem in predicting and interpreting SP signals in subsurface settings is to identify appropriate values for the coupling terms \(L_{EK}, L_{TE}\) and \(L_{EC}\). They will be described in more details in chapter 2.4.
Before the introduction of the coupling terms, models to describe the electrical conductivity of porous media will be discussed. At the continuum level, Archie’s law relates electrical conductivity to porosity and saturation:

\[
\sigma_{fs} = \phi^m \sigma_w S_w^n 
\]

where \( m \) is the cementation exponent of the rock and \( n \) is the saturation exponent. Different empirical values for \( m \) and \( n \) are appropriate for different types of rocks, for example, when \( m=1.8 \) and \( n=2 \) these values are typical of shallow, water-wet, consolidated sandstone [Anderson, 1986]. The electrical conductivity of the brine is related to the brine salinity. Archie’s law is valid for medium to coarse-grained soils and rocks and implies that the grain matrix does not contribute to the electrical current conduction, and it also neglected the surface conductivity that is related to the surface conduction of an electric double layer.

Several models take into account the effects of surface electrical conductivity, for example, an empirical correction [Ishido and Mizutani, 1981] replaces the electrolyte conductivity \( \sigma_w \) by the effective conductivity \( \sigma_{eff} \) in equation (2.8):

\[
\sigma_{eff} = F \sigma_r 
\]

where \( \sigma_r \) includes possible surface conductivity.

Many other expressions and models conducted by continuum approaches have been published (see paper published by Chelidze and Gueguen [1999] as a review), for example, different expressions proposed by Wurmstich and Morgan [1994], Guichet et al. [2003] and Moore et al. [2004]. Archie’s law can be modified to include the surface conductivity \( \sigma_s \) as shown in equation (2.9). In this study, equation (2.9) will be applied to interpret the saturation dependence of the electrical conductivity when interpreting experimental measurements of multiphase streaming potential:
\[ \sigma_{fs} = \phi^m \sigma_w \phi^n_w + \sigma_s \quad \ldots \quad (2.9) \]

### 2.4 Electrical coupling terms

When water is the only phase contributes to the transport of electrical charge, the coupling terms for the streaming, EC and TE potentials can be expressed in terms of the rock electrical conductivity \( \sigma_{fs} \) and coupling coefficients \( C_{EK} \), \( C_{TE} \) and \( C_{EC} \) as shown in equation 2.10 (a, b, c):

\[
L_{EK} = \sigma_{fs} C_{EK} \quad \ldots \quad (2.10 \text{ a})
\]

\[
L_{TE} = \sigma_{fs} C_{TE} \quad \ldots \quad (2.10 \text{ b})
\]

\[
L_{EC} = \sigma_{fs} C_{EC} \quad \ldots \quad (2.10 \text{ c})
\]

The coupling coefficients \( C_{EK} \), \( C_{TE} \) and \( C_{EC} \) are key properties that relate the magnitude of a SP signal to the associated gradient in pressure, temperature and concentration. Each coefficient is dependent upon the salinity, temperature and the fluid saturation. Up to now there are relatively sparse data available to describe the temperature and salinity dependence of coupling coefficients [Reppert and Morgan, 2003; Jaafar et al., 2009; J Saunders et al., 2012]; in particular the impacts of high temperature on the coupling coefficient is still poorly understood.

Since there is no investigation dealing with multiphase \( C_{TE} \) from experimental perspectives and only one paper described the behavior of multiphase \( C_{EC} \) [Ortiz et al., 1973], we start with multiphase \( C_{EK} \).

#### 2.4.1 Streaming coupling coefficient

To understand the behaviour of the streaming potential requires an understanding of the streaming coupling coefficient during multiphase flow. The streaming coupling coefficient is
defined as the ratio of the fluid \( \nabla P \) and streaming potential gradients \( \nabla U \) when the total current density is zero and EC, TE potentials are negligible [Sill, 1983]:

\[
C = \left. \frac{\nabla U}{\nabla P} \right|_{j=0} = -\left. \frac{C_{EK}}{\sigma_{fs}} \right|_{I=0}
\]

\[\cdots \cdots \cdots (2.11)\]

When there is more than one fluid phase present in the pore space, the coupling coefficient become a function of phase saturation, and a relative coupling coefficient \( C_r \) is introduced to describe the saturation dependence of the coupling coefficient:

\[
C_r(S_w) = \frac{C(S_w)}{C(S_w=1)}
\]

\[\cdots \cdots \cdots (2.12)\]

where \( C(S_w=1) \) is the value of the coupling coefficient when the pore space is fully saturated by the wetting phase [Revil and Cerepi, 2004]. A streaming current can be defined for each fluid phase and the total streaming current is the sum of the individual phase contributions:

\[
I_s = -\sigma r C r \nabla P_w
\]

\[\cdots \cdots \cdots (2.13)\]

where \( \sigma \) and \( C \) are the electrical conductivity and coupling coefficient when the porous medium is fully water saturated \( (S_w=1) \), so the electrical conductivity \( \sigma_r \) and coupling coefficient \( C_r \) become functions of water saturation [Jackson, 2008]. As we mentioned in Section 2.3.2, The saturation-dependent relative electrical conductivity \( \sigma_r \) (or resistivity index \( I \)) is often described using Archie’s second law or variants thereof [Dullien, 1992]. However, the saturation dependence of the relative coupling coefficient \( C_r \) remains poorly understood.

A number of experimental measurements of streaming potential during multiphase flow have also been reported (Figure 2.4) [e.g. Guichet et al., 2003; Moore et al., 2004; Revil and Cerepi, 2004; Linde et al., 2007; Revil et al., 2007; Allègre et al., 2010]. Guichet et al. [2003] measured the streaming potential during drainage under gas in a water-wet sandpack and reported a monotonic decrease in relative coupling coefficient (Figure 2.4a); however, in
similar experiments, Allègre et al. [2010] obtained the first continuous records of the variation in streaming coupling coefficient with water saturation, which shows strongly non-monotonic behaviour, with the relative coupling coefficient increasing by some two orders of magnitude before decreasing with decreasing water saturation (Figure 2.4b). Revil et al. [2007] also reported a monotonic behavior of relative coupling coefficient in dolomite core samples but, as pointed out by [Allègre et al., 2011], they calculated $C_r$ based on a value of $C(S_w=1)$ that was extrapolated from the data obtained at partial saturation. When their data are rescaled to the value of $C(S_w=1)$ reported by Revil and Cerepi [2004] for experiments on the same samples, $C_r$ again exhibits non-monotonic behaviour and exceeds the value at saturation (Figure 2.4a; compare open and closed triangles, noting the closed triangles plot against the right-hand axis).

A common feature of the studies reported above is that they observed zero streaming potential at the irreducible water saturation when water flow ceased. In contrast to these studies, Moore et al. [2004] and Vinogradov and Jackson [2011] observed a non-zero streaming potential (and, hence, coupling coefficient) at the irreducible water saturation. They measured the streaming potential during unsteady-state displacements in sandstone core samples, in which a non-aqueous, non-wetting phase (gas, oil or supercritical CO$_2$) was injected into an initially water-saturated sample during drainage, and then water was injected into the same sample at the irreducible water saturation during imbibition. Vinogradov and Jackson [2011] suggested that flow of the non-wetting phase at the irreducible water saturation drags with it small volumes of charge-rich water, giving rise to a streaming current and hence a non-zero coupling coefficient. Capillary desaturation experiments such as those conducted by Revil and Cerepi [2004], Revil et al. [2007] and Allègre et al. [2010] will always result in zero streaming potential at the irreducible saturation, because there is no flow of either the wetting or non-wetting phases.
Figure 2.4: (a, b) Experimental studies of the saturation dependence of the relative streaming potential coupling coefficient during drainage: (a) [1] data from Guichet et al. [2003]; [2-1], [2-2] data Revil and Cerepi [2004] for samples E39 and E3, respectively; [3-1] data from Revil et al. [2007] with extrapolated $C(S_w=1)$, [3-2] data from Revil et al. [2007] with $C_r$ calculated using $C(S_w=1)$ reported by Revil and Cerepi [2004]; [4-1], [4-2] data from Vinogradov and Jackson [2011] for samples Stainton and St. Bees.
respectively. (b) shows the relative coupling coefficient obtained by Allègre et al. [2010] between their electrodes 6 and 7 in experiment #1.

Limited experimental data presented contrasting behaviors of the streaming coupling coefficient at partial saturation conditions in gas/water and oil/water systems. The magnitude and general trend of the streaming coupling coefficient are still controversial. The general functional relationship between coupling coefficient and phase saturation during drainage and particularly imbibition still remains uncertain; more experimental data are needed.

A number of theoretical models have been published for the saturation dependence of $C_r$ (summarized in Table 2.1) [e.g. Wurmstich and Morgan, 1994; Perrier and Morat, 2000; Guichet et al., 2003; Darnet and Marquis, 2004; Revil and Cerepi, 2004; Linde et al., 2007; Jackson, 2010; Jougnot et al., 2012]. Wurmstich and Morgan [1994] and Darnet and Marquis [2004] both predicted that $C_r$ should increase with decreasing water saturation based on the assumption that that the non-wetting phase is transported as bubbles. However, this assumption is not appropriate when both phases are continuously distributed throughout the pore space. Guichet et al. [2003] suggested that $C_r$ varies linearly with water saturation. Revil and Cerepi [2004] developed a non-linear relationship between $C_r$ and $S_w$.

Revil and Leroy [2004] described the streaming current $I_s$ in terms of the streaming current charge density $Q_s$,

$$ I_s = Q_s q_w \quad \cdots (2.14) $$

where $Q_s$, streaming charge density that can be dragged by the flow of the pore water through the pore space of the porous media, which is also called dynamic excess charge density of the pore space. The streaming charge density is only a fraction of the total charge density $Q_t$ in the pore space including the contribution of the stern layer. It depends on the fluid and electrical charge distribution in each pore space, so a number of papers started to investigate
the behaviour of streaming charge density that controls the saturation dependence of streaming potential rather than coupling coefficient behaviour itself.

Table 2.1 Summary of published relationships for the saturation dependence of the relative coupling coefficient.

<table>
<thead>
<tr>
<th>Authors</th>
<th>Expression</th>
<th>Equation #</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wurmstich and Morgan [1994]*</td>
<td>(C_r(S_w) = \frac{(1 - w)}{\sigma_r(S_w)})</td>
<td>(2.15)</td>
</tr>
<tr>
<td>Perrier and Morat [2000]</td>
<td>(C_r(S_w) = \frac{k_{rw}(S_w)}{\sigma_r(S_w)})</td>
<td>(2.16)</td>
</tr>
<tr>
<td>Guichet et al. [2003]</td>
<td>(C_r(S_w) = S_w)</td>
<td>(2.17)</td>
</tr>
<tr>
<td>Darnet and Marquis [2004]</td>
<td>(C_r(S_w) = \frac{1}{\sigma_r(S_w)})</td>
<td>(2.18)</td>
</tr>
<tr>
<td>Revil and Cerepi [2004]**</td>
<td>(C_r(S_w) = \frac{\beta_+(\sqrt{R^2 + 1} + R) + \beta_-(\sqrt{R^2 + 1} - R)}{\beta_+(\sqrt{R^2 + 1} + R_s) + \beta_-(\sqrt{R^2 + 1} - R_s)})</td>
<td>(2.19)</td>
</tr>
<tr>
<td>Revil et al. [2007]</td>
<td>(C_r(S_w) = \frac{k_{rw}(S_w)}{S_w\sigma_r(S_w)})</td>
<td>(2.20)</td>
</tr>
<tr>
<td>Jackson [2010]</td>
<td>(C_r(S_w) = \frac{k_{rw}(S_w)Q_{rs}(S_w)}{\sigma_r(S_w)})</td>
<td>(2.21)</td>
</tr>
</tbody>
</table>

*\(w\) is the hydrodynamic resistance factor.
**\(R\) represents the excess of counter-ions in the pore water of the rock; \(\beta\) is the mobility of ions.

Titov et al. [2002] first tried to directly relate the streaming charge density with the intrinsic hydraulic conductivity, in which they collected three different types of experimental data together including streaming potential data measured using saline water, fresh water and air. They concluded that the streaming charge density is not influenced by rock and soil
permeability because those three different types of data did not show a general trend. Later, Jardani et al. [2007] proposed an empirical relationship between the streaming charge density and the intrinsic hydraulic conductivity based on experimental data measured in various rocks and saline waters. This empirical relationship was further validated by a broader variety of rocks and sediments at different salinities and pH values as shown in Figure 1 in the paper published by Soueid Ahmed et al. [2014].

Revil et al. [2007] equated $Q_s$ as excess charge density per unit pore volume in the diffuse layer (which is equal to the volumetric charge density of diffuse layer termed here $Q_v$), and argued that $Q_v$ scales inversely with water saturation as shown in equation (2.20). This model for the saturation dependence of $Q_v$ has been used to match experimental measurements of streaming potential [Linde et al. 2007]. However, this assumption is only valid when the excess charge in the diffuse layer is uniformly dragged along the pore fluid flow.

Allègre et al. [2010] first proposed two different empirical laws in two water saturation domains to match the non-monotonic measured coupling coefficient as shown in Figure 2.4 (b) during drainage only, which described coupling coefficient as an empirical power law function of effective water saturation. This study did not explain any underlying physical process. Furthermore, Allègre et al. [2014] performed a succession of drainage and imbibition cycles in a sandpack, and attempted to describe streaming current behaviour in terms of excess charge density $Q_v$ and an additional volumetric charge density demoted $Q_p$ that takes into account the polarization. Allègre et al. [2014] believed that the induced polarization in response of the development of continuous air water interface is able to explain the residual streaming potential signals at residual saturation with no macroscopic flow occurring through it.
*Jackson* [2010] built the first numerical model to describe the multiphase behavior of streaming potential at pore scale, and also proposed the thin and thick double layer assumptions to consider the impact of fluid and charge distribution at the pore scale (Figure 2.5). As demonstrated in Figure 2.5, this study described the distribution of fluid and charge in a bundle of capillary tubes with circular cross sections. The circular pore space and pore occupancy within capillary tubes model is very simple that it is easy to predict the streaming charge within each phase. Instead of direct investigation of coupling coefficient itself, Jackson proposed equation (2.21) in Table 2.1 and pointed out that the behaviour of streaming charge density is the key property to control streaming current. *Jougnot et al.* [2012] used a bundle of capillary tubes model to calculate the saturation dependence of $Q_{rs}$, iteratively adjusting the capillary size distribution to match experimentally measured water retention curves (their WR method) or relative permeability curves (their RP method). Their approach was applied successfully by *Jougnot et al.* [2015] to model field measurements of streaming potential in an agricultural test site.

However, simple pore-scale models that capture the distribution of fluids, electrical charge and flow demonstrate that $Q_v \neq Q_s$ at partial saturation, because of the heterogeneous distribution of water within pores of different sizes and the non-uniform flow field within a given pore [*Jackson*, 2008; *Linde*, 2009; *Jackson*, 2010; *Jougnot et al.*, 2012; *Jougnot et al.*, 2015]. A bundle of capillary tubes model is too simple to capture the complex pore-space topology of most geologic porous media. In this study, more realistic pore network models will be used to investigate behaviours of streaming charge density $Q_s$ and coupling coefficient via equation (2.21) in Chapter 4.
2.4.2 Electrochemical coupling coefficient

Only one study of the electrochemical potential during multiphase flow has been reported by Ortiz et al. [1973]. The results and conclusion reported in this paper are the basis for present numerical simulations to describe the saturation dependence of the EC coupling coefficient [Gulamali et al., 2011; Jackson et al., 2012b].

Ortiz et al. [1973] evaluated the change in the electrochemical potential with hydrocarbon saturation in porous media and related this change to cation exchange capacity. He reported the experimental data of the saturation dependence of electrokinetic potentials in nine samples obtained by McCall [1970], and some of them are demonstrated in Figure 2.6.
Without exception, the measured potential was increasing in the negative direction as the water saturation was decreased.

*Ortiz et al.* [1973] suggested two end-member cases. The upper limit is that of a perfect membrane, where co-ions will be largely excluded from the pore space when the water saturation is low since the transport of excess charge will be predominantly through the wetting layers sandwiches between the oil and the mineral surfaces. The voltage in the perfect membrane conditions is known as the exclusion potential ($V_E$). The lower limit is that of an uncharged porous media when most pores are occupied by water, where the electrochemical potential solely attributes to the diffusion or liquid junction potential since the transport of excess charge will be predominantly through the water outside the electrical double layer. The voltage built in the uncharged membrane conditions is known as diffusion potential ($V_{D}$). This conclusion was used to constrain the behaviour of the relative electrochemical coupling coefficient in present numerical simulations [*Gulamali et al.*, 2011; *Jackson et al.*, 2012b], however, *Ortiz et al.* [1973] only provided limited number of experimental measurements with restricted description of the experimental conditions and methodology. Further work is required.
Figure 2.6: Measured voltage against water saturation obtained by McCall [1970] by partially draining sandstone core plugs by paraffin injection. The symbol labels refer to the sample descriptions reported by Ortiz et al. [1973].

On the basis of the above discussion, the relative electrochemical coupling coefficient can be expressed as [Jackson et al., 2012b]:

\[
C_{REC} = \frac{V_{EC}(S_w) - V_E}{V_D - V_E}
\] ……… (2.22)

Using equation (2.22), Jackson et al. [2012b] modified the experimental results reported by Ortiz et al. [1973] and developed equation (2.23) to provide a reasonable match to the experimental results (Figure 2.7):

\[
C_{REC} = (1 - S_{wn})^3
\] ……… (2.23)
Figure 2.7: The relative EC coupling coefficient $C_{EC}$ is chosen to match the experimental data of McCall [1970]. The symbol labels refer to the sample descriptions reported by Ortiz et al. [1973] [Jackson, 2010].

Another saturation function of the electrochemical coupling coefficient was proposed by Gulamali et al. [2011] on the basis of the conclusion suggested by Ortiz et al. [1973]. Simple linear saturation functions of the relative coupling coefficient within four limit cases were applied in a 3-D numerical reservoir model.

In summary, there is no experimental data or numerical models to investigate and quantify the electrochemical potentials during multiphase flow except a paper published by Ortiz et al. [1973]. Present numerical simulations were all based on the conclusions proposed in this paper.
2.4.3 Thermoelectric coupling coefficient

At present, there is no published paper dealing with the thermoelectric potential during multiphase flow. However, the TE has a similar origin to the EC discussed in the previous section, which means the conclusion proposed by Ortiz et al. [1973] describing the two-member cases can be applied to describe the saturation function of the TE during multiphase flow. The exclusion and diffusion potentials are still, respectively, the upper and lower limits of the TE potential.

As defined in equation (2.22), the relative thermoelectric coupling coefficient can be described as the same saturation function with the relative electrochemical coupling coefficient. On the basis of this reason, Gulamali et al. [2011] and Jackson et al. [2012b] describe the behaviour of the TE using the same saturation function of the EC.
Chapter 3 Streaming potential during drainage and imbibition

3.1 Introduction

As we demonstrated in Section 2.4.1, unsteady-state displacements such as those conducted by Moore et al. [2004] and Vinogradov and Jackson [2011] as shown in Figure 2.4 are widely used to measure multiphase transport properties such as relative permeability, which cannot be obtained directly from the capillary desaturation experiments more typically used to measure multiphase SP. However, in such displacements, the water saturation in the sample is not uniform except at the initial (fully water saturated) condition, the irreducible water saturation and the residual non-wetting phase saturation. Consequently, the permeability, streaming potential and electrical conductivity measured across the sample are apparent values. These measured data cannot be used to interpret or model multiphase flows where it is assumed that the saturation is uniform within a Representative Elementary Volume (REV; e.g. Dullien, [1992]). Instead, it is necessary to develop and apply methods to interpret data from unsteady-state displacement experiments to determine values of the parameters of interest within a REV. An alternative to unsteady-state measurements is to use the steady-state method where both phases flow at constant rate through the porous medium of interest, but steady-state measurements are considerably more complex and time-consuming to obtain [Dullien, 1992].

Sigmund and McCaffery [1979] proposed a method to interpret the saturation dependence of relative permeability in unsteady-state displacements, in which they used numerical simulation to fit Corey-type relative permeability functions to the observed flow rate and
pressure data. In this Chapter, we develop a similar approach to interpret unsteady-state measurements of relative permeability ($k_r$), electrical conductivity ($\sigma$), the streaming potential coupling coefficient ($C$), and the streaming current charge density ($Q_s$). The approach can be used to interpret any measurements of streaming potential obtained in unsteady-state displacements.

We apply the method to the experimental data obtained during drainage and imbibition using two sandstone samples by Vinogradov and Jackson [2011] and report new data for $Q_s$ in natural geologic porous media. Few studies have interpreted $Q_s$ from experimental data and the saturation dependence of $Q_s$ in real geologic porous media is still poorly understood.

### 3.2 Methodology

To determine the saturation dependence of the coupling coefficient within a REV requires the values of $\Delta P$, $\Delta U$ and $S_w$ across each REV. To determine the streaming current charge density $Q_s$, it also requires the value of $\sigma$. These parameters were obtained here using numerical modelling to predict values across a cylindrical rock core sample ($\bar{C}$, $\bar{S_w}$, and $\bar{\sigma}$) and optimization to minimize the difference between predicted and observed values. A finite-difference approach was used to discretize the governing equations, assuming mass and current flow can be modelled in one-dimension (1-D) along the core sample. The numerical model divided the core sample into 100 equally sized grid blocks, each of which is considered to be a REV with uniform saturation and identical material properties.

The numerical modelling and optimization approach was subdivided into three steps. In step one (the ‘hydraulic optimization’), we used a commercial package [Schlumberger, 2013] to solve Darcy’s law (equation 2.1) for each phase (neglecting the electrokinetic coupling, in common with numerous similar studies; see, for example, Saunders et al. [2006] and Gulamali et al. [2011]), and the continuity equation for mass, to determine the saturation-
dependent relative permeability and capillary pressure functions applied to each REV that best match the observed pressure drop and effluent phase flow rates over the duration of the experiment. This allowed us to predict the saturation in each REV at a given time.

In step two (the ‘conductivity optimization’), we used a simple harmonic average of the electrical conductivity in each REV at a given time, to determine the saturation-dependent relative electrical conductivity function in each REV that best matches the experimentally measured electrical conductivity of the partially saturated core. This allowed us to predict the electrical conductivity in each REV at a given time. Finally, in step three (the ‘electrokinetic optimization’), we used an in-house finite-difference code to solve the modified Ohm’s Law (equation 2.6), plus the continuity equation for charge, to determine the saturation dependent relative coupling coefficient function in each REV that best matches the experimentally measured voltage drop across the partially saturated core sample at a given time. This final step yielded the desired objective: the relative coupling coefficient as a function of saturation within an REV.

Dimensions, permeability and porosity of the core samples in the numerical model were consistent with those used in the unsteady-state displacements described by Vinogradov and Jackson [2011]. They measured the pressure difference ($\Delta P$), the streaming potential ($\Delta U$), the electrical conductivity ($\bar{\sigma}$) and the average water saturation ($\bar{S}_w$) across two intact, water-wet, sandstone core samples during drainage and imbibition of undecane and water (a simple 0.01M solution of NaCl in de-ionized water). The hydraulic optimization model also includes the inlet fluid reservoir and connecting flowline (Figure 3.1). We used Darcy’s law in the same pseudo 1-D model to describe flow within the reservoir and flowline, with the permeability adjusted to yield the appropriate flow resistance for a cylindrical tube of the same diameter. In a preliminary optimization step, the compressibility of the reservoir and
flowline was adjusted to match the gradual build-up of pressure measured in the experiments at the sample inlet when the pump was switched on.

The initial and boundary conditions for the hydraulic models of drainage and imbibition matched the laboratory experiments. During drainage, the initial conditions were a uniform initial water saturation of 1 and atmospheric pressure; the boundary conditions were a fixed flow rate of undecane into the inlet fluid reservoir, determined by the flow rates applied during the experiments, and atmospheric pressure at the outlet from the core (Figure 3.1a). During imbibition, the initial conditions for the hydraulic model were uniform initial water saturation at the end of drainage \( (S_w = S_{w_{ir}}) \) and atmospheric pressure; the boundary conditions were a fixed water flow rate into the inlet fluid reservoir, determined by the flow rates applied during the experiments, and atmospheric pressure at the outlet from the core (Figure 3.1c).

The electrical model, used to optimize the electrical conductivity and electrokinetic properties, included only the core sample and was treated as a post-processing step using the outputs of pressure and saturation from the hydraulic model at a given time. The boundary conditions for the conductivity optimization were a constant (arbitrary) current through the inlet and outlet faces; the boundary conditions for the electrokinetic optimization were \( \frac{dU}{dx} = 0 \) at the inlet flow boundary, and \( U=0 \) at the outlet flow boundary. This reproduced the earthed electrode used in the experiments (Figure 3.1b).
Figure 3.1: Schematic of the 1-D numerical models used to interpret hydraulic and electrical properties measured experimentally: (a) Hydraulic model during drainage. Dashed arrows represent flow within the hydraulic model. Black bold lines represent no flow boundaries. (b) Electrical model during both drainage and imbibition to interpret the measured apparent electrical conductivity and coupling coefficient. (c) Hydraulic model during imbibition, in which the inlet flowline was modified by connecting to the base of the core sample.

3.2.1 Parameter optimization during drainage

The hydraulic optimization was to determine the relative permeability and capillary pressure in each REV that yield the best match to the measured experimental data using the hydraulic numerical model. Following the approach of Sigmund and McCaffery [1979] we assumed the following drainage functions for $k_r$ and $P_c$.
The capillary entry pressure $P_{ce}$ is computed in terms of interfacial tension, absolute permeability and porosity. The optimization problem for drainage (in which $S_{nw} = 0$) is then reduced to one of finding the values of $S_{wi}$, $\alpha$, $\beta$, $\lambda$ and $A$ that yield simulated pressure and phase flow rates that most closely match the experimentally measured values. Values of $S_{wi}$ were constrained to lie within the experimentally measured range ($S_{wi} = 0.29 \pm 0.08$ for the St Bees sample investigated by Vinogradov and Jackson [2011], and $S_{wi} = 0.44 \pm 0.08$ for the Stainton sample investigated by Vinogradov and Jackson [2011]. The problem to match simulated (subscript sim) pressure drop across the sample ($\Delta P$), total volume of produced fluid ($V_f$) and water fractional flow at the outlet ($F_w$) with observed (subscript obs) values becomes an optimization of a least-squares objective function:

$$
\begin{align*}
f_1 &= \sum \left( \frac{\Delta P_{obs} - \Delta P_{sim}}{\delta_P} \right)^2 + \sum \left( \frac{V_{f,obs} - V_{f,sim}}{\delta_V} \right)^2 + \sum \left( \frac{F_{w,obs} - F_{w,sim}}{\delta_F} \right)^2 \quad \cdots \quad (3.4)
\end{align*}
$$

We weighted each difference with the experimental uncertainties $\delta_P$, $\delta_V$, $\delta_F$ in equation (3.4) to make the quality of match of $\Delta P$, $V_f$, or $F_w$ dimensionless, and minimized the objective function ($f_1$) using constrained sequential quadratic programming (SQP) non-linear optimization [see, for example, Nocedal and Wright, 2006] implemented in Matlab [MATLAB, 2012]. We used SQP in this study because it has been shown to have high efficiency, accuracy and success over a large number of test problems [e.g. Schittkowski, 1985]. Given the highly non-linear nature of the governing equations (coupled through, for example, the saturation-dependent relative permeability and capillary pressure functions [Dullien, 1992])
the optimization solutions are likely to be non-unique and the optimization may find local rather than global minima. In an attempt to account for this, we chose the best eight sets of optimized parameters with a similar quality of match (the minimum value of $f_1 + 10\%$ variation) to take into the next step of the optimization (Figure 3.2), rather than a single set of parameters.

In the conductivity optimization, we used the simulated values of water saturation to determine the electrical conductivity of each REV. To do this requires the saturation-dependent relative electrical conductivity ($\sigma_r$) in each REV. We assumed a modified Archie’s law which accounts for surface electrical conductivity [e.g. Clavier et al., 1984; Revil and Glover, 1998; Glover et al., 2000]:

$$\sigma = a_1 \cdot S_w^n + a_2$$  \hspace{1cm} (3.5)

in which $n$ corresponds to the saturation exponent, $a_1$ corresponds to the bulk electrical conductivity when the rock is fully water saturated and $a_2$ corresponds to the surface electrical conductivity, which is assumed to be independent of saturation because the samples are strongly water-wet so water forms a continuous film along the mineral surfaces at partial saturation [Hearst and Nelson, 1985]. We constrain $a_1 + a_2 = \sigma_{obs} (S_w = 1)$ because the simulated electrical conductivity must be equal the observed electrical conductivity when the rock is fully water saturated. The objective function $f_2$ was a the sum of the weighted squared difference between observed and simulated sample electrical conductivity at a given time $t$

$$f_2 = \sum \left( \frac{\sigma_{sim}(t) - \sigma_{obs}(t)}{\delta_\sigma} \right)^2$$  \hspace{1cm} (3.6)

where $\delta_\sigma$ is the experimental uncertainty of electrical conductivity. For each of the 8 sets of optimized hydraulic parameters obtained in the previous step, we identified the values of $a_1$, $n$
and \(a_2\), and \(a_1\), \(n\) with \(a_2 = 0\), that minimized the objective function (equation 3.6). Thus sixteen sets of optimized parameters were taken into the final optimization step (Figure 3.2).

In the final step (the ‘electrokinetic optimization’) we used the simulated values of pressure, water saturation and electrical conductivity obtained using the optimized parameter sets in the previous steps to determine the streaming potential drop across each REV. The sum of these potential drops yields the total streaming potential measured across the sample. To do this requires the saturation-dependent relative streaming potential coupling coefficient \((C_r)\) in each REV. Since there is no general model to describe the saturation dependence of \(C_r\) and experimental data to date has suggested complex, non-monotonic behavior, high order functions have been tested to match the complex behavior of \(C\) measured in experiments. We varied the order of the polynomial approximation in a preliminary step and found that the quality of match to the experimental data did not significantly increase above order 4 but was significantly better than order 3, so we used an order 4 polynomial function given by:

\[
C_r = b_1 \cdot S_{wn}^4 + b_2 \cdot S_{wn}^3 + b_3 \cdot S_{wn}^2 + b_4 \cdot S_{wn} + b_5 \quad \cdots (3.7)
\]

where \(b_1\), \(b_2\), \(b_3\), \(b_4\) and \(b_5\) are fitting parameters to be adjusted in the optimization. The objective function \(f_3\) was:

\[
f_3 = \sum \left( \frac{\bar{c}_{sim}(t) - \bar{c}_{obs}(t)}{\delta C} \right)^2 \quad \cdots (3.8)
\]

where \(\delta C\) represents the measured uncertainty of the streaming potential coupling coefficient.

Although we use an arbitrary polynomial function to describe \(C_r\), we recognize that the streaming charge density in a water-wet rock must increase with decreasing water saturation, because the mobile electric charges are located within the wetting water layers and the non-wetting phase occupies the pore centers [Jackson, 2010]. We used this condition to reject some solutions for \(C_r\) obtained from the optimization; only \(C_r\) solutions in which \(Q_{rs}\)
(calculated using equation 2.21 in Table 2.1) increased monotonically were allowed, although there was no constraint placed directly on the optimization. In some cases, we added a constraint to the optimization that forced \(C_r(S_{\text{air}}) = 0\) in each REV, to determine whether this influenced the solutions obtained. For each of the 16 sets of optimized parameters obtained from the previous steps, we chose the ten sets of optimized electrokinetic parameters \(b\) with a similar quality of match (the minimum value of \(f_b + 10\%\) variation). Thus the drainage optimization finished with 160 sets of optimized parameters \(b\) that yield 160 possible functional relationships for the relative streaming potential coupling coefficient for each sample (Figure 3.2).
Figure 3.2: Flowchart showing the three optimization steps during drainage/imbibition:

- Hydraulic optimization
- Electrical conductivity optimization
- Electrokinetic optimization

Total 160 sets of optimized parameters
3.2.2 Parameter optimization during imbibition

The optimization approach during imbibition was very similar to that used during drainage, except that the relative permeability curve for water becomes

\[ k_{rw} = \frac{k(1-S_{nwr})}{k(S_w=1)} S_{wn}^\alpha \] .... (3.9)

With measured permeability \( k(1-S_{nwr}) \) at irreducible water saturation. Moreover, there is no constraint on the electrical conductivity optimization \((a_1+a_2\neq \sigma_{obs}(S_{nwr}) \) in equation (3.6)), because water saturation is less than one at the end of imbibition. Finally, the initial conditions for imbibition vary depending upon the optimization parameters chosen for drainage. We selected two different initial conditions for imbibition from the ensemble of optimized values at the end of drainage, one of which yielded a monotonic saturation dependence for \( C_r \) during drainage, and the other of which yielded a non-monotonic saturation dependence. The values of \( S_{nwr} \) during the hydraulic optimization were constrained to lie within the experimentally measured range \((S_{nwr} = 0.088 \pm 0.08 \) for the St Bees sample, and \( S_{nwr} = 0.095 \pm 0.08 \) for the Stainton sample).

The imbibition optimization finished with 160 sets of optimized parameters \( b \) for each of the two selected starting condition, thus yielding 320 possible functional relationships for the relative streaming potential coupling coefficient for each sample.

3.3 Results

3.3.1 Drainage optimization

The objective function values \((f_1, f_2 \) and \( f_3 \)) obtained at the end of the hydraulic, electrical conductivity and electrokinetic optimizations are plotted for both core samples during drainage (Figure 3.3 a,c,e) and imbibition (Figure 3.3 b,d,f).
Figure 3.3: Objective function values in hydraulic ($f_1$), electrical conductivity ($f_2$) and electrokinetic ($f_3$) optimizations: (a, c, e) objective function values from St. Bees (solid points) and Stainton samples (hollow points) during drainage; (b, d, f) objective function values in St. Bees (solid points) and Stainton samples (hollow points) during
imbibition. Case number corresponds to the 8 sets of optimized parameters obtained in the hydraulic optimization during drainage. We selected two initial conditions for imbibition from the ensemble obtained at the end of the drainage optimization (one showing monotonic behavior of $C_r$ denoted M, and the other showing non-monotonic behavior denoted NM). The error bars shown in (e, f) represent the spread in $f_3$ that yield a similar quality of match after the electrokinetic optimization.

The case numbers listed on the horizontal axis correspond to the best eight sets of parameters obtained in the hydraulic optimization during drainage; since hundreds of values of $f_3$ were obtained during the electrokinetic optimization (see Figure 3.2) we represent the range of values using the error bars in Figure 3.3 (e,f). Moreover, since we selected two different initial conditions for imbibition from the ensemble obtained at the end of drainage, the number of optimized values is doubled.

Table 3.1 Optimized values of fitting parameters during drainage shown in Figure 3.4-3.6.

<table>
<thead>
<tr>
<th>Values for Figure (3.4)-(3.6)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$A$</th>
<th>$\lambda$</th>
<th>$S_{wir}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic optimization</td>
<td>Stainton</td>
<td>3.721</td>
<td>2.316</td>
<td>0.102</td>
<td>9.321</td>
</tr>
<tr>
<td></td>
<td>St. Bees</td>
<td>3.544</td>
<td>2.475</td>
<td>0.0433</td>
<td>6.001</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_1$ (S/m)</td>
<td>Stainton</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>St. Bees</td>
<td>0.018</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_2$ (S/m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_1$</td>
<td>Stainton</td>
<td>-6.274</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>St. Bees</td>
<td>-1.740</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_2$</td>
<td></td>
<td>16.089</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.431</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_5$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Typical results from each step of the drainage optimization are shown in Figures 3.4-3.6, and the results are summarized in Table 3.1. Figure 3.4 shows typical results from the hydraulic
optimization: there is a good match within experimental error to each of the measured parameters and the two off-trend experimental data points around 15 hours in Figure 3.4f most likely reflect the accumulation of air bubbles within the core sample. The spikes in pressure observed in Figure 3.4a and 3.4b reflect the experimental measurements of streaming potential.

Figure 3.5 shows typical results from the electrical conductivity optimization for cases without (Figure 3.5 a, b) and with (Figure 3.5 c, d) surface electrical conductivity ($a_2 = 0$ and $a_2 \neq 0$ respectively); the quality of match is not significantly affected by the value of $a_2$. Both samples exhibited a rapid initial decrease in measured relative electrical conductivity with decreasing water saturation, and this was very difficult to match using an Archie-type equation; indeed, despite numerous attempts, we failed to match the data within experimental error for water saturation values over the range 0.8-1, although the mismatch is small. This may be that for, heterogeneous sandstone, a single simulation grid block does not small enough to represent a homogeneous REV in which Archie-type function can be applied. Higher order polynomial relationships between $\sigma_r$ and $S_w$ were tested, and we also tried a 3-stage Archie-type equation (in which the saturation exponent $n$ in equation (3.6) had differing values for three different ranges of saturation), but the quality of fit was not significantly improved ($f_2$ values were reduced by less than $6 \times 10^{-5}$, which is small compared to the minimum values obtained; see Figure 3.3). Higher order polynomial functions also yielded unphysical behaviour. The shift in water saturation between observed and simulated data is because we compared data at the same time step, rather than at the same saturation, as discussed above.
Figure 3.4: Typical results from the hydraulic optimization during drainage showing simulated (lines) and observed (points) data ($f_r$=4.01 and 9.58 for St.Bees and Stainton respectively): (a, b): pressure difference across the Stainton and St. Bees samples respectively; (c, d) cumulative water production from the Stainton and St. Bees samples respectively; (e, f) water injection flow.
respectively; (e, f) water fractional flow at the outlet of the Stainton and St. Bees samples. Error bars denote the typical experimental error.

Figure 3.5: Typical results from the electrical conductivity optimization during drainage for Stainton ($f_2 = 0.89 \times 10^{-3}$) (a, c) and St. Bees ($f_2 = 1.3 \times 10^{-3}$) (b, d) during drainage: (a, b) selected optimization results using Archie’s law ($a_2 = 0$); (c, d) selected optimization results using modified Archie’s law with non-zero $a_2$. The error bar denotes the typical experimental error.
Figure 3.6: Typical results from the electrokinetic optimization during drainage for (a) Stainton \((f_3=0.045)\) and (b) St. Bees \((f_3=0.068)\). The error bar denotes the typical experimental error.

Figure 3.6 shows typical results from the electrokinetic optimization, which yielded both monotonic and non-monotonic relationships between \(C_r\) and \(S_w\) with similar qualities of fit to the experimental data. Figure 3.6 shows examples of each relationship type compared to the measured data. The Stainton sample showed strongly non-monotonic behaviour at high water saturation, and it proved to be very difficult to match the initially rapid decrease in relative coupling coefficient with decreasing water saturation despite the use of a high-order polynomial, although the non-monotonic behaviour was captured. As before, the shift in water saturation between observed and simulated data is because we compared data at the same time step rather than at the same saturation. The uncertainty in \(S_w\) is shown in Figures 3.5 and 3.6, and arises from the relatively low \((\pm 0.1\text{mL})\) precision in measuring the volume of produced liquid. This uncertainty is cumulatively increased during drainage and imbibition [Vinogradov and Jackson, 2011].

### 3.3.2 Imbibition optimization

Typical results from each step of the imbibition optimization are shown in Figures 3.7-3.9, and the corresponding values are summarized in Table 3.2.
Table 3.2 Optimized values of fitting parameters shown in Figure 3.7-3.9 during imbibition.

<table>
<thead>
<tr>
<th>Values for Figure (3.7)-(3.9)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$A$</th>
<th>$\lambda$</th>
<th>$S_{nwr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic optimization</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainton</td>
<td>2.588</td>
<td>2.758</td>
<td>1.199E-5</td>
<td>65.598</td>
<td>0.038</td>
</tr>
<tr>
<td>St. Bees</td>
<td>2.000</td>
<td>3.005</td>
<td>3.269E-5</td>
<td>194.17</td>
<td>0.168</td>
</tr>
<tr>
<td>$a_1$ (S/m)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainton</td>
<td>0.007</td>
<td>0.557</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Bees</td>
<td>0.006</td>
<td>6.463</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainton</td>
<td>-27.637</td>
<td>62.379</td>
<td>-45.078</td>
<td>11.149</td>
<td>0.147</td>
</tr>
<tr>
<td>St. Bees</td>
<td>-18.135</td>
<td>41.633</td>
<td>-30.295</td>
<td>7.348</td>
<td>0.465</td>
</tr>
</tbody>
</table>

Figure 3.7 shows typical results from the hydraulic optimization; there is a generally good match within experimental error to each of the measured parameters although we were unable to obtain a good match to the late oil production (after 40 hours) observed in the St. Bees sample (Figure 3.7 (d)). The late increase in oil recovery is inconsistent with the well-established behaviour of such immiscible displacements and is most likely an experimental artefact, possibly caused by the presence of air bubbles within the core sample. There may be micro bubbles of oil trapped in the flow lines and extra oil was produced as a single slug when drops joined together. The spikes in pressure observed in Figure 3.7a and 3.7b reflect the PR measurements of streaming potential. The one off-trend experimental data point around 21 hours in Figure 3.7f most likely reflects the accumulation of air bubbles within the core sample.
Figure 3.7: Typical results from the hydraulic optimization during imbibition showing simulated (lines) and observed (points) data ($f_1$=3.48 and 5.01 for St.Bees and Stainton respectively): (a, b): pressure difference across the Stainton and St. Bees samples respectively; (c, d) cumulative water production from the Stainton and St. Bees samples respectively; (e, f) cumulative water production from the Stainton and St. Bees samples respectively.
respectively; (e, f) water fractional flow at the outlet of the Stainton and St. Bees samples. Error bars denote the typical experimental error.

Figure 3.8: Typical results from the electrical conductivity optimization during imbibition for Stainton ($f_2=0.31\times10^{-3}$) (a, c) and St. Bees ($f_2=0.63\times10^{-3}$) (b, d) during drainage: (a, b) selected optimization results using Archie’s law ($a_2 = 0$); (c, d) selected optimization results using modified Archie’s law with non-zero $a_2$. The error bar denotes the typical experimental error.

Figure 3.8 shows typical results from the electrical conductivity optimization for cases without (Figure 3.8a, b) and with (Figure 3.8c, d) surface electrical conductivity ($a_2 = 0$ and $a_2 \neq 0$ respectively); the quality of match is not significantly affected by the value of $a_2$. St. Bees exhibited a rapid initial increase in measured relative electrical conductivity with increasing water saturation at the start of imbibition, which was very difficult to match using
an Archie-type equation despite numerous attempts as we have discussed in the drainage section. Higher order polynomial functions and 3-stage Archie-type equations were also tested during imbibition, but there was no significant improvement in the quality of fit ($f_2$ values were reduced by less than $5 \times 10^{-5}$ which is small compared to the minimum values obtained; see Figure 3.3).

Figure 3.9 shows typical results from the electrokinetic optimization, which yielded both monotonic and non-monotonic relationships between $C_r$ and $S_w$ with similar qualities of fit to the experimental data; there is a good match within experimental uncertainties. As before, the shift in water saturation between observed and simulated data is because we compared data at the same time step rather than at the same saturation.

![Figures 3.9](image)

**Figure 3.9**: Typical results from the electrokinetic optimization during imbibition for (a) Stainton ($f_3=0.027$) and (b) St. Bees ($f_3=0.085$). The error bar denotes the typical experimental error.

### 3.3.3 Interpretation of optimization results

Figures 3.10-3.12 show the optimized saturation dependence of the relative permeability, capillary pressure, electrical conductivity and coupling coefficient across each REV; the spread in each (denoted by the dashed lines) reflects the range of parameter values selected at
the end of each optimization step (Figure 3.2) and the solid line shows one specific example. Parameter values are summarized in Table 3.3.

<table>
<thead>
<tr>
<th>Table 3.3 Ranges of optimized parameters from hydraulic, electrical conductivity, and electrokinetic optimization steps.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td><strong>Hydraulic optimization</strong></td>
</tr>
<tr>
<td>$a$</td>
</tr>
<tr>
<td>$b$</td>
</tr>
<tr>
<td>$A$</td>
</tr>
</tbody>
</table>

| **Electrical conductivity optimization** | | | | | | | | |
| $a$ | 0.008−2.171 | 2.845−3.541 | 0.81−0.938 | 1.516−1.617 | 0.401−0.598 | 6.123−7.346 | 0.577−0.899 | 1.23−2.412 |
| $b$ | 0.010−0.111 | 0.018 | 0.012−0.014 | 0.012−0.014 | 0.012−0.014 | 0.012−0.014 | 0.012−0.014 | 0.012−0.014 |
| $A$ | 0.004−0.066 | 0.004−0.066 | 0.004−0.066 | 0.004−0.066 | 0.004−0.066 | 0.004−0.066 | 0.004−0.066 | 0.004−0.066 |

| **Electrokinetic optimization** | | | | | | | | |
| $a$ | 0.010−0.106 | 0.015−0.185 | -19.219−2.176 | -24.466−3.692 | -53.29−4.754 | -44.922−11.961 | -3.125−9.65 | -2.105−9.65 |
| $b$ | -35.028−1.597 | -17.039−0.667 | -11.260−0.741 | -11.260−0.741 | -11.260−0.741 | -11.260−0.741 | -11.260−0.741 | -11.260−0.741 |
| $A$ | 0.132−0.457 | 0.132−0.457 | 0.132−0.457 | 0.132−0.457 | 0.132−0.457 | 0.132−0.457 | 0.132−0.457 | 0.132−0.457 |
Figure 3.10: Summary results from the hydraulic optimization showing simulated (solid and dot-dash lines) data and variations (dash lines): (a, c): relative permeability and capillary pressure of the Stainton sample during drainage and imbibition respectively, and (e) represents the comparison of relative permeability during drainage and imbibition; (b, d) relative permeability and capillary pressure of the St. Bees sample during drainage and imbibition respectively, and (f) represent the comparison of relative permeability during drainage and imbibition.
Figure 3.11: Summary results from the electrical conductivity optimization showing simulated (solid lines) data and variations (dashed lines). (a, b): relative electrical conductivity of the Stainton sample during drainage and imbibition respectively; (c, d) relative electrical conductivity of the St. Bees sample during drainage and imbibition respectively.

As expected, relative permeability and capillary pressure exhibit monotonic but hysteretic behaviour during drainage and imbibition (Figure 3.10). Hysteresis is observed because of the differing flow paths and contact angles during drainage and imbibition [e.g. Brooks and Corey, 1964; Fenwick and Blunt, 1998]. Hysteresis is also observed in the electrical conductivity, which can be related to changes in pore-scale fluid distribution caused by changes in saturation history [e.g. Longeron et al., 1989; Blunt et al., 2002]. Optimized values of the saturation exponent $n$ are often lower than the range of 1.5-2.5 typically
observed for sandstones; many experimental and numerical studies have demonstrated that the saturation exponent $n$ can be saturation-dependent, with smaller values observed at lower water saturation and values around 2 close to saturation [e.g. Knight, 1991; Roberts and Lin, 1997; Suman and Knight, 1997; Knackstedt et al., 2007].

---

**Figure 3.12:** Summary results from the electrokinetic optimization showing simulated (solid lines) coupling coefficient and variations (dash lines): (a, b): relative coupling coefficient for the Stainton sample during drainage and imbibition respectively; (c, d) relative coupling coefficient for the St. Bees sample during drainage and imbibition respectively.

The relative coupling coefficient also demonstrates hysteretic behavior during drainage and imbibition for both samples. However, the most striking result is that the relative coupling coefficient within an REV can be strongly non-monotonic and, during imbibition, can exceed
the value observed at $S_w=1$, consistent with experimental data. Moreover, the relative coupling coefficient at the REV may be zero or non-zero at the irreducible water saturation but yield a similar quality of match to the apparent values measured across the core sample.
3.4 Discussion

3.4.1 Saturation-dependence of the streaming current charge density

Using the interpreted relative permeability, electrical conductivity and streaming potential coupling coefficient functions, the saturation dependence of the relative streaming current charge density $Q_{rs}$ can be calculated using equation (2.21) (Figure 3.13). The three step optimization process adopted here yielded 160 ensembles of optimized relative permeability, electrical conductivity and coupling coefficient for each sample during drainage, and 320 ensembles during imbibition with, as discussed previously, a broad range of behaviours including both monotonic and non-monotonic variations in the relative coupling coefficient. However, the variation in relative streaming charge density with saturation interpreted from these ensembles is very narrow for a given sample and a given displacement, and the difference between samples is less than the difference between displacements i.e. the spread of $Q_{rs}$ curves is more similar for the two samples during drainage or imbibition, than it is for a given sample for drainage and imbibition.

We model the relative streaming current charge density during drainage and imbibition using a power law function given by:

$$Q_{rs} (S_{wn}) = p S_{wn}^{-q} + r \quad \text{...... (3.10)}$$

where $p$, $q$ and $r$ for a given sample and displacement are determined by curve fitting to the mean values of $Q_{rs} (S_{wn})$ at each value of water saturation; $R^2 \geq 0.99999$ for all samples and displacements reported here. We place a constraint that $p+r=1$ because the relative streaming current charge density must equal 1 when the core sample is fully saturated with water.
Values of $p$, $q$, $r$ obtained here are summarized in Table 3.4; the values are close regardless of sample for a given displacement, which suggests that the streaming current charge density is dictated by the pore-scale distribution of the two fluid phases. In the experiments reported here, this differs more significantly between drainage and imbibition than it does between the two sandstone samples for a given displacement, owing to the hysteresis in advancing and receding contact angles and differing pore-filling mechanisms [Haines, 1925; Miller and Miller, 1956].

Figure 3.13: Relative streaming charge density as a function of normalized water saturation for Stainton (solid shaded area) and St. Bees (textured shaded area) during drainage (black) and imbibition (grey); the curves are given by our power law model for the relative streaming charge density (equation 3.10) to fit the mean value of the optimized variations in each core and displacement ($R^2=0.99999$ in all cases). Fitting parameters $p$, $q$, $r$ are summarized in Table 3.4.
Table 3.4 Values of fitting parameters \((p, q, r)\) of relative streaming charge density functions with water saturation for Stainton and St. Bees during drainage and imbibition.

<table>
<thead>
<tr>
<th></th>
<th>Drainage</th>
<th>Imbibition</th>
<th>Drainage</th>
<th>Imbibition</th>
<th>Drainage</th>
<th>Imbibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainton</td>
<td>0.201</td>
<td>-3.633</td>
<td>0.799</td>
<td>0.275</td>
<td>-2.276</td>
<td>0.725</td>
</tr>
<tr>
<td>St. Bees</td>
<td>0.340</td>
<td>-3.352</td>
<td>0.660</td>
<td>0.174</td>
<td>-2.501</td>
<td>0.826</td>
</tr>
<tr>
<td>Sandstones (average)</td>
<td>0.270</td>
<td>-3.493</td>
<td>0.729</td>
<td>0.225</td>
<td>-2.388</td>
<td>0.775</td>
</tr>
</tbody>
</table>

Given the mismatch between measured and simulated electrical conductivity data at high water saturation discussed previously, we further tested higher order polynomial functions and 3-stage Archie-type functions for the electrical conductivity to determine whether changing the conductivity match significantly affected the streaming charge density and found that \(Q_{rs}\) values remained within the range already determined. Thus the small mismatch to the electrical conductivity at high water saturation has no significant influence on the \(Q_{rs}\) model we proposed here.

### 3.4.2 Comparison of our model for \(Q_{rs}\) against previous studies

The model of the saturation dependence of the streaming current charge density we propose in equation (3.10) is compared with the models proposed by Revil et al. [2007] and Jougnot et al. [2012] in Figure 3.14. The model of Jougnot et al. [2012] was applied using our interpreted capillary pressure and relative permeability curves from the Stainton and St. Bees
core samples, and the WR and RP approaches. As discussed in the introduction, the model of Revil et al. [2007] assumes that $Q_r$ scales inversely with water saturation.
Figure 3.14: Predicted variation of streaming charge density with water saturation compared against other published models: solid and long dash lines are predicted using equation (3.10) and the values of $p$, $q$ and $r$ reported in Table 5. The dotted line represents the model of Revil et al. [2007]. Models of Jougnot et al. [2012] for Stainton and St. Bees are also presented using using (a) WR and (b) RP approaches.

All three models predict that the relative streaming charge density increases monotonically with water saturation, but the $1/S_w$ model of Revil et al. [2007] predicts a lower streaming charge density at low water saturation when compared with our model and the model of Jougnot et al. [2012]; it also fails to capture the hysteric behavior between drainage and imbibition we observed here. However, in samples such as sandpacks with a narrow pore-size distribution (such as a sand-pack), the $1/S_w$ model for $Q_r$ yields reasonable predictions at high water saturation [Linde et al., 2007]. The model of Jougnot et al. [2012] predicts less hysteric behavior and lower values of $Q_r$ at intermediate and high water saturation than our interpreted data using both the WR and RP approaches. We did not expect an exact fit, since the model of Jougnot et al. [2012] is based on a bundle of capillary tubes model, which is too simple to describe the pore structure of real rock.

3.4.3 Application of the relative streaming current charge model to predict the relative streaming potential coupling coefficient

We now demonstrate the broad range of behaviours of the relative streaming potential coupling coefficient predicted using our model of the relative streaming current charge density (Sandstone average values in Table 3.4 are applied for the fitting parameters of empirical models) in conjunction with a simple Corey model of relative permeability (equations 3.1 and 3.2) and a simple Archie model for electrical conductivity (equation 3.5 with $a_2 = 0$). Recall $C_r$ is given by equation (2.21). We assume here that relative permeability, electrical conductivity and streaming charge density are independent. This may not be the
case but the dependencies for natural porous media are not well known [e.g. Dullien, 1992].

It is common to assume that relative permeability and electrical conductivity are independent, and they are often measured in separate experiments and on separate samples. Models for relative permeability and electrical conductivity are also independent.

Figure 3.15: Predicted behavior of the relative streaming potential coupling coefficient using our model of the relative streaming charge (equation 3.11) in conjunction with a simple Corey model of relative permeability ($\alpha$ and $\beta$ over range 2-5) and a simple Archie model for electrical conductivity ($n$ over range 1.5-3.5). Dash lines represent the ranges of the predicted coupling coefficients; solid lines are three selected examples (a) Example_1 represents $\alpha = 4$ and $n = 2.875$, Example_2 represents $\alpha = 4.4$ and $n = 3$ and Example_3 represents $\alpha = 5$ and $n = 3$ during drainage, and (b) Example_1 represents $\alpha = 3$ and $n = 2.75$, Example_2 represents $\alpha = 3$ and $n = 2.5$ and Example_3 represents $\alpha = 3.3$ and $n = 2.25$ during imbibition.

Figure 3.15 shows the predicted $C_r(S_w)$; the dashed lines denote the range of curves obtained using values of $\alpha$ and $\beta$ (the Corey parameters) and $n$ (the Archie parameter) varied in a simple Monte-Carlo analysis over the range typically observed in water-wet rock (including the values determined for the two sandstones investigated here) and with arbitrarily chosen values of $S_{wir} = S_{nwr} = 0.2$ (note $S_{nwr} = 0$ for drainage) (Figure 3.15 a, b). We observe that, depending on the parameters used, the $Q_{rs}$ model presented here yields both monotonic and non-monotonic variations of $C_r$ with $S_w$ as observed experimentally (Figure 2.4). In contrast,
the 1/$S_w$ model predicts only monotonic variations in $C_r$. Complex behaviors as predicted in Figure 3.15 are also consistent with model predictions [Jackson, 2010; Jougnot et al., 2012] and seismoelectric laboratory measurements [Bordes et al., 2015]. Values of $C_r$ can exceed 1 at partial saturation, although we cannot reproduce the large enhancements in $Cr$ at partial saturation observed by Allègre et al. [2010].

We suggest that the broad range of behaviour predicted here for reasonable models of $k_r$, $\sigma_r$ and $Q_{rs}$ may explain the contrasting and inconsistent experimental data reported to date (Figure 2.4). Small variations in the pore-scale distribution of the fluid phase cause variations in $k_r$, $\sigma_r$ and $Q_{rs}$ that yield complex and often non-monotonic behavior of $C_r$. Indeed, our results suggest that the relative streaming current charge density may be similar for a given displacement (drainage or imbibition) and wetting state across different samples; variability in the relative streaming potential coupling coefficient arises primarily in response to variations in relative permeability and electrical conductivity.

### 3.4.4 Implications for subsurface flow monitoring using the SP and SE methods

We propose here a simple empirical model for the saturation dependence of the relative streaming current charge density based on data interpreted from experiments on water-wet sandstones. These are the first data to be obtained using a method that makes no assumptions about the pore-space geometry. The available data suggest that variability in $Q_{rs}$ across water-wet sandstones samples is small, but that it is important to account for hysteresis between drainage and imbibition. However, further data are required to confirm this. Assuming a simple inverse water saturation function for $Q_{rs}$ does not account for hysteresis, yet such an approach has been applied in SP and SE studies of water-oil displacements which are dominated by forced or spontaneous imbibition rather than drainage ([e.g. Woodruff et al.](#))
The effect of wettability will be particularly important when predicting or modelling $Q_r(S_w)$ (and hence $C_r$): Jackson [2010] used a capillary tubes model to show that wetting state will significantly impact on $Q_r(S_w)$ if there is a difference in charge separation at the oil-water and mineral-water interfaces, while Jackson and Vinogradov [2012b] measured streaming potential in water- and oil-wet carbonate samples at the residual oil saturation, and found that the streaming current charge density in the oil-wet sample was zero within experimental error. The saturation dependence of the streaming potential is therefore best determined by fitting a model (such as equation 3.11) for the relative streaming current charge density to experimental data that specifically replicate the conditions of interest, particularly drainage versus imbibition and the wetting state. The saturation dependence of the streaming potential coupling coefficient is controlled by the saturation dependence of the relative permeability, electrical conductivity and streaming current charge density, all of which depend on the conditions of interest and how these control the pore-scale distribution of the fluid phases.

Conclusions

We present (i) a method to interpret measurements of streaming potential in multiphase flow during unsteady-state displacements of one fluid by another, and (ii) application of the method to determine the saturation dependence of the streaming potential coupling coefficient ($C$) and streaming current charge density ($Q$) using experimental data obtained during drainage and imbibition in two different sandstone core samples. We find that $C$ exhibits hysteresis between drainage and imbibition, can exhibit significant non-monotonic variations with saturation, is non-zero at the irreducible water saturation, and
can exceed the value observed at $S_w = 1$. Moreover, $Q_s$ also exhibits hysteresis, increasing with decreasing $S_w$ but not as $1/S_w$ as is often assumed. The variation in $Q_s$ with $S_w$ is very similar for a given displacement for the two sandstone samples investigated and we propose a simple empirical model for water-wet sandstones. The results presented here can be used to help interpret SP and SE measurements obtained in partially-saturated subsurface settings.

We find that the streaming current charge density increases with water saturation ($S_w$) during both drainage and imbibition, but the relative streaming current charge density ($Q_{rs}=Q(S_w)/Q(S_w=1)$) is not given by $1/S_w$ as is often assumed. Rather, the variation of relative streaming charge density $Q_{rs}$ with $S_w$ depends on the pore-level distribution of water, which is controlled by rock texture and wettability and is different for the two sandstone samples investigated here. Our results show that $C(S_w)$ exhibits complex, non-monotonic behavior, depending upon the (monotonic) saturation dependence of relative permeability, relative electrical conductivity and relative streaming current charge density.
Chapter 4 Pore network modelling of streaming potential

4.1 Introduction

Pore network models represent the void space of rocks or soil as a network of pores connected by throats, which are assigned some idealized circular or polygonal geometry. Pore network modelling can describe pertinent physical processes and multiphase fluid configurations at the pore scale. It is a promising way to describe multiphase streaming potential at the pore scale in realistic models of geological porous media. This section will give a brief introduction to network modelling and a short overview of relevant previous studies.

Network models were first constructed by Fatt [1956] who investigated the analogy between flow in porous media and a random resistor network. Realistic network models derived from real porous media have been introduced in the last two decades. Bryant and Blunt [1992] extracted network models from a random close packing of equally-size spheres. Successful predictions of relative permeability and electrical conductivity were obtained to compare with experimental data. However, the network was still based on a simple topology while rocks have more irregular structure.

In order to capture the connectivity of a real rock and reproduce this in the subsequent network model, it is necessary to obtain a three-dimensional representation of the rock itself. There are several ways to construct a three-dimensional (3D) description of the pore space. The pore space description can be directly generated using X-ray micro-tomography in which pore space can be imaged in a few microns [Dunsmuir et al.; Spanne et al., 1994; Coker et al.,
This method is direct, accurate and widely used in geologically related research and visualization of multiphase flow and reactive transport in geological porous media [e.g. Ketcham and Carlson, 2001; Andrew et al., 2014; Menke et al., 2014; Lai et al., 2015; Lin et al., 2016a; Lin et al., 2016b]. Limitations of X-ray micro-tomography are scale and the limited spatial resolution, such as carbonates where sub-micron-scale images may be required [e.g. Mangane et al., 2013; Soulaine et al., 2016]. Another approach is to use a series of two dimensional sections to form a 3D image. Even though this method is more laborious, 2D sections are often readily available in core analysis. The porosity and two-point correlation function, which measures the probability of two separate points by a distance within the same phase or pore, can be measured from the 2D sections to generate the 3D network with the same statistical properties. However, it is difficult to describe the topology of the porous medium through matching two-point statistics alone. Stochastic reconstruction algorithms have been developed to capture the underlying structure of complex porous medium, for example, Gaussian field, simulated annealing and multiple-point statistics approaches [e.g. Adler and Thovert, 1998; Yeong and Torquato, 1998; Manwart et al., 2000; Okabe and Blunt, 2004; Jiang et al., 2007].

The porous media can also be reconstructed by modelling the actual rock forming process. Figure 4.1 (a) demonstrates a 3D image of the pore space at a resolution of 3\(\mu\)m, produced by Øren and co-workers [Øren et al., 1998; Øren and Bakke, 2003]. They generated a network from micro tomographic images and simulating the geological processes including sedimentation, compaction, diagenesis and the addition of clays. From the 3D-voxel based representation as shown in Figure 4.1 (a), it is possible to construct a topologically equivalent network of pores connected by throats as shown in Figure 4.1 (b). The pores and throats within the network are assigned volumes, conductance, inscribed radii and shape factors that match the basic physical properties of the reconstructed pore spaces. This geological-process-
based approach is not suitable for carbonates and more complex systems that involve microporosity or multi sedimentary process.

Figure 4.1: Representations of the pore space of sandstone samples [Øren et al., 1998]: (a) Three-dimensional image of a sandstone; (b) a topologically equivalent network representation.
The shapes of pores and throats are very important in defining the fluid distributions within each pore to compute the transport properties. A circular shape pore or throat is not able to contain more than one phase. In real rock, the pore space is highly irregular with wetting layers remaining in the grooves and crevices of roughness in the pore space due to capillary pressure. These wetting layers have little effect on the saturation or flow, but have a significant impact on wetting phase connectivity in displacements. It is not feasible to reproduce every irregular pore space directly. Consequently, some simple shapes are assigned to the pore and throat cross-sections that accommodate wetting layers.

A variety of shapes have been proposed to represent pore spaces such as squares, triangles, and star shapes. Mason and Morrow [1991] defined a dimensionless shape factor, $G$, for each pore and throat. This is defined as the ratio of the average cross-sectional area to the perimeter length squared. A more irregular pore will then have a lower shape factor, which yields more wetting fluid retained in sharp corners and higher conductivity in the wetting layers. Then elements in the network can be defined to have circular, square or triangular cross-sections with the same shape factor as reconstructed pore space of real rocks. In most cases, the pores and throats have a triangular cross-section. Øren et al. [1998] assumed that the wetting layers are connected to adjacent pores and throats, which contributes to the connectivity spans the entire network. This assumption is also applied in the network models used here.

The wettability of porous media plays a significant impact on fluid configurations within pore spaces. For multiphase flow, the most wetting fluid always tends to resident the smallest pore space while the least wetting fluid tends to stay in the largest pore space. Hence wettability controls multiphase flow and phase trapping.
Pore-scale network modelling has been widely used to study the wettability effects on relative permeability. But most of them used a fairly simple network model that pore shapes and wetting layers are generally neglected in the pore space [e.g. McDougall and Sorbie, 1995, 1997; Dixit et al., 1999; Dixit et al., 2000]. A wettability classification system was introduced by McDougall and Sorbie [1995] to relate recovery from mixed wet systems to the fraction of oil-wet elements.

Kovscek et al. [1993] reproduced high oil recovery efficiency in mixed-wet rocks displacements conducted by Salathiel [1973] by defining a distribution of star-shaped network elements. In their study, only the interface in direct contact with oil will be altered to be oil-wet with the corners remaining water-wet. They pointed out that fluid films that are generated in different pore shapes is vital for wettability. Based on the same assumption, Blunt [1997] used square elements for both pores and throats, which allows him to explicitly model multiple wetting fluid films in each element and provided a better understanding of mixed wet and oil wet reservoir systems.

The wettling state can be broadly identified as water-wet, oil-wet or intermediate-wet in terms of contact angle where the contact angles are less than 90°, greater than 90° or around 90° respectively. Contact angles are affected by wettability alteration and the direction of flow. During primary drainage (invasion of non-wetting oil or gas), the parts of pores and throats that have been invaded by oil may alter their wettability, whereas the corners where water still resides and pores that are completely water saturated will remain water-wet. The degree of wettability alteration depends on the mineralogy of rock surface, the composition of the oil and brine, and the capillary pressure imposed during primary drainage [Radke et al., 1992; Buckley et al., 1998]. Within a given pore or throat, oil may stay in the center, or may be sandwiched by water layers in the corners. In terms of displacement, advancing contact
angles are typically larger than receding contact angles due to surface roughness [Morrow, 1975].

A brief description of how a network model computes transport and electrical properties will be provided in the methodology section. Local capillary equilibrium and the Young-Laplace equation will be used to determine the fluid configurations within pores of different shapes for a given pressure difference between phases. Capillary pressure will control the fluid configurations. In a two-phase displacement of one fluid by another, the pressure drop is applied to one of the phases whilst holding the other fixed to calculate the permeability of that phase, which yields an increase in capillary pressure. The polygonal pores and throats will be filled in order of increasing capillary entry pressure. A succession of equilibrium fluid configurations can be computed in the network.

In primary drainage, all pores are initially only saturated with water, pore scale displacements can only occur through piston-like displacement, in which pore or throat center can only be occupied if its adjacent pore or throat containing oil. During imbibition (waterflooding), the pore scale displacement become more complex, piston-like displacement, cooperative pore body filling and snap off are three possible filling processes [e.g. Øren et al., 1998; Blunt et al., 2002; Valvatne, 2004]. Saturation of one phase will be calculated via dividing the volume of that phase in each pore and throat by the total volume occupied by fluids in all pores and throats each time a new equilibrium configuration is reaches.

Empirical relations of hydraulic conductance for each phase in each pore and throat will be used to define the flow of each phase in terms of the pressure difference between pores. By applying conservation of mass in the network, transport properties such as flow rate, pressure gradient and relative permeability can be computed. Furthermore, instead of pressure
difference, electrical properties can be computed in terms of voltage difference in an analogous way as transport properties.

Figure 4.2: Comparison between experimental and predicted relative permeability for reservoir sandstone. (a) The Larger pores become preferentially oil wet. (b) The smaller pores become preferentially oil wet. (c) The oil wet pores are spatially correlated [Valvatne and Blunt, 2004].

Using 3D pore network models generated from real rocks, experimental relative permeability and capillary pressure data for two phase displacements in initially water-wet sandstones have been successfully predicted [e.g. Blunt et al., 2002; Jackson et al., 2004; Valvatne and Blunt, 2004]. Moreover, Jackson et al. [2004] and Valvatne and Blunt [2004] predicted the relative permeability for mixed wet reservoir sandstones that usually do not have available capillary pressure data from steady state measurements, and compared the predicted data with experimental data (Figure 4.2). The experimental wetting state was fairly well predicted in all cases (Figure 4.2 (a, b, c)), and the only difference between simulation cases is how wettability is characterized at the pore scale. Estimations of capillary pressure, absolute and relative permeability using pore-network models have been demonstrated by a number of researchers in sandstones and carbonates [Bryant and Blunt, 1992; Øren et al., 1998; Blunt et al., 2002; Jackson et al., 2004; Valvatne and Blunt, 2004; Tørå et al., 2012; Blunt et al., 2013].
At present, there are few published studies investigating electrical properties using realistic geological network models. These have presented promising results in describing electrical properties of geological porous media with pore-scale modelling approaches [e.g. Man and Jing, 1999; Tsakiroglou and Fleury, 1999; Man and Jing, 2000, 2001; Dalla et al., 2004; Valvatne and Blunt, 2004]. Man and Jing [2000] used a relatively realistic grain boundary pore shape to simulate the generic behavior of sandstones for two-phase flow with various wetting scenarios, which presented a close agreement with electrical resistivity measured in experiments. Based on a synthetic, non-overlapping and gravitationally stable packing-of-spheres network model, Dalla et al. [2004] simulated the flow of electrical charge via finite difference discretizations within the two-fluid and solid pore-scale distributions, and derived the bulk electrical conductivity at different saturations, which demonstrated a reasonable agreement with measured data (Figure 4.3).

![Simulated and experimental data](image)

**Figure 4.3**: Simulated bulk electrical resistivity and experimental data from Binley et al. [2002] as a function of water saturation [Dalla et al., 2004]. The solid line shows Archie’s equation with \(n=1.13\).
Bernabè [1998] first proposed an idea that using a two dimensional, 30 by 30 square networks of cylindrical capillaries with various radii oriented at 45° to investigate the single phase streaming potential distributions and behaviour for heterogeneous networks. Although the structure of cylindrical capillaries networks is simple, it is the first insight into the behaviour of streaming potential at the pore scale. Based on these successful predictions and calculations of multiphase flow properties achieved using pore network models to date, pore network modelling is a very attractive approach. We propose a methodology in this chapter to investigate and quantify the streaming potential during multiphase flow in real geological porous media at pore level by using pore network modelling approaches.
4.2 Methodology

4.2.1 Calculation of transport properties and electrical properties

Based on the work of Valvatne and Blunt [2004], we estimate transport properties in the same approach at any point during the displacement in this study. To compute the absolute and relative permeability, fluid conductance of each phase in each pore or throat needs to be defined. The flow rate $q_{p,ij}$ of phase $p$ between two pores $i$ and $j$ can be defined by:

$$q_{p,ij} = \frac{g_{p,ij}}{L_{ij}} (P_{p,i} - P_{p,j}) \quad \ldots \ (4.1)$$

where $g_{p,ij}$ is the fluid conductance between pore $i$ and $j$, $P_{p,i}$ is the pressure of phase $p$ at the centre of pore body $i$, while $L_{ij}$ is the length between two pores (centre to centre). The fluid conductance $g_p$ for single phase laminar flow in a circular pore can be computed from Poiseuille’s law:

$$g_p = \frac{1}{2} \frac{A^2 \Delta} {\mu_p} \quad \ldots \ (4.2)$$

where $\mu_p$ is the viscosity of phase $p$, $A$ is the cross-sectional area of the model. For multiphase flow in irregular pores and throats, exact analytic results are not possible, and empirical expressions are derived from solutions of Stoke’s flow for different fluid configurations. A detailed mathematic description of the calculation of conductance of water and oil layers can be found in the thesis of Valvatne [2004].

The average conductance between two pores then can be defined as the harmonic mean of each individual conductance. Then a linear set of equations will be defined from equation (4.1). It is assumed all fluid interfaces are frozen in place when the pressure of each phase is
computing separately at each equilibrium configuration. By imposing mass conservation at every pore \( i \),

\[
\sum_{j} q_{p,ij} = 0 \quad \text{(4.3)}
\]

the pressure difference of phase \( p \) across the entire network can be solved. In the network modelling software used here, the system of equations is solved using an algebraic multigrid solver [Ruge and Stueben, 1987]. When the pressures at either side of any cross-sectional plane are obtained, the total flow rate can be computed based on equation (4.1). The absolute permeability \( K \) can be found:

\[
K = \frac{\mu q t L}{A(P_{inlet}-P_{outlet})} \quad \text{(4.4)}
\]

where \( q_t \) is the total flow rate of single phase, \( L \) is the length of the model. \( P_{inlet} \) and \( P_{outlet} \) are the potential at the inlet and outlet interface. Therefore, the relative permeability at any point during displacement can be computed using the same pressure drop as for single phase flow. The relative permeability is defined as:

\[
k_{rp} = \frac{q_{mp}}{q_t} \quad \text{(4.5)}
\]

where \( q_{mp} \) is the total flow rate of phase \( p \) during multiphase flow under the same pressure difference. Saturation is computed for a given equilibrium fluid configuration within pores and throats that is controlled by the prevailing maximum in capillary pressure. At each time step, water and oil saturations, relative permeability and the capillary pressure are calculated in response to pressure boundary conditions at the inlet and outlet faces and periodic boundaries on the other faces. Drainage is assumed to complete when a target capillary pressure or saturation has been reached or when all pore spaces have been invaded by oil. To match the measured irreducible water saturations after drainage, the clay content will be
adjusted to simulate the different values of irreducible water saturations. As this part of water is assumed to be within the clay content, they do not flow. This immobile water saturation only contributes to the conduction current, but does not contribute to the streaming current. This is still a problem to properly simulate irreducible water saturation within clay and micro-porosity for complex sandstone such as St. Bees with a relatively high irreducible water saturation of 0.35.

When the pressure drop is replaced by a voltage drop, fluid flow is replaced by electrical current. The formation factor is computed analogy to absolute permeability:

\[ F = \frac{R_0}{R_w} \]  \hspace{1cm} (4.6)

where \( R_0 \) is the computed resistivity at fully water saturated network and \( R_w \) is the water resistivity. The resistivity of the network is defined from Ohm’s law,

\[ R_0 = \frac{A \Delta U}{l_{ts} I_{ts}} \]  \hspace{1cm} (4.7)

where \( \Delta U \) is the imposed voltage drop and \( l_{ts} \) is the total single phase flow of current. The electrical conductance between two pores is assumed to be the function of the cross sectional area that occupied by the conducting water (\( A_w \)), assuming water is the only conductive fluid:

\[ g_e = \frac{A_w}{R_w} \]  \hspace{1cm} (4.8)

Therefore, the electrical potential distribution across the network can be computed in an analogous way to the pressure field calculated by equations (4.1-4.2), by imposing electrical charge conservation. The resistivity index is analogy to relative permeability, given by

\[ RI = \frac{R_t}{R_w} \]  \hspace{1cm} (4.9)

where \( R_t \) is the resistivity at any given water saturation.
Clay minerals are typically found to also conduct electricity. In this study, we take clay conductivity into account by defining the clay volume and clay resistivity following the approach of Valvatne [2004] who described the clay distribution by defining a continuous correlation function with pore or throat radius or distributed the clay content uniformly across the network. Furthermore, surface conductivity is defined proportional to the perimeter of water content in each pore and throat. Therefore, electrical conductivity is composed of water conductivity, clay conductivity and surface conductivity.

4.2.2 Calculation of streaming potential

To estimate the streaming potential it is required to solve for the induced voltage \((U_{\text{inlet}} - U_{\text{outlet}})\) at any point during displacement for the imposed pressure drop \(\Delta P\) across the entire network. The convection current induced by the flow of water is termed the streaming current \((I_s)\) and the conduction current \((I_c)\) is established simultaneously and correspondingly to maintain electrical neutrality. Charge conservation means that no electrical charge is allowed to accumulate at a given pore \(i\) so,

\[
\sum_j I_{t,ij} = 0 \quad \cdots \quad (4.10)
\]

where \(j\) runs over all the pores connected to pore \(i\). The total electrical current \(I_{t,ij}\) between pore \(i\) and \(j\) is given by

\[
I_{t,ij} = -M_{ij}\Delta P_{ij} - S_{ij}\Delta U_{ij} \quad \cdots \quad (4.11)
\]

where the first term \(M_{ij}\Delta P_{ij}\) is the streaming current and \(M_{ij}\) represents the streaming coupling term while the second term \(S_{ij}\Delta U_{ij}\) is the conduction current and \(S_{ij}\) is the electrical conductance; \(\Delta U\) is the voltage drop.
Each connection between pore $i$ and $j$ is composed of pore body $i$, throat and pore body $j$ as shown in Figure 4.4. The total electrical current ($I = I_e + I_c$) remains constant through the connection between pore $i$ and pore $j$ because of the electrical continuity. The streaming potential drop between two pore bodies is:

$$\Delta U_{SP,ij} = \sum (\Delta U)_k = \Delta U_i + \Delta U_{throat} + \Delta U_j, \quad k = i, \text{throat, } j \quad \cdots \quad (4.12)$$

Therefore, the total streaming potential drop between pore $i$ throat and $j$ can be computed as:

$$\Delta U_{SP,ij} = \sum \frac{I_{tk}}{S_k} + \sum \frac{M_k \Delta P_k}{S_k} \quad , k = i, \text{throat, } j \quad \cdots \quad (4.13)$$

Since $I_{ti} = I_{t,throat} = I_{tk,j} = I_{t,ij}$ remains constant, equation (4.13) can be expressed as:

$$\Delta U_{SP,ij} = I_{t,ij} \sum \frac{1}{S_k} + \sum \frac{M_k \Delta P_k}{S_k} \quad \cdots \quad (4.14)$$

Hence, the total electrical current between pores bodies $i$ and $j$ is:

$$I_{t,ij} = \frac{\Delta U_{SP,ij}}{\sum \frac{1}{S_k}} + \frac{\sum \frac{M_k \Delta P_k}{S_k}}{\sum \frac{1}{S_k}} \quad \cdots \quad (4.15)$$

Figure 4.4: Streaming potential between two pores: pore body $i$, throat and pore body $j$.

The electrical conductance $S_{ij}$ is computed for each pore and throat when we are solving for the electrical conductivity. $\Delta P_{ij}$ is solved when we compute the relative permeability as described in section 4.2.1. The boundary conditions to calculate the streaming potential are a fixed electrical potential ($U$) at the outlet and no current through any boundaries ($I_{t, inlet} = 0$).
We are able to solve the $\Delta U_{SP,ij}$ across over the pore network by combing equations (4.10) and (4.15) with a properly defined streaming coupling term $M_i$ for each pore and throat. The following paragraphs will describe the streaming coupling terms for multiphase flow in polygonal pores and throats.

Zhang et al. [2015] is the only paper at present to model streaming current using a 3-D pore network model. They solved the electrical potential and net charge density distribution in a single capillary, and then computed the velocity field by solving the Navier-Stokes equation. They further calculated fluid and electrical coefficient ($M_{ij}$ and $S_{ij}$ in equation (4.6)) in a single capillary. This scheme can also be applied to capillaries with arbitrary geometries. However, when they extended the fluid and electrical coefficients in a single capillary to a 3-D pore network extracted from micro-CT images of core samples, they used the harmonic mean to average fluid and electrical coefficients for connected pores as shown in equation (15) in their paper. This is a reasonable assumption when fluid and electrical coefficients are non-zero and variations in the coupling terms are not large between pores. However, fluid and electrical coefficients can vary a lot and the streaming coupling term can have opposite polarity at different surfaces that have different wettability and interfaces that contacts with different fluids as observed by Jackson et al. [2016]. When the streaming potential coupling terms of two connected pores have different signs because the local zeta potentials have opposing polarity, the harmonic mean approach is inappropriate that cannot be applied for the average of negative values. Therefore, the scheme proposed by Zhang et al. [2015] is not appropriate for the study of streaming potential during multiphase flow where there are variations in the polarity of the surface charge or zeta potential. The next section will introduce the description of streaming current at each individual pore and throat.
4.2.2.1 Description of streaming current

The streaming current can be calculated under thin and thick double-layer assumptions. The thick double layer assumption requires that the thickness of the diffuse layer as we introduced in Chapter 2.1 is comparable to the radius of the capillary so that the excess charge is uniformly distributed across each capillary, while the thin double layer assumes the thickness of the diffuse layer is much less than the capillary radius. The thick double layer assumption is valid in some cases such as mudstone [Leinov and Jackson, 2014], but here we assume a thin double layer. Based on the thin double layer assumption, Hunter [1981a] derived the equation for the streaming current for a single capillary tube with circular cross-sectional area.

We apply the revised equation to pore body \(i\) as below:

\[
I_{s,i} = -M_i(\Delta P)_i = \frac{\epsilon \zeta_{wri}/owi}{2\mu} \frac{P_r r \Delta P_i}{l_i} \quad \ldots (4.16)
\]

in which \(\zeta_{wri}/owi\) is the zeta potential at the water-rock or oil-water interface; \(P_r\) is the perimeter of water-rock or oil-water interfaces and \(r\) is the corresponding inscribed radius of the interfaces. For a circular capillary with \((P_r r)/2 = \pi r^2\), equation (4.16) is same as the streaming current equation for a single capillary derived by Hunter [1981a]. As the shape factors of pores and throats increases, equation (4.16) will slightly overestimate the streaming current because the product of perimeter and the inscribed radius will overestimate the cross sectional area as the pores and throats become more irregular. However, this approximation will have no effect on the conductance current.

Since zeta potential is strongly correlated with the mineral interface, wettability and brine composition, it is reasonable to compute different interface perimeters and the corresponding inscribed radius allowing different zeta potentials in each pore and throat instead of the fraction of the cross sectional area occupied by the phase with single zeta potential for all interfaces [Jackson and Vinogradov, 2012a; Mahani et al., 2015; Alroudhan et al., 2016].
Furthermore, Jackson et al. [2016] presented experimental data suggesting that oil-wet mineral surfaces can be positively or negatively charged in aged carbonate samples. Hence, we will also investigate strongly water-wet carbonates during drainage and aged oil-wet carbonates with different initial water saturations during imbibition to mimic experimental data.

In multiphase conditions, an individual pore or throat may contain both oil and water. Expressions for fluid distributions in element pore or throat centres and distribution in water and oil layers are needed to compute the perimeters and inscribed radius of each part. Because we will also consider wettability alteration, polygonal pores and throats are classified as strongly water-wet elements and oil-wet or mixed-wet elements during imbibition. In the next section, we will discuss how to compute different perimeters and the corresponding inscribed radii for water-wet and oil-wet polygonal pores and throats.

4.2.2.2 Computing perimeters and corresponding inscribed radius

Prior to drainage, all pores and throats are initially water saturated and strongly water-wet. In most network models, only a very few pores and throats have a circular or square cross section. All other pores and throats are represented by triangles as shown in Figure 4.5 (a). During primary drainage, oil enters the pore network. Oil invades in an invasion percolation processes, entering the centres of the largest connected pores and throats and water remains in the corners. Figure 4.5 (b) shows one single corner of a triangular pore occupied by two phases (blue water and white oil). A fraction of the pores and throats will remain water-saturated during, and at the end of, primary drainage.
Figure 4.5: (a) Cross-sectional view of water in a water-wet pore; (b) cross-sectional view of a single corner in a triangular pore. $L_{w r}$ represent the total water-rock interface in a single corner; $\beta$ is the half contact angle; $a_i$ is the contacting interface on one side of the corner; $L_{ow}$ is the oil-water interface; $r_{ow}$ is the corresponding inscribed radius of the oil-water interface.

For water-wet pores only containing water, the water-rock contacting perimeter $P_{r-wr}$ is computed as the perimeter of the pore via equation (4.17):

$$P_{r-wr} = \sqrt{\frac{A_i}{G}}$$

where $A_i$ and $G$ is the area and shape factor of pores and throats respectively. The corresponding radius is the inscribed radius of the polygonal pore.

For water-wet elements containing both water and oil, $L_{wr}$ as shown in Figure 4.5 (b) is the total water-rock contacting interface in each corner, which can be computed in terms of pore radius, curvature, shape factor and contact angle as derived by Valvatne [2004] in his paper equation (3.12). Because $L_{wr}$ is not the perimeter of a closed polygon, the corresponding radius in this corner is then assumed to be the inscribed radius of the water in the corner. As shown in Figure 4.5 (b), the contact angle is $\theta$, and the water-rock contacting length in one side is $a_i$. The corresponding inscribed radius $r_{wc}$ of water contend in a single corner can be computed by the half corner angle $\beta$, contact angle $\theta$ and $a_i$ using equation (4.18–4.20).
\[ r_{ow} = \frac{1}{\cos(\theta + \beta)/(a_i \sin \beta)} \]…… (4.18)

where \( r_{ow} \) is the radius of curvature of the oil-water interface (\( L_{ow} \)) that is shown in Figure 4.5 (b).

\[ H_c = a_i \cos \beta + r_{ow} \cos(90 - \theta - \beta) \]…… (4.19)

where \( H_c \) is the length from the corner to the centre of the inscribed circle with the radius \( r_{ow} \),

\[ r_{wc} = \frac{(H_c - r_{ow}) \sin \beta}{1 + \sin \beta} \]…… (4.20)

When we compute the streaming current in a single pore or throat that results from charge separation at the water-rock interface using equation (4.18-4.20), we sum the product of \( L_{wr} r_{wc} \) in each corner as \( \sum_i (L_{wr} r_{wc}) \).

\( L_{ow} \) is the oil-water interface in a single corner and can be computed in terms of capillary pressure (\( P_c \)), interfacial tension (\( \sigma_{ow} \)) and contact angle \( \theta \) derived from the Young-Laplace equation:

\[ L_{ow} = \frac{2\sigma_{ow}}{P_c} \left( \frac{\pi}{2} - \theta - \beta \right) \]…… (4.21)

The streaming current in a single pore or throat induced by charge separation at the oil-water interface can be computed in terms of the sum of product of \( L_{ow} R \) in each single corner \( R \sum_i L_{ow} \), in which \( R \) is the radius of the pore or throat.

Therefore, with zeta potentials defined at the water-rock and water-oil interfaces (denoted \( \zeta_{wr} \) and \( \zeta_{ow} \) respectively), we can compute the streaming coupling term \( M_i \) and hence the streaming current using equation (4.16) that is induced by charge separation at the water-rock and water-oil interfaces in each pore and throat for any fluid configuration in all pores and throats in pore network. The total streaming current is the sum of those two components.
Since we will also investigate displacements after aging and wettability alteration, we assume that the wettability of pore surfaces in direct contact with oil may be altered after aging, while the corners of pores that are still occupied by water will remain strongly water-wet as shown in Figure 4.5. We model wettability alteration by changing the contact angle (water-wet is $<90^\circ$, intermediate-wet is close to $90^\circ$ and oil-wet is $>90^\circ$). After aging, the three main displacement processes during imbibition are piston-like displacement, cooperative pore body filling and snap off [e.g. Øren et al., 1998; Blunt et al., 2002; Valvatne, 2004]. Three possible fluid configurations are illustrated in Figure 4.6.

When oil is in the pore centre and water remains in the corners, the water-rock perimeter is the total corner length $L_{wr}$ that remains strongly water-wet and the corresponding inscribed radius can be computed using equations (4.18-4.20) as in the water-wet case. Calculations of the length of oil water interface will be exactly the same as we described in the water-wet case with altered contact angles.

Figure 4.6: Possible fluid configurations modified from Valvatne and Blunt [2004] and Jackson et al. [2016] (a) Initially strongly water-wet pore only filled with water; (b)
After primary drainage, the part of pore in contact with oil may be altered to oil-wet, which is highlighted by bold lines $b_i$; (c) During imbibition, the pore can be completely filled with water again, but part of it can retain altered wettability; (d) Oil may become sandwiched between water in the corner and the centre. Figure d shows postulated wettability of water-rock and oil-water interfaces in polygons saturated with water and oil. Oil may have a negatively charged oil-brine interface or a positively charged interface as shown respectively.

When a pore is only occupied by water but part of the pore has been altered to be oil-wet, the water-rock perimeter will only include the corner length that remains water-wet. The oil-wet length $b_i$, is treated as the oil-wet water-rock interface $\sum b_i$, and the inscribed radius of oil-wet water-rock interface will be computed for each corner using equation (4.18-4.20). Furthermore, we must define a third zeta potential $\zeta_{wr}$ to denote the oil-wet, water-rock interface that reflects the changed properties of the mineral surface after wettability alteration. The corresponding radius of the non-closed shape composed by water-rock interfaces $\sum b_i$ is the pore or throat inscribed radius.

When the oil is sandwiched between water in the corners and water in the centre of a pore as shown in Figure 4.6 (d), we compute the water-rock and oil-water perimeters and inscribed radii (two oil-water interfaces in each single corner) in the same way as the case we have discussed earlier where oil is in the centre and water remains in corners. Furthermore, the perimeter of oil-wet water-rock interfaces are computed as $\sum b_i$.

With predefined $\zeta$ representing water-wet water-rock interfaces, oil-wet water-rock interfaces, and oil-water interfaces, we can compute the streaming current based on equation (4.16) induced by the flow of water in each pore and throat for any configuration of water-wet, oil-wet or mixed-wet pores in the network. In total, streaming current in a single polygonal pore and throat needs to be computed in terms of wettability and interfaces. Then a linear set of equations will be defined from equation (4.15). By imposing electrical charge conservation at
every pore $i$ as shown in equation (4.10), the electrical potential difference across the entire network can be solved using the same algebraic multigrid solver [Ruge and Stueben, 1987].
4.2.3 Network model of St. Bees sandstones

In the last chapter, we interpreted experimental measurements of streaming potential during unsteady-state displacements in two sandstone samples (Stainton and St. Bees) using an inversion approach. Pore network modelling can describe the behaviour of the coupling coefficient and streaming current charge density based on a pore-scale model of flow and charge transport. In order to compare the interpreted inversion results with the pore network modelling results, in this section we will outline the image acquisition and processing to construct a pore network model of the St. Bees sandstone sample.

Apparatus and sample preparation

The sample comprised a cylindrical core of 6 mm in diameter and 10 mm in length. The core sample was put into a Perspex holder and was scanned using a Versa XRM-500 X-Ray Microscope (Zeiss X-Ray Microscopy, Pleasanton, CA, USA) as shown in Figure 3 of Lin et al. [2016a].

Image acquisition

3D images were reconstructed using proprietary software on the Versa system. The voxel size (resolution) of the image is 5 µm. The dimension of the entire scan is around $1000^3$ voxels. The scanning volume was reconstructed from a set of 2001 projections, taking about 2 hours to acquire.

Image processing

After image acquisition, the image was filtered using a non-local mean edge preserving filter [Buades et al., 2005; Buades et al., 2008]. The image was then segmented into two phases, namely the grain phase and pore phase. The segmentation was carried out using a watershed algorithm computed off a seed generated using a 2D histogram [Vincent and Soille, 1991;
Jones et al., 2007; Andrew et al., 2014]. The image processing workflow for the St. Bees sample is shown in Figure 4.7.

Figure 4.7: A) Entire scan of St. Bees sandstone with dimension of 2000³. B) Sub-volume image with dimension of 1000³. C) The sub-volume image after applying non-local mean filter. D) The red area represents pores and blue area represents grains. E) Segmented image.
Network Extraction

The network extraction algorithm is based on a maximal ball algorithm by Dong and Blunt [2009] and Raeini et al. [2017]. In this algorithm, the distance of void voxel from the nearest solid voxel is first obtained. The distance map is calculated as the distance from the void voxel centre to the centre of the nearest solid voxel minus half the voxel length. Then maximal balls are assigned to each voxel on the medial axis of the void space -- the set of points equidistant from at least two solid voxels. The locations of pore centres are defined as the local maximal of the distance map which is obtained by generating a hierarchy of the maximal balls. The maximal-ball hierarchy is obtained by finding the pairs of maximal-balls that partially overlap and assigning the bigger ball as the parent of the smaller maximal-ball. The maximal-balls that have no parent are located at local maxima of the distance map and are recorded as pore centres. Pore throats are identified using a water-shed segmentation of a distance map. Throat surfaces are obtained by collecting all the voxel faces connecting each two adjacent pores. The voxel face with the largest value of the distance map is defined as the throat centre and its distance map defines the throats inscribed radius.

The length and volume between each pore and throat centres is divided based on their distance to the pore/throat centre so that the resulting single-phase properties, formation factor and absolute permeability, match that of direct simulations closely for some benchmark cases. The voxels are assigned to the throat if their distance to the throat centre is less than 0.25 times the distance between the pore and the throat centre. The shape factor, $G$, is computed using the following equation:

$$ G = \frac{R^2}{4A} \ldots (4.22) $$

This equation produces the same value as the equation used by Øren et al. [1998] for triangular elements, which is the dominant type of element in the network. The advantage of
this equation, however, is that it is less sensitive to the surface roughness and image resolution [Raeini et al., 2017].
4.3 Results and Discussion

This section is composed of three parts. First, the streaming-potential behaviour obtained using pore network modelling was tested using a Berea sandstone network. Predicted relative permeability for primary flooding cycles will be first compared to steady-state experimental data by Oak [1990] to obtain an appropriate range of intrinsic contact angles. Then predicted electrical properties, streaming potential and streaming current charge density behaviours will be computed and discussed during drainage and imbibition both in water-wet Berea sandstone. Second, we mimicked the experimental process of Jackson et al. [2016] in a carbonate sample to investigate the relationship between measured zeta potential and wettability. Finally, the St. Bees pore network described previously was used to investigate the coupling coefficient and streaming current charge density and compare the model results against the inversion results shown in the last chapter.

4.3.1 Berea sandstone network model

Berea sandstone is a simple granular system consisting of quartz with minor amounts of dolomite and clays. This sandstone has been widely used for core analysis because of its fine grained and well understood characteristics bedding [Okabe and Blunt, 2004]. The Berea network model we are using here was extracted by Valvatne and Blunt [2004] and the code can be accessed from the Imperial College website. The properties of 3D network model were listed in Table 4.1. Before we make any prediction for multiphase streaming potential, we first tested the ability of pore network modelling of predicting the single phase streaming potential at fully water saturated conditions.

The single phase coupling coefficient was first calculated when the Berea network model was only saturated with water and strongly water-wet. The predicted single phase coupling coefficient of fully saturated Berea network is $1.96273 \times 10^{-8}$ V/Pa. When surface conductivity
is negligible, the Helmholtz-Smoluchowski equation can be used to compute the apparent zeta potential across the network [Hunter, 1981a]:

\[
\zeta = \frac{C \mu_w \sigma_w}{\varepsilon_w} \quad \ldots \quad (4.25)
\]

where \( \sigma_w \) is the electrical conductivity of the brine saturating the rock and \( \varepsilon_w = \varepsilon_r \varepsilon_0 \) is the dielectric permittivity of the brine, which is related to the relative permittivity of the brine \( (\varepsilon_r=80.1) \) and the vacuum permittivity \( (\varepsilon_0=8.8541878176 \times 10^{-12}) \). Based on equation (4.24), the corresponding apparent zeta potential is -27.7 mV, which is very close to the input zeta potential we defined of -28 mV. This demonstrates that the pore network modelling approach we developed in this study is able to recover the input zeta potential for single phase flow.

| Table 4.1: Properties of the Berea pore network |
|-----------------|-----------------|
| Estaillades     | Pore network    |
| **Volume**      | 27 mm³          |
| **Porosity**    | 0.24            |
| **Permeability**| 2.5 Darcy       |
| **Average coordination number** | 4.19 |
| **Number of pores** | 12349 |
| **Number of throats** | 26146 |

| Table 4.2: Fluid properties applied in pore network modelling |
|-----------------|-----------------|-----------------|
| **Fluid**       | **Oil**         | **Water**       |
| **Density**     | 8100 kg/m³      | 1000 kg/m³      |
| **Viscosity**   | 1.39×10⁻³ Pa·s  | 1.05×10⁻³ Pa·s  |
| **Resistivity** | 1000 Ω·m        | 1Ω·m            |

For multiphase flow in pore network modelling, Valvatne and Blunt [2004] have matched steady-state experimental data of relative permeability in gas/water and oil/water displacement cycles using the water-wet Berea sandstone network that we will apply in this
section. We assigned the same contact angle, irreducible water saturation and fluid properties for the oil-displacements to validate our predictions of relative permeability in the first step. The fluid properties are listed in the Table 4.2 and the interfacial tension is 30 mN/m.

Figure 4.8: Predicted relative permeability for water-wet Berea sandstones in oil-water displacements during drainage and imbibition (lines) compared to experimental data by Oak [1990] (circles).
The predictions shown in Figure 4.8 were obtained with intrinsic receding contact angle of 0° and uniformly distributed advancing contact between 50 and 60 degrees for the oil-water displacements because of the roughness of surface and potential minor wettability alteration.

We did not obtain the exactly same predictions as Valvatne and Blunt [2004] demonstrated in Figure 8 because there predictions are the mean of 20 realizations with the same assigned contact angle range and slightly different random contact angle distributions within the range. As they pointed out, small changes in the distribution of contact angles did not affect the results significantly as long as the contact angle remains within the range. Therefore, Figure 4.8 in this section only demonstrated one realization results in water-wet Berea network and demonstrated a good match with measured experimental data during both drainage and imbibition. It gives us the validated first step to further predict resistivity index and streaming potential properties with reasonable contact angles and irreducible water saturation values.

The input zeta potential was determined in terms of brine salinity as Vinogradov et al. [2010] demonstrated a function of zeta potential (ζ) with brine salinity (Cf) as listed in equation (4.23). With the input brine conductivity 1 S/m, we related the brine salinity with conductivity by an empirical correlation and published data at 23°C [Worthington et al.; Weast, 1989]:

\[
C_f = 5.9738 \times 10^{-7}\sigma^6 - 3.5136 \times 10^{-5}\sigma^5 + 7.823 \times 10^{-4}\sigma^4 - 8.0334 \times 10^{-3}\sigma^3 + 4.0791 \times 10^{-2}\sigma^2 + 3.4996 \times 10^{-2}\sigma + 3.6104 \times 10^{-2} \quad \quad \quad \ldots (4.23)
\]

The computed salinity then acts as input for an empirical relation of zeta potential as shown [Vinogradov et al., 2010]:

\[
\zeta = a + b \log C_f, C_f < 0.4M \quad \quad \quad \ldots (4.24a)
\]

\[
\zeta = c, C_f \geq 0.4M \quad \quad \quad \ldots (4.24b)
\]
The values of fitting parameters that we used to compute the zeta potentials are $a = -9.67$ mV, $b = 19.02$ mV, and $c = -17$ mV, which were obtained by Vinogradov et al. [2010] from fitting to the data for silica, quartz, glass in NaCl brine and sandstones in natural and artificial brines as shown in their Figure 11. Based on equations (4.23, 4.24), the input zeta potential at water rock interfaces was defined to be -28 mV when brine conductivity is 1 S/m.

Figure 4.9 demonstrates capillary pressure and resistivity index as functions of water saturation during drainage and imbibition with the receding and advancing contact angles to be 0° and 50-60°, respectively. Capillary pressure exhibit hysteretic behaviour during drainage and imbibition, because fluids have different fluid distributions that is related to different contact angles [Brooks and Corey, 1964; Fenwick and Blunt, 1998]. Hysteresis is not observed in the resistivity index as demonstrated in Figure 4.9 (b). In experiments, the hysteretic behaviour in resistivity index Berea sandstones is not obvious at low water saturations as the adsorption and desorption of water process are reversible during imbibition and drainage while water tends to swell the water layers during imbibition [Knight, 1991]. At high water saturations, the non-hysteretic behaviour in resistivity index is likely because the receding and advancing contact angles remains less than 90° and the wettability is not altered during drainage and imbibition. Therefore, the connected flowing paths at higher water saturations during drainage and imbibition are likely to be identical in pore network modelling.
Figure 4.9 (a, b): Capillary pressure and resistivity index as functions of water saturation during drainage and imbibition in water-wet Berea network model.

Figure 4.10 demonstrates the predicted relative coupling coefficient in water-wet Berea network as a function of water saturation during drainage and imbibition. The predicted relative coupling coefficient gradually decreases as the water saturation decreases and falls to zero at the end of drainage (Figure 4.10). This is the same as predicted by Jackson [2010] using the bundle of capillary tube model for the water-wet cases. This is because as the water saturation decreases, elements occupied by the non-conductive oil contribute to neither the streaming current nor conduction current. This causes the electrical conductivity and relative coupling coefficient to gradually decrease. When it is approaching the irreducible water saturation, the small elements occupied by the irreducible water saturation do not contribute to the streaming current but only to the conduction current. Then the streaming current decreases more rapidly than the conduction current as water saturation decreases. When it reaches the irreducible water saturation, there is no mobile water within the pore network that yields the zero value at the end of displacement. The hysteretic behaviour was observed in the relative coupling coefficient as shown in Figure 4.10, which is likely due to different contact angles and fluid distribution at pore level during drainage and imbibition.
Relative streaming current charge density can be computed in terms of predicted relative permeability, relative electrical conductivity and relative coupling coefficient based on equation (2.21) in Chapter 2. Figure 4.11(a) demonstrates the computed relative streaming current charge density as a function of water saturation for the water-wet Berea model during drainage and imbibition. The relative streaming current charge density gradually increases as water saturation increases and rapidly goes up to extremely high value as it is approaching the irreducible water saturation. It is the same as what we observed in the inversion Chapter 3 because the constant number of excess charges is constrained within a very thin water layer at low water saturation, which gives a much higher streaming charge density in the end of displacement. The predicted streaming charge density also exhibits hysteric behaviour during drainage and imbibition as transport and electrical properties during drainage and imbibition.
In chapter 3, an empirical relationship between $Q_r$ and $S_w$ was proposed based on experimental data from two sandstones samples (Stainton and St. Bees). This empirical model (fitting parameters are listed in Table 3.1), is shown for comparison with predicted results in Figure 4.11 (b). The relative streaming current charge density obtained using pore network modelling exhibits a similar exponential trend as the empirical model obtained using the inversion approach. They both predict that the relative streaming charge density gradually increases as water saturation decreases at high and intermediate normalized water saturation (>0.2) and sharply increases when $S_w$ approaches the irreducible water saturation. However, the empirical functions both yield higher values of $Q_r$ at low normalized water saturation (<0.2) than the network model predictions, and lower values at high water saturation. Furthermore, empirical functions demonstrate a slightly more pronounced hysteretic behaviour than predicted results of pore network modelling. Even though the empirical functions are not derived from experiments on Berea sandstone and we do not expect an exact quantitative match, the comparison still confirms the exponential behaviour of streaming charge density as indicted by empirical functions from the inversion approach and gives us a reasonable match. The streaming current charge density is highly dependent on fluid distribution at the pore level and the pore structure [Jackson, 2008, 2010; Jougnot and Linde, 2013; Jackson et al., 2016].
Figure 4.11: (a) Predicted relative streaming current charge density during drainage and imbibition in the water-wet Berea network; (b) A comparison of predicted relative streaming charge density from the inversion and pore network modelling approaches.
4.3.2 Estaillades carbonates network model

The Estaillades network model we are using here was extracted by Gharbi et al. [2013] and can be accessed from the Imperial College website. The properties of pore network and comparison with experimental core sample are listed in Table 4.3. But there is a huge discrepancy in properties. First, it is because they are not the same kind of carbonates as we demonstrated in description in the table. Furthermore, the miss-match is likely originated from imaging and segmentation errors and the network model does not incorporate micro-porosity yet. The average coordination number is 3.91. Oil brine displacements are simulated for primary drainage and imbibition. Fluid properties used in this network are same as those in Berea network.

Table 4.3: Properties of the Estaillades pore network and the Estaillades core sample that was used by Jackson et al. [2016].

<table>
<thead>
<tr>
<th>Estaillades</th>
<th>Experiment</th>
<th>Pore Network</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Description</strong></td>
<td>Upper Cretaceous limestone from France</td>
<td>Micro-porosity are not included in the network</td>
</tr>
<tr>
<td><strong>Porosity</strong></td>
<td>28% ±0.5</td>
<td>10.9%</td>
</tr>
<tr>
<td><strong>Permeability</strong></td>
<td>0.13 Darcy ±0.2</td>
<td>0.218 Darcy</td>
</tr>
<tr>
<td><strong>Formation Factor (F)</strong></td>
<td>12.92 ±0.5</td>
<td>115.6</td>
</tr>
<tr>
<td><strong>Dimensions</strong></td>
<td>Length (L) =0.0762 m, Diameter (D) =0.0381 m</td>
<td>27 mm $^3$</td>
</tr>
</tbody>
</table>

Jackson et al. [2016] developed an approach that used streaming potential measurements to relate zeta potential with brine composition, wettability and oil recovery during controlled salinity waterflooding (CSW) with consistent materials and experimental conditions. They observed that wettability (as defined by the Amott Water Wetting Index) is closely correlated with the zeta potential measured on carbonate rock samples. They observed two distinct trends in zeta potential with wettability: one is increasingly positive as the intact sample
becomes more oil-wet, and the other one is increasingly negative with the decreasing wettability index. Based on this observation, Jackson et al. [2016] suggested that the oil-water interface can be positively or negatively charged in carbonates at the high pH and ionic strength. However, there is no other experiment or model to support or confirm this hypothesis. In this section, a Estaillades network whose properties have been listed in Table 4.3 will be used to test the hypothesis proposed by Jackson et al. [2016].

Figure 4.12 (a) demonstrates the correlation between zeta potential and wettability obtained experimentally by Jackson et al. [2016]. In experiments, the fully water saturated Estaillades model was drained to different water saturations and then aged at 80°C for four weeks to induce wettability alteration before imbibition. In some cases, the sample was aged in the absence of water (dry-aged samples). There are two obvious trends. The apparent zeta potential of the sample saturated with brine and Oil B becomes increasingly positive as the sample becomes more oil-wet, while the apparent zeta potential of the sample saturated with brine and Oils C, D and E follows the opposite trend, in which the apparent zeta becomes more negative as the sample become more oil-wet.

We mimicked this experimental process by stopping the simulation of primary drainage at a pre-defined water saturation that is consistent with the experimentally measured initial water saturations, then adjusting the contact angles to 120°-140° prior to imbibition. Consequently, based on the hypothesis they proposed, we begin by defining two sets of input zeta potentials in the pore network modelling defined at oil-wet water-rock interfaces and oil-water interfaces: one set is more positive than the zeta potential at the water-wet water-rock interface, and the other is more negative. Since Jackson et al. [2016] obtained 7 mV as the apparent zeta potential for the fully water saturated rock sample in water-wet conditions (as shown in Figure 4.12 (a) by the hollow diamond), we defined the input zeta potential at water-wet water-rock interfaces to be 7 mV.
Figure 4.12: (a) Zeta potential as a function of Amott water wetting index for each of the four oils tested (B-E) using the Estaillades samples saturated with formation brine and residual oil saturation. Empty circles represent aging in the absence of water (‘oil-only’), empty squares represent aged samples in the presence of water, filled square represents non-aged sample and the diamond symbol represents the water-only sample; (b) Zeta potential as a function of water wetting index using the Estaillades pore
network model. Empty squares represent model prediction after drainage to different initial water saturations; empty circles represent predictions of dry models (no initial water present).

Wettability alteration was modelled in two ways to capture the measured wettability index of these samples. For samples aged in the presence of water, we drained the pore network to the same irreducible water saturation as in the experiment. The pores that had been invaded by oil were selected to be oil-wet and the others remained water-wet during imbibition. The fraction of selected pores is the adjustable parameter to match the experimental wettability index. Contact angles of oil-wet pores were changed to 120° - 140°. For samples dry aged in the absence of water, imbibition was modelled started from zero initial water saturation. The majority of pores were assumed to be oil-wet after dry aging and a fraction of pores was specified to remain water-wet. The fraction of pores selected to remain water-wet was the adjustable parameter used to match the measured wettability index of the dry aged samples. The modelled zeta potential at oil-wet water-rock interfaces and oil-water interfaces was the adjustable parameter used to match the measured apparent zeta potential for a given wetting state. A given oil (B-D) was constrained to have the same zeta potential at all interfaces. The results from the Estaillades network modelling are shown in Figure 4.12 (b).

We are able to match the wettability index within 5%. We also obtain a good match to the measured apparent zeta potential within 10%. The corresponding values of wettability index and zeta potential are listed in Table 4.4. $\zeta_{ow}$ denotes zeta potential at oil-water interface while $\zeta_{wr}$ denotes zeta potential at water-rock interface.
Table 4.4. Summary of pore network modelling values to match the experimental initial water saturation, wettability index and measured zeta potential in carbonates

<table>
<thead>
<tr>
<th>$\zeta_{wr}$ (mV)</th>
<th>$S_{wi}$</th>
<th>$I_w$</th>
<th>log($I_w$)</th>
<th>$C$ (V/Pa)</th>
<th>$\zeta_{calculated}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>4.95E-09</td>
<td>6.98</td>
</tr>
</tbody>
</table>

When $\zeta_{ow} > \zeta_{wr}$

<table>
<thead>
<tr>
<th>$\zeta_{ow}$ (mV)</th>
<th>$S_{wi}$</th>
<th>$I_w$</th>
<th>log($I_w$)</th>
<th>$C$ (V/Pa)</th>
<th>$\zeta_{calculated}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>0.35</td>
<td>0.090668</td>
<td>-1.04255</td>
<td>6.94E-09</td>
<td>9.79</td>
</tr>
<tr>
<td>22</td>
<td>0.71</td>
<td>0.146431</td>
<td>-0.83437</td>
<td>5.95E-09</td>
<td>8.40</td>
</tr>
<tr>
<td>22</td>
<td>0.67</td>
<td>0.186045</td>
<td>-0.73038</td>
<td>5.86E-09</td>
<td>8.26</td>
</tr>
<tr>
<td>22</td>
<td>0</td>
<td>2.90E-02</td>
<td>-1.53774</td>
<td>8.57E-09</td>
<td>12.1</td>
</tr>
</tbody>
</table>

When $\zeta_{ow} < \zeta_{wr}$

<table>
<thead>
<tr>
<th>$\zeta_{ow}$ (mV)</th>
<th>$S_{wi}$</th>
<th>$I_w$</th>
<th>log($I_w$)</th>
<th>$C$ (V/Pa)</th>
<th>$\zeta_{calculated}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-2.4</td>
<td>0</td>
<td>0.029326</td>
<td>-1.53273</td>
<td>7.21E-10</td>
<td>1.02</td>
</tr>
<tr>
<td>-2.4</td>
<td>0</td>
<td>0.051967</td>
<td>-1.28427</td>
<td>1.68E-09</td>
<td>2.38</td>
</tr>
<tr>
<td>-2.4</td>
<td>0</td>
<td>0.040822</td>
<td>-1.38910</td>
<td>1.28E-09</td>
<td>1.81</td>
</tr>
<tr>
<td>-2.4</td>
<td>0.42</td>
<td>0.059769</td>
<td>-1.22352</td>
<td>2.66E-09</td>
<td>3.76</td>
</tr>
<tr>
<td>-2.4</td>
<td>0.46</td>
<td>0.108944</td>
<td>-0.9628</td>
<td>2.88E-09</td>
<td>4.06</td>
</tr>
</tbody>
</table>

Two clear and distinct trends in zeta potential with wettability index are observed in the pore network model results that reproduce the experimental trends. When the zeta potential at the oil-wet rock-water and oil-water interfaces is more positive than at the water-wet water-rock interface (i.e. for Oil B) (22 mV as listed in Table 4.4), pore network modelling predicts a more positive apparent zeta potential across the entire network. When the zeta potential at the oil-wet rock-water and oil-water interfaces is more negative (-2.4 mV), the apparent zeta potential can still be positive (Figure 4.12b). However, the apparent zeta potential becomes more negative as the wettability index decreases. This is because the number of oil-wet water-rock interfaces increases with increasing oil wettability (decreasing water wettability). The predictions are consistent with the measured data Figure (4.12a).
Figure 4.13 and 4.14 demonstrate relative permeability, capillary pressure, resistivity index and relative coupling coefficient as functions of water saturation in the Estaillades model during drainage and during imbibition after aging in the presence of water with $S_{wi} = 0.35$ and $0.42$ as shown in Table 4.4. The corresponding wettability index of Figure 4.13 and 4.14 are also listed in Table 4.4. Transport properties, resistivity index and relative coupling coefficient all exhibit hysteretic behavior. The only difference between Figure 4.13 and 4.14 is the input zeta potential for oil-wet water-rock and oil-water interfaces. When the zeta potential at oil-wet interfaces becomes more positive (Figure 4.13), there is an obvious jump in the relative coupling coefficient at the beginning of imbibition which represents the alteration of wetting state. This is because the magnitude of the zeta potential for oil-wet water-rock interfaces is larger than for water-wet water-rock interfaces. The relative coupling coefficient then starts to decreases with increasing water saturation because most of the change in water saturation change occurs through the water-wet connected flow paths. The relative coupling coefficient starts to increase rapidly after the water saturation reaches 0.8 as water increasingly occupies the oil-wet pores. Figure 4.14 (d) presents the opposite trend of relative coupling coefficient due to the more negative zeta potential at oil-wet water-rock and oil-water interfaces. An immediate drop of relative coupling coefficient is caused by the wettability alteration and the coupling coefficient increases as water saturation increases, followed by a sharp drop at high water saturation ($> 0.8$ water saturation). The more negative zeta potential at oil-wet water-rock and oil-water interfaces yields a more negative relative coupling coefficient at the end of imbibition.
Figure 4.13: Relative permeability, capillary pressure, resistivity index and relative coupling coefficient as functions of water saturation during drainage and oil wet imbibition in the Estaillades pore network with the more positive zeta potential at oil-wet water-rock and oil-water interfaces (22 mV). The initial water saturation ($S_{wir}$) is 0.35 for imbibition and no surface conductivity is included. The corresponding wettability index is 0.090668 as shown in Table 4.4.
Figure 4.14: Relative permeability, capillary pressure, resistivity index and relative coupling coefficient as functions of water saturation during drainage and oil wet imbibition in the Estaillades pore network with the more negative zeta potential at oil-wet water-rock and oil-water interfaces (-2.4 mV). The initial water saturation ($S_{wi}$) is 0.42 for imbibition and no surface conductivity is included. The corresponding wettability index is 0.059769 as shown in Table 4.4.
4.3.3 St. Bees sandstone network model

In the last section we investigate the streaming potential in St. Bees using pore network modelling. The St. Bees network model we are using here is extracted from a cylindrical core 6 mm in diameter and 10 mm in length, which is a part of the intact core sample (37.1 mm in diameter and 77.6 mm in length) that has been used by Vinogradov and Jackson [2011]. Entire scanning domain is 1 cm$^3$ containing 32293 pores and 56493 throats. Compared to the grid block size 0.84 cm$^3$ we simulated in Chapter 3, both of them are small enough to represent a REV with uniform rock properties and saturations. The process to construct St. Bees network has been detailed described in section 4.2.3.

We begin by running single phase flow simulation in the constructed St. Bees network to match the measured porosity, absolute permeability and formation factor. Here we distribute clay content randomly as an adjustable parameter to match formation factor and resistivity index that is obtained in St. Bees displacement experiments [Vinogradov and Jackson, 2011]. A 30% portion of the void space has been randomly assigned to be clay content to match the irreducible water saturation and the measured absolute permeability, and clay resistivity was assumed to be the same as the brine resistivity to match and formation factor. Furthermore, in order to obtain this best match, a scaling factor for the distribution of shape factors of elements has been applied to be 0.65. Table 4.5 demonstrates the best matched properties of St. Bees network with comparison of properties of measured intact core sample, and the input file for the best match is attached in the appendix as a reference. The porosity and permeability are well predicted while the formation factor is slightly over-predicted. It is likely because we distributed clay content within the network model in order to match the relatively low measured permeability, which yields a higher predicted formation factor.
The receding and advancing contact angle is 0° and 30° during drainage and imbibition, respectively. Experimental displacements were conducted using brine and undecane, so the wettability during drainage and imbibition was assumed to be identical without any wetting state alteration. However, it has to be noticed that the measured residual oil saturation obtained by Vinogradov and Jackson [2011] is very low for a water-wet sandstone core sample ($S_{or} =0.087$), so it will not be possible to match the measured low residual oil saturation using a network model. Therefore, instead of defining the wettability to be purely water-wet, a fraction of pores that have been invaded by oil is assumed to be oil-wet with the contact angle between 120° to 140° in order to match the measured residual oil saturation at the end of imbibition. The fraction of altered pores acted as an adjustable parameter to match the residual oil saturation. The measured coupling coefficient at initial fully water saturated conditions ($3.58 \times 10^{-8}$ V/Pa) was used to compute the input zeta potential at water-rock interfaces. As a first step, we assume the zeta potential at oil-water and oil-wet water-rock interface is same as the water-rock interface.

**Table 4.5: Properties of St. Bees predicted by pore network modelling (PNM) and measured in experiments [Vinogradov and Jackson, 2011].**

<table>
<thead>
<tr>
<th>St. Bees</th>
<th>Predicted by PNM</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute permeability (mD)</td>
<td>73</td>
<td>70±2</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.16</td>
<td>0.19±0.002</td>
</tr>
<tr>
<td>Formation Factor</td>
<td>28</td>
<td>18±0.5</td>
</tr>
</tbody>
</table>

Relative permeability predicted by pore network modelling is plotted as a function of water saturation during drainage and imbibition in Figure 4.15 (a, b). As a comparison, the interpreted relative permeability which yields the best match with experimental pressure and production data is also plotted. We did not obtain a good match of relative permeability curves. The relative permeability curves from the inversion approach and from pore network...
modelling are similar during drainage, but present more distinct behaviours during imbibition.

In general, predictions from pore network modelling tend to yield more water-wet behaviour.

Figure 4.15: (a, b) comparisons of relative permeability interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition, respectively; (c, d) comparison of resistivity index interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition respectively. Measured apparent resistivity index across the core samples are represented by stars for reference.

Resistivity index predicted by pore network modelling is plotted as a function of normalized water saturation to compare with the interpreted experimental results during drainage and
imbibition in Figure 4.15 (c, d). Pore network modelling predicts higher resistivity index at partial normalized water saturation. The gradient of resistivity index, which is the Archie exponent, from the inversion approach and pore network modelling are both around 0.5, which is lower than the typical range for sandstones 1.5-2.5.

Figure 4.16 (a) demonstrates the relative coupling coefficient predicted by pore network modelling as a function of normalized water saturation and the interpreted results from the experimental data. Since Vinogradov and Jackson [2011] observed non-zero streaming potential at the end of drainage, the interpreted results from experimental data has a non-zero coupling coefficient at the end of drainage. However, there is no moving water in the pore network modelling that can produce a streaming current at the end of drainage, which might be the reason of non-zero streaming coupling coefficient at unsteady-state displacements. Consequently, the predicted relative coupling coefficient from pore network modelling falls to zero at the end of drainage. Furthermore, pore network modelling does not predict the non-monotonic behavior interpreted from the experimental data. We observe hysteresis in both results.

Figure 4.16: (a) comparisons of relative coupling coefficient interpreted from experimental data using inversion approach and pore network modelling predictions
During drainage and imbibition, respectively; (b) comparison of relative streaming charge density model that interpreted from experimental data using inversion approach and pore network modelling predictions during drainage and imbibition respectively.

Based on equation (2.21), we computed the relative streaming current charge density using the relative permeability, electrical conductivity and streaming potential coupling coefficient predicted by the pore network model, and compared it as a function of normalized water saturation with the interpreted data from the St. Bees experiments. Comparisons are shown in Figure 4.16 (b). Both interpreted and predicted data exhibit hysteresis during drainage and imbibition and have lower relative streaming charge density during imbibition than drainage. Since pore network modelling predicted more water-wet transport properties in Figure 4.15, the streaming charge density predicted by pore network modelling increases less rapidly as water saturation decreases than the interpreted experimental data. The St. Bees pore network was very difficult to match with the measured transport properties and low resistivity index of experiments. If we can have a better match in relative permeability, it may be possible to have a better match with the streaming potential coupling coefficient and streaming charge density interpreted from experimental measurements.
4.4 Conclusions

We present a method to investigate multiphase streaming potential using pore network models that represent real geological porous media, and applications of the method to determine the saturation dependence of the streaming potential coupling coefficient ($C$) and streaming current charge density ($Q_s$) during drainage and imbibition in two sandstones (Berea and St. Bees) and a carbonate (Estaillades) network. Key findings from this chapter are demonstrated as below:

1. Pore network modelling can predict the single phase coupling coefficient successfully and present similar multiphase coupling coefficient behaviors in water-wet network as predicted by Jackson [2010] using the bundle of capillary tube model. With predefined input zeta potential, pore network modelling predicts hysteric multiphase coupling coefficient between drainage and imbibition in water-wet and oil-wet conditions for all networks.

2. Pore network modelling is able to reproduce the observed correlation between apparent zeta potential across the core sample and the wettability of Estaillades. It confirms their hypothesis that zeta potential at oil-water interface can be positive or negative, depending on the composition of the oil and brine.

3. Although using St. Bees pore network is difficult to match with the measured transport properties and electrical resistivity in this study, the predicted variation in $Q_s$ with $S_w$ is similar to the interpreted empirical model obtained by the inversion approach from Chapter 3. The streaming current density predicted using pore network modelling increases as water saturation decreases and goes up to infinite rapidly when it is close to the irreducible water saturation and exhibit hysteric behavior during drainage and imbibition.
4. Pore network modelling approach provides a new insight from the pore scale perspectives to investigate the underlining mechanism in fluids rock system.
Chapter 5 Conclusions and Future work

5.1 Conclusions

The aim of this study was not simply to match experimental data, but to develop new methods to investigate the fundamental behaviour of streaming potential during multiphase flow in complex geological media from continuum and pore scale perspectives. The behaviour of multiphase streaming potential is closely related to the electrical charge distribution within the double layer adjacent to the solid fluid interface. This study provides an insight into the fundamental explanation of various inconsistent streaming potential measurements during multiphase flow, and confirms streaming potential during multiphase flow highly depends on the pore-level fluid distribution which is controlled by rock texture and wettability.

A new inversion approach has been presented to interpret multiphase streaming potential dependence on water saturation during unsteady-state displacements of one fluid by another. It is not only able to be applied to determine the saturation dependence of the streaming potential coupling coefficient, but also to investigate the streaming current charge density behaviour. Compared to the other theoretic models listed in the Table 2.1, this inversion approach can be applied to interpret any SP measurements obtained by any unsteady state displacements in any rock, acts as a routine post-processing step to investigate the real saturation dependence of SP signals of subsurface settings. Interpreted results will be very helpful to detect water fronts for the further smart well control, monitoring in reservoirs during water flooding in oil recovery and acting as a nonintrusive vadose zone water content sensor. The interpreted behaviour can also be applied to interpret and evaluate seismoelectric (SE) signals [Warden et al., 2013; Revil et al., 2014].
Predicted variation of relative streaming charge density with water saturation is relatively small compared to that of streaming coupling coefficient. Instead of investigating apparent coupling coefficient, the streaming current density controlled by rock texture and fluid properties is the key property to be modelled because it behaves similarly for a given displacement in similar rocks. The empirical streaming current density model proposed here can be used to help predict SP and SE measurements obtained in partially-saturated subsurface settings.

By developing a new method that combines pore networks containing realistic rock topologies with the description of streaming current, we successfully predicted single and multi-phase coupling coefficient and streaming current charge density during drainage and imbibition in Berea, St. Bees and Estaillades networks. The implementation of the pore scale modelling was validated using experimental data from Estaillades carbonate and St. Bees sandstone. It confirms their hypothesis that zeta potential at oil-water interface can be positive or negative.

Even though some experiments and theoretical models have attempted to investigate the behaviour of multiphase streaming potential, there is no pore-scale modelling method at present to explain the underlying mechanism of SP. The investigation of fluids and electrical charge displacements within each pore is vital to explain, support and confirm continuum observations and models. Current pore level theoretical models are all established on simple networks with oversimplified pore structure such as the bundle of capillary tube model, in which there is no variation in pore shape and interconnections between tubes. This study is the first attempt to investigate streaming current behaviour in complex rock networks. Pore network modelling provides a new promising tool to investigate the fundamental mechanism of various SP behaviours at partial saturations in complex porous media.
5.2 Future work

Most of published measurements of streaming potential during multiphase flow were conducted by unsteady-state displacements, in which the saturations within the sample are not uniform except at the initial fully saturated condition, the irreducible water saturation and the residual non-wetting phase saturation. In this study, we proposed a post-processing inversion method to interpret unsteady-state measurements of streaming potential within a REV where the saturation is uniform. In the future, a potential alternative to unsteady-state measurements is to use the steady-state method where both phases flow at constant rate through the porous media of interest. Even though steady-state measurements are considerably more complex and time consuming, it reflects the intrinsic behaviours of any measured transport and electrical properties because the saturations are uniform along the core sample during the whole process of displacements. The measured values will directly reflect multiphase spontaneous potentials behaviour with water saturations in real rocks without post-process interpretation step.

Furthermore, current measurements of streaming potential are all conducted in water-wet fluid rock systems. Only one theoretical model attempted to model streaming potential in oil-wet systems based on the bundle of capillary tube model [Jackson, 2010]. This study simulated streaming current in oil-wet sandstones and carbonates networks including the contribution of the electrical double layers in oil-water interfaces, which is an appropriate assumption for the oil-wet cases because the hydrocarbon components that cause wettability alteration are polar. More measurements of streaming potential for multiphase flow are needed to validate our pore network modelling predictions in oil-wet conditions and to investigate multiphase streaming potential behaviour.
As we discussed in Chapter 4, rigorous pore-scale modelling of complex sandstone and carbonate rock samples that contains micro-porosity and clay contents is still an ongoing research problem. An improved model needs to be developed incorporating micro-porosity and appropriate distribution of clay contend and its contributions to electrical conductivity.

We implemented pore network modelling with the mathematical description of streaming current that revised from the bundle of capillary tube model, which is still an approximation regardless of shapes of pores and throats. Exact analytical descriptions of streaming current for multiphase flow in arbitrary shapes of pores and throats are necessary for a more accurate and powerful pore network modelling approach. Use of direct simulation on rock images is a potential next step to solve the streaming potential problems at pore-scale level.

Last, we only focused on the streaming potential simulation in this study rather than the total SP including thermoelectric and electrochemical potentials. It would be of great value if we can incorporate those two components into the pore network modelling in the future.


MATLAB (2012), version 8.0.0.783 (R2012b), The MathWorks Inc., Natick, Massachusetts.


Worthington, A. E. P., J. H. Hedges, and N. Pallatt Part I -guidelines For Preparation Of Brine And Determination Of Brine Resistivity For Use In Electrical Resistivity Measurements; Sca Guidelines For Sample Preparation And Porosity Measurement Of Electrical Resistivity Samples.


