Measurements, modelling and applications of the electro-kinetic properties of rocks

Paul Glover
Université Laval, Québec, Canada
Plan

- Introduction
- Origin
- Theory
- Laboratory determinations
- Applications
- Conclusions
- Future directions
- Acknowledgments
Introduction
Introduction

What are electro-kinetic properties?

**Electro-kinetic phenomena**

The generation of an electrical potential difference across a porous medium by the flow of fluid through it, or vice versa

- Flow causes potential ➔ Electro-kinetics
- Potential causes flow ➔ Electro-osmosis

**Electro-seismic phenomena**

The generation of an electro-magnetic wave in a porous medium by the passage of an elastic wave through it, or vice versa

- Elastic wave causes EM wave ➔ Seismo-electric conversion
- EM wave causes elastic wave ➔ Electro-seismic conversion
Introduction II

Principal applications

- **Electro-kinetic phenomena**
  - Hydrocarbon production
  - Water reservoir management
  - Remediation of polluted soils
  - Volcano prediction
  - Earthquake prediction
  - Synthetic earthquakes

Polymer sciences, membrane sciences, catalysis, microfluidics, food science, medical science

- **Electro-seismic phenomena**
  - Hydrocarbon exploration & production
  - Water reservoir management
  - Volcano prediction
  - Earthquake prediction
Origins
The electrical “double” layer
Debye thickness
Surface conduction
Electro-seismic conversion
Origin - The electrical double layer

Plan
- Introduction
- Origin
- Theory
- Apparatus
- Laboratory determination
- Applications
- Conclusions
- Future directions

8 of 72
There exists:

An undisturbed central zone of laminar flow,

and

A surface boundary layer of turbulent flow,

and

Zero flow at the rock surface
There exists:
- A -ve charged rock surface,
- A layer of +ve adsorbed ions,
- A net –ve diffuse layer [thickness/(salinity)],
- Net neutral bulk fluid.
Origin - The electrical double layer

Boundary of moveable fluids is in diffuse layer
Flow separates – ve charges to the right
and
+ve charges are left behind
this
 generates a potential difference called the
STREAMING POTENTIAL

Immobile Fluid
+ve > -ve

Shear plane

Moveable Fluid
-ve > +ve

Shear plane

Net +ve

Net -ve

Streaming Potential
Debye thickness \( \chi_d \) is given by:

\[
\chi_d = \frac{2 \sqrt{\frac{\varepsilon_f k_b T N_A}{2000 e^2 C_f}}}{}
\]
Origin
Debye thickness II

Plan
Introduction
Origin
Theory
Apparatus
Laboratory determination
Applications
Conclusions
Future directions

13 of 72
PET Visualisation of the electrical double layer
Two conduction mechanisms

A. via the bulk fluid

B. via the diffuse and Stern layers

The latter is surface conduction

Surface conduction more effective than bulk fluid conduction

At low salinities – the EDL is thick – Surface conductivity dominates
Origin

Electro-seismic conversion

Haines et al. (2007)
Theory

- DC Theory
- The Helmholtz-Smoluchowski equation
- Formulation in continuous media
- What controls the zeta potential?
- AC Theory
Theory

DC theory - Historical

- **Helmholtz (1879)**: Simple mineral surface neutralized by a monolayer of counterions from the fluid.

- **Gouy (1910) & Chapman (1913)**: Replaces monolayer with a diffuse layer composed of counterions and coions (monolayer affected by thermal agitation).

- **Stern (1924)**: Proposes amalgamation of the two previous models.
Theory

The Helmholtz-Smoluchowski equation

By equating the convective and conductive currents (Overbeek, 1952)

\[
\Delta V = - \frac{\varepsilon \zeta}{\eta \left( \sigma_f + \frac{2 \Sigma_s}{\Lambda} \right)} \Delta P
\]

\(C_s\) is the electro-kinetic coupling coefficient is defined as the ratio of the streaming potential to the fluid pressure difference that created it (V/Pa)

\[
C_s = \frac{\Delta V}{\Delta P} = \frac{\varepsilon \zeta}{\eta \sigma^*} \quad \text{where} \quad \sigma^* = \sigma_f + \frac{2 \Sigma_s}{\Lambda}
\]

Sources of error

1. Not including surface conduction
2. Using \(\varepsilon = 80\) at low fluid salinities
3. Using bulk fluid pH (zeta potential is a strong function of pH)
Theory

Formulation in continuous media

Darcy’s law, \( L_{11} = k/\eta \)

\[
\begin{bmatrix}
Q \\
J
\end{bmatrix} = - \begin{bmatrix}
L_{11} & L_{12} \\
L_{21} & L_{22}
\end{bmatrix} \begin{bmatrix}
\nabla P \\
\nabla \phi
\end{bmatrix}
\]

Electro-kinetic phenomena
\( L_{21} = L_{12} = \varepsilon \zeta/\eta \)

Ohm’s law, \( L_{22} = \sigma_f \)

\( k \) permeability (m²)
\( \sigma_f \) fluid conductivity (S/m)
\( \varepsilon \) fluid dielectric constant
\( \zeta \) zeta potential (V)
\( \eta \) fluid viscosity (Pa.s)
\( P \) fluid pressure (Pa)
\( \varphi \) electrical potential (V)
\( Q \) fluid flow (L/m²),
\( J \) electric current density (A/m²)

or

\[
J = \frac{\varepsilon \zeta}{\eta} \nabla P - \sigma_f \nabla \varphi
\]

and

\[
Q = -\frac{k}{\eta} \nabla P + \frac{\varepsilon \zeta}{\eta} \nabla \varphi
\]

✓ OK for capillaries ✗ To be verified for rocks
Theory

What controls the zeta potential?

The streaming potential depends upon 4 parameters:

- Fluid* dielectric constant
- Fluid* viscosity
- Fluid* conductivity
- Zeta potential

Therefore any control of the streaming potential exercised by the rock rests in the zeta potential.
Theory

Controls on the zeta potential

- Salinity
- pH
- Porosity
- Pore microstructure – connectedness
- Flow rate
- Fluid viscosity
- Pore/fracture surface roughness
- Saturation
- Temperature, applied, pore and effective pressure
- Chemical composition of mineral and fluid
We propose

\[
\frac{\Delta V}{\Delta P} = f^* (\omega) \frac{\varepsilon_f \zeta}{\eta_f \sigma_f^*}
\]

Glover (2007)

For the hydraulic coupling coefficient

\[
\nu(\omega) = \frac{1}{\eta lk^2} \left[ \frac{2}{\eta lk^2} \frac{J_1(ka)}{ka J_0(ka)} - 1 \right]
\]

Packard (1953)

The streaming potential coupling coefficient becomes

\[
C(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{\varepsilon_f \zeta}{\eta_f \sigma_f^*} \left[ -2 \frac{J_1(ka)}{ka J_0(ka)} \right]
\]

Packard (1953)

\[
C(\omega) = \frac{\Delta V(\omega)}{\Delta P(\omega)} = \frac{\varepsilon_f \zeta}{\eta_f \sigma_f^*} \left[ 1 - \frac{2}{a \sqrt{\omega \rho_f}} \left( \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}} i \right) \right]
\]

Reppert & Morgan (2001)
Theory
AC Theory II

Hydraulic coupling coefficient is almost Debye-like

Streaming coupling coefficient is not Debye-like

The smaller the grain size the higher the frequency of the dispersion
Apparatus
Apparatus

- Early DC measurement cells
- DC measurement cells at ULaval
- Early AC measurement cells
- AC measurement cells at ULaval
Apparatus

Early DC cells

• From two existing cells:
  → Jouniaux et al. (2000)
  → Glover (2001)
Apparatus

DC measurement cells
Apparatus

DC measurement cells
Apparatus

DC measurement cells
Mark 3 cell can be used at higher Confining pressures within the same hydraulic press
Apparatus

Early AC measurement cells

Fig. 2. Cross-sectional view of main test chamber with test cell attached.

Fig. 3. Diagrammatic view of test cell, showing capillary unit. Dimensions of test cell: internal diameter: 1.75 in.; outer diameter: 3.00 in.; height polystyrene body: 1 1/4 in.; distance between electrodes: 1 1/4 in.; length platinum electrodes: 1 1/4 in.; diameter platinum electrodes: 0.016 in.; thickness threaded section: 1/8 in.; diameter threaded section: 1/8 in.

Packard (1953)
Electrical potential from a fluid pulse: The « Hammer test »

**Apparatus**

**Early AC measurement cells**

Vertical scale: 1 square = 1 V
Horizontal scale: 1 square = 5 ms

Ottawa sand
Grain diameter between 0.1 mm and mm
Satured with 0.1M de NaCl
Glover (2007)
Apparatus

AC measurement cells

The design takes a piston or a rubber membrane.

An LVDT allows a servo-locked amplifier to control the shaker with precision.

Measurements can be made with or without an imposed DC fluid flow.
Apparatus

AC measurement cells
Apparatus
AC measurement cells

Holes for fluid circulation or pressure transducers
Spring
Non-consolidated sample
Site for electrodes for electrical potential measurements

Precision shaker
Piston
Membrane
Perforated end piece

Section of the set-up
Laboratory determinations
Laboratory determinations

- Pore fluid chemistry
- Pore fluid salinity
- Pore fluid pH
- Mineralogy
- Grain size
- Temperature
- Saturation
- Frequency
Laboratory determinations

Pore fluid chemistry

Plan
- Introduction
- Origin
- Theory
- Apparatus
- Laboratory determination
- Applications
- Conclusions
- Future directions

Lorne et al. (1999)

Morgan et al. (1989)

Graph showing the relationship between potential zeta (ζ) and pH for different salts (KCl, K_2SO_4, CaCl_2, CaSO_4) as a function of resistivity (Ω.m) of the saturating fluid in pores.
Laboratory determinations

Pore fluid salinity I

\[ \zeta = 8 + 26 \log_{10} C_f \quad \text{Pride and Morgan (1991)} \]

\[ \zeta = -16.606 + 16.175 \log_{10} C_f \quad \text{Saunders et al. (2008)} \]
Laboratory determinations

Pore fluid salinity II

Plan

Introduction
Origin
Theory
Apparatus
Laboratory determination
Applications
Conclusions
Future directions

Saunders et al. (2008)
Laboratory determinations

Pore fluid pH I

Quartz 28x65 mesh
Eau distillée KNO₃ 10⁻³ N
Température 45°C

Potentiel électrocinétique (mV)
Pression appliquée (cm Hg)

-60
-40
-20
0

pH=8.7
6.1
4.2
10.8
3.2
0
5
10

Ishido et Mizutani (1981)

Zeta potential (mV)

Pression appliquée (cm Hg)

-100
-75
-50
-25
0

2 4 6 8 10 12

pH

10⁻³ M

10⁻² M

10⁻¹ M

Athabasca sand
Fisher silica

Cerda & Non-Chhom (1989)
Laboratory determinations
Pore fluid pH II

Scales et al. (1992)
Kosmulski & Matijevic (1992)
Kirby & Hasselbrink (2004)

pH dependence of temperature-corrected (20°C), normalized zeta potential

Zeta potential measured as a function of pH and counterion concentration
Laboratory determinations

Mineralogy I

- Potential (mV)
- Surface conductivity (mS/m)
- pH

Laboratory determinations

Plan
Introduction
Origin
Theory
Apparatus
Laboratory determination
Applications
Conclusions
Future directions

Saunders et al. (2008)
Laboratory determinations

Grain size

\[ C_s = -\frac{d \varepsilon_f \zeta}{\eta_f (d \sigma_f + 6 \Sigma_s (F-1))} \]
\[ \Lambda = \frac{d}{3(F-1)} \quad \text{(Revil et al. (1999))} \]

\[ C_s = -\frac{d \varepsilon_f \zeta}{\eta_f (d \sigma_f + 4 \Sigma_s mF)} \]
\[ \Lambda = \frac{d}{2mF} \quad \text{(Glover et al. (2006))} \]

\[ C_s = -\frac{r \varepsilon_f \zeta \sqrt{a}}{\eta_f \left( r \sigma_f \sqrt{a} + 4 \Sigma_s \sqrt{2} \right)} \]
\[ \Lambda = r \sqrt{\frac{a}{8}} \quad \text{(Glover and Walker (2009))} \]
The coupling coefficient varies significantly, but erratically with temperature.

Stability is the main experimental problem.

The calculated zeta potential may be a function of temperature.

However, its form is controlled by the effect of temperature on the fluid conductivity.
Laboratory determinations

Saturation I

\[ J_i = -\sigma \sigma_{ri} C C_{ri} \nabla P_i \]

\[ \sigma_{ri} = S_i^n \]

\[ C_{ri} = ? \]

Many attempts at finding a solution

\[ C_r = \frac{1}{S_w^{n+1}} \left( \frac{S_w - S^{r}}{1 - S^{r}_w} \right)^{(2 + 3\lambda)/\lambda} \]

Revil et al. (2007)

\[ C_r = \frac{Q_w k_{rw}}{\mu_w \sigma_r} \quad \text{where} \quad C = \frac{k}{\sigma} \]

Jackson (2008)

\[ C_r = S_w^{n+2} \left( \frac{S_w - S^{r}}{1 - S^{r}_w} \right)^{1/\lambda} \]

Glover (2009)

\[ C_r = \frac{Q_w k_{rw} + Q_o k_{ro}}{\mu_w \mu_o \sigma_r} \]

Jackson (2008)
Laboratory determinations

Saturation II

\[
\log_{10} \text{Relative coupling coefficient } (C_r) = f(S_w)
\]

- Linde et al. (2007)
- Jackson (2008)
- Glover (2009)

Water saturation \((S_w)\) vs. \(\log_{10} \text{Relative coupling coefficient } (C_r)\)

Plan
- Introduction
- Origin
- Theory
- Apparatus
- Laboratory determination
- Applications
- Conclusions
- Future directions

50 of 72
Laboratory determinations

Frequency (AC measurements) I

No reliable data exists for rocks in the public domain
Here is the best data made on silica filters

Filter A (72.5-87 μm). Modelled transition frequency (269 Hz) corresponds to a pore radius of 65 μm.

Filter B (35-50 μm). Modelled transition frequency (710 Hz) corresponds to a pore radius of 40 μm.
Laboratory determinations

Frequency (AC measurements) II

First data available for Ottawa sand using the Université Laval Petrophysics AC cell Mk 2

- Applied pressure difference in red
- Streaming potential in blue

15 Hz – some improvement of S/N ratio required
20 Hz – Problems with cavitation. Calculations have been carried out to avoid this phenomenon.
Applications
Applications

- Hydrocarbon exploration & production
- Water reservoir management
- Remediation of polluted soils
- Permafrost monitoring
- Acid mine drainage monitoring
- Volcano prediction
- Earthquake prediction
- Synthetic earthquakes
- Geothermal HDR reservoir monitoring
- Monitoring of CO₂ sequestering
- Soil stabilisation

...many others
There are many impressive examples of the use of seismoelectric and electro-kinetic prospection of hydrocarbon reservoirs.

All are impossible to publish!!!

Here is an application to mining instead – the discovery of zinc ore by electroseismics.
As water approaches the borehole it may be predicted by measuring the increasing streaming potential.

The well can be shut to improve the reservoir production.
Applications
CO₂ Sequestration

Injection of CO₂ produces a dramatic decrease in the coupling coefficient

-300 mV/MPa → -30 mV/MPa

These differences would be easily detectable by measuring surface SP

- Progressive injection of a reservoir with CO₂ could be monitored
- CO₂ leaking from a sequestration reservoir may also be detected before it appears at the surface
Applications

Remediation of polluted soils

Electrolysis of ions
Electro-osmosis of water
Electrophoresis of colloids

Electro-kinetic water extraction is also used to strengthen soils

Electro-kinetic processes are used to
A. Extract polluted fluids and ions, or
B. Move polluted fluids into contact with bioremediation or other active agents

Active from ppt upwards
First create a 2D finite element model in Comsol Multiphysics.
Applications

Volcano prediction II

First create a 2D finite element model in Comsol Multiphysics

Colour: Temperature (K)
Arrows: Total heat flux

Colour: Fluid pressure (Pa)
Arrows: Fluid velocity field (m/s)

Colour: Fluid density (kg/m³)
Arrows: Fluid velocity field (m/s)

293.15 - 844.846
670 - 891

Plan
Introduction
Origin
Theory
Apparatus
Laboratory determination
Applications
Conclusions
Future directions

60 of 72

Courtesy of Emile Walker
Modelling is still at an early stage. Need to develop convective flow. A map of the electric potential across the surface will then be compared to The measured SP values.

Time dependent injection of magma will then be modelled to see the SP values change with time.
Applications - Earthquake prediction I

- Initial fault is submitted to a shear stress
- However, it is locked
  - by its surface geometry and
  - by the effective stress perpendicular to the fault
- Fluid flowing into a fault increases the fluid pressure
- It decreases the effective stress on the fault
- Unlocks the fault for it to fail
- Lubricates the faulting process

What causes the fluid flow?
What can the fluid flow cause?
Applications

Earthquake prediction II

- The inflow may cause an electrical potential difference hence generating a streaming current and hence a magnetic field by electro-kinetic processes generating electro-magnetic and SP precursors

- The fluid flow can be caused by electrical potential differences within the crust associated with natural telluric currents induced by ionospheric currents by electro-osmosis

- The fluid flow may be caused by elastic waves set in motion by other earthquakes

Understanding these links may lead to improvement in our ability to predict the time of earthquakes
Red seismic stations received arrivals from small local earthquakes that was triggered by a large distant earthquake (those in blue did not) Independent of tectonic province – mediated by surface waves!
Applications
Synthetic earthquakes I

MHD Generators – The Earthquake machine

- Weight 18,000 kg
- Maximum power 15 MW
- Runtime 2 & 7 seconds
- Output 1.5 kA at 1350 V

Graph showing number of local earthquakes before and after MHD run (days).
Fluid flow into the fault reduces the effective pressure, triggering the earthquake.

Pressure in the fault increases at one rate and decreases at another. Fracture fluid pressure may be over a critical level for several days after current injection.
Conclusions

Bailey et al., 2008
Conclusions I

- The electro-kinetic and (seismo-electric) phenomena are well understood conceptually and qualitatively.

- Unfortunately we do not have a sufficient database of measurements to fully understand quantitatively these phenomena in rocks.

- Despite this fundamental lack both phenomena have been pressed into practical application.
However, high quality apparatus is being developed in a number of laboratories worldwide.

Future data should give us a better quantitative basis for the phenomena.

Applications for the phenomena are huge with a potential market amounting to billions of euros.

The properties as a function of frequency and saturation are particularly important.
Future directions

- Development of AC electrical theory in rocks
- Development of AC electro-kinetic and seismo-electric theory
- Better basic measurements made over a large range of rocks and parameters
- Particular importance given to AC measurements and saturation measurements
- Open research with industry
- Ensure applications use the latest developments and data
## Acknowledgments

<table>
<thead>
<tr>
<th>Country</th>
<th>Contributors</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Canada</strong></td>
<td>Emilie Walker &amp; Eric Tardif, Jean Ruel, John Hadjigeorgiou &amp; Tom Ransford, Guillaume Lalande, Melissa Jodouin, Marc Blouin, Nicholas Déry &amp; Simon Marcil</td>
</tr>
<tr>
<td><strong>Scotland</strong></td>
<td>Steven Ogilvie, Evgeny Isakov, Malcolm Hole &amp; Colin Taylor, Ibrahim Al-Zadjali, Kellie Frew, Steven Cuddy &amp; Hesham Al-Qassab, Peter Bormann &amp; Gregor Bächle</td>
</tr>
<tr>
<td><strong>Hungary</strong></td>
<td>Antal Adám</td>
</tr>
<tr>
<td><strong>Spain</strong></td>
<td>Jaume Pous &amp; Javier Gomez</td>
</tr>
<tr>
<td><strong>Japan</strong></td>
<td>Koji Matsuki, Kazuo Hayashi &amp; Toshiyuki Hashida</td>
</tr>
<tr>
<td><strong>France</strong></td>
<td>André Revil, David Mainprice, Philippe Pezard, Benoît Iledefonse, Yves Guéguen, Yves Bernabé, Michel Darot, Thierry Reuschlé &amp; Patrick Baud</td>
</tr>
<tr>
<td><strong>UCL</strong></td>
<td>Philip Meredith, Stan Murrell &amp; Steve Boon</td>
</tr>
<tr>
<td>UEA &amp; Newcastle upon Tyne</td>
<td>Fred Vine FRS, Keith Runcorn &amp; Russell Ross</td>
</tr>
</tbody>
</table>