Work In the Framework of
Eurad-2 WP6 STREAM

European Partnership
on Radioactive Waste Management

Corrosion of Magnesium alloy in geopolymer: In situ corrosion and mechanical alteration monitoring

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Plan

1. Context
2. Magnesium Corrosion: Key Concepts
3. Experimental Study
4. Numerical Study
5. Conclusion

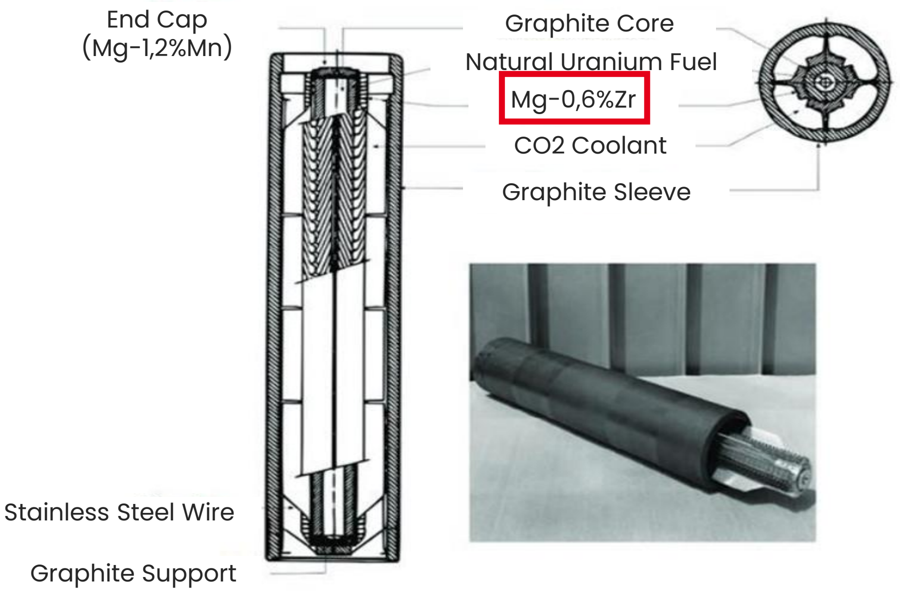
Context

Uranium Natural Graphite Gaz
UNGG Reactors

- ***Fuel:*** **Natural Uranium**
- ***Moderator:*** **Graphite**
- ***Coolant:*** **CO_2**

UNGG Assemblies

- **Metallic Uranium Rod**
- **MgZr alloy Cladding**
- ***Two MgMn alloy end caps***
- ***Tubular Graphite Sleeves***

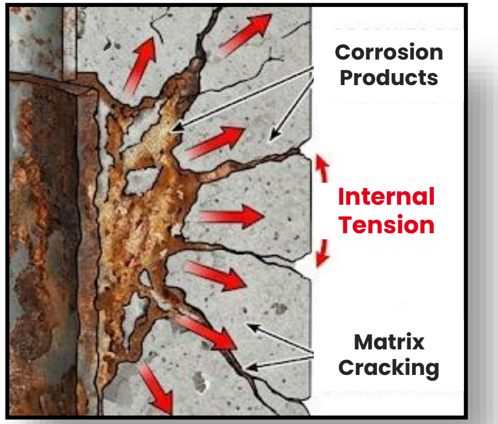


UNGG Fuel Element

Generation of Reactive Nuclear Waste

Mg-Zr alloy cladding embedded in a geopolymer matrix [ANDRA-DECIMAL]

If poor binder formulation: Metal corrosion



Context

Phenomenon

Generation of expansive products due to corrosion

Risk

Degradation of the mechanical properties of the waste package

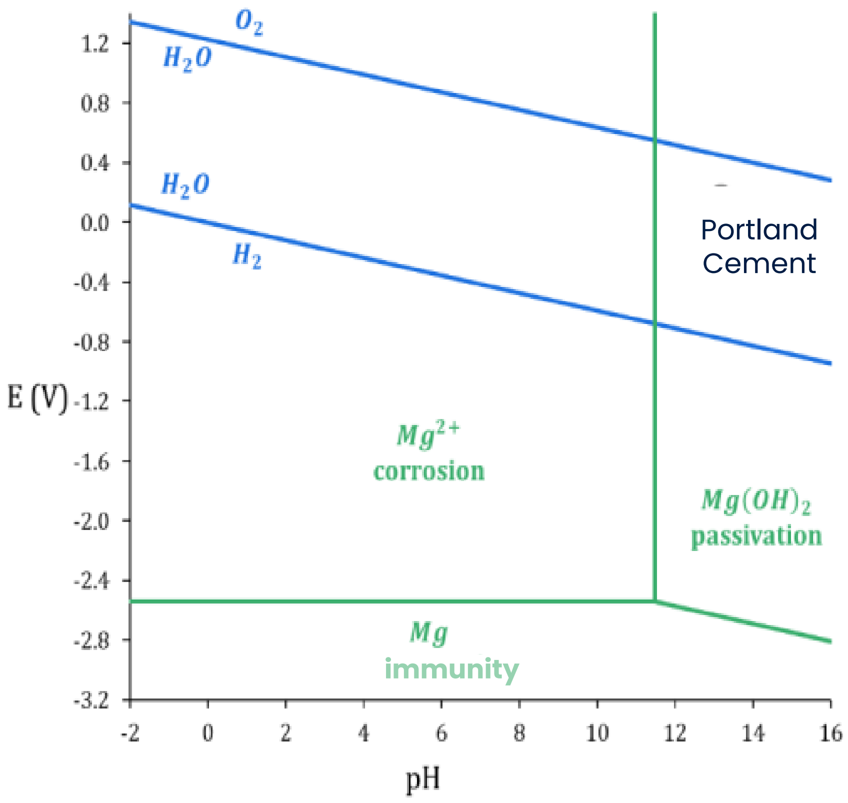
Challenge

Experimentally reproduce and model the hydro-chemo-mechanical interactions between the metal and its binder to ensure storage safety

Outline

- State of the art on Magnesium Corrosion and its monitoring in nuclear waste conditioning matrices
- Experimental Study of Magnesium Corrosion in Geopolymer Matrices
- Development of a First, Simplified Hydro-Chemo-Mechanical Model Based on Experimental Results

Magnesium Corrosion: Key Concepts



Pourbaix's Diagram

$$A\ pH < 11{,}5 : Mg + 2H^+ \rightarrow Mg^{2+} + H_2$$

$$A\ pH > 11{,}5 : Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

Galvanic Corrosion of Magnesium

$$Mg + 2H_2O \rightarrow Mg^{2+} + H_2 + 2HO^- \rightarrow Mg(OH)_2 + H_2$$

Formation of expansive corrosion products

Hydrogen gas generation

What is a Geopolymer?

$$M_n\{-(SiO_2)_z - AlO_2\}_n . wH_2O$$

Cation (Na, K, Cs)

Degree of polycondensation

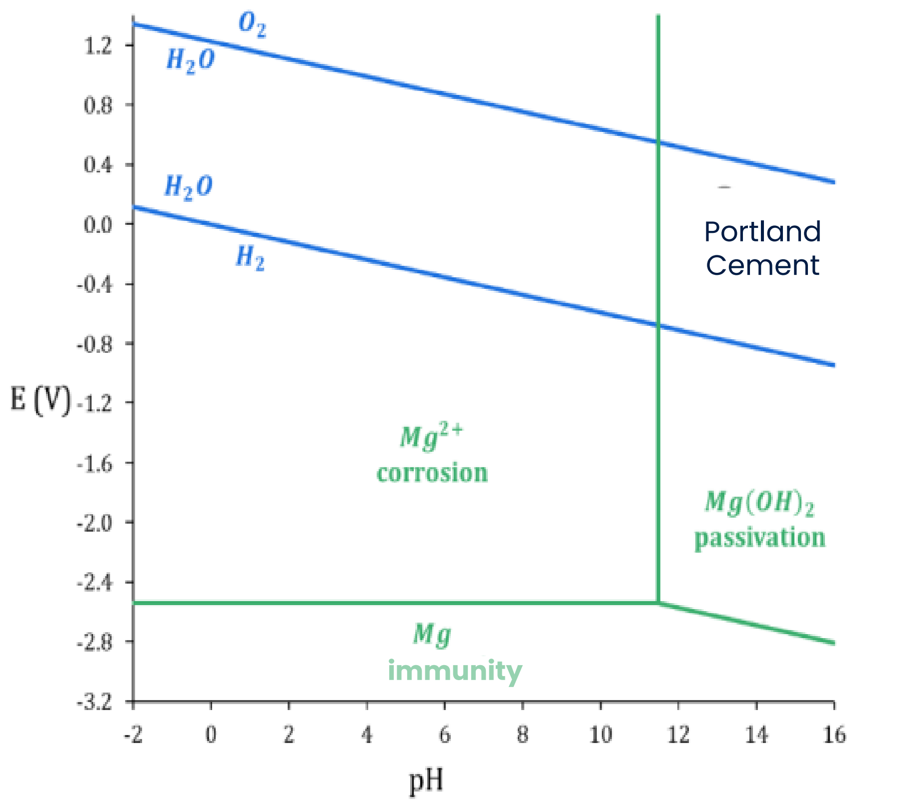
Si/Al Ratio (1-3)

Water Molecules

Aluminosilicate-based material activated with alkaline solutions

$\boxed{1Na_2O\text{-}3{,}96SiO_2\text{-}1Al_2O_3\text{-}12{,}5H_2O}$

Magnesium Corrosion: Key Concepts



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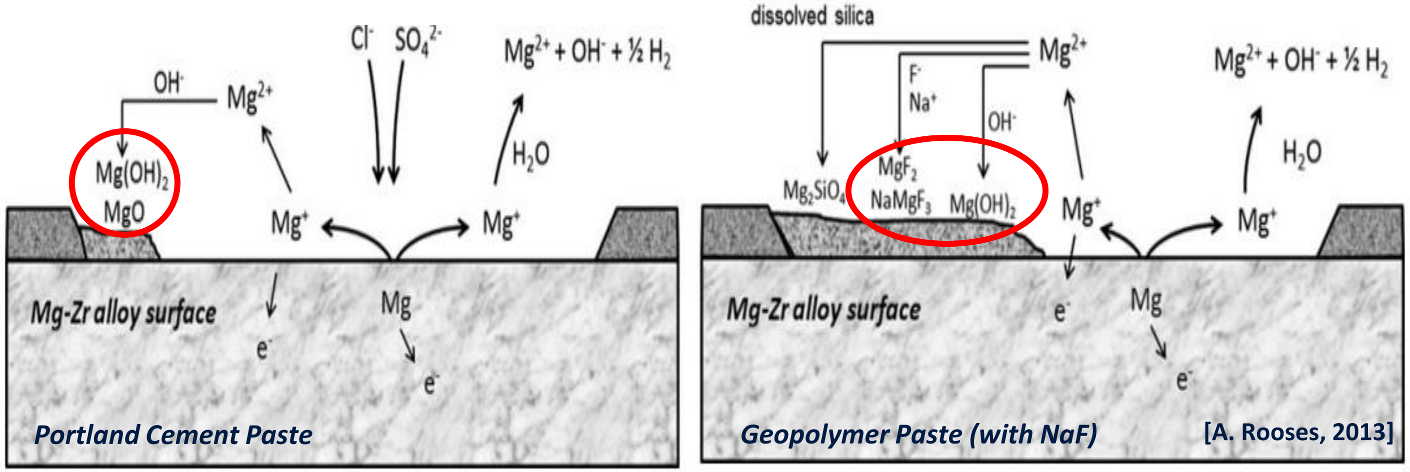
Formation of expansive corrosion products

Hydrogen gas generation

Why The Geopolymer?

- ph>11 → Passivation domain
- NaF → More protective layers than $Mg(OH)_2$



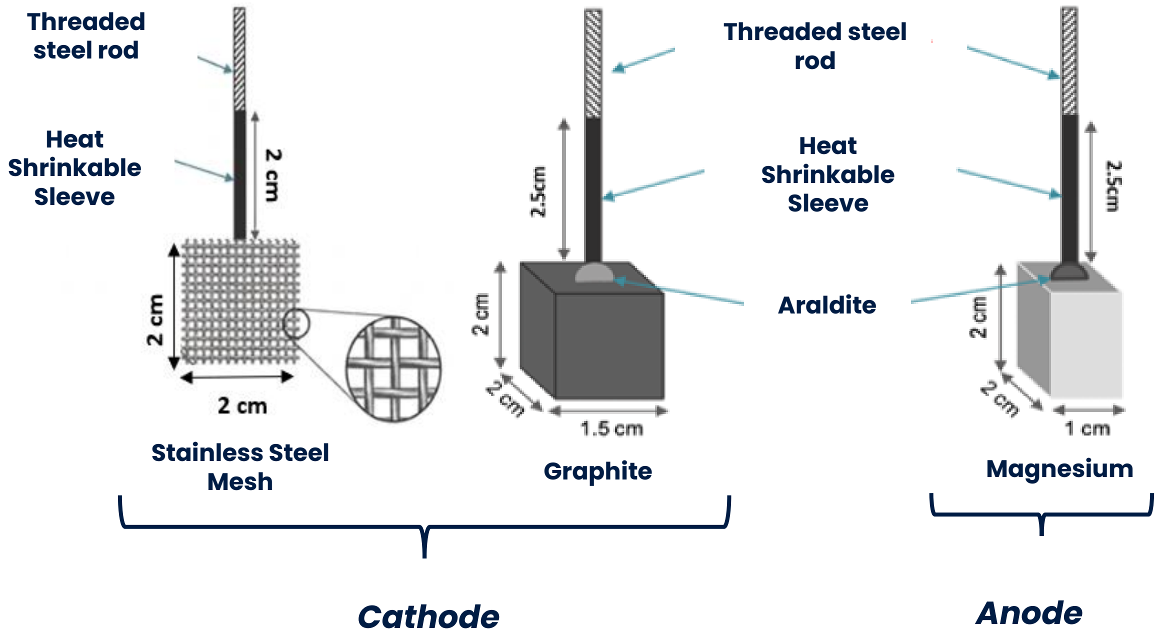
[A. Rooses, 2013]

Experimental Study

Study of Mg–graphite or Mg–stainless steel galvanic couples in geopolymers for future electrochemical testing

More Significant Corrosion – Easier To Measure

Electrodes



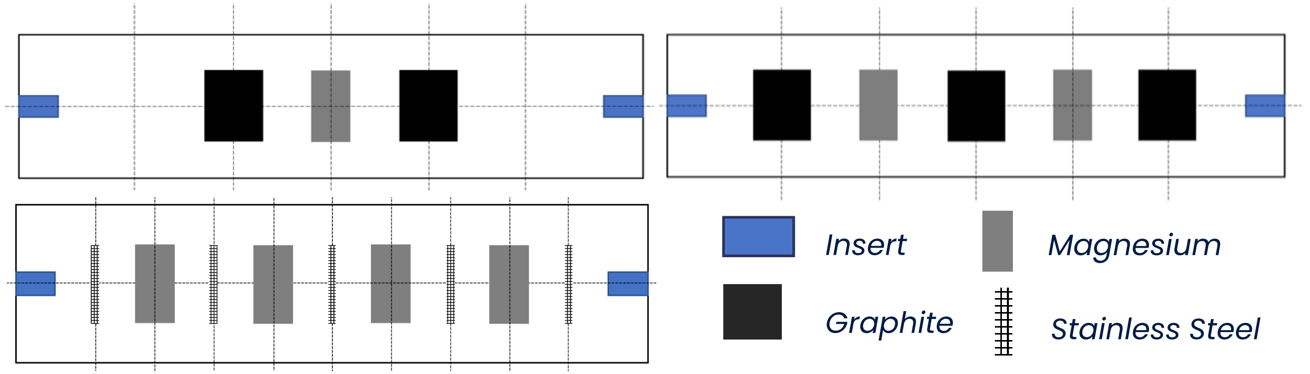
Choice Of Geometry

Mechanical + Corrosion

Displacements Measurements

Electrochemical tests

4*4*16cm Specimen



Configurations proposed to optimize specimen displacement based on numerical simulations

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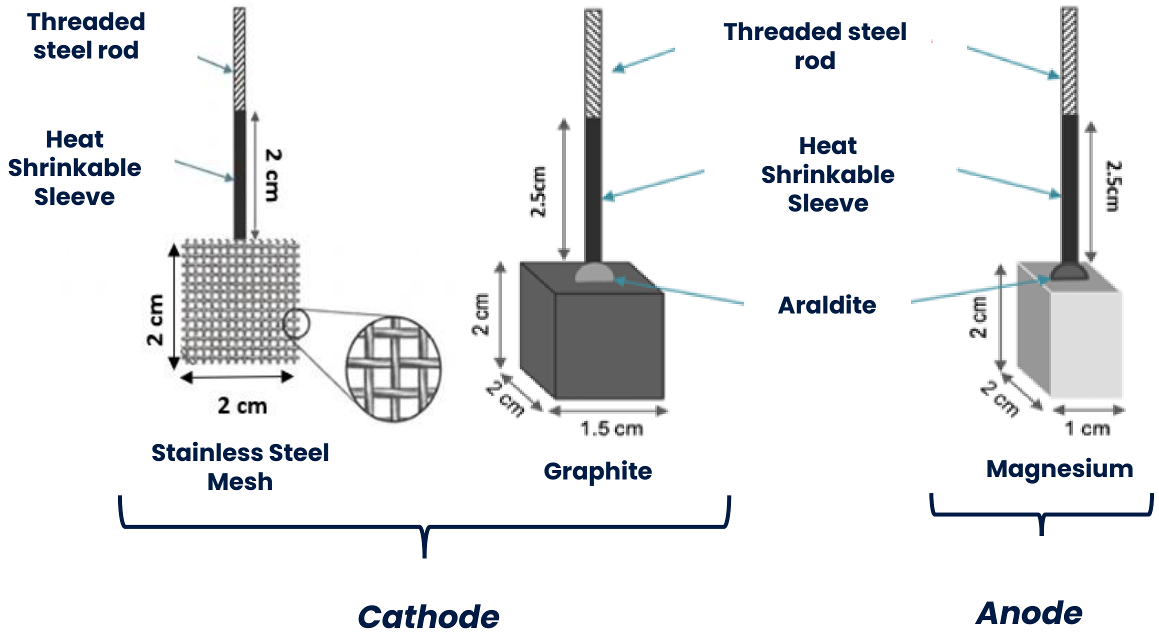
More Significant Corrosion – Easier To Measure

Electrodes



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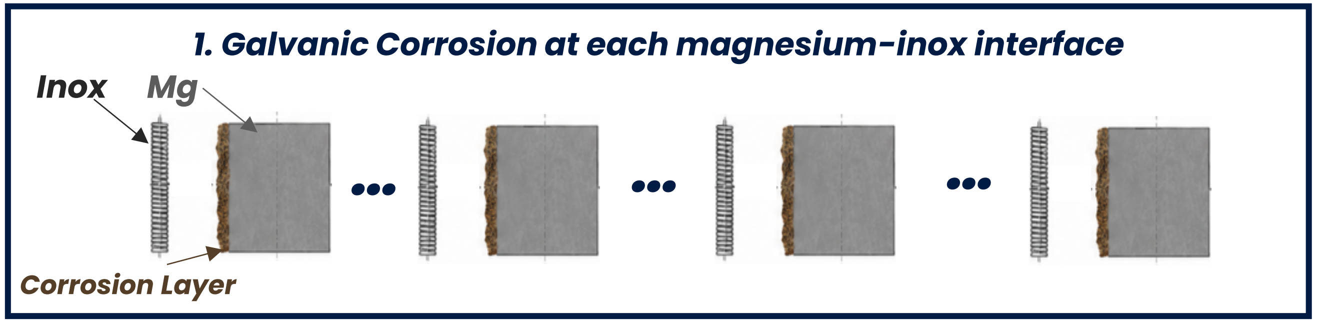
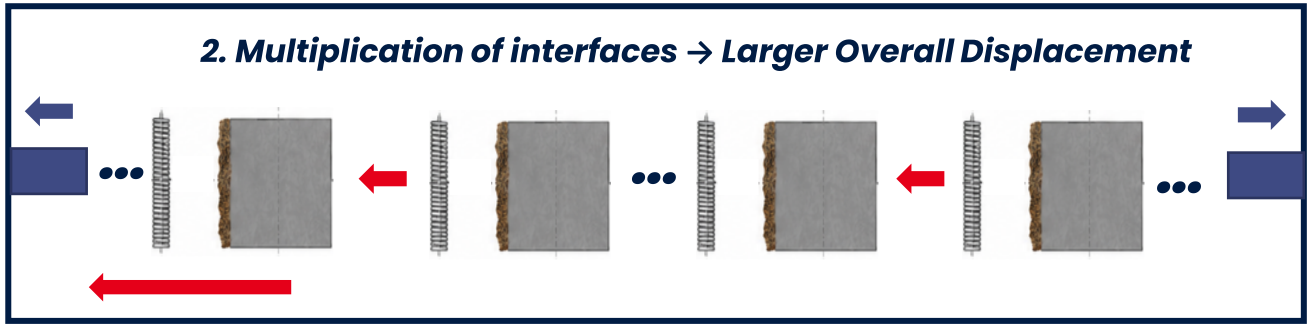


Each Mg-Inox interface corrodes → Local material degradation & displacement



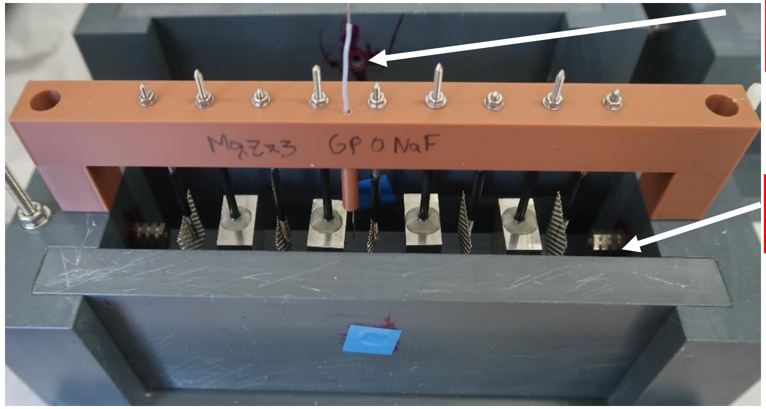
Corrosion at multiple interfaces accumulates → Larger displacement

Cumulative expansion across many interfaces

Experimental Study

Methodology for all configurations

Custom-designed standardized molds



Platinum wire as reference

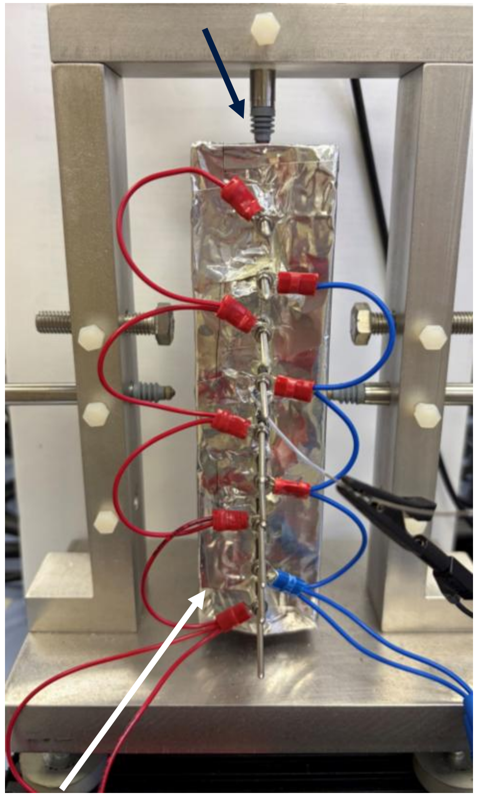
Inserts for LVDTs

LVDT: Linear Variable Differential Transformer (Displacement Sensor)

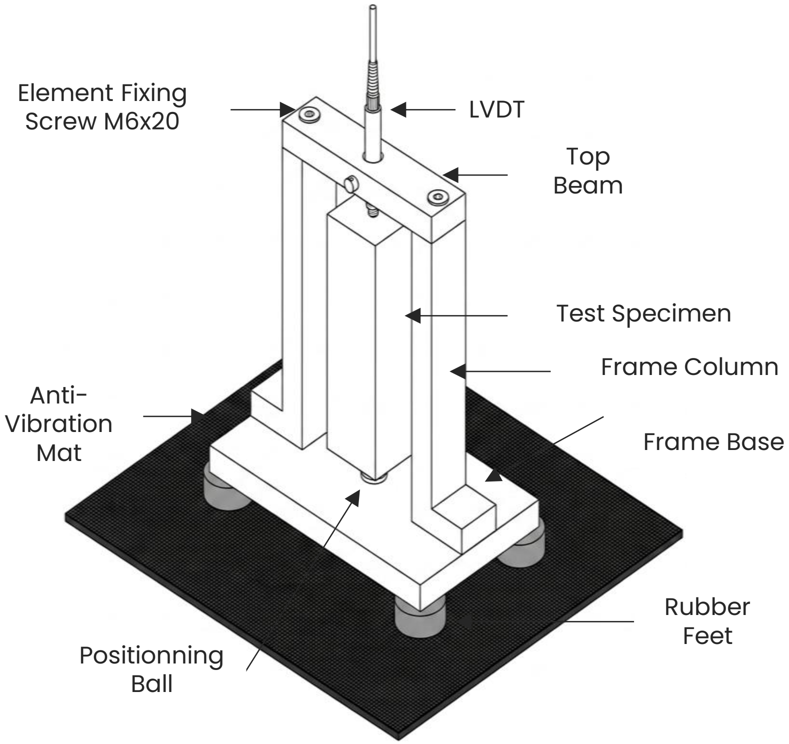
4 × 4 × 16 cm specimens for electrochemical tests

Reference Specimens
(Mg_Mn covered with varnish)

LVDT



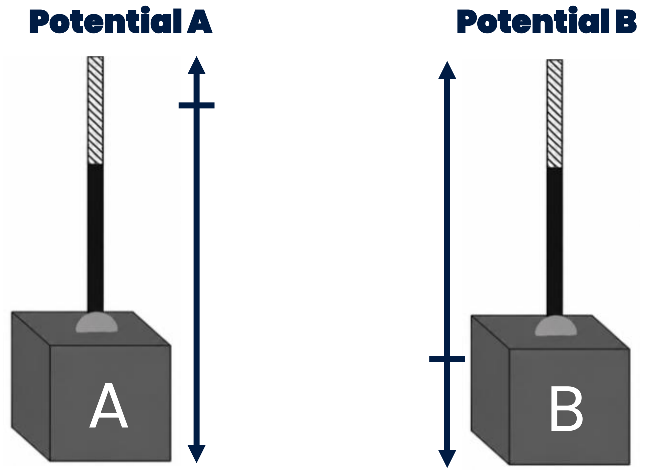
Potentiostat-linked connectors



Specimen placement in a custom-designed frame for electrochemical tests and displacement measurements

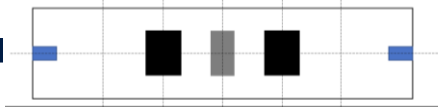
Experimental Study

Electrochemical Method:
Zero Resistance Ammeter (ZRA)



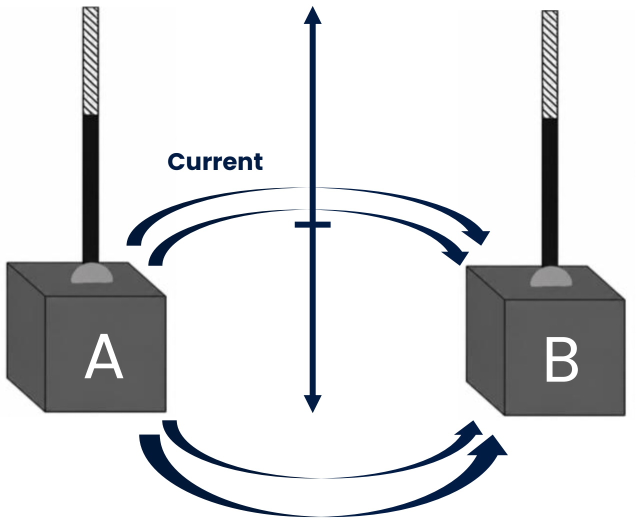
Experimental Study

Configuration 1

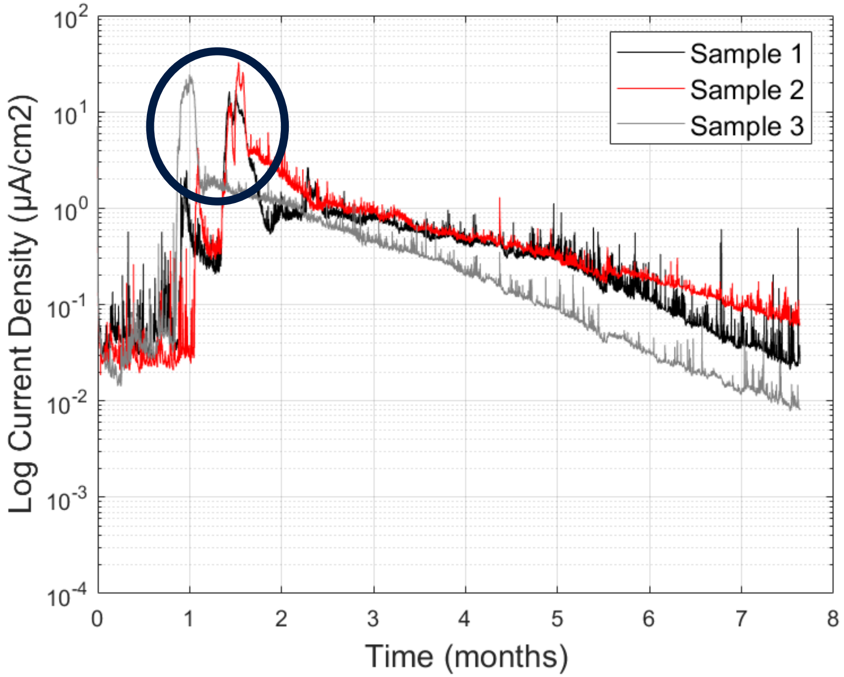


Electrochemical Method:
Zero Resistance Ammeter (ZRA)

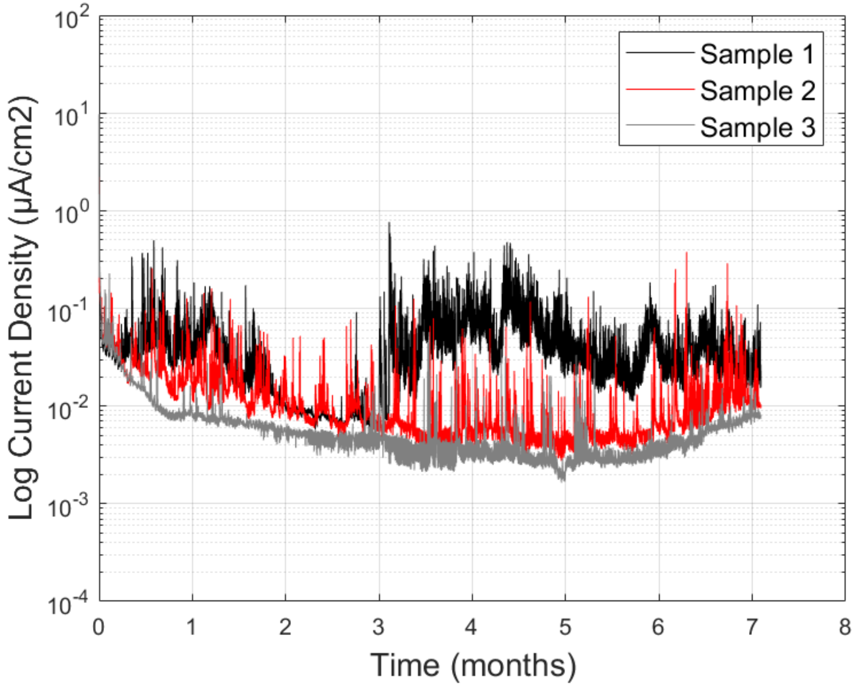
Potential A **Potential B**



Without NaF



With NaF



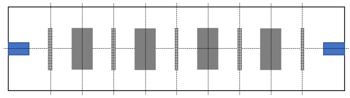
Calculated quantities	GP 0 NaF			GP 1,25 NaF		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Charge (Coulombs)	222	295	236	10,5	3,75	2,57
Mass of corrosion products (mg)	27,9	37,2	29,7	1,3	0,47	0,32
Equivalent thickness of corroded metal (µm)	10	13,4	10,7	0,48	0,17	0,12
Average corrosion rate (µm/year)	16	21,4	17,1	0,81	0,29	0,2

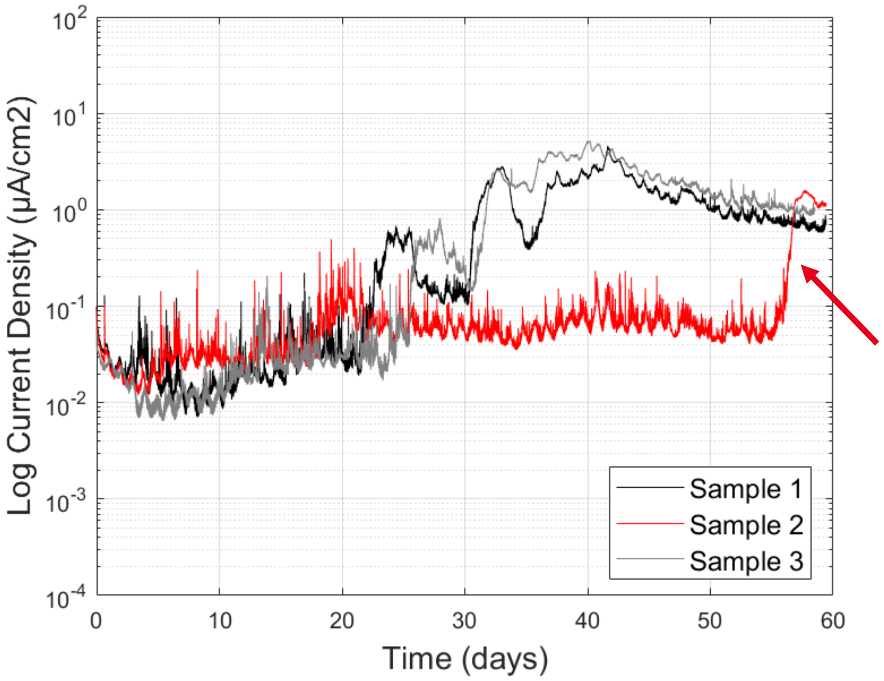
For 7 months

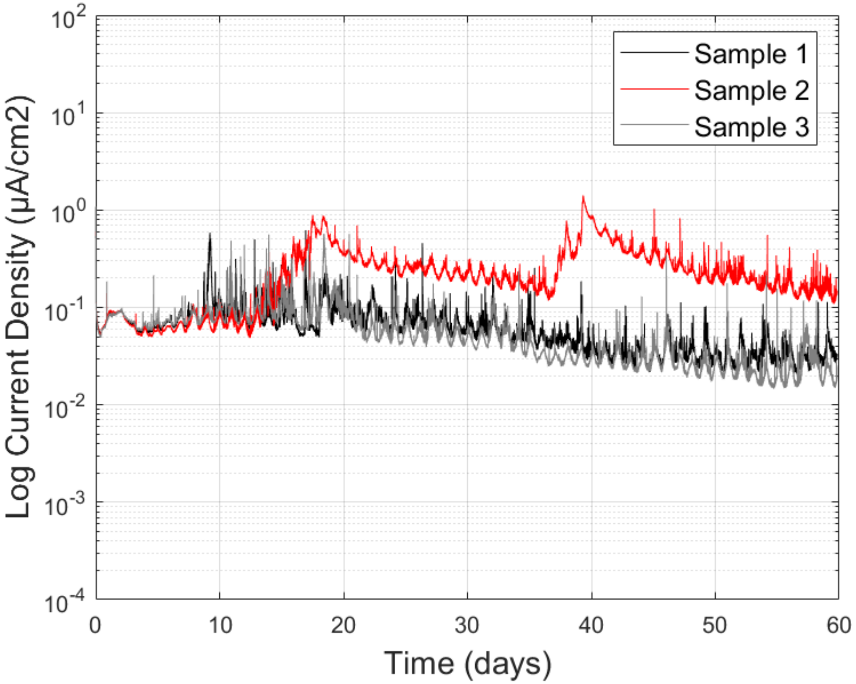
→ **NaF shows corrosion-inhibiting behavior**

Experimental Study

Configuration 2







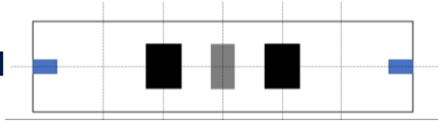
Calculated quantities	GP 0 NaF			GP 1,25 NaF		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Charge (Coulombs)	244	36,84	342,37	20,19	78,15	18,13
Mass of corrosion products (mg)	3,07	0,46	4,31	0,25	0,98	0,23
Equivalent thickness of corroded metal (µm)	1,10	0,17	1,55	0,09	0,35	0,08
Average corrosion rate (µm/year)	6,79	1,02	9,52	0,56	2,15	0,50

For 2 months

→ **NaF shows corrosion-inhibiting behavior (Further monitoring is required, as corrosion is a slow process)**

Experimental Study

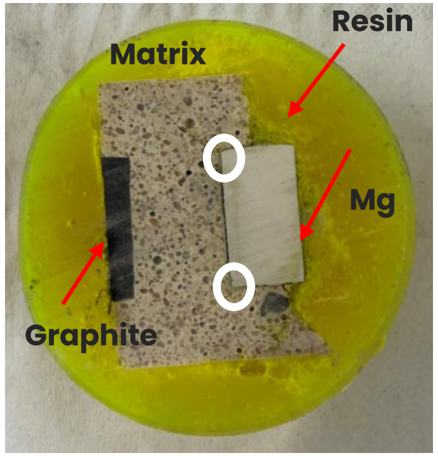
Configuration 1



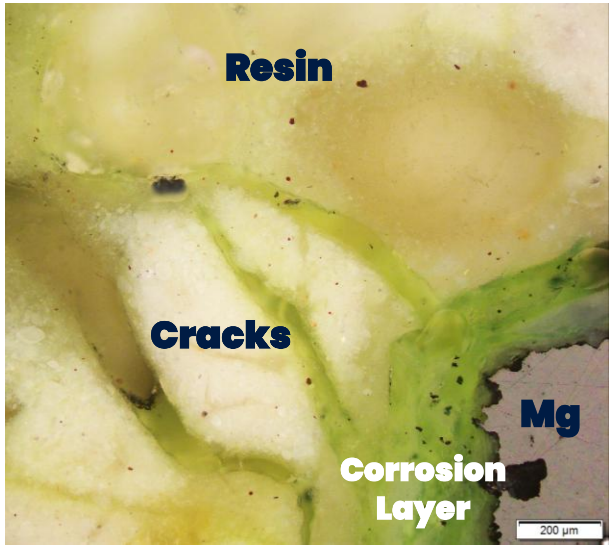
Without NaF : Specimen Fractured in two pieces

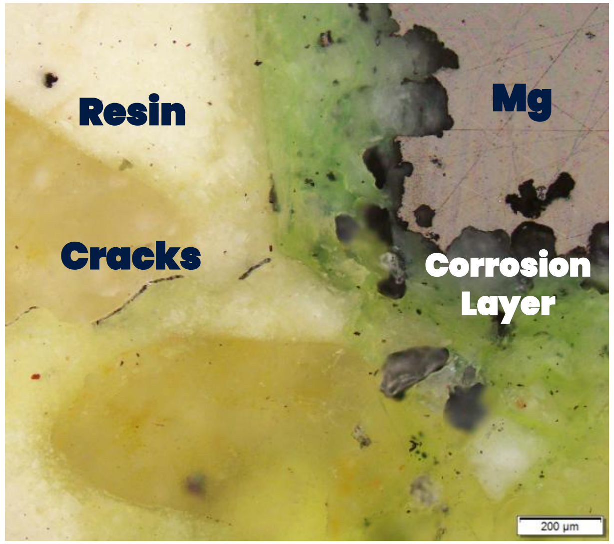
Visible Cracks

Significant Mg Corrosion



With NaF : Specimen remained intact

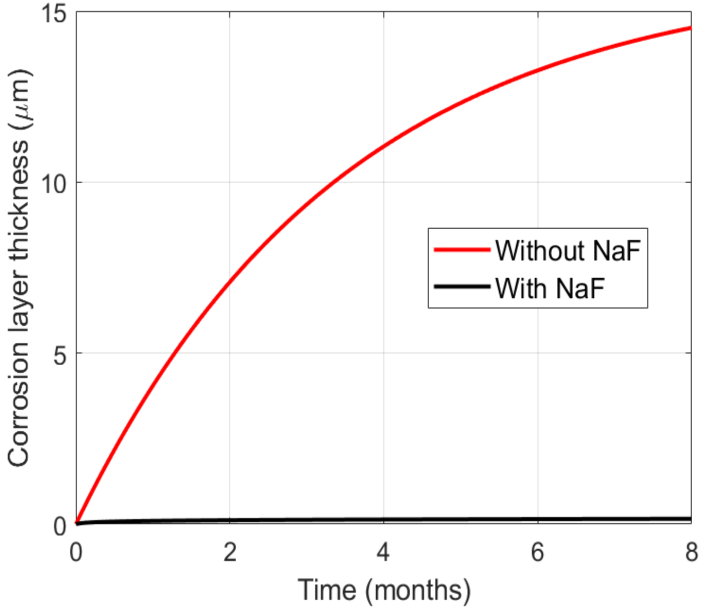




Corroded magnesium surface in GP without NaF – optical microscopy

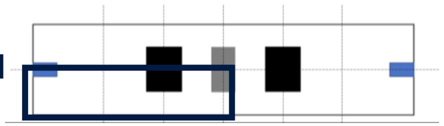
Numerical Study

Loading: Evolution of corrosion layer thickness



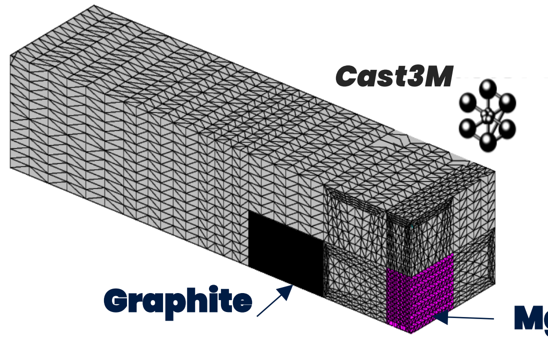
Mechanical Properties / Material	Young's Modulus (GPa)	Poisson's Coefficient
Magnesium	44	0,35
Graphite	20	0,2
Geopolymer	18	0,2

Configuration 1



Algorithm 1 Numerical modeling of corrosion by equivalent expansion

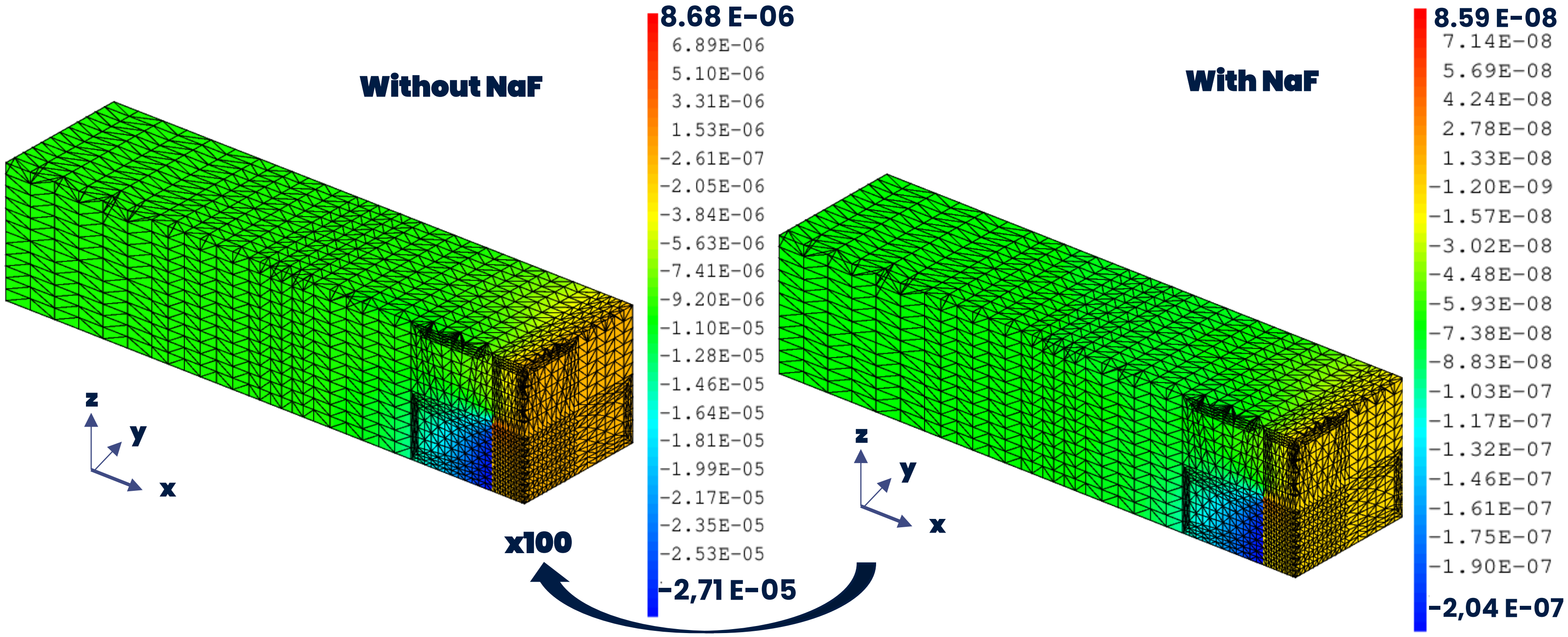
1: Generate the mesh of the study domain
2: Create interface elements between magnesium and matrix
3: Assign an elastic model and mechanical properties to each element
4: Apply boundary conditions related to symmetry
5: Model corrosion by equivalent expansion at the interface
6: Display the results



$$\boxed{\tilde{k}_n = \frac{2\tilde{\mu}_c(1-\tilde{\nu}_c)}{h(1-2\tilde{\nu}_c)}}$$

$$\boxed{\tilde{k}_t = \frac{\tilde{\mu}_c}{h}}$$

Displacements Ux of the 4 x 4 x 16 cm specimen



Numerical Study

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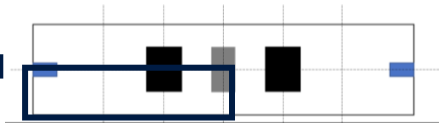

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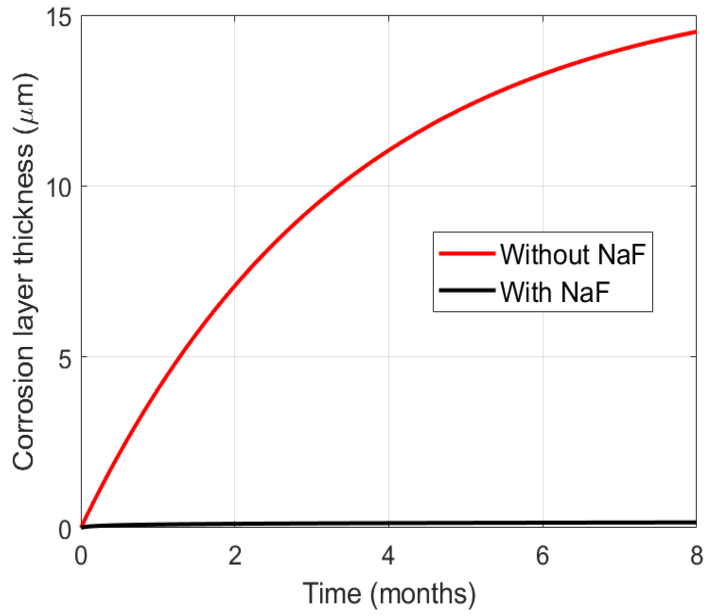

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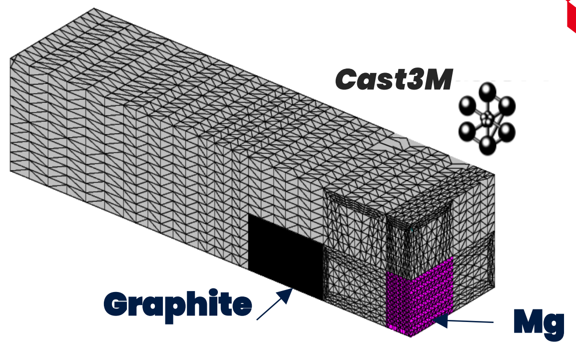

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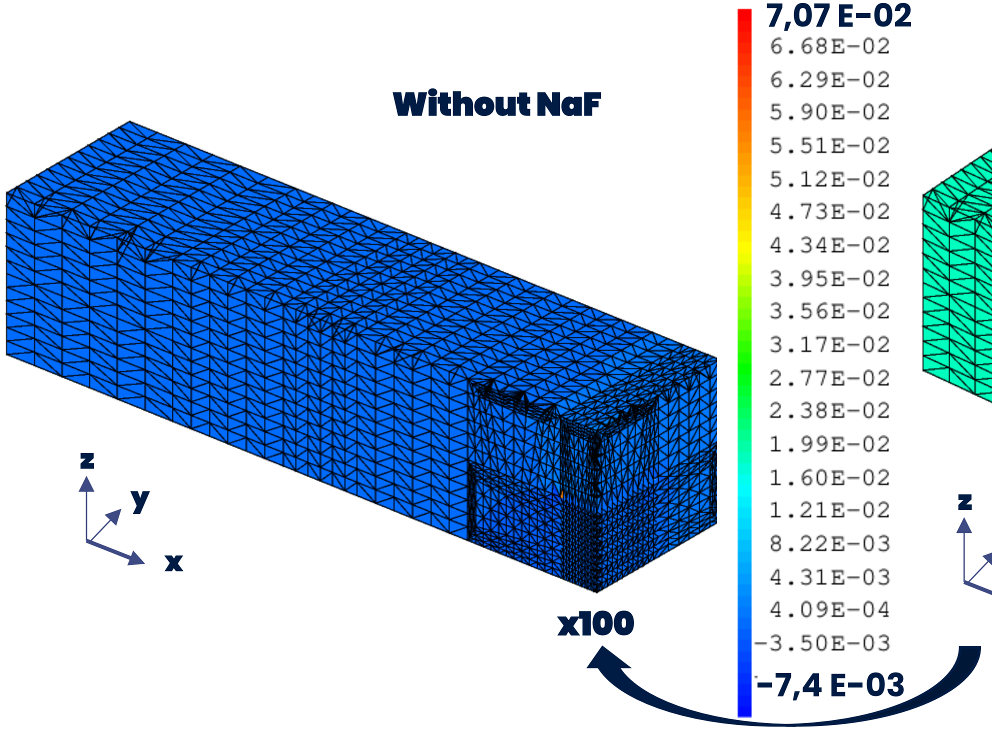
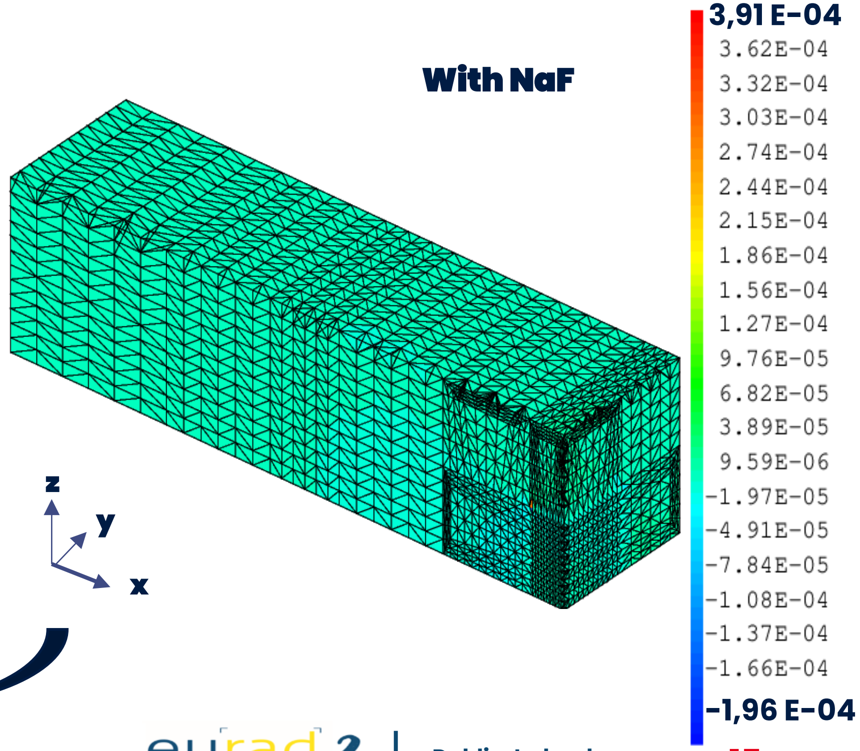
Deformations Ux of the 4 x 4 x 16 cm specimen





Conclusion

- **Different experimental configurations were investigated to improve corrosion monitoring.**
- **NaF addition significantly reduces Mg corrosion in the geopolymer matrix.**
- **The coupling between experimental measurements and numerical modelling is key to better understanding and predicting Mg corrosion and the resulting material response.**

Future Work

- **Incorporate drying shrinkage, creep, and a damage variable into the numerical model.**
- **Use Portland cement as the encapsulation matrix to achieve a greater corrosion layer thickness.**
- **Characterize the corrosion products using nanoindentation measurements.**

Thank you !

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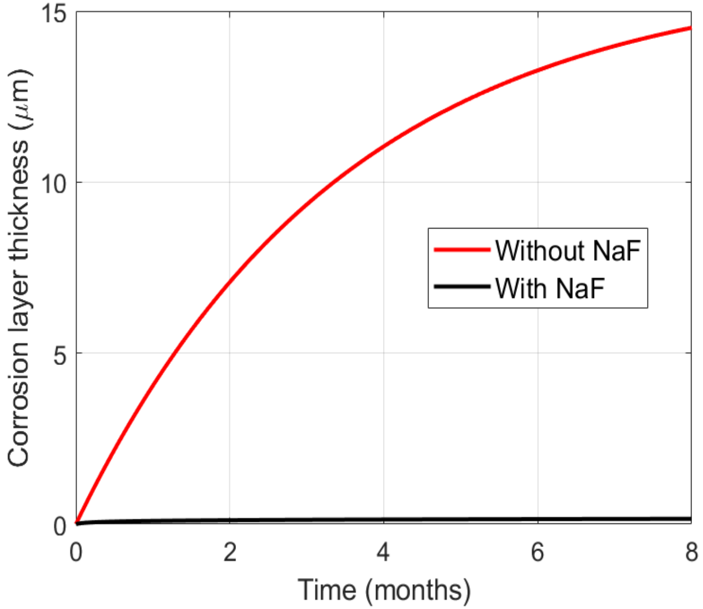
Numerical Study

Loading: Evolution of corrosion layer thickness



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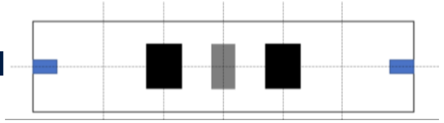

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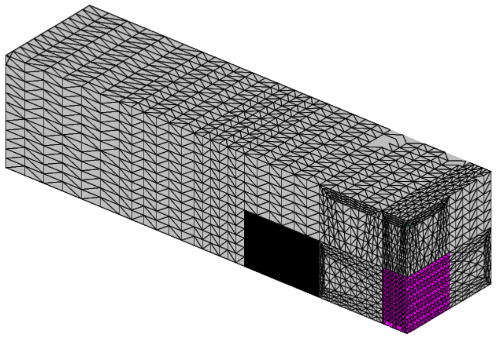

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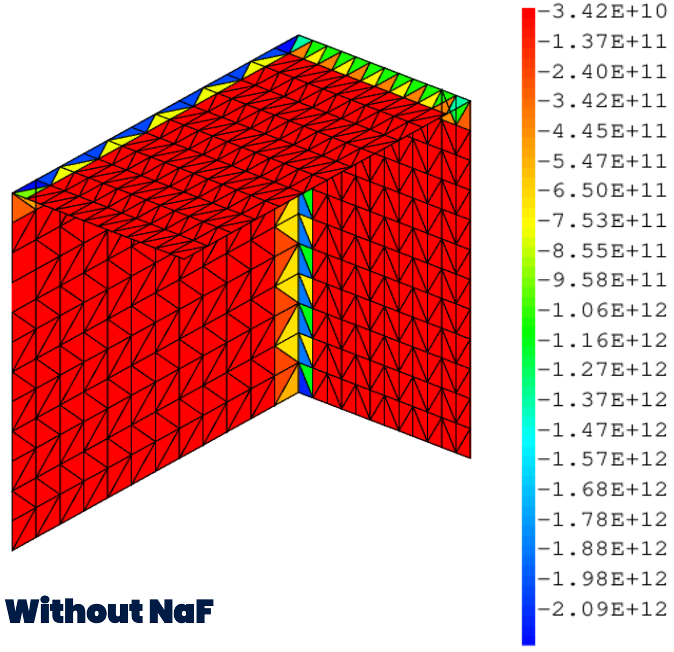
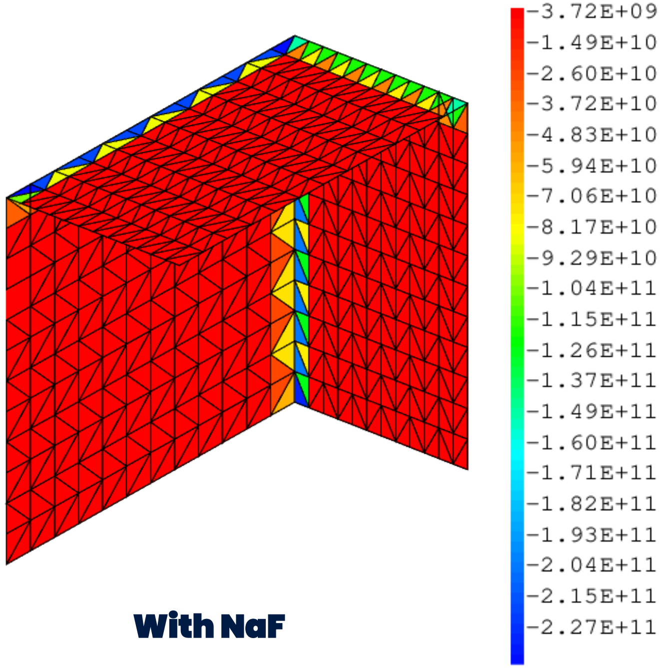
Normal Stress Field on interface elements



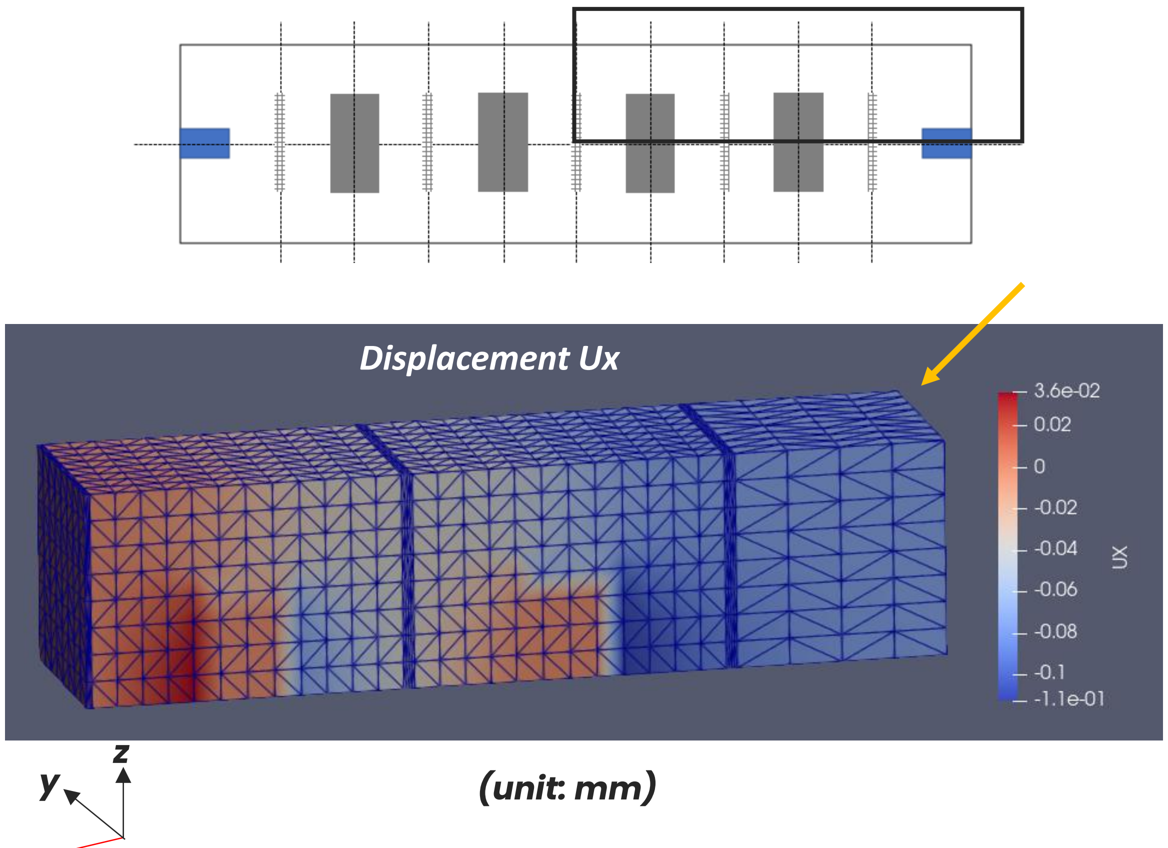
Without NaF



With NaF

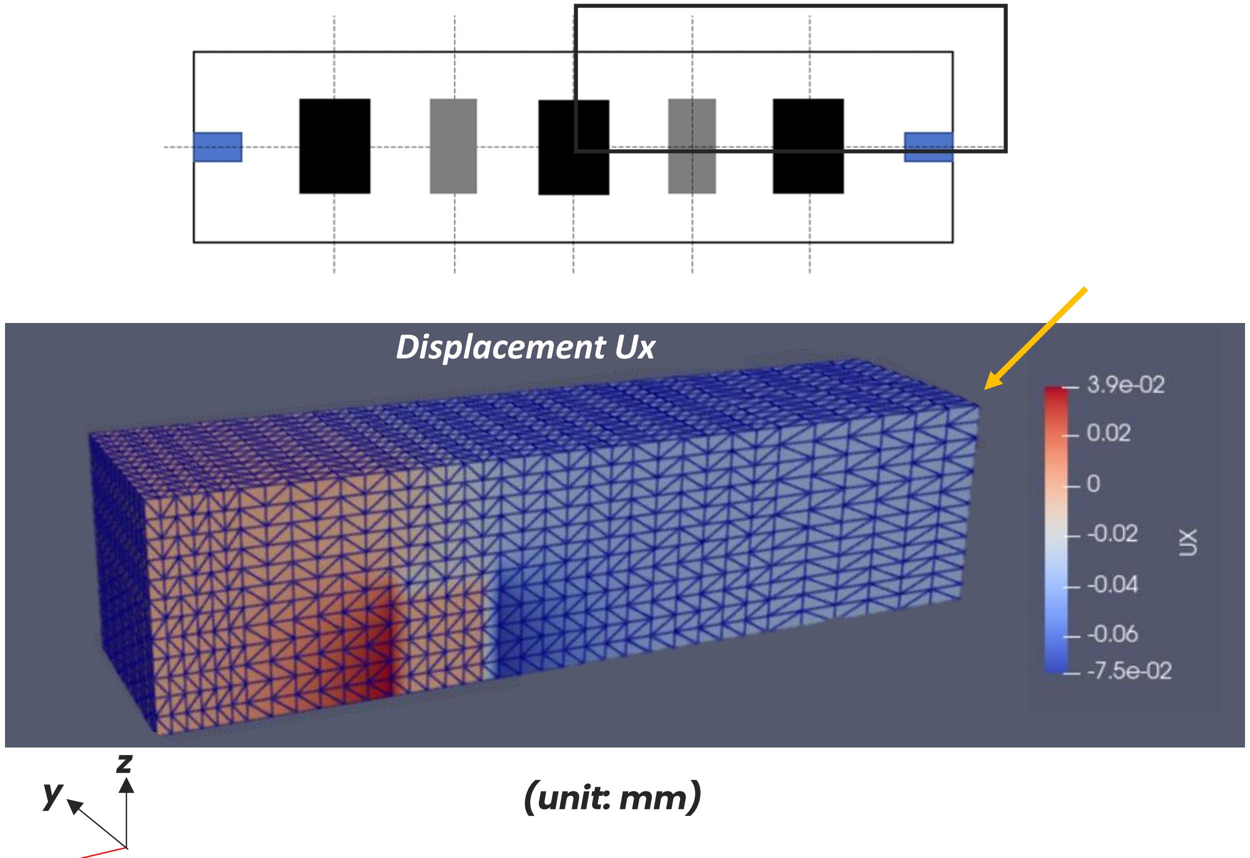
Numerical Study

Numerical optimization of the configuration to improve LVDT measurements (Cast3M)
(For the same applied load)



(unit: mm)

~ 80 µm after 2 months



(unit: mm)

~ 40 µm after 2 months