A THEORETICAL MODEL OF STREAMING POTENTIAL AND ZETA POTENTIAL IN ROCKS

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Introduction

- The classical Helmholtz-Smoluchowski equation relates the streaming potential coupling coefficient (SPCC) to
  - zeta potential
  - Pore fluid dielectric permittivity
  - Pore fluid conductivity
  - Pore fluid viscosity

$$C_s = \frac{\varepsilon_f \zeta}{\eta_f \left(\sigma_f + 2\Sigma_s / \Lambda\right)}$$

- Developped for capillary tubes
- Commonly applied to rocks
- However, never been validated for rocks (no measure of zeta potential)
- Never even been a theoretical model applied to real rocks
- DESPITE most of the theoretical tools being available since 1998

Introduction

❖ In this presentation:

Development of the required theoretical tools

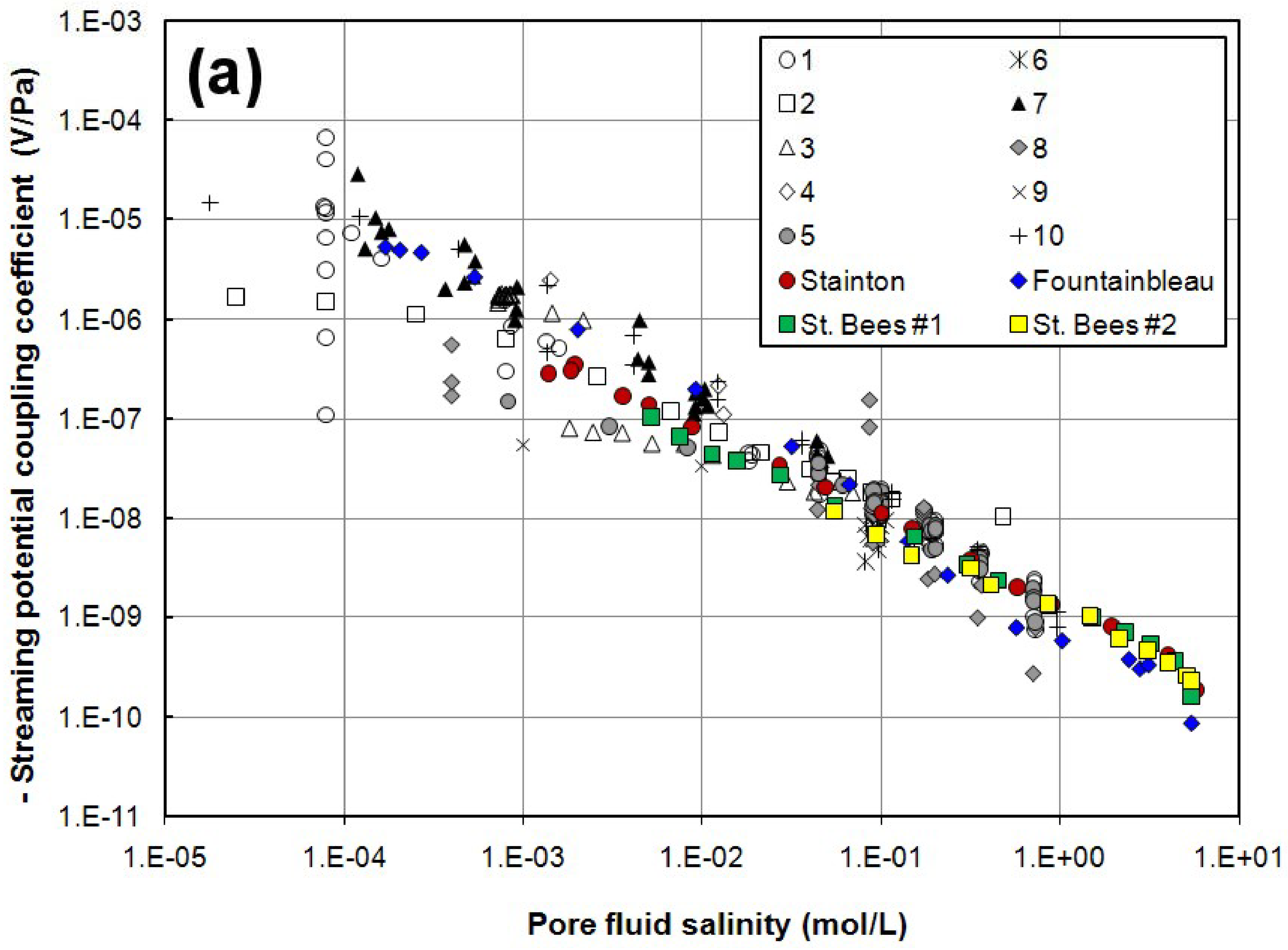
Compilation of a SPCC dataset for rocks

Compilation of a zeta potential dataset for rocks

Modelling SPCC of rocks as a function of salinity

Modelling ζ of rocks as a function of salinity

Database



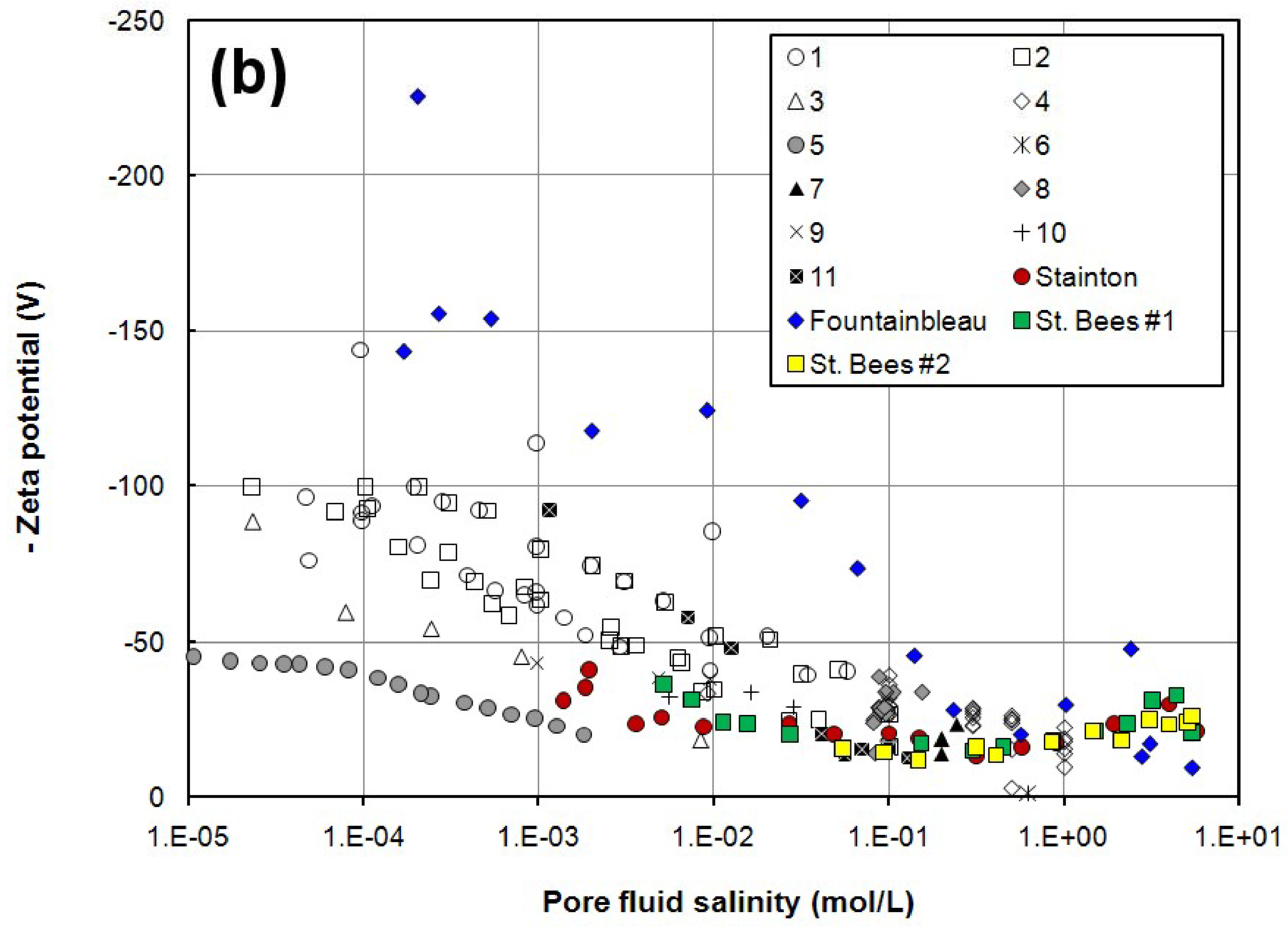
SPCC vs. Pore fluid salinity

Silica, glass, sand and sandstone

11 sources

Acknowledgments to Jaafar (2009)

Database



Zeta potential vs. Pore fluid salinity

Silica, glass, sand and sandstone

7 sources

Acknowledgments to Jaafar (2009)

Theoretical model

The method is as follows:

1. Calculate the pore fluid conductivity (salinity and temperature)

$$\sigma_f\left(T,C_f\right)=\left(d_1+d_2T+d_3T^2\right)C_f-\left(\frac{d_4+d_5T}{1+d_6C_f}\right)C_f^{3/2}$$

Sen and Goode (1992)

2. Calculate the pore fluid relative permittivity (salinity and temperature)

$$\varepsilon_f\left(T,C_f\right)=\varepsilon_o\left(a_0+a_1T+a_2T^2+a_3T^3+c_1C_f+c_2C_f^2+c_3C_f^3\right)$$

Olhoeft (1980)

3. Calculate the pore fluid viscosity (salinity and temperature)

$$\eta_f\left(T,C_f\right)=e_1+e_2\exp\left(\alpha_1T\right)+e_3\exp\left(\alpha_2C_f^m\right)+e_4\exp\left(\alpha_3T+\alpha_4C_f^m\right)$$

Phillips et al. (1978)

Theoretical model

4. Define the physical chemistry of the double layer

$$>\mathrm{SiOH^o} \overset{K_{(-)}}{\Leftrightarrow} >\mathrm{SiO^-} + \mathrm{H^+}$$

$$>\mathrm{SiOH^o} + \mathrm{Me^+} \overset{K_{Me}}{\Leftrightarrow} >\mathrm{SiOMe^o} + \mathrm{H^+}$$

5. Calculate or set the pore fluid pH (SiO_2-H_2O-CO_2)

$$C_{H^+}^3 - \left(C_a - C_b\right)C_{H^+}^2 - \left(K_w + K_1\right)C_{H^+} - 2K_1K_2 = 0$$

$$K_w = 6.9978\times10^{-16} + 5.0178\times10^{-16}T - 2.4434\times10^{-17}T^2 + 7.1948\times10^{-19}T^3$$

Lide (2009); Revil et al. (1999)

6. Calculate the Debye screening length and shear plane distance

$$\chi_d = \sqrt{\frac{\varepsilon_o\varepsilon_r k_b T}{2000\mathrm{N}e^2 I_f}} \quad \text{and} \quad I_f = \frac{1}{2}\sum_i^n Z_i^2 C_i^f \qquad \chi_\zeta = 2.4\times10^{-10}\ \mathrm{m}$$

Theoretical model

7. Calculate the Stern plane potential

$$\varphi_d = \frac{2k_bT}{3e}\ln\left(\frac{\sqrt{8\times10^3\varepsilon_r\varepsilon_o k_b T \mathrm{N}}\left(10^{-pH}+K_{Me}C_f\right)}{2e\Gamma_s^o K_-}\left[\frac{C_a+C_b+C_f+10^{-pH}}{\sqrt{I_f}}\right]\right)$$

Revil and Glover (1997; 1998)

8. Calculate the zeta potential

$$\zeta = \varphi_d \exp\left(-\chi_\zeta / \chi_d\right)$$

Revil and Glover (1997; 1998)

Theoretical model

9. Calculate the surface conductance $\Sigma_s = \Sigma_s^{EDL} + \Sigma_s^{Prot} + \Sigma_s^{Stern}$

$$\Sigma_s^{Stern} = \frac{e\beta_s \Gamma_s^o K_{Me} C_f}{\left(10^{-pH} + K_- \left(\frac{\sqrt{8\times10^{-3}\varepsilon_r\varepsilon_o k_b T N}\left(10^{-pH} + K_{Me}C_f\right)}{2e\Gamma_s^o K_-}\left[\frac{C_a + C_b + C_f + 10^{-pH}}{\sqrt{I_f}}\right]\right)^{2/3} + K_{Me}C_f\right)}$$

$$\Sigma_s^{EDL} = R\left[\left[\left(B_{Na^+}C_f + B_{H^+}10^{-pH}\right)\left(\left(S\left(\frac{10^{-pH} + C_f K_{Me}}{2e\Gamma_s^o K_-}\right)\right)^{-1/3} - 1\right)\right] + \left[\left(B_{Cl^-}C_f + B_{OH^-}10^{pH-pK_f}\right)\left(\left(S\left(\frac{10^{-pH} + C_f K_{Me}}{2e\Gamma_s^o K_-}\right)\right)^{+1/3} - 1\right)\right]\right]$$

$$R = \sqrt{\frac{2\times10^{-3}\varepsilon_r\varepsilon_o k_b T N}{C_f + 10^{-pH}}}$$

$$S = \sqrt{8\times10^{-3}\varepsilon_r\varepsilon_o k_b T N\left(C_f + 10^{-pH} + 10^{pH-pK_w}\right)}$$

Revil and Glover (1997; 1998)

Theoretical model

10. Calculate the SPCC

$$C_s = \frac{\Delta V}{\Delta P} = \frac{d\,\varepsilon_f\,\zeta}{\eta_f\left(d\,\sigma_f + 4\Sigma_s\,m\,F\right)}$$

Glover and Déry (in press)

- Fundamental constants (k_b and N_A etc.).
- Environmental conditions (T etc.).
- Fluid parameters (salinity, pH, pK_w, pK_1 *and* pK_2 etc.).
- Rock microstructure parameters (F, m, ϕ, d etc.).
- Rock-fluid interface parameters, i.e., the electro-chemical parameters associated with surface adsorption reactions (pK_{me}, pK_{-} etc.).

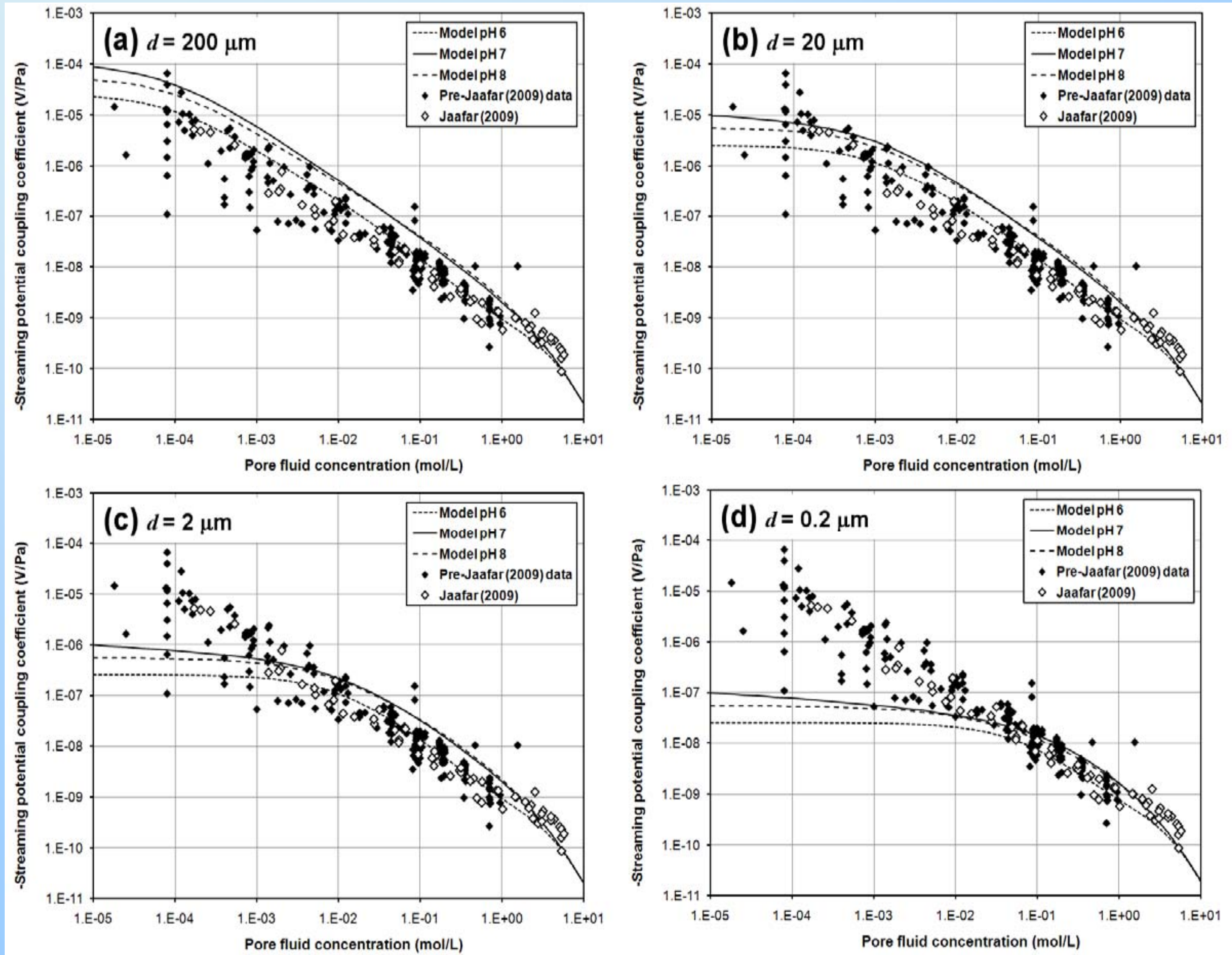
Theoretical model

Parameter	Symbol	Value or range	Units	Reference
Model variables				
Temperature	T	25	°C	Experimental condition
Pore fluid salinity	C_f	10^{-5} – 3.98	mol/L	Varied between limits
Pore fluid pH	pH	6 - 8	(-)	Varied between limits
Fundamental constants				
Dielectric permittivity in vacuo	ε_o	8.854×10^{-12}	F/m	Lide (2009)
Boltzmann's constant	k_b	1.381×10^{-23}	J/K	Lide (2009)
Charge on an electron	e	1.602×10^{-19}	C	Lide (2009)
Avagadro's number	N	$6.02\times10^{+23}$	/mol	Lide (2009)
Fluid parameters				
Added acid concentration	C_a	variable	mol/L	Calculated from pH
Added base concentration	C_b	variable	mol/L	Calculated from pH
Surface mobility	β_s	5×10^{-9}	$m^2/s/V$	Revil and Glover (1997)
Reaction constant carbonisation	pK_1	7.53	(-)	Wu et al. (1991)
Reaction constant dehydrogenisation	pK_2	10.3	(-)	Wu et al. (1991)

Theoretical model

Parameter	Symbol	Value or range	Units	Reference
Rock parameters				
Grain size (diameter)	d	2×10^{-4}	m	St Bee's SST (Jaafar et al., 2009)
Cementation exponent	m	1.86	(-)	Calculated $m = -\log F / \log \phi$
Formation factor	F	19.80	(-)	St Bee's SST (Jaafar et al., 2009)
Porosity	ϕ	0.19	(-)	St Bee's SST (Jaafar et al., 2009)
Rock/fluid interface parameters				
Surface site density	Γ_s^o	$1\times10^{+19}$	sites/m^2	Adjusted to fit data
Binding constant for cation (sodium) adsorption on quartz	pK_{me}	7.1	(-)	Adjusted to fit data
Disassociation constant for dehydrogenisation of SiOH	$pK_{(-)}$	7.5	(-)	Adjusted to fit data
Shear plane distance	χ_ζ	2.4×10^{-10}	m	Revil and Glover (1997)
Surface conduction (protonic)	Σ_s^{Prot}	2.4×10^{-9}	S	Revil and Glover (1997)
Surface mobility	β_s	5×10^{-9}	m^2/s/V	Revil and Glover (1997)

Plenary Model



SPCC vs. Pore fluid salinity

Silica, glass, sand and sandstone

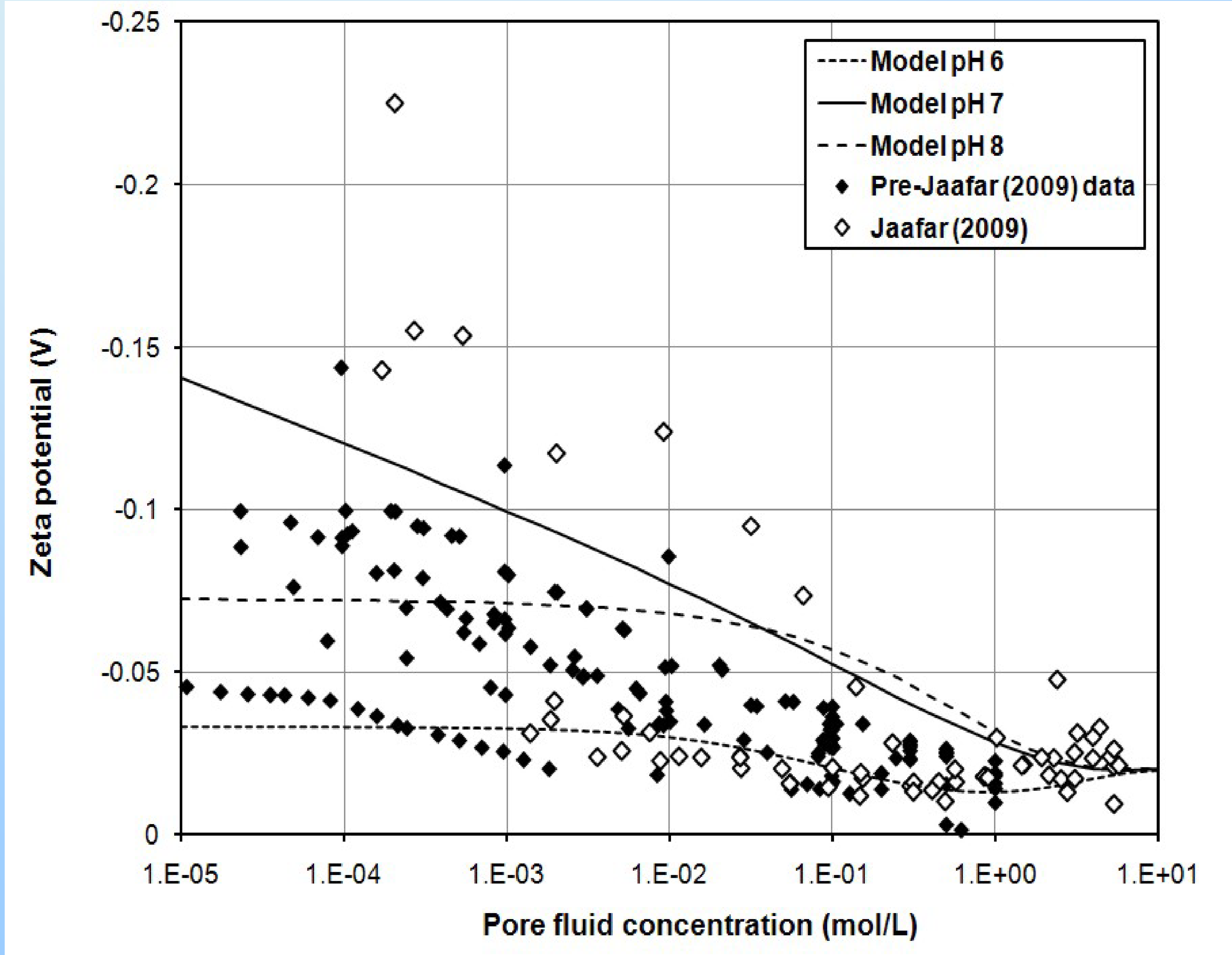
3 different pHs

4 different grain sizes

General properties of the SPCC database and absolute values are well described

Grain size can be extremely important

Plenary Model



Zeta potential vs. Pore fluid salinity

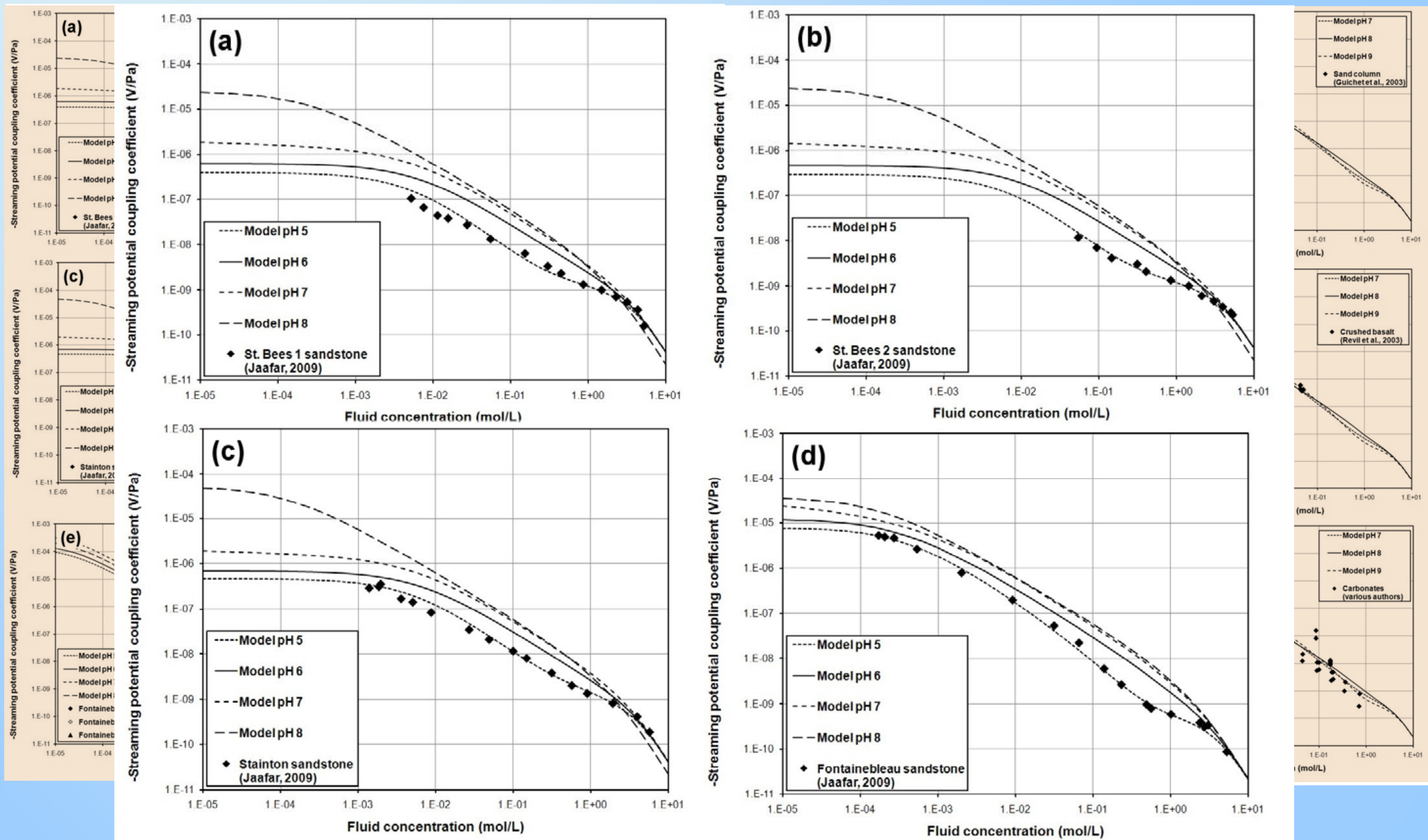
Silica, glass, sand and sandstone

3 different pHs

Database measurements are very scattered

Highly sensitive to changes in pH

Individual Model



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Individual Model

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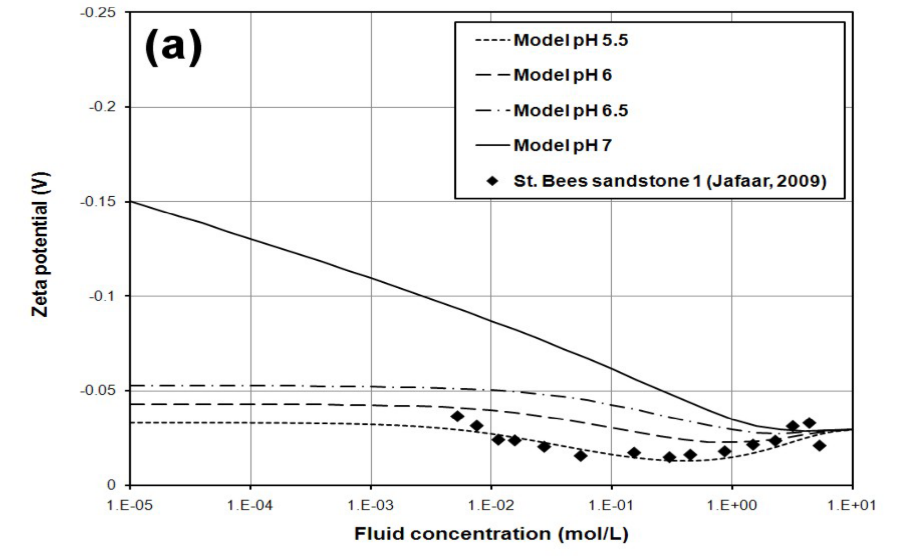

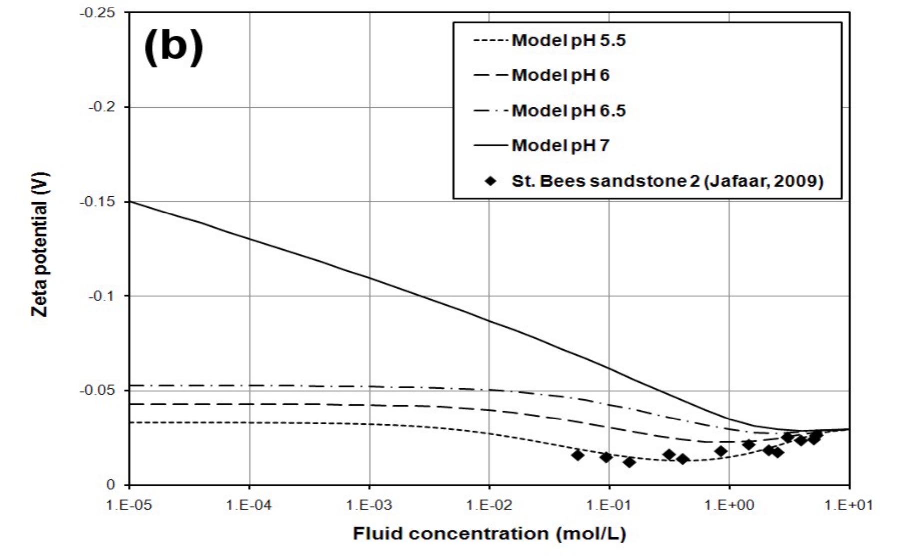

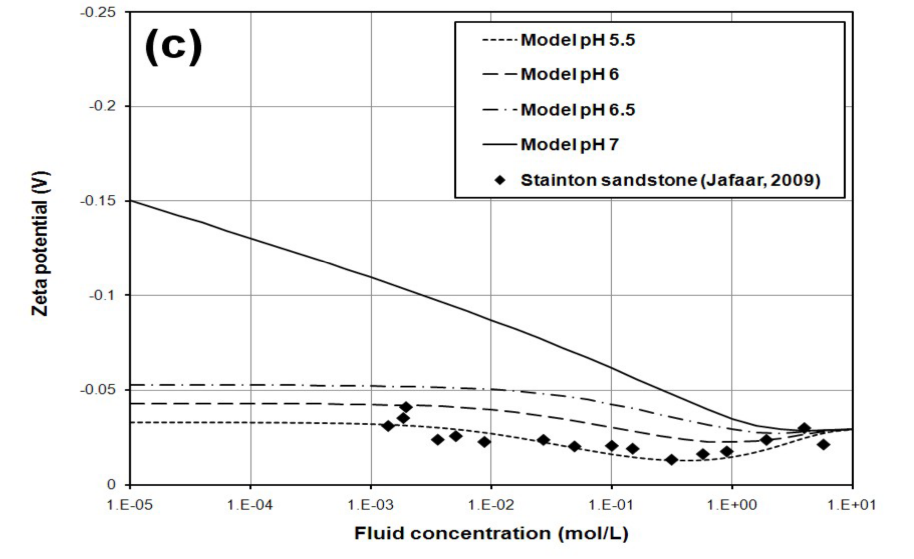

Individual modelling suggests that the operating pH is low (about pH 5.5).

Conclusions

- Compiled: A database of SPCC vs. pore fluid salinity for silica-based rocks
- Compiled: A database of zeta potential vs. pore fluid salinity for silica-based rocks
- Developped: A method for modelling the SPCC and zeta potential of porous media as a function of pore fluid salinity
- Theoretical model: Shows systematic variations with pH and grain size
- Using whole database: The theoretical approach is capable of describing the general properties of the database as well as the absolute values of SPCC and zeta potential
- Using individual rocks: The theoretical approach is capable of describing some of the fine structure apparent in the individual SPCC and zeta potential determinations as a function of salinity

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