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Preparation and Application of Calcined Mg/Al Layered Double Hydroxides in Organic Coatings and Chloride Removal

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The adsorption of infiltrated chloride ions by layered double hydroxide (LDH) is expected to improve the corrosion resistance of organic coatings. Mg/Al layered double hydroxide (LDH) with a Mg/Al molar ratio of 4:1 was prepared using the co-precipitation method. The calcined layered double hydroxide (CLDH) was placed in NaCl solution to investigate its effect upon the adsorption of Cl⁻, then, the product was added to a two-component epoxy coating, to study its effect upon corrosion resistance. The CLDH powder product was characterized using XRD and FT-IR, and the corrosion resistance of the coatings was investigated by EIS and NSS tests. The experimental results show that CLDH can effectively adsorb Cl⁻ from a NaCl solution via its memory effect, and the corrosion resistance of the epoxy coating can be improved by adding 1.0-2.0 wt. % CLDH.

Keywords: Mg/Al CLDH; Cl⁻ adsorption; epoxy coating; corrosion resistance.

1. INTRODUCTION

As the most popular corrosion protection technology in marine environments, organic coatings play a role in mitigating corrosion, by blocking the diffusion of water and corrosive media (e.g. chloride ions) to the protected metal substrate [1]. However, with prolonged service lifetimes, the polymer resin in the coating gradually ages and fails, which reduces the barrier effect of the coating against water and corrosive media. Previous studies have focused on improving the crosslinking density, medium resistance, and aging resistance of resins, however, little research has been done on how to prevent the diffusion of corrosive media such as chloride ions from the coating to the metal substrate [2]. In this study, the preparation of Mg/Al hydrotalcite intercalation materials to adsorb chloride ions in organic coatings provides a new idea for improving the barrier properties of coatings against chloride ion

corrosive media and delaying the corrosion of metal substrates. Natural hydrotalcite is an anionic clay with the formula of $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$. It features a positively charged metal hydroxide layer with anions and water molecules in between [3]. Its structure is similar to brucite, a flake-mineral-type filler; the flake-type fillers have better shielding properties than the granular and fibrous fillers [4]. Layered double hydroxides (LDHs) is a synthetic hydrotalcite, and the general formula can be denoted as $[(M^{2+})_{1+x}(M^{3+})_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$; they are collectively referred to as hydrotalcite-like compounds (HTLcs) [5]. The layered structure of LDH determines its interlayer anion exchangeability and memory effect. Based on these properties, LDHs have important application prospects in the field of metal anti-corrosion, and they have attracted the attention of many researchers [5].

Alibakhshi et al. [6] separately incorporated ZnAl-PO₄³⁻ LDHs and ZnAl-NO₃⁻ LDHs into a composite silane primer layer covered by an epoxy-polyamide topcoat layer. The coatings were crosshatched, to facilitate investigation of their activity inhibiting properties. The results showed that the doped LDH in the silane layer enhanced the active anticorrosion performance of the coating system when the coating was scratched. Over time, the coating resistance in the presence of the ZnAl-PO₄³⁻ LDHs increased sharply, forming a passivation film on the defect area. A Zn/Al-NO₃⁻ LDHs film was prepared by Wang et al. [7] on an AZ91D magnesium alloy via a hydrothermal synthesis method, and the LDHs were modified with Cl⁻ and VO₃⁻. The concentration gradient of chloride anions in the Zn-Al-Cl LDHs film successfully delayed the diffusion of chloride ions on the surface of the magnesium alloy. Of these modifiers, VO_3^- plays a key role as a corrosion inhibitor. Zn-Al-VO_x LDHs films not only absorb chloride ions but also release corrosion inhibiting anions into the solution. The above mentioned studies mainly utilized the layered structure and ion-exchange properties of LDHs to either store corrosion inhibitors (and thereby obtain LDHs films) or to function as coating fillers. This is also the key research direction of LDHs in the field of metal anti-corrosion [8-16]. However, few studies have used the memory effect of LDHs, instead focusing on the corrosion protection of concrete reinforcement [17-19]. Yoon et al. [20] added calcined Mg/Al LDHs to the cement slurry coating and found that the composite cement slurry coating has an increased saturation adsorption capacity for Cl⁻; furthermore, the restoration of the layered structure of the calcined filler could effectively prevent Cl⁻ erosion.

In this study, Mg/Al LDH was prepared using a co-precipitation method, and the adsorption behavior of calcined products for Cl⁻ in NaCl solution was explored. The calcined product was added to the salt solution to investigate its adsorption behavior to Cl⁻; then, it was added to a two-component epoxy resin coating, to investigate its effect on the coating's anti-corrosion performance.

2. EXPERIMENTAL

2.1 Synthesis of LDH materials

Co-precipitation is the most popular method to produce LDHs in a laboratory at low cost and with simple operation [3, 21-22]. According to relevant literatures [23-24], the Cl⁻ adsorption effect is optimal when the molar ratio of Mg/Al is 4:1. In this paper, Solution A was prepared using Al(NO₃)₃·9H₂O (0.25M, 7.5 g), Mg(NO₃)₂·6H₂O (1M, 20.48 g) and H₂O (100 mL), and Solution B was

prepared using NaOH (2M, 8 g), Na₂CO₃ (0.5M, 5.3 g), and H₂O (100 ml). Solution A and B were slowly dripped into 200 mL H₂O in a 70 °C water bath. Meanwhile, the stirring speed was controlled at 2600 rpm, and the pH was controlled at 8±0.05 during the dripping process. After the dropwise addition was completed, stirring was continued for 2 h; thereafter, the product was allowed to stand for 12 h in a water bath at 70 °C to age. After suction filtration, the precipitate was washed 2–3 times with deionized water and dried at 80°C. The dried precipitate was ground into a powder to obtain the prepared Mg/Al-CO₃²⁻ LDH ((hereafter referred as LDH).

The Mg/Al-CO₃²⁻ LDHs was placed in a muffle furnace and kilned separately at 300, 400, 500, 550, 600, and 700°C for 4 h, to obtain Mg/Al CLDH ((hereafter referred to as CLDH).

2.2 Cl⁻ adsorption performance test

The NaCl solution was prepared in deionized water with CO₂ removed, and CLDH was added and stirred at 400 rpm for 6 h. After removal by centrifugation, the supernatant was collected for Cl⁻ concentration measurement. The centrifuged pellet was washed 2-3 times with deionized water and dried. We took 25 mL of the supernatant and added 50mL H₂O, and 1 mL K₂CrO₄ (5 wt. %). A standard AgNO₃ solution was then added dropwise under shaking conditions. The titration was completed when the solution turned orange-red.

The concentration of Cl⁻ was calculated as follows: $c = \frac{c_n(v_2 - v_1) \times 35.5}{v_1} \times 1000.$

Here, c is the chlorine content in the sample solution (mg/L), c_n is the concentration of AgNO₃ standard solution (mol/L), v is the volume of sample solution (mL), v_1 is the volume of the AgNO₃ standard solution adsorbed by deionized water (mL), v_2 is the volume of AgNO₃ standard solution consumed by the sample solution (mL)

The equilibrium adsorption capacity of Cl⁻ is $q_e = \frac{(c_0 - c_e)V}{m}$. The adsorption amount of Cl⁻ at time t is $q_t = \frac{(c_0 - c_t)V}{m}$.

Here, c_0 is the initial concentration of chloride ion (mg/L), c_e is the concentration of chloride ion at equilibrium (mg/L), c_t is the concentration of chloride ion at time t (mg/L), V is the volume of salt solution (L), and *m* is the mass of CLDH added (g).

2.3 Coating Preparation

The Q235 steel sample was ground using 600# sandpaper, washed with absolute ethanol, and placed in a drying box. The CLDH was added to the epoxy resin in quantities of 0.5, 1.0, 2.0, and 4.0 wt.%, respectively. The CLDH was then uniformly dispersed in epoxy resin via ball milling with xylene diluent for 24 h. After adding an appropriate amount of curing agent, the coating was evenly coated on the surface of Q235 carbon steel. The coating thickness was controlled at 90 \pm 5 μ m to obtain five different coatings (hereinafter referred to as EP, EP-0.5, EP-1.0, EP-2.0, and EP-4.0).

2.4 Performance tests

The electrochemical impedance spectroscopy (EIS) test specimens consisted of Q235 steel with an epoxy coating with dimensions of 5 cm \times 5 cm. The EIS test was conducted on a PAR 2273 electrochemical workstation using a three-electrode system in a 3.5 wt.% NaCl solution. The test specimen was assembled as the working electrode, a platinum foil was used as the auxiliary electrode, and a saturated calomel electrode was used as the reference electrode. During the measurement, a sinusoidal AC potential disturbance of 20 mV (voltage peak value) with respect to the open-circuit potential was applied to the coated steel system, and the measurement frequency ranged from 100 kHz to 10 mHz. All experiments were performed at room temperature (20-27°C). The experimental data were analyzed using ZSimpWin software.

The salt-spray resistance of the coating samples was determined using a neutral salt spray test. X-ray diffraction (XRD) measurements were taken to determine the crystal structure of the clay particles; this was realized using an X'Pert PRO X-ray diffractometer with Cu K- α rays (1.54 Å), operating at 40 kV and 40 mA and a scanning range of 5–90°. Fourier transform infrared (FTIR) tests were conducted using a Thermo IS10 infrared spectrometer in the scanning range of 4000–400 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

The XRD patterns of the LDHs are shown in Figure 1a. Sharp symmetrical diffraction peaks appeared at low angles. The characteristic diffraction peaks at 2θ angles of 11.20° and 22.61° corresponded to the characteristic diffraction peaks of the 003 and 006 crystal planes, respectively. The reflection patterns were identified by the previous reports [25-27]. No other impurity peaks appeared in the curve, indicating that the synthesized LDH had a single crystal orientation. According to the Bragg equation, the interlayer spacing d₀₀₃ was 0.727 nm.



Figure 1. XRD patterns of LDH at different calcination temperatures: (a) non-calcined, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C, and (f) 600 °C.

It can be seen from Figure 1 b–f that the main characteristic peak of LDH remains present when the calcination temperature is below 300 °C; however, the peak intensity is weakened and shifted to a higher angle direction. This is attributable to the removal of surface and interlayer water in this temperature range. As the calcination temperature continued to increase, the diffraction peak of LDH disappeared at 400 °C, indicating that the layered structure had collapsed. Simultaneously, two new diffraction peaks corresponding to the Mg/Al composite oxide appeared, and the peak intensity increased with increasing temperature.

3.2 CLDH dechlorination

3.2.1 CLDH dechlorination mechanism

Figure 2c shows the XRD spectrum for CLDH after dechlorination in NaCl solution. Compared with the CLDH spectrum, a low-angle symmetrical diffraction peak reappeared, indicating that the layered structure was restored after the adsorption of inorganic anions and water molecules in the solution. However, compared with the LDH spectrum, the diffraction peak had a wider peak shape and lower peak height, indicating a reduced degree of crystallinity. Meanwhile, the low-angle diffraction peak shifted to the right, and the corresponding interlayer spacing d_{003} value increased from 0.727 to 0.813nm, which was caused by the increase of interlayer Cl⁻ content (In the Reference [27], the d_{003} value from 0.727 to 0.781-0.789 nm).



Figure 2. XRD patterns of (a) Mg/Al-CO₃ LDH, (b) CLDH, and (c) CLDH after adsorption.

Figure 3a shows the FTIR curve of the Mg/Al- CO_3^{2-} LDH. The peaks at 3532.75 cm⁻¹ and 1635.10 cm⁻¹ are attributable to the stretching and bending vibrations of the hydroxyl group, respectively. The peaks at 1383.10 cm⁻¹ and 625.65 cm⁻¹ are attributable to the stretching and bending vibrations of CO_3^{2-} , respectively; the peak at 400–800 cm⁻¹ corresponds to the skeleton vibration of the laminate's metal-oxygen bond. The above peaks are characteristic of LDH and consistent with the FTIR spectra reported in the literature [3]. As shown in Figure 3b, the absorption vibration peaks of –OH and CO_3^{2-} are significantly weakened owing to the separation of interlayer water and CO_3^{2-} after high-temperature

roasting. Figure 3c shows the FTIR spectrum after adsorption of CLDH. The stretching vibration peak of carbonate exhibits a redshift, attributable to the interaction of chloride ions entering the interlayer with CO_3^{2-} [28].



Figure 3. FTIR spectra for (a) LDH, (b) CLDH, and (c) CLDH after adsorption.

The above results indicate that the adsorption of Cl⁻ by CLDH primarily depends on the memory effect of the LDH; that is, the Cl⁻ in the solution re-enters the molecular layers of CLDH materials, such that the structure can be partially restored to an ordered layered structure.

3.2.2 Effect of calcined temperature

We added 0.5 g of CLDH to 250 mL NaCl solution (350 mg/L). The calcination temperatures of CLDH were 300, 400, 500, 550, 600, and 700 °C, respectively. After stirring in a 35 °C water bath at 400 rpm for 6 h, the supernatant was taken for Cl⁻ concentration measurement.



Figure 4. Effect of LDHs calcination temperature on Cl⁻ removal.

As shown in Figure 4, the dechlorination performance of CLDH exhibited an increase and then a decrease under an increase in roasting temperature. The dechlorination performance was superior in the calcination temperature range of 500–600 °C. The highest Cl⁻ adsorption was achieved at 550 °C with 121 mg/g, and the adsorption ratio was almost 70% (The best calcination temperature for Natural organic matters is 500 °C in Reference [29]). When the calcination temperature was 200–500 °C, an increase in the calcination temperature lead to the gradual removal of interlayer water and carbonate anions, and the absorbability gradually increased. Further increasing the calcination temperature to 600 °C gradually transformed the structure into the spinel phase (which lacks a memory effect), and the adsorption performance decreased.

3.2.3 Effect of additive quantity

We added 0.125, 0.25, 0.375, 0.5, 0.625, and 0.75 g CLDH to 250 mL NaCl solution (350 mg/L), stirred it for 6 h at 400 rpm in a 35 °C water bath, then took the supernatant liquid detection Cl^{-} concentration.



Figure 5. Effect of additive quantity of LDHs upon Cl⁻ removal.

As shown in Figure 5, when the amount of CLDH increased, the adsorption rate continued to increase; however, the adsorption amount presented a trend of initial increase and subsequent decrease. This phenomenon is related to the adsorption sites. When the dosage was too low, there were few adsorption sites, and the adsorption effect was poor. However, when the dosage was too high, the adsorption amount tended to balance, resulting in a corresponding decrease in the amount of CLDH adsorption per unit mass.

3.2.4 CLDH dechlorination equilibrium isotherm

The equilibrium isotherm data obtained under different Cl⁻ initial concentrations (100–600 mg/L)

at 35 °C were fitted to the Langmuir equation,

$$\frac{\tilde{C}_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \qquad (1)$$

and Freundlich's empirical formula,

$$lnq_e = lnK_F + nlnC_e$$
 (2)

The fitting results are shown in Figure 6.



Figure 6. Equilibrium isotherm of Cl⁻ adsorption.

The fitting results show that $R_L^2 > R_F^2$, indicating that the Cl⁻ adsorption isotherm of CLDH is more consistent with the Langmuir model. The maximum adsorption q_m was calculated as 153 mg/g, close to the theoretical adsorption of Cl⁻ (168 mg/g) by CLDH [28]. In the Langmuir equation, *n* was 0.24, which was in the range of 0.1–0.5, indicating that the Cl⁻ adsorption by CLDH was effective.

The maximum Cl⁻ adsorption capacities on CLDH, as obtained by different researchers, are listed in Table 1. The data in the table show that the CLDH prepared in this experiment has a good adsorption effect on Cl⁻.

Table 1. Comparison of the maximum adsorption capacities of CLDH materials for Cl⁻

CLDH	$q_m \ (mg/g)$ Reference	
Double hydrous oxide (Fe ₂ O ₃ • Al ₂ O ₃ • xH ₂ O)	70	Chubar et al. [30]
Mg-Al oxide (Mg/Al molar ration of 3)	102.6	Kameda et al. [31]
CLDH (Mg _{0.80} A1 _{0.20} O _{1.1})	149.5	Lv Liang[28]
CLDH (Mg/Al molar ration of 4)	1866.6	Ma Shuangchen[32]
CLDH (Mg/Al molar ration of 4)	153	This work

3.2.5 CLDH dechlorination kinetics

2 g CLDH was added to 1 L NaCl solution with Cl⁻ concentrations of 100, 200, 300, 400, 500, and 600 mg/L respectively; the result was stirred at 400 rpm and 35 °C. A certain quantity of the solution was extracted at intervals for centrifugation, the Cl⁻ content of the supernatant was measured, and the adsorption amount q_t at time *t* was calculated. The data are summarized in Figure 7.

The obtained data were fitted with first- and second-order kinetic models, and the fitting results are shown in Figure 8 and Table 2.

First-order kinetic model: $\frac{dq_t}{dt} = k_1(q_e - q_t), \frac{dq_t}{dt} = k_1(q_e - q_t).$ Converted into a linear equation: $ln(q_e - q_t) = lnq_e - k_1t.$ Second -order kinetic model: $\frac{dq_t}{dt} = k_2(q_e - q_t)^2.$ Converted into a linear equation: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}.$

Here, k_1 is the first-order rate constant (min⁻¹), and k_2 is the second-order rate constant (g·mg⁻¹·min⁻¹).



Figure 7. Dechlorination effect of CLDH in different concentrations of NaCl solutions.



Figure 8. (a) First- and (b) second-order kinetic models.

It can be seen from Figure 7 that the dechlorination amount gradually increased as the reaction progressed; then, it tended to stabilize. Meanwhile, the de-chlorination effect of CLDH decreased under increasing chloride ion concentration.

As shown in Figure 8 and Table 2, the second-order kinetic fitting data exhibited a good linear relationship, and the removal rate decreased as the initial concentration increased.

Concentration	First-order kinetic model		Second -order kinetic model			
of $C1^{-}/(mg/L)$	$q_e/({ m mg/g})$	k_1	R^2	$q_e/({ m mg/g})$	$k_{2} \times 10^{-4}$	R^2
100	55.18052	0.02832	0.93986	54.23	7.33463	0.99434
200	56.61817	0.01365	0.91617	93.72	3.94487	0.99737
300	134.0805	0.01362	0.95306	155.04	0.428428	0.96668
400	157.5212	0.01733	0.95266	155.52	0.707718	0.98466
500	154.2462	0.01058	0.97044	186.22	0.408576	0.98349
600	158.4406	0.01021	0.9028	201.62	0.468816	0.98784

Table 2. Fitting data of dechlorination kinetic models.

3.3 EIS tests

It can be seen from Figure 9 that at the initial stage of immersion, the impedance spectrum of the coating/metal system gradually deviated from the pure capacitive behavior, owing to the water absorption of the coating; then, the resistive behavior began to appear in the low-frequency region. Meanwhile, the coating showed a higher impedance, indicating that water did not completely penetrate it. This is the first time that this constant has been reported. The electrical parameters of the coating/metal system at this stage can be obtained by fitting the impedance data using equivalent circuit Model A (Figure 10), where R_s is the solution resistance, Q_c is the coating capacitance, and R_c is the coating resistance.

When the immersion time increased, the capacitive reactance arc radius of the EP Nyquist diagram gradually decreased. The phase angle in the low-frequency region was significantly reduced, and the peak value in the low-frequency region moved to the middle- and high-frequency regions. The impedance modulus in the low-frequency region decreased, and the frequency range of the horizontal segment (representing the resistance characteristic) increased. This is the second time constant; it indicates that the corrosion reaction zone at the coating–metal interface gradually expands.





Figure 9. EIS spectra of the coatings after immersion in 3.5 wt.% NaCl solution: (a, b) EP, (c, d) EP-0.5, (e, f) EP-1.0, (g, h) EP-2.0, and (I, j) EP-4.0.

The equivalent circuit model shown in Model B (Figure 10) was used to fit the EP coating impedance data, where Q_{dl} denotes the double-layer capacitance of the substrate metal corrosion reaction, R_t is the charge transfer resistance of that reaction, and the coating resistance R_c is replaced by the microporous resistance R_{po} . In the later stage, because of the accumulation of metal corrosion reaction products on the surface of the metal substrate, the size of the capacitance arc was further reduced. In the Bode diagram, the peaks in the mid- and low-frequency regions were shifted to the mid- and high-frequency regions. Owing to the coating coverage, the corrosion products were difficult to diffuse, and mass transfer occurred in the control process of the interface Faraday process. The equivalent circuit model shown in Model C was used for fitting, where Z_w is the Warburg impedance. As the corrosion reaction proceeded, a large quantity of corrosion products accumulated, and the coating gradually became thinner but not completely invalid. Model D was established for fitting.



Figure 10. Equivalent circuit models.

After the CLDH was added, the capacitive arc radius of the coating first decreased and then increased slightly before finally decreasing during immersion. This may be attributable to the fact that the CLDH added to the coating absorbs H_2O , Cl^- , and CO_2 during the immersion process to restore the ordered layered structure; this not only reduces the invasion of Cl^- but also exerts a certain shielding effect on water and other corrosive ions. Moreover, under the increase in additive quantity, the longer increasing trend was maintained, and this feature was more obvious in the EP-4.0 coating. However, owing to the addition of more CLDH, agglomeration occurred, which produced an increase in coating defects and provided channels for the transmission of water and other corrosive ions.



Figure 11. |Z|_{0.01Hz} values of the coating immersed in 3.5 wt.% NaCl solution.



Figure 12 *R* values of the coating after immersion in 3.5 wt.%NaCl solution for 24h and 25 days.

Compared with the other coatings, the EP-1.0 and EP-2.0 coatings still showed larger capacitive reactance arc radii and higher resistance values after prolonged immersion. This is because the CLDH material was added to the coating, which absorbs water molecules and Cl⁻ in the corrosive solution to restore the layered structure and slows the rate of penetration of the solution into the coating. Meanwhile,

the appropriate amount of CLDH added did not appear to agglomerate in the EP-4.0 coating, which exhibited a better protective performance.

The low-frequency impedance modulus ($|Z|_{0.01Hz}$) and fitted coating resistance (*R*) values of the coating after immersion in 3.5 wt.% NaCl solution are depicted in Figures 11 and 12. The EP-1.0 and EP-2.0 coatings exhibited higher $|Z|_{0.01Hz}$ and *R* values after 24 hours of soaking, and they could still reach more than $10^{11} \Omega \cdot \text{cm}^2$ after 25 days. As the immersion time increased, the EP coating $|Z|_{0.01Hz}$ and *R* decreased most, by up to three orders of magnitude. The *R* values of coatings EP-1.0 and EP-4.0 increased to varying degrees during long-term immersion. The above results are related to the absorption of water and Cl⁻ by the coating, and CLDH restores the layered structure, which has a blocking effect on the diffusion of the electrolyte solution. This indicates that the addition of CLDH as a filler to the epoxy coating can effectively improve the coating's corrosion resistance.

3.4 Salt spray test



Figure 13 depicts the failure process of the epoxy coatings with different CLDH contents after the NSS tests.

Figure 13. NSS test results of the coatings with different spray times, (a) EP, (b) EP-0.5, (c) EP-1.0, (d) EP-2.0, and (e) EP-4.0.



Figure 14. NSS test results of scratched coatings with different spray times, (a) EP, (b) EP-0.5, (c) EP-1.0, (d) EP-2.0, and (e) EP-4.0.

When the NSS test lasted 312 h, slight corrosion occurred under the EP coating (Figure 13a). At this time, the Q235 substrate coated with CLDH did not exhibit obvious corrosion. When the test reached 1000 h, the corrosion of the EP coating substrate was more severe, with a larger corrosion area and denser corrosion points; meanwhile, the corrosion point area on the substrate of the coating with added CLDH was smaller and more scattered. Compared with the other additives, the EP-4.0 coating substrate exhibited more corrosion points.

Figure 14 shows the NSS test results of the epoxy coatings with different CLDH contents after scratching. The EP coating degenerated after 48 h (Figure 14a). With the addition of CLDH, all coatings exhibited good protection against the Q235 steel substrates. Among them, the EP-1.0 coating exhibited the best protection effect, and the corrosion area showed almost no further expansion.

The above phenomena indicate that the corrosion resistance of the epoxy coating was significantly improved by the addition of CLDH. This may be because the material has a certain adsorption effect on Cl⁻, which reduces the diffusion of free Cl⁻. Meanwhile, CLDH also has a good physical shielding effect when it slowly recovers into a layered structure. The salt spray test results show that when the added quantity of CLDH reaches 1.0%, the coating exhibits the optimal anti-corrosion performance; this can effectively inhibit further expansion of the corrosion area. When the CLDH content in the coating increased to a certain extent, the anti-corrosion performance of the coating decreased. This may be attributable to agglomeration when the amount of added CLDH is too large; this leads to an increase in coating defects and a decrease in the barrier's performance against corrosive media.

4. CONCLUSION

A Mg/Al-CO₃²⁻ LDH material was successfully prepared, as verified by XRD and FTIR results.

The adsorption effect of the CLDHs on chloride ions primarily relied on its memory effect; that is, the Cl⁻ and water molecules in the solution re-entered the CLDH material, which could be partially restored to an ordered layered structure. When the calcination temperature was 550 °C, the adsorption effect of CLDHs on chloride ions was superior. In a NaCl solution with a temperature of 35 °C and a concentration of 350 mg/L, adding 2 g/L CLDH caused the adsorption capacity of chloride ions to increase to as much as 121 mg/g, with an adsorption rate approaching 70%. The adsorption process of CLDH to Cl⁻ was aligned with the second-order kinetic model and Langmuir isotherm equation, and the fitted maximum adsorption capacity q_m was 153 mg/g, close to the theoretical dechlorination capacity of CLDH (168 mg/g). The results of the EIS and NSS tests show that the CLDH-added epoxy coating can effectively alleviate the corrosion rate of the metal substrate. The optimal anti-corrosion effect was obtained when the CLDH content in the epoxy coating was 1.0–2.0 wt.%. This may be attributable to the absorption of H₂O and Cl⁻ by CLDH and the restored layer structure of CLDH, which plays a role in shielding and blocking corrosive media.

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