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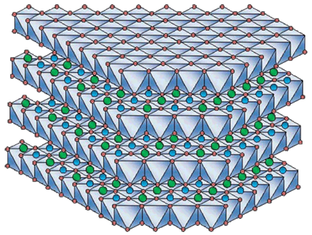
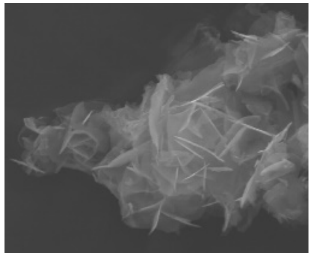
The effect of layered double hydroxides (LDH) on the corrosion resistance of reinforcement steel in concrete





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CICECO – Aveiro Institute of Materials
Universidade de Aveiro, 3810-193 Aveiro, Portugal
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Steel in concrete

Reinforced concrete is shaping buildings and landscapes all over the globe.

Jean Bouin stadium, Paris, France

In 2015:

Cement: **3.7 x 10^{12} Kg**

Concrete: **20 x 10^{12} Kg**

Concrete is the most used structural construction material in the world.

Degradation of concrete structures

- Physical damage
- Aggregate expansion
- Shrinkage
- Abrasion / erosion
- Fire / heat
- Freeze-thaw
- Chemical damage (acids, carbonation,…)
- Calcium leaching
- Bacterial attack
- Natural hazards (seismic, wind, loss of foundations, etc)
- Imposed degradations (demolitions, etc)
- **Steel rebars corrosion**.

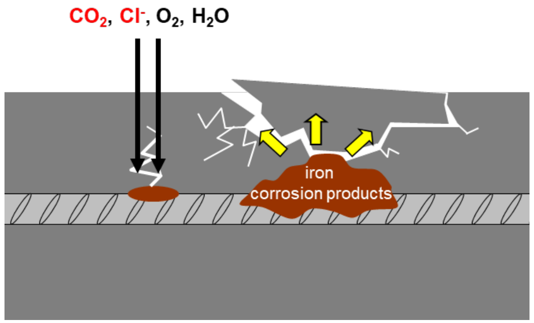
Corrosion of steel in concrete

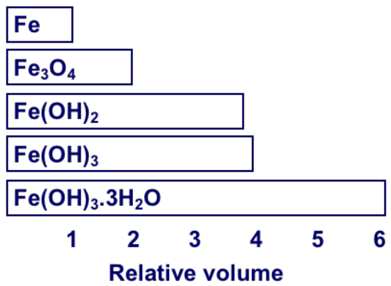
The pH of concrete varies between 12.6 and 13.5, optimal conditions for the passivation of reinforcing steel.

CO_2 ⟶ carbonation ⟶ low pH ⟶ depassivation ⟶ uniform corrosion

Cl^- ⟶ localized corrosion

The volume expansion of corrosion products causes cracking, delamination and spalling.





Corrosion of steel rebars dramatically limits the service life of reinforced concrete.

Control of steel corrosion inside concrete

- Alternative reinforcing materials (stainless steel, polymer composites,...)

- Coatings on the rebars: epoxy paint or galvanized (zinc) layer

- Cathodic protection

- Use of demineralised water and "clean" sand and aggregates

- Higher thickness of concrete cover

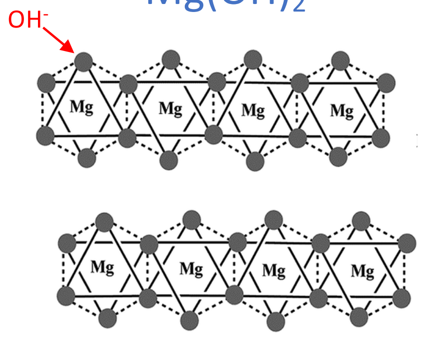
- Painting the external surface

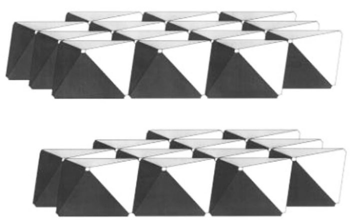
- Corrosion inhibitors →
  - calcium nitrite
  - sodium benzoate
  - chromates
  - phosphates and polyphosphates
  - silicates
  - polycarboxylic acids
  - fatty acids emulsions
  - alkanolamines

Layered double hydroxides (LDH)

Brucite

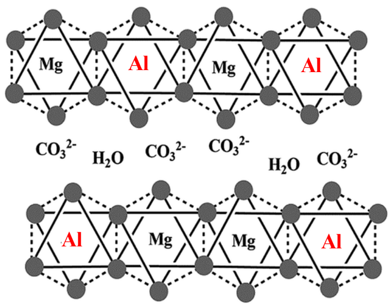
$Mg(OH)_2$

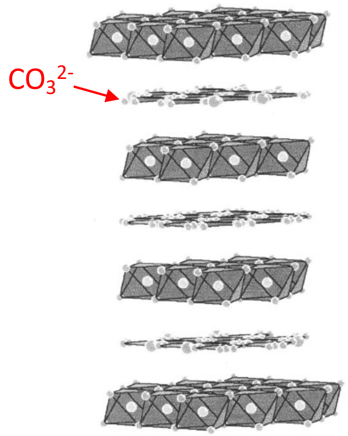




Hydrotalcite

$[Mg_6Al_2(OH)_{16}]CO_3.4H_2O$

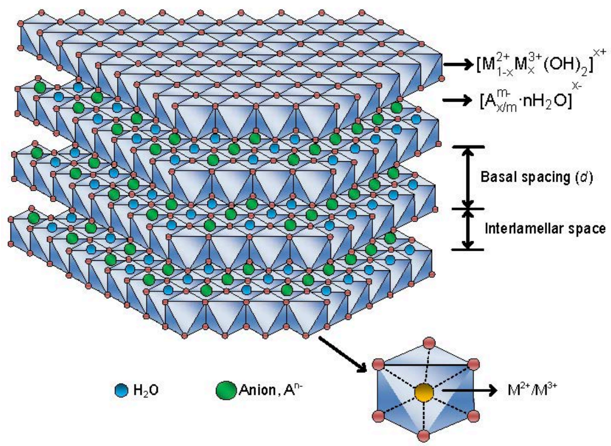




LDH

$[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^+[A^{n-}]_{x/n}.yH_2O$

$M^{2+} = Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2}+$, …
$M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}$,…
$A^{n-} = CO_3^{2-} < OH^- < Cl^- < NO_2^- < NO_3^-$



RSC Adv. 5 (2015) 98853
Proc. Indian Acad. Sci. (Chem. Sci.), 113 (2001) 671

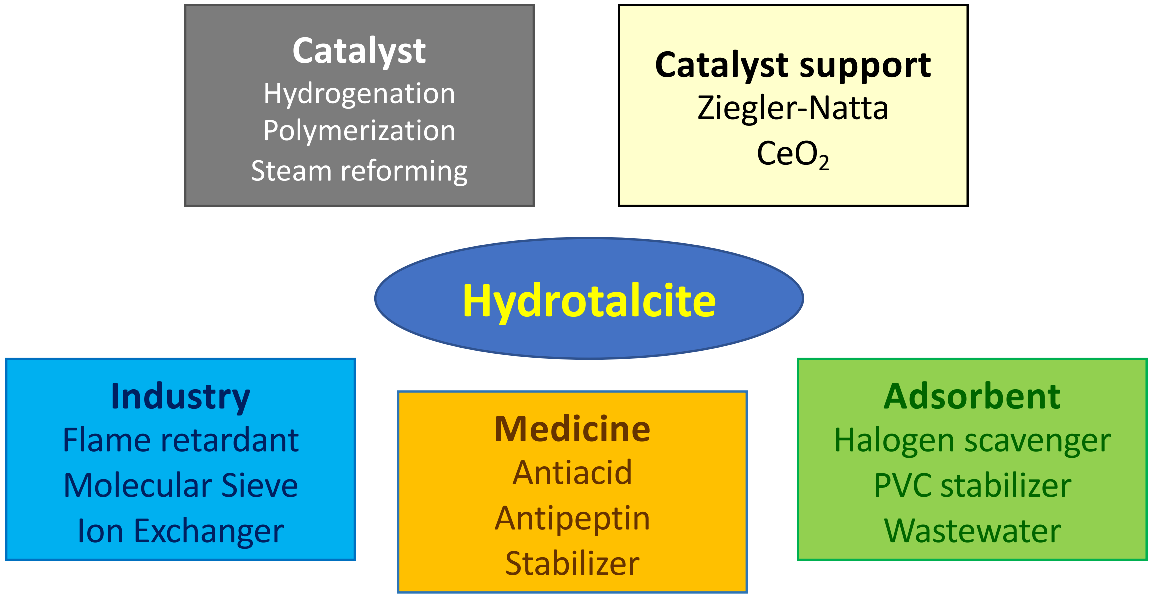
J. Tronto *et al.*, Conducting Polymers / Layered Double Hydroxides Intercalated Nanocomposites, *in* Materials Science - Advanced Topics, Y. Mastai (Ed.), InTech Pub, 2013.

Layered double hydroxides (LDH)

Hydrotalcite

$[Mg_6Al_2(OH)_{16}]CO_3.4H_2O$

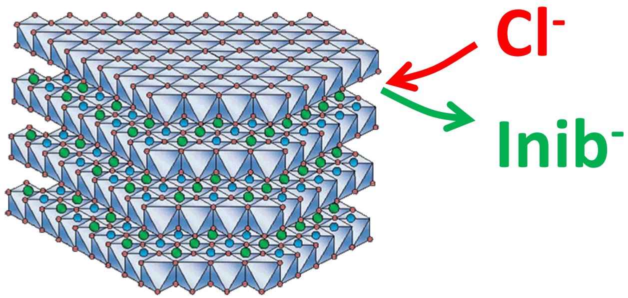
Sweden, ~1842



Catalysis Today 11 (1991) 173

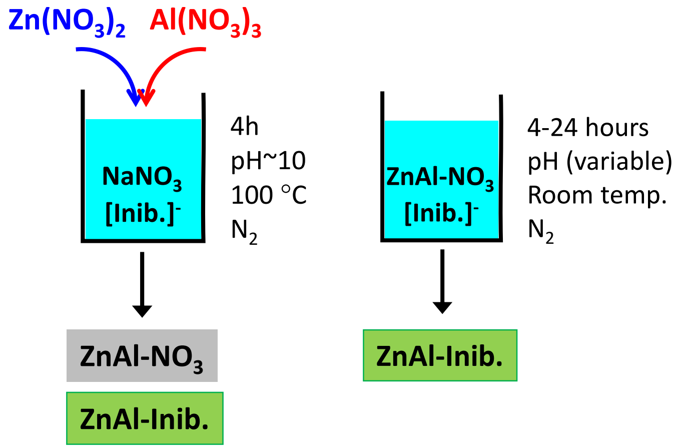
LDH in corrosion protection

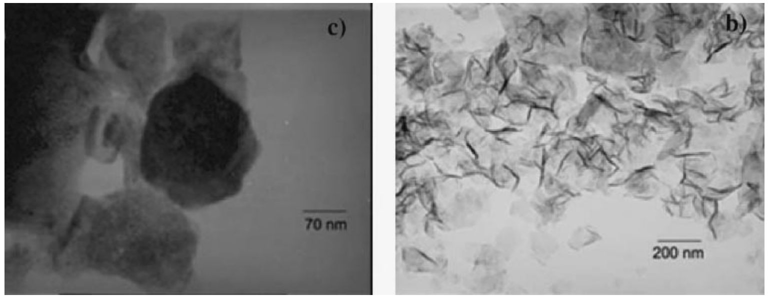
Micro- / Nano-containers with corrosion inhibitors



R.G. Buchheit *et al.*
Prog. Org. Coat. 47 (2003) 174

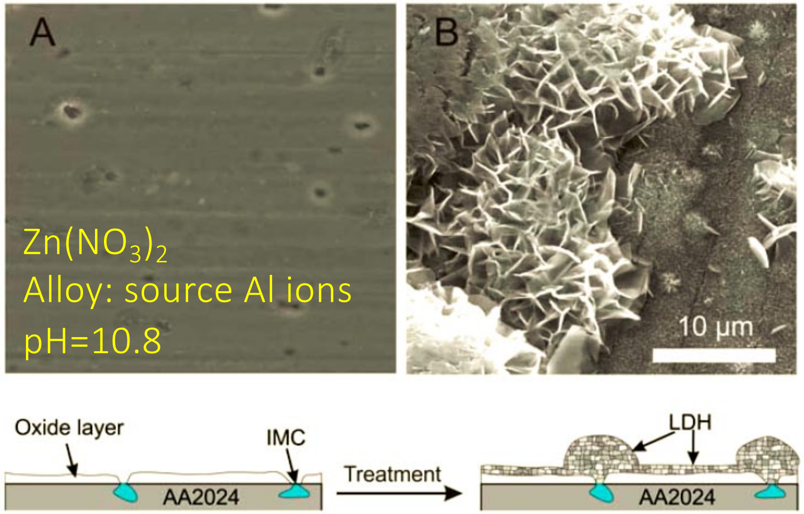
Corros. Sci. 52 (2010) 602
ACS App. Mater. Interf. 1 (2009) 2352
ACS App. Mater. Interf. 2 (2010) 1528



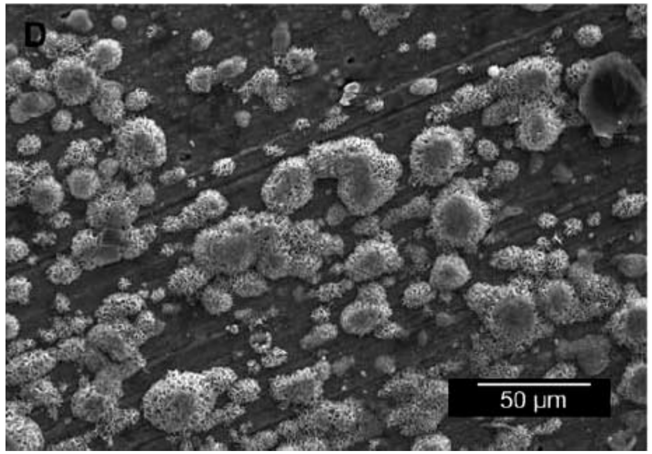


LDH in corrosion protection

Surface conversion



J. Mater. Chem. 21 (2011) 15464
Electrochim. Acta 117 (2014) 164
Electrochim. Acta 210 (2016) 215
J. Colloid Interf. Sci. 468 (2016) 86



SMALLMATEK

Long Lasting Reinforced Concrete for Energy Infrastructure under Severe Operating Conditions.

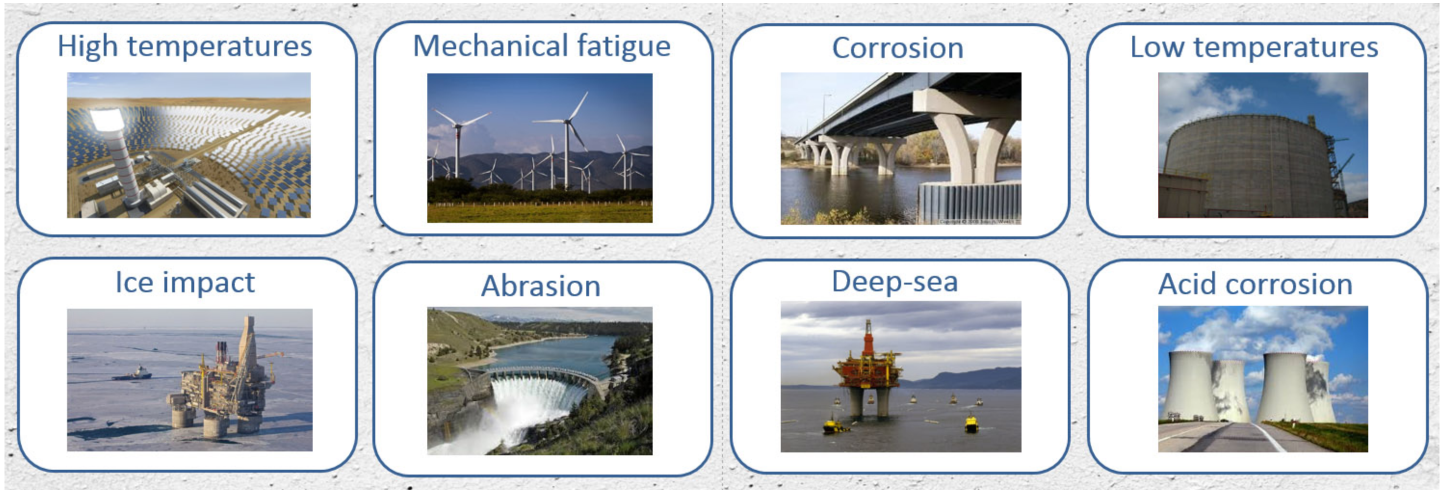
Horizon 2020 collaborative project Grant agreement nº 685445.

LORCENIS

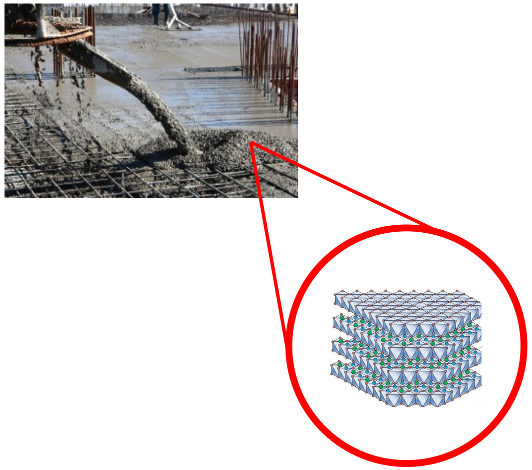
www.lorcenis-eu.com

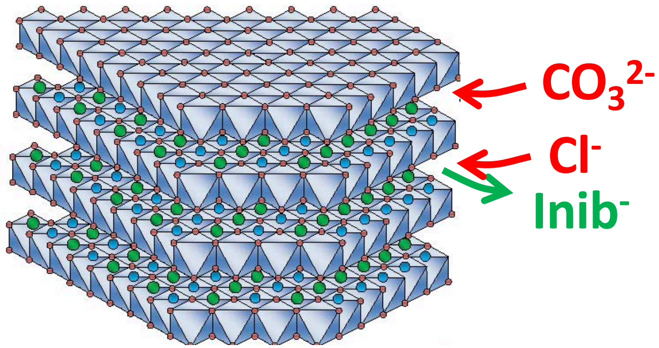
Objective: extend the durability of concrete structures in harsh conditions.

Self-Healing, Self-Sealing, Self-Sensing, Self-Curing



The concept in concrete





Capture of aggressive species (Cl^-, CO_3^{2-})

Release of corrosion inhibitors (only in the presence of aggressive species)

LDH in concrete

Around 20 papers since 2004

Cement and Concrete Research 34 (2004) 1717
Applied Clay Science 163 (2018) 129
Materials and Corrosion 64 (2013) 1
Materials and Corrosion 67 (2016) 721
Corrosion Science 126 (2017) 166
Applied Clay Science 158 (2018) 123
Applied Clay Science 163 (2018) 129

Materials Letters 236 (2019) 517
ZnAl-NO_2
Exchange studies
EIS with steel in solution
ZnAl-NO_2 vs $NaNO_2$

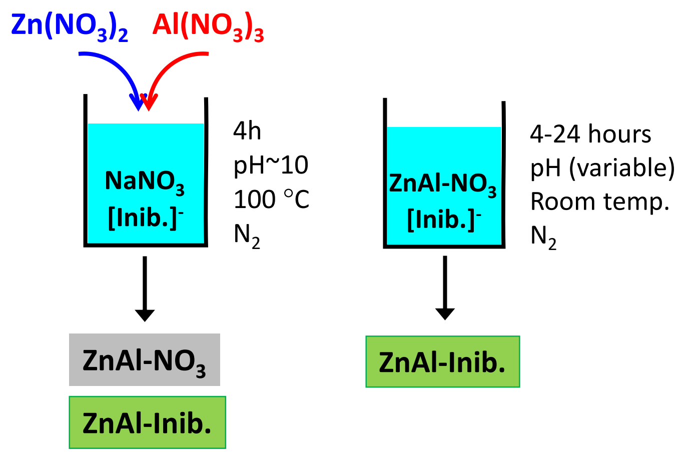
LDH Type	Intercalated ions	Tests	Corrosion studies
Hydrotalcite (HT)	CO_3^{2-}	Hydration, curing,…	E_{corr}, i_{corr} (pol. res.), EIS
MgAl-…	NO_3^-	Mechanical properties	Steel in solution and in mortar
CaAl-…	NO_2^-	Exchange kinetics	
	Organics (anionic)	Binding capacity, isotherms,…	
		Cl^- migration and diffusion	

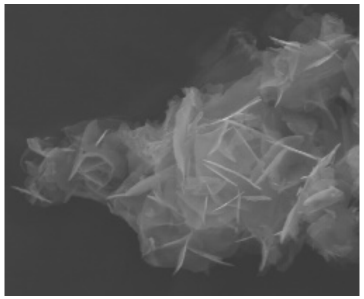
This communication

LDH

$Zn_2Al(OH)_2NO_3.2H_2O$ (LDH-NO_3)

$Zn_2Al(OH)_2NO_2.2H_2O$ (LDH-NO_2)





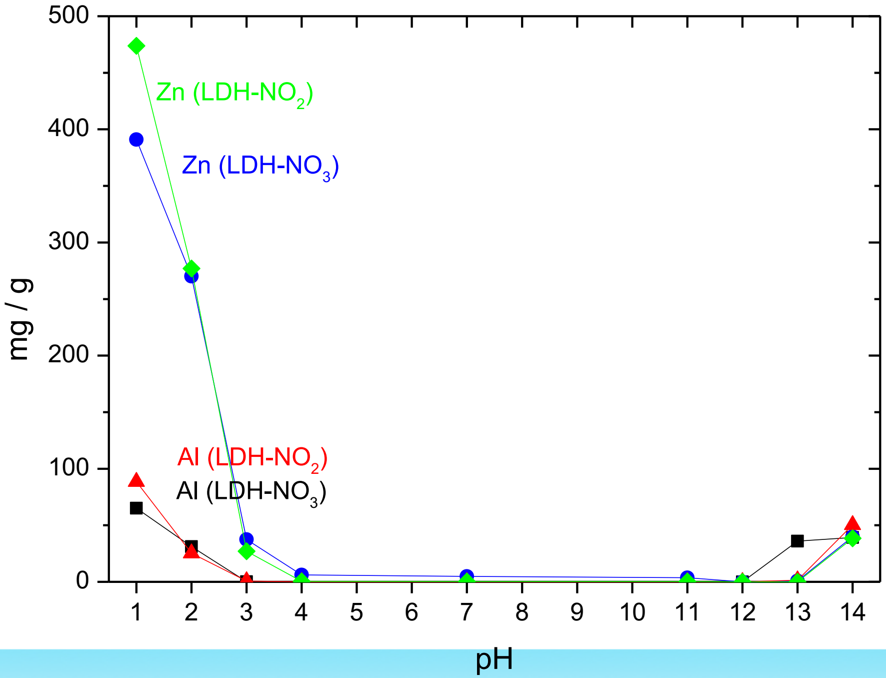
- XRD, FTIR, Chemical analysis, TGA
- Particle size distribution, zeta-potential
- Stability in water at different pH
- Stability in cement paste and mortar
- Effect on setting, hydration and rheology
- Effect on mechanical properties (ex: compressive strength)
- Ionic exchange (capture/release)
- Binding capacity
- Chloride threshold measurements
- Field exposure of concrete samples with LDH
- Chloride ingress on mortars with LDH
- EIS of steel concrete samples with LDH
- EIS of steel on mortar samples with LDH
- EIS of steel samples in NaCl solutions

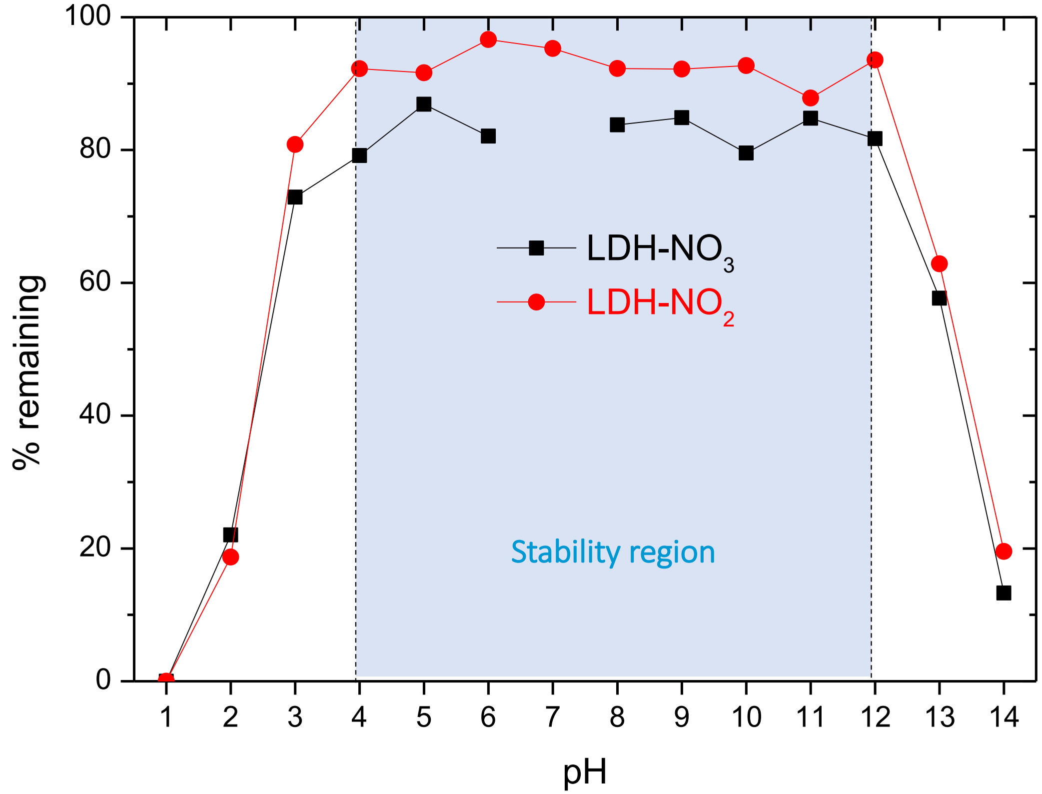
SMALLMATEK

LDH stability in solution

1 g LDH in 50 mL H_2O with different pH during 30 days. Then:

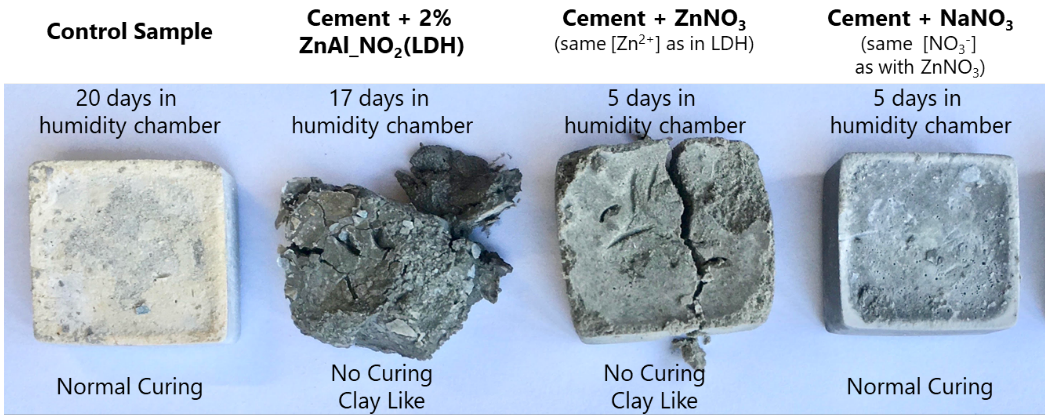
a) Visual examination
b) Mass variation
c) Chemical analysis of solution
d) XRD on remaining powder



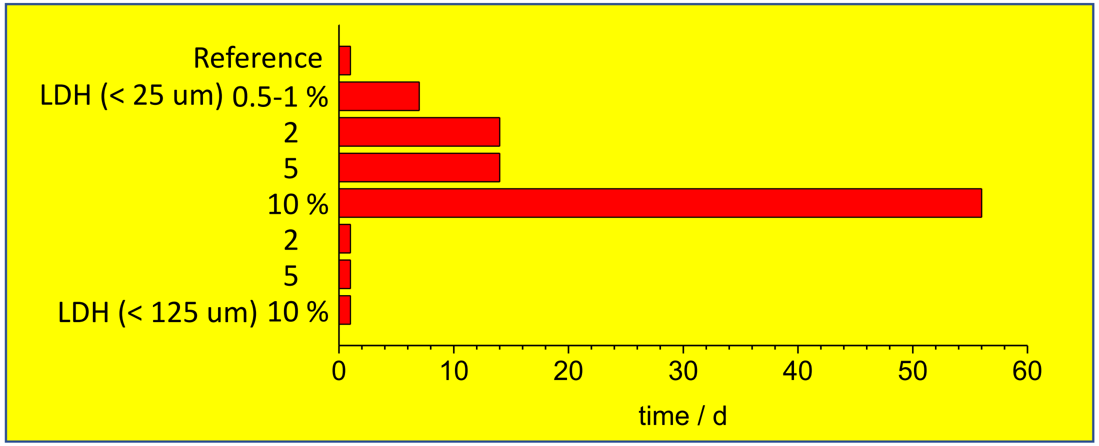


LDH stability in concrete

2% (w/w) LDH in 10 g cement paste samples. Samples were cast with w/c = 0.5 ratio and cured in a humidity chamber.



Time to harden for demoulding:

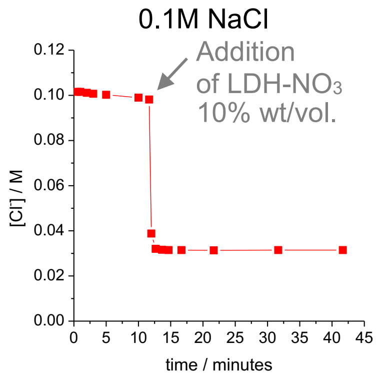


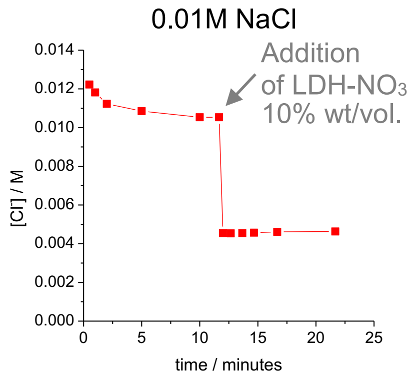
Materials Research 10 (2007) 331, Hydration Study of Ordinary Portland Cement in the Presence of zinc ions.

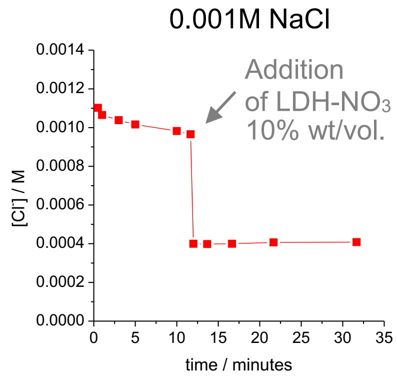
LDH release/exchange kinetics

10% LDH:
2.5 g LDH in
25 mL solution

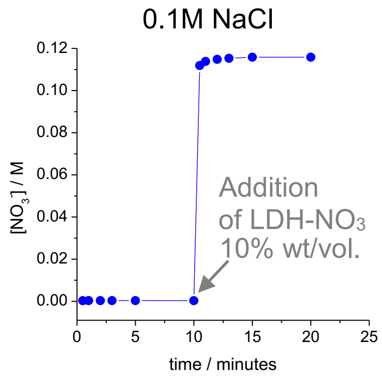
Capture of Cl^-

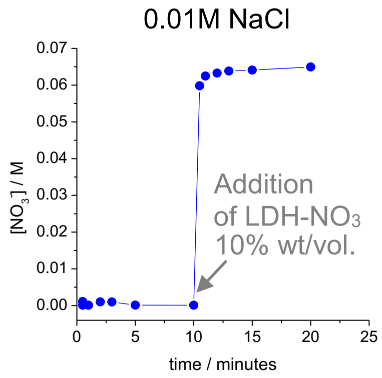


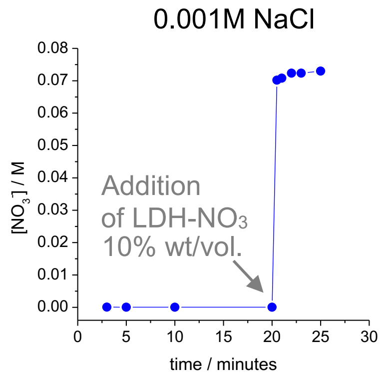




Release of NO_3^-

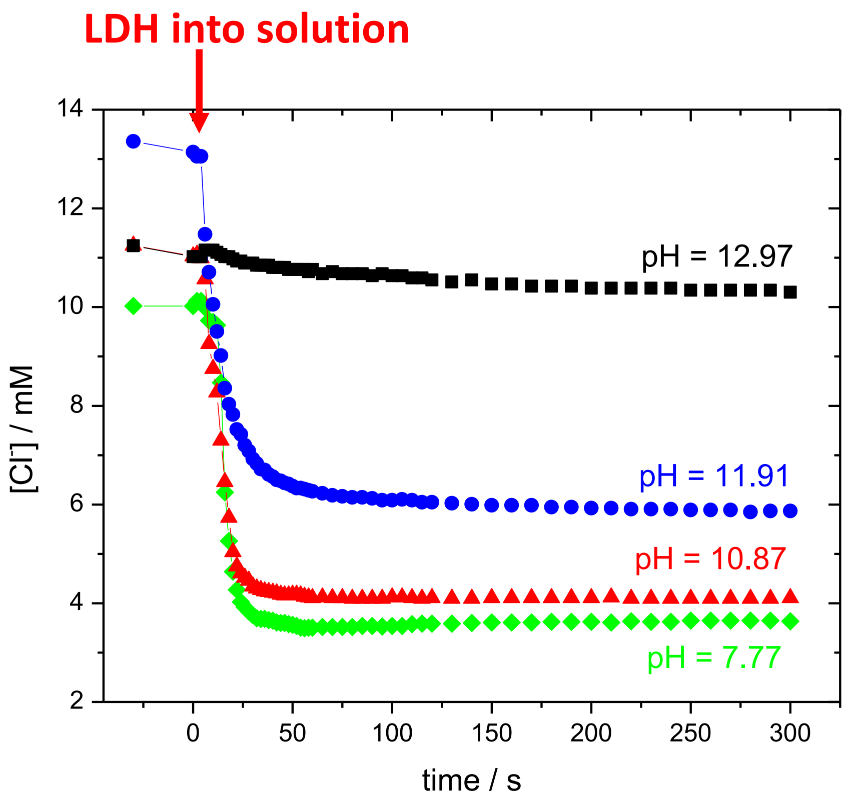




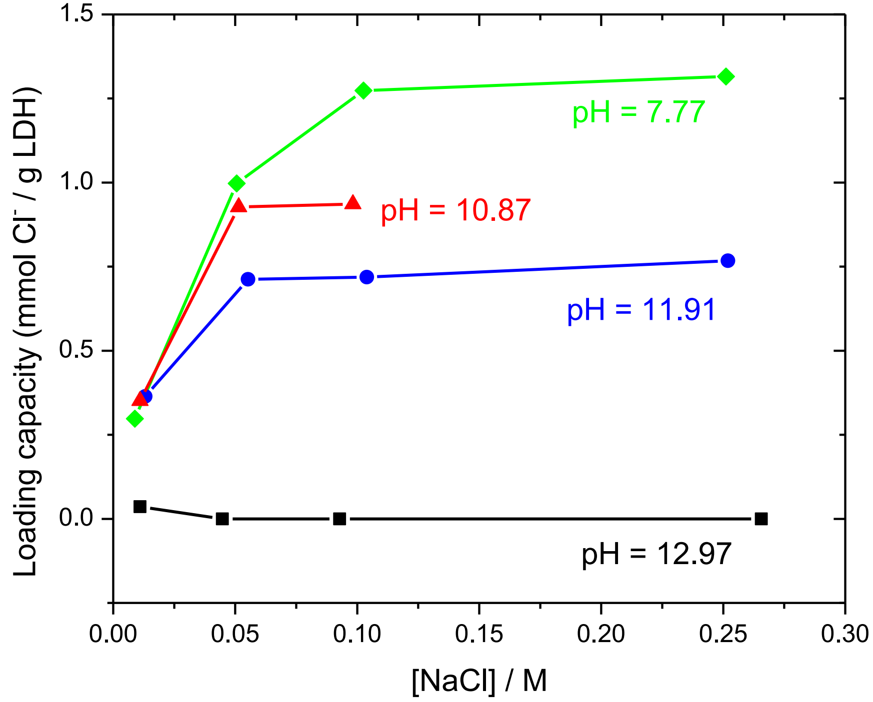


LDH release/exchange kinetics

1g LDH in 50 mL solution

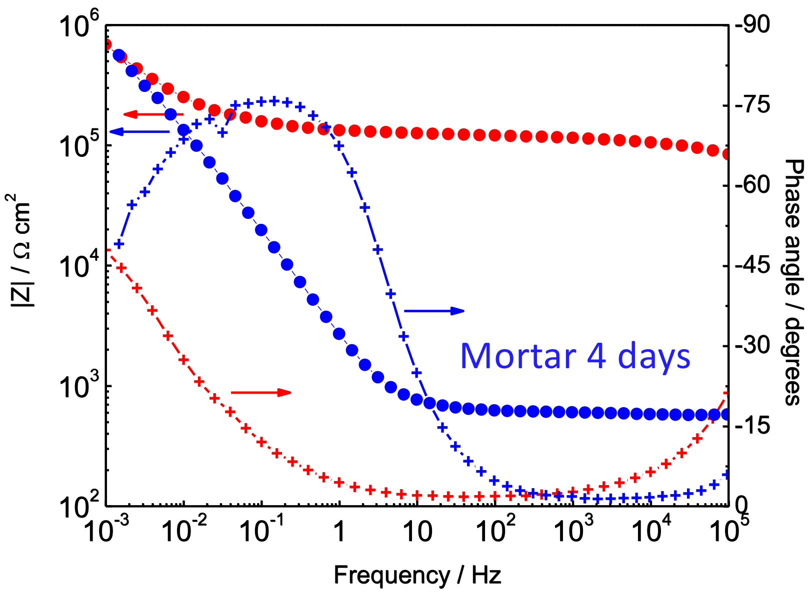


$$\text{Binding Capacity} = \left(\frac{(\text{Ci} - \text{Cf})\ \text{Vsol}}{\text{m}_{\text{LDH}}}\right)$$



EIS of steel in concrete and in mortar

Concrete composition		
CEM I 52.5 R	350	kg/m³
Fly Ash	140	kg/m³
Sand 0-4	1090	kg/m³
Gravel 4-8	115	kg/m³
Gravel 8-16	460	kg/m³
Tap water	170	kg/m³
ViscoFlow 45	1	% by CEM
AerSolid	2	kg/m³
Binder content	490	
w/b - ratio	0.35	

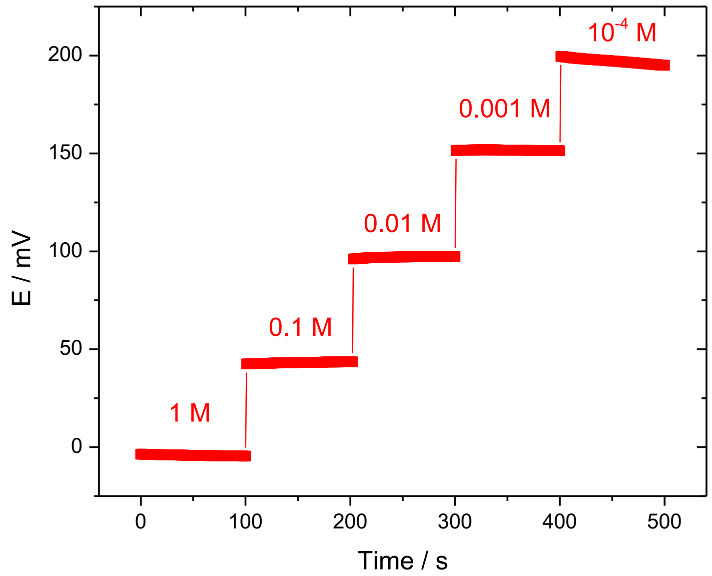


Mortar composition	kg
CEM II / B-L 325 N	1
LDH (>125 um)	0.02-0.05
Sand 0-2 mm	5
Dist. water	0.9
w/c	0.9
s/c	5

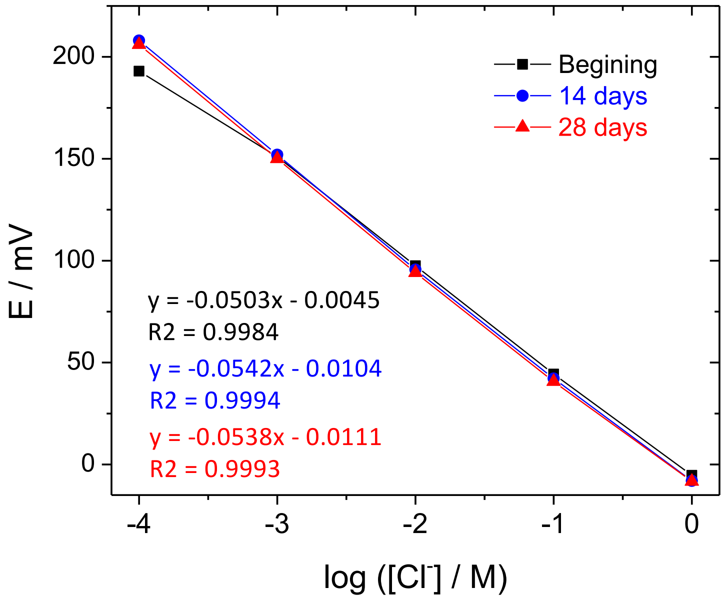
Curing: 2 days in mould + 6 days in water

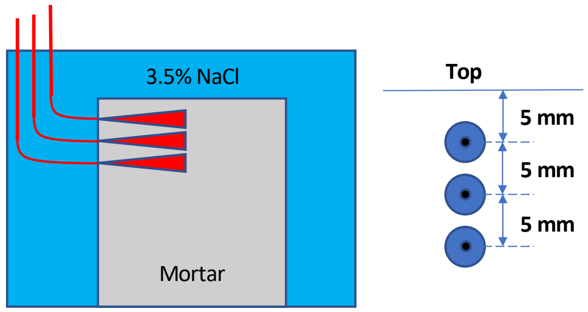
Chloride sensors

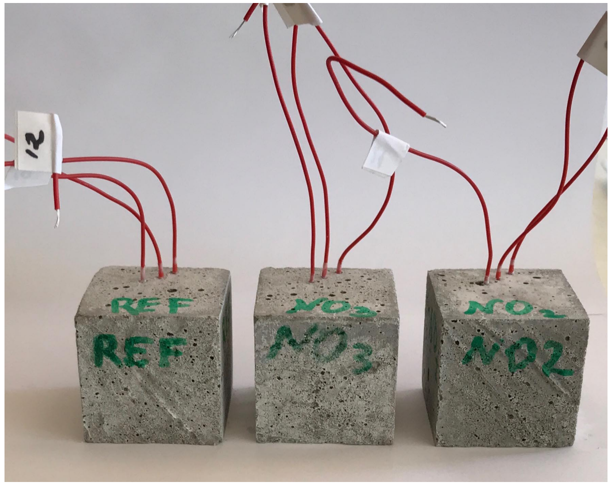
Ag wire 0.8 mm diameter
Galvanostatic polarization
(30 min; 2 mA cm^{-2}; 0.1 M HCl)



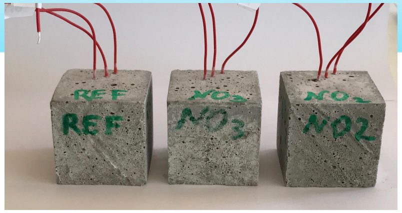
Calib. after electrode stored in pH=13



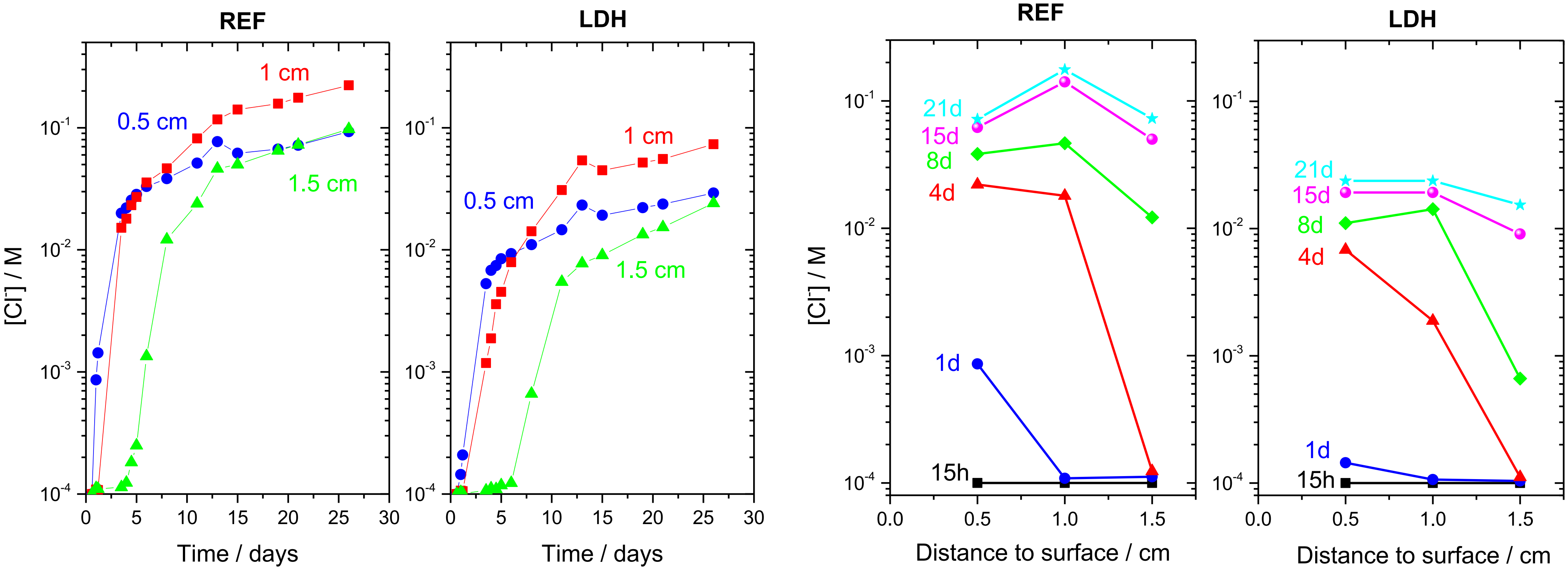




Chloride sensors

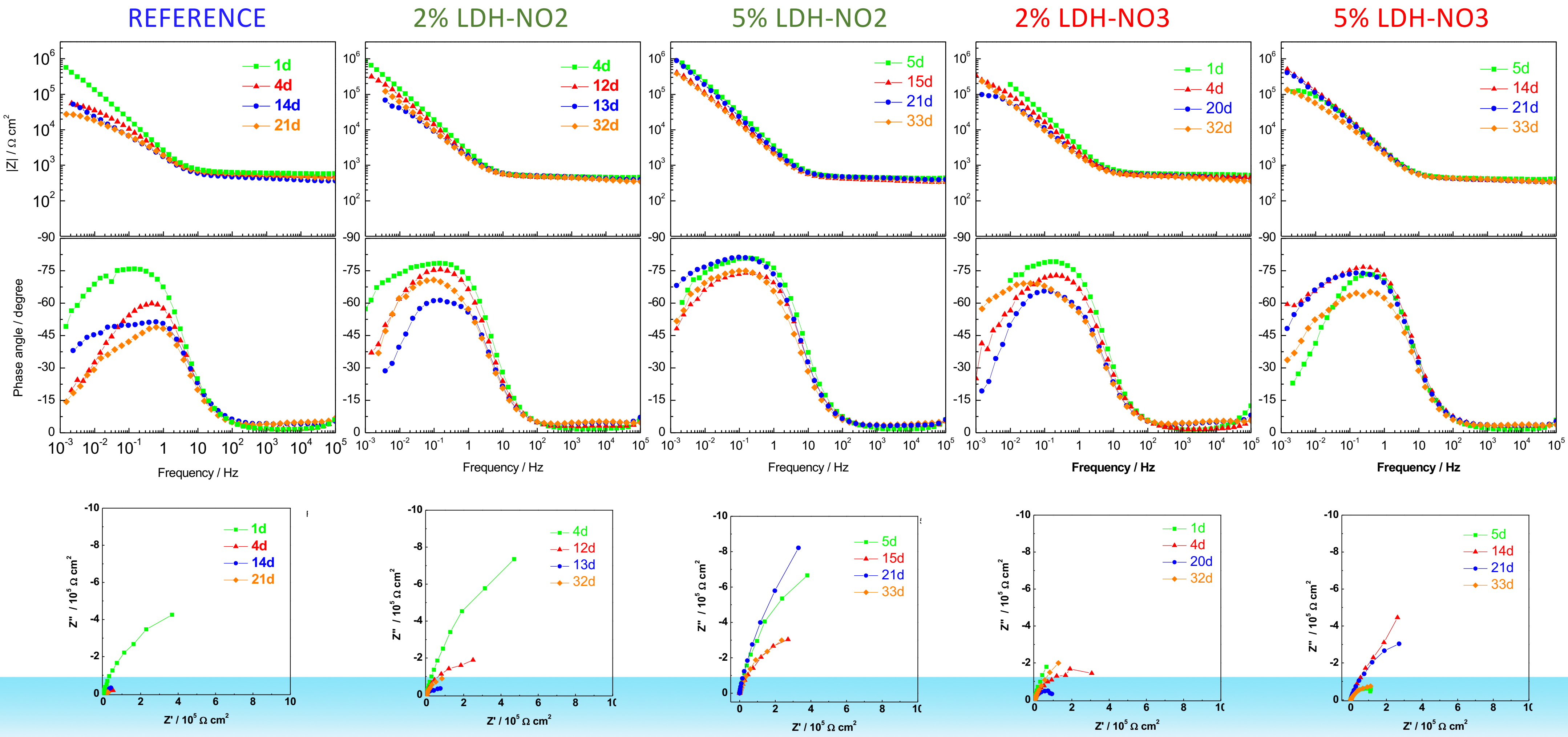


Mortars immersed in 3.5% NaCl

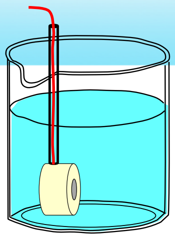


EIS of steel in mortar

immersed in 3.5% NaCl

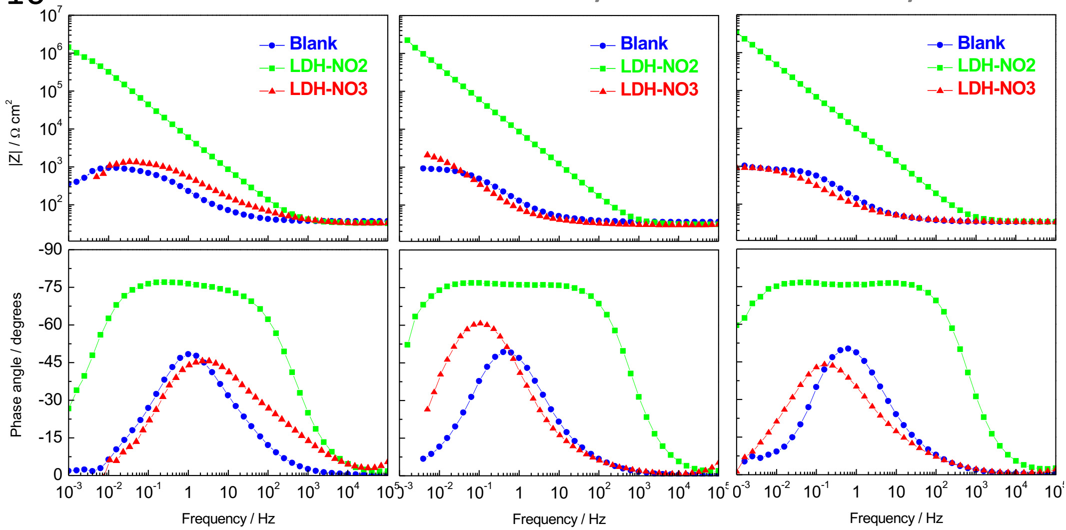


EIS of steel in solution with 0.5% LDH



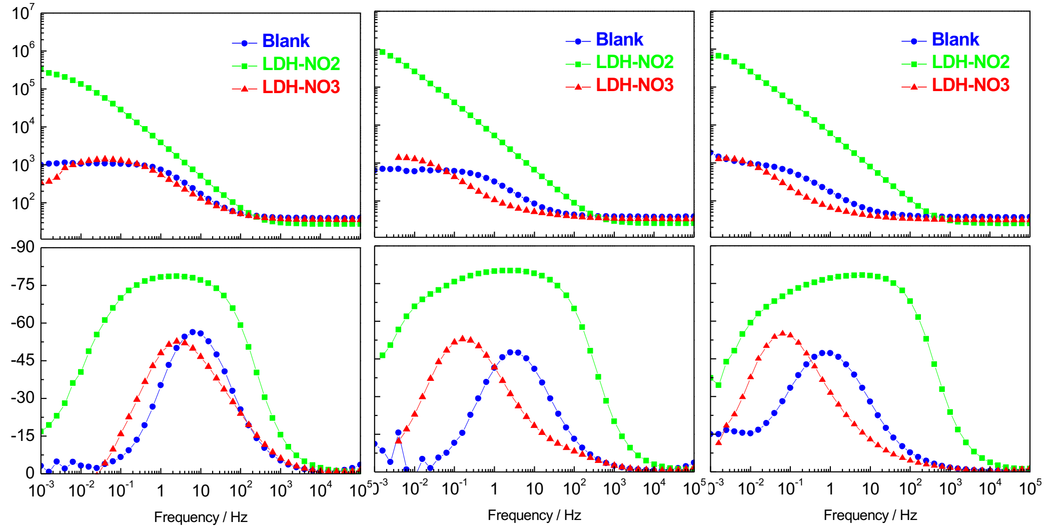
0.05M NaCl (pH=6-7)

1 hour | 1 day | 6 days



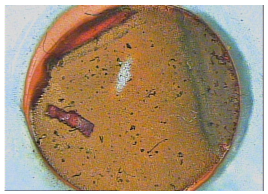
0.05M NaCl (pH=11... ...7-9)

1 hour | 1 day | 6 days



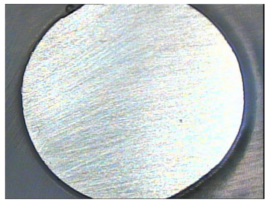
Blank

LDH-NO3

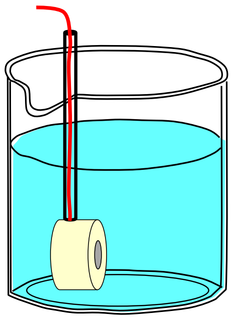


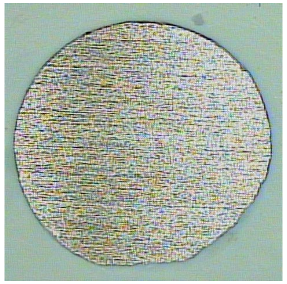
5 mm

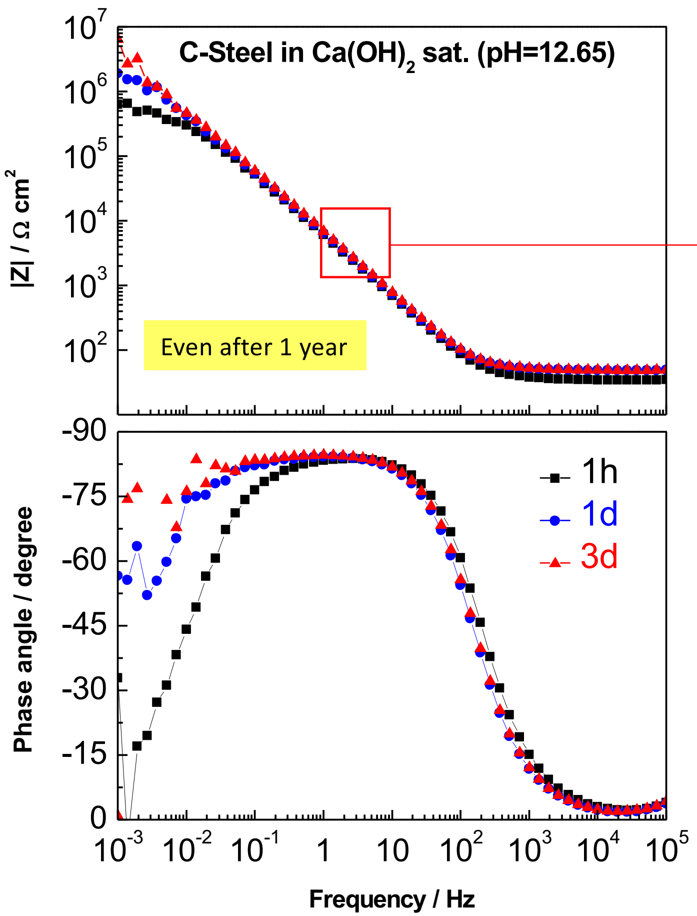
LDH-NO2

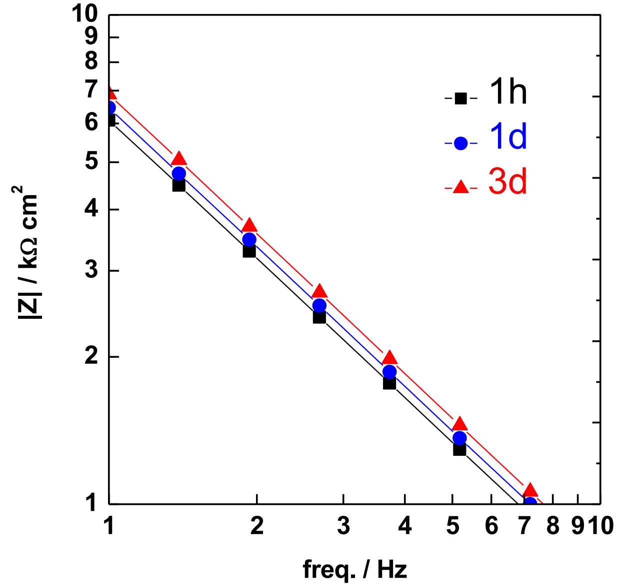


EIS of steel in solution









Conclusions, Discussion, Work for future

- In solution, chloride ions are captured by LDH and nitrate/nitrite ions are released.
- This process stops at high pH.
- ZnAl-LDH dissolves partially at pH>13.
- However, chloride ingress in mortar is slower when LDH is present.
- Higher corrosion resistance is observed in samples containing LDH-NO_2.
- LDH-NO_3 does not seem to provide any significant difference.

Open questions:

- Optimal LDH amount / concentration.
- Effect of particle size.
- Does the LDH remain in concrete? It might dissolve, release the nitrite ions and still capture chloride by the formation of Friedel's Salt (or others). Compare with $Ca(NO_2)_2$ in concrete.

Conclusions, Discussion, Work for future

The real question is:

"Can LDH be used to extend the service life of reinforced concrete?"

This is yet to be confirmed.

- Concrete samples with LDH are being tested but the changes are too slow.

- Measurements with a modified mortar composition are about to be started.
- Chloride threshold is being determined by RILEM TC 235-CTC "Corrosion Initiating Chloride Threshold Concentrations in Concrete".

- Slabs with 100 x 70 x 10 cm^3 were placed in a site in Sweden for field exposure but tests are expected to extend for the next 10-20 years.

Acknowledgements

This work was supported by the HORIZON 2020 Collaborative project "LORCENIS" (Long Lasting Reinforced Concrete for Energy Infrastructure under Severe Operating Conditions", Grant agreement nº 685445).

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