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Spectral induced polarization in a sandy medium containing semiconductor materials: study of the polarization mechanism

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Preface

- The polarization mechanism in mineralized medium is not completely understood yet.

- Diffusion of charge carriers inside the semi-conductor grain or around it in the electrolyte: which one is determinant?

- The basic equation is not valid in mineralized medium:

$$\boldsymbol{\tau} = \frac{a^2}{D}$$

(after Gurin et al.2015; Revil et al. 2015)

Objectives

- New experimental study of the polarization phenomena in mineralized medium (semi-conductors).

- New numerical modelling based on Poisson-Nernst-Planck equations has been applied.

Background

- Wong (1979) attributes the polarization observed over mineralized medium to two mechanisms:

  1- Redox-active ions at the grain surface.

  2- Flow of inactive ion in the solution.

- Revil et al. (2015 a, b) attribute the polarization in presence of semi-conductor minerals to the diffusion and accumulation of charges (electrons and holes) inside the metallic grains (in absence of redox activity).

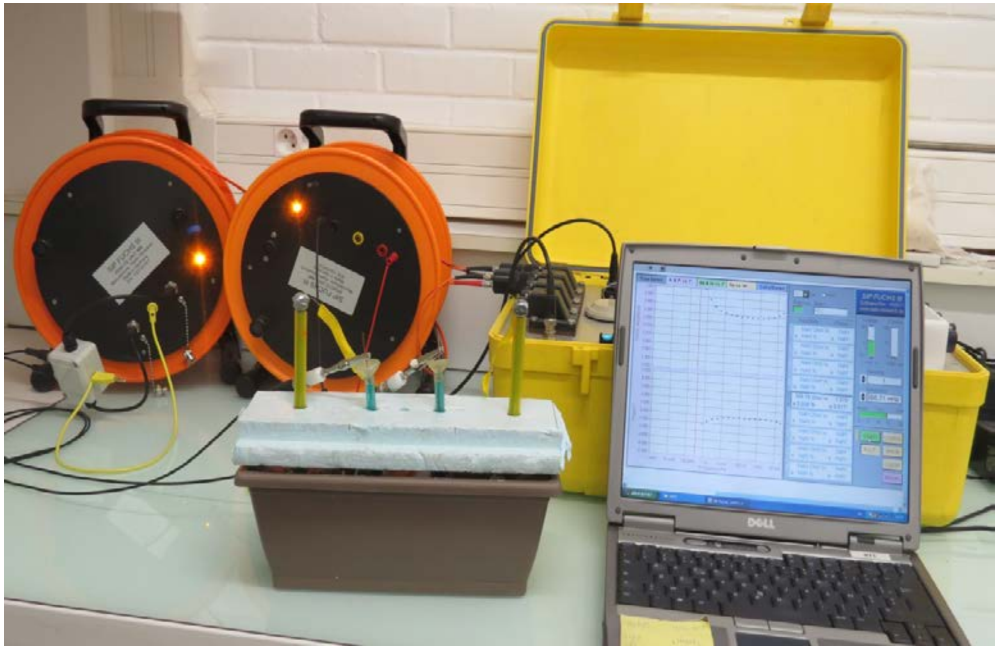
- Both studies show that the metal grain behaves like isolator at lower frequency.

Experiments setup

- Measurements: Complex resistivity of uncosolidated sandy medium
- Variables:
  1- semi-conductor content.
  2- electrolyte type and concentration (0.001 to 0.5 mol/l).
  3- semi-conductor type (galena, pyrite, chalcopyrite and graphite).
  4- grain size.

- Background medium
  - Fine grain sand
    (negligible polarization)
  - Full saturated medium

- Assumption
  - no oxidization.



Calculated parameters

- Chargeability: $\boldsymbol{M} = \frac{\rho_0 - \rho_\infty}{\rho_0}$

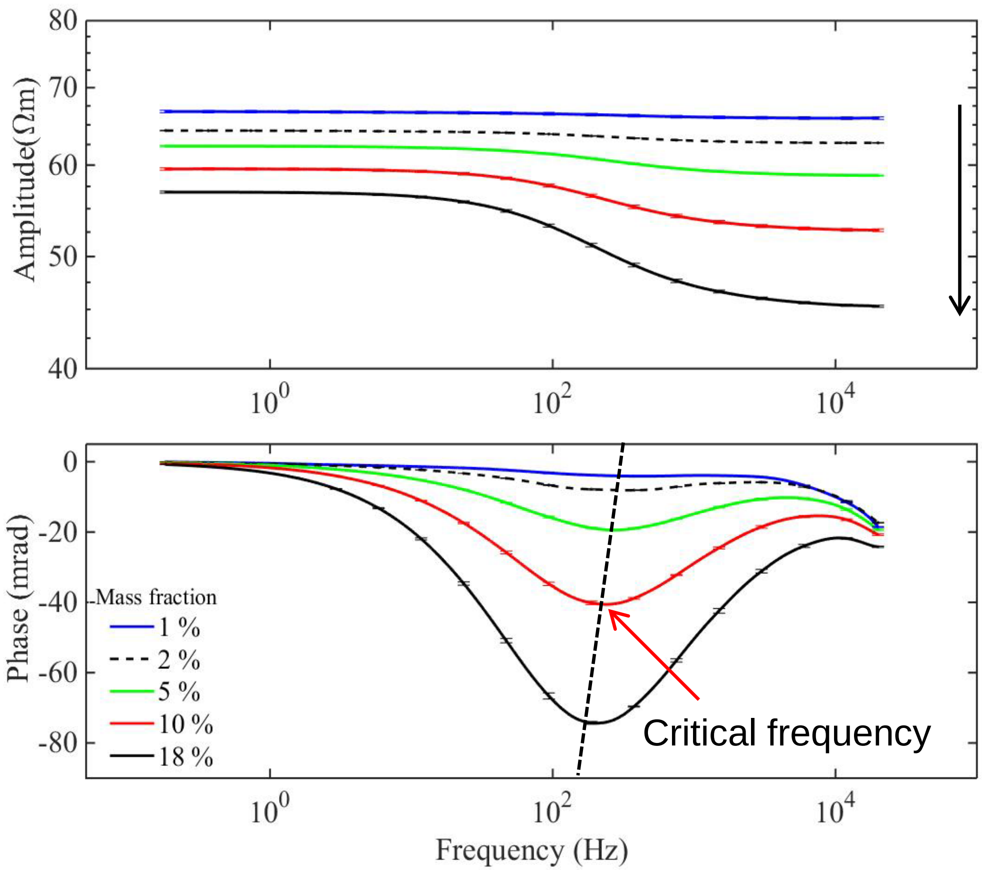
ρ_0 and ρ_∞ are amplitude of the complex resistivity at lower and higher frequency.

- The relaxation time: $\boldsymbol{\tau} = \frac{1}{2\pi f_{peak}}$

f_{peak} is the critical frequency (the frequency of the phase peak).

Semi-conductor content

❑ Example: measurements on Galena of 0.5 mm grain size.

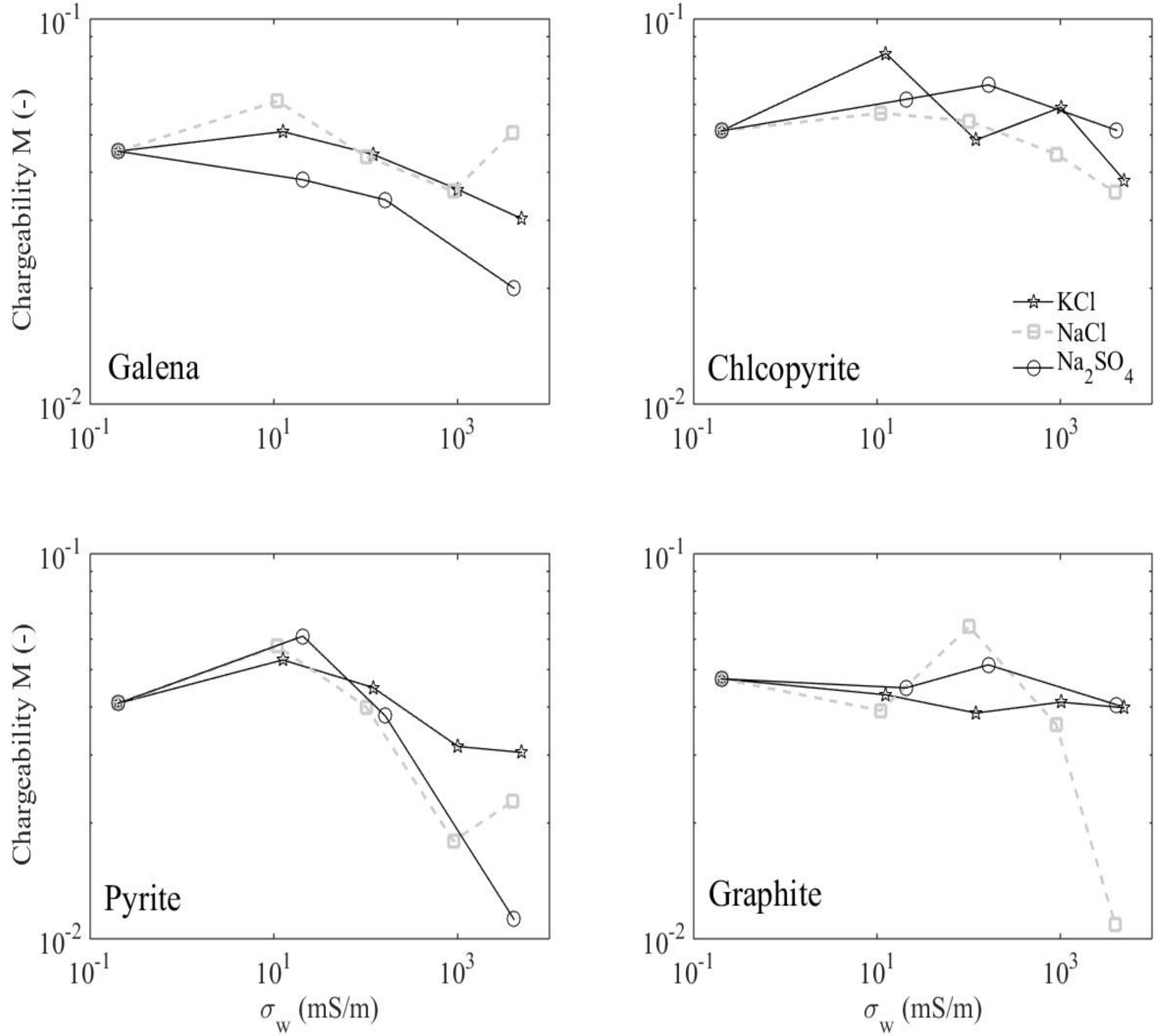


Little increase of semi-conductor content, results in a slight decrease in CR amplitude. (Mahan et al.1986; Hupfer et al. 2016).

✓ Linear relationship between (***M***) and the volume content semi-conductor.

Electrolyte concentration vs chargeability

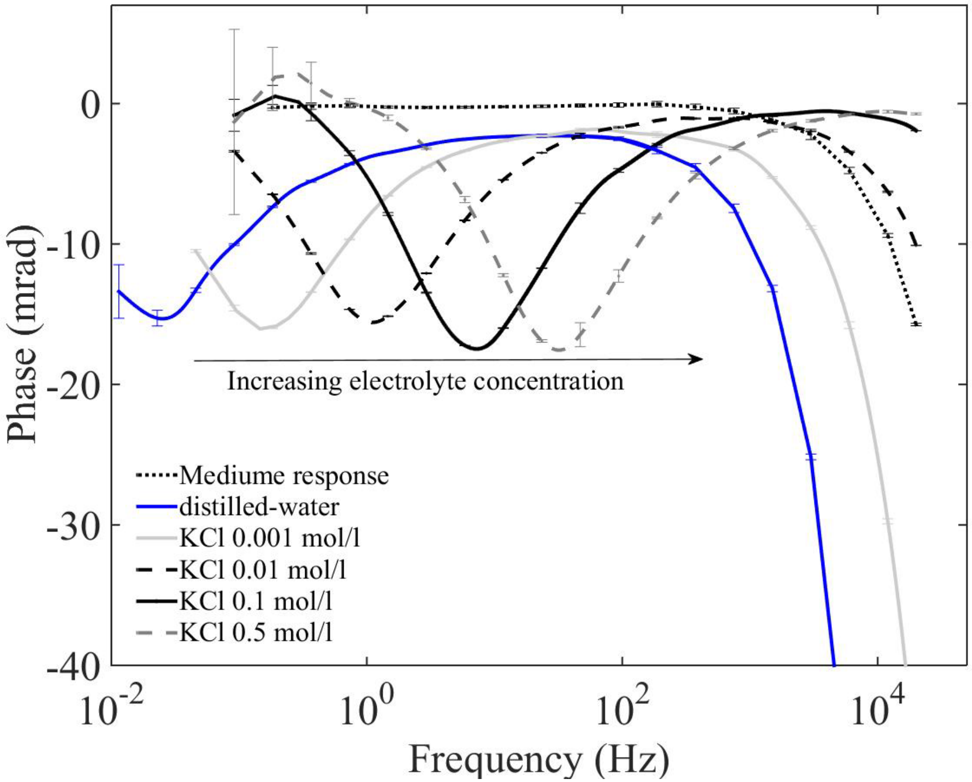
1% volume of semi-conductor

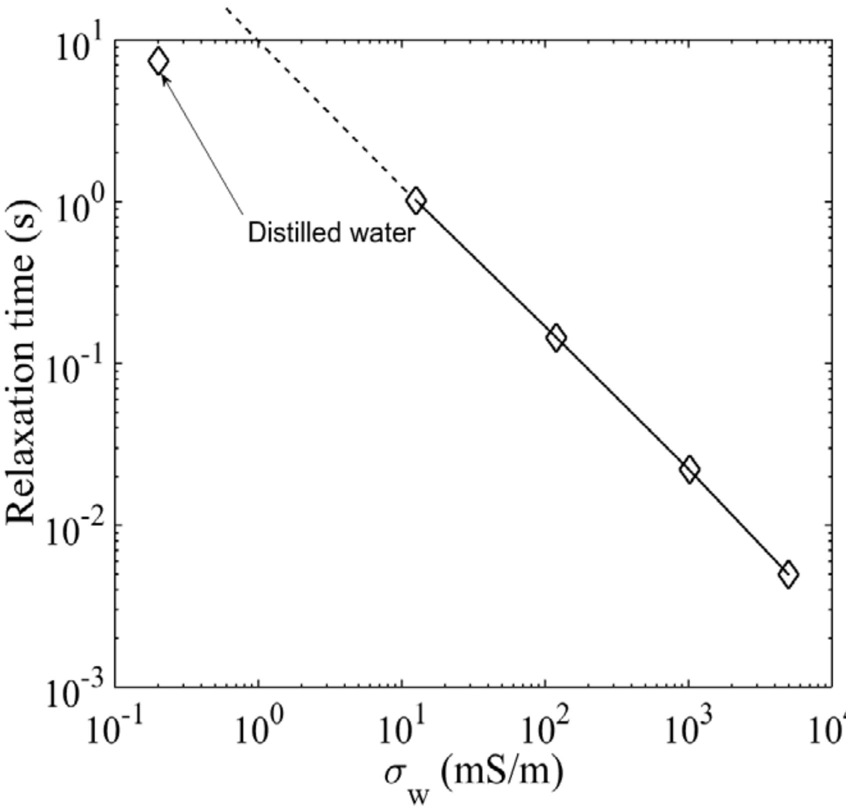


✓ No relation between ***M*** and the electrolyte type or concentration.

Electrolyte concentration vs relaxation time

- Example: measurements on 1% volume of Graphite with 10-15 mm grain size.





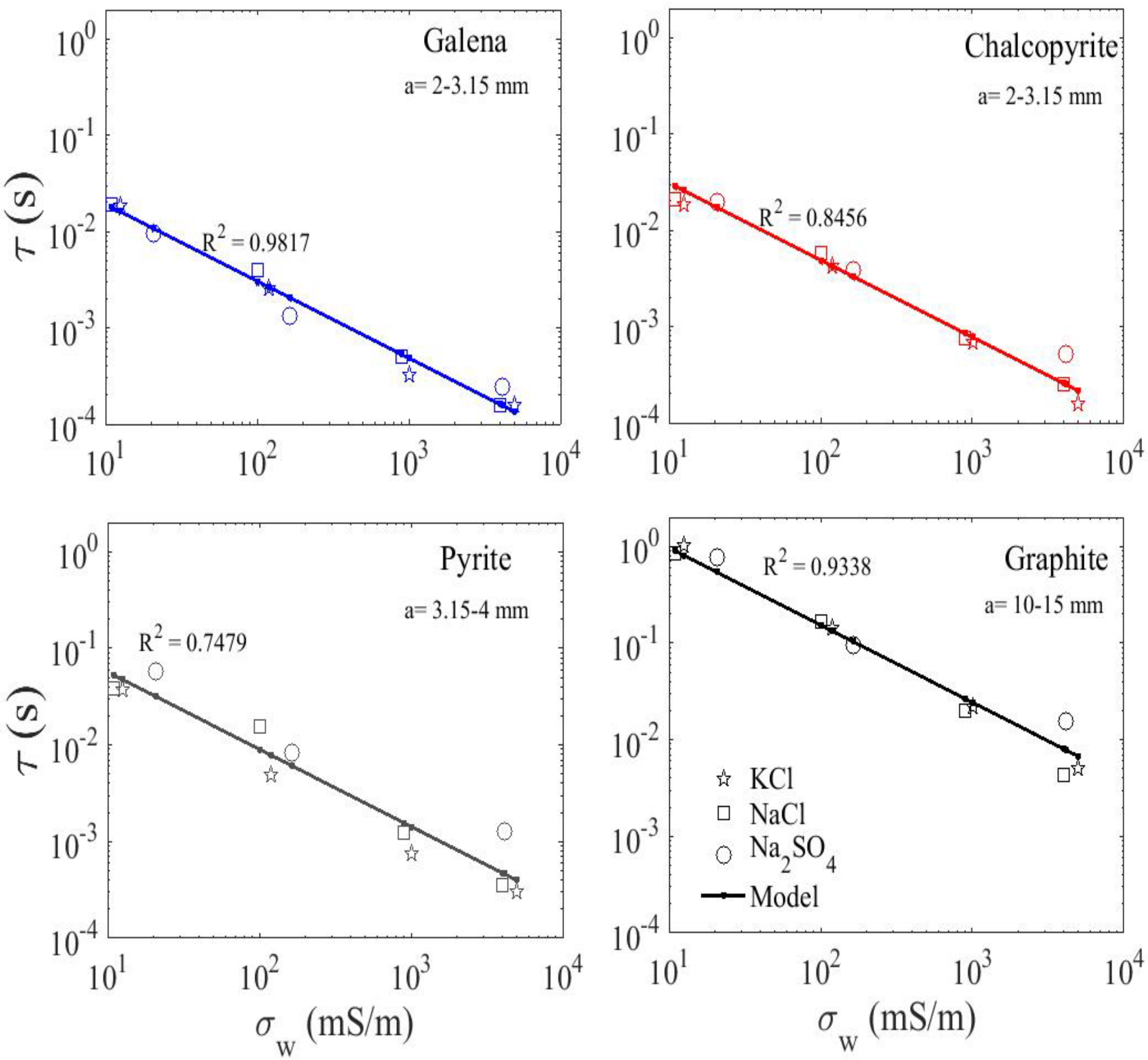
- ✓ Linear relationship between (τ) and solution conductivity (σ_w).
- ✓ No change in the phase shape and phase amplitude.

Electrolyte type vs mineral type

- ✓ The conductivity strongly impacts the time constant $\boldsymbol{\tau}$.

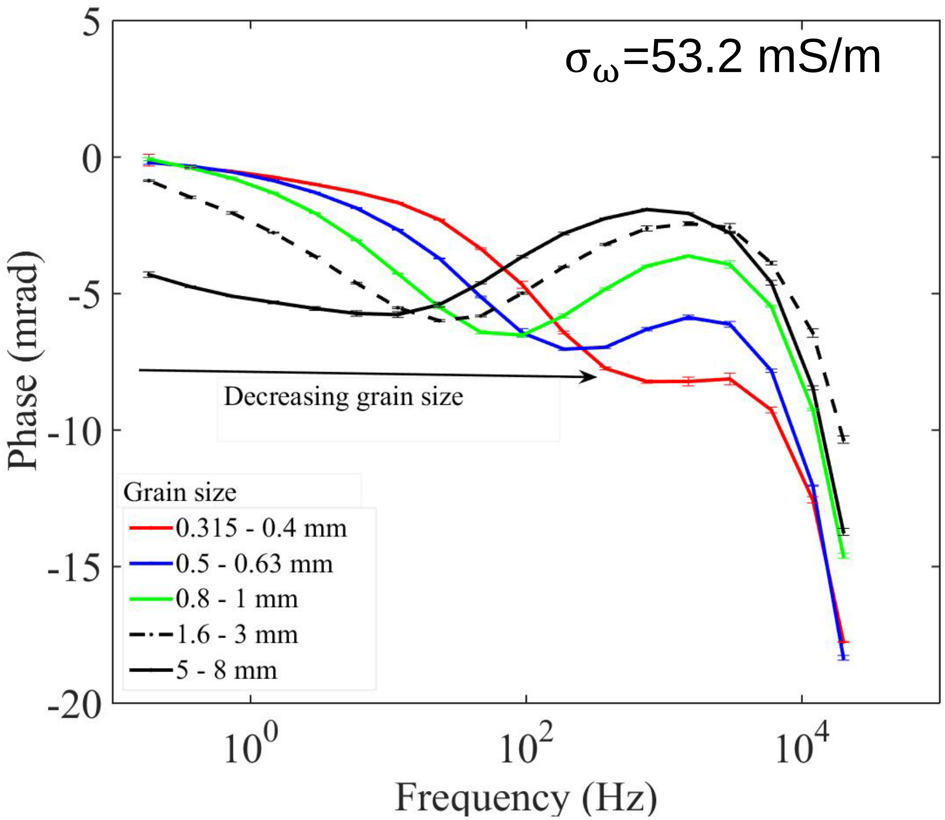
$$\log_{10}(\boldsymbol{\tau}) = -0.8\log_{10}(\sigma_w) + B$$

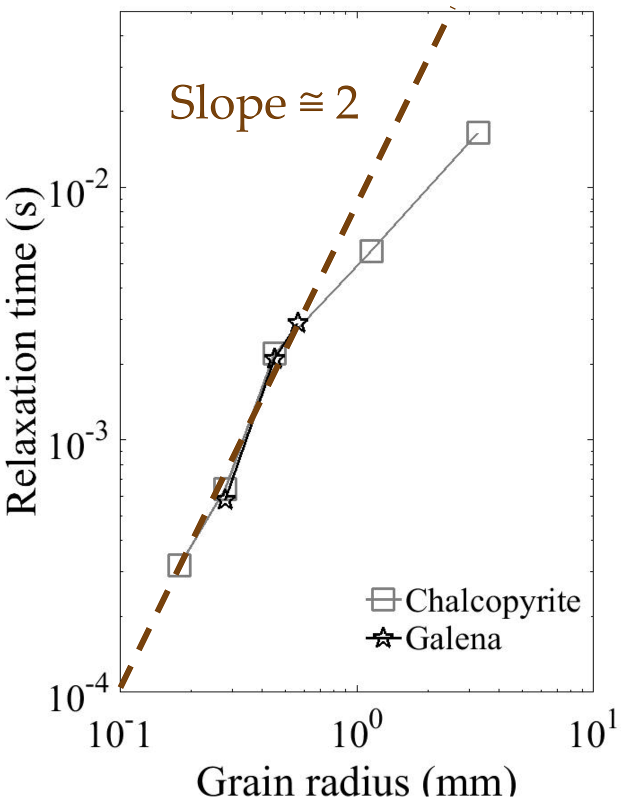
B is dependent on the grain size and mineral type.



Semi-conductor grain size

- ❑ Example: measurements on Chalcopyrite with different grain size.





- ✓ Log – log relationship between ($\boldsymbol{\tau}$) and a^2.
- ✓ Negligible change of ($\boldsymbol{\tau}$) with mineral type (Galena and Chalcopyrite).

Modelling assumptions

- Poisson-Nernst-Planck equations (PNP):

$$\begin{cases} \dfrac{\partial c_i}{\partial t} = \nabla\left(D_i \nabla c_i + \dfrac{z_i e}{k_B T} c_i \nabla V \right); \qquad i = 1, \ldots.. N \\ \nabla\left(\varepsilon \nabla V\right) + \sum_i z_i e c_i = 0 \end{cases}$$

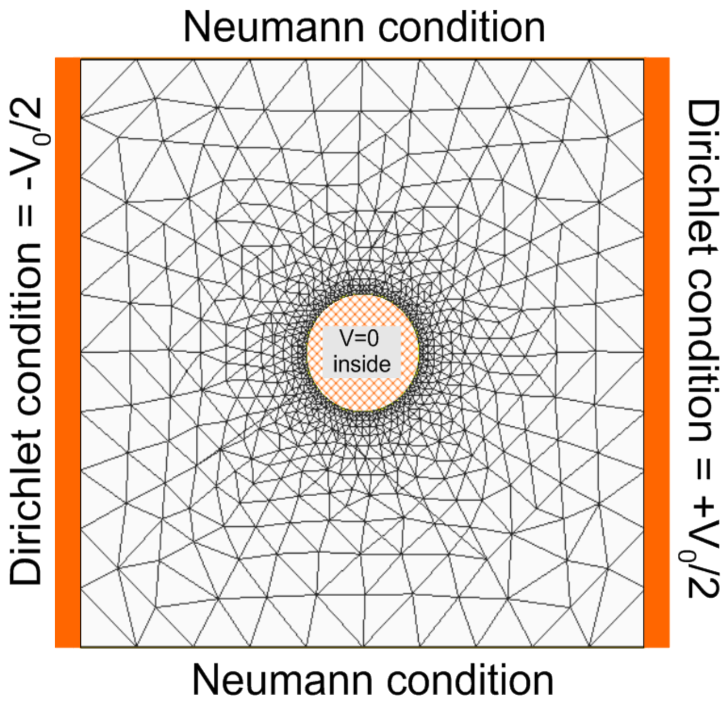
- This couple of equations describe the influence of the ionic concentration and the electrical potential on the flux of charge-carriers in the medium.

- The PNP equations have been applied to model the electromigration diffusion of charge carriers in electrolyte and in semi-conductors.

Numerical calculation

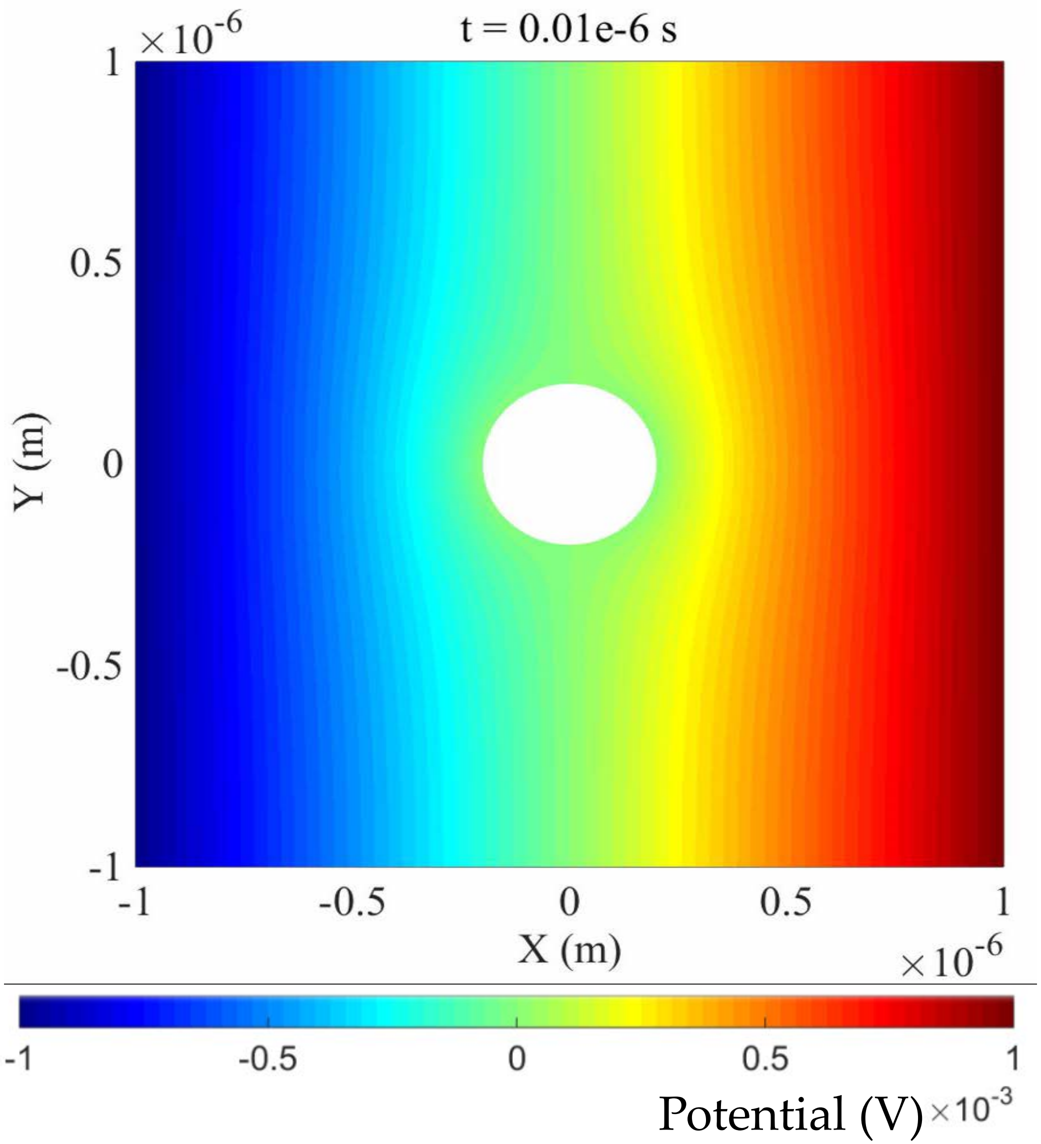
- The time dependent problem solved by using the finite difference approximation in time (Euler's method).

- The space dependent problem solved by using the finite element method.



- **Freefem++** software is used to perform the numerical computation. (http://www.freefem.org/).

Results of numerical calculation



- ❑ Assumptions:

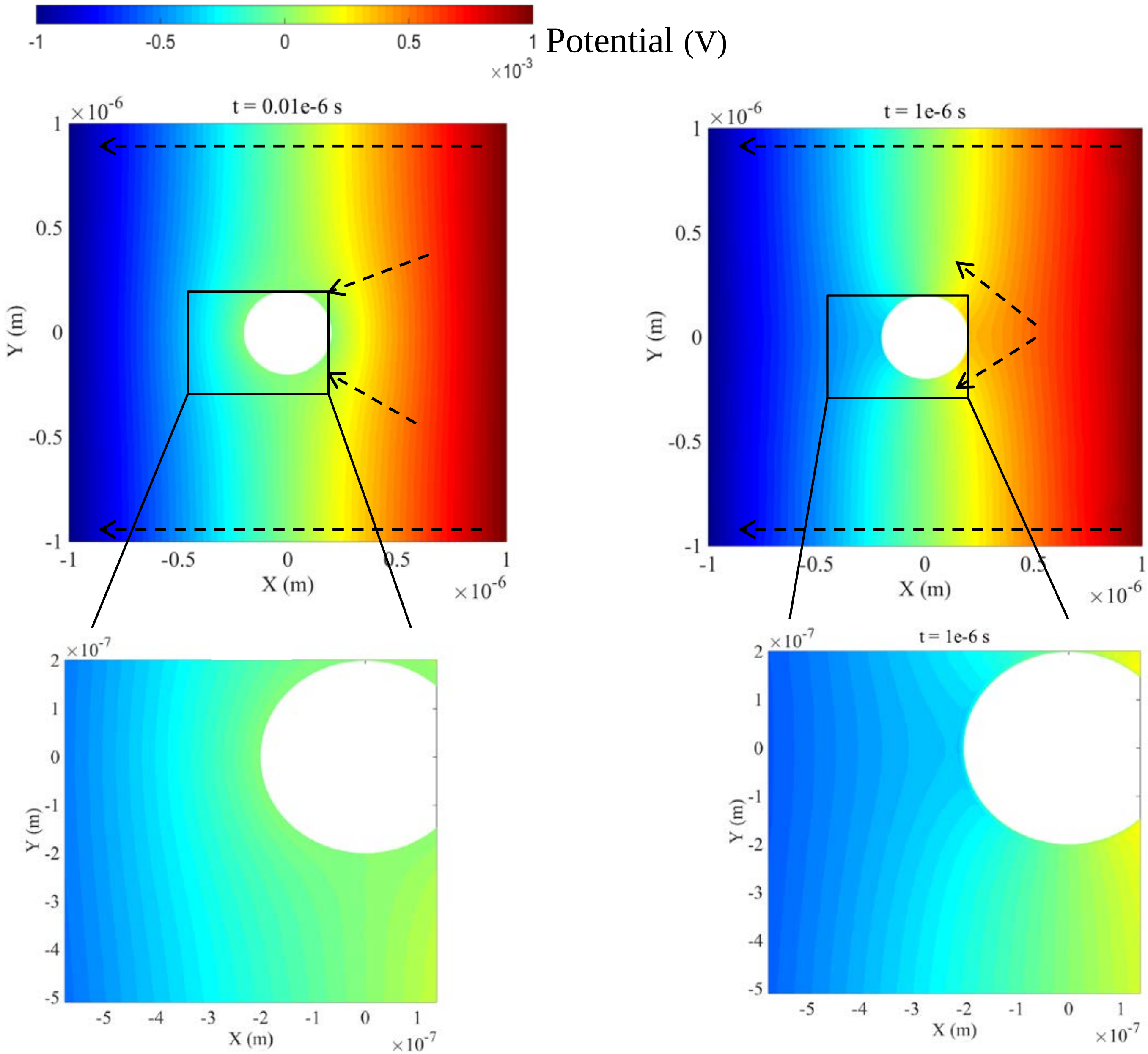
1- Before injection:

- Potential is zero everywhere in medium
- Homogeneous ions concentration.

2- After injection:

- When the particle at center: its own potential is zero all time. (simplification)

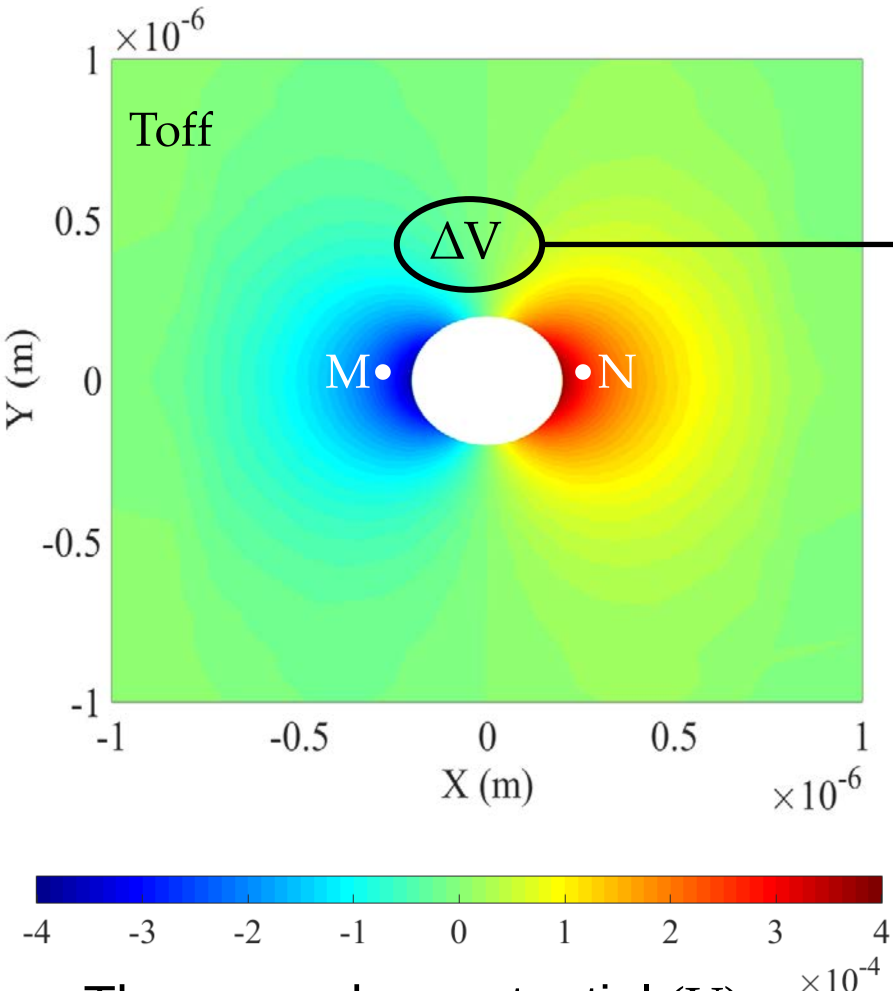
Potential distribution



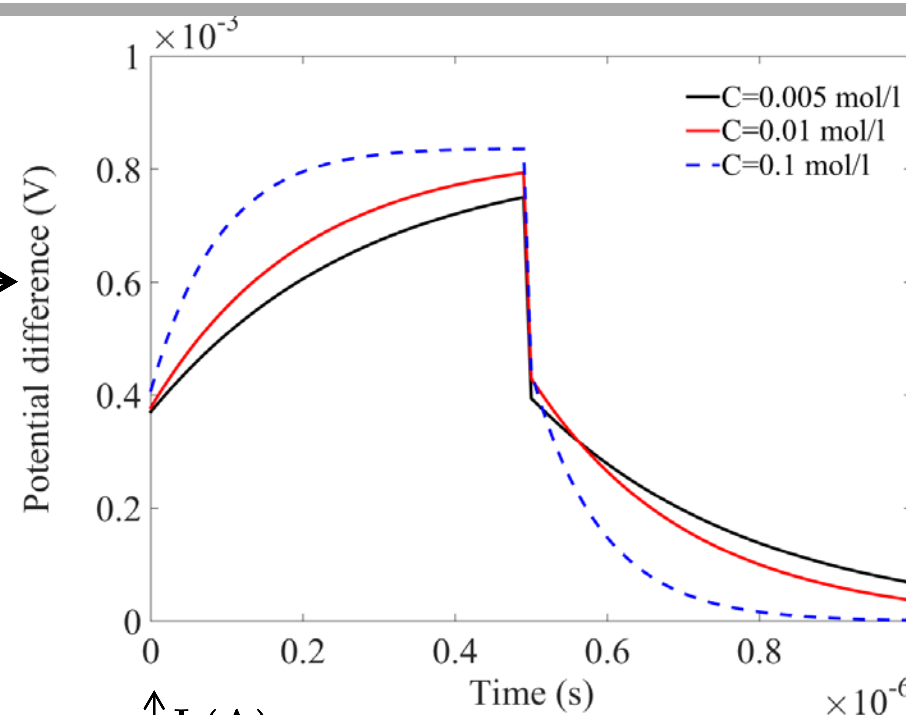
Grain conductor looks like isolator after sometimes.

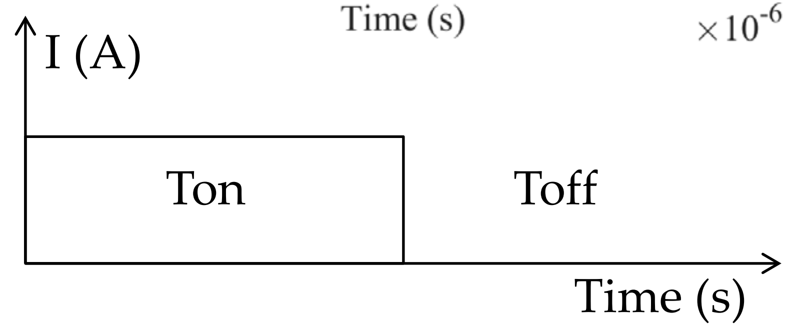
But at micro-scale it is always conductor. (just scale problem).

Changing the concentration-Numerically



The secondary potential (V)
Case of KCl electrolyte.

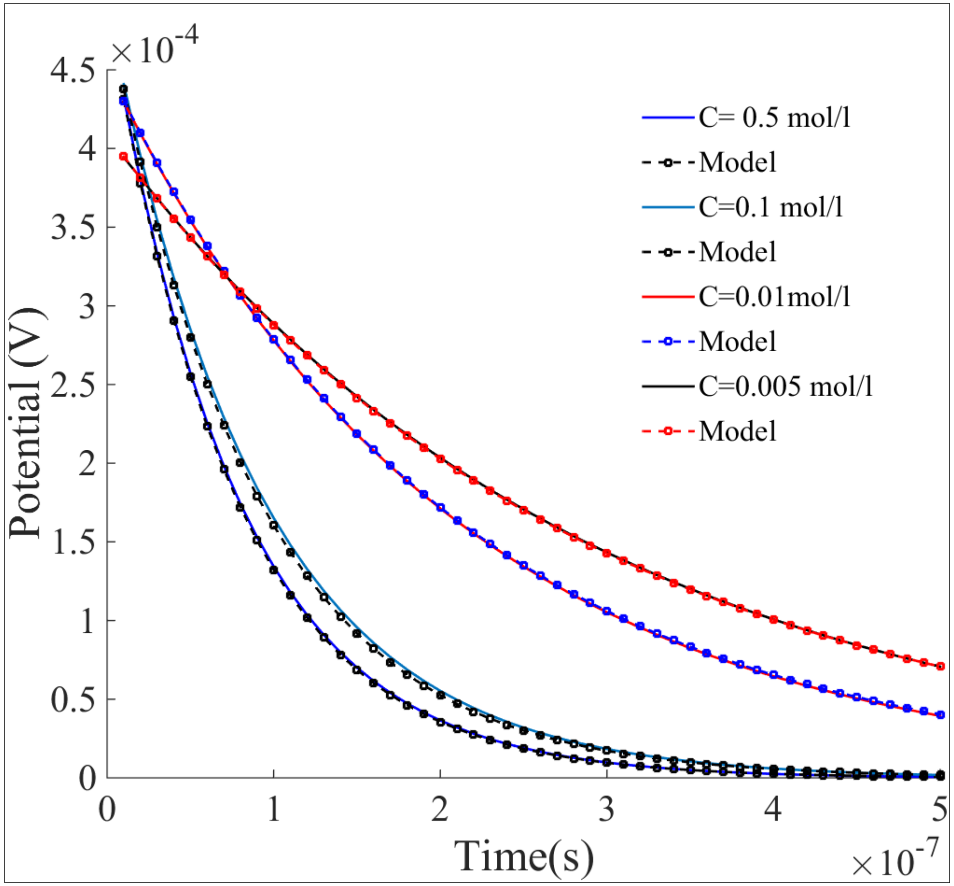




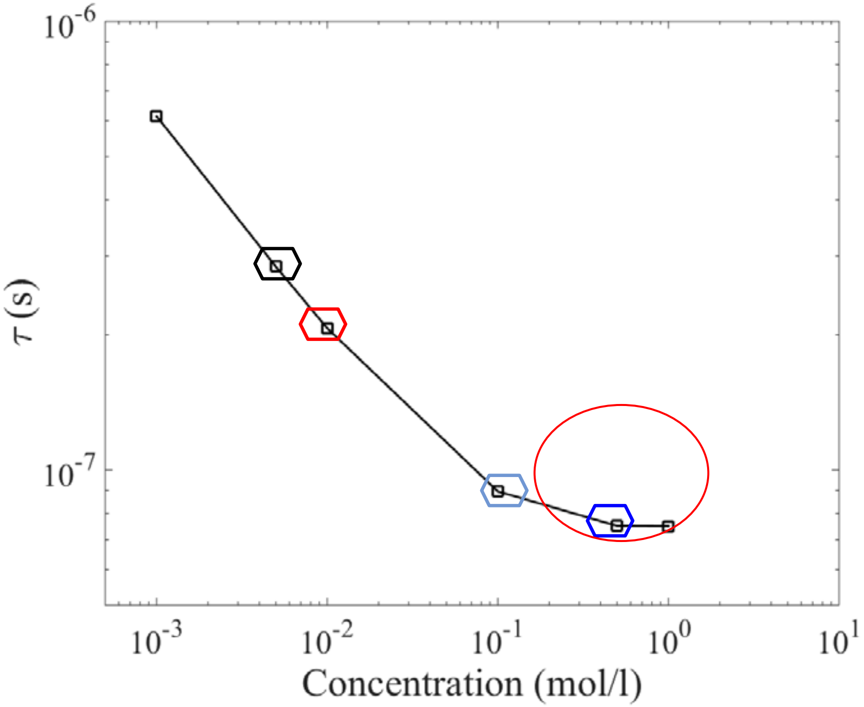
The potential difference between M and N during a cycle of Ton and Toff.

Changing the concentration

Decay curve fitted with exponential function.



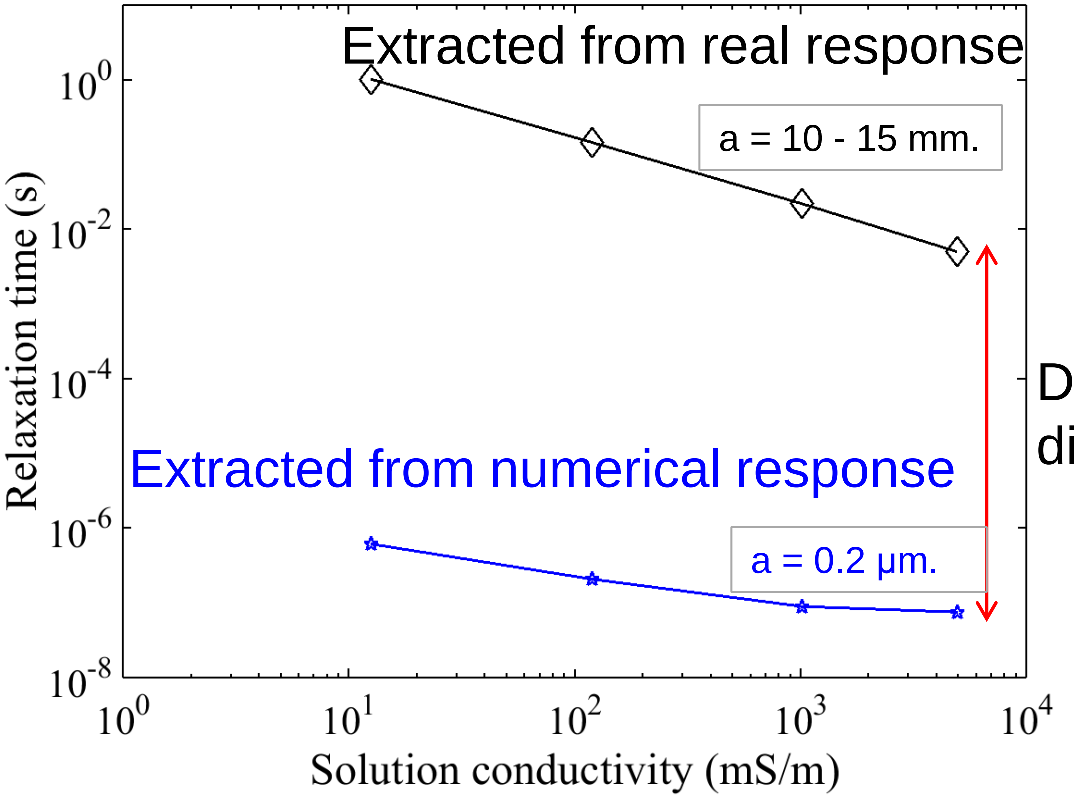
Relaxation time at different Concentration.



✓ Correlation in the relation between with the measurements

Qualitative Comparison (Numerical vs experimental)

- Measurements and modelling in presence of KCl electrolyte.



Difference because of different grain size.

Conclusions

- ✓ ***M*** is a function of the metal volume and independent of the electrolyte type and concentration.
- ✓ **τ** is a function to grain radius, electrolyte conductivity, and slightly to mineral type.
- ✓ The electric dipole formed inside the semi-conductor induces a diffusion of charge carriers in its vicinity.
- ✓ The amount of charge carriers affected by the electric dipole will exist in a smaller zone at higher concentration that's possibly why **τ** decreases.
- ✓ At lower frequency the numerical calculation shows that the grain behaves as isolator.
- ✓ Numerical calculations is in agreement with experimental results and shows a dependence of relaxation time on the electrolyte concentration.

THANK YOU FOR YOU ATTENTION

Outlook

- ✓ Improvement of the numerical model
- ✓ Make computation in frequency domain.
- ✓ Managing the FreeFem++ up scaling to reach more realistic simulation
- ✓ Managing a semi-empiricale model the same as the model of realistic parameters.