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Synthesis and characterization of functional nanocontainers for active corrosion protection

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1. Introduction

Direct incorporation of corrosion inhibitors in coating formulations can lead to several problems:

-**detrimental interaction** between inhibitors and coating matrix (**technical**)

-**constant/spontaneous leaching** of inhibitors into the environment (**environmental and economical**)

Limitation of the coating protective action in time and magnitude

Nanocontainer

Corrosion inhibitor

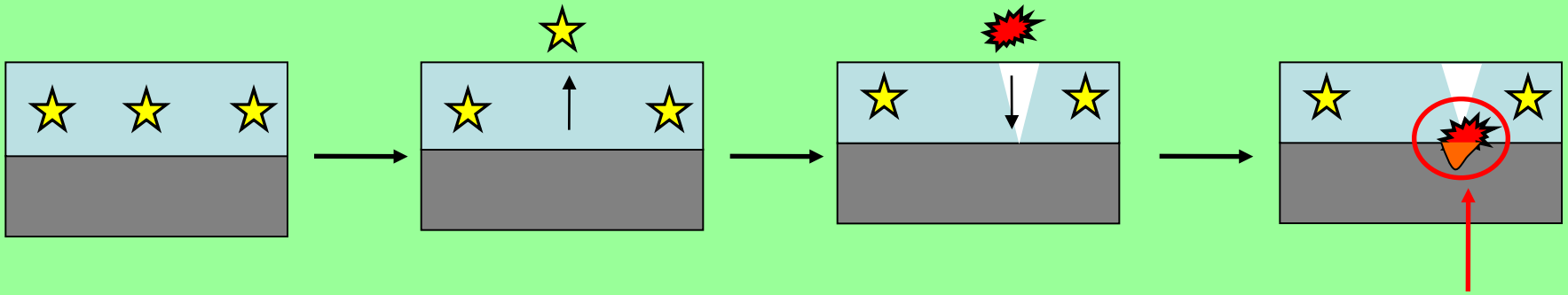
Coating

Metallic substrate

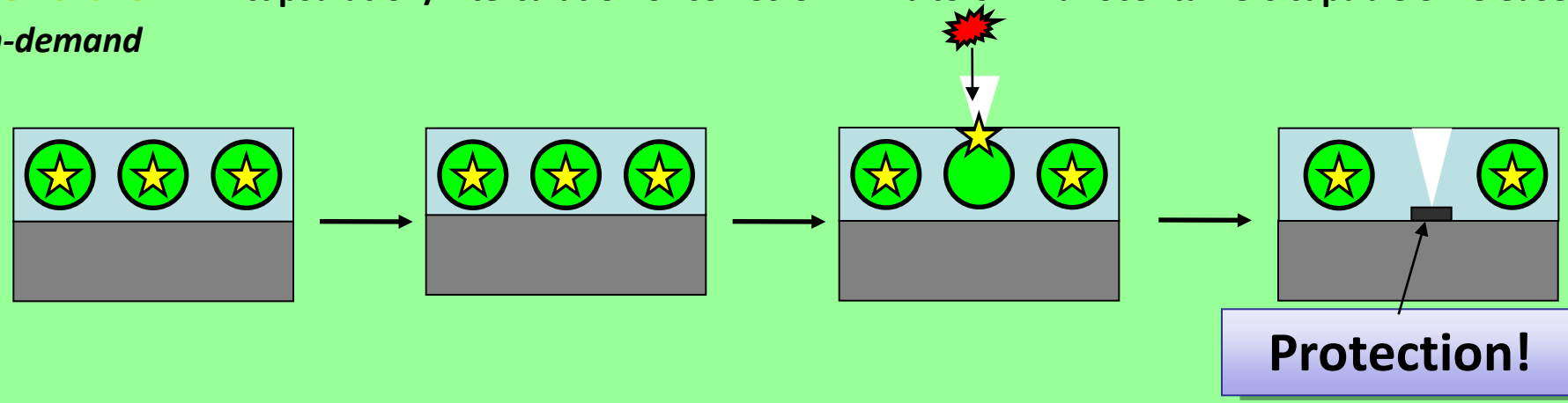
Aggressive species

Corrosion products

Protective film



Solution Encapsulation/intercalation of corrosion inhibitors in nanocontainers capable of *release-on-demand*



Micro/nanocontainer + Corrosion inhibitor >= Chromates

Inert, hosting structures

Release mechanisms

Active protection

Low toxicity

Types of containers:

-inorganic, organic, hybrid

Release mechanisms:

-mechanical impact

-pH -H_2O

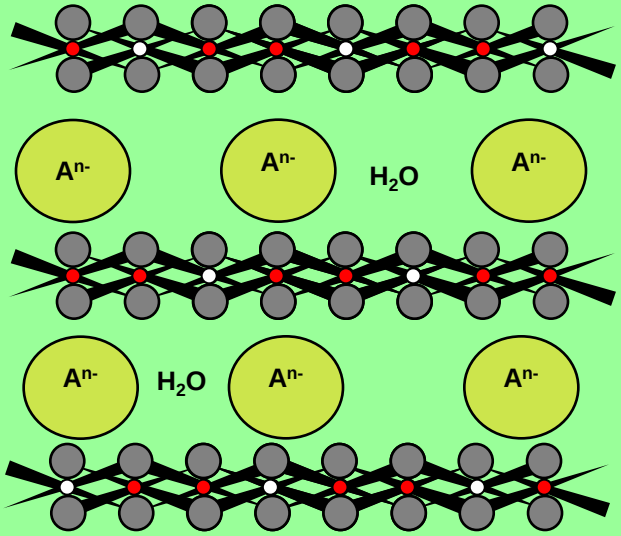
-presence of aggressive species (e.g. chlorides)

Potential advantages related to this strategy:

- improvement of coating integrity
- smaller amounts of inhibitor required
- development of new value-added products
- comply with environmental law regulations

Layered double hydroxides (LDHs)

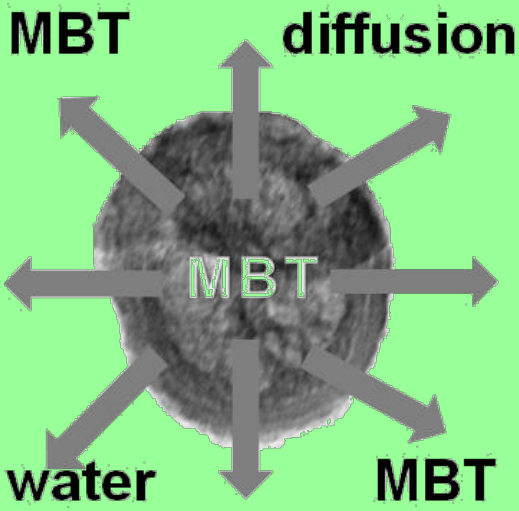
$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$



Applications:

Sorbents, Drug-delivery systems, Polymer stabilizers, Heterogeneous catalysis

Silica nanocapsules (SiO_2)



Applications:

Drug-delivery systems

Transport carriers

Nano-reactors

2. Experimental

- **Synthesis of LDHs**

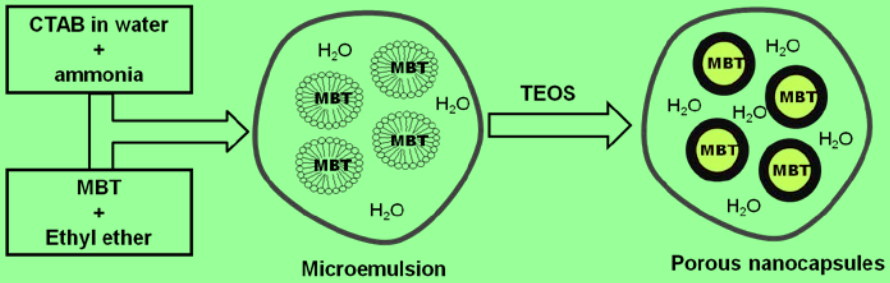
-methodologies applied: ion-exchange, calcination-rehydration

-corrosion inhibitors intercalated: MoO_4^{2-}, VO_3^-, MBT

- **Synthesis of SiO_2**

-oil-in-water microemulsion

-corrosion inhibitor: MBT



- **Structural/morphological characterization**

XRD, SEM, TEM

- **Release studies**

HLPC

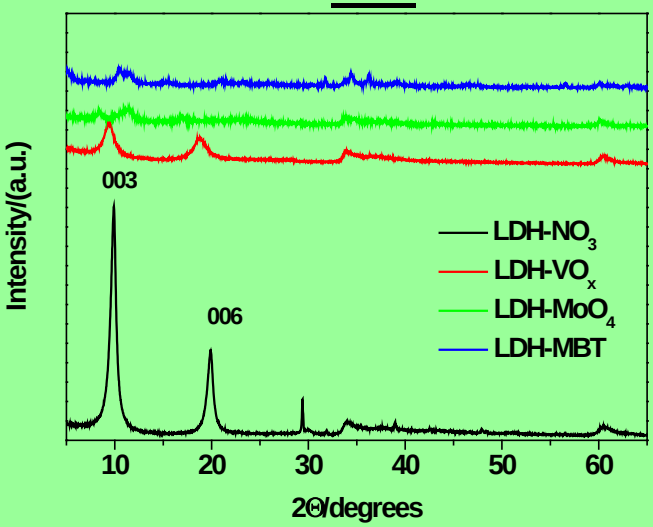
- **Corrosion studies**

EIS

3. Struture and morphology

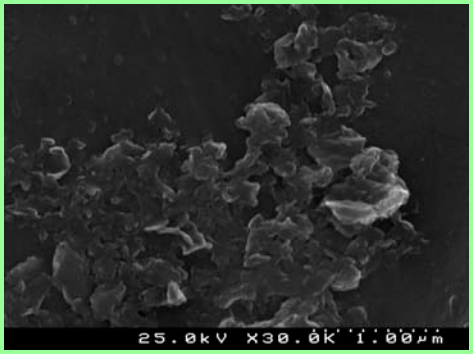
LDHs

XRD

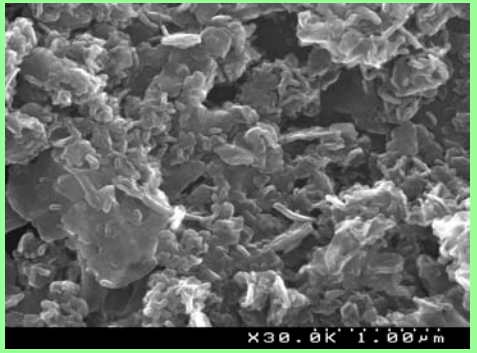


- Peak positions at low angles: information on the gallery height (anion size and orientation)

SEM

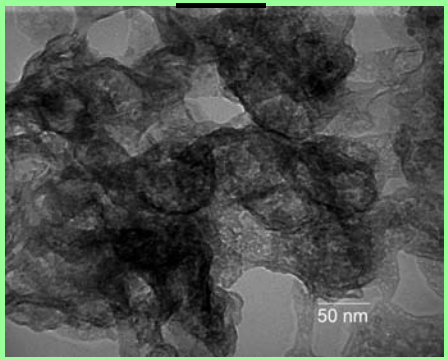


LDH-NO_3



LDH-VO_x

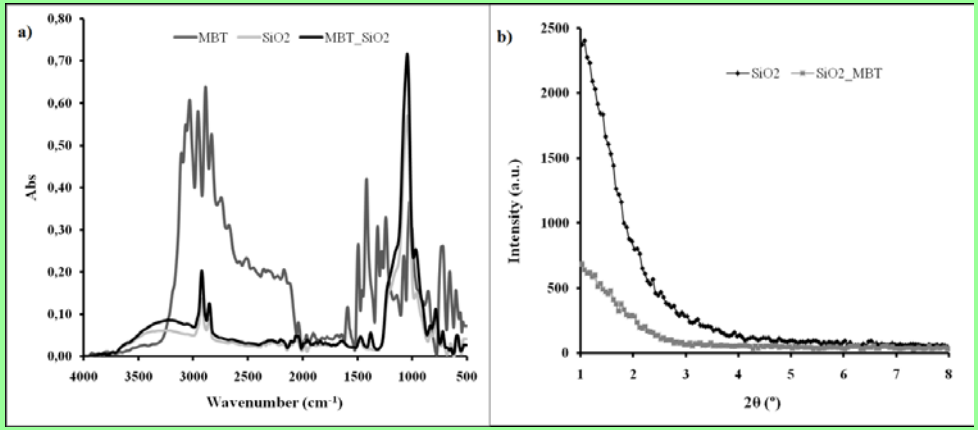
TEM



- Plate-like morphology
- LDH particles: 200-400 nm diameter and 20-40 nm height

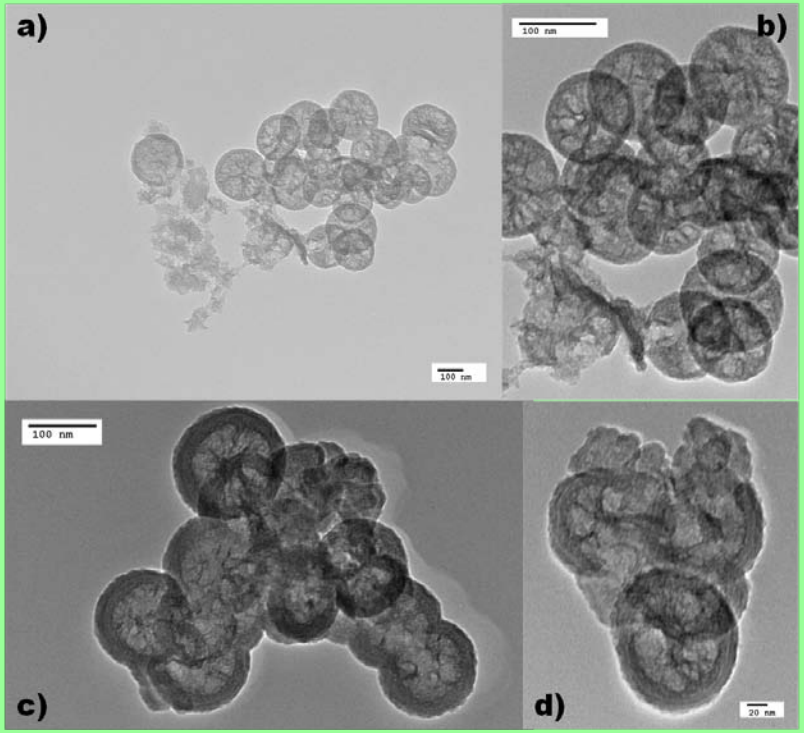
SiO_2

FTIR

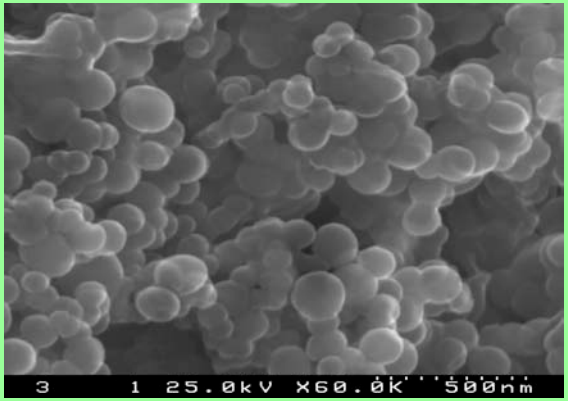


XRD

TEM

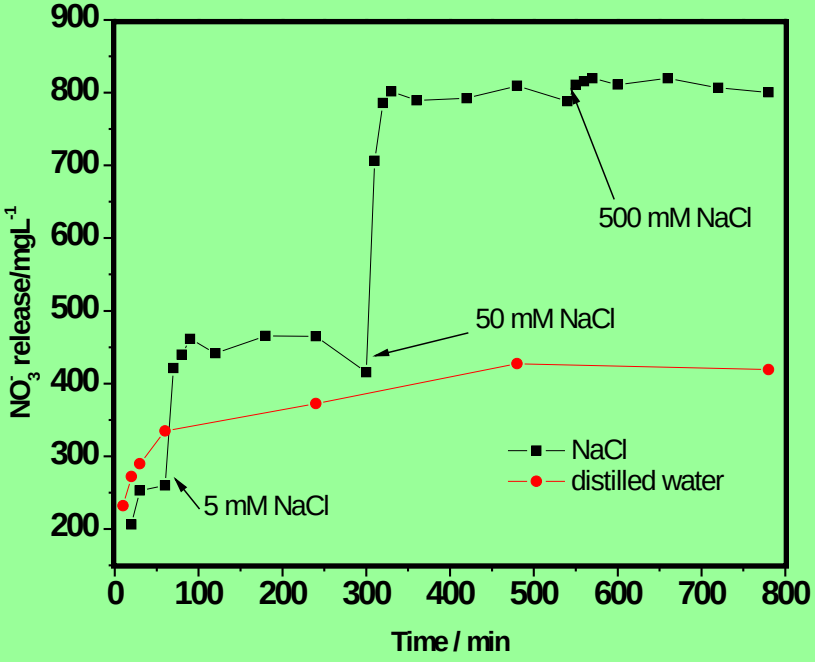


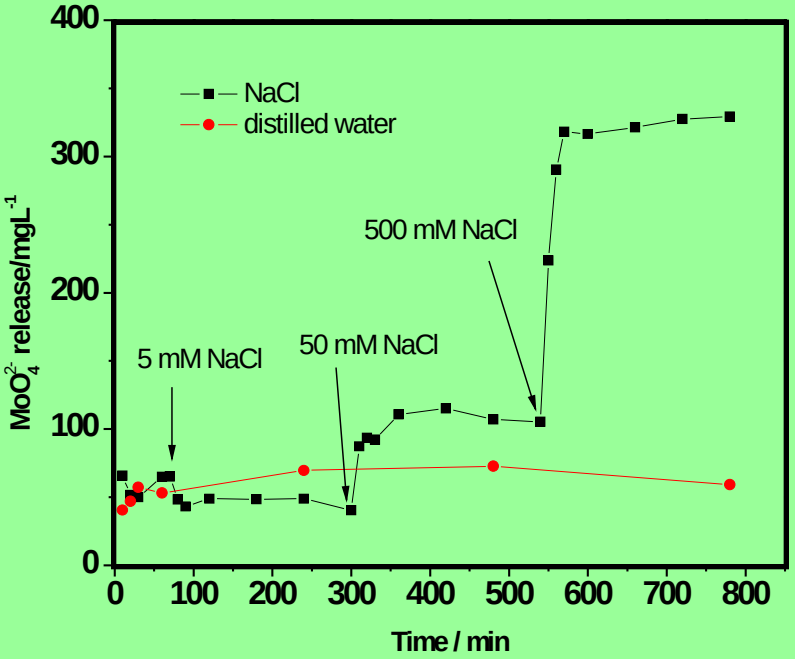
SEM



- **Porous, spherical particles 150 nm diameter**
- **Different core/shell porosities**

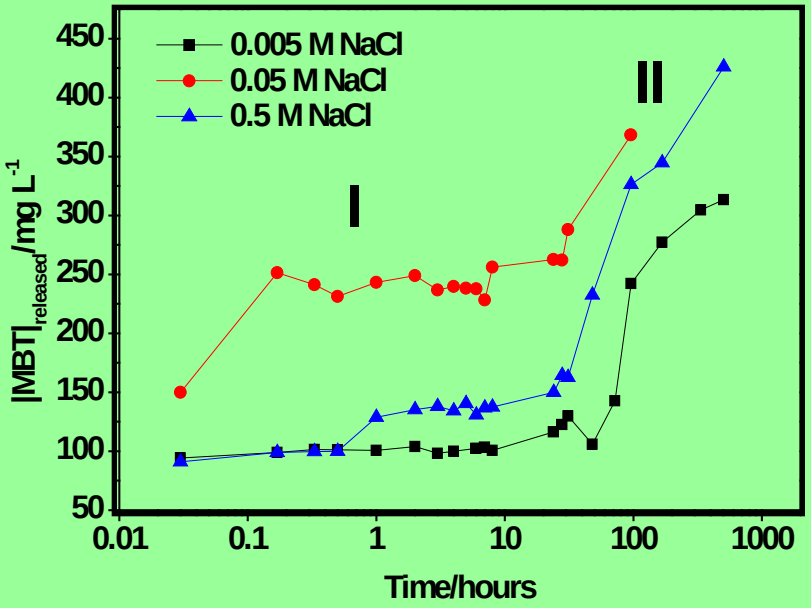
4. Release studies-LDHs



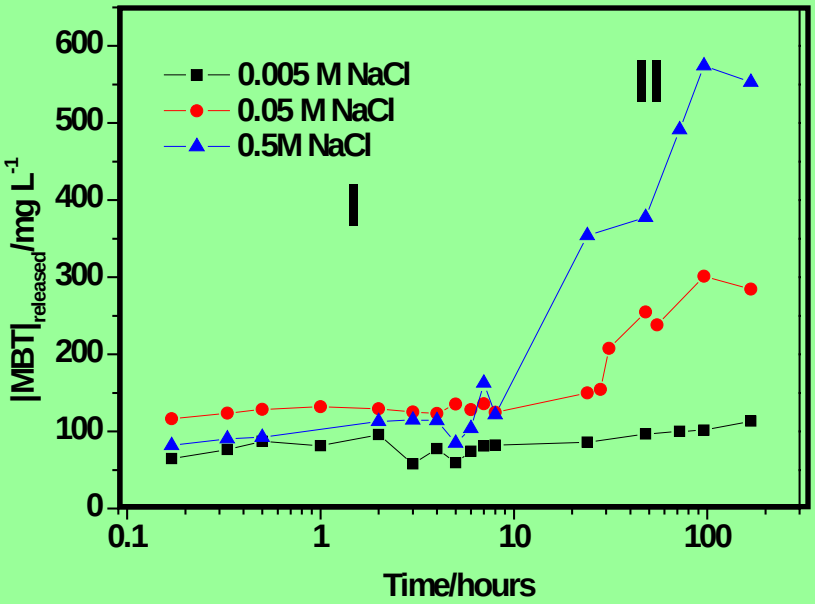


- **The release of NO_3^- and MoO_4^{2-} anions is triggered by the presence of chloride anions**

SH-MBT

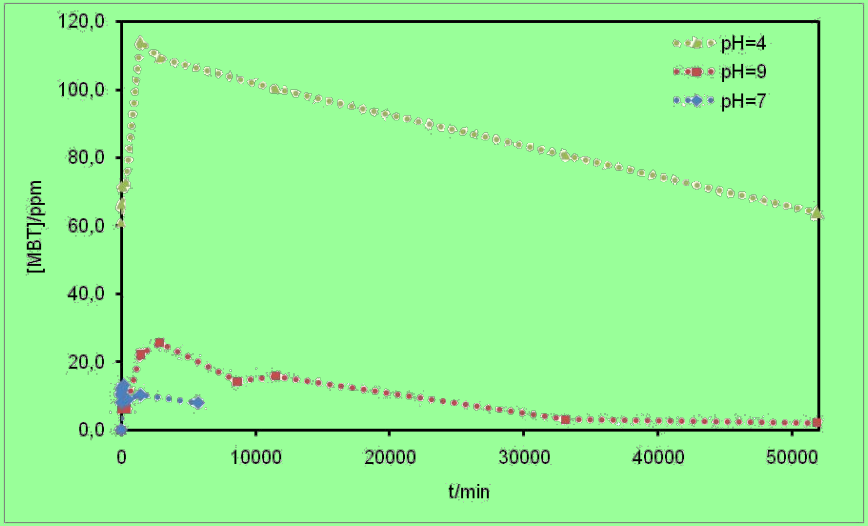


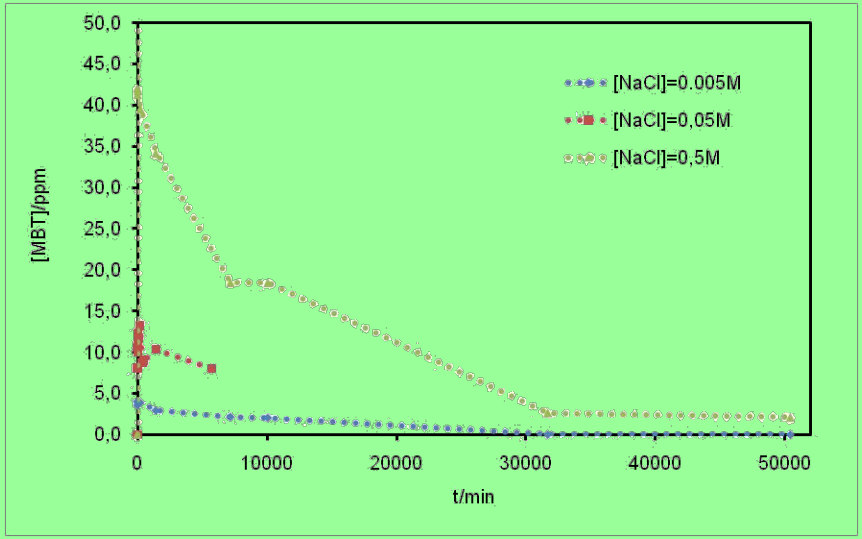
Zn(2)-Al-MBT



- **Two release profiles are observed: short (1-2h) and long timescales (>100 h)**
- **Profile at short timescales is not sensitive to the concentration of Cl^-**

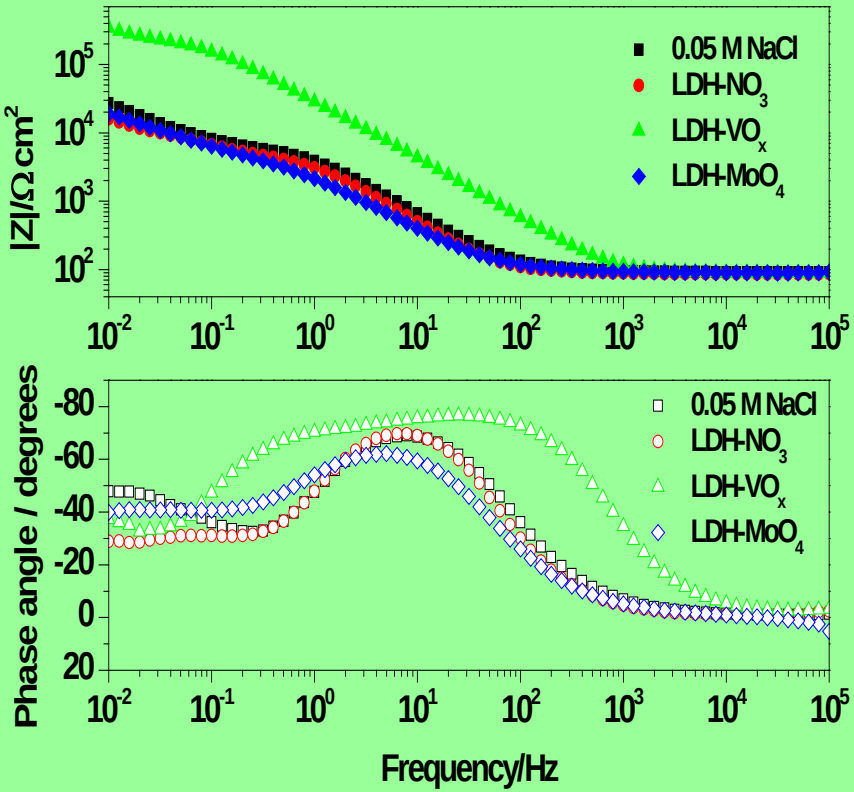
4. Release studies-SiO_2

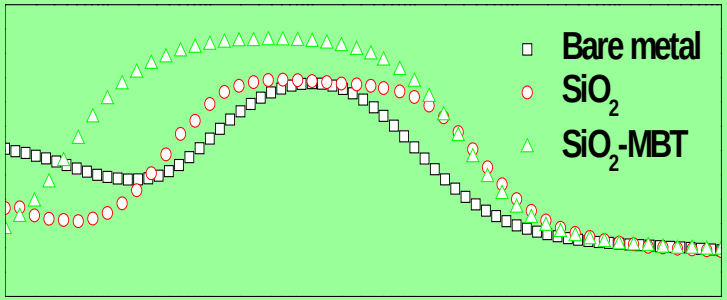




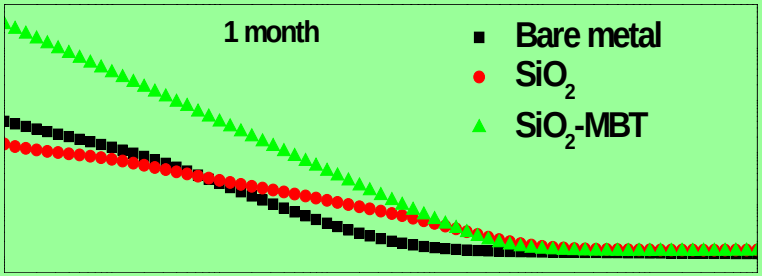
- **MBT released preferentially in concentrated NaCl solutions and acidic conditions**

5. Assessment of anticorrosion performance-EIS

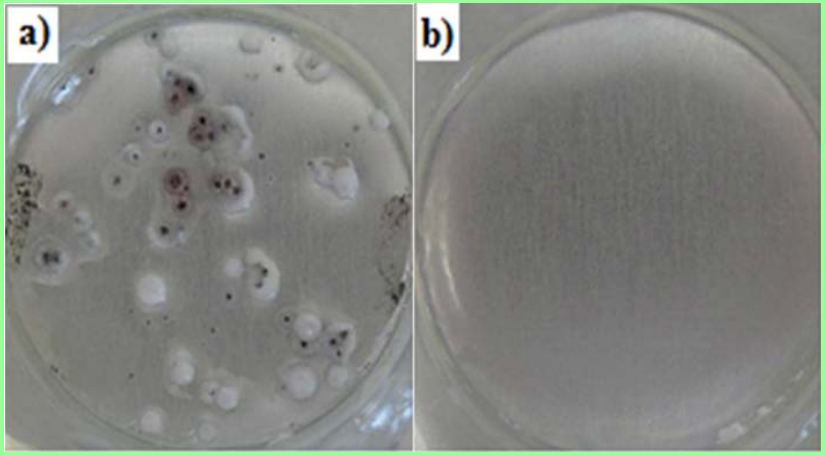




- **EIS spectra for bare AA2024 after 1 day of immersion in 0.05 M NaCl**



SiO_2 SiO_2-MBT



1 month of immersion in 0.05 M NaCl

- **The presence of inhibitor determines the (active) protection of the metal substrate**

Concluding Remarks

- LDH nanocontainers and SiO_2 nanocapsules were synthesized and corrosion inhibitors successfully intercalated/ encapsulated
- Release studies showed that the optimal conditions for the release of corrosion inhibitors are

  -LDHs (NaCl) -SiO_2 (pH and NaCl)
- The anticorrosion activity in solution depends on the strength of the inhibitor

Future perspectives

- Incorporation of corrosion inhibitor/nanocontainer 'pigments' in coating formulations from aeronautical, automotive and maritime industry

  -dispersion optimization via surface modification

  -assessment of the protection performance of the coatings

- Optimization of the nanocontainers for specific applications

  -action on the release response

  -screening of inhibitors, combination of inhibitors displaying synergistic effects

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