

Mg-Zr alloy corrosion in Na-geopolymer and its synthetic pore solution

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DE LA RECHERCHE À L'INDUSTRIE

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Mg-Zr alloy corrosion in Na-geopolymer and its synthetic pore solution

E. Schmucker[1], B. Muzeau[2], C. Bataillon[1]

[1] *Den-Service de Corrosion et du Comportement des Matériaux dans leur Environnement (SCCME), CEA, Université Paris-Saclay, 91191 Gif-sur-Yvette, France*

[2] *Den-Service d'Etude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, 91191 Gif-sur-Yvette, France*

EUROCORR 2018

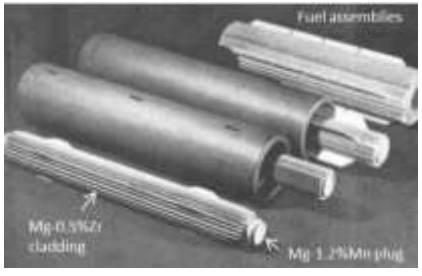
9-13 SEPTEMBER 2018

KRAKOW, POLAND

CONTEXT: METALLIC NUCLEAR WASTES

- **UNGG-Natural Uranium Graphite Gas reactor**
  - From the 60's until the 90's in France
  - Mg alloys used for fuel claddings









- **Mg alloys wastes conditioning strategy :** encapsulation of the Mg-wastes in an hydraulic binder inside a metallic container
  - Exposition to alkaline environment
  - Contact with graphite (AquaDAG ®) or steel (container) leading to galvanic coupling

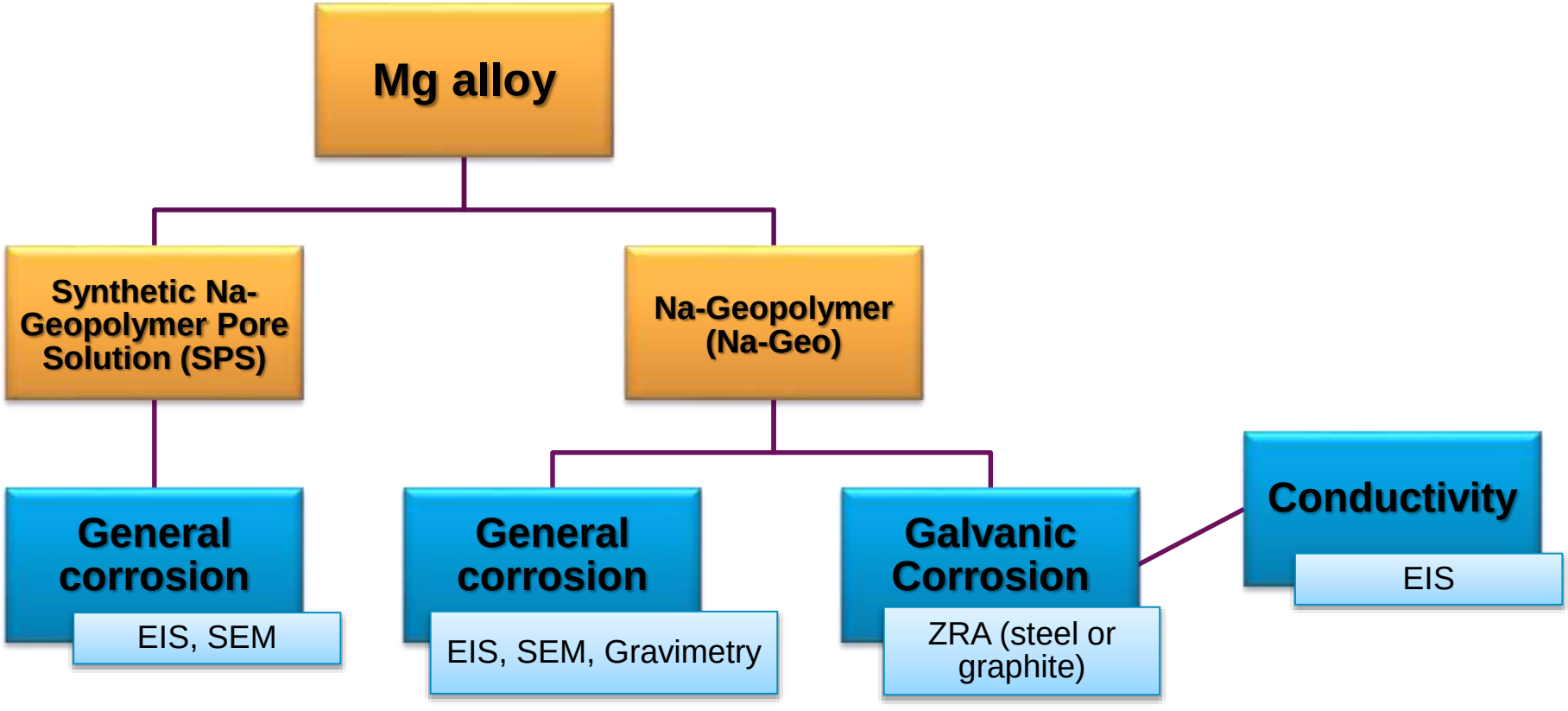


Corrosion of Mg alloys → hydrogen evolution reaction and corrosion products formation

OUTLINE

- Introduction
- **Experimental methodology**
- Corrosion of Mg-alloy in Synthetic Pore Solution
  - *General corrosion*
- Corrosion of Mg-alloy in Na-Geopolymer Mortar
  - *General corrosion*
  - *Galvanic corrosion*
  - *Conductivity measurements*
- Conclusion

EXPERIMENTAL METHODOLOGY



EXPERIMENTAL METHODOLOGY

Alloy composition:

Mg-0.5Zr (wt.%)

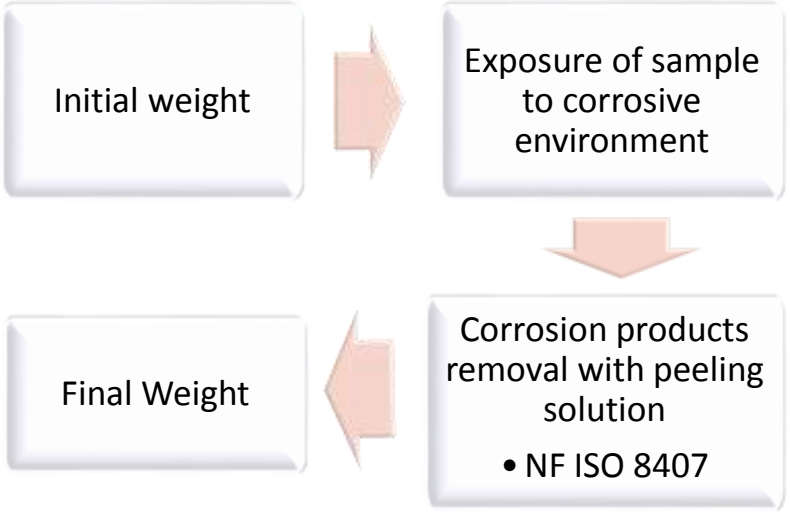
Na-Geopolymer/NaF mortar:

$1Na_2O\text{-}3.96SiO_2\text{-}1Al_2O_3\text{-}12.5H_2O$ +1.25M NaF + Sand

Synthetic Pore Solution:

NaF ; $AlF_3,3H_2O$; KOH ; NaCl ; $Na_2SO_4,10H_2O$; NaH_2PO_4,H_2O ; $Na_2SiO_3,5H_2O$

Weight loss measurements:



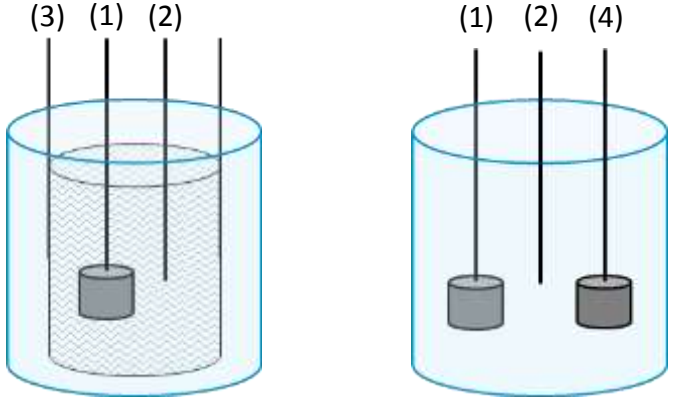
Electrochemical set-up:

3 electrodes electrochemical cell:

⇒ **WE:** Mg-0.5%Zr cylinder (1)

⇒ **RE:** Pt wire (2)

⇒ **CE:** Ti mesh for general corrosion (3)
S235JR steel or graphite (4) for galvanic corrosion



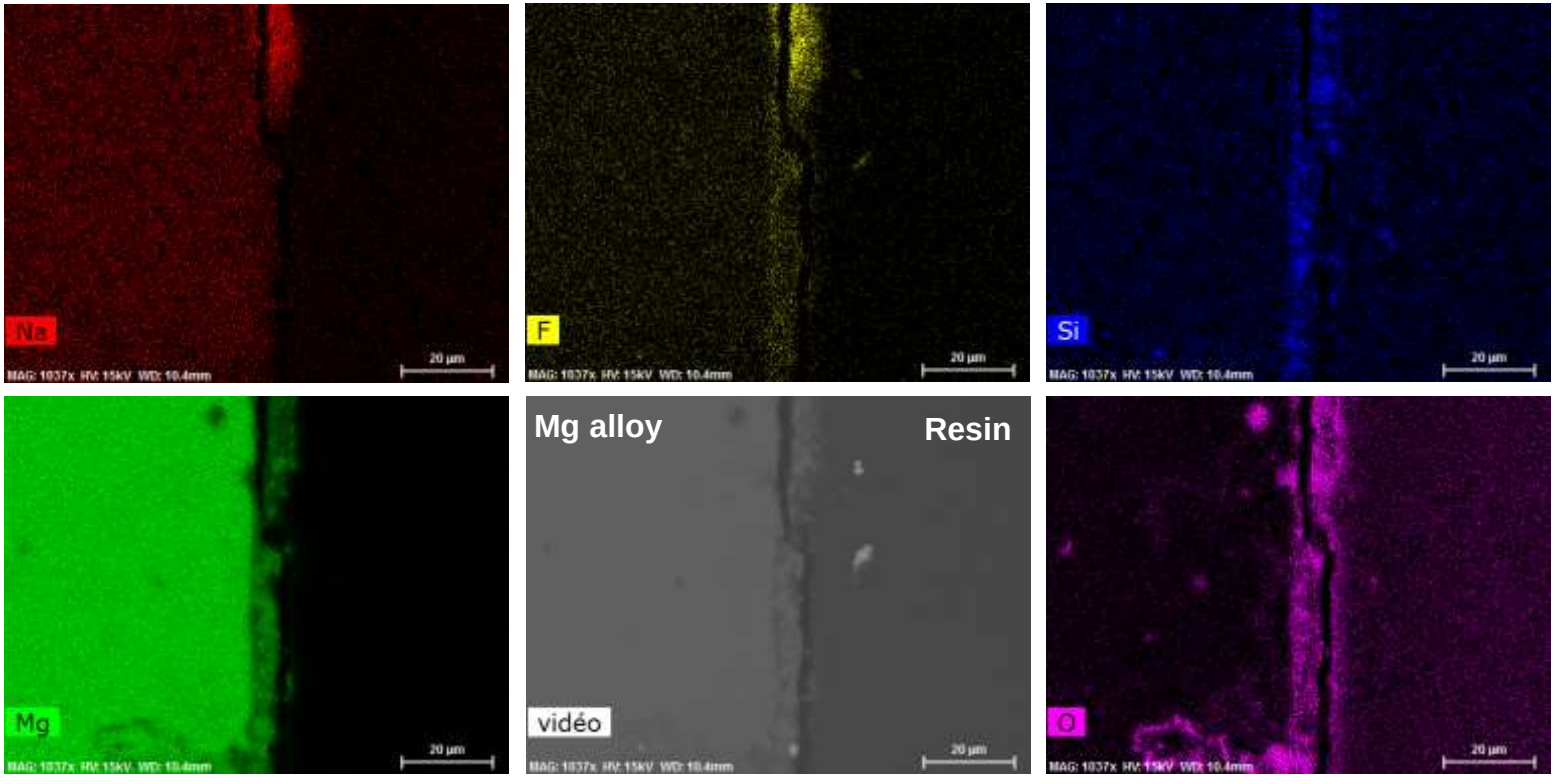
Ecorr / EIS *ZRA*

OUTLINE

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- Conclusion

GENERAL CORROSION IN PORE SOLUTION

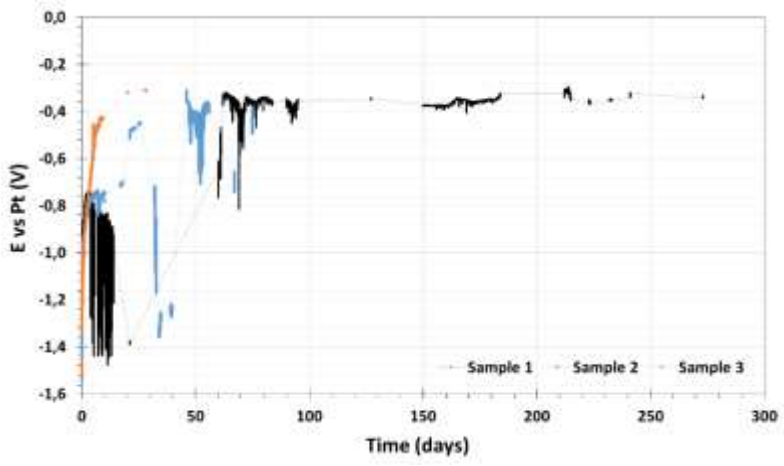
Elementary X-ray Mapping - (after 6 months exposure)



Presence of two different phases: 4-5 µm thick

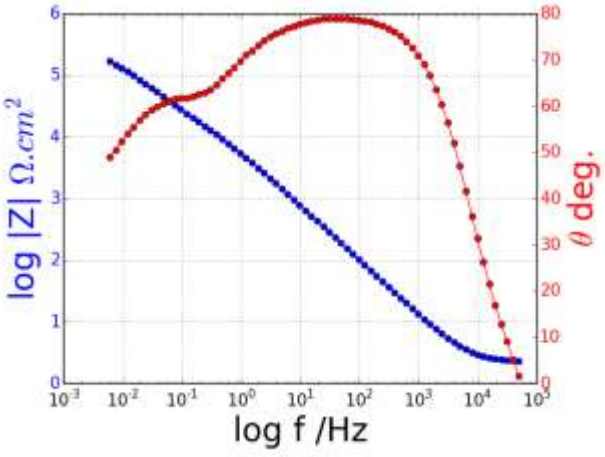
- Mg and O rich → brucite $Mg(OH)_2$ or MgO
- Mg, O, Na, F rich → mixture of $Mg(OH)_2$, NaF, MgF_2, $NaMgF_3$, oxyfluorides, silicates… ?

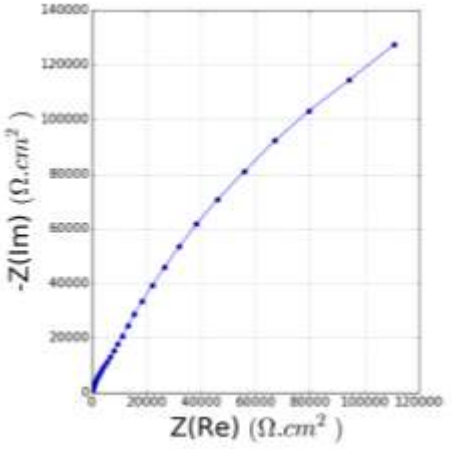
GENERAL CORROSION IN PORE SOLUTION



Corrosion potential monitoring:

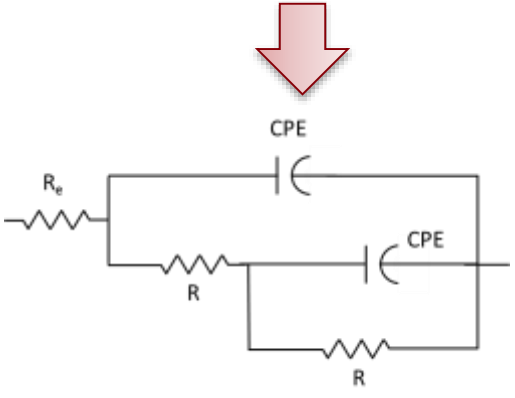
- Increase to anodic potentials
- Instabilities for short durations



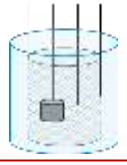


Electrochemical Impedance Spectroscopy:

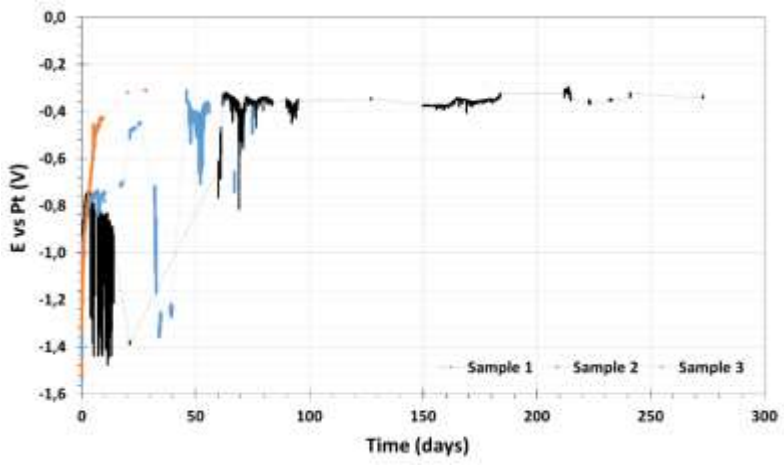
- 2 capacitive loops
- Analysis and deconvolution with IAO software (developped at CEA-LECA lab)
- Fitting with Simad software (developped at LISE laboratory, UPMC Paris)



Equivalent circuit
for MgZr / SPS
corrosion modelling

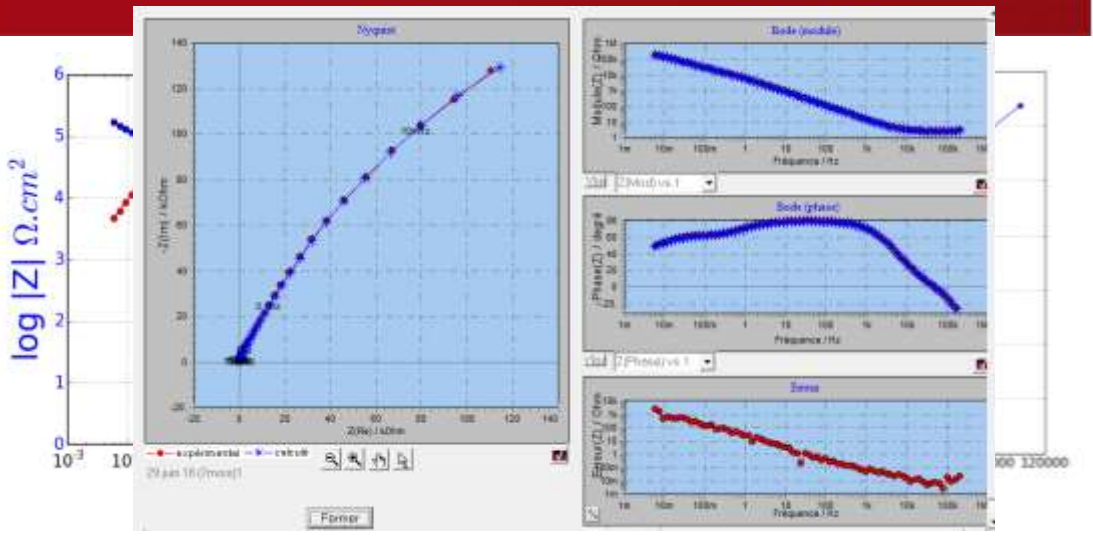


GENERAL CORROSION IN PORE SOLUTION



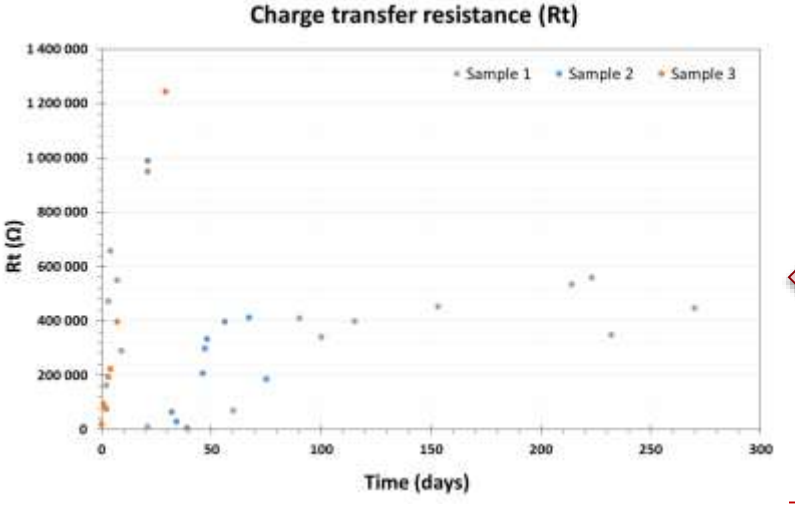
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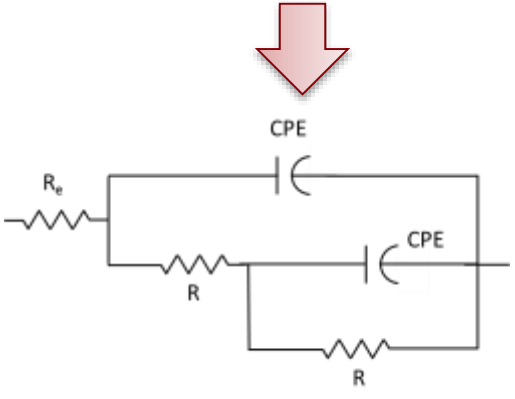
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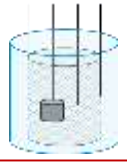
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Equivalent circuit
for MgZr / SPS
corrosion modelling



GENERAL CORROSION IN PORE SOLUTION

Conclusions

- Heterogeneous surface film composition
  - Brucite $Mg(OH)_2$ or MgO
  - Na, F, Si rich phase

- Equivalent circuit with two R//CPE contributions consistent with the film morphology

➡ Further characterisations of the film are still required (Raman, XRD, XPS…)
What is the formation mechanism of the film ?

- Order of magnitude for corrosion rate ≈ 0.1 µm/year

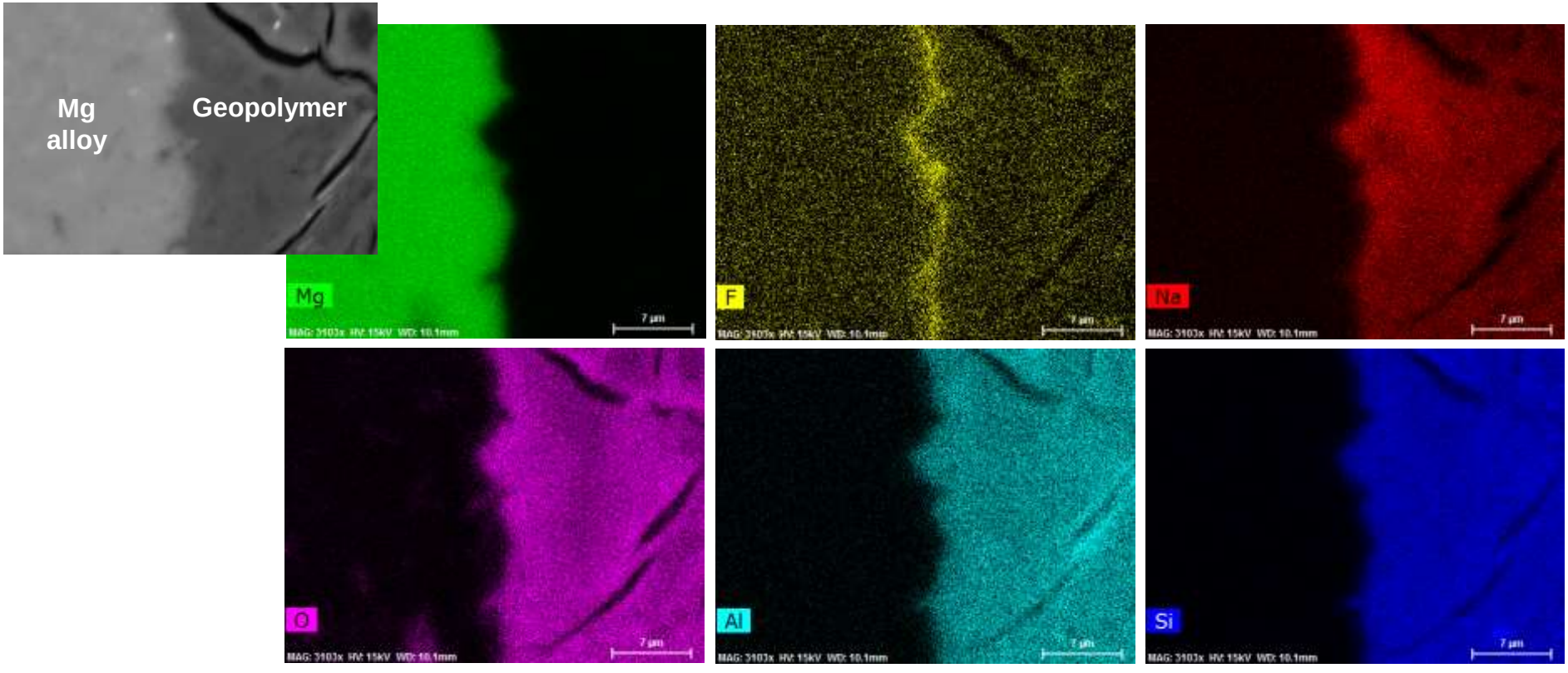
- Several experiments are required for repetability

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GENERAL CORROSION IN GEOPOLYMER MORTAR

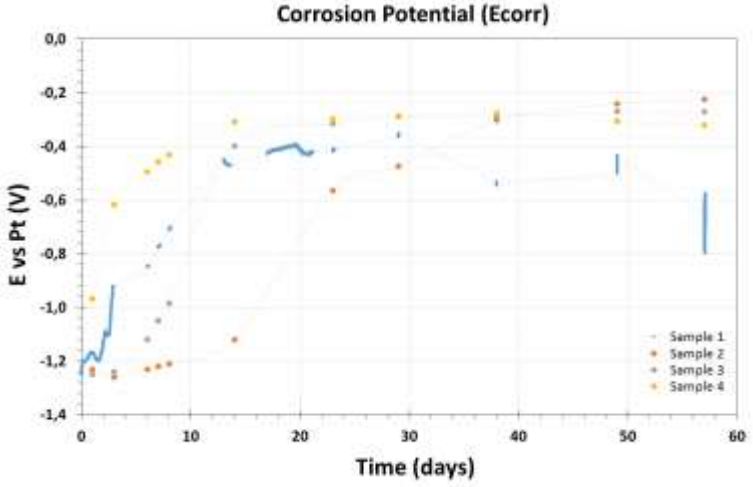
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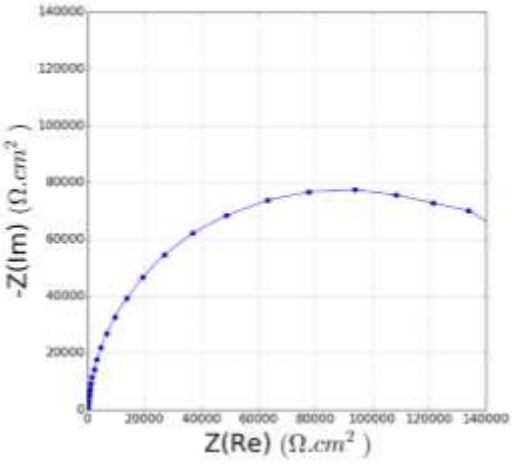


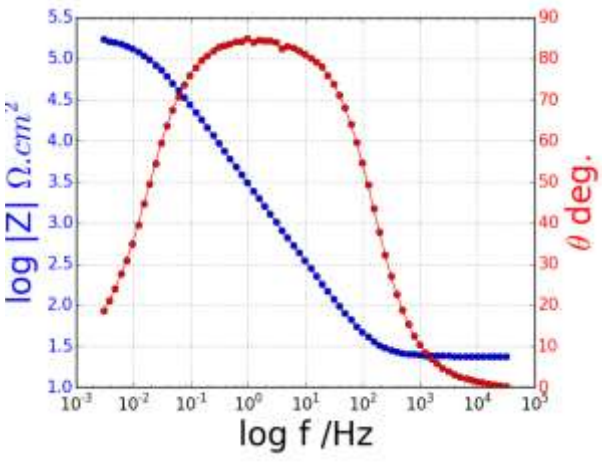
F-rich layer evidenced at the Mg alloy / Na-Geopolymer interface

- MgF_2 or $NaMgF_3$ layer

GENERAL CORROSION IN GEOPOLYMER MORTAR





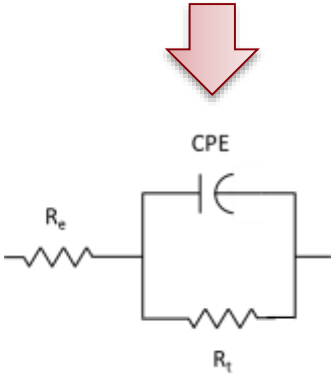


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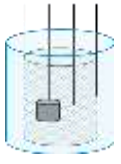
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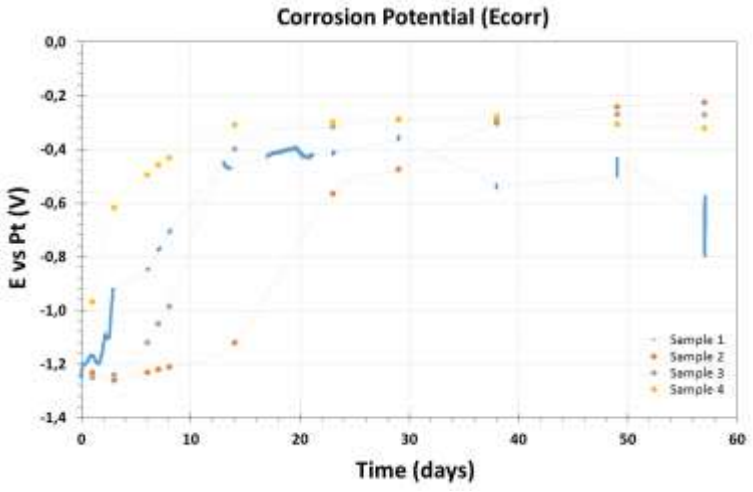
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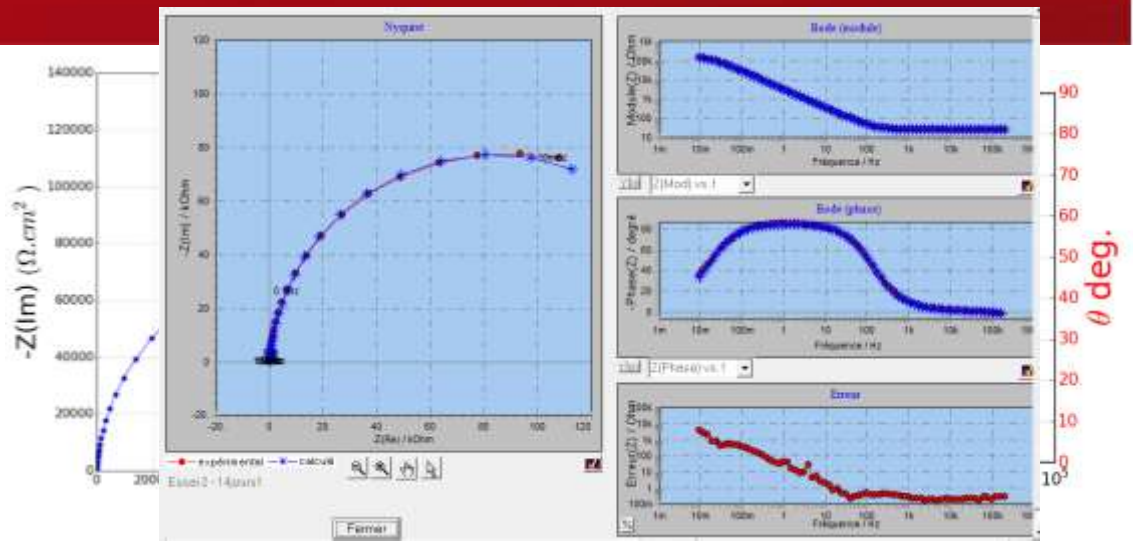


Equivalent circuit
for MgZr / Na-Geo
corrosion modelling



GENERAL CORROSION IN GEOPOLYMER MORTAR



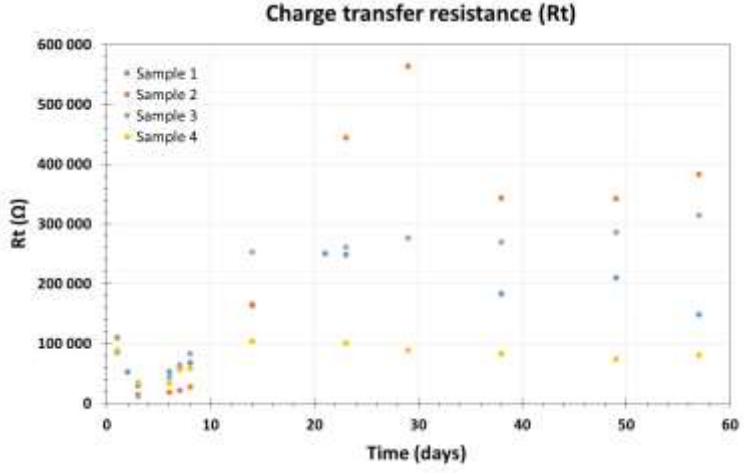


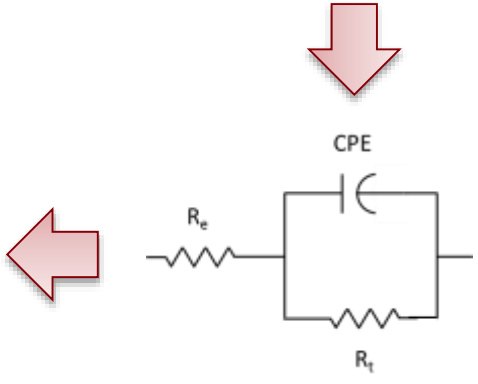
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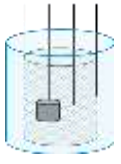
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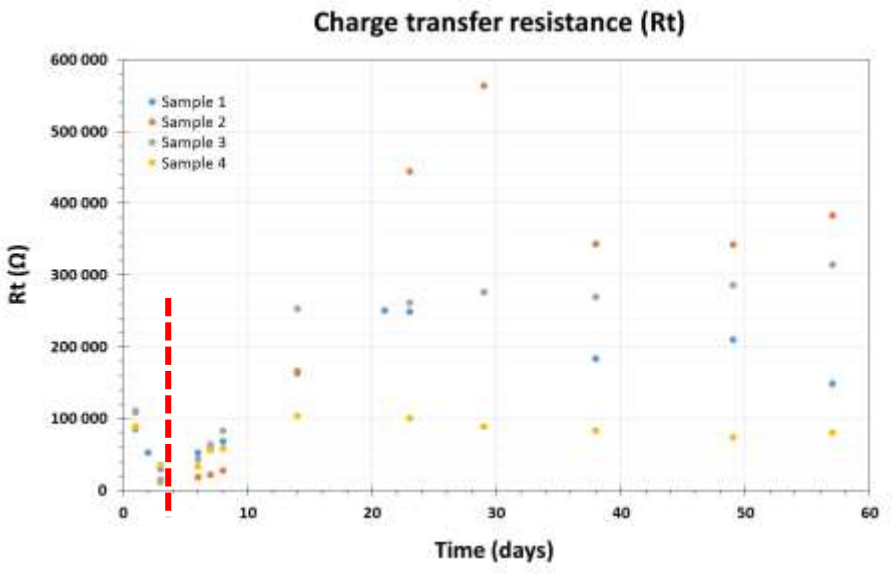


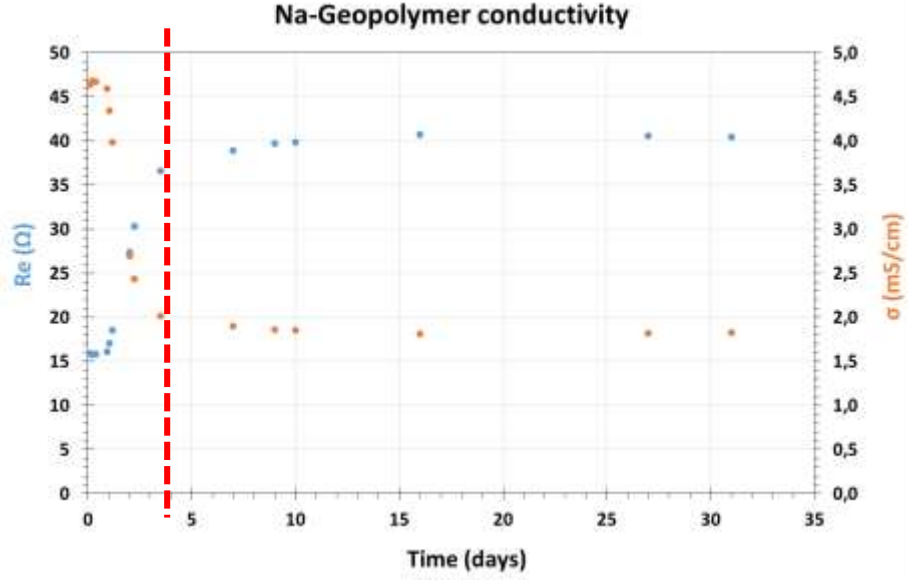
Equivalent circuit
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NA-GEOPOLYMER MORTAR CONDUCTIVITY

Correlation between geopolymer evolution and Charge transfer resistance





- Rapid evolution of the geopolymer conductivity within the first days and stabilisation at about 1.8 mS cm^{-1}
- Shift of conductivity between day 1 and day 3
- Correlation between geopolymer structuration and local minimum of Rt values

GENERAL CORROSION IN GEOPOLYMER MORTAR

Conclusions

- Homogeneous surface film composition
  - Probably MgF_2 or $NaMgF_3$

  ➡ Further characterisations of the film are still required (Raman, XRD, XPS…)

- Equivalent circuit with a single R//CPE contribution consistent with the film morphology

- Local minimum in Rt values at ≈ 3 days corresponding to the geopolymer structuration

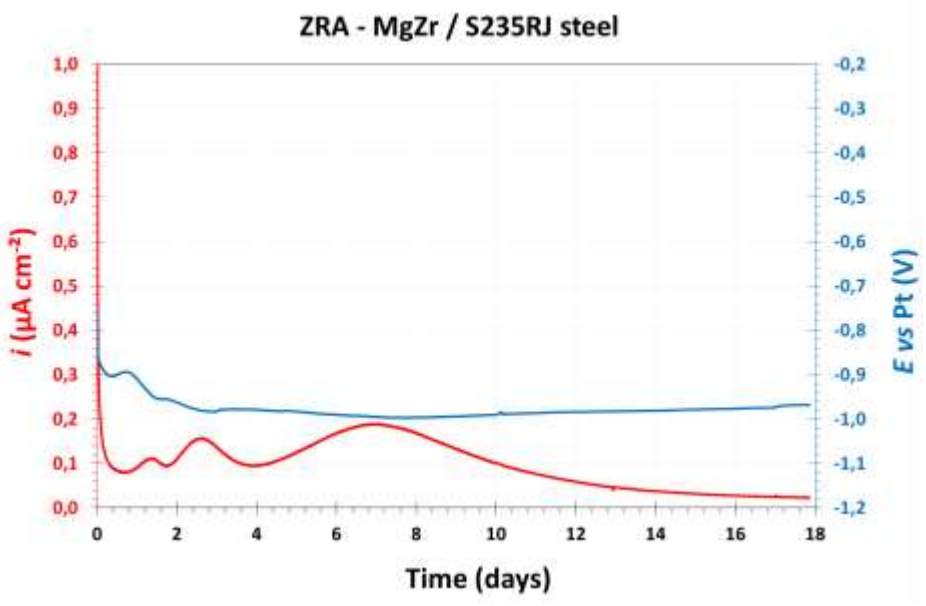
- Order of magnitude for corrosion rate ≈ 0.1 µm/year

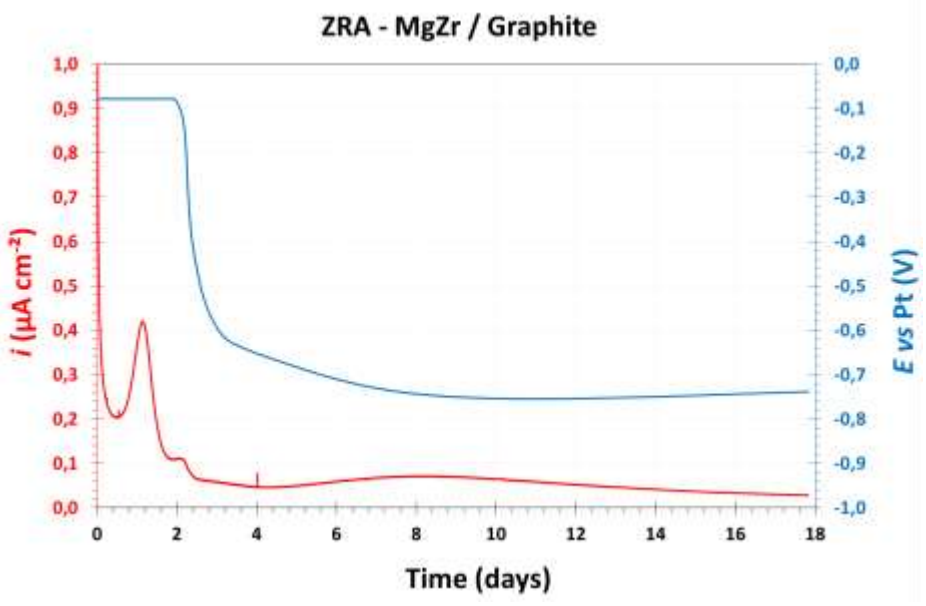
- Several experiments are required for repeatability / statistics

GALVANIC CORROSION IN GEOPOLYMER MORTAR

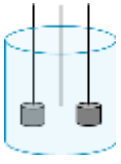
Galvanic coupling with steel or graphite

- ✓ Simulate the interaction between Mg wastes and the steel container or Aquadag
- ✓ Electrochemical method: Zero Resistance Ammeter (ZRA)
- ✓ Anode / Cathode surface ratio = 1/1





- ➢ Stabilisation of the system within a few days in both cases
- ➢ Galvanic current densities are about 20-30 nA cm^{-2} after 18 days



CORROSION RATES IN NA-GEOPOLYMER MORTAR

Corrosion rate for general corrosion in Na-geopolymer mortar:

- From EIS (instantaneous rate):

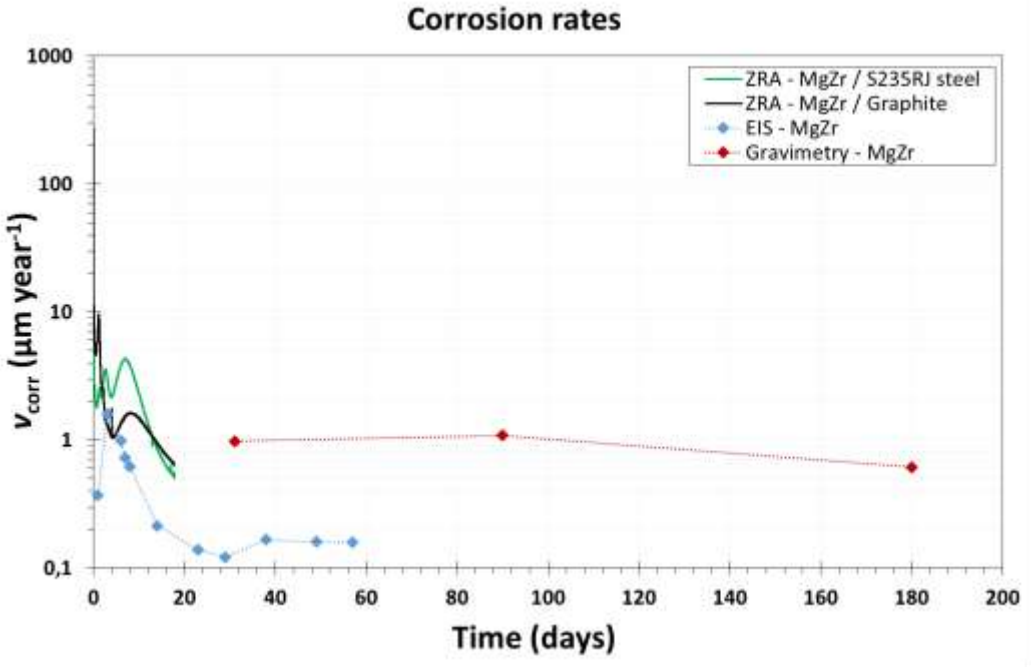
$$i_{corr} = \frac{1}{n_a \alpha_a + n_c \alpha_c} \frac{RT}{F} \frac{1}{R_t}$$

- From Weight loss measurements: (average rate)

$$v_{corr} = \frac{\Delta m / S}{\rho_{Mg} . t}$$

Corrosion rate for galvanic corrosion:

$$v_{corr} = \frac{i_{corr} M_{Mg}}{n F \rho_{Mg}}$$



Corrosion rates of MgZr in NaGeo mortar:

- Low corrosion rates: 0.1 - 1 µm year^{-1}
- Small increase due to galvanic coupling (A/C = 1/1)
- H_2 evolution = 0.016 - 0.16 mL cm^{-2} year^{-1}

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  - *General corrosion*
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  - *Conductivity measurements*
- **Conclusions**

CONCLUSIONS

Synthetic Na-geopolymer/NaF pore solution	Na-geopolymer/NaF mortar
Surface film	
Multiple surface film composition: $Mg(OH)_2$; Na, F, Si rich layer ?	Surface film composition: F-rich layer: MgF_2 or NaMgF3 ?
2 capacitive loops for equivalent circuit	1 single capacitive loop for equivalent circuit
General corrosion	
Charge transfer resistances (i.e. corrosion rates) of same order of magnitude	
	Higher rates obtained by weight loss measurements
Galvanic corrosion	
	Anode / Cathode ratio 1:1
	Galvanic corrosion rates ≥ General corrosion rates

Thank you for your attention !

Commissariat à l'énergie atomique et aux énergies alternatives
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