

Beyond solution corrosion inhibitors tests: Evaluating the smart ion-exchange performance of Ca—Al LDH pigments within organic coatings[☆]

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ABSTRACT

This study proposes a novel quantitative methodology to investigate the in situ release kinetics and barrier properties of “smart” ion-exchange pigments within organic coatings, addressing a critical methodological gap in active corrosion monitoring. Hydrothermally synthesized calcium-aluminum layered double hydroxide (LDH) nanocontainers were intercalated with disodium sebacate (SB) inhibitor, yielding high-aspect-ratio (9.76) hexagonal platelets with a total inhibitor payload of 50 wt%. Thermogravimetric analysis confirmed exceptional thermal stability up to 700 °C driven by interlayer host-guest interactions. In aqueous solution, chloride scavenging followed a Langmuir chemisorption isotherm ($R^2 > 0.98$) with near-instantaneous, diffusion-limited exchange kinetics.

When incorporated into free-standing bilayer acrylic films using a custom two-chamber diffusion cell, the hybrid LDH/Seb²⁻ system effectively mitigated the filler-induced defectivity observed in traditional nitrate-LDH counterparts. Total organic carbon and potentiometric monitoring revealed a highly synchronized, coupled mechanism: the active entrapment of permeating chlorides within the inorganic galleries simultaneously triggered a controlled, sigmoidal delivery of the organic inhibitor to the simulated substrate interface. Unlike free-SB controls that exhibited a detrimental “burst release,” the hybrid nanocontainers provided a gradual supply of inhibitor (55 ppm/cm² after 28 days). Crucially, the intercalated dicarboxylate provided a structural pillaring effect that stabilized the Ca—Al framework against re-dissolution, ensuring permanent halide immobilization. Confining the active pigments within the primer layer beneath an unpigmented top-coat maximized the environment-to-interface delivery efficiency while preventing wasteful external leaching, demonstrating a highly optimized smart coating architecture for long-term active corrosion protection.

1. Introduction

Corrosion-related degradation of metallic structures represents a persistent global issue, imposing substantial economic burdens and raising significant safety concerns across industrial, architectural, and transport sectors [1,2]. While organic coatings traditionally serve as the primary defense, offering passive barrier protection by limiting the ingress of aggressive species (such as water, oxygen, and chlorides), the inevitable mechanical damage or localized failure of the polymer matrix initiates corrosion at the metal/coating interface. This vulnerability necessitates a strategic transition from purely passive defense mechanisms to advanced active corrosion protection strategies.

Recent advancements focus on engineering “smart” or responsive coatings capable of delivering active agents directly to the site of damage. This approach involves incorporating smart pigments or nanocontainers, materials designed to encapsulate corrosion inhibitors and release them upon the detection of an environmental trigger [3,4]. The fundamental principle of ‘on-demand’ delivery relies on safeguarding the active agents within a protective host architecture, preventing premature leaching while ensuring localized, fast-responsive release when stimulated by specific chemical or physical changes [5]. Depending on the carrier material, this mechanism can follow different pathways [5]. For instance, polymeric micro/nanospheres can achieve triggered delivery via mechanical rupture or shell degradation under physical stress

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or localized pH variations [3,6]. Alternatively, advanced porous architectures, such as mesoporous silica [7], zeolites [8], and Metal-Organic Frameworks (MOFs) [9], exploit reversible diffusion and molecular gating effects within highly ordered crystalline networks to trap and selectively release inhibitors upon exposure to target chemical cues, including pH shifts or the presence of specific ions.

Among the most investigated and effective smart pigments are Layered Double Hydroxides (LDHs). These hydrotalcite-like compounds possess a positively charged hydroxide layer structure, allowing them to host various anionic corrosion inhibitors in their interlayers [10,11]. Structurally, these materials consist of brucite-like octahedral sheets where the isomorphic substitution of divalent cations by trivalent ones generates a net positive surface charge, which is neutralized by the presence of exchangeable anions and water molecules within the hydrated interlayer galleries. This unique architecture not only provides a reservoir for inhibitors but also enables a highly controlled ion-exchange mechanism driven by the presence of aggressive species like chlorides [12].

This active protection is governed by the anion exchange mechanism. Upon the infiltration of aggressive halides, particularly chlorides (Cl^-), the host framework effectively sequesters these species within its galleries, a process that simultaneously triggers the displacement and release of the pre-intercalated inhibitor ions [13,14]. This controlled ion exchange acts as a localized, stimuli-responsive release vehicle, activating the inhibitor precisely when and where the corrosive threat is detected [15,16]. Extensive studies have demonstrated the high capacity of various LDH formulations, including CaAl-LDH, to serve as effective inhibitor reservoirs and chloride entrapment agents [17–19].

In this study, disodium sebacate (SB) was selected for intercalation as sebacate anions (Seb^{2-}) within the CaAl-LDH framework due to its proven efficacy in steel protection and structural compatibility with the host lattice [17,20]. A major challenge in smart coatings is the environmental degradation or premature leaching of organic inhibitors when directly dispersed in the polymer matrix. By encapsulating Seb^{2-} within the LDH galleries, these stability issues are mitigated, effectively shielding the inhibitor until it is needed. The performance of the released dicarboxylate is then governed by its chain length: while longer chains improve surface adsorption, SB's ten-carbon structure ($\text{C}_{10}\text{H}_{16}\text{Na}_2\text{O}_4$) represents an optimal balance between high interfacial hydrophobicity and sufficient solubility, ensuring an immediate and effective active defense upon triggering [21].

In aerated, near-neutral environments, the released Seb^{2-} acts as an effective anodic inhibitor [22,23]. The protection mechanism is twofold: first, Seb^{2-} facilitates a “pore-plugging” effect by promoting the formation of sparingly soluble Fe(III)–carboxylate complexes at oxide layer defects, effectively sealing potential corrosion sites and stabilizing the passive film [24,25]. Second, in the presence of aggressive species like chlorides, Seb^{2-} hinders the anodic dissolution of iron by preventing the formation of soluble chloride complexes, instead favoring the development of protective surface deposits that limit further metal solubility [26]. Furthermore, the intercalation of these voluminous Seb^{2-} may exert a stabilizing effect on the LDH lamellar framework, enhancing structural regularity compared to simple nitrate-intercalated precursors. Finally, the use of long-chain anions like Seb^{2-} represents a strategic approach to enhance the compatibility between the LDH filler and the organic polymer matrix, promoting better particle dispersion and improving the overall stability of the resulting nanocomposite coating [27].

Despite the compelling evidence confirming the enhanced anti-corrosion performance afforded by these smart systems, a critical methodological gap severely limits the rational development and optimization of such coatings: the lack of a reliable, quantitative procedure for measuring inhibitor release kinetics in situ at the actual coating/substrate interface [28,29]. Current experimental campaigns typically rely on: (i) testing the bare inhibitor in solution, which fails to replicate the restrictive environment of the polymer matrix; or (ii)

electrochemical measurements on coated substrates (e.g., open circuit potential, impedance spectroscopy, polarization curves). While the latter electrochemical methods provide valuable quantitative insights into interfacial property changes, including the calculation of surface coverage, inhibitor adsorption isotherms, and protective layer thickness derived from double layer capacitance and distinct time constants, they inherently monitor the net consequences of protection at the metal surface. Consequently, a significant analytical challenge remains in resolving the structural mismatch between the absolute dose of inhibitor migrating through the polymer matrix and the exact fraction that undergoes chemisorption or local secondary reactions with the substrate and electrolyte ions. This underscores the necessity of viewing electrochemical interface testing and mass-transport monitoring as complementary frameworks: while traditional electrochemical parameters quantify the localized interfacial binding efficiency, they cannot independently measure the underlying mass-flux kinetics of the active species during their migration through the binder matrix [30].

Addressing this lacuna is paramount for advancing the field. This study proposes a novel experimental methodology designed to accurately monitor and quantify the mass of the organic inhibitor released from CaAl-LDH smart pigments. Our approach isolates the inhibitor release process from the electrochemical response of the substrate by utilizing a custom-designed two-chamber diffusion cell, which is an adaptation of the setup initially proposed by other authors [31]. A similar potentiometric approach, primarily focused on monitoring chloride permeation and entrapment within free-standing films, was previously validated by Tedim et al. for ZnAl-based LDH nanocontainers [28]. The polymer coating, prepared as a free-standing film, separates the aggressive exterior solution from a collection solution that accurately models the environment at the metal/paint interface. Inhibitor molecules released into the collection chamber are then precisely quantified using Total Organic Carbon (TOC) analysis, while the simultaneous chloride capture is monitored via potentiometry. By leveraging these advanced quantitative procedures, this work provides a robust and necessary tool to determine the true release efficiency and kinetics of LDH nanocontainers, offering a clear pathway for the science-based formulation of high-performance active coatings. It is important to emphasize that isolating the coating as a free-standing matrix is a mandatory requirement to decouple the transport phenomena from the electrochemical contribution of a corroding metal substrate, thereby transforming qualitative interface evaluation into an exact, chemically resolved transport model. Specifically, the key scientific problem addressed herein revolves around the current inability to establish a simultaneous, real-time mass balance between the aggressive halide influx and the corresponding protective counter-flux at the actual coating/substrate boundary. The core innovation of this work rests on the development of a synchronized electrochemical and TOC monitoring framework. By decoupling the mass transport kinetics from the substrate's contribution, this study provides the first quantitative validation of a coupled “scavenging-release” mechanism within a bilayer protective matrix, transforming empirical barrier evaluation into a transport-phenomena model.

2. Materials and methods

2.1. Hydrothermal synthesis of Ca–Al LDH and LDH/ Seb^{2-} hybrid pigments

CaAl-LDH pigments were synthesized via a hydrothermal route. Two precursor solutions were prepared: Solution A, containing 6.25 g of NaOH and 9.1 g of NaNO_3 in 44 mL of demineralized water; and Solution B, containing 11.7 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 17 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in 80 mL of demineralized water. Both solutions were sonicated to ensure complete dissolution. To minimize carbonate contamination, Solution A was purged with N_2 for 10 min under magnetic stirring before the addition of Solution B. Solution B was then added dropwise into Solution

A under continuous N_2 bubbling (reaching a pH of 10.5 at room temperature). The temperature was stepwise increased to 80 °C and maintained for 1 h. The resulting suspension was centrifuged (4500 rpm, 2 min), washed twice with demineralized water and twice with acetone to isolate the solid phase. The product was dried at 40 °C for 24 h and ground into a fine powder. Similarly, the hybrid pigment (LDH/Seb²⁻) was synthesized following the identical protocol, replacing $NaNO_3$ in Solution A with 7 g of SB to facilitate the intercalation of the organic inhibitor. An excess of organic inhibitor was employed to ensure effective intercalation. All chemical reagents used throughout the experimental campaign were of analytical grade and were purchased from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany).

2.2. Physicochemical and morphological characterization

The crystalline structure of the powders was analyzed via X-ray diffraction (XRD) using an X'Pert High Score diffractometer (Rigaku, Japan) with a Cu K α source ($\lambda = 1.54056 \text{ \AA}$), operated at 30 kV and 10 mA. Phase identification was performed by comparison with the reference pattern JCPDS #87-0493, corresponding to CaAl-LDH. Surface morphology was examined by scanning electron microscopy (SEM, JSM-IT300, JEOL, Japan). Thermal stability and inhibitor content were evaluated through thermogravimetric analysis (TGA) (by NETZSCH STA449 F3) by heating 15 mg samples from 30 °C to 900 °C at 20 °C/min under N_2 flux (50 mL/min). Additionally, the anion-exchange capacity was investigated by dispersing the LDH and LDH/Seb²⁻ pigments in a 0.5 M NaCl solution under continuous stirring for 48 h; the resulting exchanged phases were washed with demineralized water, dried following the post-synthesis protocol, and subsequently analyzed via XRD and TGA to evaluate the structural and thermal changes associated with the chloride capture.

2.3. Formulation and preparation of free-standing acrylic films

Free-standing films were prepared using a clear water-borne acrylic paint (V33 Group, Domblans, France) to facilitate rapid electrolyte permeation. The LDH/Seb²⁻ pigments were added at 5 wt% loading (referring to wet paint). To ensure uniform distribution, the powders were first sonicated in 5 mL of demineralized water (UP400S Ultrasonic Processor, Hielscher) before being incorporated into the resin.

For comparison purposes, control samples containing only the free SB inhibitor (not intercalated in LDHs) were also prepared. These films were formulated with a 2.5 wt% loading of SB. This concentration was chosen to be comparable to the actual amount of inhibitor present in the LDH/Seb²⁻-pigmented coatings, as the Seb²⁻ content in the synthesized LDH particles was estimated to be approximately 50 wt% via TGA analysis and in a previous study [20].

The mixture was deposited onto a polyethylene support using an automatic spreader and dried overnight. A topcoat was applied using a similar procedure to seal potential defects and reach a final overall coating thickness of 150 μm . Once dried, the films were peeled off, cut

into 2 cm diameter discs, and characterized by thickness measurements (Karl Deutsch Leptoskop) before immersion tests.

The resulting discs were mounted in a diffusion cell (Fig. 1) to investigate the ion-exchange and permeation processes. The side corresponding to the topcoat was exposed to a 0.1 M NaCl solution, simulating an aggressive external environment. Conversely, the inner side was kept in contact with a chloride-free 0.1 M Na_2SO_4 solution to simulate the coating/substrate interface. The sulphate solution was employed to provide a stable, non-interfering ionic background capable of balancing the charge of the chloride and inhibitor ions permeating through the film, mimicking the role of counter-cations during electrolyte transport. It must be emphasized that while a neutral 0.1 M Na_2SO_4 solution cannot replicate the highly dynamic chemical features of a real metallic interface, such as localized pH shifts and the release of hydrolysable metallic cations, this simplified electrolyte is a mandatory requirement for this transport-focused setup. Introducing active metallic cations (e.g., Fe^{2+} or Fe^{3+}) would trigger the immediate precipitation of insoluble metal-carboxylate complexes, depleting the dissolved inhibitor concentration and rendering its quantification via TOC impossible. Therefore, this configuration is designed to isolate the baseline mass-transport kinetics of the active species while continuously maintaining electroneutrality via sodium counter-ion migration, without attempting to simulate the complex secondary reaction kinetics occurring at an active corroding substrate [28]. Specifically, as Cl^- or released Seb²⁻ anions migrate through the polymer matrix, their transport is coupled with the migration of Na^+ counter-ions from the common sodium-rich reservoirs on both sides, ensuring that local electroneutrality is continuously maintained without establishing artificial diffusion potentials.

Furthermore, sodium sulphate represents a highly effective trade-off: the sulphate anion is sufficiently large to minimize aggressive competitive exchange with the intercalated Seb²⁻ within the galleries, ensuring that the measured smart response is exclusively driven by the chloride-pigment interaction. A thermodynamic non-interference is supported by the established LDH anion exchange selectivity series ($CO_3^{2-} > Seb^{2-} > OH^- > F^- > Cl^- > NO_3^- > SO_4^{2-}$) [12,32].

While the difference in ionic strength between the 0.1 M NaCl chamber ($I = 0.1 \text{ M}$) and the 0.1 M Na_2SO_4 chamber ($I = 0.3 \text{ M}$) slightly alters the local ion activity coefficients, the overall transport rates remain heavily dominated by the high physical restrictiveness of the crosslinked binder network and anion concentration gradients rather than the thermodynamic properties of the bulk boundary solutions.

During immersion, the concentration of permeated chlorides and the released organic carbon (attributable to both the binder degradation and the inhibitor release) were periodically measured on both sides of the cell (up to 28 days). Since the organic carbon measurement is a destructive technique, at least three replicates were tested for each sampling time to ensure reproducibility.

2.4. Quantitative evaluation of chloride scavenging and inhibitor release

The chloride capture capacity of the pigments was evaluated through

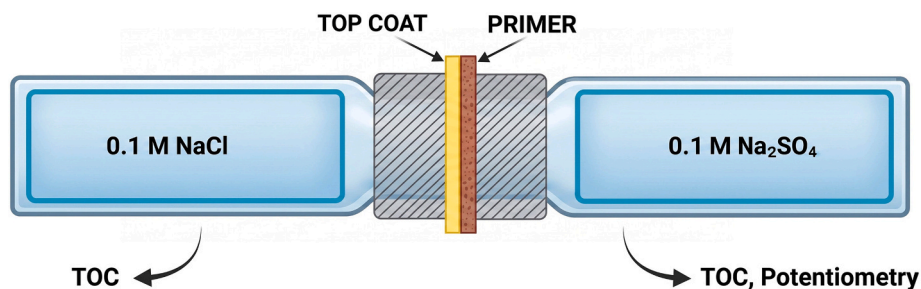


Fig. 1. Experimental setup of the two-chamber permeation cell. The bilayer free-standing coating separates the aggressive 0.1 M NaCl medium from the chloride-free 0.1 M Na_2SO_4 receptor solution. Sampling pathways for Total Organic Carbon (TOC) to measure external inhibitor leakage (left) and combined TOC/potentiometry to monitor interface-directed inhibitor release and chloride permeation (right) are highlighted.

Open Circuit Potentiometry (OCP). A custom-made ion-selective electrode (ISE) was prepared as the working electrode by immersing a pure silver bar in sodium hypochlorite for 10 min. This was paired with an Ag/AgCl 3 M KCl reference electrode and connected to an Autolab 302 N potentiostat. Calibration was performed before each session using known chloride-containing solutions (10, 100, and 1000 ppm Cl^-). To account for the influence of the ionic strength and the presence of interfering ions, two distinct calibration curves were recorded using NaCl: one in ultrapure water and another in a 0.1 M Na_2SO_4 background solution. The latter was specifically used to ensure accurate measurements on the collection side of the permeation cell, which contained the same sulfate electrolyte. Calibration curves are reported in Fig. 2.

For entrapment tests of particles dispersed in a liquid environment, pigments (3 g/L) were dispersed in ultrapure water and sonicated. Known amounts of NaCl were added to reach nominal concentrations of 35, 175, 350, and 1000 ppm Cl^- . After 5 min of stirring (time sufficient to consider the anion-exchange process to be completed), the residual Cl^- concentration was measured, and the amount entrapped was estimated by difference.

Inhibitor release of Seb^{2-} from the organic layer was assessed via Total Organic Carbon (TOC) analysis (Shimadzu TOC-L, Japan) after different times of immersion in the permeation cell. Measurements were performed on both sides of the cell to check both for the inhibitor reaching the interface-simulating cell and the leakage in the surrounding environment. For each immersion time, 3 replicates consisting of 3 different free-film samples were tested. The net organic carbon signal ($C_{\text{net, ppmC}}$) attributable exclusively to the released organic inhibitor was obtained by subtracting the baseline organic carbon contribution of the neat polymer degradation ($C_{\text{Blank, ppmC}}$) from the total measured organic carbon ($C_{\text{Total, ppmC}}$), Eq. (1):

$$C_{\text{net, ppmC}} = C_{\text{Total, ppmC}} - C_{\text{Blank, ppmC}} \quad (1)$$

To convert the net carbon concentration into the effective mass of active Seb^{2-} ($M = 200.23 \text{ g/mol}$), we apply a conversion factor derived from the exact mass fraction of carbon within the Seb^{2-} structure ($120.11 \text{ g C} / 200.23 \text{ g Seb}^{2-} = 0.5998$, i.e., 59.98 wt%C), Eq. (2):

$$C_{\text{net, Seb}^{2-}} = \frac{C_{\text{net, ppmC}}}{0.5998} \quad (2)$$

All release profiles are normalized over the exposed film surface area.

3. Results and discussion

3.1. Surface morphology

The morphology and particle size of the synthesized LDH and LDH/ Seb^{2-} pigments were evaluated via SEM. Secondary electron imaging was prioritized to achieve superior topographical contrast, essential for characterizing the surface features and edges of the powders. As shown in Fig. 3, both pigments exhibit the characteristic plate-like habit typical of hydrotalcite-like structures.

The pristine nitrate-intercalated LDH particles (Fig. 3a) show well-defined hexagonal habits with sharp, delineated sides. Image analysis performed via ImageJ allowed for a precise quantification of the dimensions (Table 1), revealing an average particle width of $1.45 \pm 0.20 \mu\text{m}$ and a thickness of $0.354 \pm 0.09 \mu\text{m}$. These results are in excellent agreement with the morphological characteristics reported in previous literature for CaAl-LDH systems [33,34].

Upon intercalation of the organic inhibitor, the LDH/ Seb^{2-} hybrid pigment (Fig. 3b) maintains its lamellar integrity, although a noticeable shift in dimensions is observed. The presence of the voluminous Seb^{2-} during the synthesis/intercalation stage appears to influence the crystal growth kinetics. Specifically, the platelets undergo a lateral expansion (reaching $2.05 \pm 0.21 \mu\text{m}$) coupled with a reduction in thickness ($0.21 \pm 0.07 \mu\text{m}$). This shift toward a higher aspect ratio (ratio between the mean lateral width and the particle thickness) is likely due to the Seb^{2-} acting as capping agents or surface-active species that selectively adsorb onto the (001) basal planes. By hindering the vertical stacking regularity while allowing lateral growth, the organic chains promote the formation of wider, thinner flakes, which is a significant functional advantage for creating a tortuous diffusion path in coatings [35]. The resulting high aspect ratio of the LDH/ Seb^{2-} platelets (~ 9.76), significantly higher than that of the pristine nitrate form (~ 4.09), constitutes a key functional advantage for coating applications. Such a morphological configuration is instrumental in promoting a 'tortuous path' effect within the polymer matrix, which enhances the passive barrier properties by forcing aggressive species to follow a more convoluted diffusion path. Simultaneously, the increased lateral dimension provides an extensive active surface area, which is essential for ensuring the rapid and efficient ion exchange kinetics required for active corrosion protection.

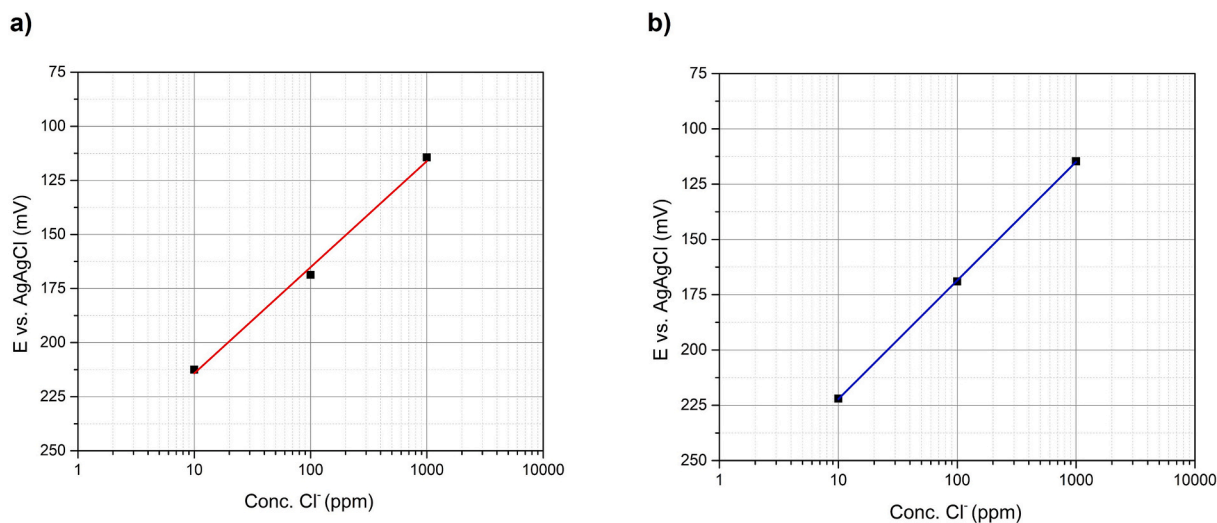


Fig. 2. Potentiometric calibration of the homemade chloride ion-selective electrode (ISE) in different electrolytes. (a) Calibration curve obtained using NaCl standards (10, 100, and 1000 ppm Cl^-) in ultrapure water. (b) Calibration curve recorded using the same chloride standards in a 0.1 M Na_2SO_4 background solution.

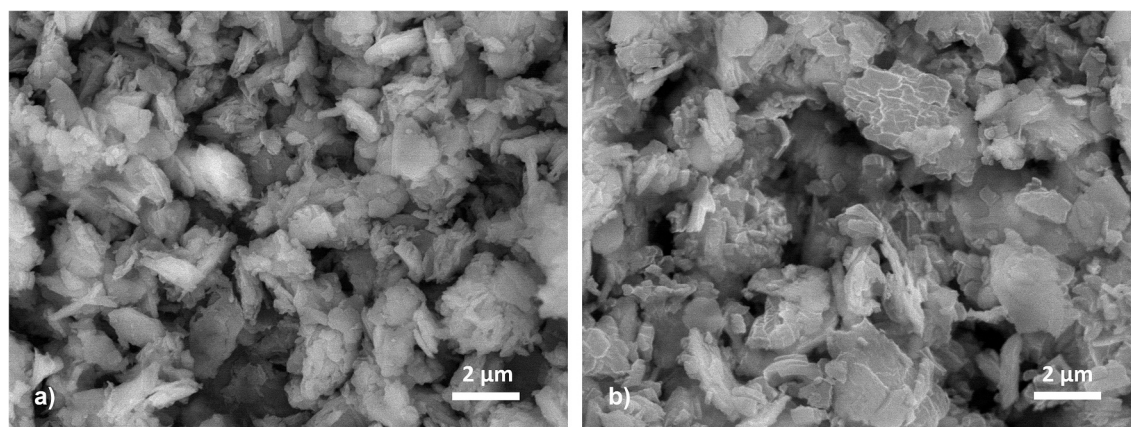


Fig. 3. SEM micrographs of the synthesized pigments. (a) Pristine nitrate-intercalated CaAl-LDH showing characteristic hexagonal platelets with well-defined edges. (b) Hybrid LDH/Seb²⁻ pigments exhibiting the preserved lamellar morphology and a noticeable lateral expansion following the intercalation of the voluminous Seb²⁻ anions.

Table 1

Morphological parameters of the synthesized LDH pigments were determined via SEM image analysis.

Pigment	Width (μm)	Thickness (μm)	Aspect ratio
LDH	1.45 ± 0.20	0.354 ± 0.09	4.09 ± 1.2
LDH/Seb ²⁻	2.05 ± 0.21	0.210 ± 0.07	9.76 ± 3.4

3.2. Crystalline structure and anionic exchange efficiency (XRD)

The crystalline structure and anion intercalation of the synthesized pigments were evaluated via X-ray diffraction, as illustrated in the full-range patterns (Fig. 4a) and the low-angle zoom focusing on the basal reflections (Fig. 4b). The pristine LDH (red line) exhibits characteristic (003) basal reflections centered at $2\theta \approx 9.94^\circ$ ($d = 0.89$ nm), consistent with the nitrate-intercalated CaAl-LDH phase (JCPDS #87-0493). The observable splitting of the nitrate peak, with components at 9.8° and 10.2° , is attributed to distinct hydration states or specific anion orientations within the Ca–Al hydroxide interlayer galleries [36,37]. A

minor reflection at 11.0° indicates a slight carbonate-LDH contamination (JCPDS 41-0219), likely arising from residual atmospheric CO_2 during the hydrothermal synthesis and representing a thermodynamically stable fraction that does not participate in the subsequent ion-exchange process [27,38,39].

Upon intercalation of the organic inhibitor, a substantial lattice expansion is observed, with the primary basal reflection shifting to $2\theta \approx 5.61^\circ$, corresponding to a significantly expanded d -spacing of 1.58 nm [20,40,41]. The presence of well-resolved higher-order reflections, specifically (006) at 11.2° , (009) at 16.9° , and (012) at 22° , demonstrates a highly ordered and periodic lamellar stacking [27,42]. Notably, the intercalation of Seb^{2-} appears to exert a stabilizing effect on the lamellar framework [17]; while residual nitrate signals persist, the enhanced definition of the (00 l) series in LDH/ Seb^{2-} suggests superior structural regularity compared to the nitrate-only precursor.

The efficiency of the anionic exchange process is corroborated by the patterns of LDH-Cl⁻ and LDH/Seb²⁻-Cl⁻. Following exposure to an excess of chlorides (0.5 M NaCl), the original reflections from nitrate and Seb²⁻ intercalated phases disappear, being replaced by a dominant (003) reflection at 11.4° (*d* ≈ 0.78 nm). This shift marks the formation of

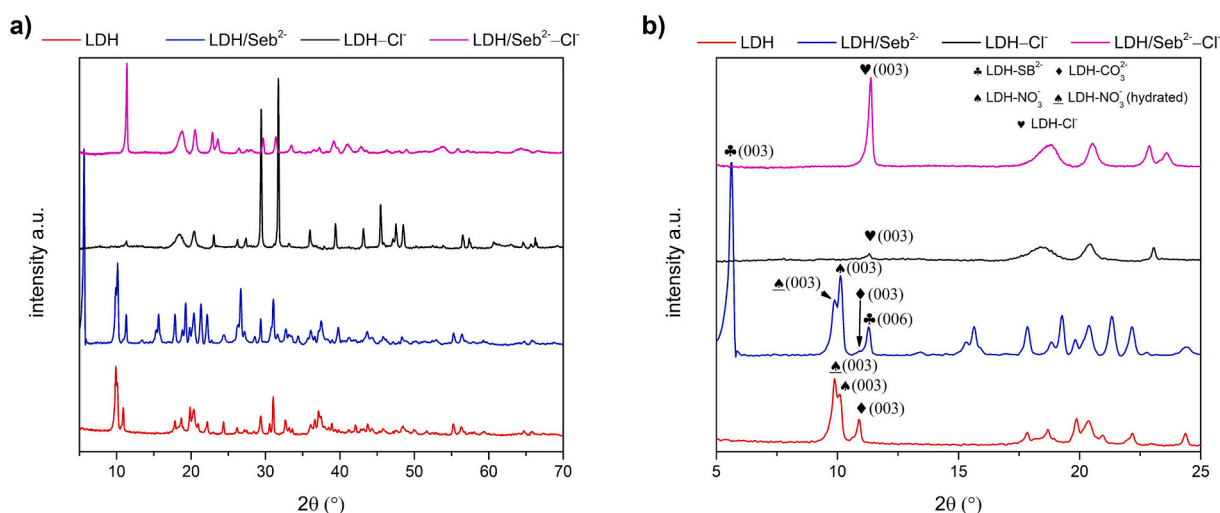


Fig. 4. X-ray diffraction patterns of the synthesized pigments. (a) Full-range XRD patterns (2θ 5–70°) and (b) low-angle zoom (2θ 5–25°) focused on the basal reflections (00 l) of pristine LDH (red), LDH/Seb²⁻ hybrid (blue), and the corresponding chloride-exchanged phases, LDH-Cl⁻ (black) and LDH/Seb²⁻-Cl⁻ (magenta). The shift of the (003) reflection in LDH/Seb²⁻ to lower angles (5.61°) indicates successful intercalation of Seb²⁻, while the disappearance of precursor peaks and the emergence of the monochloroaluminate reflection at 11.4° in the exchanged samples confirm the efficiency of the anion-exchange process. Side phases associated with Portlandite and Calcite are also identified. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Friedel's salt (monochloroaluminate, JCPDS 19-0202) [37,43], representing the LDH structure that has successfully captured and immobilized chloride ions from the environment. The marked increase in peak intensity and the sharpening of the structural reflections at $2\theta = 31.6^\circ$ – 31.8° (corresponding to the (110) and (112) diffraction planes of Friedel's salt, $d \approx 0.28$ nm, validated against Renaudin's CIF database and JCPDS 19-0202 [37]) suggest a chloride-induced recrystallization or ordering process, leading to enhanced crystallinity [44].

The lower intensity of the (003) reflection for the chloride-exchanged nitrate-LDH, compared to the LDH/Seb²⁻-Cl⁻ counterpart, suggests a loss of long-range crystalline order, likely linked to the lower structural stability of the Ca–Al framework when initially intercalated with labile nitrate anions. This behavior is strongly related to the well-known tendency of Ca–Al LDH structures to undergo partial dissolution and structural relaxation when exposed to neutral aqueous environments, a phenomenon strictly governed by local pH variations and the nature of the chemical buffer as established in previous work [20]. While plain nitrate precursors offer limited protection against framework degradation, the intercalation of bulky organic Seb²⁻ anions exerts a powerful screening and pillaring effect on the inorganic sheets. This structural stabilization effectively mitigates local dissolution pathways and locks the aggressive halide species permanently within the crystalline galleries, as confirmed by the superior long-range order and macroscopic structural integrity observed for the hybrid system.

Regarding parasitic phases (corresponding patterns reported in Fig. S1 in the Supplementary Material), all synthesized powders exhibit reflections associated with Portlandite (Ca(OH)₂ JCPDS 04-0733, (100) at 18.1 degrees) and Calcite (CaCO₃ JCPDS 05-0586, (104) at 29.4 degrees), which match the included reference patterns [39,45]. The persistence of these side phases throughout the ion-exchange process indicates they are stable by-products resulting from the high reactivity of the calcium precursors. In the chloride-exchanged samples, the signal at 29.4° is still attributed to the (104) reflection of the calcite by-product, making it one of the tallest peaks alongside the primary (003) basal reflection of Friedel's salt at 11.4° and the sharp structural reflections of the chlorinated phase in the 31–32° range.

While the XRD shift confirms the successful intercalation of Seb²⁻ into the LDH galleries, it is worth noting that a secondary fraction of the inhibitor may be associated with the parasitic phases. Due to the high surface reactivity of Portlandite and Calcite, a portion of the total Seb²⁻ could be adsorbed onto their surfaces via surface complexation. This non-intercalated fraction, although minor, might contribute to an initial rapid release observed in the TOC profiles, acting in synergy with the ion-exchange mechanism of the LDH host.

To provide a more rigorous assessment of the pigment composition, a semi-quantitative phase analysis was conducted by integrating the net areas of the diagnostic reflections for each phase (Table 2). In the pristine system (LDH), the nitrate-intercalated phase represents the dominant component (77.2 wt%), while a secondary reflection of carbonate-LDH (LDH-CO₃²⁻) phase accounts for 5.9 wt%. The remaining

composition is attributed to external parasitic phases, namely calcite (12.5 wt%) and portlandite (4.4 wt%). In the hybrid system, the quantitative distribution confirms a high intercalation efficiency, with the expanded LDH/Seb²⁻ phase accounting for 51.5 wt% of the total powder. The residual LDH fraction (34.1 wt%) comprises unexchanged nitrates (LDH-NO₃⁻) and carbonate domains (LDH-CO₃²⁻), which represent 'dead' sites thermodynamically locked by carbonate ions. When accounting for these non-reactive domains, the phase distribution reflects an exchange of approximately 60% of available sites (calculated as the ratio of the newly intercalated LDH/Seb²⁻ phase to the total potentially active framework: 51.5 wt% / [51.5 wt% + 34.1 wt%]). Finally, stable parasitic phases account for the remaining 14.4 wt%, providing a supplementary alkaline buffer. The comparison between the two systems reveals a significant reduction in the external calcite fraction within the hybrid pigment (6.0 wt% vs 12.5 wt%), suggesting that the bulky organic Seb²⁻ chains provide a shielding effect against further atmospheric carbonation. Consequently, the limited competition of carbonate species for the host's active sites safeguards the structural integrity of the nanocontainers, ensuring a high effective ion-exchange capacity for responsive chloride sequestration.

3.3. Thermal stability and host-guest interactions

The thermal behavior and composition of the synthesized pigments were evaluated through thermogravimetric analysis (TGA). The resulting profiles for pristine LDH, hybrid LDH/Seb²⁻, and pure SB, alongside the chloride-exchanged phases, are illustrated in Fig. 5.

The thermal degradation of the CaAl-LDH framework typically proceeds through three main stages. Below 150 °C, all samples undergo an initial mass loss corresponding to the removal of physisorbed water and interlayer hydration molecules [46,47]. For the nitrate-intercalated LDH (red solid line), a second significant event occurs between 150 °C and 350 °C, involving the dehydroxylation of the brucite-like layers and the simultaneous decomposition of NO₃⁻ anions into volatile nitrogen oxides (NO_x) [17,48]. The subsequent mass loss drop observed in the 450–600 °C region for this pristine system corresponds to the terminal decomposition and evacuation of the residual interlayer nitrate groups into volatile nitrogen oxides, overlapping with the final loss of structural hydroxyl groups. This terminal thermal event triggers the irreversible collapse of the lamellar hydrotalcite framework, leading to the subsequent phase transformation into stable mixed calcium-aluminum oxides [49].

The LDH/Seb²⁻ hybrid pigment (blue solid line) exhibits a distinct multi-step decomposition pattern compared to both the unfunctionalized matrix and the free salt. While pure SB (black line) degrades completely in a single, abrupt step between 450 °C and 550 °C, the LDH/Seb²⁻ pigment displays a prolonged, two-stage organic degradation profile. Following initial physisorbed water release below 200 °C and a minor loss event between 200 °C and 300 °C, attributable to residual unexchanged NO₃⁻ anion decomposition and early Al-OH

Table 2

Semi-quantitative phase composition (wt%) of the pristine LDH and hybrid LDH/Seb²⁻ pigments. Values were determined via XRD peak area integration using a modified Reference Intensity Ratio (RIR) approach. The d-spacing values for the (003) basal reflections and main parasitic signals are reported for structural comparison. For the LDH/Seb²⁻ system, the residual fraction includes unexchanged nitrate-LDH (LDH-NO₃⁻) and persistent LDH-carbonate domains (LDH-CO₃²⁻).

Phase	Reflection (hkl)	2θ position (°)	d-spacing (nm)	Reference	LDH (wt%)	LDH/Seb ²⁻ (wt%)
LDH-NO ₃ ⁻	(003)	10.34	0.86	JCPDS 87-0493	77.2	30.1
LDH-Seb ²⁻	(003)	5.61	1.57	Basal expansion [20]	–	51.5
LDH-CO ₃ ²⁻	(003)	10.9–11.0	0.80	JCPDS 41-0219	5.9	4.0
Portlandite	(100)	18.1	0.49 ^a	JCPDS 04-0733	4.4	8.4
Calcite	(104)	29.4	0.30 ^a	JCPDS 05-0586	12.5	6.0
Friedel's salt	(003)	11.4	0.78 ^b	JCPDS 19-0202	— ^b	— ^b

^a For non-lamellar secondary phases (Portlandite and Calcite), d-spacing values refer to the characteristic interplanar distances of the main crystallographic planes (e.g., (104) for Calcite and (001) for Portlandite) used for phase identification and fingerprinting against ICDD standards, rather than being indicative of interlayer expansion.

^b Friedel's salt is not present in the as-synthesized powders and forms exclusively upon chloride exchange.

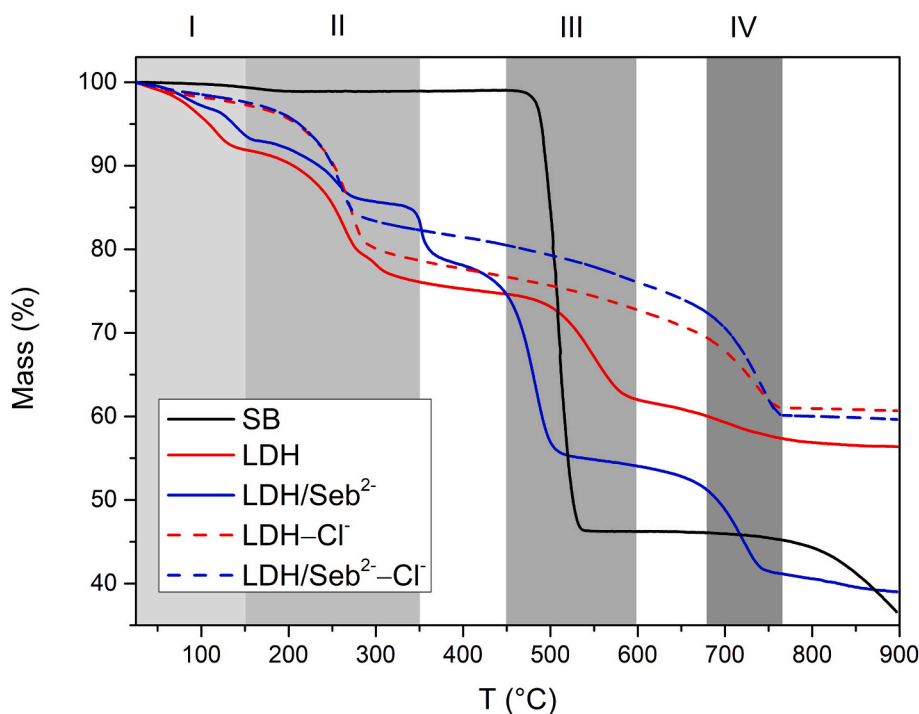


Fig. 5. Thermogravimetric (TGA) profiles of the synthesized pigments before (solid lines) and after (dotted lines) 48 h chloride exchange, including pure disodium sebacate (SB, black), pristine LDH (red), and hybrid LDH/Seb²⁻ (blue). The shaded overlays define the four primary temperature regions where distinct decomposition processes occur: (Region I, <150 °C) Initial mass loss corresponding to the removal of physisorbed water and interlayer hydration molecules across all lamellar samples. (Region II, 150–350 °C) Main dehydroxylation of the Ca–Al hydroxide sheets coupled with the initial breakdown of intercalated nitrates into volatile nitrogen oxides for the pristine precursor. (Region III, 450–600 °C) Complete single-step oxidative decomposition of bulk SB (black curve), which corresponds to the degradation of a more labile, surface-complexed Seb²⁻ pool bound through a bidentate chelating mode to Ca²⁺ sites within the hybrid pigment, as well as the terminal evacuation of residual nitrate groups in the pristine framework. (Region IV, 680–760 °C) Final high-temperature window marking the terminal structural collapse, deep dehydroxylation, and phase transformation of the Ca–Al hydrotalcite-like host lattice into stable mixed metal oxides. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dihydroxylation, the organic fraction degrades in two distinct temperature regimes. In addition to a primary loss step in the 450–550 °C range, a secondary mass loss drop is significantly shifted to higher temperatures, in the 680–760 °C window [17].

This high-temperature window marks the intrinsic terminal structural collapse, deep dehydroxylation, and phase transformation of the inorganic Ca–Al hydrotalcite-like framework into mixed oxides [17,20,50]. Because this lattice degradation is a fundamental property of the inorganic host itself, it occurs across all investigated Ca–Al lamellar phases, explaining why the organic-free chloride-exchanged sample (LDH-Cl⁻, Friedel's salt) also exhibits a prominent mass loss in this identical temperature region. For the hybrid LDH/Seb²⁻ pigment, the pyrolytic destruction of the strongly stabilized interlayer Seb²⁻ core (anchored via bidentate bridging to Al³⁺ sheets) electrostatically overlaps with this terminal framework decomposition, confirming an advanced host-guest stabilization effect that shelters the intercalated dicarboxylate up to lattice breakdown.

The quantitative estimation of the intercalated Seb²⁻ content from TGA data requires a careful evaluation of the carbonaceous residue (*char*) formed during the pyrolysis of the organic moiety under nitrogen flux [51,52]. Quantitatively, the estimation of the total Seb²⁻ content (loading) requires accounting for both the intercalated anions and the fraction adsorbed on the external surfaces of the LDH and parasitic phases. Considering the variable carbonaceous residue (*char*), a sensitivity analysis yields a calculated total Seb²⁻ total loading between 41.8 wt% and 66.6 wt%. A representative loading of 50 wt% was adopted for the following research steps, which is in accordance with previous studies employing other techniques [20,23], confirming the superior capacity of CaAl-LDH nanocontainers for organic dicarboxylates. This choice ensures a conservative yet scientifically grounded representation

of the inhibitor reservoir available within the nanocontainers, accounting for the inherent complexity of the organic-inorganic thermal interaction.

Interestingly, comparing this result with the semi-quantitative XRD data reveals a compelling mass balance discrepancy that clarifies the pigment structure. While XRD identifies a 51.5 wt% fraction of the expanded hybrid LDH phase within the total crystalline powder, this crystalline fraction alone cannot account for the massive 50 wt% total Seb²⁻ content estimated via TGA. This mass balance discrepancy suggests the presence of a substantial fraction of surface-adsorbed Seb²⁻, which remains amorphous or highly disordered and is therefore untraceable by conventional X-ray diffraction. Consequently, this synergistic distribution is highly advantageous for active corrosion protection, as it effectively combines a rapid initial inhibitor release from the external surfaces with a sustained, 'smart' on-demand delivery from the interlayer galleries, whose ultimate thermal evacuation merges with the final lattice decomposition profile above 650 °C.

The effectiveness of the ion-exchange process was confirmed by analyzing the powders after 48 h of exposure to 0.5 M NaCl (dotted lines). In both the LDH-Cl⁻ and LDH/Seb²⁻-Cl⁻ samples, the disappearance of mass loss events in the 450–650 °C range demonstrates the successful replacement of the original nitrate and Seb²⁻ anions with chloride ions. The exchanged phases exhibit a simplified profile, with a final mass loss at ~750 °C associated with the structural collapse of the Friedel's salt phase, as identified in the XRD patterns [53,54]. Furthermore, the observed increase in the final residue for the chloride-exchanged samples compared to the starting LDH/Seb²⁻ further corroborates the exchange process: the replacement of the voluminous organic anions with smaller, denser chloride ions leads to a relative enrichment of the stable inorganic oxide phase in the final residue.

3.4. Solution-phase chloride scavenging and sequestration isotherms

To characterize the chloride removal process in aqueous solution, the chloride sequestration isotherms for both pristine LDH and LDH/Seb²⁻ were analyzed to evaluate their entrapment efficiency, revealing a remarkably similar uptake capacity between the two systems. As shown in Fig. 6, the experimental data for chloride removal were modeled using the Langmuir isotherm (Eq. (3)), which provided an excellent fit (R^2 of 0.988 and 0.996, respectively, in Table 3). While the Langmuir equation is conventionally associated with 2D monolayer adsorption on finite identical sites, in this context, it is strictly employed as an effective empirical model to quantify the apparent macroscopic equilibrium. The high correlation coefficient suggests that the overall process kinetics are initially dominated by the rapid saturation of the available exchange sites on the external surface of the LDH platelets. This surface saturation acts as a kinetic bottleneck for the subsequent intracrystalline diffusion [19,54,55]. Indeed, as unequivocally demonstrated by the XRD structural analysis, the actual underlying sequestration mechanism is not restricted to a surface monolayer, but rather involves a 3D volumetric intercalation driven by highly efficient ion-exchange and the subsequent neoformation of a stable crystalline phase (Friedel's salt). Such a volumetric phase transformation facilitates a robust immobilization of the aggressive species. Furthermore, the reaction occurred within tens of seconds and was limited by the diffusion of the anions, indicating that the “trapping” functionality is nearly instantaneous upon chloride contact with the pigment outer surface [56].

$$Q = \frac{K \cdot Q_{\max} \cdot C_{Cl}}{1 + K \cdot C_{Cl}} \quad (3)$$

In the reported non-linear isotherm (Eq. (3)), $Q_{\max}$ represents the maximum apparent entrapment capacity (ppm), and K is the Langmuir adsorption constant, while C_{Cl} and Q denote the equilibrium chloride concentration and the entrapped fraction, respectively [57–60]. $Q_{\max}$ reached 173.9 ppm for the nitrate-based LDH and 194.2 ppm for LDH/Seb²⁻, confirming that the structural modification does not compromise the framework's intrinsic ability to trap halides. This parity in performance indicates that the absolute entrapment capacity is primarily determined by the density of available positively charged sites on the

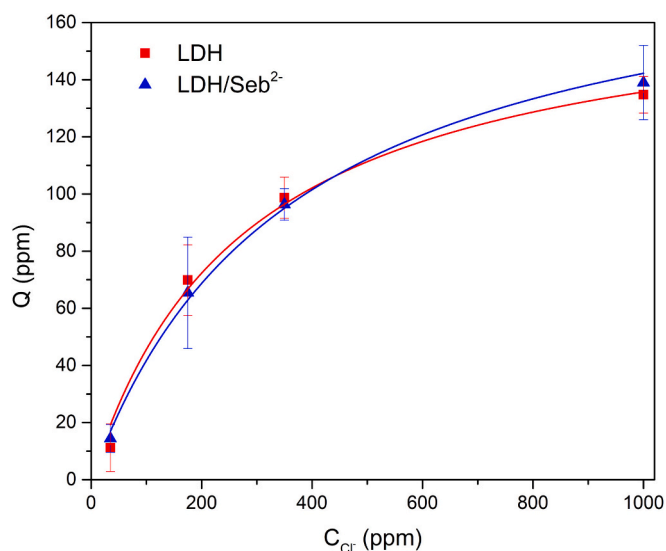


Fig. 6. Chloride entrapment isotherms for pristine CaAl-LDH and LDH/Seb²⁻ pigments. The experimental data points represent the absolute value of entrapped Cl^- (Q) as a function of the initial chlorides available in solution (C_{Cl}). The solid lines indicate the non-linear regression based on the Langmuir adsorption model, showing the high affinity of both lamellar structures for halide sequestration. Error bars represent the standard deviation of at least three independent measurements for each sampling time.

Table 3

Langmuir isotherm fitting parameters for chloride sequestration on CaAl-LDH and LDH/Seb²⁻ samples. $Q_{\max}$ represents the calculated maximum adsorption capacity, K is the Langmuir adsorption constant related to the binding energy, and R^2 denotes the correlation coefficient of the non-linear fit.

Pigment	$Q_{\max}$ (ppm)	K	R^2
LDH	173.9	0.00356	0.988
LDH/Seb ²⁻	194.2	0.00274	0.996

lamellar surfaces rather than the weight percentage of the initial guest anion. While the pristine LDH structure hosts a higher molar quantity of monovalent nitrates, the divalent nature of the Seb²⁻ allows a single anion to balance two positive charges within the interlayer space, effectively equalizing the exchange potential compared to the nitrate-only configuration. Furthermore, structural characterization via XRD confirms that the Seb²⁻ intercalation is partially incomplete, leaving residual nitrates within the LDH/Seb²⁻ interlayers, which actively contribute to the total quantity of sequestered chlorides. The slightly lower Langmuir constant (K) observed for the LDH/Seb²⁻ system (0.00274 compared to 0.00356 for LDH) may be attributed to the increased steric hindrance and diffusion limitations imposed by the bulkier organic chains during the exchange process. Consequently, the integration of organic inhibitors into the CaAl-LDH framework achieves a dual functionality: Seb²⁻-mediated corrosion inhibition and efficient chloride sequestration, without significantly altering the trapping capacity of the inorganic host.

Indeed, the comparative analysis of chloride scavenging performance reveals a fundamental divergence in the long-term stability of the entrapped phases. While both systems exhibit near-instantaneous uptake upon initial contact, real-time potentiometric monitoring (Fig. 7) highlights a “leakage” effect exclusive to the nitrate-precursor system. The gradual increase in chloride activity observed for nitrate-LDH suggests a partial dissolution or structural relaxation of the newly formed Friedel's salt in neutral aqueous media. In contrast, the LDH/Seb²⁻ system maintains a steady-state, indicating that the intercalated Seb²⁻ anions, beyond their role as inhibitors, act as structural “pillars”. This stabilization, corroborated by the higher crystallinity of the (003) reflection in the XRD patterns of the exchanged LDH/Seb²⁻- Cl^- , effectively locks the aggressive species within the galleries, preventing their re-release and ensuring a permanent sequestration of chlorides. Consequently, the integration of organic inhibitors into the CaAl-LDH framework achieves a dual functionality: Seb²⁻-mediated corrosion inhibition and superior stabilization of the entrapped halides.

3.5. Two-chamber diffusion cell: in situ release kinetics and barrier properties

The mass transport properties and the responsive “smart” behavior of the pigmented coatings were investigated using free-standing acrylic films mounted in a custom-designed two-chamber diffusion cell. This experimental configuration allows for the precise evaluation of chloride permeation kinetics and inhibitor release. Fig. 8 presents the cumulative concentration of chlorides permeated into the collection chamber over a 28-day immersion period. The experimental data follow a characteristic sigmoidal progression, modeled using Boltzmann-type fitting. This trend describes a well-defined initial lag phase, representing the time required for the aggressive species to saturate the polymer matrix, followed by a pseudo-steady-state diffusion regime [61].

A critical analysis of the permeation profiles reveals that the incorporation of both free SB and pristine nitrate-LDH leads to a significant increase, about four times, in chloride flux compared to the neat paint (Blank) after 28 days. Crucially, while a fraction of this transport acceleration could be ascribed to initial filler-induced defectivity, a purely physical mismatch at the polymer/particle interface would trigger an

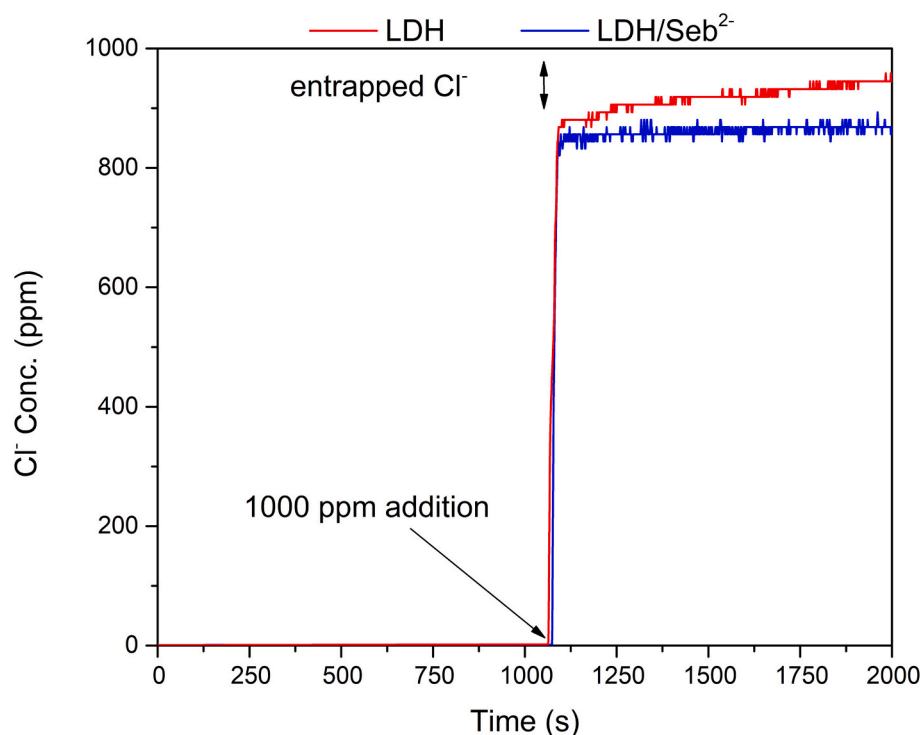


Fig. 7. Real-time evolution of chloride concentration in a 3 g/L LDH/Seb²⁻ aqueous dispersion. Upon the addition of 1000 ppm Cl⁻ (indicated by the arrow), the system exhibits an immediate response, reaching a steady-state. The difference between the nominal added concentration and the measured equilibrium value corresponds to the amount of entrapped chloride ions by the LDH particles.

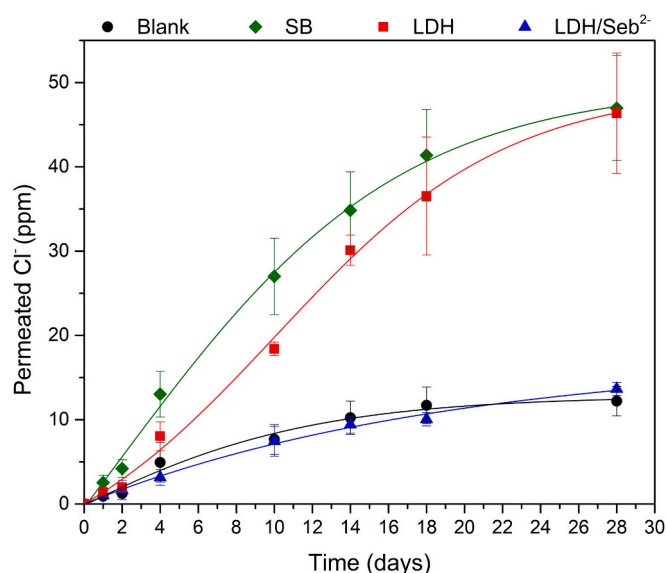


Fig. 8. Permeated Cl⁻ concentration measured in the collection chamber as a function of immersion time. The data compare the chloride transport through free-standing acrylic films: neat resin (Blank), 5 wt% LDH/Seb²⁻-pigmented coating, 5 wt% LDH-pigmented coating, and 2.5 wt% free SB control. The tests were performed in a two-chamber diffusion cell, with the topcoat side exposed to 0.1 M NaCl and the collection side containing 0.1 M Na₂SO₄. The curves illustrate the active chloride scavenging effect of the intercalated LDH pigments compared to the passive barrier of the neat resin and the inhibitor-only control. Error bars represent the standard deviation of at least three independent replicates for each sampling time.

immediate increase in permeation within the first 48 h. Instead, the pristine nitrate-LDH profile diverges significantly only at later

immersion times. This delayed acceleration is directly linked to the progressive chemical degradation of the unstable Ca—Al hydrotalcite-like host matrix when exposed to neutral saline environments.

As halide permeation proceeds, the nitrate-LDH undergoes an anion-exchange process, but the newly formed chlorinated phase is thermodynamically susceptible to partial dissolution and framework relaxation under neutral conditions. This dynamic degradation is corroborated by the post-exchange XRD patterns (Section 3.2), where the chloride-exchanged nitrate precursor (LDH-Cl⁻) exhibits a drastically lower basal reflection intensity, indicating a loss of long-range structural order. The gradual in situ dissolution of the inorganic platelets over long-term exposure creates localized porous pathways and structural micro-voids within the cured acrylic binder, which actively promote and accelerate subsequent chloride transport.

In stark contrast, the LDH/Seb²⁻-Cl⁻ hybrid system remains highly stable. The bulky, hydrophobic aliphatic chains of the intercalated dicarboxylate act as structural pillars and steric shields, preventing the local dissolution of the Ca—Al layers. This stabilization ensures that the crystalline framework remains intact during the phase transition to Friedel's salt, permanently trapping the aggressive species within the galleries without generating conductive ionic pathways, thereby maintaining the baseline barrier properties of the coating throughout the 28-day exposure.

This highly favorable transport trend can be rationalized by considering two synergistic effects: geometric barrier enhancement and interfacial surface modification. Morphologically, the significantly higher aspect ratio of the LDH/Seb²⁻ platelets (9.76 vs 4.09 for the nitrate precursor) physically enforces a markedly more tortuous diffusion pathway for incoming aggressive species, extending the tortuous lag phase. Interfacially, while pristine LDH clusters are inherently hydrophilic and undergo poor wet-out within the carbon-rich acrylic resin (favoring interfacial micro-voids), the hybrid system hosts a voluminous network of aliphatic dicarboxylate chains complexed on its external facets that function as an in situ compatibilizer during film formation.

It must be emphasized that direct in situ visualization of interfacial

micro-porosity, wetting angle evolution, and particle/binder interface morphology within the fully cured polymer network is technically restricted by inherent experimental boundaries (such as electron-beam-induced degradation and melting of the acrylic matrix during high-magnification cross-sectional tracking). Therefore, while the surface organophilization and interfacial void-sealing mechanism is proposed here as a working thermodynamic hypothesis, this model is strongly corroborated by direct macroscopic evidence: the significant extension of the chemical lag time, the 4-fold suppression of steady-state chloride flux, and the preservation of crystalline framework integrity confirmed by post-exchange XRD analysis. By coupling this increased physical tortuosity with active halide sequestration, the system effectively maintains the chloride flux below the critical threshold for corrosion initiation throughout the entire test duration.

To establish epistemological transparency, the level of evidence supporting this transport mechanism is categorized into directly measured physical data and inferred working hypotheses. The physical quantities directly measured in this investigation include the potentiometric chloride permeation curves and steady-state fluxes, the cumulative TOC carbon release profiles, the crystallographic reflections, d-spacings, and post-exchange peak retention (XRD), the multi-step pyrolytic mass losses (TGA), and the particle aspect ratio dimensions (SEM). Conversely, sub-nanometric interfacial phenomena, specifically the “organophilic compatibilization/void-sealing” and the “structural pillaring” models, represent inferred working hypotheses that provide a self-consistent thermodynamic explanation for the observed macroscopic transport suppression and framework stability. Finally, the main sources of experimental uncertainty in this setup arise from minor sample-to-sample membrane thickness variations ($\approx 150 \pm 5 \mu\text{m}$), the destructive nature of TOC sampling across independent film triplicates, the logarithmic sensitivity constraints of potentiometric ISE tracking at high ionic concentrations (1000 ppm Cl^-), and the baseline subtraction of polymer binder leaching.

These findings are highly consistent with the structural and thermal evidence previously discussed. The notably higher aspect ratio of the LDH/Seb²⁻ platelets, compared to the pristine nitrate-precursor, acts in synergy with their superior long-range architectural order to provide a more efficient physical obstruction to the diffusive flux. This optimized geometry, combined with the formation of a stable Friedel's salt phase as confirmed by XRD (Section 3.2), ensures that the entrapped chlorides are permanently ‘locked’ within the crystalline framework. Simultaneously, the robust host-guest stabilization evidenced by TGA (Section 3.3) guarantees that the nanocontainers maintain their structural integrity and chemical reactivity throughout the exposure period. Ultimately, the LDH/Seb²⁻ hybrid represents the only system capable of restoring the baseline barrier performance of the binder, effectively transforming a potential structural vulnerability into a functional advantage that combines high-capacity chloride sequestration with the simultaneous, on-demand release of the organic inhibitor.

A similar potentiometric approach, primarily focused on monitoring chloride permeation and entrapment within free-standing films, was previously validated by Tedim et al. for ZnAl-based LDH nanocontainers [28]. A direct comparison between the two experimental approaches highlights a significant advancement in data reliability and trend identification. In the reference study, because the permeation profile was reported as the continuous monitoring of a single sample over time, extracting a generalized kinetic model remains difficult, even though a linear progression was empirically suggested [28]. In contrast, by employing a rigorous destructive testing protocol with multiple independent replicates for each immersion interval, our setup unequivocally captures a reproducible sigmoidal trend. This statistical resolution allows us to clearly distinguish a definitive chemical lag phase from the subsequent diffusion regime. Crucially, while their framework focused exclusively on tracking this single chloride trigger, our configuration is strategically designed to expand this paradigm, paving the way for the simultaneous evaluation of the displaced organic inhibitor release

discussed below.

The quantitative assessment of the organic inhibitor dose delivered to the simulated coating/substrate interface (Fig. 9) reveals a profound divergence in release mechanisms. The cumulative TOC concentration for the neat acrylic resin (Blank) establishes a consistent baseline ($\sim 25 \text{ ppmC/cm}^2$ at 28 days), attributable to the natural leaching of low-molecular-weight fractions or partial degradation of the polymer binder [62,63].

When comparing the inhibitor-loaded systems (LDH/Seb²⁻), the free SB control exhibits a characteristic “burst release” profile. Within the first 24 to 48 h, a sharp, uncontrolled spike in organic carbon is detected at the interface, indicating that the free salt, governed purely by its solubility and the rapid infiltration of the electrolyte, immediately saturates the local environment.

It is worth noting that while Fig. 9 displays the raw, uncorrected TOC values (where the background contribution from the neat paint is plotted independently as the “Blank” curve), a mathematical baseline subtraction is performed using Eqs. (1) and (2) to isolate the net active agent. For instance, after 28 days of immersion, the raw TOC concentration for the hybrid LDH/Seb²⁻ coating reaches 57.0 ppmC/cm^2 , while the polymer baseline background ($C_{\text{Blank, ppmC}}$) accounts for 24.1 ppmC/cm^2 , yielding a net carbon release of $C_{\text{net, ppmC}} = 32.9 \text{ ppmC/cm}^2$. Applying the stoichiometric factor, this directly equates to an active delivered dose of 54.8 ppm/cm^2 of structural Seb²⁻ anions delivered to the simulated substrate interface.

From a coating science perspective, such a burst effect is detrimental to long-term performance [5]; it risks premature exhaustion of the inhibitor reservoir [64]. The direct incorporation of free SB into organic binders is often limited by its high solubility in aqueous environments, which can trigger localized osmotic pressure gradients at the coating-substrate interface during water uptake. Although direct mechanical adhesion evaluations, such as ASTM D3359 cross-cut or pull-off tests, were not performed in this study, literature on barrier degradation suggests that such osmotic pathways can promote local water accumulation, leading to blistering and eventual loss of wet adhesion. By contrast, hosting the dicarboxylate guest within the layered Ca–Al framework regulates the interfacial ionic concentration on demand, mitigating the thermodynamic driving force for osmotic blistering and preserving the integrity of the protective bilayer matrix [65].

In contrast, the LDH/Seb²⁻-pigmented coating effectively transforms the release profile into a gradual, sigmoidal progression. This “smart” behavior is intrinsically linked to the host-guest stabilization previously evidenced by TGA (Section 3.3), where the steric confinement within the inorganic galleries shields the Seb²⁻ anions from immediate dissolution. The inhibitor release kinetics exhibit a direct coupling with the chloride permeation profiles (Fig. 8), reflecting the synchronized nature of the anion-exchange process. Specifically for the hybrid LDH/Seb²⁻ system, the lag phase in chloride release perfectly overlaps with the active delivery of Seb²⁻, as the LDH galleries function as a reactive sink that sequesters incoming halides while simultaneously displacing the guest inhibitor. The eventual kinetic deceleration observed in the TOC release curve for the sample LDH/Seb²⁻ (Fig. 9) marks the progressive exhaustion of the ion-exchange capacity; the LDH host is gradually saturated with chlorides, triggering the transition from a chemically active barrier to a purely physical diffusion regime, which aligns with the onset of the chloride steady-state flux. After 28 days of immersion, the amount of inhibitor released is slightly lower than the level of the free-SB loaded paint; notably, the cumulative mass of active species delivered to the interface reaches approximately 57 ppmC/cm^2 , which corresponds to 55 ppm/cm^2 of structurally active Seb²⁻ anions. This value highlights a trend wherein the hybrid system progressively approaches the final release threshold established by the plain-SB control, yet does so through a significantly more gradual and sustained delivery profile over time, confirming the excellent controlled-release efficiency afforded by the crystalline framework.

Ultimately, this controlled delivery ensures that the inhibitor is not

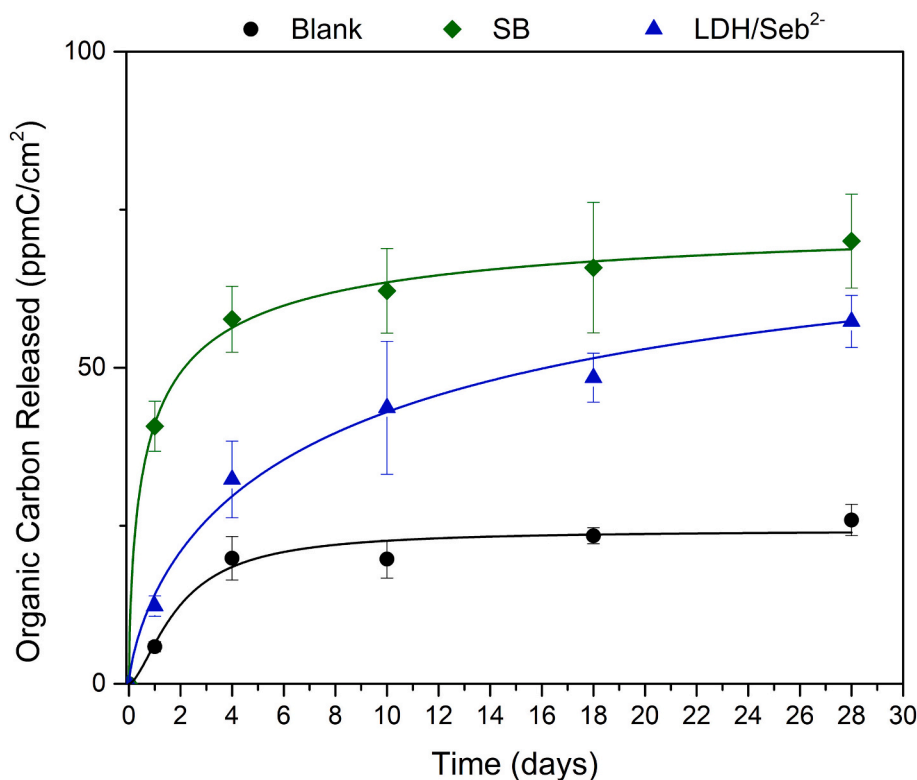


Fig. 9. Cumulative Total Organic Carbon (TOC) concentration detected in the collection chamber as a function of immersion time. This side represents the simulated coating/substrate interface, initially containing a chloride-free 0.1 M Na₂SO₄ solution. The plot compares the organic signal originating from the neat acrylic resin, the 5 wt% LDH/Seb²⁻-pigmented film, and the 2.5 wt% free SB control. Note: The plotted curves display raw, uncorrected TOC values ($C_{Total, ppmC}$), where the organic carbon contribution from the neat polymer degradation (Blank, $C_{Blank, ppmC}$) is plotted independently for direct comparison. The measured TOC values represent the effective dose of carbon derived from Seb²⁻ inhibitor delivered to the interface, alongside the background carbon contribution resulting from the partial degradation or leaching of the polymer binder. The net carbon contribution from the active Seb²⁻ inhibitor dose ($C_{net, ppmC}$) is calculated mathematically via Eqs. (1) and (2) by subtracting the Blank baseline and dividing by the stoichiometric carbon conversion factor (0.5998). Error bars indicate the standard deviation calculated from at least three independent replicates. The results are normalized over the exposed paint area.

wasted during the early stages of exposure. By avoiding the initial burst effect, the LDH/Seb²⁻ system maintains interfacial integrity while providing a functionally superior dose of active protection that scales with the environmental threat, a key requirement for the next generation of high-performance organic coatings.

Beyond the successful delivery of active agents to the simulated metal/coating interface, the prevention of excessive inhibitor leaching into the bulk electrolyte is a prerequisite for both environmental sustainability and the long-term preservation of the active reservoir. The organic signal detected on the external immersion side (Fig. 10) is significantly lower than that measured at the simulated interface side, regardless of the system tested. For the neat acrylic resin (Blank), the baseline leakage (~20 ppmC/cm²) reflects the unavoidable leaching of mobile polymer fractions through the topcoat. The magnitude of the carbon release in this cell is comparable to the value measured in the solution exposed to the primer side of the unloaded coating system.

The transport behavior of the LDH/Seb²⁻ system indicates that while a functional dose of the inhibitor is delivered to the primer/substrate interface, external leaching remains limited and lower than that of the free-SB control. This trend suggests that confining the active LDH pigments within the primer layer allows the unpigmented top-coat to act as a physical barrier, which increases the diffusion path for the released Seb²⁻ toward the external electrolyte. Furthermore, ion exchange ensures that Seb²⁻ is primarily released only when triggered by incoming chlorides, rather than through uncontrolled concentration-driven diffusion. This strategic containment not only minimizes the environmental impact but also maximizes the durability of the coating by preventing the “wasteful” depletion of the inhibitor reservoir, ensuring that

the active defense remains localized where the corrosive threat is most imminent.

Ultimately, the high-affinity sequestration capacity established in the solution phase acts as the thermodynamic prerequisite for the favorable Interface-to-Environment Delivery Efficiency Ratio (RI/E) observed in the subsequent diffusion cell tests. To provide a rigorous mathematical definition of this architectural containment, a quantitative ratio can be formulated as Eq. (4):

$$RI/E = C_{Interface} / C_{Environment} \quad (4)$$

where $C_{Interface}$ and $C_{Environment}$ denote the cumulative mass of active Seb²⁻ delivered to the simulated interface (Fig. 9) and leached to the external solution (Fig. 10) at the 28-day steady-state threshold, respectively, after subtracting the polymer binder's baseline background. For the hybrid LDH/Seb²⁻ system, the net interface delivery reaches approximately 55 ppm/cm², while the net external leaching is restricted to a minor pool of approximately 2.5 ppm/cm². This results in a remarkable RI/E value of approximately 22, proving that the environment-to-interface transport pathway is highly asymmetric. By directing 22 times more active species toward the simulated metallic substrate rather than allowing wasteful depletion into the external environment, this parameter quantitatively substantiates the superior efficiency of the primer-confined smart architecture for targeted active corrosion protection. This ensures that the smart reservoir is primarily utilized for the localized protection of the metallic substrate rather than being wastefully depleted into the external environment. To summarize, the schematic model illustrated in Fig. 11 elucidates the scavenging-release architecture achieved by the localization of LDH/Seb²⁻

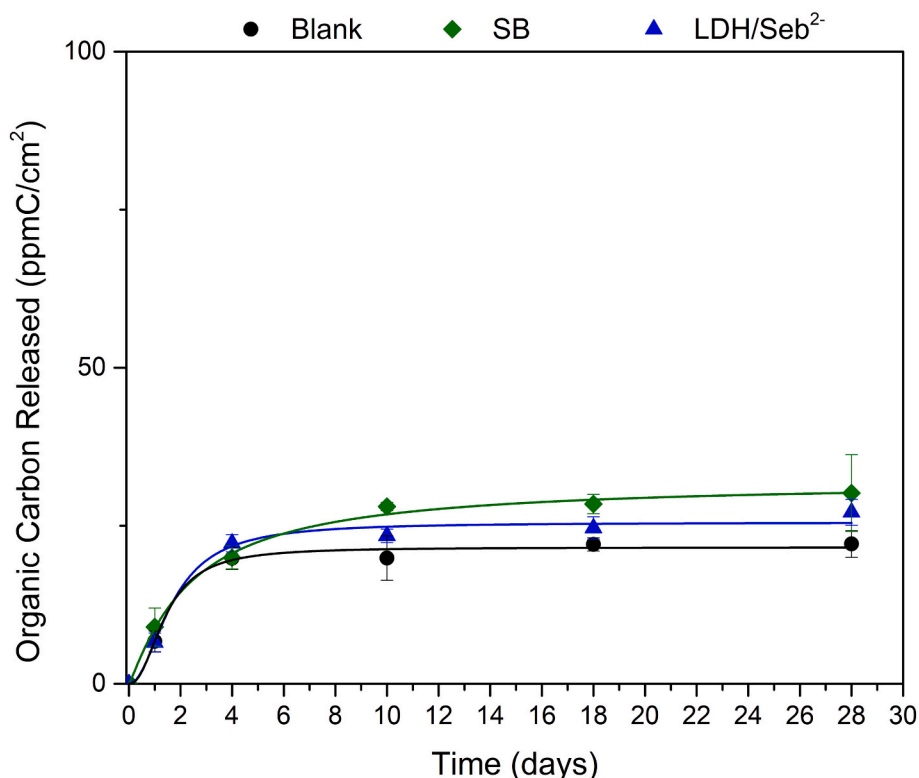


Fig. 10. Cumulative Total Organic Carbon (TOC) concentration detected in the outer cell as a function of immersion time. This immersion side corresponds to the top coat surface exposed to the aggressive 0.1 M NaCl solution. The measured TOC values account for the organic species leached from the acrylic binder and the fraction of Seb^{2-} inhibitor released toward the external environment (leakage). The plot compares the organic carbon contribution from the neat acrylic resin, the 5 wt% LDH/ Seb^{2-} -pigmented film, and the 2.5 wt% free SB control. Note: The plotted curves display raw, uncorrected TOC values (C_{Total} , ppmC), where the organic carbon contribution from the neat polymer degradation (Blank, C_{Blank} , ppmC) is plotted independently for direct comparison. The measured TOC values represent the effective dose of carbon derived from Seb^{2-} inhibitor delivered to the interface, alongside the background carbon contribution resulting from the partial degradation or leaching of the polymer binder. The net carbon contribution from the active Seb^{2-} inhibitor dose (C_{net} , ppmC) is calculated mathematically via Eqs. (1) and (2) by subtracting the Blank baseline and dividing by the stoichiometric carbon conversion factor (0.5998). Error bars indicate the standard deviation calculated from at least three independent replicates. The results are normalized over the exposed paint area.

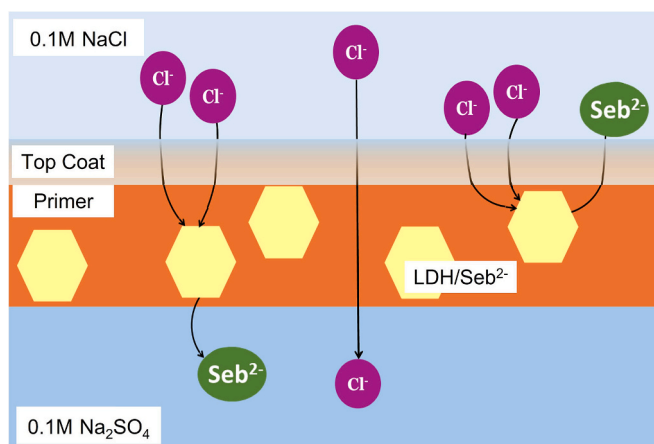


Fig. 11. Mechanistic model of the “smart” ion-exchange behavior and architectural containment of LDH/ Seb^{2-} hybrid pigments within the bilayer acrylic coating. The diagram highlights the synchronized coupling between chloride sequestration and sebacate anion (Seb^{2-}) release: as Cl^- ions diffuse through the top-coat, they are actively entrapped within the inorganic galleries of the primer-localized nanocontainers. This process simultaneously triggers the targeted release of the organic inhibitor toward the simulated metal/coating interface (bottom chamber) while the bilayer stratigraphy effectively minimizes the wasteful leakage of active species into the external environment.

pigments within the primer layer. As aggressive chloride ions infiltrate

through the unpigmented top-coat, the LDH framework acts as a reactive chemical filter that sequesters the halides while simultaneously triggering a directional delivery of Seb^{2-} toward the critical substrate interface, in this case, a simulated sodium sulphate solution.

4. Conclusions

This study successfully demonstrates a robust methodology for the quantitative assessment of the in situ performance of “smart” ion-exchange pigments within organic coatings. The hydrothermal synthesis of CaAl-LDH/Seb^{2-} hybrid pigments yielded high-aspect-ratio hexagonal platelets that not only promote a physical tortuous path effect within the polymer matrix but also provide a significant active surface area for anion exchange. A substantial inhibitor reservoir was achieved, with a total Seb^{2-} loading of approximately 50 wt%. This reservoir is composed of a synergistic dual distribution, where a robustly protected core of specifically intercalated anions within the interlayer galleries coexists with a significant surface-adsorbed population.

The experimental data validated a synchronized ‘scavenging-release’ mechanism, where near-instantaneous, diffusion-limited chloride sequestration follows an adsorption process described by the Langmuir model ($R^2 > 0.98$). Critically, chloride entrapment is directly coupled to inhibitor release; as halides infiltrate the coating, the LDH galleries act as a reactive sink, displacing the guest Seb^{2-} toward the metal/coating interface. Crucially, the intercalated Seb^{2-} anions exert a structural pillaring effect that stabilizes the Ca-Al framework against redissolution. Unlike traditional nitrate-LDH precursors, which exhibit

structural instability and subsequent chloride leakage over time, the hybrid system permanently locks the aggressive halides within the crystalline galleries via the stabilization of the newly formed Friedel's salt phase.

In situ monitoring via custom diffusion cells confirms that this chloride entrapment in the hybrid pigments-loaded free film (LDH/Seb²⁻) is coupled to the release of the Seb²⁻ inhibitor at the simulated coating-substrate interface. Unlike the detrimental “burst effect” observed in the free-SB control, which poses severe risks of localized osmotic pressure peaks and adhesion loss, the total organic carbon (TOC) profile of the LDH/Seb²⁻ system exhibits a controlled, sigmoidal progression. After 28 days of exposure, the delivered dose reaches 57 ppmC/cm², equating to 55 ppm/cm² of active Seb²⁻. This kinetic trend demonstrates that the hybrid nanocontainers progressively converge toward the final release threshold of the free inhibitor control, yet accomplish this through a significantly more gradual delivery. Such an optimized profile indicates a substantial initial kinetic attenuation, which effectively extends the chemical lag time and prolongs the service life of the protective matrix.

Finally, this work demonstrates the high efficacy of the combined diffusion cell, potentiometry, and TOC methodological approach. This setup provides a robust, quantitative tool to monitor organic inhibitor release kinetics directly coupled with chloride-trapping ion-exchange mechanisms, offering a clear pathway for the rational design of long-term active protective coatings.

CRedit authorship contribution statement

Andrea Cristoforetti: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Elisa Callegaro:** Investigation, Data curation. **Michele Fedel:** Writing – review & editing, Validation, Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.porgcoat.2026.110558>.

Data availability

Data will be made available on request.

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