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Search for a cementitious matrix to stabilize and solidify radwaste containing beryllium metal

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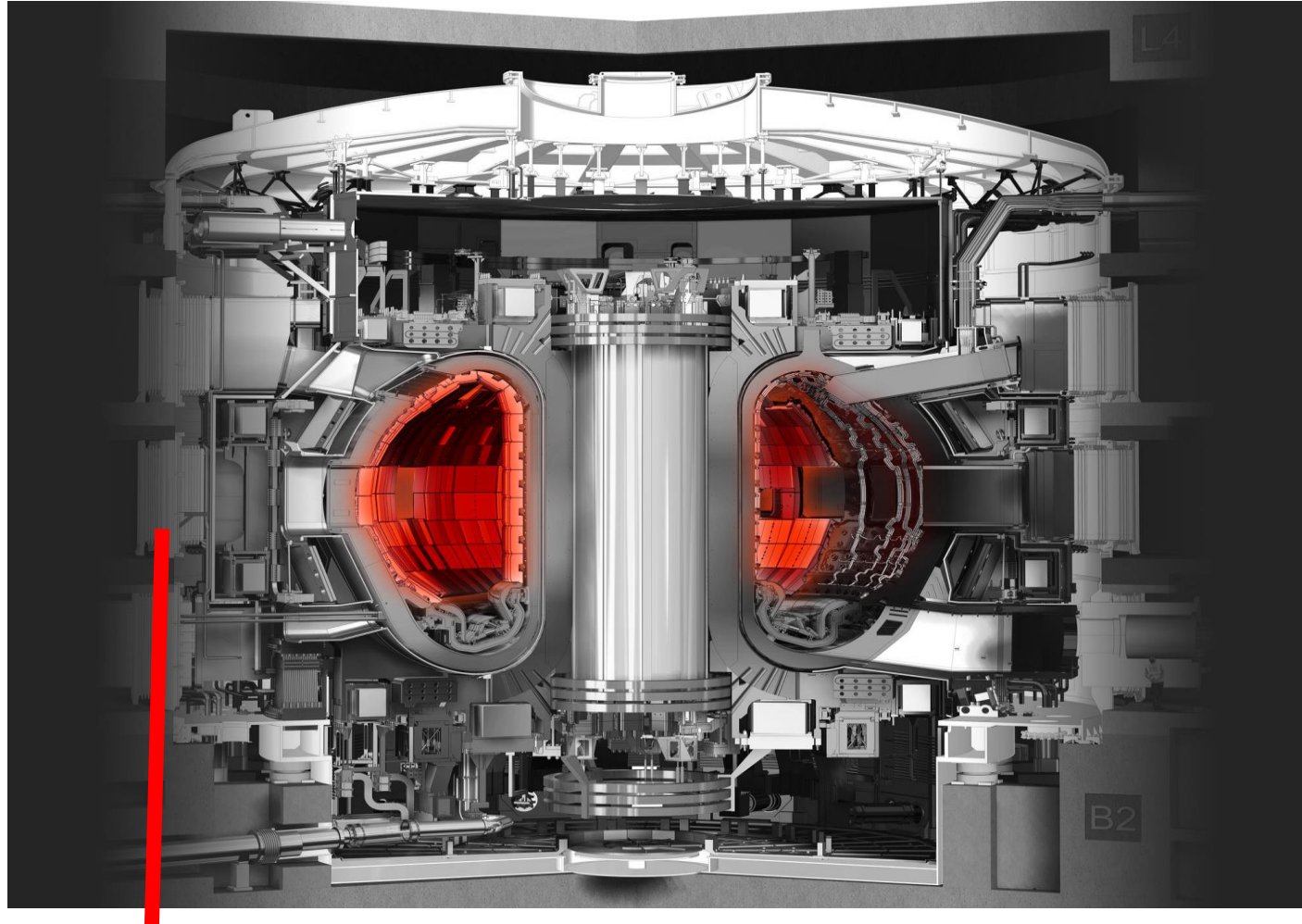
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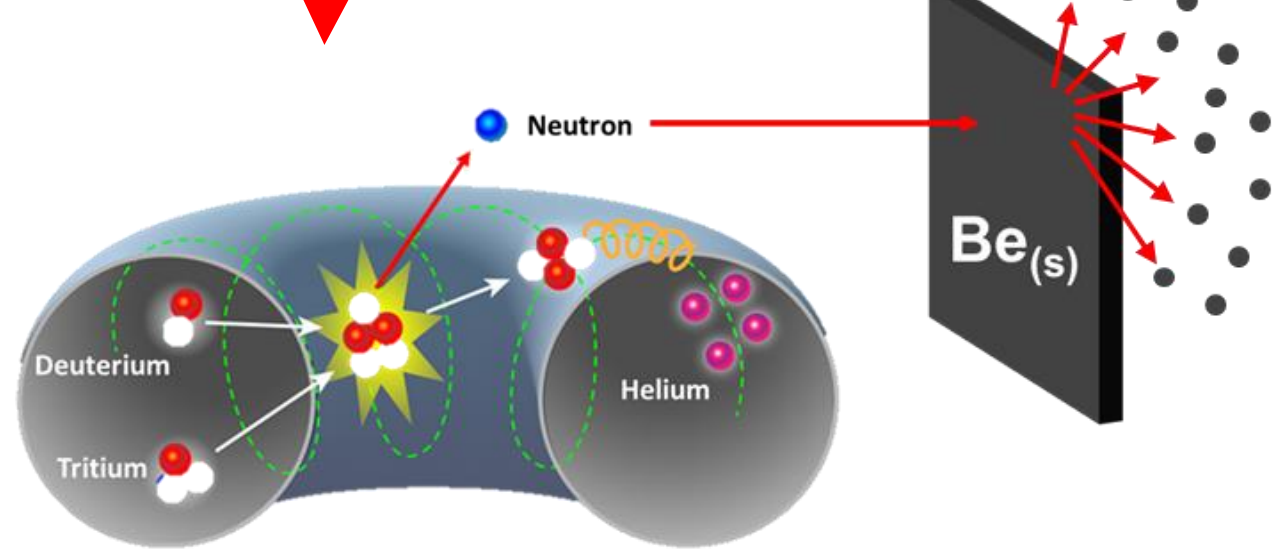
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Origin of the waste



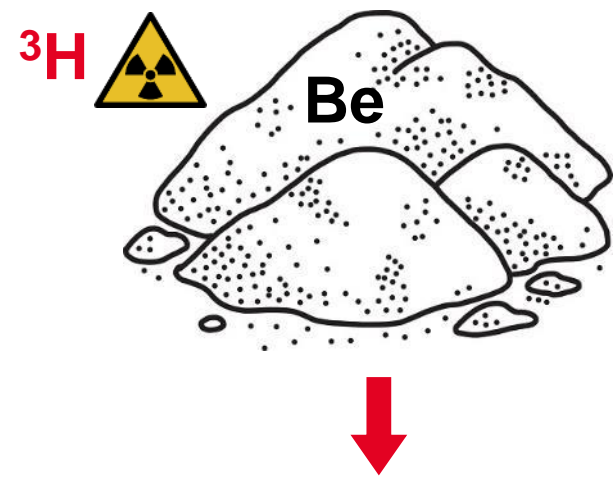
Beryllium in fusion power plants :

- ↳ Tritium contamination due to plasma exposure
- ↳ Blankets are eroded to dust by high-energy neutrons impact
- ↳ Low or intermediate level radioactive waste



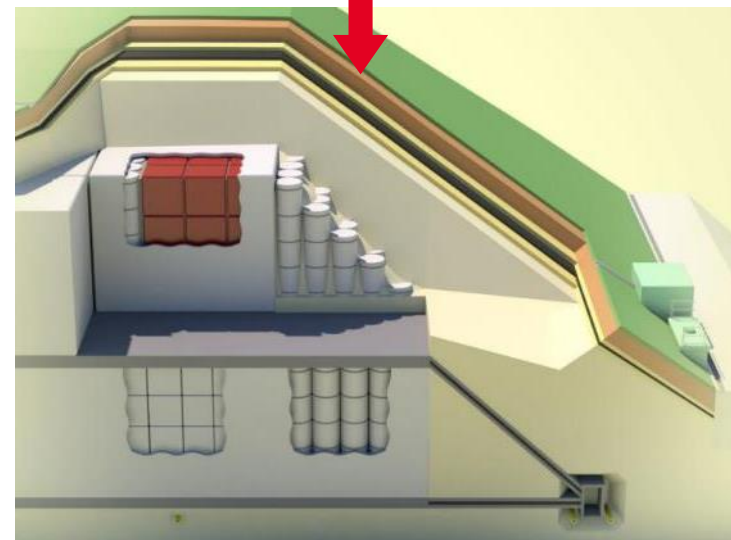
Background

Waste management

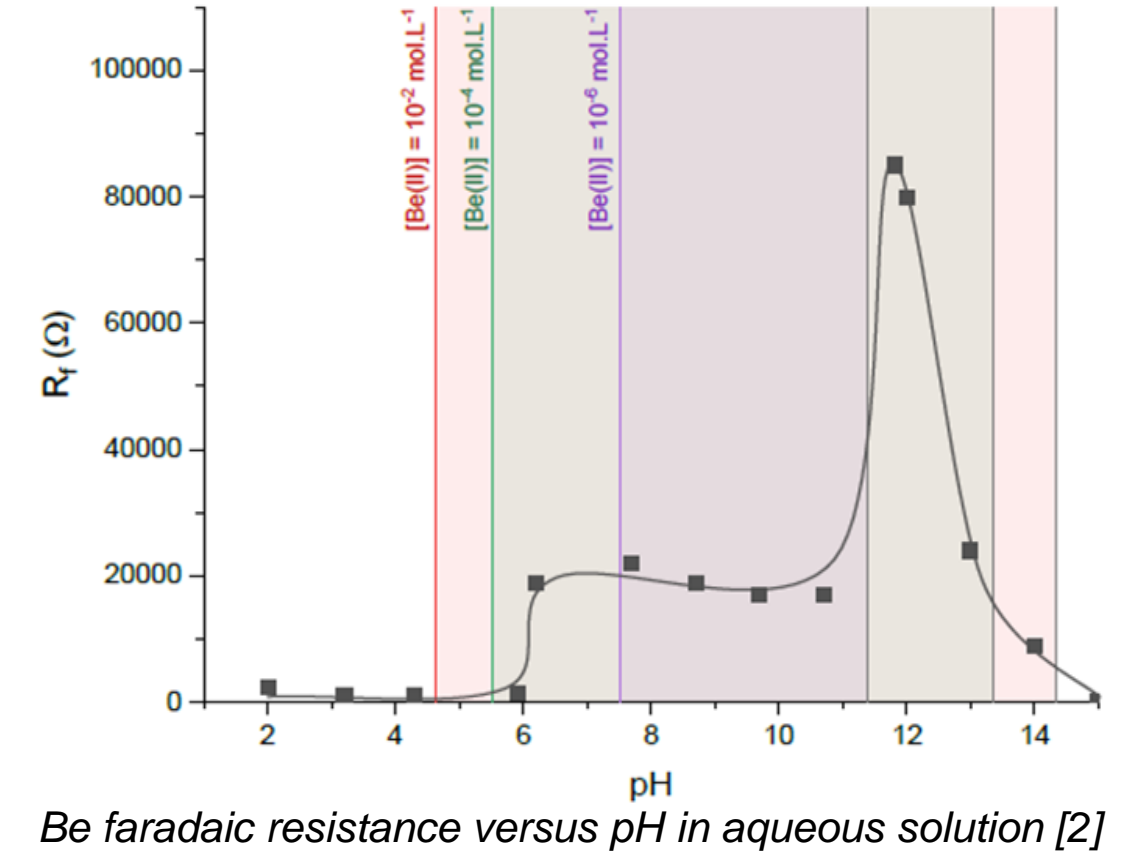
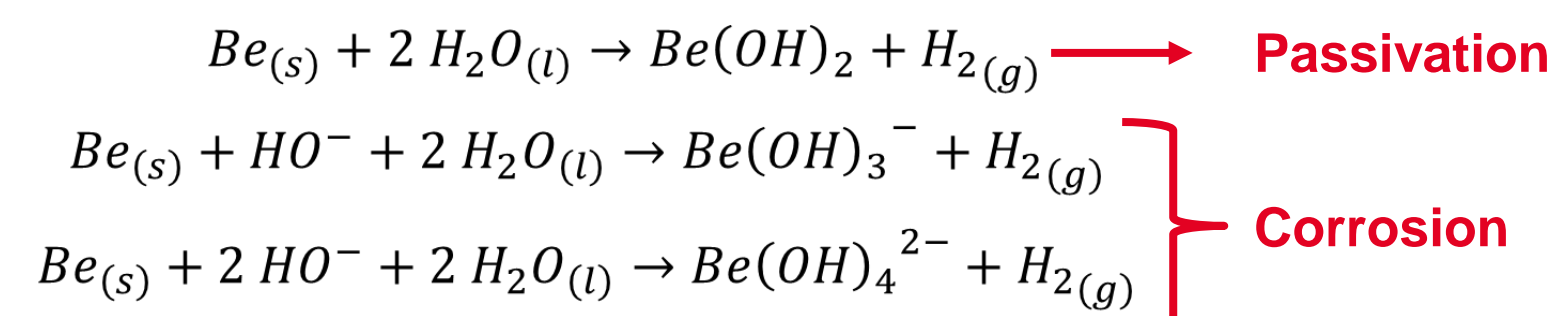
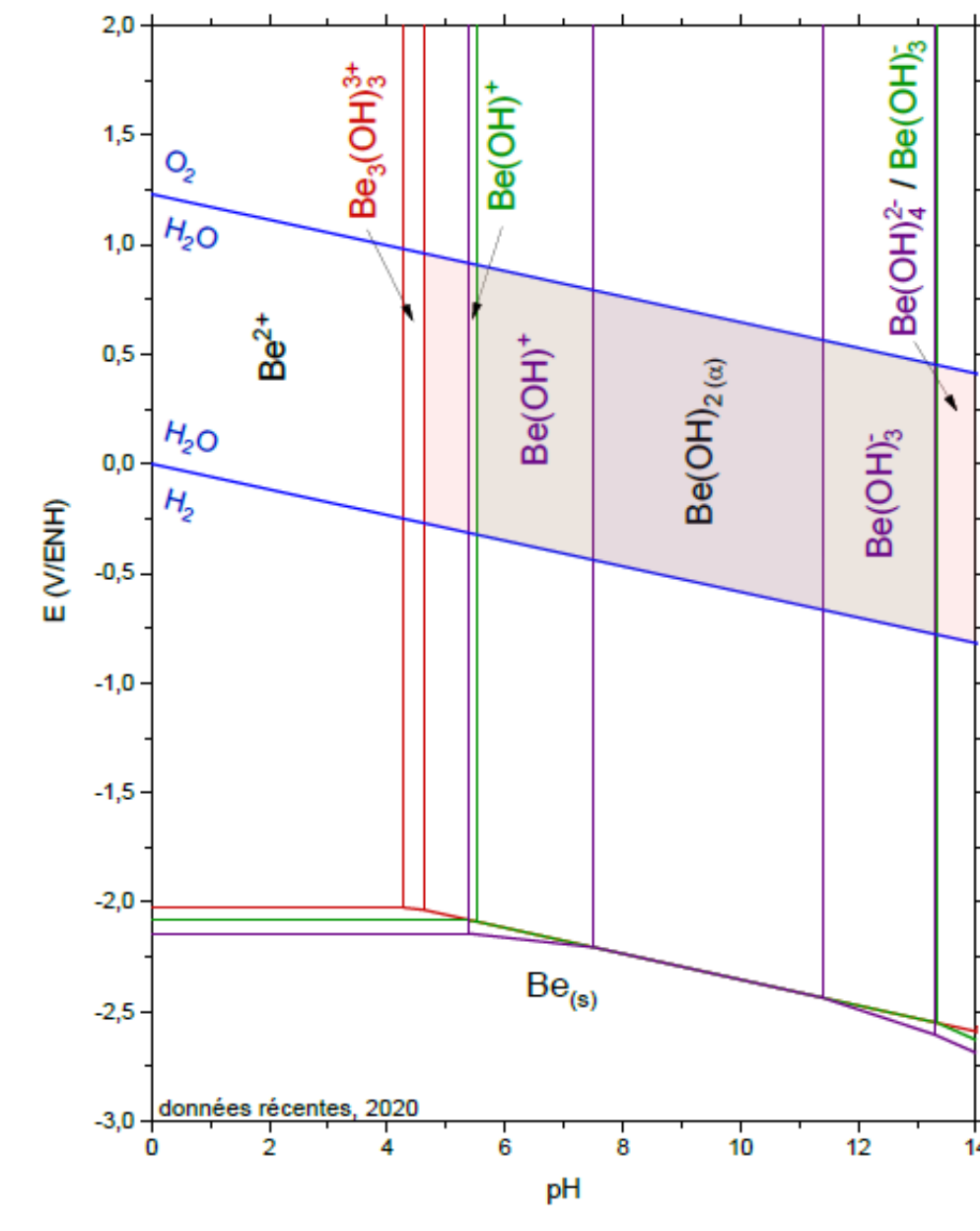


Waste

Conditioning in cement matrix



Cement/waste interactions



- ✓ Passivation at $8 < \text{pH} < 12$ due to $\text{Be}(\text{OH})_2$ precipitation
- ✓ Higher corrosion resistance at $\text{pH} 12$ [2]

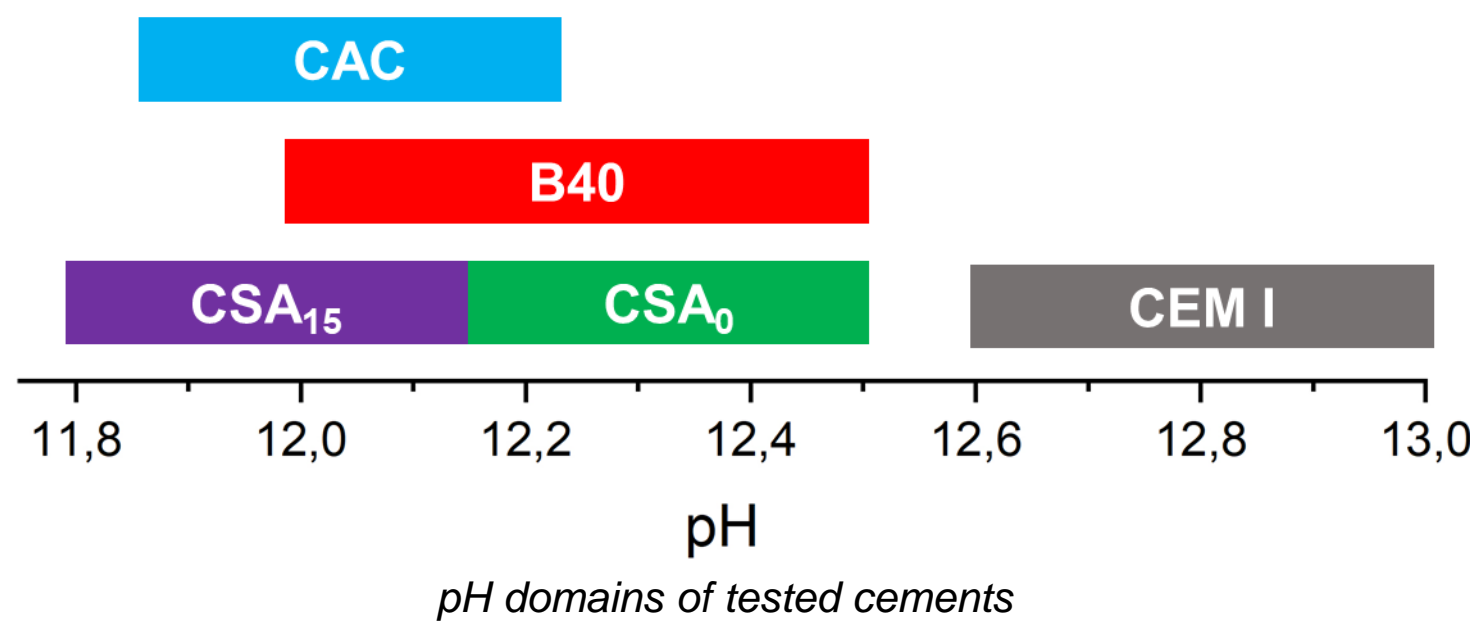
- ⚠ Explosion and fire hazard at repositories
- ⚠ Possible damage on cement matrix (pressure build-up, expansive corrosion products)
- ⚠ Highly reactive waste due to its high surface area

Experimental approach

Materials

Tested cements

- CEM I : Portland cement CEM I 52,5 N CE PM-ES-CP2 NF
- B40 : 60% CEM I + 40% silica fume (Condensil 595 DM)
- CAC : Calcium Aluminate Cement (Fondu)
- CSA₀ : 100% Sulfo-aluminate cement Alpenat CK (55% ye'elimite, 30% belite)
- CSA₁₅ : 85% Sulfo-aluminate cement Alpenat CK, 15% anhydrite



1. Monitoring corrosion in cement suspensions

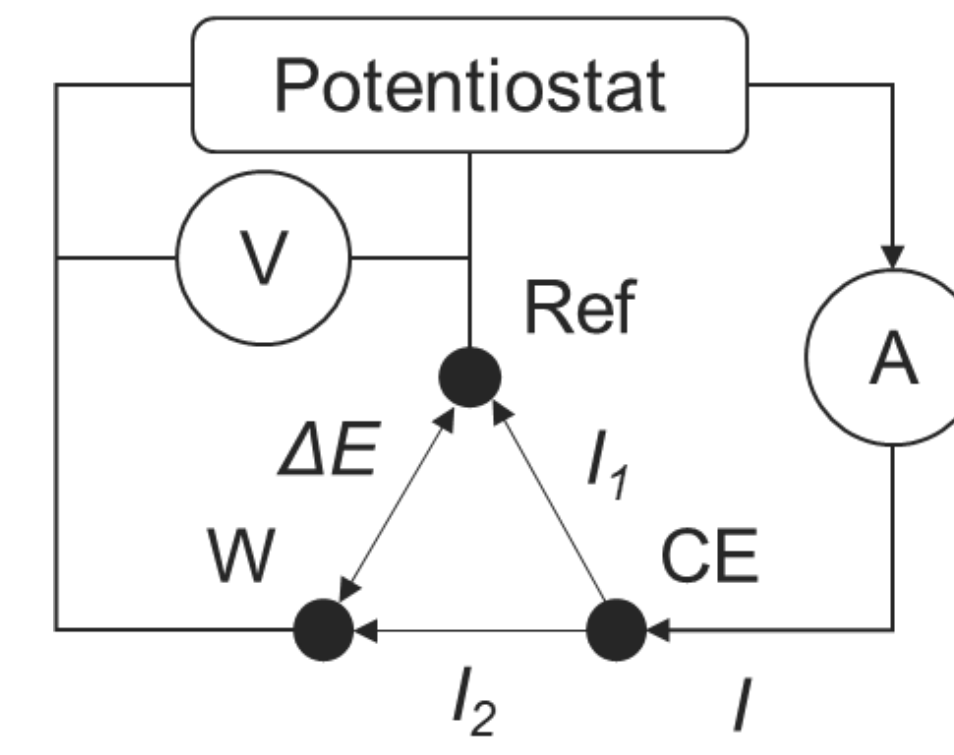
- Goal : select the best binder to limit Be corrosion
- pH fixed by the buffering effect of cement hydrates
- No limitation of corrosion by lack of water
- Preparation of suspensions :
 - Grinding and sieving ($d \leq 2 \text{ mm}$) of hydrated pastes (>28 days)
 - L/S = 5

2. EIS measurements in selected cement pastes

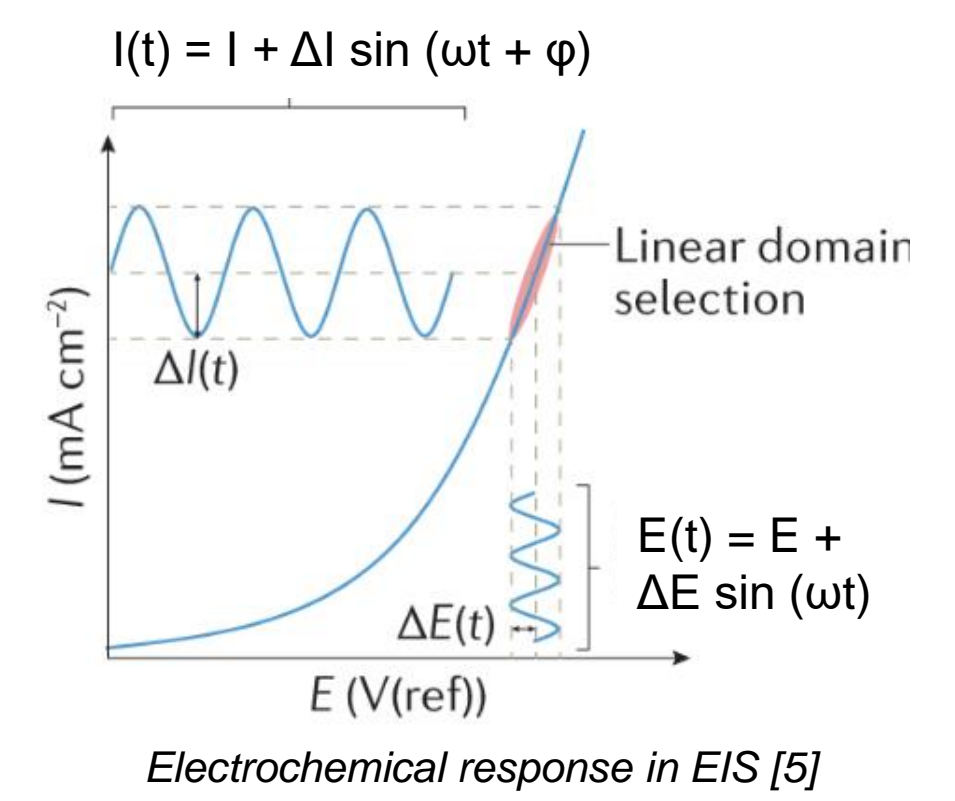
- Assess the duration of transitory period before cement chemistry can ensure beryllium passivation
- Determine the corrosion kinetics at early and later ages and associated hydrogen outgassing

Electrochemical methods

- ↳ Voltammetry
- ↳ OCP (Open Circuit Potential)
- ↳ Electrochemical Impedance Spectroscopy (EIS) at OCP



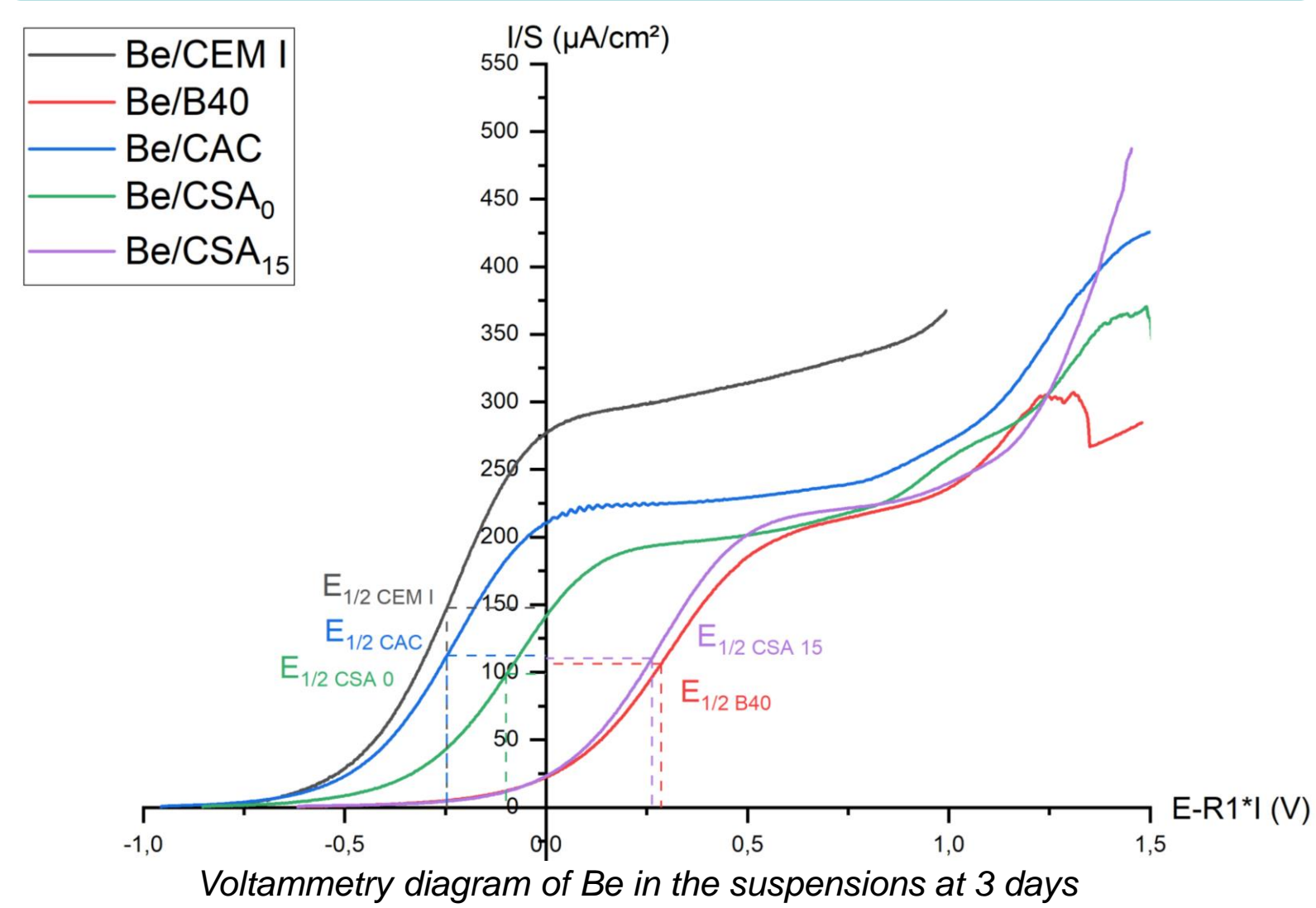
- Ref : reference electrode
- CE : counter-electrode
- W : beryllium working electrode



- Calculating the impedance : $Z = \frac{\Delta E}{\Delta I}$
- Plotting of impedance spectra :
 - Nyquist : Z_{imag} vs Z_{real}
 - Bode : $|Z|$ vs freq / ϕ vs freq

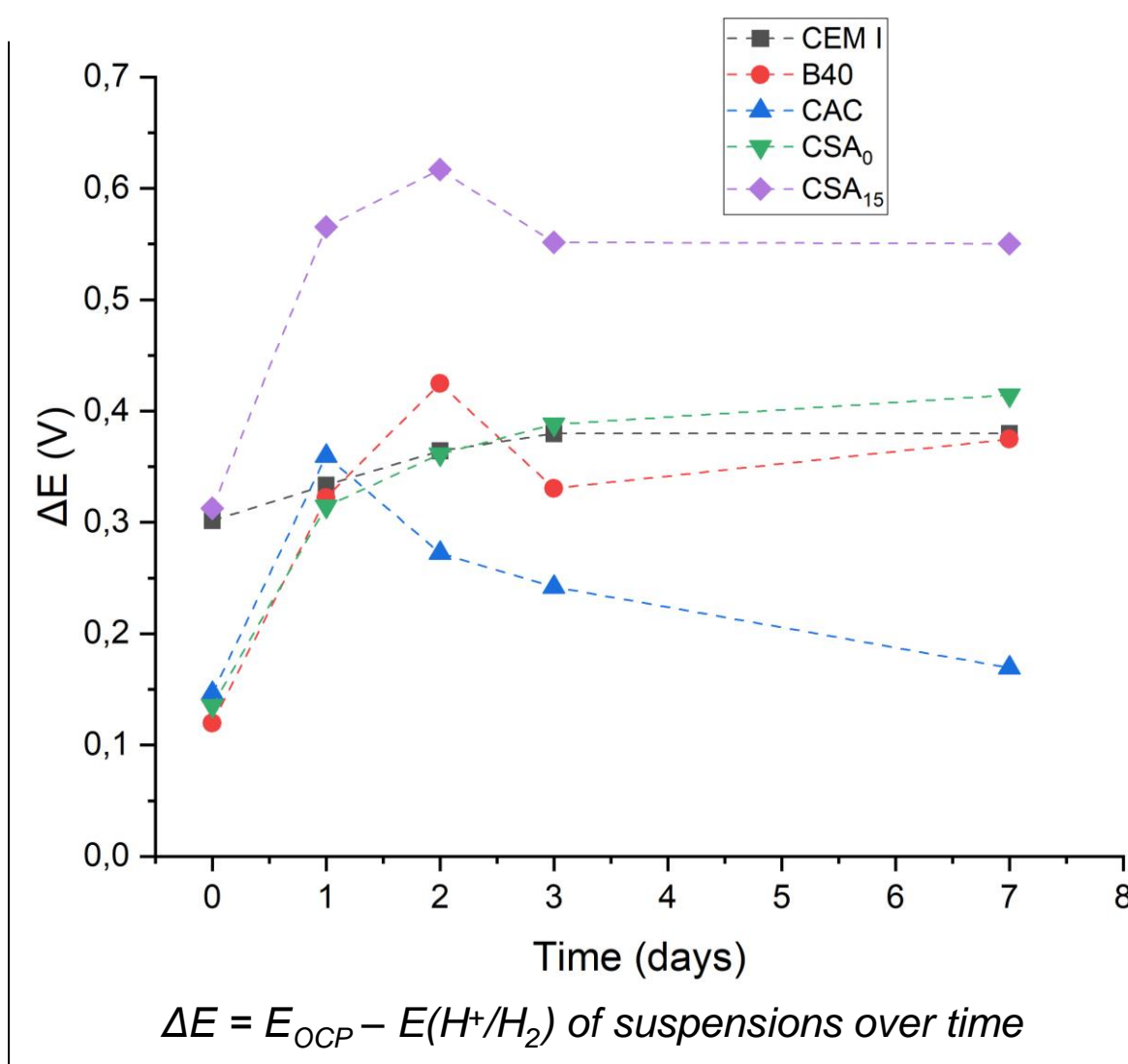
Beryllium in cement suspension

Voltammetry



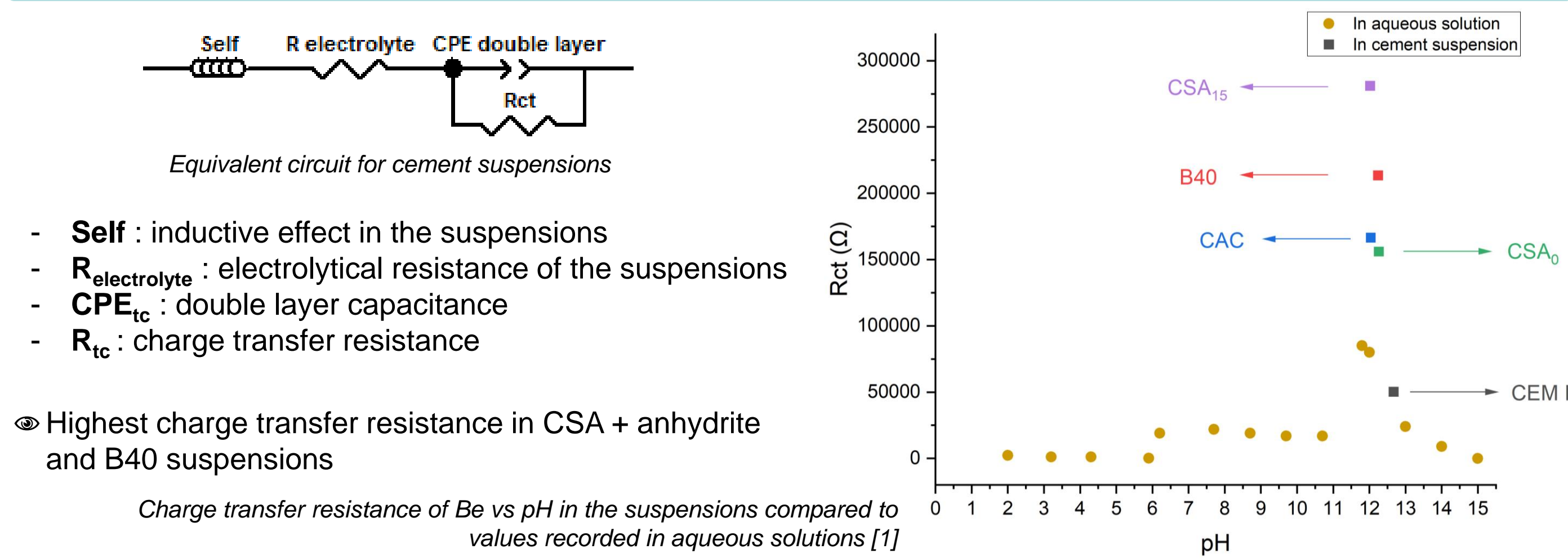
- ⊕ Occurrence of diffusion plateaus on the sigmoidal steady-state voltammetry diagram indicating Be is passivated
- ⊕ Be is better passivated in CSA₁₅ and B40 suspensions
 - Higher E_{1/2} value for CSA + anhydrite and B40 suspensions
 - Plateaus at lower corrosion currents

OCP



- ⊕ Higher value of ΔE in CSA + anhydrite suspensions
 - Be is less reactive in CSA₁₅ suspension

EIS

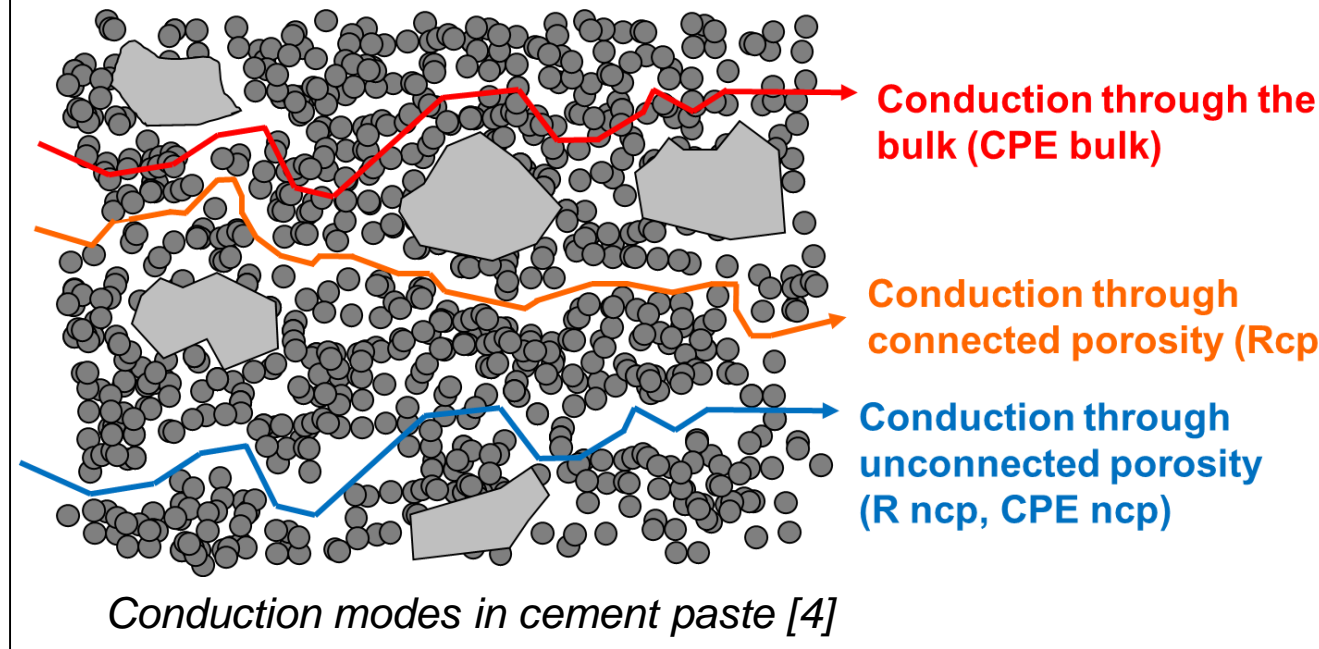


- Self : inductive effect in the suspensions
- R_{electrolyte} : electrolytical resistance of the suspensions
- CPE_{ic} : double layer capacitance
- R_{ic} : charge transfer resistance
- ⊕ Highest charge transfer resistance in CSA + anhydrite and B40 suspensions

↳ CSA₁₅ and B40 selected for measurements in cement paste

Beryllium in cement pastes

In the cement matrix (ionic/electronic conduction)

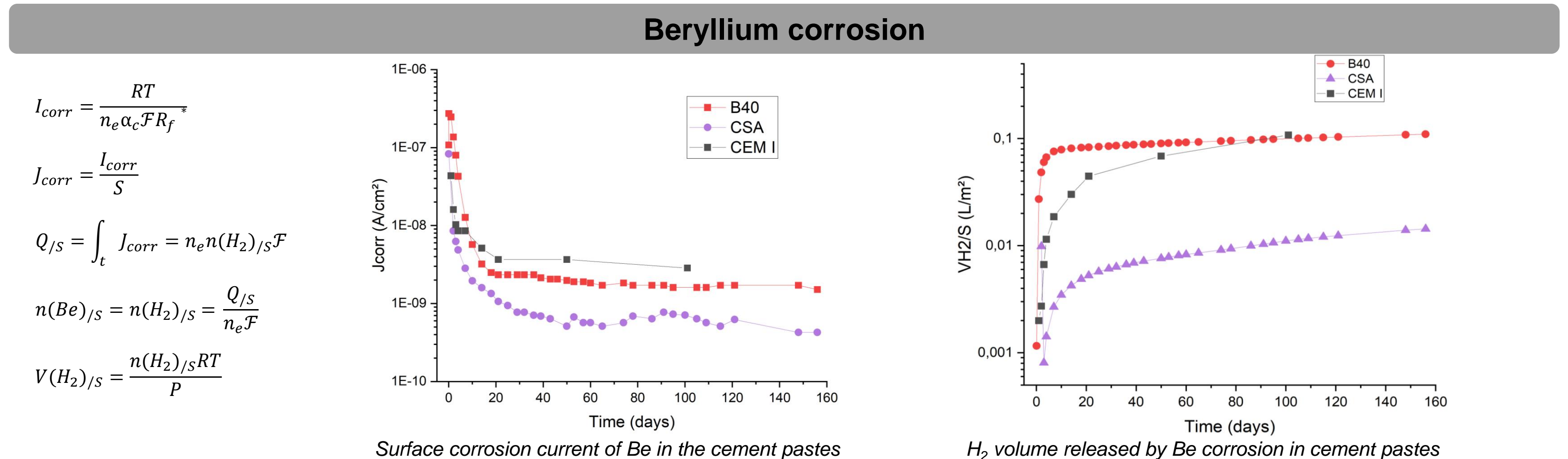
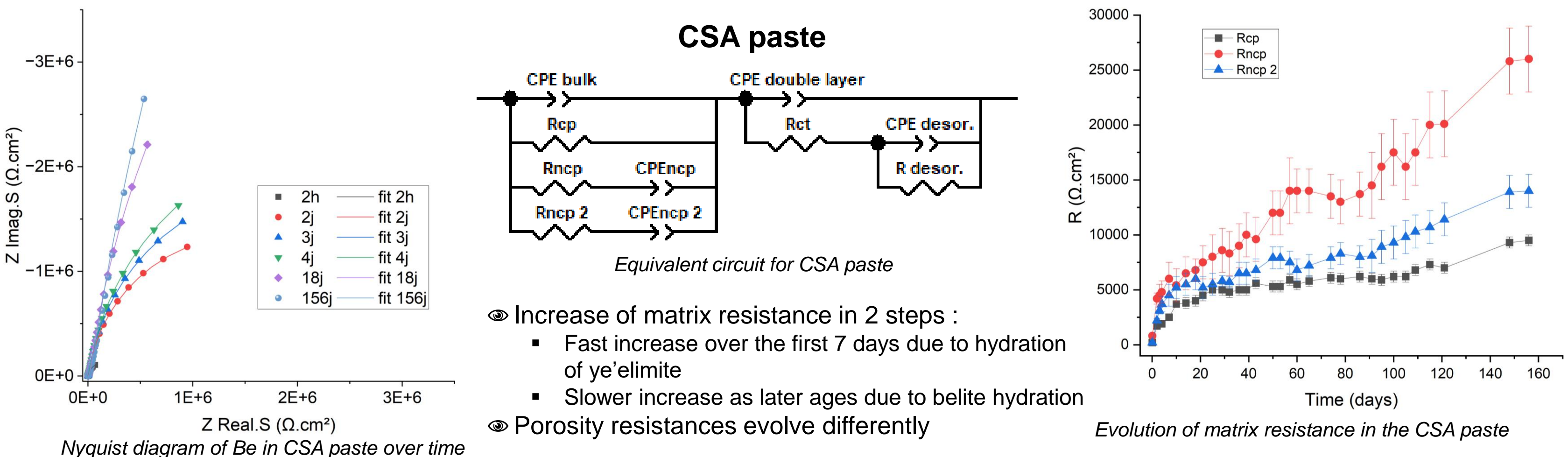
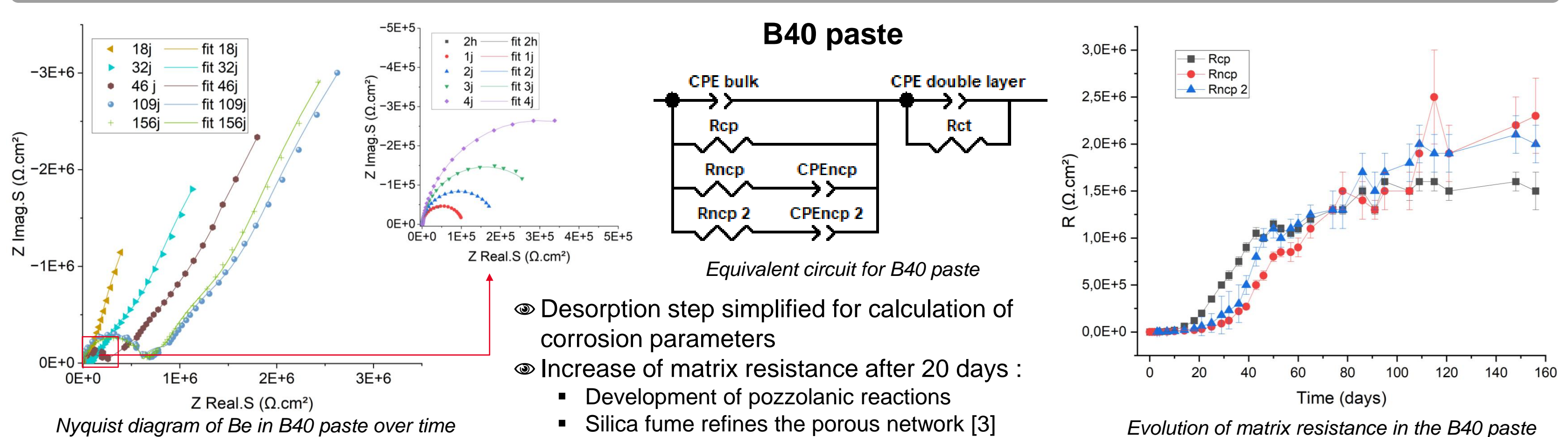


- ↳ SIE provides information both on the cement matrix and Be corrosion
- At the metal/matrix interface

Postulated corrosion mechanism :

- Beryllium oxidation into Be²⁺ : $\text{Be}_{(s)} \rightarrow \text{Be}^{2+}_{(\text{aq})} + 2e^-$
- Water reduction : $2 \text{H}_2\text{O}_{(l)} + 2e^- \rightarrow \text{H}_2_{(g)} + 2 \text{HO}^-_{(\text{aq})}$
- Desorption (renewal of electro-active sites) : $\text{Be}^{2+}_{(\text{aq})} \text{el} \rightarrow \text{Be}^{2+}_{(\text{aq})} \text{sol}$
- Precipitation of Be(OH)₂ : $\text{Be}^{2+}_{(\text{aq})} + 2 \text{HO}^-_{(\text{aq})} \rightarrow \text{Be}(\text{OH})_2$

Matrix evolution



Conclusion and outlooks

- ✓ Optimizing the cement composition enables to mitigate beryllium corrosion
- ✓ Reduction of the corrosion rate by a factor ~ 10 in a CSA cement paste as compared to CEM I
- ✓ Interest of B40 paste for long-term corrosion : pozzolanic reactions reduces the pH and refines the pore network

- ↳ Measurement of H₂ outgassing by gas chromatography to confirm EIS calculations
- ↳ Influence of porosity resaturation on beryllium corrosion

Mentioned references

- [1] N. Çevirm-Papaioannou et al., Applied Geochemistry 123 (2020) 104775
- [2] P. Bouhier, PhD report, Paris-Saclay University (2022)
- [3] B. J. Christensen et al., Journal of the American Ceramic Society 75[4], 939-45 (1992)
- [4] G.-L. Song, Cement and Concrete Research 30 (2000) 1723-1730
- [5] Wang, S. et al., Electrochemical impedance spectroscopy. Nat Rev Methods Primers 1, 41 (2021).

- ↳ Be corrosion current in CSA reduced by a factor ~ 10 compared to Portland cement [1]
- ↳ B40 enables to reduce slightly long-term corrosion