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Bilayer Zn-primer/Cu₂O-topcoat ethyl silicate coating: a promising approach for combined marine corrosion and fouling resistance

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ABSTRACT

Protecting marine metallic structures requires coatings that provide both corrosion resistance and antifouling. This research investigated multifunctional ethyl silicate coatings combining zinc (Zn) and copper(I) oxide (Cu₂O). We compared four systems: Zn-only, Cu₂O-only, a single-layer Zn/Cu composite, and a bilayer Zn+Cu structure (Zn primer/Cu₂O topcoat). Comprehensive evaluations included electrochemical corrosion behavior (DC polarization, 60-day EIS in 3.5 wt% NaCl), ion release kinetics, and long-term antifouling efficacy via 12-month natural marine exposure. Results revealed distinct performance profiles. The Zn coating provided excellent short-term corrosion protection but failed antifouling tests. Conversely, the Cu₂O coating showed good initial antifouling via effective Cu release (~12–14 µg/cm².day) but had poor corrosion resistance. The composite Zn/Cu coating exhibited intermediate properties. Significantly, the bilayer Zn+Cu system demonstrated the most favorable synergy, offering the best long-term corrosion resistance (highest impedance via EIS after 60 days), superior adhesion, sustained effective copper release (3.41 µg/cm².day), and outstanding antifouling performance over 12 months. This study underscores the decisive role of coating architecture, identifying the bilayer Zn+Cu structure as a highly promising configuration for developing durable, multifunctional protective coatings for maritime applications.

Keywords: Ethyl silicate coating, corrosion protection, antifouling coating, Zn/Cu₂O, bilayer structure.

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Introduction

The harsh marine environment, which covers the majority of Earth's surface, poses significant engineering challenges for structures and vessels, such as ships, offshore platforms, and coastal installations, due to corrosion and biofouling [1]. Electrochemical corrosion, particularly of steel in seawater, causes substantial economic losses through structural degradation and repair costs [2, 3]. Concurrently, biofouling - the unwanted accumulation of microorganisms, plants, and animals on submerged surfaces - leads to severe consequences: increased hydrodynamic drag (resulting in higher fuel consumption and emissions), pipeline blockage, sensor interference, and Microbiologically Influenced Corrosion (MIC) [4].

To counteract these issues, applying protective coatings is the most prevalent and effective solution [4]. For corrosion protection, zinc-rich coatings (ZRCs) are widely employed for steel [5, 6]. They primarily function via sacrificial protection: zinc, being more electrochemically active (anodic) than steel, corrodes preferentially, thereby protecting the steel substrate [7]. The efficiency of ZRCs depends on factors such as zinc content, particle morphology and size (spherical vs. lamellar), dispersion, and electrical connectivity within the binder matrix [8]. Inorganic binders, such as ethyl silicate, are often used for demanding applications requiring high temperature and solvent resistance, though they can be brittle [9].

Conversely, antifouling coatings are used to combat biofouling [7]. The dominant technology relies on the controlled release of biocidal compounds, typically copper(I) oxide (Cu_2O), into the surrounding water [10–12]. The mechanism involves the slow dissolution of Cu_2O , which leaches copper ions ($\text{Cu}^+/\text{Cu}^{2+}$) into the boundary layer, where they reach concentrations toxic to settling organisms [13, 14]. A minimum critical release rate of approximately $10 \mu\text{g}/\text{cm}^2\cdot\text{day}$ is considered necessary for efficacy [15]. However, the use of biocides, especially copper, raises environmental concerns due to the accumulation of heavy metals [16, 17]. Furthermore, their

effectiveness is limited by the finite biocide reservoir and its release rate, leading to a limited service life.

In practice, marine structures often require both corrosion and antifouling protection simultaneously. Coatings optimized for only one function typically fail to meet this dual requirement. While ZRCs offer good corrosion protection, their antifouling properties are very limited; indeed, their surface and corrosion products can sometimes promote fouling [18]. Conversely, conventional copper-based antifouling coatings are typically not designed to provide optimal corrosion protection for the underlying metal substrate. Therefore, developing multifunctional coating systems that effectively combine both capabilities represents a crucial research direction.

One approach involves incorporating both anticorrosive (zinc) and antifouling (Cu_2O) components into a single coating system [18, 19]. However, this raises critical questions regarding component interactions and the optimal coating architecture. Specifically, the current work examines whether a simple blend of zinc and Cu_2O particles in a single matrix (composite system) is effective, or whether a layered structure, employing a zinc-rich primer for corrosion protection and a Cu_2O -containing topcoat for antifouling (bilayer system), would perform better. The analysis also considers how potential electrochemical interactions between the more active zinc and the nobler copper might influence zinc's corrosion rate and copper's release rate. Finally, we investigate the role of the specific binder, in this case, ethyl silicate, in controlling particle dispersion, mechanical properties, durability, and ion release kinetics [20].

Consequently, this study systematically investigates the effects of combining zinc particles (a mixture of lamellar ZnAl and spherical types) and cubic Cu_2O particles within an ethyl silicate binder matrix. We fabricated and compared four distinct coating systems: (i) containing only zinc (Zn), (ii) containing only Cu_2O (Cu), (iii) a single-layer composite coating containing both zinc and Cu_2O (Zn/Cu), and (iv) a bilayer coating system with a zinc-rich primer and a Cu_2O -containing topcoat (Zn+Cu). This research

comprehensively evaluated key properties, including mechanical characteristics (adhesion, impact resistance), surface properties (water contact angle), phase composition and chemical structure (XRD, FTIR), microstructure (SEM), corrosion protection performance (DC polarization, EIS over time), ion release kinetics (Zn and Cu), and practical antifouling efficacy. The ultimate objective is to elucidate the structure-composition-performance relationships for these systems, thereby identifying an optimal configuration capable of providing effective simultaneous corrosion and antifouling protection for marine applications.

Materials and methods

Materials

CT3 steel panels measuring 10 cm × 15 cm × 0.2 cm were used as the substrate material. The chemicals, including Ethyl silicate 40, ethanol, and hydrochloric acid (HCl, 37%), were purchased from Jinan Finer Chemical Co., Ltd. (China). Mica powder was supplied by Hebei Chida Co., Ltd. (China). Spherical zinc (Zn) particles (Zn/ZnO ratio 50.3:49.7, particle size 5–7 µm) were supplied by Jotun Paints (Vietnam). Lamellar Zinc-Aluminum (ZnAl) alloy flakes (Zn/Al ratio 80:20, particle size 5–7 µm) were obtained from Hunan Jinhao New Material Technology Co. (China). Copper(I) oxide (Cu₂O) was supplied by Yixin Chemical Co. (Shanghai, China).

Coating preparation

The CT3 steel substrates underwent a surface pretreatment process comprising three steps: degreasing with a hot alkaline solution, rust removal in HCl, and surface roughening with 600-grit abrasive paper. The ethyl silicate binder was synthesized via the sol-gel method from a mixture comprising 45.4 wt% ethanol, 1.8 wt% water (H₂O), 0.022 wt% HCl, 33.71 wt% mica powder, and 19.07 wt% TEOS (by weight) [21]. This mixture was allowed to stabilize for 24 hours at room temperature before use.

Four different pigment formulations were prepared to create the corresponding coatings. Sample Zn (containing 40 wt% spherical Zn and 5 wt% lamellar ZnAl alloy), sample Cu (containing 30 wt% Cu₂O), sample Zn/Cu (containing 40 wt% spherical Zn, 5 wt% lamellar ZnAl alloy, and 10 wt% Cu₂O, homogeneously mixed) and sample Zn+Cu (Fabricated as a two-layer system: the primer layer contained 40 wt% spherical Zn and 5 wt% lamellar ZnAl alloy; the topcoat contained 10 wt% Cu₂O).

The respective pigment formulation was dispersed into the prepared ethyl silicate binder, subsequently filtered, and then coated onto the pretreated steel substrates using a dip-coating method. The coatings were allowed to dry naturally in air (cured under ambient conditions) for seven days before subsequent corrosion and antifouling testing. The dry film thickness (DFT) of the coatings was controlled to be approximately 100 ± 10 µm, except for the Zn+Cu sample, which had a DFT of 120 ± 10 µm due to its bilayer structure.

Analytical and testing methods

Physicochemical and mechanical characterization

Surface wettability was evaluated by measuring the water contact angle (WCA) using an OCA 50 contact angle goniometer (Dataphysics, Germany). The average value was calculated from three replicate measurements per sample. The adhesion strength of the coating to the steel substrate was determined using the pull-off method according to the ASTM D4541 standard, utilizing a Defelsko PosiTest AT adhesion tester. Measurements were performed at three different locations on each sample. The impact resistance of the coating was assessed using an Elcometer 1615 Impact Tester, following the procedure outlined in ISO 6272-2:2011.

Structural and morphological analysis

The crystalline phase composition of the coatings was analyzed by X-ray diffraction (XRD) using a Bruker D8 Advance AXS diffractometer with Cu Kα radiation over a 2θ range of 10° to

80°. The surface morphology and microstructure of the coatings were observed using a JSM-IT-200 scanning electron microscope (SEM) (Jeol Ltd., Japan). The chemical functional groups present in the coatings were identified by Fourier-transform infrared spectroscopy (FTIR) using a Tensor 27 spectrometer (Bruker, Germany), scanning in the wavenumber range from 4,000 cm⁻¹ to 400 cm⁻¹.

Electrochemical and corrosion resistance assessment

The corrosion resistance of the coatings was evaluated by electrochemical impedance spectroscopy (EIS) and polarization curve measurements using an Autolab PGSTAT 204N electrochemical workstation with a standard three-electrode cell setup. The coated sample served as the working electrode (WE), a Platinum (Pt) mesh as the counter electrode (CE), and an Ag/AgCl electrode as the reference electrode (RE). The test electrolyte was a 3.5 wt% NaCl solution. The exposed surface area of the sample to the electrolyte was 3.46 cm². EIS measurements were performed over a frequency range from 100 kHz to 0.01 Hz, with an AC perturbation amplitude of 10 mV at the open-circuit potential (OCP). EIS measurements were repeated over 60 days of immersion to monitor the evolution of protective performance. Potentiodynamic polarization curves were recorded by scanning the electrode potential from -150 mV to +150 mV versus OCP at a scan rate of 0.01 V/s (10 mV/s). From these curves, the corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined. Electrochemical data were processed using Nova 2.0 software. Triplicate measurements were performed for each condition to ensure statistical reliability.

Metal ion release rate measurement

Statistical analyses. The release rates of Zinc (Zn²⁺) and Copper (Cu²⁺) ions from the coatings were determined by Atomic Absorption Spectroscopy (AAS) using an AA-6800 instrument (Shimadzu, Japan). Coated samples (dimensions 5 cm × 10 cm × 0.2 cm)

were immersed in artificial seawater. The concentration of metal ions in the solution was analyzed after immersion periods of 2, 15, and 30 days. The metal ion release rate (R , in µg/cm².day) was calculated using the formula:

$$R = (\rho \times V \times 24) / (t \times A) \quad (1)$$

where: ρ is the cumulative concentration of the metal ion (µg/L); V is the volume of the solution (L); t is the testing time (h); and A is the surface area of the coating exposed to the solution (cm²).

Natural environment antifouling test

The antifouling efficacy of the coatings was evaluated directly in a natural marine environment at Dam Bay, Hon Tre Island, Nha Trang, Vietnam. Sample panels were hung at a depth of 1.0 meters below the sea surface and monitored for 1, 4.5, and 12 months. Parameters of seawater samples, including pH, temperature (°C), and salinity (‰), were determined to be 8.0 ± 0.3, 28.4 ± 2.3°C, and 3.5 ± 0.1‰.

Results

Physicochemical and mechanical characterization

This study evaluates the physicochemical and surface properties of four coating systems based on an ethyl silicate binder, including variations containing zinc (Zn), copper(I) oxide (Cu₂O), a mixture (Zn/Cu), and a bilayer structure (Zn+Cu). The results, presented in Figure 1, show a distinct influence of the coating composition and structure on adhesion strength, impact resistance, and water contact angle.

Adhesion strength (Fig. 1a) is a critical factor determining the service life and protective efficiency of a coating [22]. In this study, the Zn+Cu coating with its bilayer structure exhibited the highest adhesion strength (~ 3.5 MPa), followed by the Zn coating (~ 3.1 MPa). Previous studies have reported good adhesion of zinc-rich coatings based on silicate binders, often attributing this

to the formation of chemical bonds between silanol groups ($-\text{Si}-\text{OH}$) in the hydrolyzed coating film and the metal substrate's surface oxides, as well as mechanical interlocking [23]. The use of a zinc-rich primer in the Zn+Cu sample appeared to optimize this interaction, resulting in superior adhesion compared to the other systems. Conversely, the coating containing only Cu_2O (Sample Cu) had the

lowest adhesion strength (~ 1.7 MPa). This may be related to weaker interactions between Cu_2O particles and the ethyl silicate matrix, or between the Cu_2O coating and the substrate, compared to those in the zinc-containing systems [24]. The Zn/Cu composite sample exhibited intermediate adhesion, suggesting contributions from both Zn and Cu_2O .

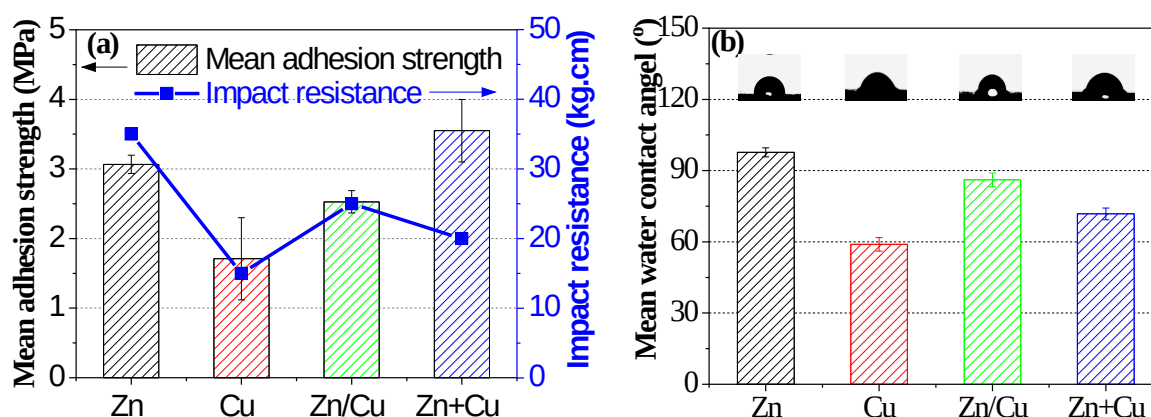


Figure 1. Adhesion strength and impact resistance (a) and Water contact angle (b) of the coatings

Regarding impact resistance (Fig. 1a), the Zn coating demonstrated the best performance (~ 34 kg.cm). Zinc particles, especially the lamellar ZnAl flakes, are known for their ability to enhance toughness and dissipate impact energy within the coating matrix [5]. The low impact resistance of the Cu coating (~ 15 kg.cm) may reflect the more brittle nature of Cu_2O or weaker cohesion within the system [24]. Interestingly, the Zn+Cu coating, despite having the highest adhesion, exhibited significantly lower impact resistance (~ 20 kg.cm) than the Zn coating. This phenomenon is not uncommon in multilayer systems, where incompatibility between layers or interface stress can reduce overall impact resistance, even when adhesion to the substrate remains good [25]. The Cu_2O topcoat in the Zn+Cu system may be the limiting factor for its impact resistance.

Surface wettability, assessed via contact angle (Fig. 1b), is an important property affecting the coating's interaction with the environment, such as its corrosion or antifouling performance [26]. The Zn coating exhibited distinct hydrophobicity (contact angle $\sim 98^\circ$).

This aligns with reports that zinc or zinc oxide surfaces (often naturally formed on zinc) can exhibit hydrophobic behavior [23]. In contrast, the Cu_2O coating (sample Cu) was hydrophilic (contact angle $\sim 59^\circ$), a characteristic commonly observed for metal oxides such as Cu_2O [10]. Incorporating both components in the Zn/Cu ($\sim 87^\circ$) and Zn+Cu ($\sim 75^\circ$) samples resulted in intermediate wettability. Although both have Cu_2O at the exposed surface (in the mixture or as the top layer), they were still considerably more hydrophobic than the pure Cu sample, suggesting an underlying influence of the silicate matrix and/or the remaining zinc components. The slight difference between Zn/Cu and Zn+Cu might be related to differences in surface microstructure or the proportion of components at the air-facing surface [26].

Structural and morphological analysis

To gain further insight into the phase composition and chemical bonding structure of the prepared coatings, X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy

(FTIR) analyses were conducted, as presented in Figure 2.

XRD analysis reveals the crystalline phases present in the materials (Fig. 2a). For the Zn coating, the diffractogram shows the presence of distinct diffraction peaks corresponding to the crystalline metallic zinc (Zn) phase (e.g., peaks around 36.4° (002), 39.1° (100), 43.3° (101), 54.4° (102), 70.7° (103)), consistent with standard data (JCPDS 04-0831) [27], and the presence of a broad, low-intensity diffraction hump at low 2θ angles (around $20\text{--}30^\circ$) is characteristic of the amorphous phase of silica (SiO_2) formed from the hydrolysis and condensation of TEOS in the ethyl silicate matrix [28]. Regarding the Cu coating, the pattern for this sample predominantly displays characteristic diffraction peaks for the cubic copper(I) oxide (Cu_2O) phase (peaks around 36.5° (111), 42.4° (200), 61.5° (220), 73.7° (311)), matching well with reference data (JCPDS 05-0667) [29]; no diffraction peaks for zinc were detected, confirming the expected composition of this coating, and the amorphous SiO_2 background was also observed. For the Zn/Cu coating, this diffractogram is a combination of

the two previous samples, clearly showing the coexistence of diffraction peaks from both metallic Zn and Cu_2O , confirming that, in this single-layer composite coating, both additive components are dispersed as separate crystalline phases within the silicate matrix. In the case of the Zn+Cu coating, the pattern for this bilayer sample is very similar to that of the pure Zn sample, with the diffraction peaks of metallic Zn being dominant, while characteristic peaks for Cu_2O are very weak, if present at all, or indistinguishable from the background. This can be explained in several ways: (i) the Cu_2O topcoat is relatively thin compared to the penetration depth of the X-rays, causing the signal from the underlying Zn primer to dominate; (ii) the Cu_2O layer might have lower crystallinity compared to the pure Cu sample; or (iii) preferred orientation of the Zn crystals in the primer layer. However, this result confirms the presence of the crystalline Zn primer. Overall, XRD analysis successfully confirmed the presence of the expected crystalline phases (metallic Zn and/or Cu_2O) in the respective coatings, along with the amorphous SiO_2 background from the binder.

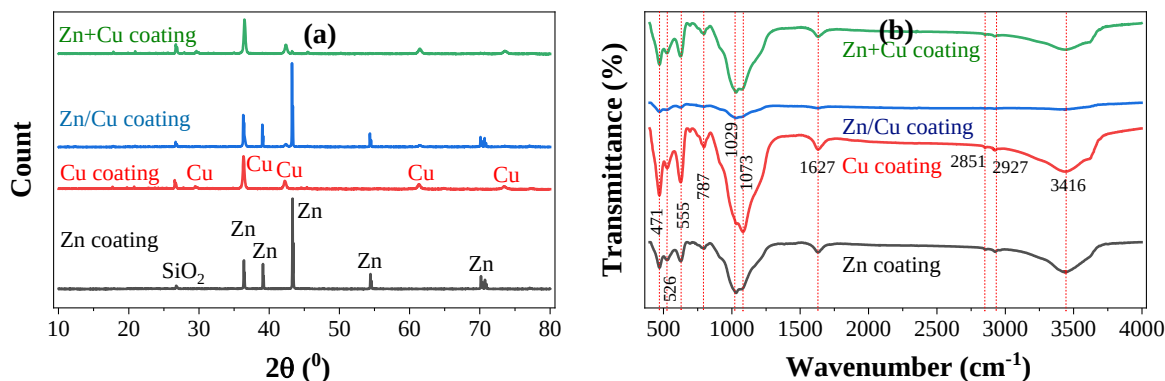


Figure 2. XRD patterns (a) and FTIR spectra (b) of the coatings

FTIR spectroscopy provides information about the functional groups and chemical bonds present in the coatings (Fig. 2b). All spectra exhibit strong characteristic absorption bands of the silica (SiO_2) network, the main component of the ethyl silicate binder after hydrolysis and condensation. Key absorption bands include: symmetric and asymmetric stretching vibrations of Si-O-Si bonds (observed around 1029--

$1,073\text{ cm}^{-1}$ and a shoulder at $\sim 1,200\text{ cm}^{-1}$), bending vibration of Si-O-Si bonds (around $787\text{--}800\text{ cm}^{-1}$), and bending vibration of O-Si-O bonds (around $471\text{--}555\text{ cm}^{-1}$) [30, 31].

A broad absorption band around $3,416\text{ cm}^{-1}$ and a weaker peak around $1,627\text{ cm}^{-1}$ are attributed to O-H stretching vibrations and H-O-H bending vibrations of water molecules, respectively. Their presence indicates the

persistence of incompletely condensed silanol groups (Si-OH) or physically adsorbed water within the porous structure of the silica matrix [32].

Weak peaks around 2,851 and 2,927 cm^{-1} can be assigned to C-H stretching vibrations from residual ethoxy groups ($-\text{OCH}_2\text{CH}_3$) from

incompletely hydrolyzed or condensed TEOS precursor [33].

Identifying characteristic absorption bands specific to Zn-O or Cu-O in this infrared region is difficult, as they typically lie at low wavenumbers ($< 650 \text{ cm}^{-1}$) and can be obscured by or overlap with the strong Si-O network vibrations [34].

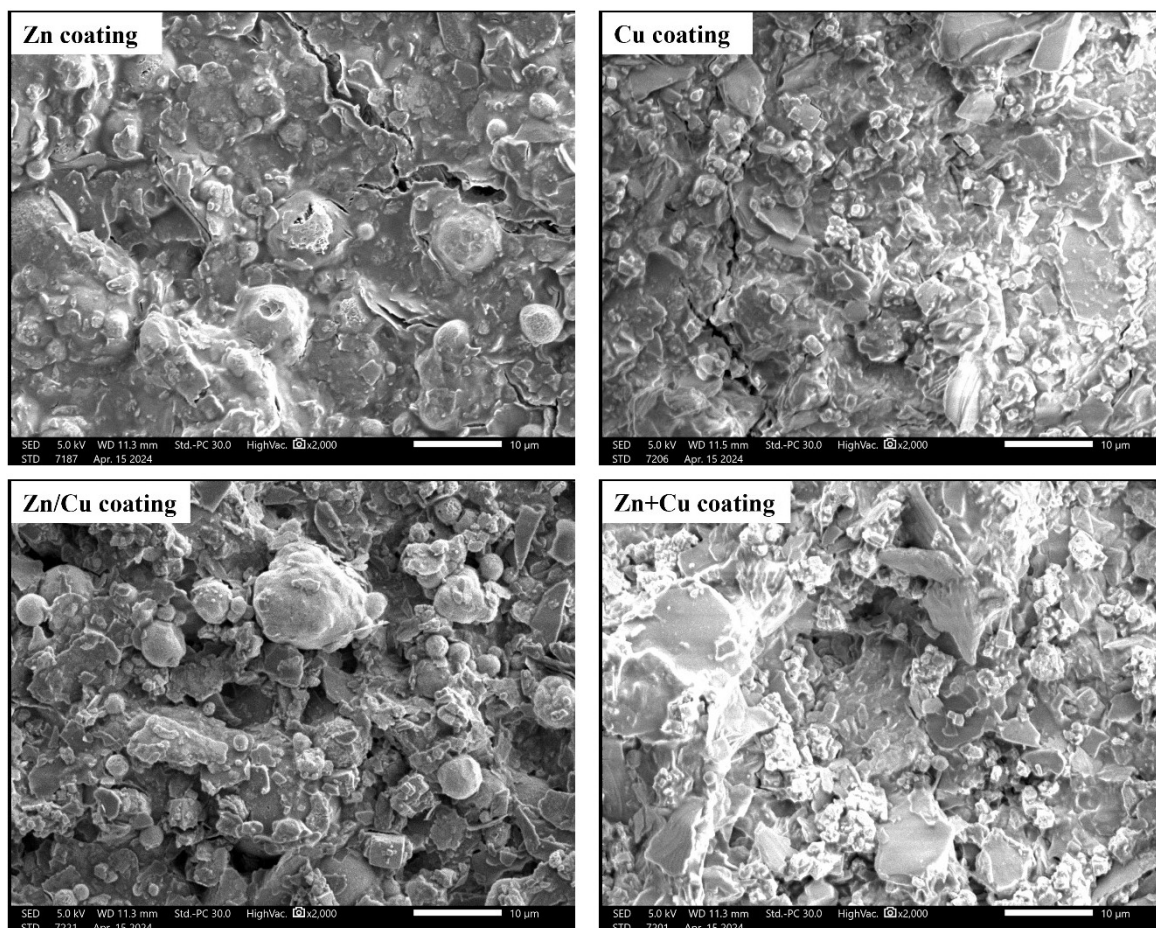


Figure 3. SEM images of coatings

FTIR analysis primarily confirms the chemical structure of the silicate matrix formed from TEOS. The significant similarity between the spectra indicates that the binder is the dominant component determining the main absorption features in the investigated infrared range.

Scanning electron microscopy (SEM) images in Figure 3 clearly show the differences in surface morphology and microstructure among the four fabricated coating types, helping to

explain the mechanical properties and wettability presented in Figures 1 and 2. The Zn coating has a relatively rough, non-uniform surface, containing spherical zinc particles and flake-like structures (possibly flake ZnAl) dispersed in an ethyl silicate matrix. The zinc particles are only partially covered by the binder. Notably, microcracks are present; this morphology, with the distribution of zinc particles and cracks, is typically observed in zinc-rich silicate-based coatings [18]. The cracks may

form due to shrinkage stress during the curing of the filler-rich silicate film [18, 33]. Although the cracks might affect long-term durability, the high density of zinc particles explains the good impact resistance (Figure 1a) due to their energy-dissipating capability. Conversely, the Cu coating exhibits a fairly uniform granular structure of Cu_2O particles (variously shaped), embedded in the silicate matrix at high density. This morphology is distinctly different from that of the Zn coating, reflecting the distinct nature and size of the Cu_2O additive particles. This granular structure might be responsible for the lower adhesion and impact resistance (Fig. 1a) compared to the zinc system, possibly due to weaker interaction between Cu_2O particles and the matrix or the brittle nature of the particles. The Zn/Cu (mixed) coating's surface morphology is complex, featuring the simultaneous presence of larger spherical zinc particles and smaller, more angular Cu_2O particles/clusters, randomly distributed within the silicate matrix, consistent with the mixing of components within the same layer. This explains the intermediate mechanical properties and wettability observed (Fig. 1). For the Zn+Cu double-layer sample, the surface morphology is primarily determined by the

outermost Cu_2O -containing layer, appearing rough and non-uniform. This surface differs from the pure Cu coating, possibly due to the lower Cu_2O concentration (10% vs 30%) and/or influence from the rough structure of the underlying Zn primer layer. The surface appears less densely packed with Cu_2O particles than the Cu sample. However, this roughness and structure might contribute to the highest adhesion strength observed (Fig. 1a), potentially through enhanced mechanical interlocking or reduced internal stress.

Electrochemical and corrosion resistance assessment

Table 1 provides the quantitative electrochemical parameters extracted from the polarization curves (Fig. 4), offering a detailed evaluation of the corrosion protection performance of four types of coatings after 7 days of immersion in a 3.5 wt% NaCl solution. These parameters include corrosion potential (E_{corr} , mV vs Ag/AgCl), corrosion current density (i_{corr} , $\mu\text{A}/\text{cm}^2$), anodic (β_a) and cathodic (β_c) Tafel slopes (mV/dec), and polarization resistance (R_p , $\Omega\cdot\text{cm}^2$).

Table 1. Data obtained from DC polarization for coatings after 7 days of exposure to a 3.5 wt% NaCl solution

Sample	E_{corr} (mV vs Ag/AgCl)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/dec)	$-\beta_c$ (mV/dec)	R_p ($\Omega\cdot\text{cm}^2$)
Zn	-745.08	0.837	102.61	252.69	37,852
Cu	-561.26	326.91	146.41	419.86	144.21
Zn/Cu	-658.15	2.205	107.46	273.5	15,189
Zn+Cu	-815.01	1.237	144.29	190.06	28,796

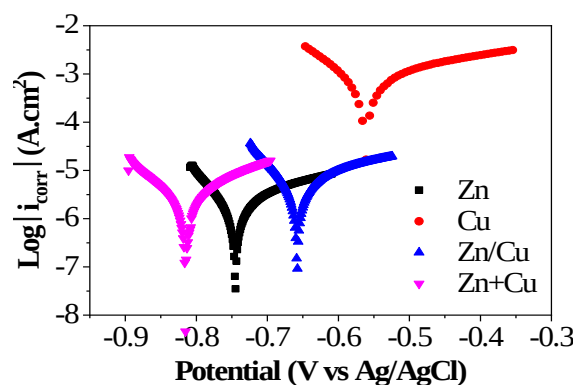


Figure 4. Polarization curves of coatings after 7 days of exposure to 3.5 wt% NaCl solution

The corrosion rate, reflected by the corrosion current density, indicates that the Zn coating has the lowest value ($0.837 \mu\text{A}/\text{cm}^2$), confirming its superior protective capability. In contrast, the Cu coating exhibits an extremely high value ($326.91 \mu\text{A}/\text{cm}^2$, approximately 390 times higher), indicating very poor protection. The combined coatings, Zn+Cu ($1.237 \mu\text{A}/\text{cm}^2$) and Zn/Cu ($2.205 \mu\text{A}/\text{cm}^2$), have significantly lower corrosion rates than Cu but still higher than Zn (about 1.5 and 2.6 times, respectively). Notably, the bilayer Zn+Cu structure shows a lower corrosion rate (better protection) than the mixed Zn/Cu coating.

Polarization resistance (R_p), an inverse measure of corrosion rate, follows the same trend as the corrosion current density: the Zn coating has the highest R_p (37,852 $\Omega \cdot \text{cm}^2$), followed by Zn+Cu (28,796 $\Omega \cdot \text{cm}^2$), Zn/Cu (15,189 $\Omega \cdot \text{cm}^2$), and finally Cu with a very low R_p (144.21 $\Omega \cdot \text{cm}^2$). This protective effectiveness ranking (Zn > Zn+Cu > Zn/Cu >> Cu) once again confirms the superiority of the Zn coating and highlights the greater effectiveness of the bilayer structure compared to the mixed one in reducing corrosion rates.

Analysis of corrosion potential and reaction kinetics reveals that the Cu coating shows the most positive (or least negative) corrosion potential (-561.26 mV) compared to the other coatings, while the Zn-containing coatings are significantly more active: Zn/Cu (-658.15 mV), Zn (-745.08 mV), and Zn+Cu (-815.01 mV) are the most active. All these E_{corr} values are more negative than that of carbon steel, indicating that all three Zn-containing coatings are capable of providing sacrificial protection to the steel substrate [6], with Zn+Cu showing the strongest sacrificial tendency thermodynamically.

The Tafel slope values offer insights into the anodic (metal dissolution) and cathodic (oxygen reduction) reaction kinetics [5, 35]. For the Zn coating, β_a (102.61 mV/dec) is close to the theoretical value for activation-controlled Zn dissolution, while β_c (252.69 mV/dec) is relatively high, possibly indicating mixed control or oxygen diffusion effects. The Cu coating has both β_a (146.41 mV/dec) and β_c (419.86 mV/dec) at relatively high levels, suggesting complex reaction steps or hindered kinetics, despite the overall high rate.

The Zn/Cu coating shows β_a (107.46 mV/dec) and β_c (273.5 mV/dec), similar to those of the Zn coating, indicating potentially similar control mechanisms but with a higher overall rate. The Zn+Cu coating shows higher β_a (144.29 mV/dec) and lower β_c (190.06 mV/dec) than Zn; the lower β_c may indicate easier cathodic reactions on the Cu_2O -containing surface [29]. However, the corrosion current density of Zn+Cu is still lower than that of Zn/Cu, indicating that while the cathodic reaction may be kinetically easier, the overall effective active area or anodic reaction may be better controlled in this bilayer system.

Therefore, the quantitative data in Table 1 strongly support the previous analyses. The superior protective performance of the Zn coating (lowest i_{corr} , highest R_p , sufficiently negative E_{corr}) aligns well with the sacrificial protection mechanism of zinc. The poor performance of the Cu coating (highest i_{corr} , lowest R_p) is associated with its morphology (Fig. 3) and electrochemical nature. A key finding is that the Zn+Cu bilayer structure provides better performance (lower i_{corr} , higher R_p) than the Zn/Cu mixed structure, despite having a more negative E_{corr} . This could be due to the bilayer structure optimizing the balance between the sacrificial activity of the Zn underlayer and a degree of barrier protection or cathodic reaction control provided by the outer Cu_2O layer.

Periodic electrochemical impedance spectroscopy (EIS) measurements evaluated the long-term protection durability over 60 days in 3.5 wt% NaCl on Zn, Zn/Cu, and Zn+Cu coatings (excluding Cu due to poor performance). Figure 5 presents the evolution of impedance at 10 mHz and phase angle at 100 kHz.

Impedance at 10 mHz reflects overall corrosion resistance [18]. Initially, Zn+Cu showed the highest impedance ($\sim 4.65 \log|Z|$), followed by Zn (~ 4.3) and Zn/Cu (~ 4.25). All coatings exhibited a significant increase in impedance during the first 20–30 days, attributed to the formation of protective zinc corrosion products that blocked defects [6]. Subsequently, Zn+Cu maintained the highest impedance (peak > 5.0 $\log|Z|$), followed by Zn (~ 4.9) and then Zn/Cu (~ 4.7). The 60-day performance ranking based on impedance is Zn+Cu > Zn > Zn/Cu, indicating the bilayer structure offers the most sustainable protection.

The phase angle at 100 kHz indicates coating integrity [5]. Initially higher for Zn and Zn+Cu ($\sim 48^\circ$) than Zn/Cu ($\sim 30^\circ$), the phase angles for all coatings increased over the first 30 days, suggesting improved barrier function due to pore blocking by corrosion products [23]. Long-term, Zn and Zn+Cu stabilized at similarly high angles (65–68 $^\circ$), while Zn/Cu remained slightly lower (63–64 $^\circ$), confirming better sustained integrity for Zn and Zn+Cu systems.

These dynamic EIS results complement the instantaneous DC polarization data (Table 1). The long-term impedance ranking ($\text{Zn+Cu} > \text{Zn} > \text{Zn/Cu}$) differs slightly from the day 7 corrosion rate ranking ($\text{Zn} > \text{Zn+Cu} > \text{Zn/Cu}$), suggesting that initial performance may not predict long-term durability, as protective layers evolve. However, both methods identify Zn/Cu as the least protective among the three.

The superior long-term performance of the Zn+Cu bilayer (Fig. 3) likely arises from an optimized balance between the primer's sacrificial action and the topcoat's barrier effect or control over product formation/release. The general improvement observed across all Zn-containing systems suggests self-healing, as Zn corrosion products seal initial coating defects [19].

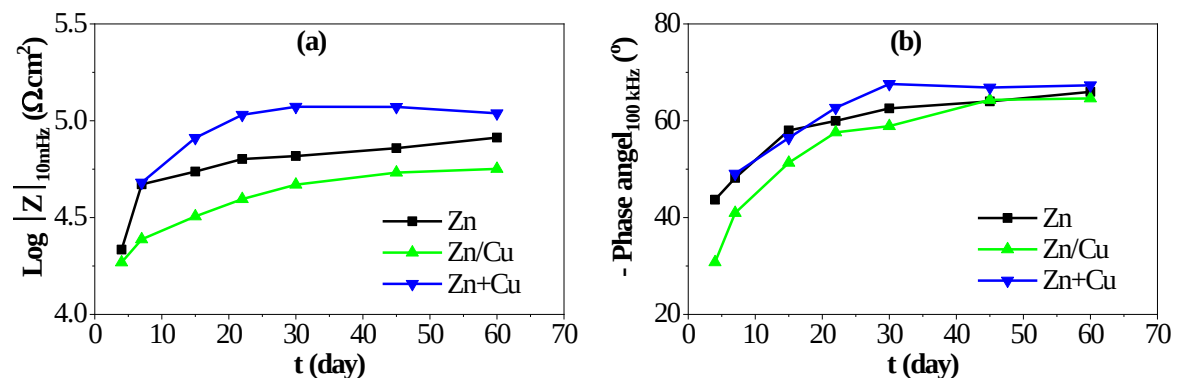


Figure 5. The plots of total impedance (10 mHz) (a) and phase angle (100 kHz) (b) versus immersion time of the coatings obtained from the Bode plot

Metal ion release rate

Figure 6 shows the release rates of zinc (Zn) (Fig. 6a) and copper (Cu) (Fig. 6b) from various coating systems during 30-day immersion in

seawater under laboratory conditions. These data offer important insights into the dissolution behavior of active components related to corrosion protection (Zn) and antifouling effectiveness (Cu).

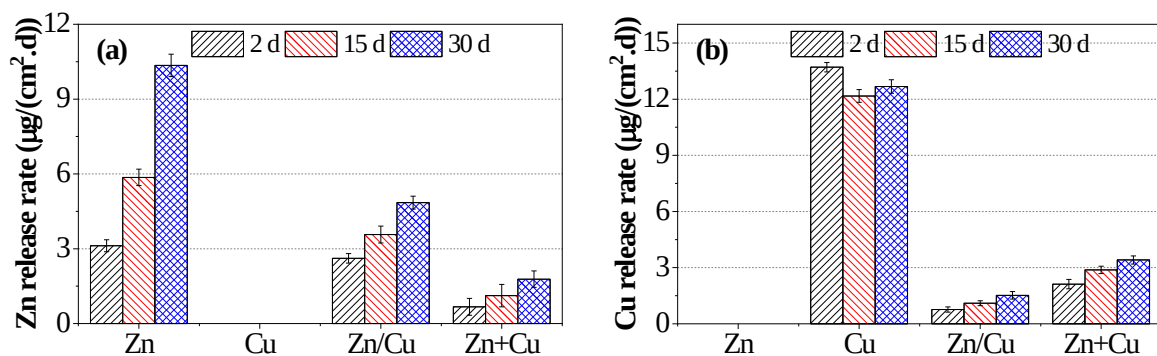


Figure 6. Zn (a) and Cu (b) release rates of coatings during 30 days of immersion in seawater in the laboratory

The Zn coating exhibited the highest Zn release, increasing from $3.12 \mu\text{g}/\text{cm}^2\cdot\text{day}$ after 2 days to over $10.35 \mu\text{g}/\text{cm}^2\cdot\text{day}$ after 30 days. This reflects the sacrificial corrosion mechanism of Zn particles [7], with the increasing rate possibly due to enhanced

permeability or to corrosion products affecting dissolution kinetics. The Zn/Cu coating showed a lower Zn release ($4.85 \mu\text{g}/\text{cm}^2\cdot\text{day}$ after 30 days), possibly due to Cu_2O altering the microenvironment or competitive dissolution. The Zn+Cu bilayer exhibited the lowest Zn

release ($1.78 \mu\text{g}/\text{cm}^2\cdot\text{day}$), consistent with the barrier effect of the Cu_2O -rich topcoat that limits seawater exposure. The Cu coating, as expected, released no Zn.

In terms of Cu release (Fig. 6b), the Cu coating maintained a high and stable rate ($12\text{--}14 \mu\text{g}/\text{cm}^2\cdot\text{day}$) over 30 days, typical for Cu_2O -based antifouling coatings designed to provide sufficient toxic Cu ion flux [36]. This rate aligns with effective antifouling thresholds ($\sim 10 \mu\text{g}/\text{cm}^2\cdot\text{day}$) [15]. The Zn/Cu coating, with only 10 wt% Cu_2O , showed a much lower Cu release ($1.52 \mu\text{g}/\text{cm}^2\cdot\text{day}$), while the Zn+Cu coating, also containing 10 wt% Cu_2O , released more ($3.41 \mu\text{g}/\text{cm}^2\cdot\text{day}$). This suggests that localizing Cu_2O in the outer layer enhances release efficiency, potentially due to increased exposure or galvanic interaction between the Zn primer (anode) and the Cu_2O -rich topcoat (cathode). The Zn coating showed no Cu release.

These findings support electrochemical results and enhance understanding of coating performance. High Zn release in the Zn coating confirms its active protection role. In contrast, the low Zn release in the Zn+Cu system reflects effective shielding, correlating with improved corrosion resistance in EIS data (Fig. 5). Although the Cu coating provides strong antifouling performance, its poor corrosion resistance (Table 1) limits its overall effectiveness. Zn/Cu and Zn+Cu systems offer better corrosion protection but lower Cu release, raising concerns about antifouling efficacy. However, soluble Zn species may also contribute biocidal effects. The Zn+Cu bilayer, with better corrosion resistance and higher Cu release than Zn/Cu, shows potential to balance protection and bioactivity.

Natural environment antifouling test

Figure 7 provides a visual overview of the surface condition of coated panels after different exposure durations (0, 1, 4.5, and 12 months) in a natural marine environment, enabling assessment of the practical antifouling performance of coatings under real-world conditions.

At 0 months, all samples appeared clean, showing the original surface. After 1 month, Cu

and Zn+Cu coatings maintained mostly clean surfaces, with only minor biofilm, while Zn and Zn/Cu began showing early signs of fouling and/or corrosion. By 4.5 months, significant differences emerged: Zn and Zn/Cu showed heavy fouling, including macroorganisms such as barnacles. Cu also showed macrofouling, while Zn+Cu demonstrated significantly better antifouling performance, with minor biofouling and large areas still uncovered. At 12 months (images available for Zn, Zn/Cu, and Zn+Cu), Zn and Zn/Cu were heavily fouled, nearly covering the entire surface. Zn+Cu continued to show the best performance, with more fouling than at 4.5 months, but still less severe in coverage and organism size than the other two. Based on visual assessment, the antifouling effectiveness after 12 months follows the order: Zn+Cu > Zn/Cu $\approx$ Zn. While Cu initially performed well, its effectiveness declined over time.

These observations correlate with the ion release rates analyzed in Figure 6. The Cu coating, with a high Cu release rate ($\sim 12\text{--}14 \mu\text{g}/\text{cm}^2\cdot\text{day}$), initially inhibited fouling but failed to maintain effectiveness beyond the early months, possibly due to coating degradation or insufficient long-term protection against all fouling types [10]. In contrast, Zn+Cu, with a moderate Cu release ($3.41 \mu\text{g}/\text{cm}^2\cdot\text{day}$), exhibited the best long-term antifouling performance. This suggests that a lower but stable and sustained Cu ion release, combined with coating durability (as supported by EIS data in Fig. 5), can yield better overall protection over time [12]. The Zn/Cu sample, with a lower Cu release ($1.52 \mu\text{g}/\text{cm}^2\cdot\text{day}$), had limited antifouling effectiveness, comparable to Zn. The Zn coating, which released no Cu, also lacked antifouling capacity. Although Zn compounds may have some biocidal effects [19], the measured Zn release and corrosion products were insufficient to prevent diverse marine biofouling under these test conditions.

The antifouling mechanism primarily relies on the release of Cu ions from Cu_2O , which are toxic to larvae and spores [37]. The superior long-term performance of Zn+Cu compared to Cu (despite lower Cu_2O content) and Zn/Cu (with the same Cu_2O content) underscores the importance of coating architecture.

Concentrating Cu_2O in the outer layer of the Zn+Cu bilayer likely enhances and stabilizes Cu release more effectively than dispersion in the Zn/Cu hybrid layer. Furthermore, Zn+Cu's improved structural integrity over time (as inferred from Figure 5) may also contribute to its sustained antifouling efficiency. Natural

exposure also indirectly reflects coating durability. Coatings with heavy fouling (Zn, Zn/Cu, Cu) may over time face under-deposit corrosion, reducing service life [38]. In contrast, Zn+Cu's superior antifouling capacity can help preserve structural integrity and prolong the protective function of the Zn-rich primer.

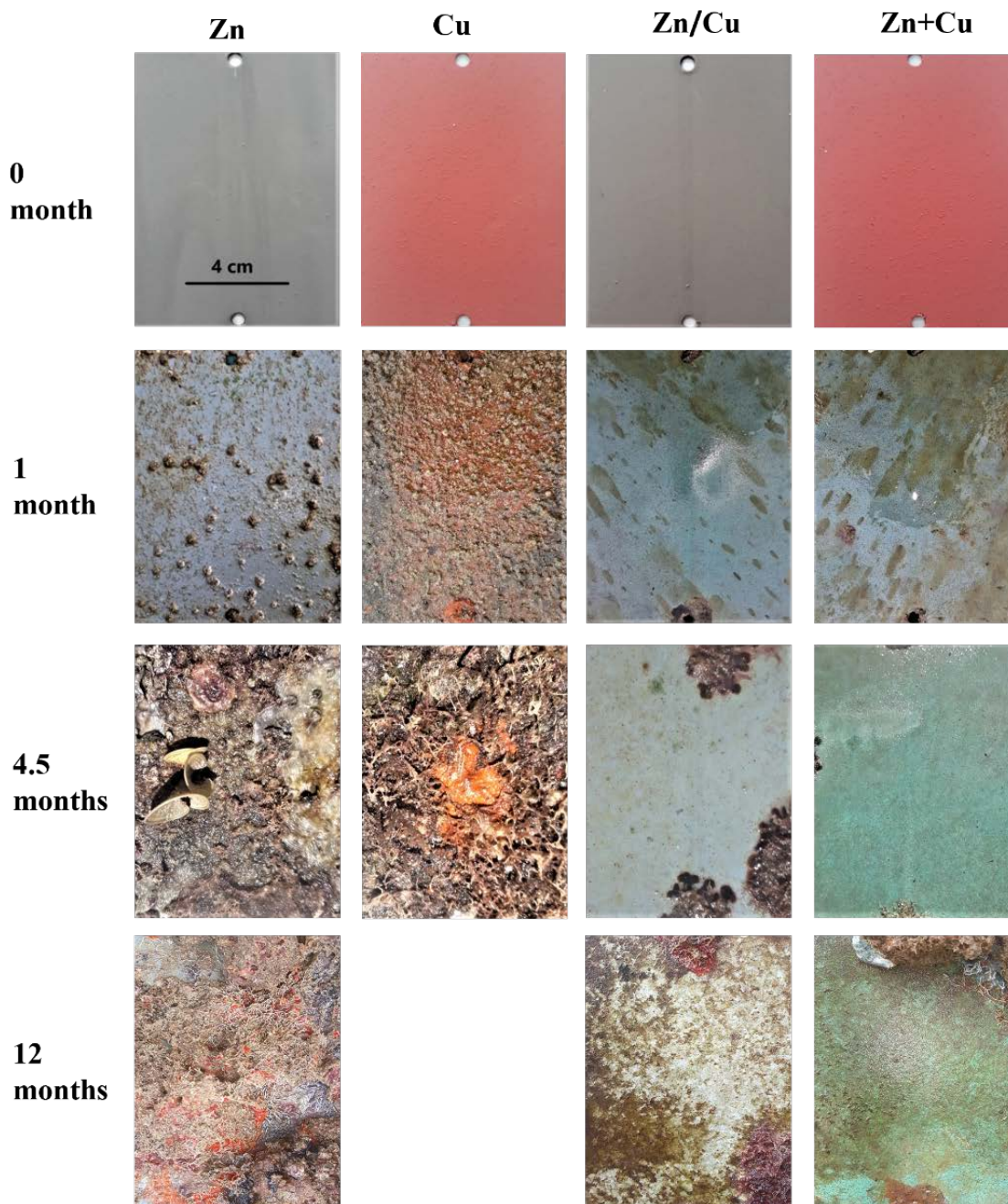


Figure 7. Images showing the fouling surfaces of coatings after undergoing natural testing for different durations

Conclusion

This study systematically evaluated and compared the protective performance of four types of ethyl silicate-based coatings containing Zinc (Zn) and/or Copper(I) oxide (Cu_2O), including Zn-only, Cu-only, mixed Zn/Cu, and bilayer Zn+Cu coatings, for marine applications. Results showed that the Zn-only coating provided effective sacrificial corrosion protection but failed in antifouling performance. Conversely, the Cu coating exhibited good initial antifouling ability due to a high copper release rate, but possessed very poor corrosion resistance, and its antifouling efficacy decreased over time.

Combining Zn and Cu_2O improved the balance between the two functions; however, the coating structure played a decisive role. The bilayer Zn+Cu coating (Zn primer, Cu_2O topcoat) demonstrated superior overall performance compared to the mixed Zn/Cu coating and the single-component coatings. The Zn+Cu system not only exhibited the best adhesion and superior long-term corrosion resistance (indicated by the highest electrochemical impedance after 60 days of immersion), but also released copper effectively and provided the best antifouling performance in the 12-month field exposure test. These results confirm that the bilayer structure is an effective strategy for simultaneously optimizing corrosion protection and antifouling properties, opening potential avenues for developing sustainable, multifunctional ethyl silicate coating systems for marine applications.

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