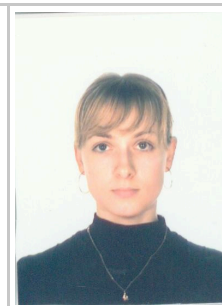


P-095 Investigation of release of active species from inert nanomaterials

Kuznetsova A.¹, Tedim J.¹, Salak A.¹, Zheludkevich M.L.¹, Ferreira M.G.S.¹¹CICECO, Dep. Ceramics and Glass Eng., 3810-193, Aveiro, Portugal

alena@ua.pt



INTRODUCTION AND OBJECTIVES

Nowadays, the encapsulation and release of active species from inert, “hosting” nanostructured materials is a relevant topic in distinct areas of science such as medicine, biology, biochemistry and corrosion (Broz 2006), (Shchukin 2006). Materials scientists have been focused on the development of nanostructured materials (nanocarriers, nanocontainers) because they offer the opportunity for storage, release and delivery of targeted species in a specified time and location. The release process depends on various factors, intimately associated with the structure and properties of the “hosting” nanomaterials. The main challenge is, thus, to find a match between the triggers and the specific purposes onto which the active species must perform, in order to maximise the effectiveness of the latter.

The main goal of the present work is to investigate and tune the release of active species (corrosion inhibitors) from ion-exchanging, materials including layered double hydroxides-LDHs (anions), bentonite clays and zeolites (cations). In spite of the current work being directed towards anticorrosion applications, the concepts are general and relevant to many different areas, as long as different active species are used (e.g. drugs, nutrients).

LDHs are crystalline inorganic structures generically represented by the formula $[M^{II}_x M^{III}_{1-x} (OH)_2]_{intra} [A^{m-}_{x/m} \cdot nH_2O]_{inter}$, where M^{II} and M^{III} are divalent and trivalent metal cations, A^{m-} is the anion, and the *intra* and *inter* subscripts denote the intralayer domain and the interlayer space, respectively (Figure 1). LDHs have a vast number of potential applications, all of them exploring the anion-exchange abilities of these systems: separation chemistry, polymer additives and catalysis (Leroux 2001).

Bentonite clays occur naturally as easily mined, mineral deposits. The structure of individual bentonite layers comprises three tiers, two of tetrahedral bonded silica sandwiching a layer of octahedrally bonded alumina. The charged layers form multilayer stacks, which are held together by electrostatic forces with compensating cations necessary for charge neutrality residing between them. The layers exhibit isomorphic substitution, where atoms at particular locations are replaced by a variety of dissimilar atoms having a similar ionic radius (Loveridge 2006).

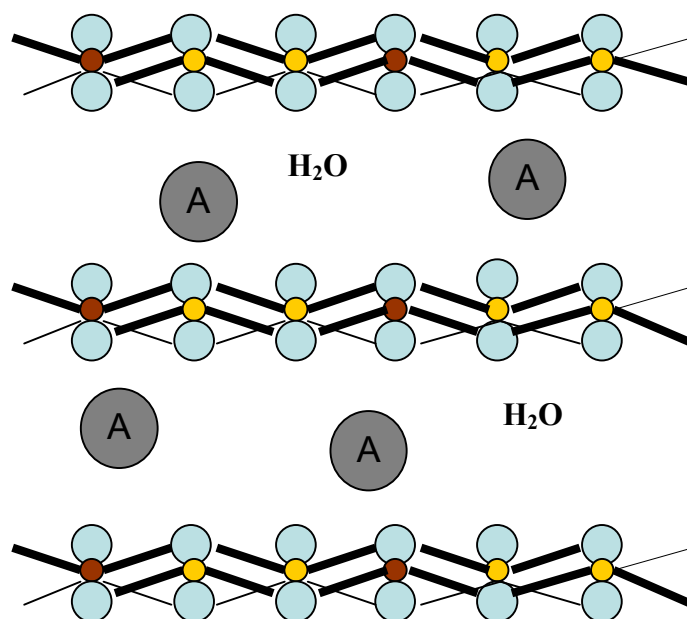


Figure 1: Scheme of LDH structure

Zeolites are microporous crystalline solids with well-defined structures. Naturally occurring zeolites are hydrated aluminosilicate materials with high cation exchange capacity (Shareef. 2009)

MATERIALS AND METHODS

All the chemicals were obtained from Aldrich, Fluka and Riedel - de Häen, with $\geq 98\%$ of ground substance, and used as received (Tedim 2010).

In the present work, different types of LDHs, containing anionic corrosion inhibitors are prepared using two different routes: anion-exchange and calcination of the LDH precursor. The procedures are described in the literature (Tedim J. 2010, Newman 1998).

Metal cations Ca^{2+} , Ce^{3+} , Zn^{2+} are intercalated into bentonite clays according to procedures described elsewhere (Loveridge 2006).

The synthesized powders are analysed by X-ray diffraction, electron microscopies (SEM, TEM), Fourier transform infrared spectroscopy (FTIR), and optical techniques for determination of particle size distributions.

The release of inhibitors is investigated by HPLC and UV-visible spectrophotometry under different conditions relevant for corrosion, including pH changes and presence of aggressive species such as chlorides.

RESULTS AND DISCUSSION

XRD results show that the prepared LDHs are crystalline, single-phased systems. Position of diffraction peaks at low 2 Theta angles can be correlated with size and orientation of guest anions within the LDH galleries.

Moreover, FTIR bands (Figure 2) can be assigned to vibration modes associated with the presence of various groups in the LDH structure (metal – oxygen groups in LDH sheets, hydroxyl groups from layers and intercalated anions and water).

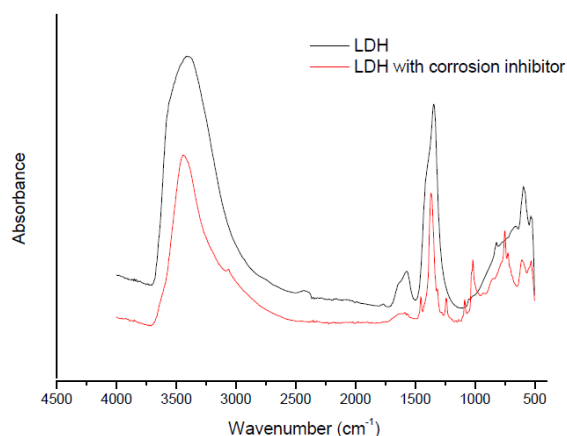


Figure 2: FTIR spectra of prepared LDHs

SEM results (Figure 3) show that LDHs have a plate-like morphology, with tendency for agglomeration.

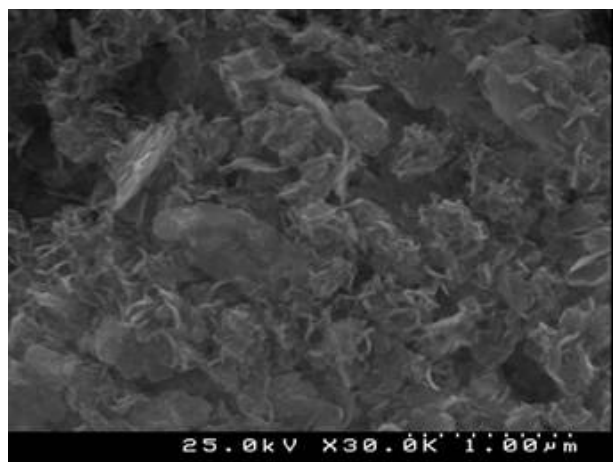


Figure 3: SEM image of LDH intercalated with corrosion inhibitor

The study of the release of anions and cations with corrosion inhibiting properties will be performed using spectrophotometric and chromatographic methods (Figure 4-preliminary results).

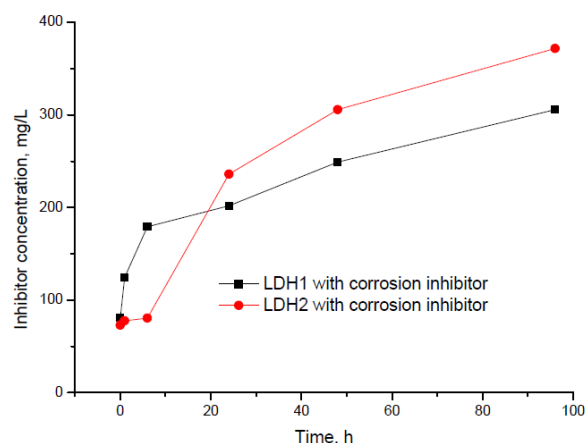


Figure 4: Kinetic curves of corrosion inhibitor release in 0.05 M NaCl solution

CONCLUSIONS

In the present work, dependences between type and concentration of active species and their release ability from hosting structures under different conditions will be defined.

The results will show that the extent of released species is not only a function of the type of inhibitors (density of charge) and structure of the hosting material (loading capacity and ion-exchange ability), but also of the experimental conditions (concentration of corrosion-relevant species in the environment and pH).

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