DE LA RECHERCHE À L'INDUSTRIE

Projet CEDAL

Développement d'une matrice à base de ciment phospho-magnésien pour le conditionnement de l'aluminium métallique

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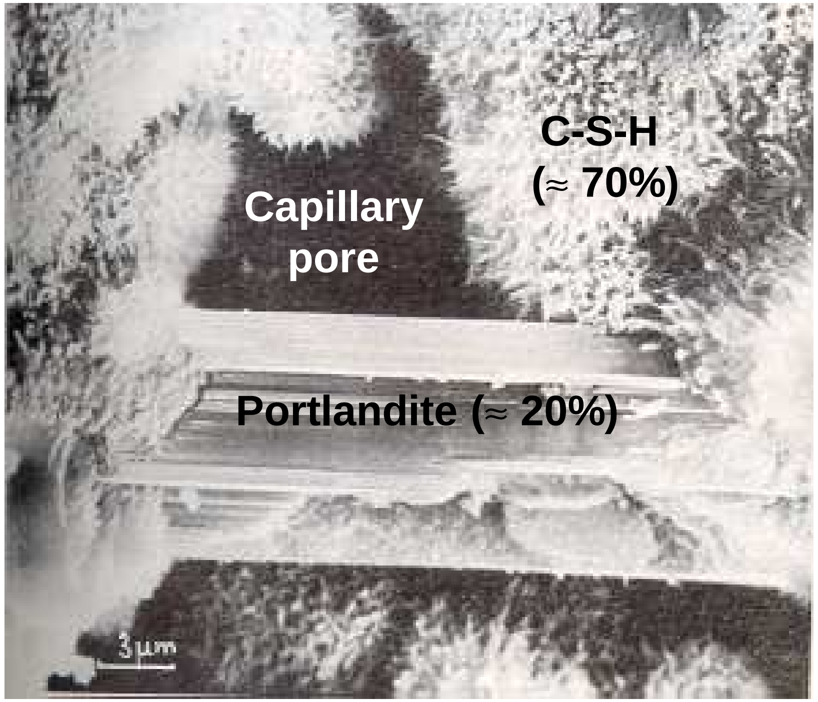
1. Introduction: hardened paste of Portland cement

- **Portland cement paste = porous, hydrates and alkaline medium**



+ Hydrated aluminates (≈10%)

Alkaline pore water

Concentrations in mg/kg of extracted solution

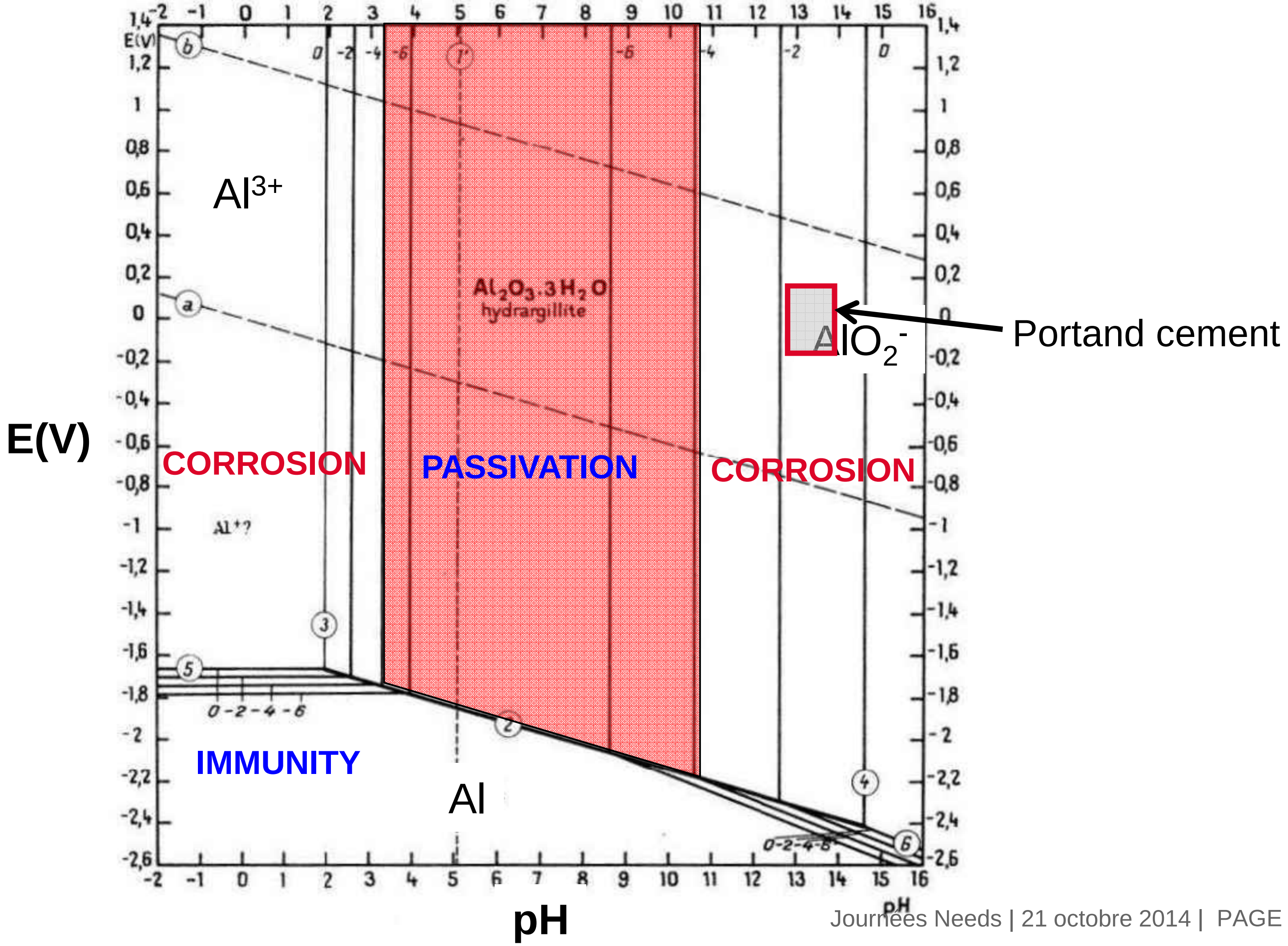
SiO_2	SO_3	Na_2O	K_2O	pH
22	844	4430	26100	13.6

OPC paste (clinker 95.5% - gypsum 4.5%) - W/C 0.5 - curing at 20°C in air-tight bag for 13 months *(Longuet, 1973)*

1. Introduction: redox properties of aluminium

$2\,Al + 6\,H^+ \rightarrow 2\,Al^{3+} + 3\,H_2$

$2\,Al + 2\,OH^- + 2\,H_2O \rightarrow 2\,AlO_2^- + 3\,H_2$



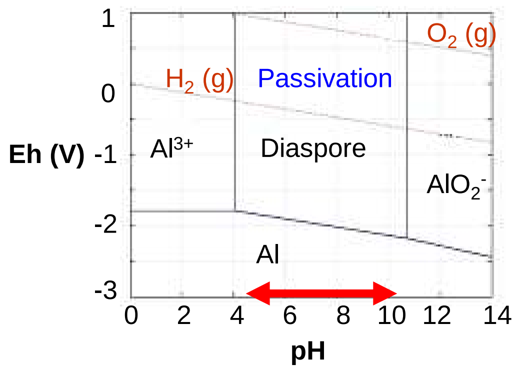
1. Introduction: ANDRA specifications

- **Specifications for low- and intermediate-level and short lived radioactive waste (CSFMA waste disposal facility)**

	Maximum surface area of Al per 330L-canister
Al directly embedded in cement	0.1 m^2
Al in a canister to be compacted	0.5 m^2
Al isolated from cement by a material like vinyl	1 m^2

1. Introduction: which strategy for Al encapsulation?

2 complementary approaches



Aluminium (1E-4 mol/L)

❶ Use of alternative cements, yielding pore solutions with a pH close to neutrality

❷ Addition of corrosion inhibitors

1. Outline

➊ **Literature survey : search for alternative binders to calcium silicate cements**

➋ **Experimental screening of binders**

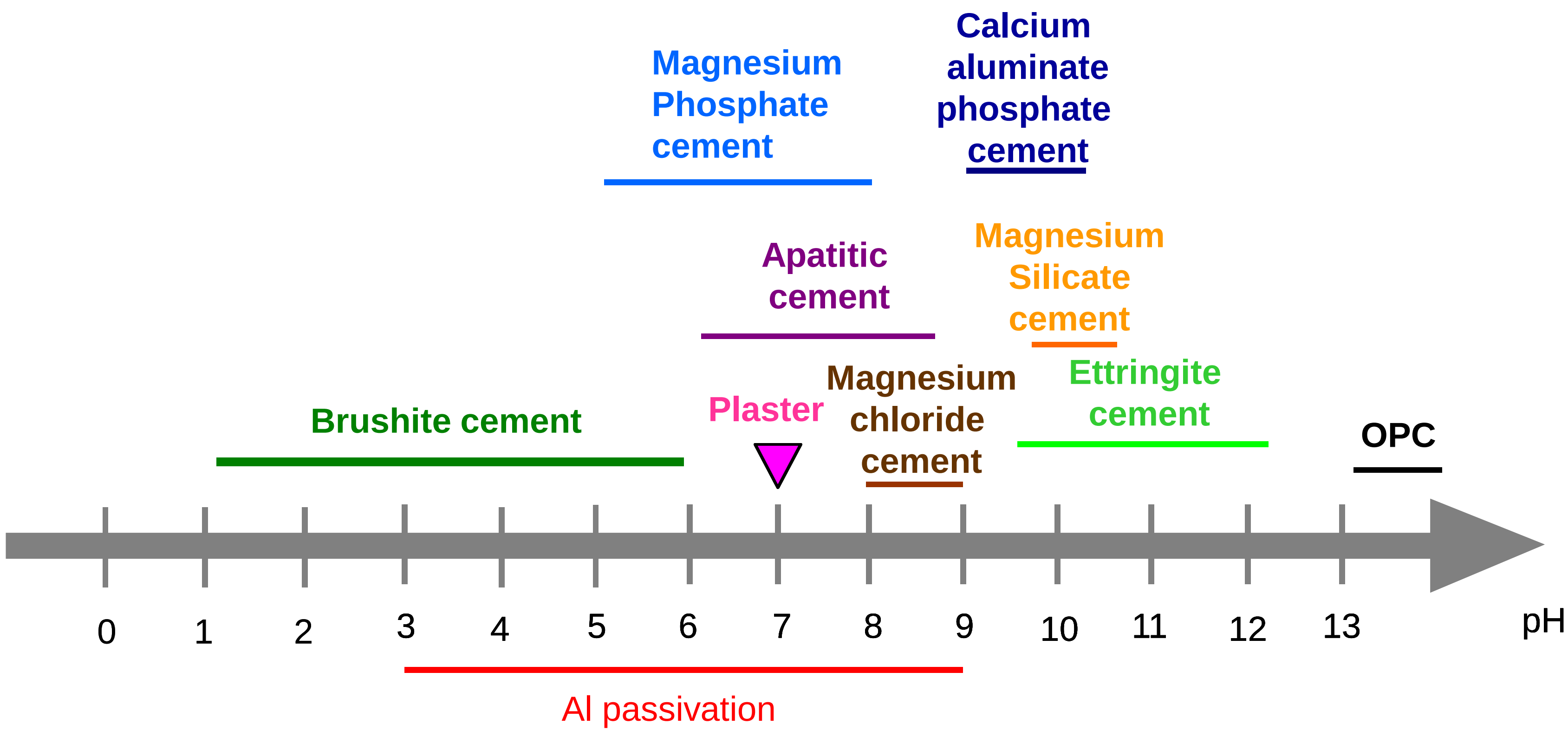
➌ **Factors controlling the cement reactivity**

➍ **Processes responsible for setting and hardening**

➎ **Electrochemical behavior of metallic aluminum in a magnesium phosphate binder**

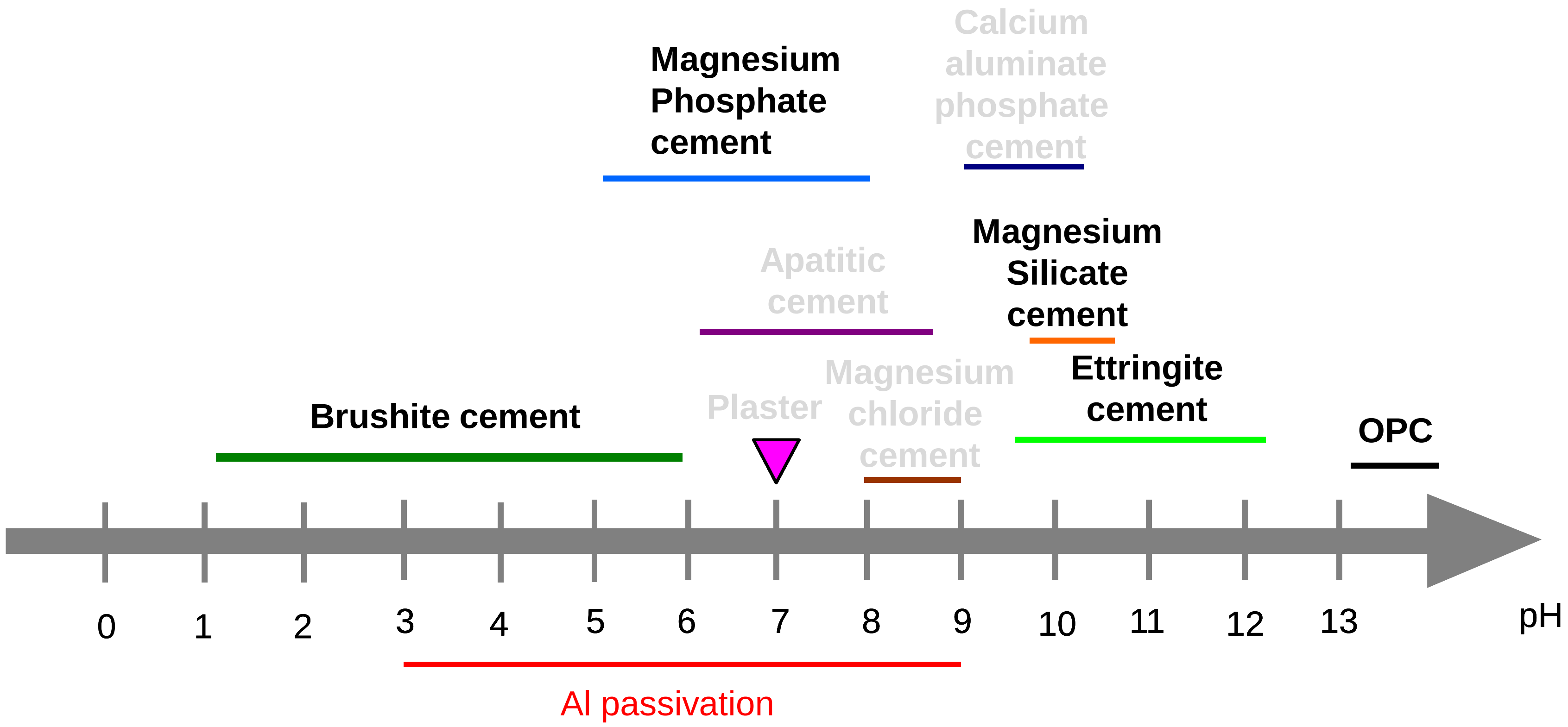
2. Literature survey : search for alternative binders to calcium silicate cements

- **Comparison of pore solution pH generated by different cement systems**



2. Literature survey : conclusion

- **Selection of binders for an experimental study**



- **Experimental study to measure under identical conditions the hydrogen release due to corrosion of an aluminum rod embedded in the selected cement pastes**

3. Experimental screening of binders

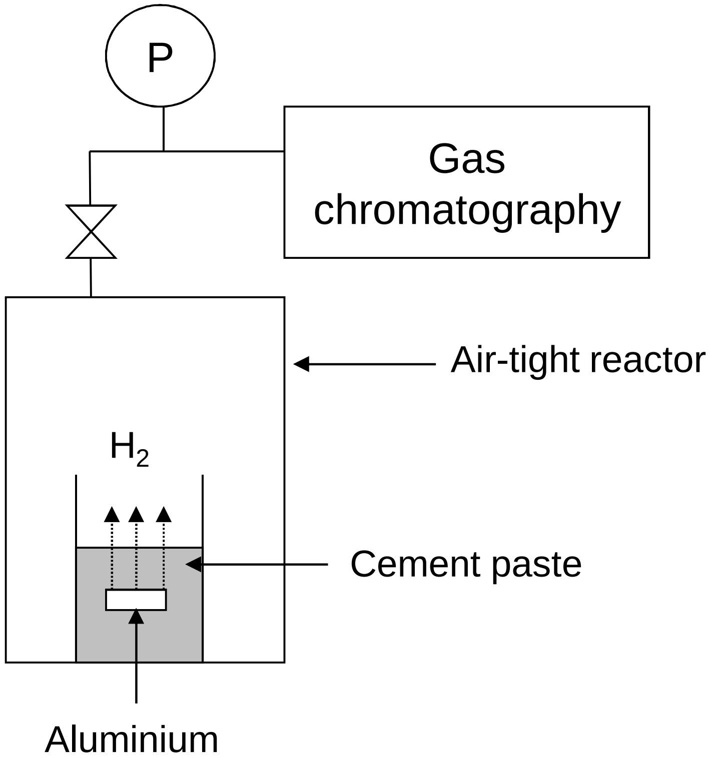
Simulated waste

Aluminum rod (99.99% Al) (ϕ = 1 cm, h = 3 cm)
Depassivated by immersion in H_2SO_4 (20%) and rinsed with demineralized water just before the experiment

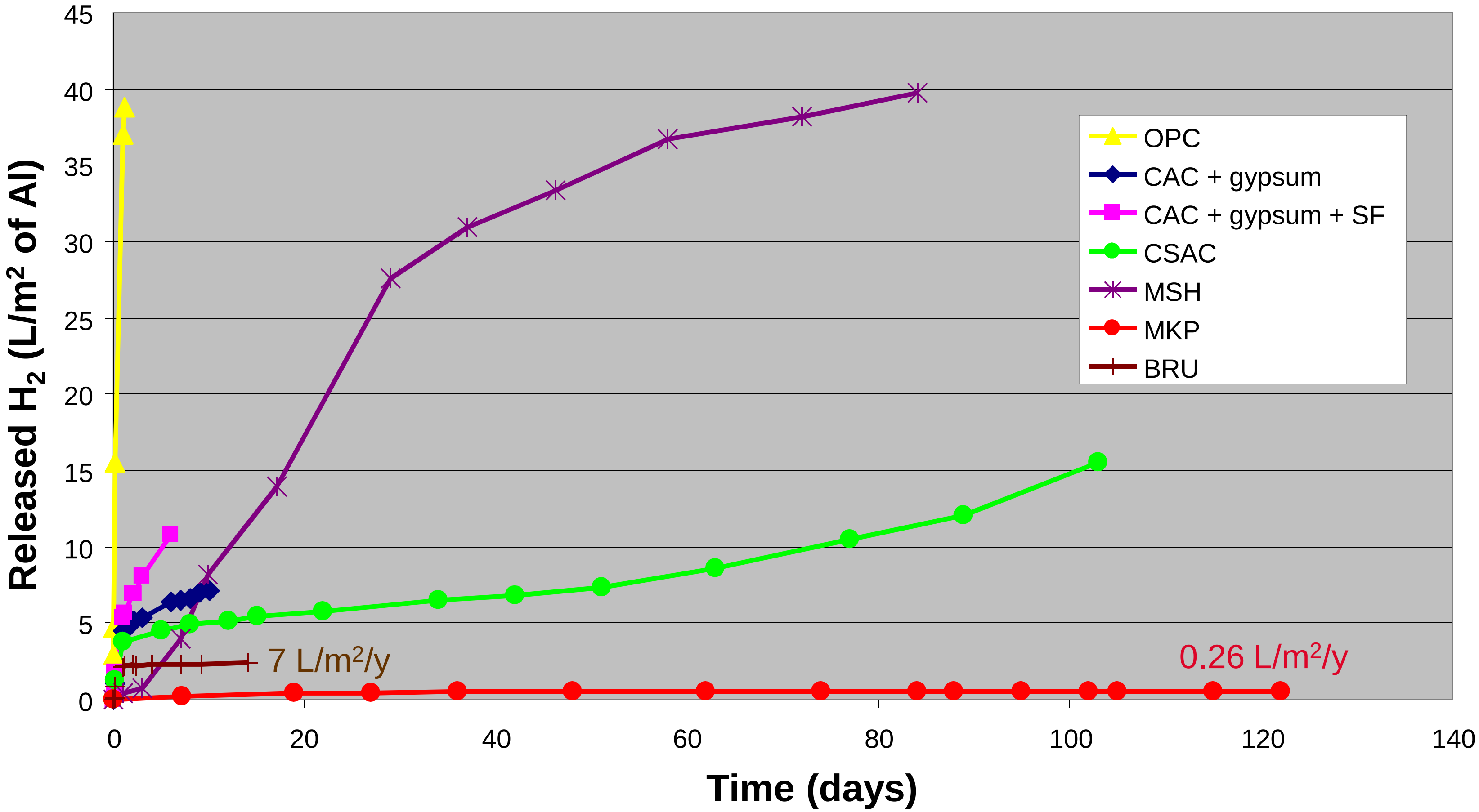
Investigated binders

Binder	Reference and producer	W/C ratio (g/g)	Reference
Portland cement	CEM I 52.5 PM ES CP2 (Lafarge Le Teil)	0.4	OPC
Calcium aluminate cement + gypsum (67 :33 g/g)	Fondu (Kerneos)	0.48	CAC + gypsum
Calcium aluminate cement + gypsum + silica fume(60 :30:10 g/g)	Fondu (Kerneos) SF S95DM (Condensil)	0.60	CAC + gypsum + SF
Calcium sulfoaluminate cement (75% clinker, 25% gypsum)	KTS 100 (Belitex)	0.55	CSAC
Magnesium silicate binder (40% MgO, 10% $MgCO_3$, 50% SiO_2)	MgO, $MgCO_3$ (VWR) SF S95DM (Condensil)	0.35	MSH
Magnesium phosphate cement (MgO: KH_2PO_4 1:1 mol/mol)	MgO MagChem 10 CR (MAF Magnesite BV) KH_2PO_4 (VWR)	0.51	MKP
Brushite cement (wollastonite + phosphoric acid solution)	FOTIMINE (Sulitec)	0.80	BRU

- **Experimental device for H_2 measurement**



H_2 production

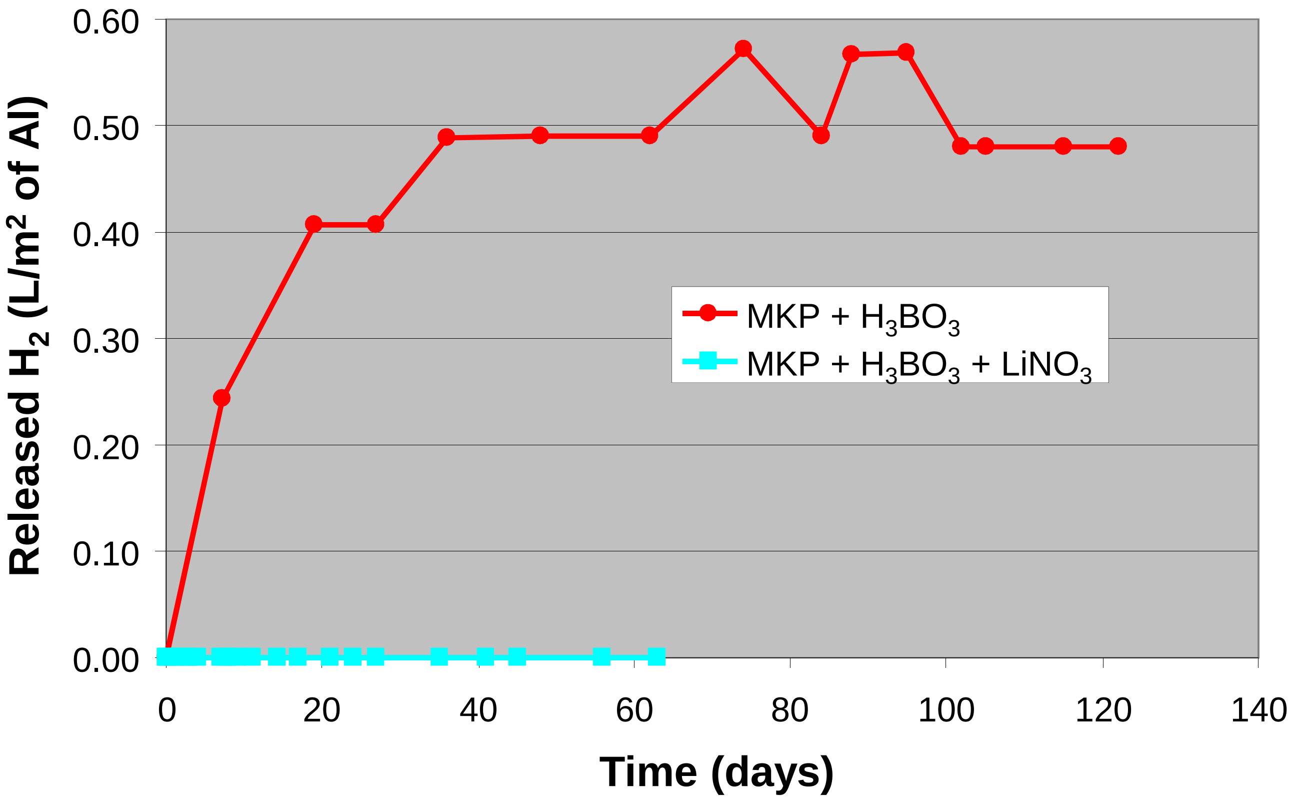


Most promising binder: magnesium phosphate binder

$MgO + KH_2PO_4 + 5\ H_2O \rightarrow MgKPO_4.6H_2O$

3. Experimental screening of binders

H_2 production



With $LiNO_3$: released H_2 < detection limit of the analytical method
Extrapolation over 1 year : $H_2 < 2.28 \times 10^{-4}$ L/(m².year)

Formation of a protective insoluble layer of $LiH(AlO_2)_2.5H_2O$ at the surface of the metal (*Matsuo et al., 1995*)

Conclusion

Selection of the **magnesium-phosphate cement** for the next step of the project

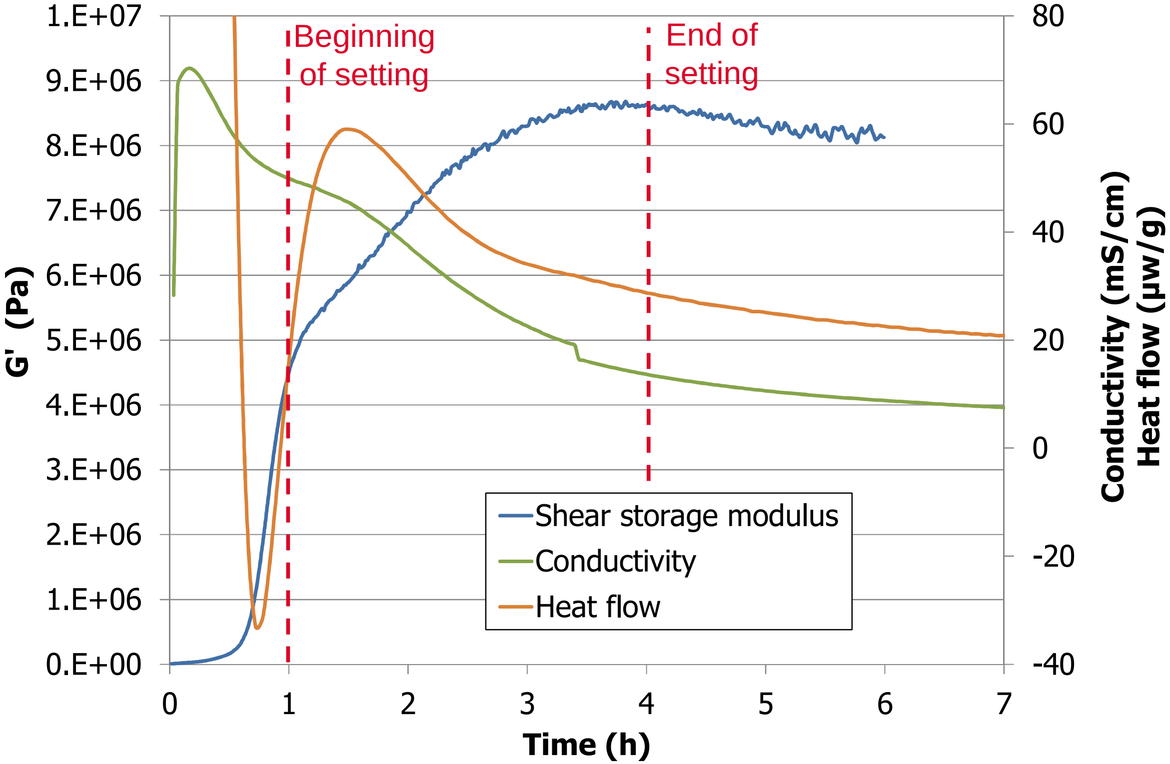
4. Control of the cement reactivity

Critical parameters for a formulation

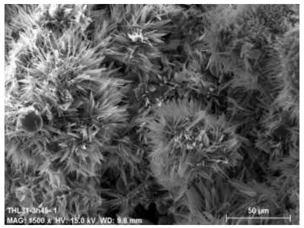
- MgO characteristics (particle size, specific surface area)
  - Hardburnt (S < 1 m^2/g)
- MgO / KH_2PO_4 ratio
  - 1
- Type and content of filler
  - Low CaO fly ash
- Type and content of sand
  - Siliceous sand
- Use of admixtures
  - H_3BO_3, $LiNO_3$

4. Processes responsible for the setting and hardening

Mechanisms of setting and hardening
System {$MgO + KH_2PO_4$ + Fly ash}



Thèse de Hugo Lahalle en cours

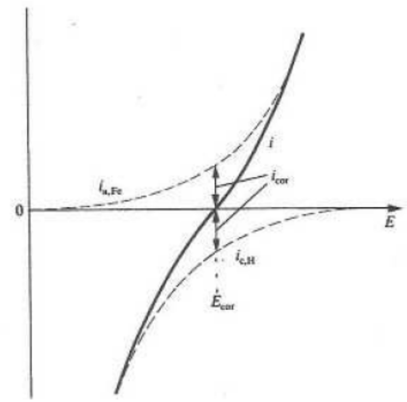


- 0 min – 5 h 30 min: KH_2PO_4
- 15 min – 26 j: K-struvite
- 15 min – 3 h 45 min: Poorly crystallized phase ($Mg_2KH(PO_4)_2(H_2O)_{15}$?)
- 3 h 45 min – 26 j: Other secondary phases ($MgHPO_4.7H_2O$, $AlPO_4.xH_2O$, ?)

5. Electrochemical behaviour of aluminium in a magnesium phosphate binder

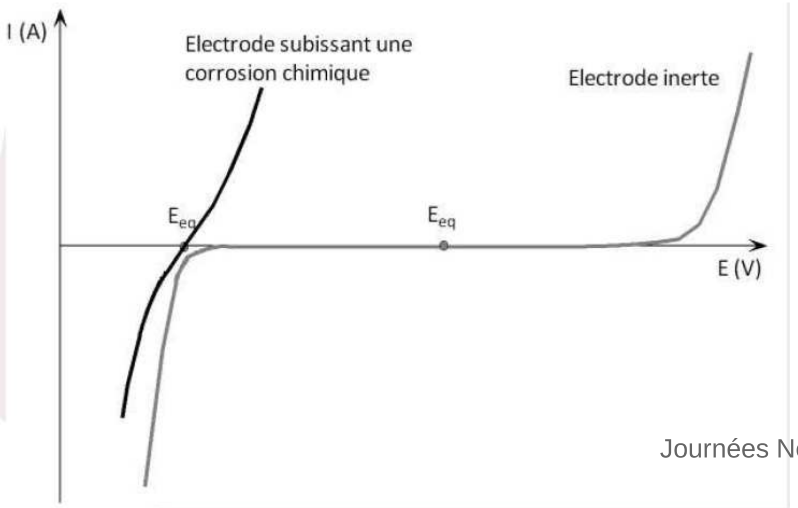
L'électrochimie pour l'étude de la corrosion in situ

Corrosion chimique :
Réaction chimique entre le métal (Al) et le milieu (H_2O)



Le courant de corrosion permet de déterminer la quantité d'aluminium oxydé et donc la quantité d'hydrogène produit.

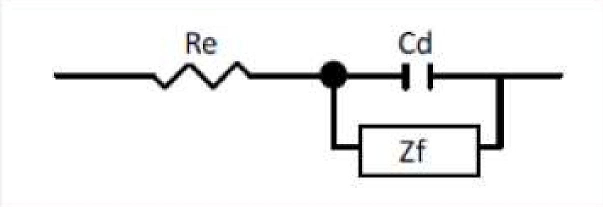
Qualitativement, la « pente » de la courbe i=f(E) est fonction du courant de corrosion et donc de la vitesse de corrosion.



La spectroscopie d'impédance pour l'étude de la corrosion chimique in situ

L'interface solution/matériau se comporte comme un circuit électrique composé d'éléments: R, C, L,...

$I = I_c + I_f$ (courant capacitif + courant faradique)



En mesurant l'impédance à $E = E_{eq}$ (conditions non destructrices et pas de corrosion forcée)

- Electrode en zone d'immunité (inerte) ou électrode recouverte d'une couche protectrice (empêchant le contact entre solution et matériau: $Z_f \rightarrow \infty$: circuit électrique Re // Cd

- Electrode qui subit une corrosion chimique: $Z_f \neq \infty$: l'impédance à une allure classique de schéma réactionnel électrochimique (résistance de transfert de charge, boucles capacitives, impédance de diffusion…)

5. Electrochemical behaviour of aluminium in a magnesium phosphate binder

Déroulement de l'étude

Influence de l'inhibiteur de corrosion $LiNO_3$

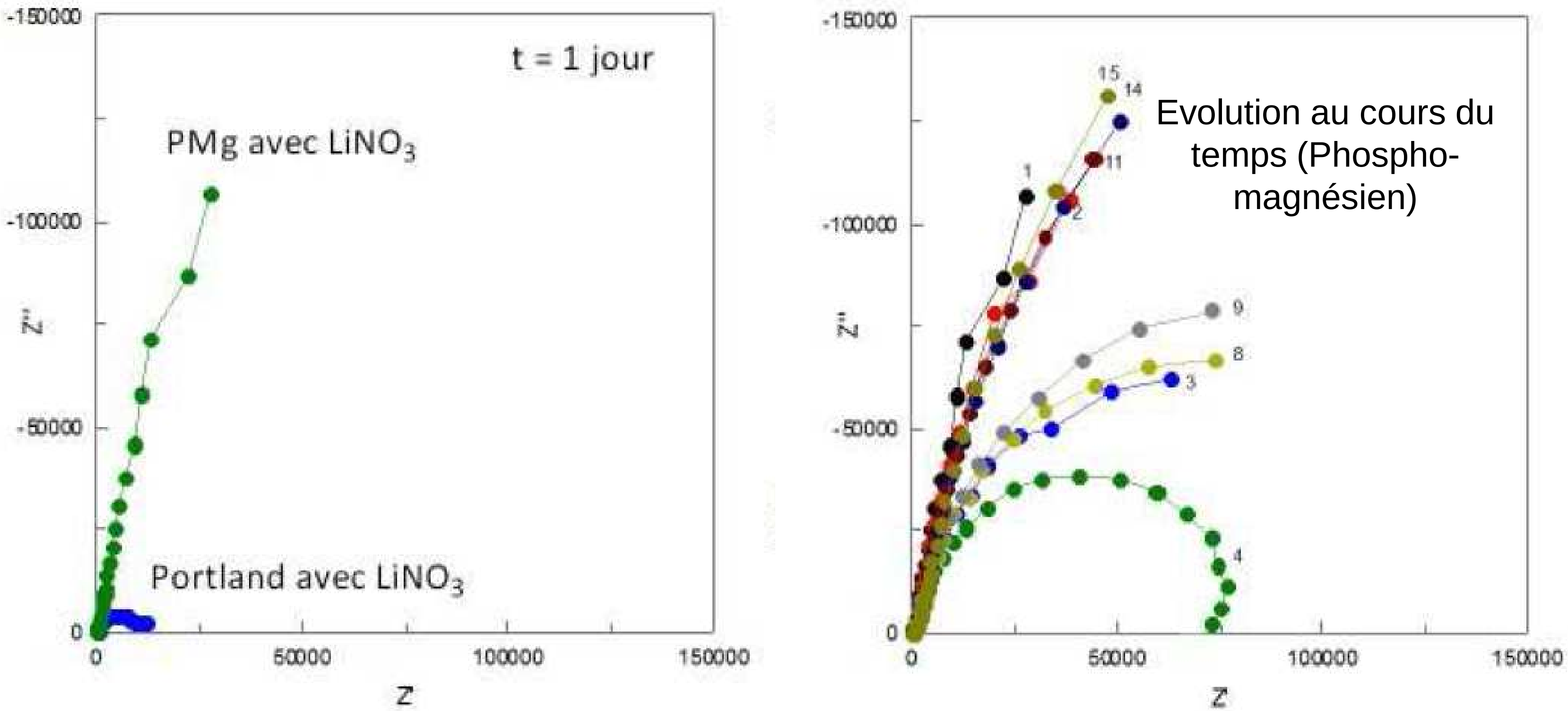
- en milieu aqueux basique (pH=13)
- dans les ciments Portland et Phosphomagnésien

Dispositifs expérimentaux

	PMg	PMg + $LiNO_3$	Portland	Portland + $LiNO_3$
Al/Pt/Pt/Pt	CV	CV	CV	CV
Al/Pt/Pt/Pt	EIS	EIS	EIS	EIS

5. Electrochemical behaviour of aluminium in a magnesium phosphate binder

Pâtes de ciment phospho-magnésien et Portland : diagrammes d'impédance



Portland avec $LiNO_3$: impédance caractéristique d'un phénomène de corrosion

Phospho-magnésien avec $LiNO_3$: diminution de l'impedance pendant les 4 premiers jours puis augmentation => Il est probable que la couche d'oxyde qui protège initialement Al soit progressivement remplacée par l'aluminate de lithium, plus stable et protecteur

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5. Conclusion

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- Magnesium phosphate cements appear to be the most promising binders (among those tested) for the encapsulation of metallic aluminium

- Corrosion of aluminium can be reduced still further by adding a corrosion inhibitor (lithium nitrate): **Brevet Français**, C.Cau dit Coumes, D.Lambertin, P.Antonucci, M.Charlot,*« Liant et son utilisation pour le conditionnement de déchets contenant de l'aluminium métallique»,* N° FR3003252A1
- Critical parameters controlling the cement reactivity :
  - type of MgO (calcination temperature, specific surface area)
  - type of filler used
  - MgO / KH_2PO_4 ratio
  - L/S ratio
  - type and amount of admixtures
- The electrochemical measurements (determination of the open circuit potential and electrochemical impedance spectroscopy) confirm that aluminum is corroded when it is encapsulated in a Portland cement paste, whereas it tends to a passive state in the magnesium phosphate binder

C. Cau Dit Coumes, D. Lambertin, H. Lahalle, P. Antonucci, C. Cannes, S. Delpech, Selection of a mineral binder with potentialities for the stabilization / solidification of aluminum metal, Journal of Nuclear Materials 453 [1-3] (2014) 31-40

5. Prospects

- Analysis of the EIS data by using judicious equivalent electrical circuits to get more information on the aluminum corrosion (mechanism, rate)

- Understanding of the influence of admixtures (H_3BO_3, $LiNO_3$) on cement hydration

- Design and characterization of an injection grout in view of blocking massive aluminum pieces

3.3 m² d'aluminium métal

- Use of the electrochemical method developed in this project to study the encapsulation of other reactive metals