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Belgian Nuclear Research Centre

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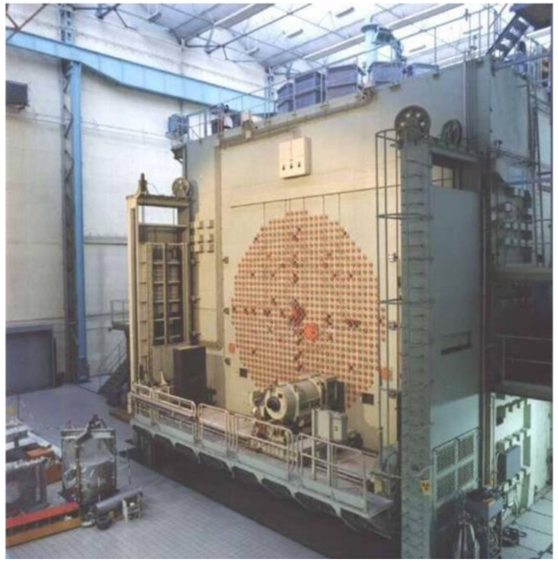
Impedance spectroscopy study of aluminium alloy 1100 encapsulated in ordinary Portland cement pastes

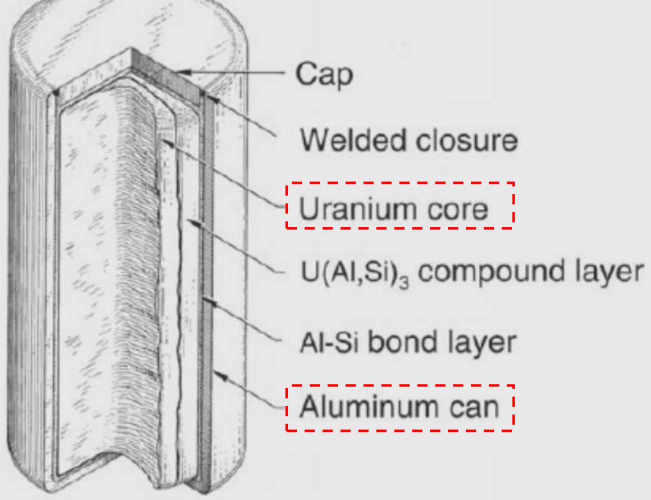
- Context
- Materials & method
- Corrosion
- Cement paste
- Conclusion

Context

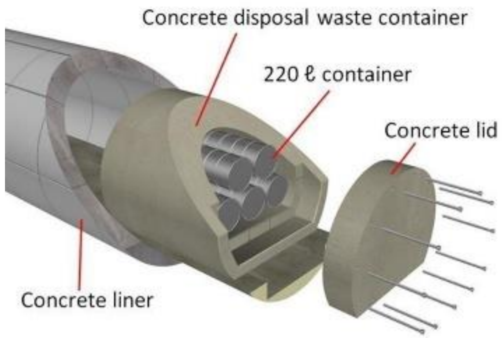
Geological disposal of BR1 fuel



BR1 fuel structure



Disposal route: the direct emplacement of the spent fuel capsules in a cementitious matrix



<u>The key problem</u>: the corrosion of Al layer in the highly alkaline cementitious matrix

The addition of $LiNO_3$ or Li_2CO_3 (Li-Al layered double hydroxide (LDH) film)

- **Electrochemical techniques**
  EIS (Electrochemical Impedance Spectroscopy) & Tafel Polarization
- **GC (Gas Chromatography)**
- **SEM (Scanning Electron Microscopy)**
- **MIP (Mercury Intrusion Porosimetry)**

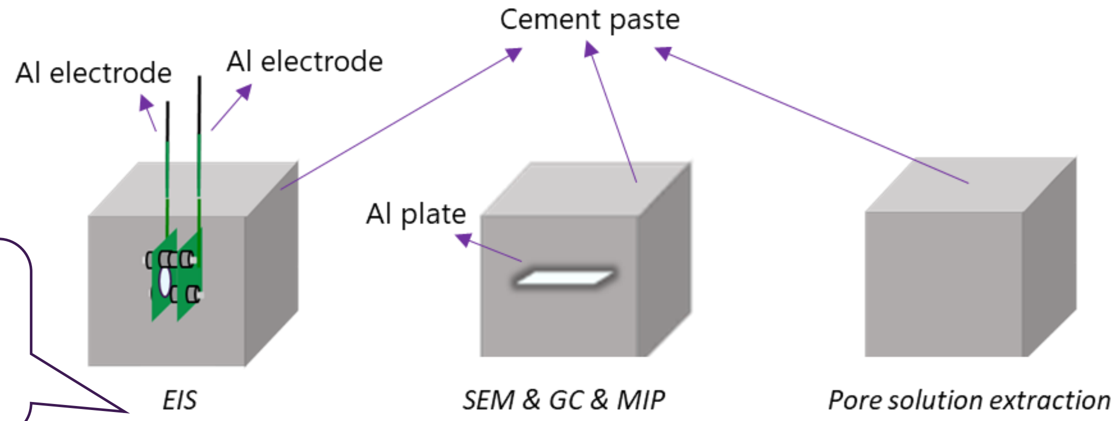
Materials & method

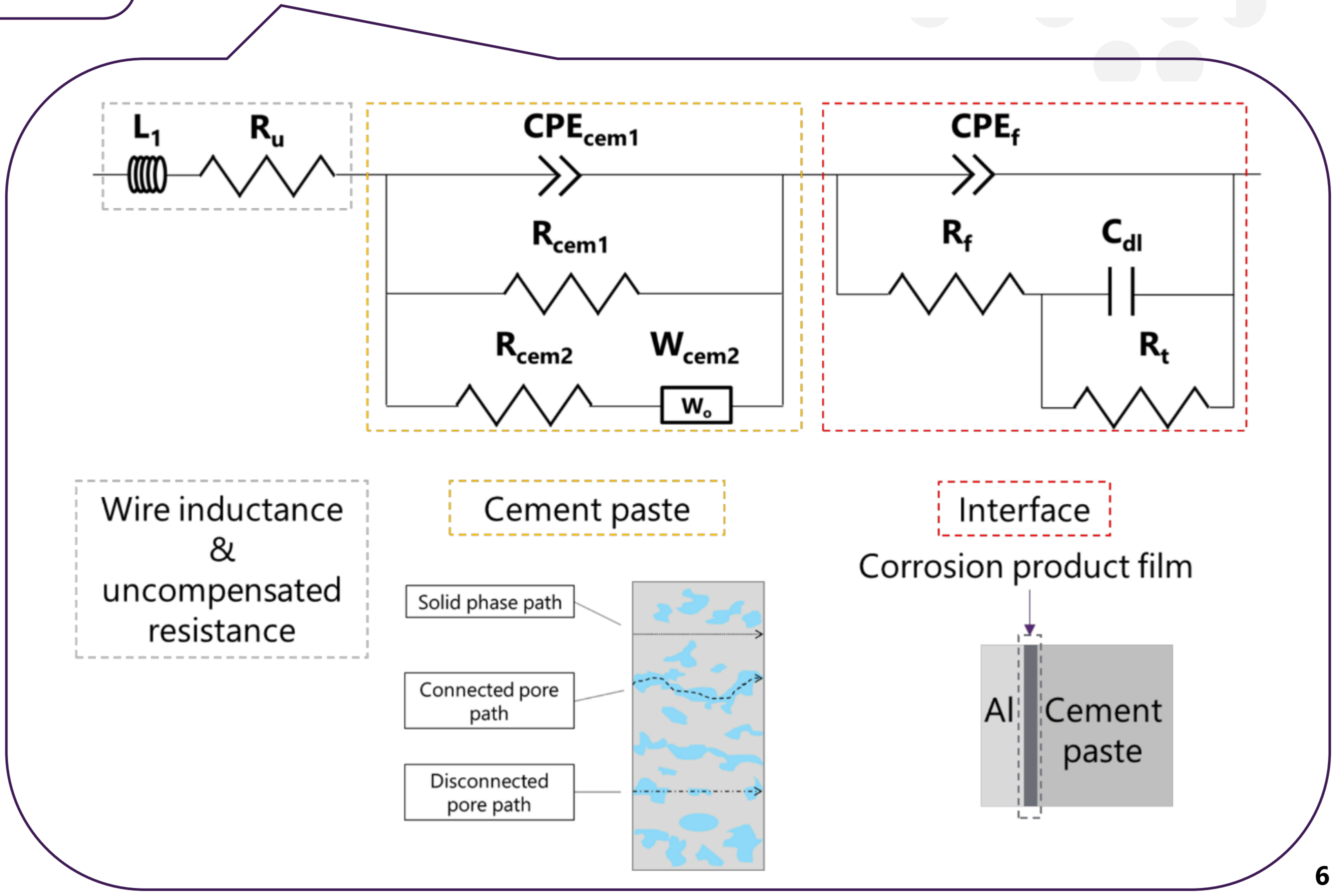
Materials & method

Sample setups:

- Aluminium alloy 1100
- EC:
  - two identical electrodes
  - an exposed area of 2.26 cm^2
- SEM & GC & MIP:
  - one 15×15×1 mm^3 Al plate
- Pore solution extraction:
  - one 40×40×40 mm^3 bulk

EIS testing:
- 1 MHz - 0.01 Hz
- 10 mv





Cement pastes:

- 0.36 w/c OPC
- 0.36 w/c OPC+3 wt.% $LiNO_3$
- 0.50 w/c OPC+1.607 wt.% Li_2CO_3

Paste blocks:

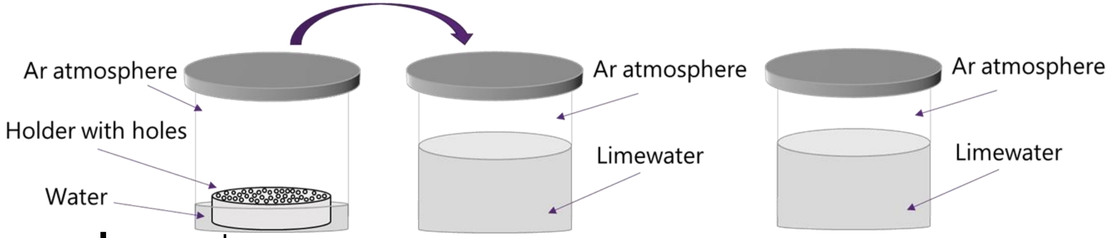
- 40×40×40 mm^3
- 1d in molds

Curing conditions:

Condition 1

Simulate the possible intrusion of underground water

Condition 2



Corrosion rate: comparison between EIS, GC and SEM

Methods used to calculate the corrosion rate

EIS:

$$I_{corr} = \frac{I_{appl}}{2.3\Delta\emptyset}\left(\frac{\beta_a\beta_c}{\beta_a+\beta_c}\right) = \frac{B}{R_t}$$

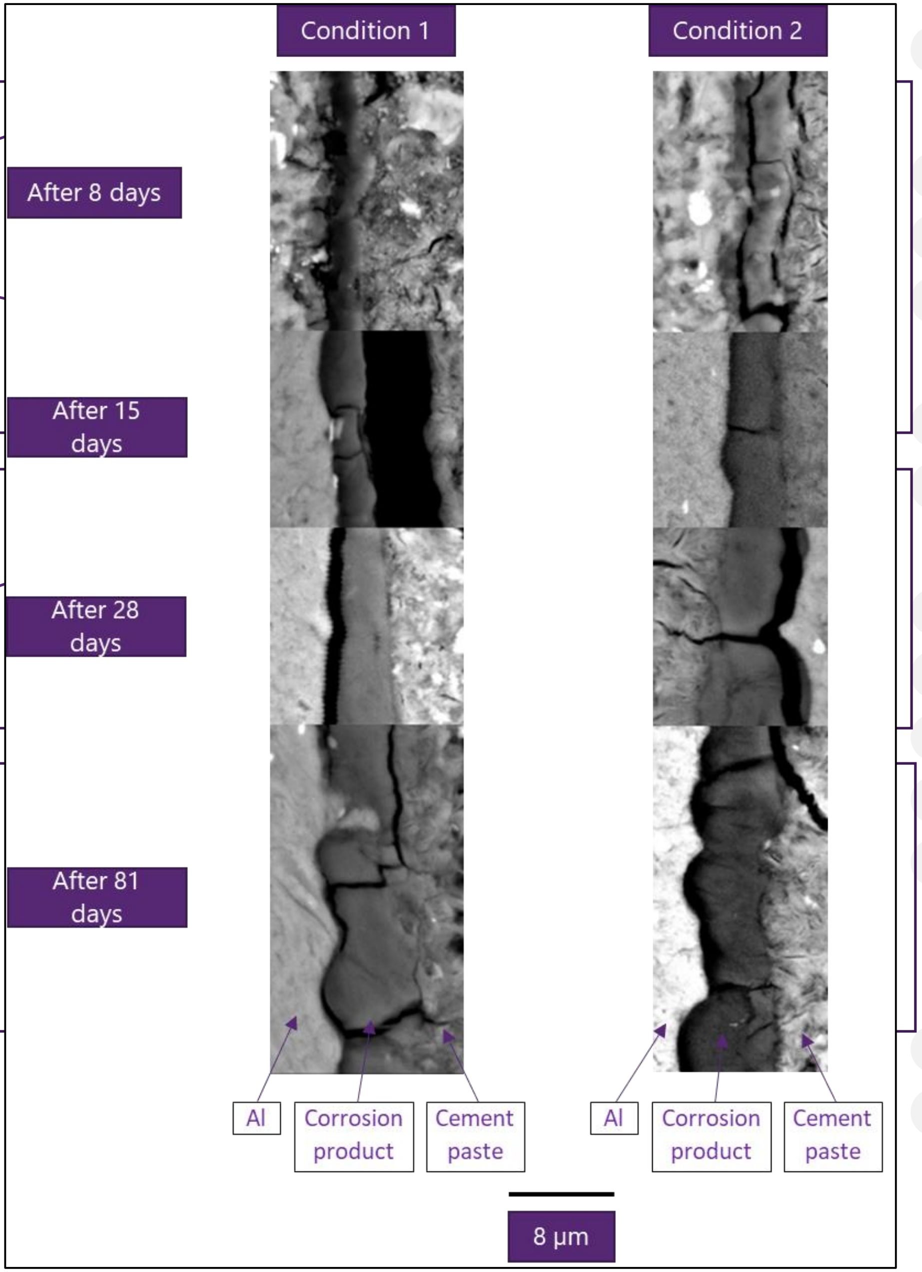
$$\nu_{corr}\ (in\ \mu m/y) = 3.27 \times \frac{I_{corr}}{\rho} \times EW$$

GC:

$$Al + OH^- + 3H_2O \rightarrow Al(OH)_4^- + \frac{3}{2}H_2 \uparrow$$

SEM:

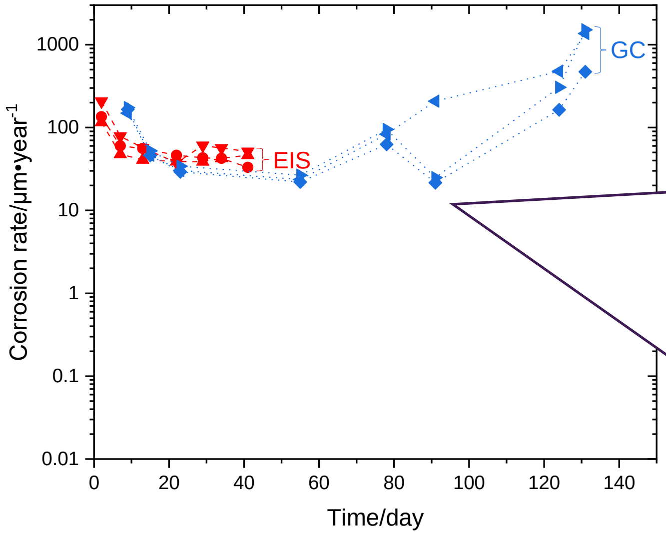
$$\nu_{corr}\ (in\ \mu m/y) = \frac{d_{t2}-d_{t1}}{t_2-t_1}$$

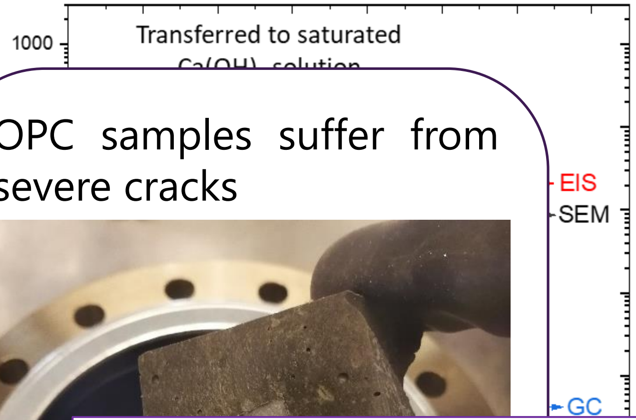


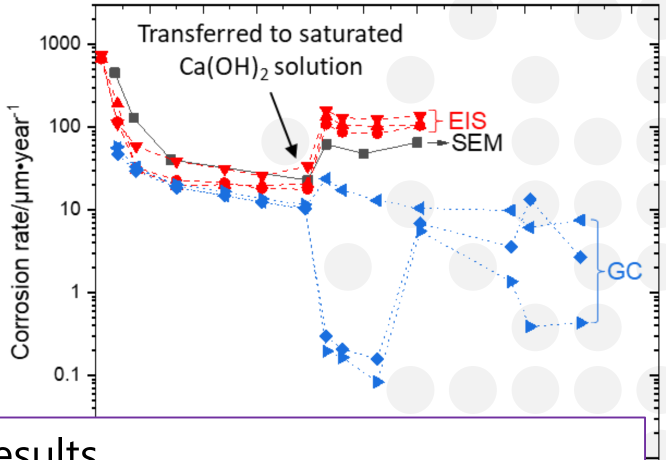
Comparison of the corrosion rate obtained by EIS, SEM and GC

0.36 w/c samples | **0.36 w/c OPC+3% $LiNO_3$ samples** | **0.50 w/c OPC+1.607% Li_2CO_3 samples**

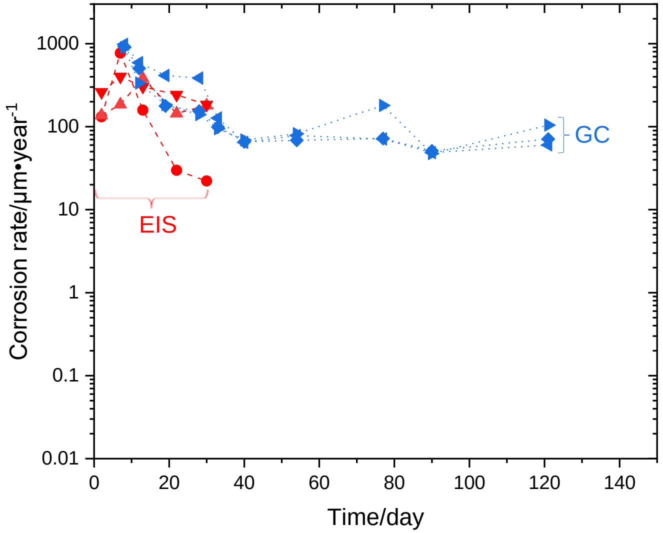
Condition 1

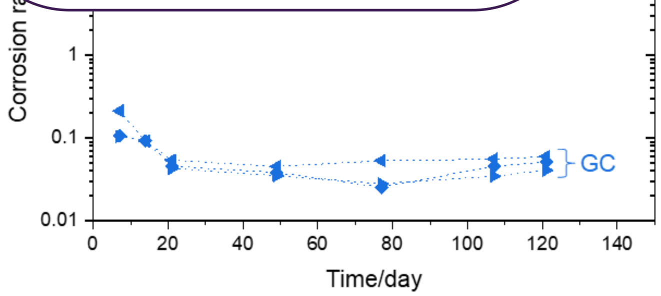


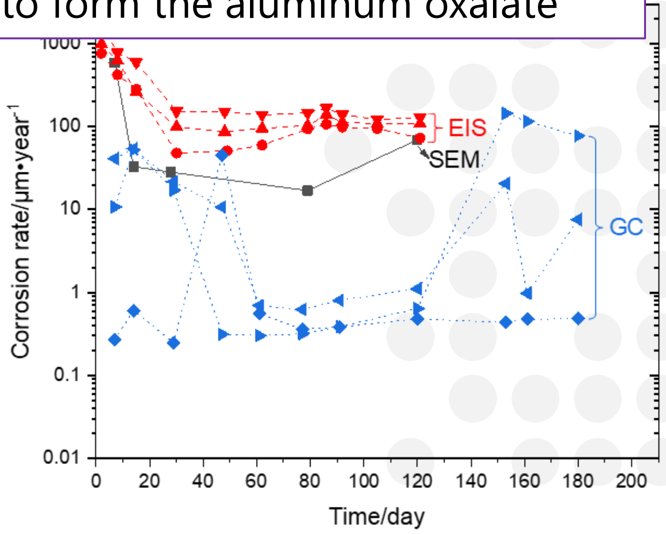




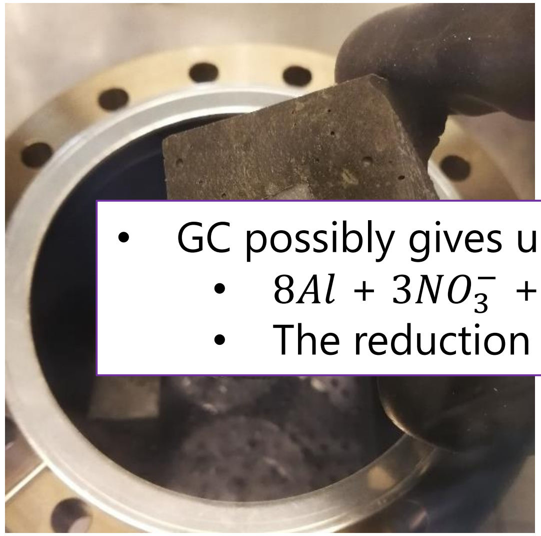
Condition 2







OPC samples suffer from severe cracks



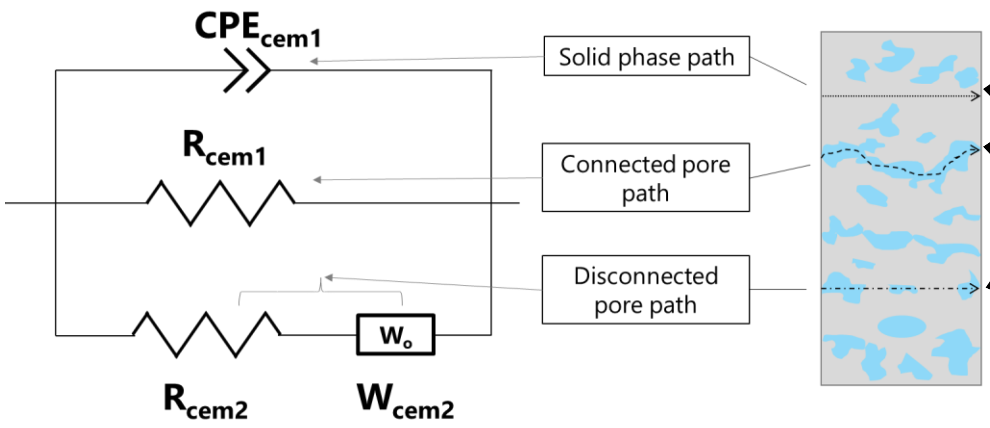
- GC possibly gives unreliable results
  - $8Al + 3NO_3^- + 5OH^- + 18H_2O \rightarrow 8Al(OH)_4^- + 3NH_3 \uparrow$
  - The reduction of to CO_3^- to form the aluminum oxalate

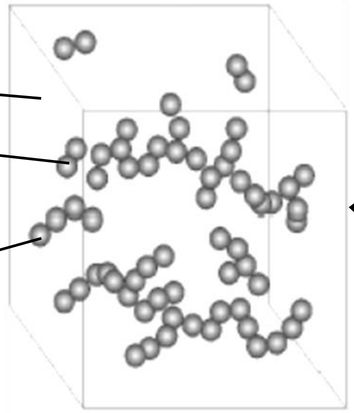
Cement paste: combination of EIS and GEM

Effective Medium Theory (EMT)

EIS model

Composite material: Conductive powders in an insulating matrix.

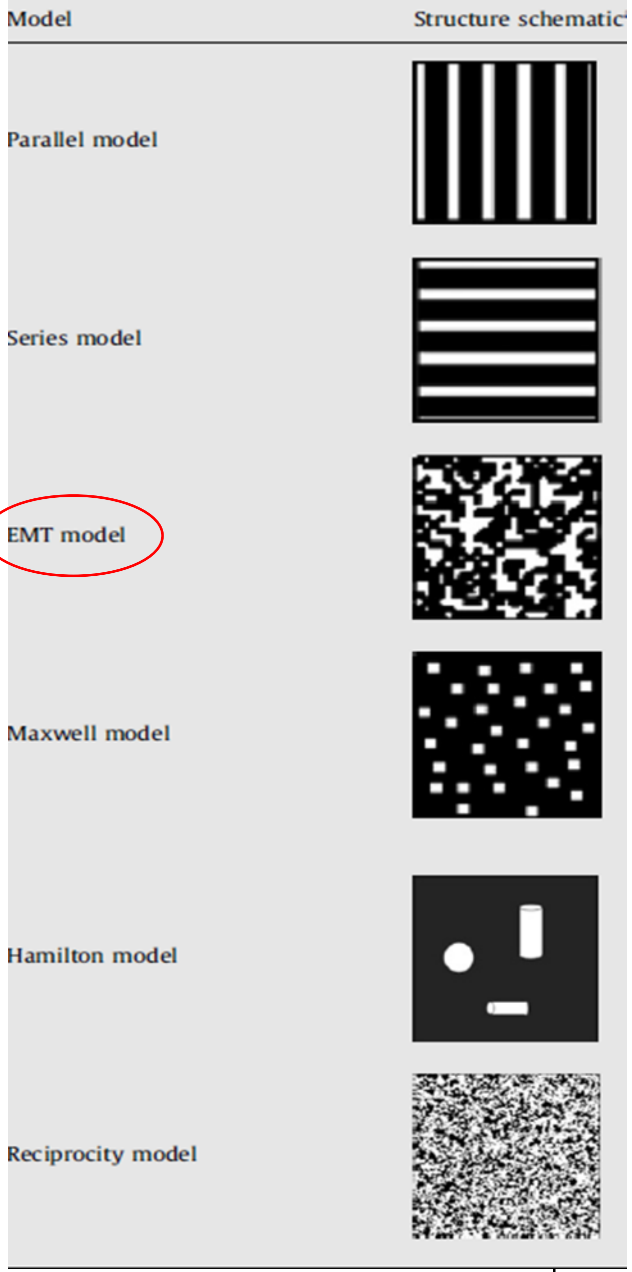




Cement pores are full of pore solution. The resistivity of solid gel is much larger than that of pore solution.

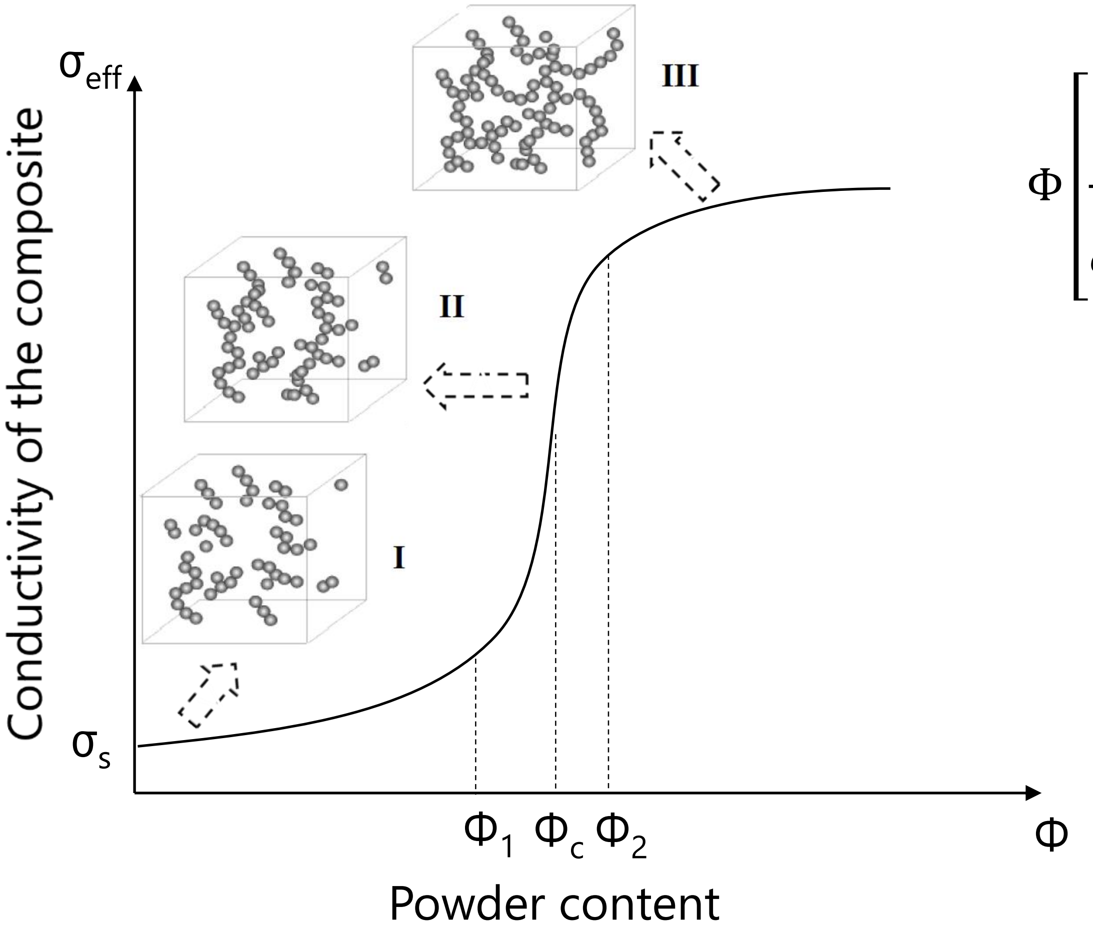
Effective Medium Theory (EMT) model tackles materials with a completely random distribution of all the components. It gives **the relationship between powder content and conductivity** of the system.

Two-phase models



Model	Structure schematic
Parallel model	
Series model	
EMT model	
Maxwell model	
Hamilton model	
Reciprocity model	

General Effective Medium (GEM) = EMT +percolation theories



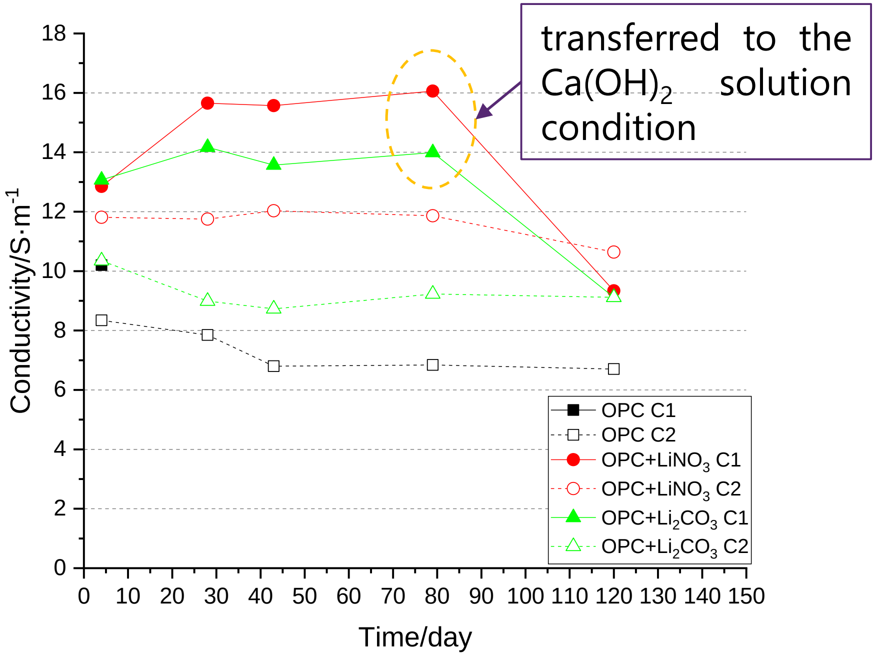
$$\Phi\left[\frac{\left(\sigma_p^{\frac{1}{t}}-\sigma_{eff}^{\frac{1}{t}}\right)}{\sigma_p^{\frac{1}{t}}+\sigma_{eff}^{\frac{1}{t}}\left(\frac{1-\phi_c}{\phi_c}\right)}\right]+(1-\phi)\left[\frac{\left(\sigma_s^{\frac{1}{t}}-\sigma_{eff}^{\frac{1}{t}}\right)}{\sigma_s^{\frac{1}{t}}+\sigma_{eff}^{\frac{1}{t}}\left(\frac{1-\phi_c}{\phi_c}\right)}\right]=0$$

σ_{eff}: the effective conductivity of the system;
σ_p: the conductivity of the pore solution;
σ_s: the conductivity of the solid phase;
Φ_c: the percolation threshold of capillary pores;
t: a critical exponent characterizing the conductivity of the conducting regions in the microstructure (similar to a tortuosity parameter) ;
Φ: the porosity.

General Effective Medium (GEM)

$$\Phi = \frac{\left[\left(\frac{\sigma_p}{\sigma_{eff}}\right)^{\frac{1}{t}} + \left(\frac{1-\Phi_c}{\Phi_c}\right)\right] * \left[\left(\frac{\sigma_s}{\sigma_{eff}}\right)^{\frac{1}{t}} - 1\right]}{\left[\left(\frac{\sigma_p}{\sigma_{eff}}\right)^{\frac{1}{t}} + \left(\frac{1-\Phi_c}{\Phi_c}\right)\right] * \left[\left(\frac{\sigma_s}{\sigma_{eff}}\right)^{\frac{1}{t}} - 1\right] - \left[\left(\frac{\sigma_p}{\sigma_{eff}}\right)^{\frac{1}{t}} - 1\right] * \left[\left(\frac{\sigma_s}{\sigma_{eff}}\right)^{\frac{1}{t}} + \left(\frac{1-\Phi_c}{\Phi_c}\right)\right]}$$

- $\boldsymbol{\sigma_p}$: the conductivity of the capillary pore phase, which is approximated by the conductivity of pore fluids in capillary pores.



- $\boldsymbol{\sigma_s}$: the conductivity of the solid phase 1/400 of $\boldsymbol{\sigma_p}$ i.e. **0.0008** S/m is chosen.
- **t**: a critical exponent characterizing the conductivity of the conducting region in the microstructure. **2** for a 3-D system is used.
- $\boldsymbol{\Phi_c}$: the critical porosity at which the pore network first percolates. **0.104** is chosen.
- $\boldsymbol{\sigma_{eff}}$: the effective conductivity of the system i.e. the overall conductivity of cement paste.

$$\sigma_{eff} = \frac{K}{R_{eff}}$$

K: cell constant

Φ: cement paste porosity

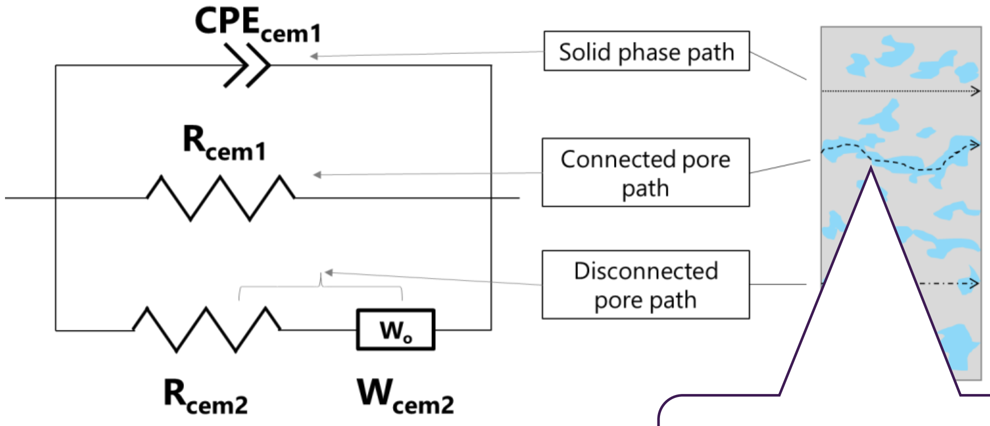
Determination of σ_{eff}

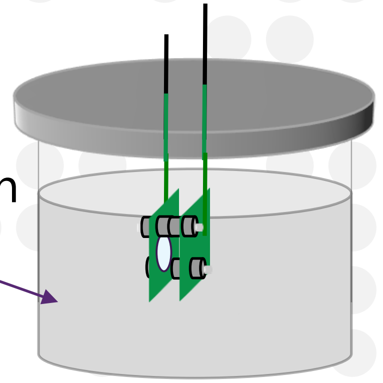
- **σ_{eff}**: the effective conductivity of the system i.e. the overall conductivity of cement paste

$$\sigma_{eff} = \frac{K}{R_{eff}}$$

K of the specific cell is fixed. The resistance of the cell in saturated $Ca(OH)_2$ solution is around 100 Ω, its conductivity is 1.03 S/m. K value should be 103.

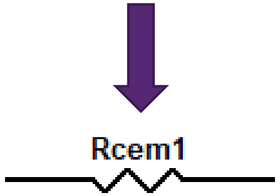
R_{eff} is the overall resistance of the cement paste in DC, i.e. when the input signal frequency is 0 Hz.

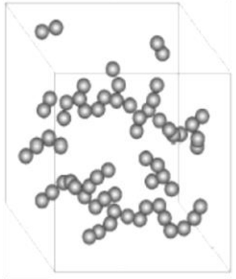




Since the pore phase is much more conductive, $R_{eff} \approx R_{cem1}$

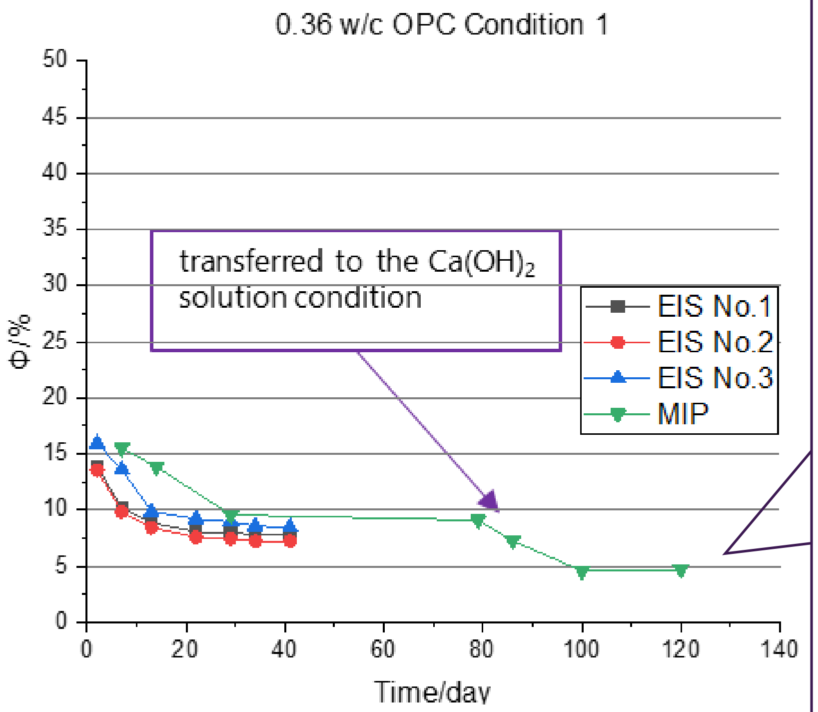
at a low frequency region



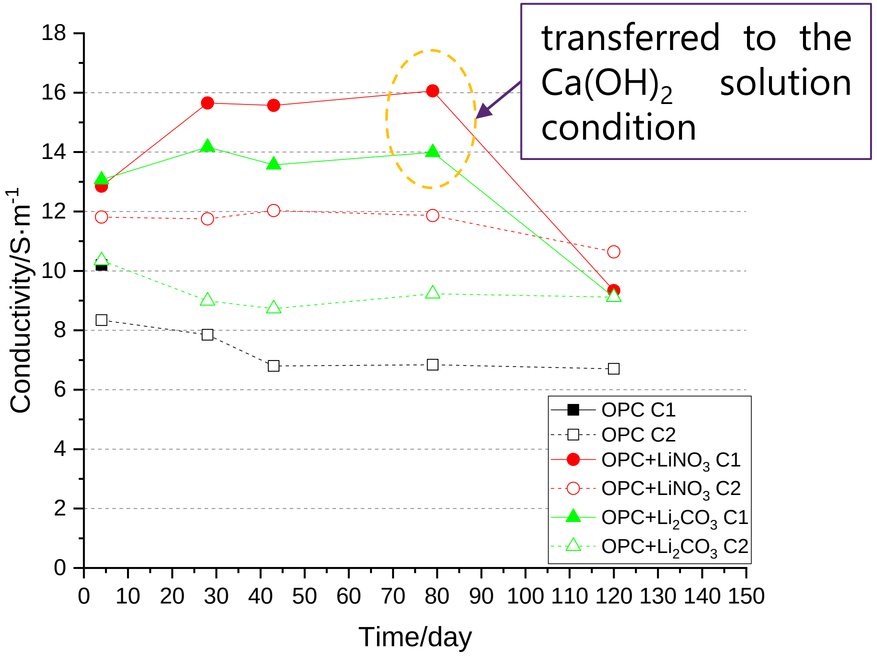


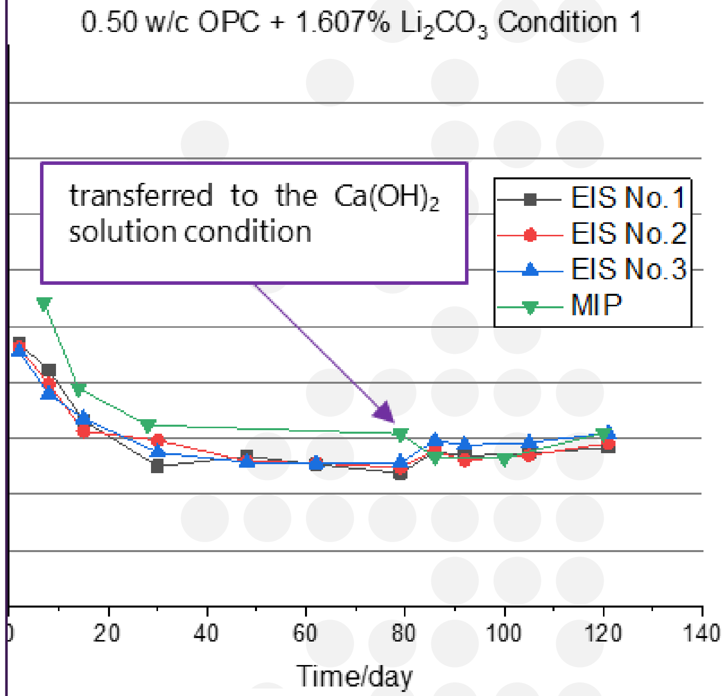
Cement paste: porosity measured by EIS/GEM and MIP

Porosity comparison of specimens in condition 1



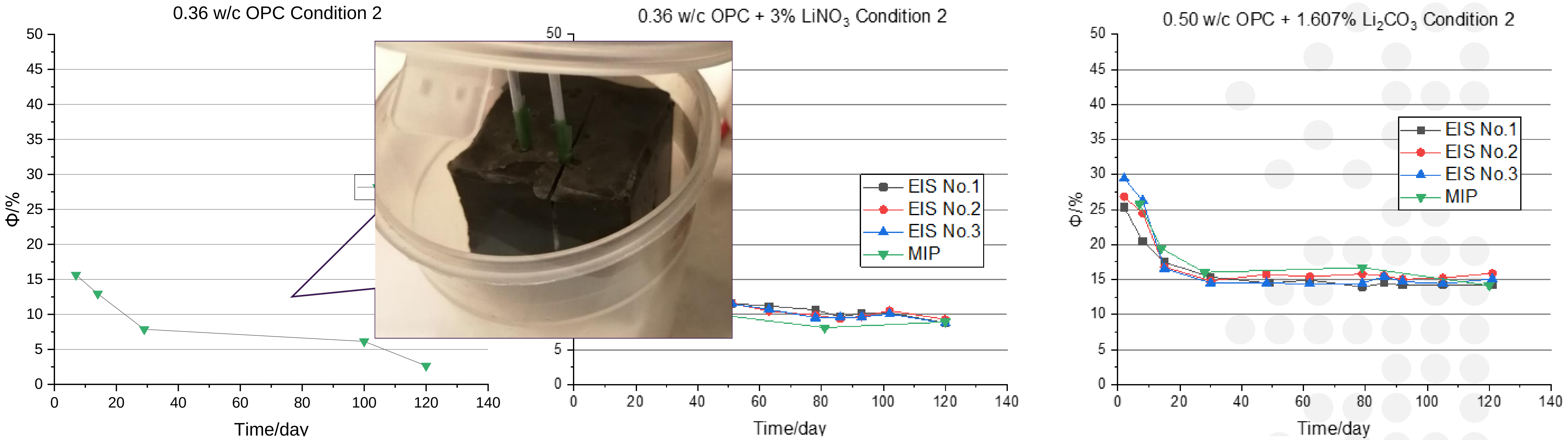
- **σ_p**: the conductivity of the capillary pore phase, which is approximated by the





- OPC samples suffer from severe cracks
- The partly saturated pores lead to an underestimation of the total porosity
- OPC+$LiNO_3$ contain enough pore solution to fill all the capillary pores, which is probably attributed to the addition of $LiNO_3$

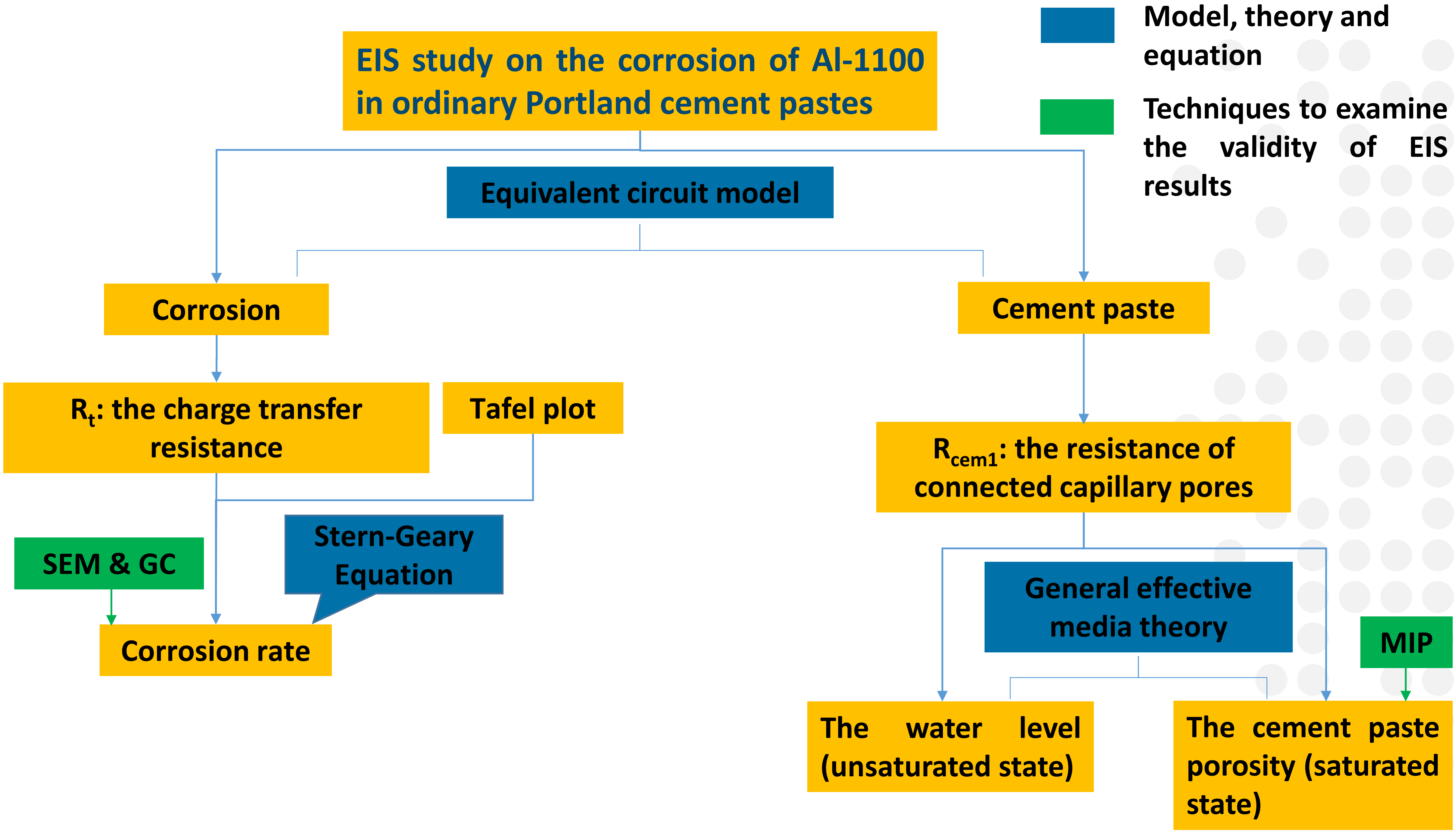
Porosity comparison of specimens in condition 2



- OPC samples suffer from severe cracks
- The porosity results obtained from EIS and MIP are in good agreement.

Conclusion

Conclusion



Model, theory and equation
Techniques to examine the validity of EIS results
EIS study on the corrosion of Al-1100 in ordinary Portland cement pastes
Equivalent circuit model
Corrosion
Cement paste
R_t: the charge transfer resistance
Tafel plot
R_{cem1}: the resistance of connected capillary pores
SEM & GC
Stern-Geary Equation
Corrosion rate
General effective media theory
MIP
The water level (unsaturated state)
The cement paste porosity (saturated state)

Thank you!

Caveat:

The proposed approach and obtained results in no way entail a decision of ONDRAF/NIRAS whatsoever on this approach as a solution for the long-term management of this waste.