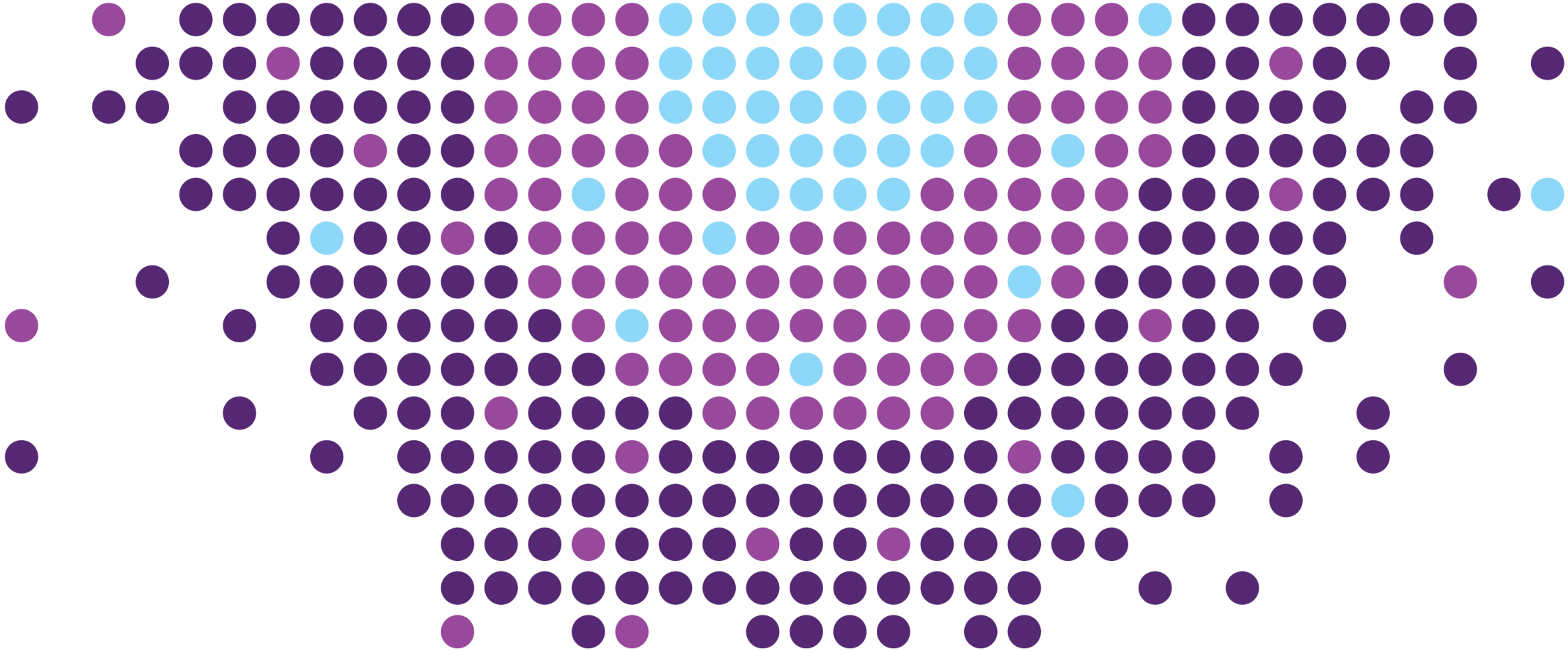

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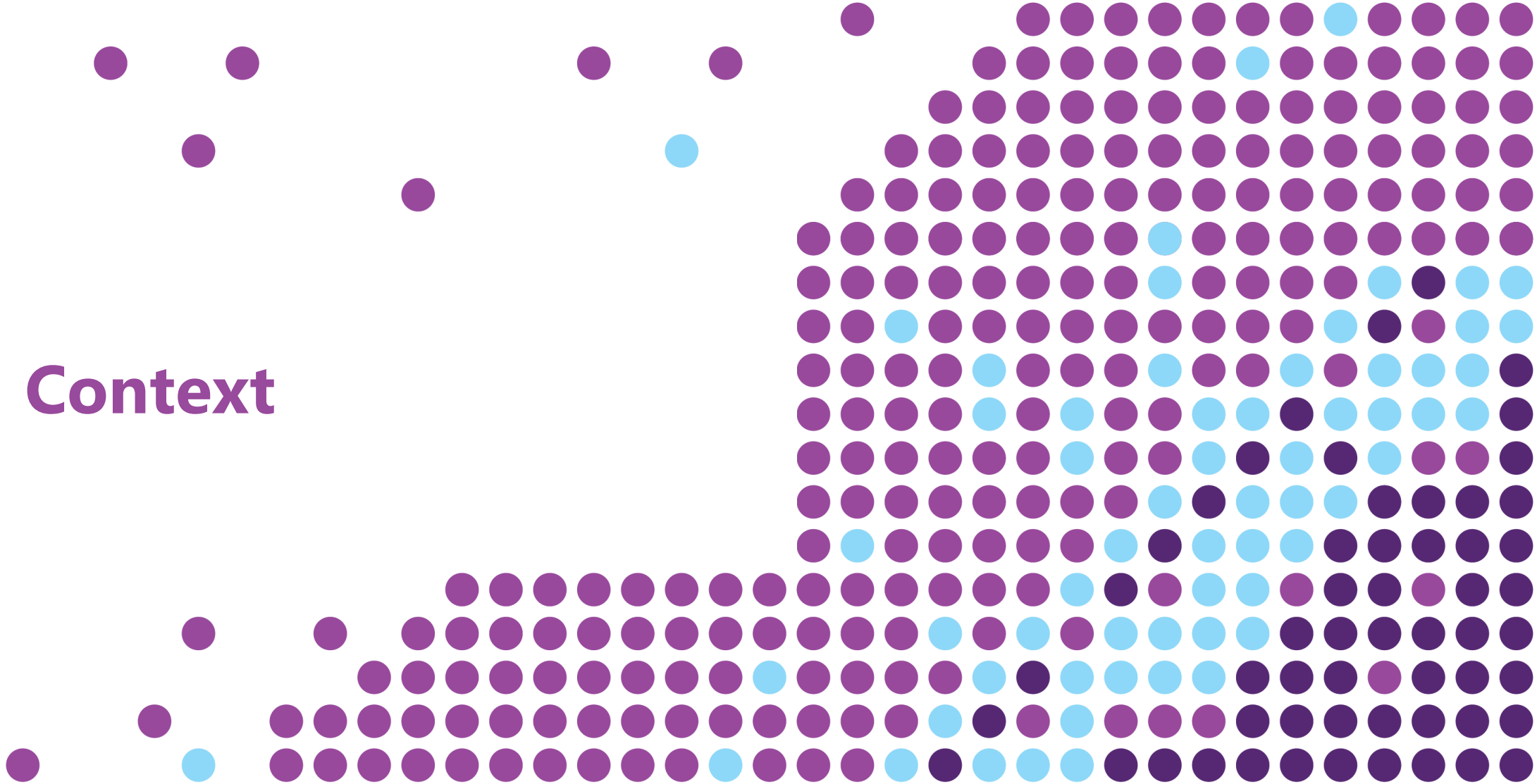
Belgian Nuclear Research Centre

X. Li, S. Caes, T. Pardoen, G. De Schutter, B. Kursten - 29/08/2022

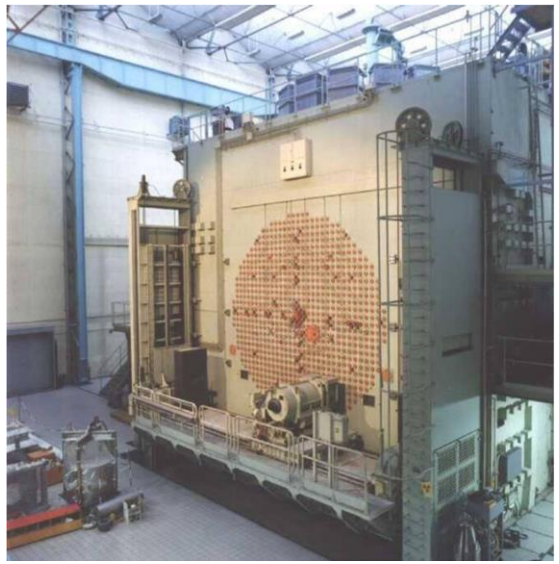
Influence of the lithium salts as corrosion inhibitors on the corrosion process of aluminium in OPC matrix

- Context
- Materials & method
- Variation of R_f
- Corrosion rate
- Microscopy
- Conclusion

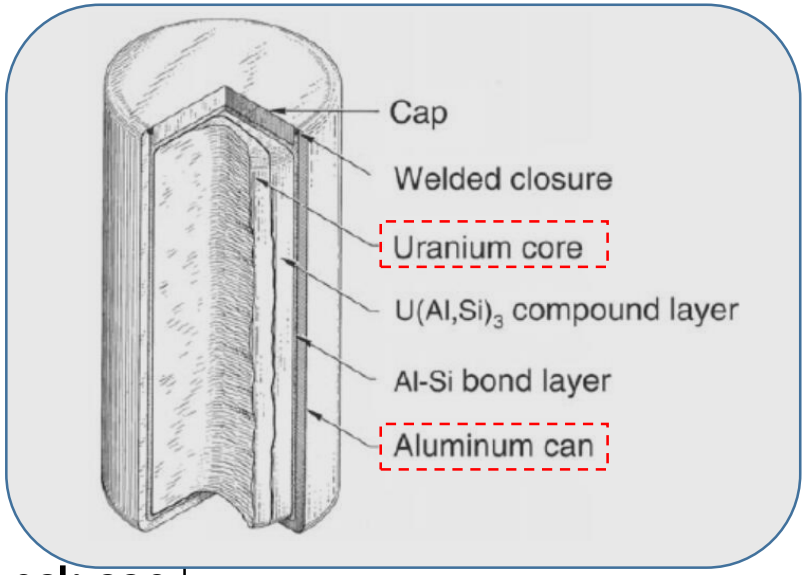
Context



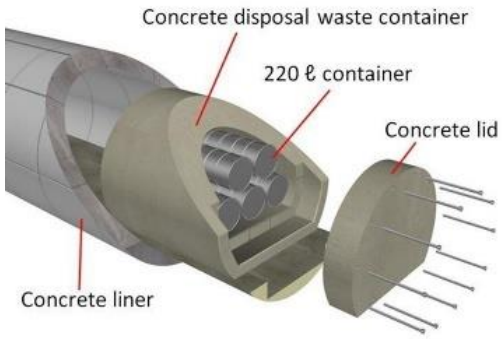
Geological disposal of BR1 fuel



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

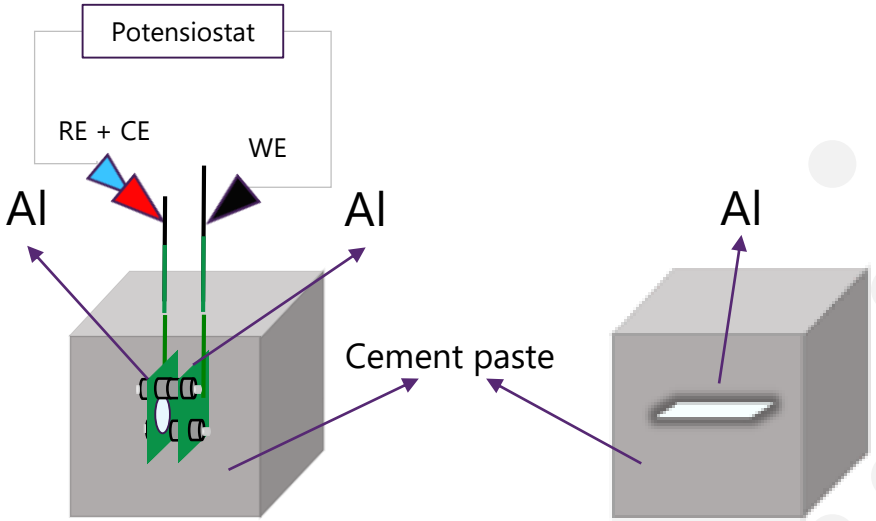
The addition of $LiNO_3$ or Li_2CO_3 (Li-Al layered double hydroxide (LDH) film)

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

Materials & method

Sample Preparation

Sample setups:
- Aluminium alloy 1100
- EC:
  - two identical electrodes
  - an exposed area of 2.26 cm^2
- GC and SEM:
  - one 15×15×1 mm^3 Al plate



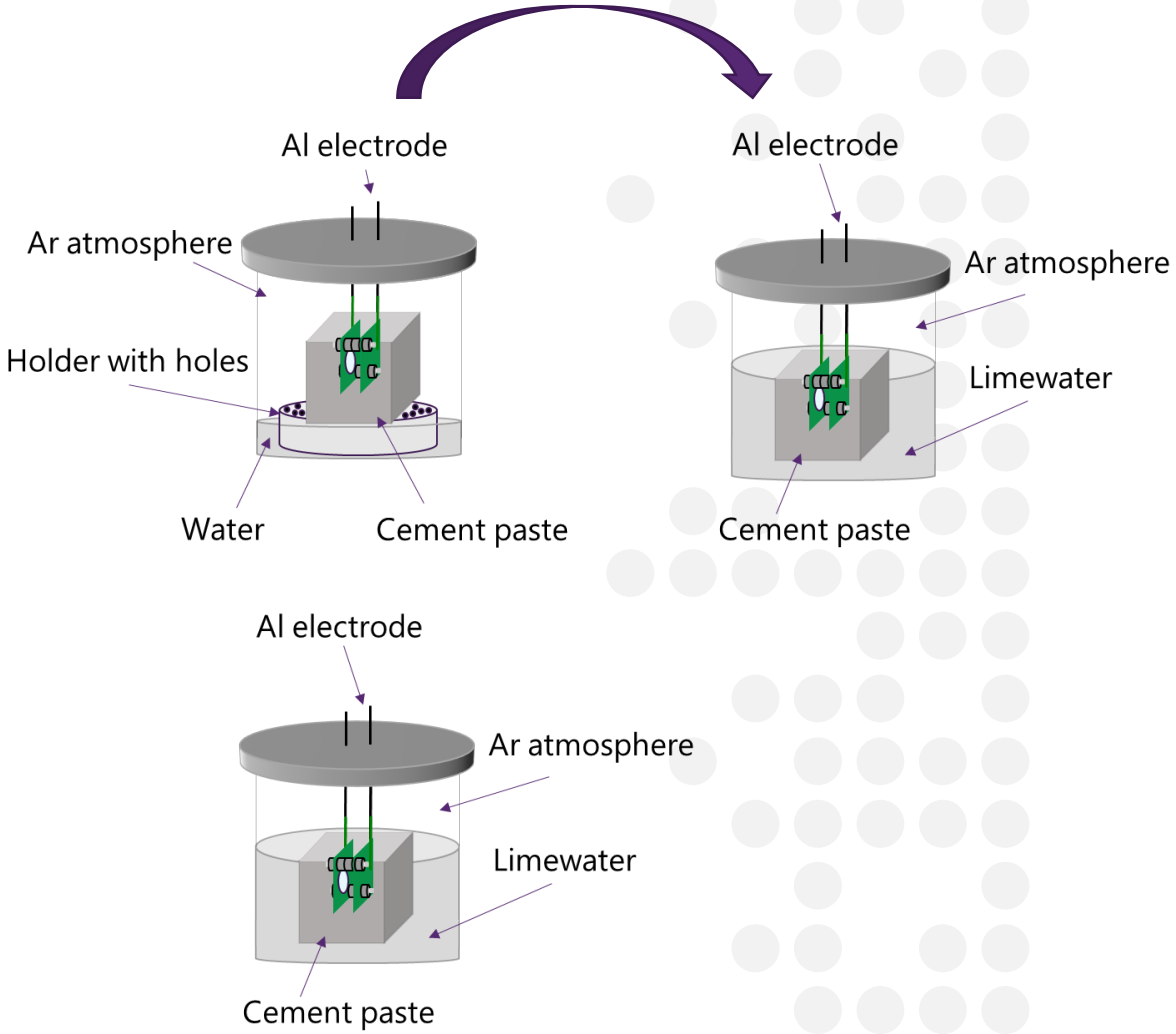
Cement pastes:
- 0.36 w/c OPC
- 0.36 w/c OPC+3 wt.% $LiNO_3$
- 0.50 w/c OPC+1.607 wt.% Li_2CO_3

Paste blocks:
- 40×40×40 mm^3
- 1d in molds

Anaerobic conditions:
- In a glove box under Ar atmosphere
- < 1 ppm O_2 in gas atmosphere ; < 1 ppb O_2 in solutions

Curing conditions

Simulate the possible intrusion of underground water



Condition 1:

- in a humid Ar atmosphere at the beginning
- transferred to saturate $Ca(OH)_2$ solution

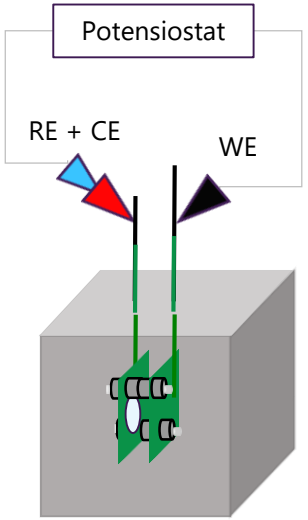
Condition 2:

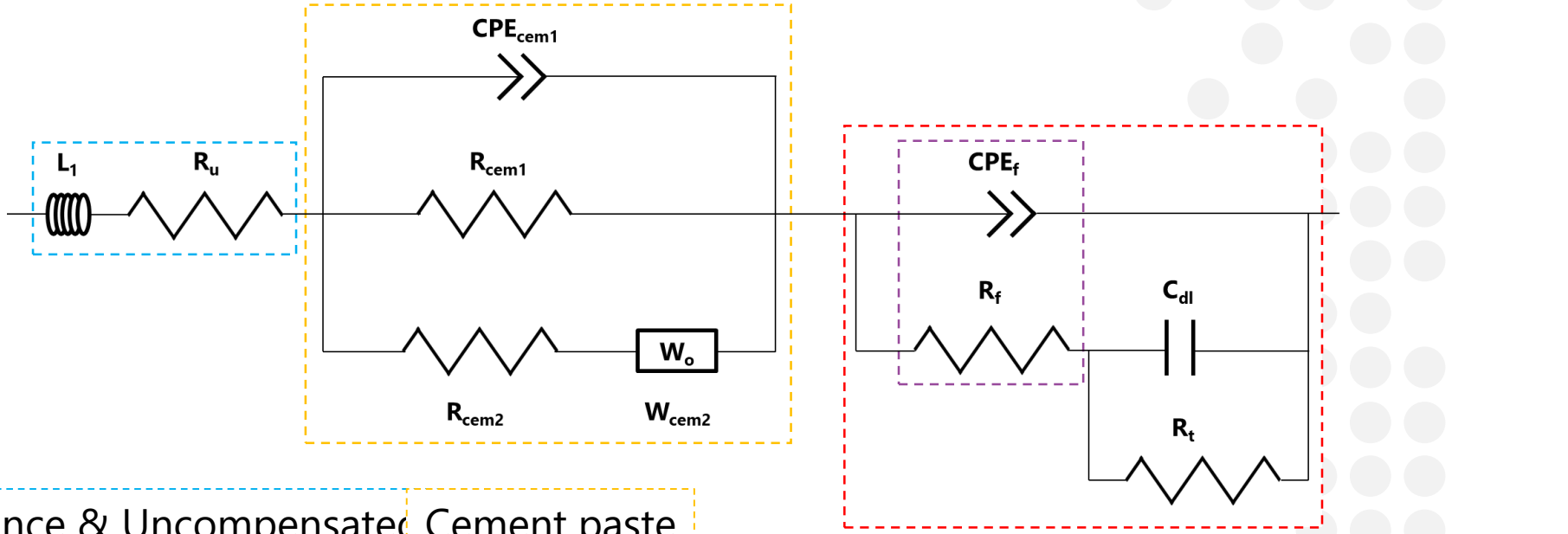
- in saturate $Ca(OH)_2$ solution from the beginning

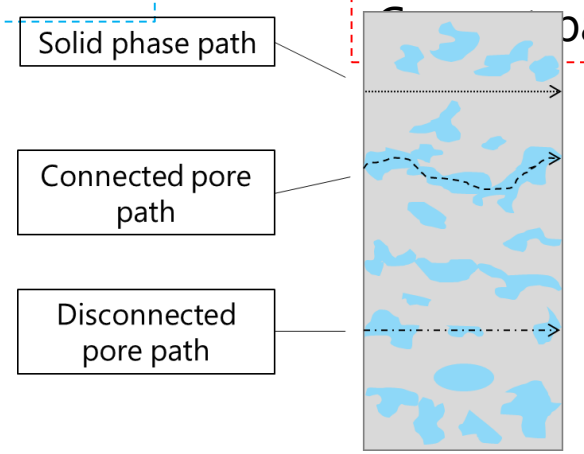
Electrochemical Impedance Spectroscopy (EIS)

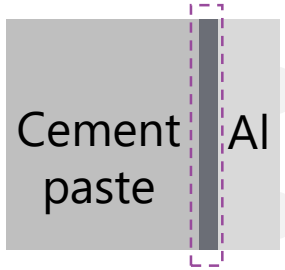
Testing conditions

- 1 MHz - 0.01 Hz
- 10 mv







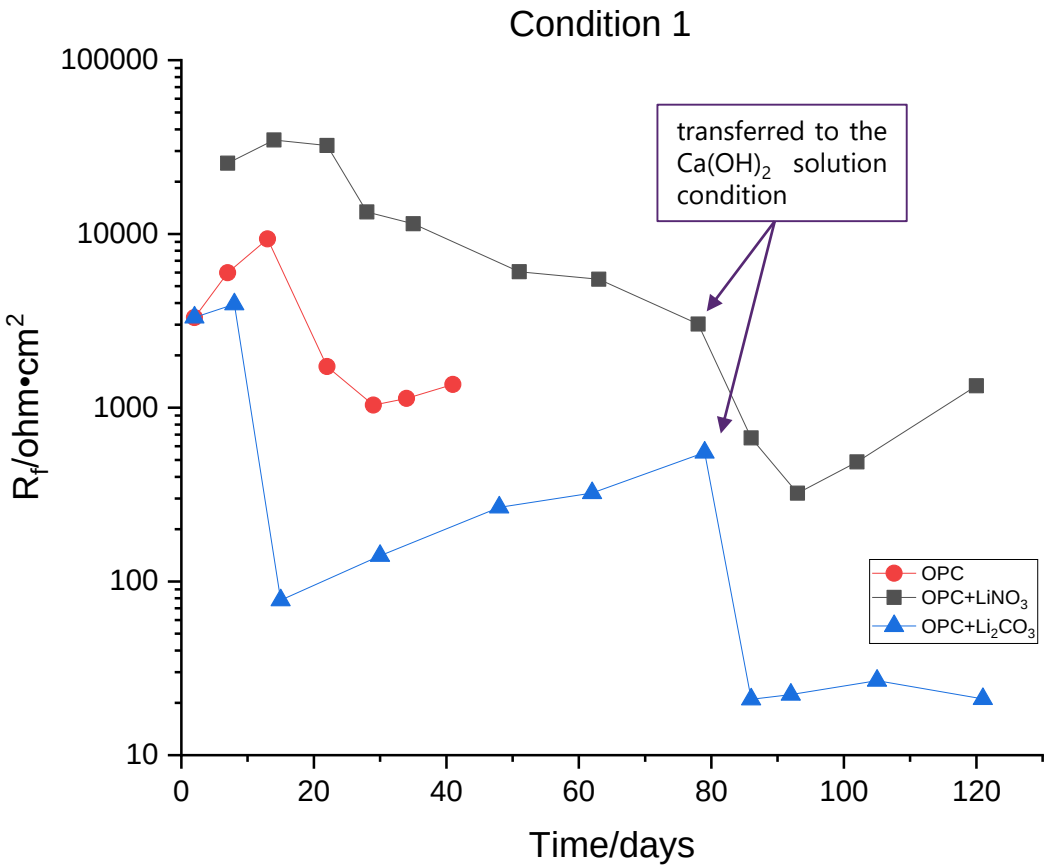


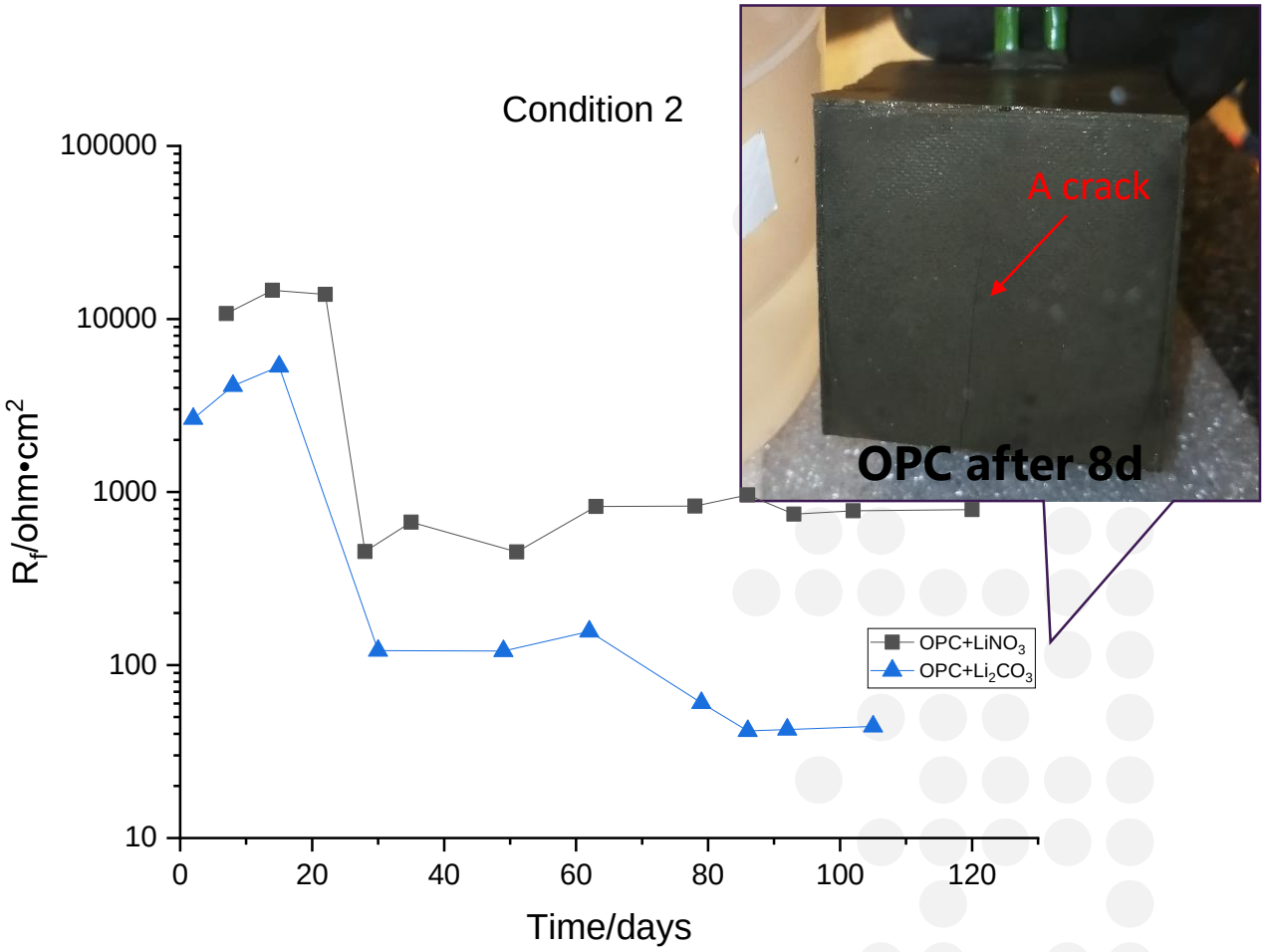
Variation of R_f

The resistance of the corrosion product film

Variation of R_f

reveals the evolution of LDH films





- The long saturation process of LDH films
- The transfer further decreases R_f in Condition 1
- $OPC+LiNO_3$ samples have the largest R_f values
- R_f values are close in both conditions at the end

Corrosion rate

The determination of the corrosion rate

EIS:

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

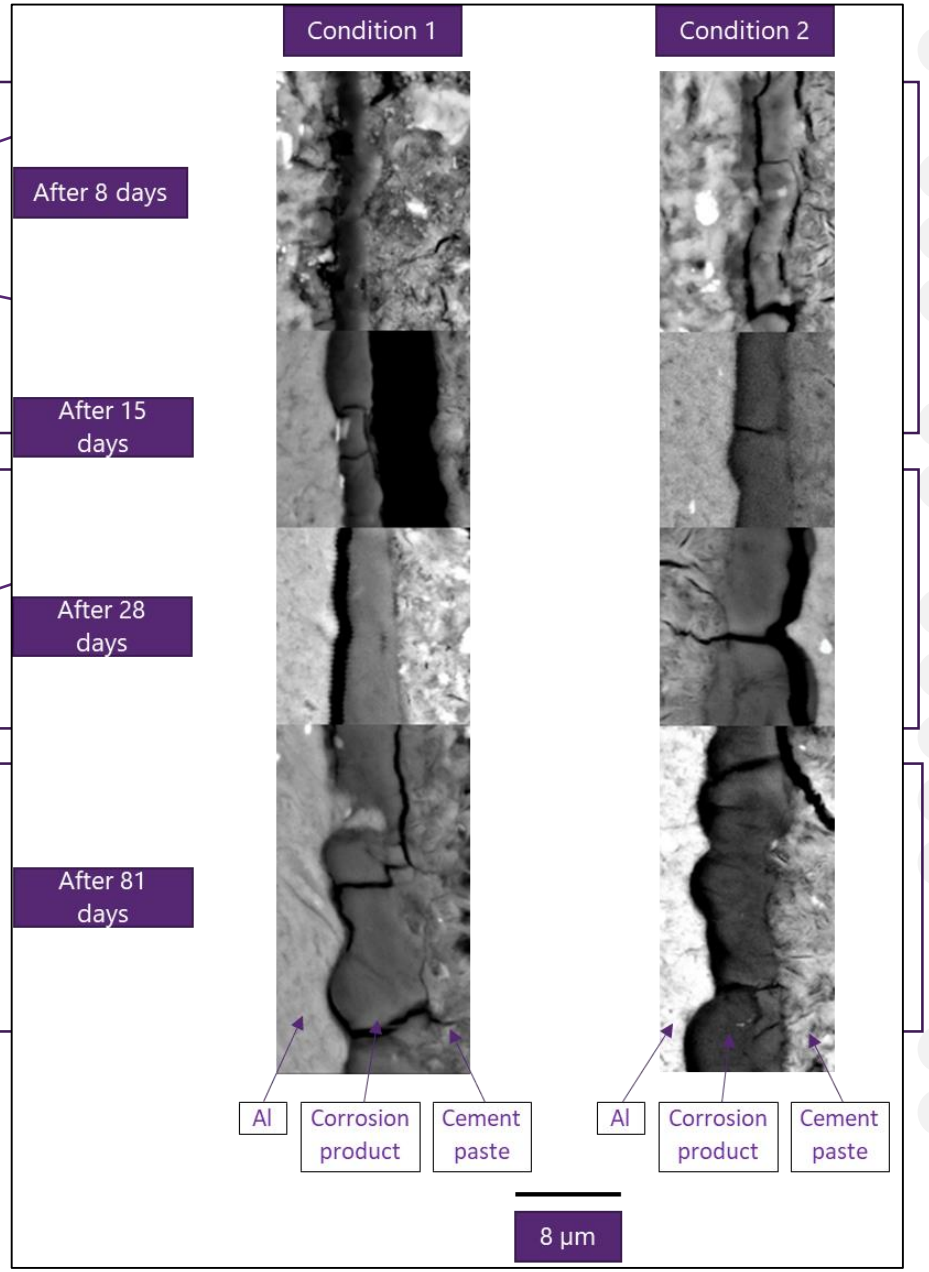
$$\nu_{corr}\ (in\ \mu m/y) = 3.27 \times \frac{I_{corr}}{\rho} \times EW$$

GC:

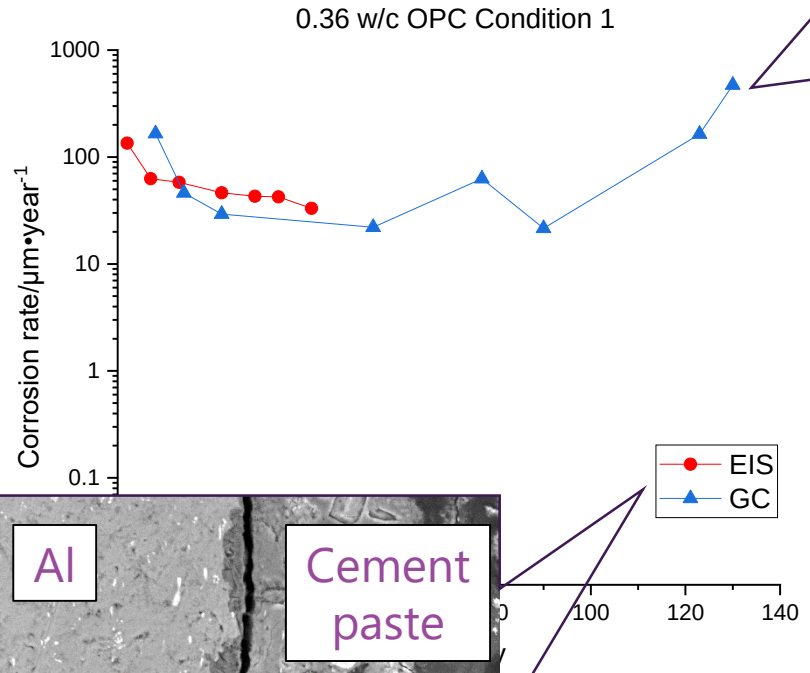
$$Al + OH^- + 3H_2O \rightarrow Al(OH)_4^- + \frac{3}{2}H_2 \uparrow$$

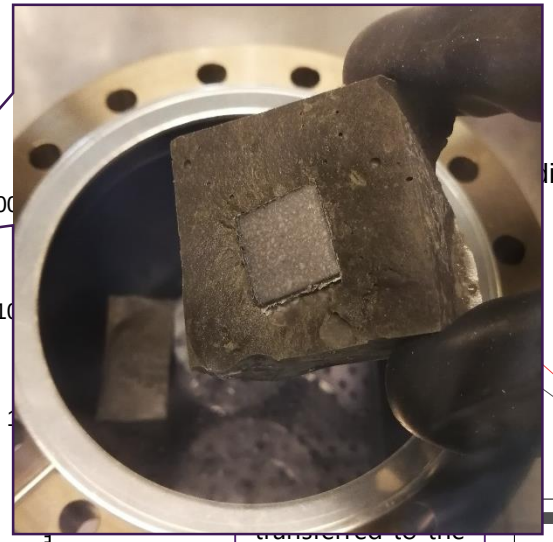
SEM:

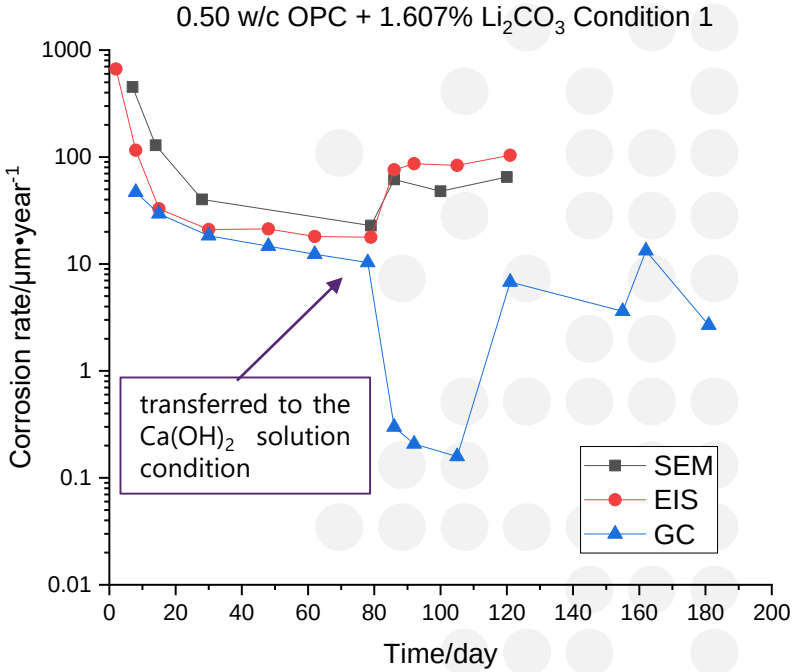
$$\nu_{corr}\ (in\ \mu m/y) = \frac{d_{t2} - d_{t1}}{t_2 - t_1}$$

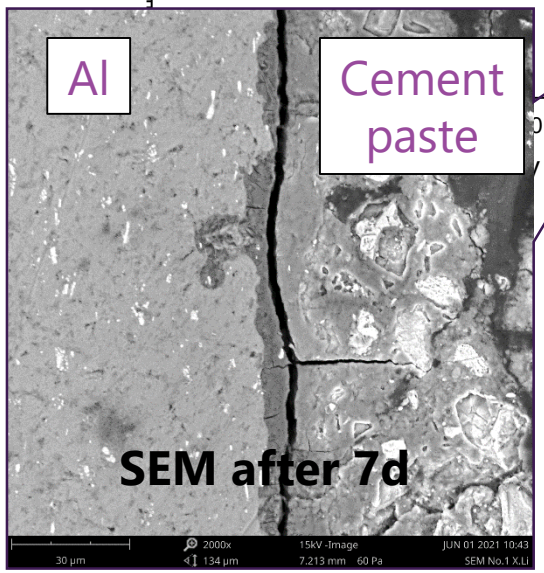


Corrosion rate



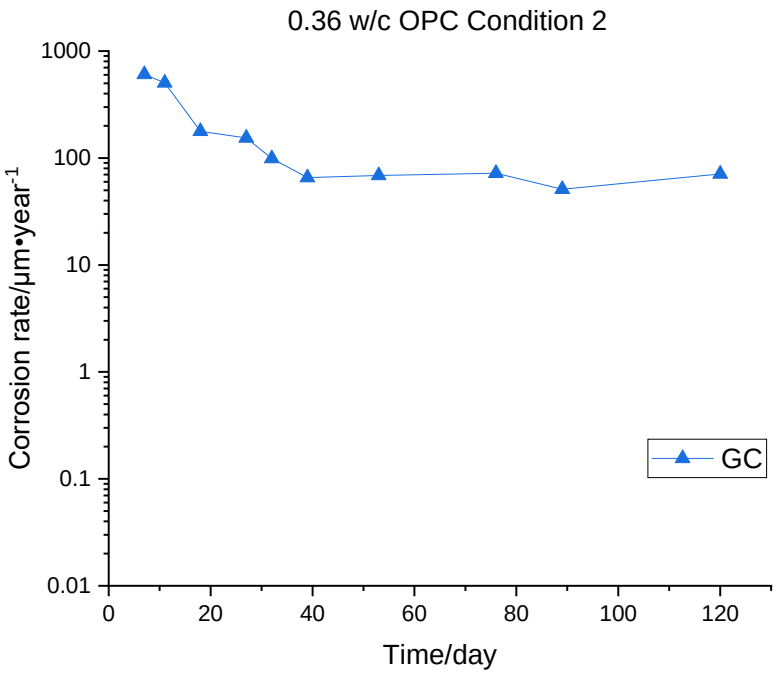


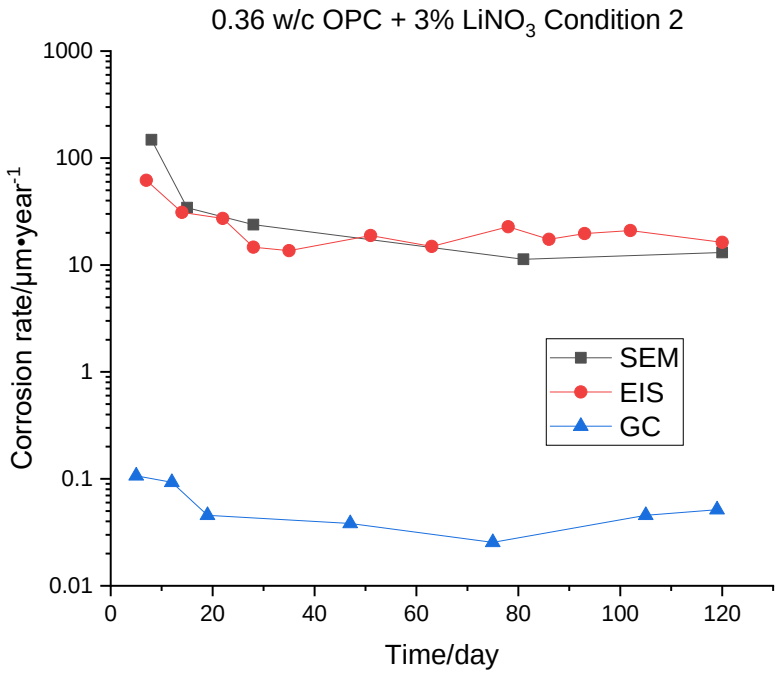


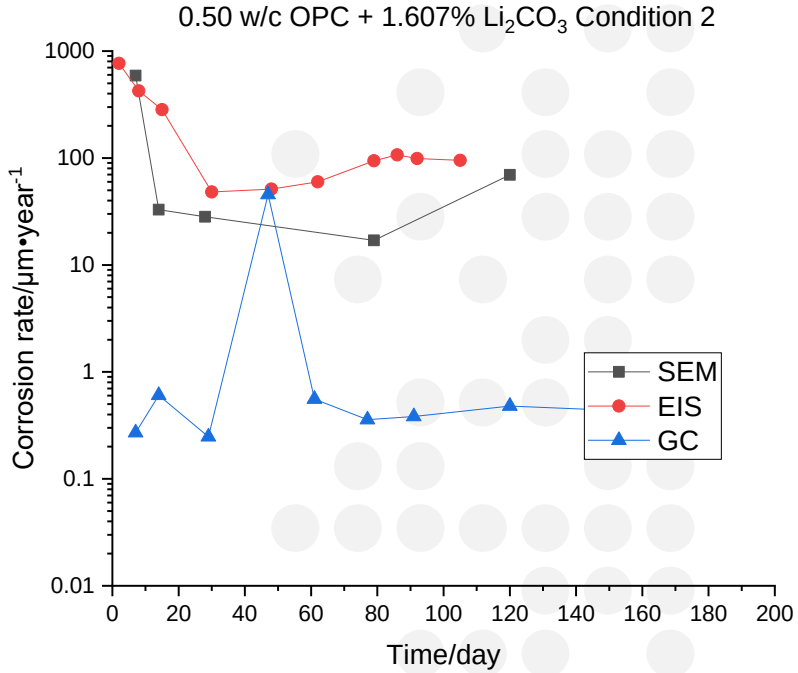


- OPC samples suffer from severe cracks
- OPC+$LiNO_3$ samples have the best performance
- GC possibly gives unreliable results
  - $8Al + 3NO_3^- + 5OH^- + 18H_2O \rightarrow 8Al(OH)_4^- + 3NH_3 \uparrow$
  - The reduction of to CO_3^- to form the aluminum oxalate
- The immersion of $Ca(OH)_2$ solution increases the corrosion rate
- Corrosion rates are reliable

Corrosion rate







- No visible cracks are observed in GC in OPC samples
- OPC+$LiNO_3$ samples have the best performance
- 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
- OPC+$LiNO_3$ and OPC+Li_2CO_3 have similar corrosion rates to that in Condition 1
- Corrosion rates are reliable

Microscopy

SEM observation

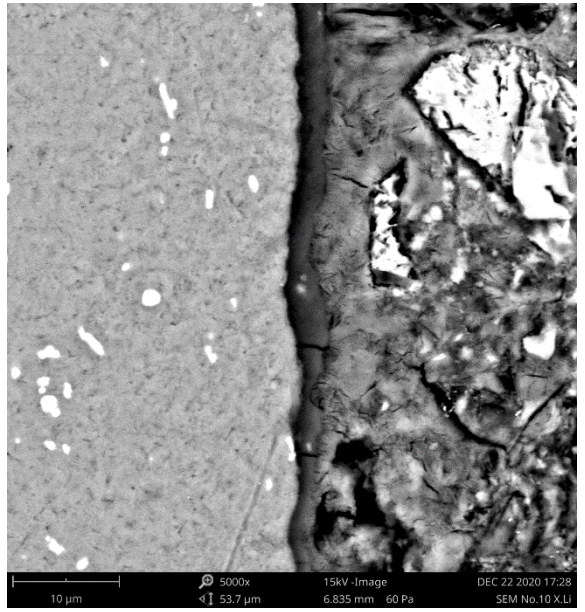
- The delamination in OPC+Li_2CO_3 samples might be caused by the larger thickness

SEM images of OPC+$LiNO_3$ samples in Condition 2

SEM images of OPC+Li_2CO_3 samples in Condition 2

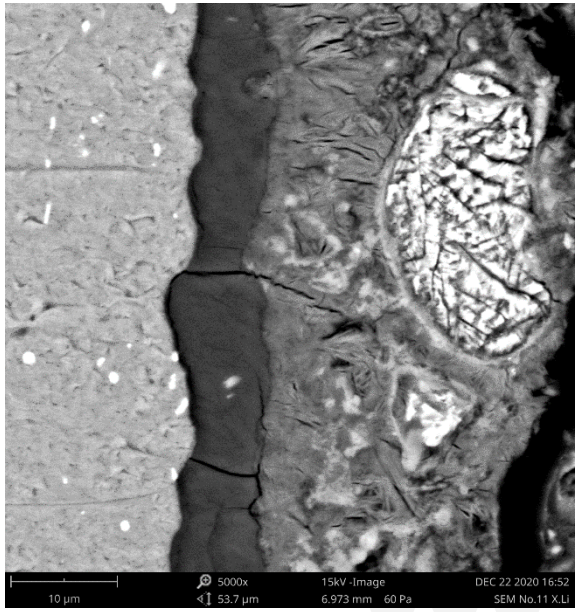
After 28d

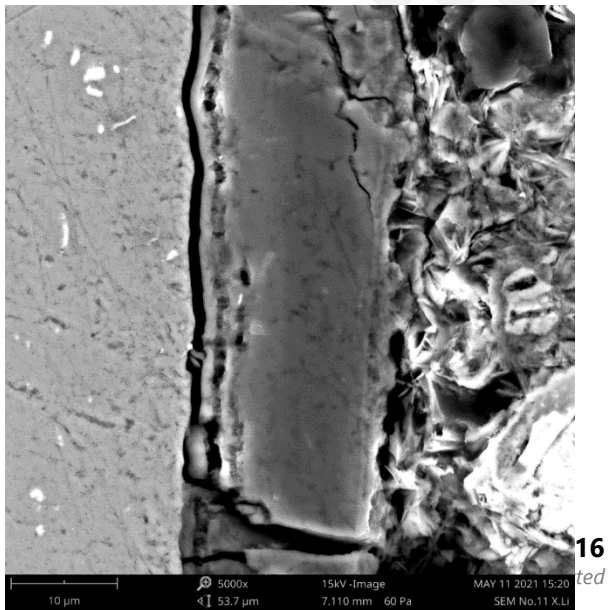
Al | Li-Al LDH film | Cement paste



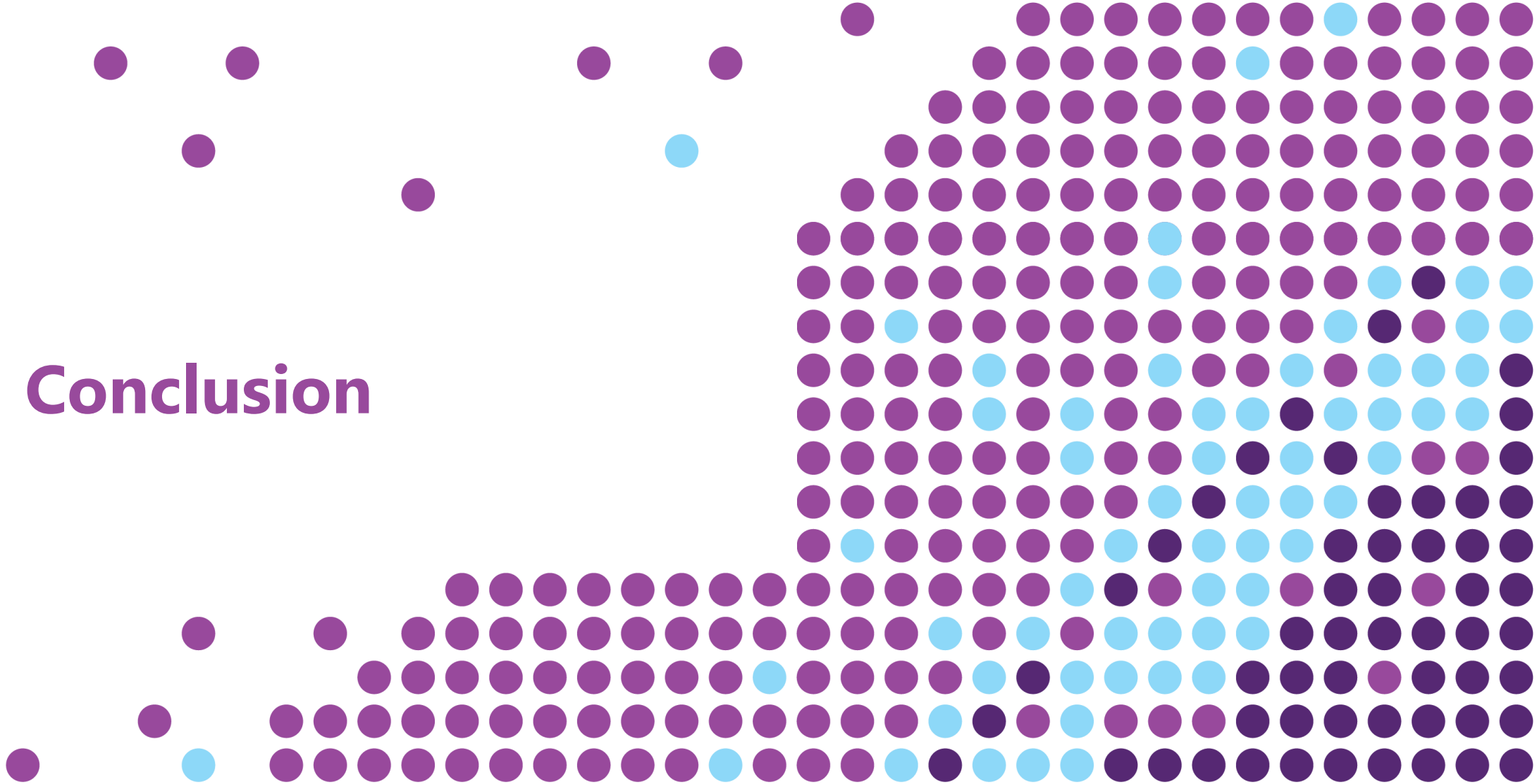
After 79d

Al | Li-Al LDH film | Cement paste





Conclusion

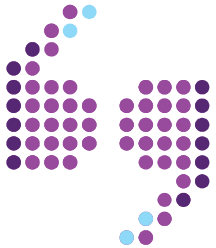


Conclusion

- The application of $LiNO_3$ inhibits the corrosion effectively
  - Less hydrogen generation
  - Lower corrosion rate
  - No cracks
- The variation of R_f proves the saturation process of LDH film
- The corrosion rate results obtained from the EIS fitting are comparable to that from other techniques, i.e. SEM and GC
- The delamination of Li-Al LDH film in the OPC+Li_2CO_3 samples is possibly attributed to the larger thickness of the film

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.



Thank you!