



Comparative study of azole-based corrosion inhibitors for nickel and copper–nickel alloys in NaCl solution

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ABSTRACT

The corrosion-inhibition performance of seven organic inhibitors on Ni metal, and on CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀ alloys was studied in 3 wt% NaCl. Electrochemical tests and XPS analyses revealed strong alloy-dependent inhibition. While Ni showed poor response, Cu-rich alloys formed protective Cu-inhibitor layers, with BTAH, SH-Thd-Me, and SH-BimH being optimal for CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀, respectively. Surface enrichment of Cu is a decisive factor in forming a protective layer with inhibitors. Inhibitor structure and alloy composition jointly influenced film morphology and bonding, highlighting the critical role of alloying in designing corrosion inhibitor protection strategies.

1. Introduction

CuNi alloys are extensively used in marine and chloride-containing environments (e.g. desalination plants, ship hulls, heat exchangers, and seawater piping) due to their excellent corrosion resistance in seawater [1]. This inherent resistance is attributed to the formation of protective surface films: an inner barrier layer rich in cuprous oxide (Cu₂O) with some Ni incorporated, and an outer layer of cuprous chloride (CuCl), which together shield the alloy from aggressive chloride attack [2–5]. Increasing the Ni content in Cu improves the stability of these protective films by reducing vacancies at the inner barrier layer; for example, a CuNi₃₀ cupronickel (70 wt% Cu, 30 wt% Ni) forms a Ni-enriched Cu₂O layer that imparts superior seawater corrosion resistance compared to lower-Ni alloys [5,6]. However, Milošev and Metikoš-Huković found that variations in Cl[−] concentration also influence the corrosion resistance of CuNi alloys, which does not simply increase with Ni content [5]. At low Cl[−] concentrations, corrosion resistance may even slightly decrease [5]. Although the surface film alleviates corrosion attack, long-term corrosion risks and the demand for further reduction in corrosion rate persist. Therefore, CuNi alloys require flexible corrosion protection strategies that maintain good electrical and thermal conductivity. Conventional approaches, such as organic coatings, are often ineffective. In this context, organic corrosion inhibitors have emerged as a promising and highly adaptable option also for Cu-based alloys [7–9].

Organic corrosion inhibitors, typically containing heteroatoms (such

as N, O, S), can adsorb onto metal surfaces and markedly reduce corrosion rates by forming protective films [10]. A classic example is benzotriazole (BTAH), which has been extensively used to inhibit Cu corrosion by adsorbing and forming a mono- or multi-layer barrier on the Cu surface [11–13]. The inhibition mechanism of BTAH and related azole compounds is generally understood to involve chemisorption with surface metal atoms (e.g. forming Cu(I)–BTA film), thereby creating an adherent film that blocks aggressive species [8,14]. Numerous organic inhibitors – from small synthetic molecules (e.g. triazoles, thiazoles, amines) to large biomolecules and plant extracts – have been investigated for Cu in chloride media and show high inhibition efficiencies [15–22].

Various corrosion inhibitors have been studied in chloride media for CuNi alloys. In particular, azole-based compounds (such as benzotriazole and other triazoles) are well known for their high inhibition efficiency against corrosion of Cu and CuNi alloys. BTAH shows outstanding performance on CuNi₁₀ alloy, yielding ~99% inhibition efficiency (IE) in synthetic seawater even with 10 ppm sulfide by forming a protective inhibitor layer [23,24]. Similarly, triazole derivatives, such as 3-amino–1,2,4-triazole–5-thiol (ATT), afford high inhibition on Cu₇₀Ni₃₀ alloy in 3 wt% NaCl. Polarization results show that ATT is a mixed-type inhibitor that greatly reduces the corrosion current and achieves 98–99% IE at 0.5 mM even under flow conditions [25]. Some triazole and isoxazole compounds also show good inhibition in the cooling water system [26]. Moreover, eco-friendly inhibitors, such as lentil seed extract, yielded nearly 98% inhibition for CuNi₁₀ (wt%) in

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3.5 wt% NaCl at 300 ppm, thereby significantly reducing the corrosion rate [27]. Similarly, carob fruit extract achieved up to 92.6% and 83.2% inhibition efficiency for CuNi₁₀ and CuNi₃₀ (wt%) alloys, respectively, in 3.5 wt% NaCl solution at a 300 ppm dosage [28]. Despite these advances, several aspects of corrosion inhibition for CuNi alloys remain insufficiently understood. One key knowledge gap is the influence of alloy composition on inhibitor performance. Most prior investigations have focused on a single metal or a specific alloy composition, and direct comparisons across different CuNi-based alloys are lacking. Alloying can modify the surface film chemistry – for example, Ni metal in cupronickel contributes to a different oxide/chloride film structure than Cu metal, which in turn could affect how inhibitors interact with the surface. Further, data on inhibitor action on the CuNi₁₈Zn₂₀ alloy (nickel silver) are not available, but their behavior in chloride-containing media has been investigated previously [29–31].

Since the passive oxide film on Cu alloys is predominantly a Cu-rich layer [4,5], the corrosion-inhibition performance of organic inhibitors is expected to be closely related to their effectiveness on Cu metal. Therefore, the selection of inhibitors for CuNi alloys can be guided by those that demonstrate high inhibition on Cu metal. However, the optimal inhibitor for a Cu alloy does not necessarily coincide with that for Cu metal, as it is influenced by the alloying elements and their content [32,33]. The extensive linear polarization resistance (R_p) data accumulated in our laboratory for various corrosion inhibitors on Cu metal, as presented in Fig. 1, serve as a valuable reference for the preliminary screening of candidate inhibitors [29–38]. The y-axis represents the R_p value after immersion for 1 h in a 3 wt% NaCl solution containing 1 mM inhibitor, with error bars indicating the standard deviation of three or more measurements. This reflects the short-term adsorption behavior and the initial corrosion-inhibition efficiency on the Cu surface. The x-axis indicates the average R_p values measured over 24–100 h, with the corresponding standard deviation as error bars, reflecting the time-dependent evolution of inhibition efficiency and the long-term stability of the inhibitor. The "Blank" denotes the R_p value measured in a 3 wt% NaCl solution without any inhibitor. In Fig. 1, inhibitors that accelerate corrosion or exhibit low inhibition are circled with a black dashed line, those with moderate but insufficient performance are marked with a blue dashed circle, and those within the green dashed circle exhibit superior inhibition performance and are expected to be effective on Cu-based alloys. The inhibitors applied in this study are labeled with red color in the figure.

In the present work, we address the above-mentioned gaps on IE on CuNi alloys by investigating the corrosion-inhibition behavior of seven

azole-based organic inhibitors on Ni metal and three CuNi-based alloys in 3 wt% NaCl solution. The selection of inhibitors was based on their ability to inhibit corrosion of Cu metal, as shown in Fig. 1. The materials studied include Ni metal, CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀ alloy (wt%). Unlike previous studies that predominantly focused on individual inhibitors for single metals, the core novelty of this work lies in exploring the alloy composition-driven inhibition performance. Using a combination of electrochemical techniques and X-ray photoelectron spectroscopy (XPS) surface analysis, we evaluate the inhibition efficiency of each inhibitor over up to 120 h of immersion. This long (5-day) exposure allows us to track the time-dependent evolution of protective performance on each alloy, providing insight into the stability and longevity of the inhibitor films. More importantly, the rigorous XPS analysis, in conjunction with the electrochemical results, explicitly uncovers how varying alloying elements (Ni, Zn) and subsequent surface elemental redistributions dictate the metal–inhibitor interaction and the protective film bonding on different alloy surfaces. Overall, the results provide new insights into selecting and optimizing corrosion inhibitors for various CuNi alloy systems in chloride environments.

2. Materials and methods

The following materials were used in this study: Ni foil (2 mm, 99.0%, annealed, Goodfellow Cambridge Limited), Cu₉₀Ni₁₀ alloy (wt%, CuNi₁₀, Zlatarna Celje, Slovenia), Cu₇₀Ni₃₀ alloy (wt%, CuNi₃₀, 1.6 mm foil, as rolled, Zlatarna Celje, Slovenia), and Cu₆₂Ni₁₈Zn₂₀ alloy (wt%, CuNi₁₈Zn₂₀, 0.6 mm foil, as-rolled, Goodfellow Cambridge Limited). All samples were cut into 15 mm-diameter discs. For electrochemical experiments, the specimens were ground sequentially with SiC papers of grits P320, P1200, P2400, and P4000, ultrasonically cleaned in acetone for 5 min, rinsed with ethanol (Supelco, 99.99%), and dried with clean compressed air for electrochemical experiments. For immersion experiments followed by XPS characterization, the samples were polished to P4000 grit and further mirror-polished with 6 μ m, 3 μ m and 1 μ m diamond suspensions, then ultrasonically cleaned in acetone, rinsed with high-purity ethanol, and dried. These as-polished samples were designated as Bare.

Azole-based organic compounds were evaluated as potential corrosion inhibitors, as shown in Fig. 2. The tested compounds include:

- 2-Mercaptobenzimidazole (SH-BimH, Sigma-Aldrich, 98%),
- 2-(Methylthio)benzimidazole (Me-S-BimH, Fluorochem, 95%),

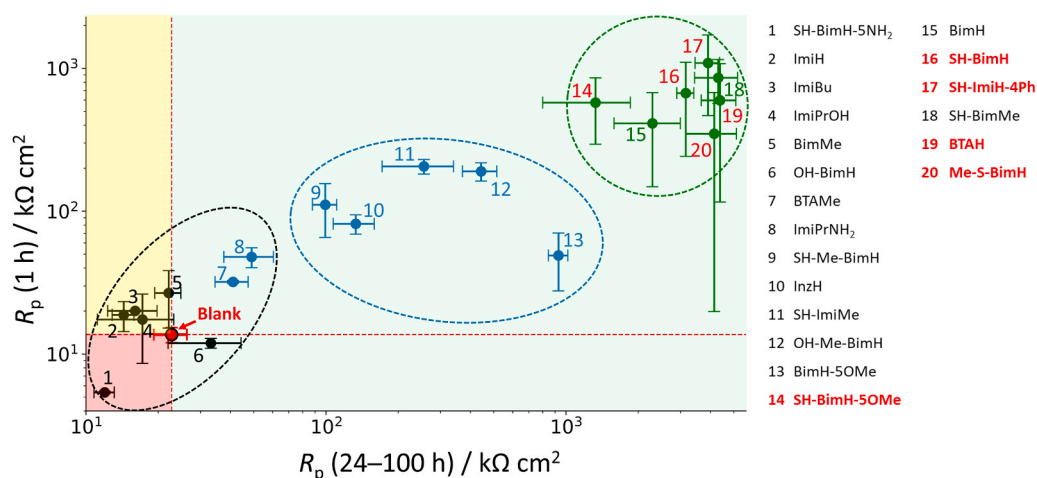


Fig. 1. The R_p values of Cu in 3 wt% NaCl solution with and without corrosion inhibitors from previous research in our group [32,33,35,36–38]. The x-axis represents the average R_p values measured multiple times during immersion over 24–100/120 h, with standard deviations shown as error bars. The y-axis displays the average R_p values after 1 h of immersion, with error bars derived from three tests. These values reflect the short- and long-term inhibition efficiency and stability of the inhibitors for Cu. Full chemical names and their respective abbreviations are shown in Supporting Information (Table S1).

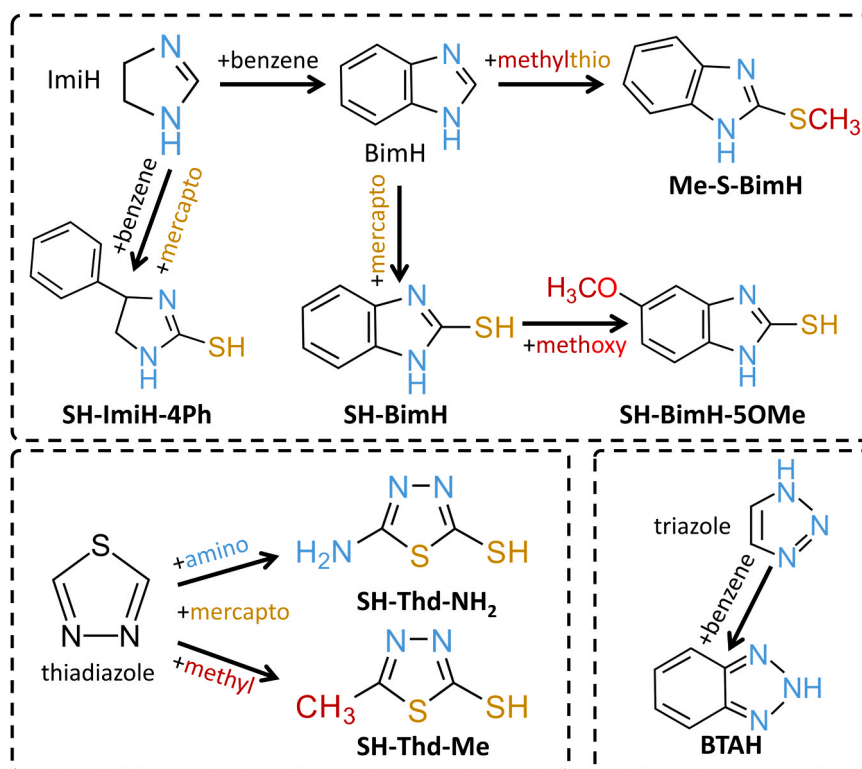


Fig. 2. The chemical structures of the seven organic compounds used in this study (highlighted in bold).

- 5-Methoxy-1H-benzo[d]imidazole-2-thiol (SH-BimH-5OMe, Fluorochem, 95%),
- 4-Phenylimidazole-2-thiol (SH-ImiH-4Ph, Sigma-Aldrich, 97%),
- 1H-Benzotriazole (BTAH, Fluka Analytical, $\geq 99.0\%$),
- 5-Methyl-1,3,4-thiadiazole-2-thiol (SH-Thd-Me, Sigma-Aldrich, 99%), and
- 5-Amino-1,3,4-thiadiazole-2-thiol (SH-Thd-NH₂, Sigma-Aldrich, 95%).

The selection of these compounds was strategically designed to systematically investigate the structure–performance relationships on CuNi alloys. Building upon fundamental insights derived from pure Cu inhibition, this selection aims to explore how specific functional groups, electronic modulation, and multi-dentate anchoring capacities adapt to alloyed surfaces. The structural selection rationale (Fig. 2) follows three design strategies:

1. Commercial benchmark: BTAH was selected as the industry-standard inhibitor for copper. It serves as the baseline, representing traditional inhibitors that rely predominantly on N-heteroatom coordination.
2. Synergistic multi-dentate bonding: A series of thiol-substituted azoles was selected to evaluate the efficiency of synergistic N and S multi-dentate anchoring. This library spans distinct structures: SH-BimH, imidazole containing a hindered phenyl group (SH-ImiH-4Ph), and thiadiazole rings featuring intrinsic ring-sulfur atoms (SH-Thd-Me, SH-Thd-NH₂). The distinct heteroatom distributions in these compounds enable the investigation of various spatial configurations, including the highly compact, horizontal "lying-down" adsorption mode (e.g., thiadiazoles).
3. Electronic and steric effects: To further decode the structure–performance dependencies, two derivatives of the benzimidazole core were systematically tested. SH-BimH-5OMe was included to evaluate how modifying the electron density of the scaffold via a strong electron-donating methoxy group ($-OCH_3$) influences adsorption stability. Me-S-BimH was incorporated to investigate the

effect of substituting the free active thiol ($-SH$) with a methylthio group ($-SCH_3$). This derivative explicitly tests how altering the protonation capability and introducing local steric hindrance at the sulfur binding site impacts the inhibition on alloyed substrates.

A 3 wt% NaCl solution (Chemlab, 99.8%) prepared with 18.2 MΩ cm deionized water was used as the baseline electrolyte (Blank), consistent with previous research in our lab. Inhibitor-containing solutions were prepared by adding 1 mM of the respective compound in NaCl solution for electrochemical and immersion tests. The fixed 1 mM concentration was selected [35]. This concentration provides measurable differentiation among related molecular structures while remaining below the aqueous solubility limits of all compounds investigated in the present study. Lower concentrations (e.g., 0.1 mM) fail to adequately differentiate structural effects due to incomplete surface coverage, whereas higher concentrations (e.g., 10 mM) are experimentally precluded by the aqueous solubility limits of the molecules, such as SH-BimH (solubility limit < 6.7 mM at room temperature) [35]. Therefore, utilizing 1 mM as a standardized baseline strictly isolates the molecular structure as the sole variable, enabling a rigorous comparison of the bonding mechanisms across the alloys.

2.1. Electrochemical testing and data processing

Electrochemical measurements in 3 wt% NaCl were conducted in a three-electrode cell (~ 200 mL) with a multipotentiostat/galvanostat (Autolab PGSTAT M204, Metrohm Autolab, Nova 2.1.6, Utrecht, The Netherlands) at room temperature. Electrochemical measurements were performed in a three-compartment set-up: the sample as a working electrode (WE) was attached to the bottom by pressing it against an o-ring, an Ag/AgCl (3.5 M KCl, $+0.205$ V vs. SHE at 25 °C) electrode served as the reference, and a graphite rod ($d \approx 7$ mm) as the counter electrode. Samples acted as working electrodes with an exposed area of ~ 1 cm². For the 1h-period tests, open-circuit potential (OCP) was recorded for 1 h before further measurements, which were then

performed sequentially: (i) linear polarization resistance (LPR), (ii) measurements of electrochemical impedance spectra (EIS), and (iii) measurements of potentiodynamic polarization (PDP) curves. In LPR, three repetitions were conducted by scanning the potential from -10 mV to $+10$ mV vs. OCP at a potential scan rate of 0.1 mV s^{-1} . R_p was determined via linear regression. EIS was conducted at OCP over a frequency range of 10^5 – 10^{-2} Hz using a 10 mV AC perturbation (rms).

In this study, the low-frequency impedance modulus at 0.01 Hz ($|Z|_{0.01 \text{ Hz}}$) was used as a directly measured, model-independent descriptor to complement and cross-check the inhibition trends obtained from R_p . A fully resistive low-frequency plateau was not reached for every investigated system at 0.01 Hz, as the corresponding phase angles remained appreciably different from 0° in some cases. Therefore, $|Z|_{0.01 \text{ Hz}}$ is not interpreted as an exact R_p , film resistance (R_f), charge-transfer resistance (R_{ct}), or total barrier resistance. Instead, it was used solely for comparative evaluation of samples measured under identical experimental conditions [39]. No R_f , R_{ct} , or double-layer capacitance (C_{dl}) values were derived directly from $|Z|_{0.01 \text{ Hz}}$. Equivalent electrical circuits (EECs) fitting was not applied because the number, degree of separation, and temporal evolution of the apparent time constants varied substantially with alloy composition, inhibitor, and immersion time, preventing the use of a common circuit model that would yield consistently comparable physical parameters across the complete experimental matrix [40].

To ensure statistical reliability and reproducibility, the LPR measurements were strictly performed in triplicate. The comprehensive statistical data for these measurements, including the calculated mean values and their corresponding standard deviations (SD), are tabulated in the [Supplementary Information \(Table S2\)](#). Due to the extensive experimental matrix and the prolonged 120-h continuous immersion, EIS measurements were performed on representative samples. The EIS data ($|Z|_{0.01 \text{ Hz}}$) served as an orthogonal functional cross-validation to independently corroborate the inhibition trends established by the triplicate LPR measurements.

PDP measurements were recorded with the potential scanned from -250 mV to $+650$ mV vs. OCP at 1 mV s^{-1} . Tafel parameters, corrosion potential (E_{corr}), apparent corrosion current density (j_{corr}) were determined by non-linear fitting using Nova software. Because well-defined linear Tafel regions were not observed for several inhibited systems, conventional anodic and cathodic Tafel slopes are not reported. The apparent j_{corr} values are used only as model-dependent, semi-quantitative descriptors and are not interpreted as independently validated absolute corrosion rates.

Complementary electrochemical measurements, including R_p and EIS, were recorded at 3-hour intervals over a 24-hour immersion period. The R_p and EIS data are omitted in the article for brevity, but a final PDP test conducted at 24 h to evaluate the evolution of polarization behavior is presented.

In the 120h-period tests, R_p and EIS were recorded approximately every 24 h, with PDP performed after 120 h. The extended 120 h test provides a more accurate and reliable evaluation of inhibitor performance, as previously demonstrated in our manuscript in preparation [38].

Inhibitor efficiency was assessed based on R_p and $|Z|_{0.01 \text{ Hz}}$. For cross-comparison among inhibitors in 120-hour tests, the inhibition power (P , also denoted as P_{inh}), calculated from the R_p and $|Z|_{0.01 \text{ Hz}}$ as shown in [Eq. 1](#), was used [36]. The 1 h P_{inh} values were obtained as the average of nine values conducted at 1 h (including 1-h, 24-h and 120-h period experiments).

$$P_{inh} = 10 \log \frac{R_p^{inh}}{R_p^{Blank}} \text{ or } P_{inh} = 10 \log \frac{|Z|_{0.01 \text{ Hz}}^{inh}}{|Z|_{0.01 \text{ Hz}}^{Blank}} \quad (1)$$

where $R_p^{inh}/|Z|_{0.01 \text{ Hz}}^{inh}$ is the $R_p/|Z|_{0.01 \text{ Hz}}$ of the inhibitor-treated sample and $R_p^{Blank}/|Z|_{0.01 \text{ Hz}}^{Blank}$ is the $R_p/|Z|_{0.01 \text{ Hz}}$ of the sample in 3 wt% NaCl

solution only. The inhibition power is measured in decibels (dB). Accordingly, an inhibitor that shows a gain of 10 dB increases the polarization resistance by a factor of 10 relative to the Blank solution.

2.2. X-ray Photoelectron Spectroscopy (XPS)

XPS was performed under ultra-high vacuum using a TFA Physical Electronics spectrometer with a hemispherical analyzer and an Al K_α source (1486.6 eV). The analysis area was $400 \mu\text{m}$ in diameter. High-resolution spectra were acquired with 0.1 eV steps and a pass energy of 27 eV for C 1 s and O 1 s spectra, and 55 eV for N 1 s, S 2p, Cl 2p, Na 1 s, Cu (2p & LMM), Ni (2p) and Zn (2p & LMM) spectra. XPS was performed on selected inhibitor-immersed samples (120 h)—SH-BimH, SH-ImiH-4Ph, BTAH, SH-Thd-Me—along with the sample after polishing (Bare) and immersed only in 3 wt% NaCl (Blank). Elements analyzed included Ni 2p, O 1 s, Cl 2p, C 1 s, N 1 s, and S 2p for alloys and Ni metal; Cu 2p and Cu LMM for Cu-containing alloys; and Zn 2p and Zn LMM for CuNi₁₈Zn₂₀ alloy. XPS spectra were calibrated to the adventitious C 1 s peak at a binding energy (BE) of 284.8 eV due to the surface charging effects. However, the adventitious C 1 s peak of SH-Thd-Me-treated CuNi₁₀ and CuNi₃₀ alloys was not the dominant peak; thus, the Cu 2p_{3/2} peak (932.5 eV) was used for charge correction. This alternative calibration is justified by the specific surface chemistry discussed in [Section 3.3.2](#).

Surface compositions were determined from high-resolution C 1 s, O 1 s, N 1 s, S 2p, Cl 2p, Cu 2p, Ni 2p, Zn 2p spectra using MultiPak software (v9.9.2). Qualitative analysis was performed based on literature references, with curves normalized and overlaid one above the other for clarity. Due to the complexity of overlapping peaks and the key role of surface-bond N and S, only N 1 s and S 2p spectra were fitted and presented.

3. Results and discussions

3.1. Linear polarization resistance and impedance modulus at 0.01 Hz

Organic corrosion inhibitors exhibit time-dependent adsorption kinetics, often evolving from physisorption to more stable chemisorption to enhance inhibition power. The resistance to mass and charge transfer at the metal/electrolyte interface is accurately reflected by R_p and $|Z|_{0.01 \text{ Hz}}$ values. Utilizing these metrics after a 1 h immersion period in 3 wt% NaCl allows for efficient screening of inhibitors. Comparative measurements for Cu and Zn metal and CuZn alloys are given in ref. [33, 38]. As shown in [Fig. 3](#), the performance of Ni metal, CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀ alloys across all tested inhibitors after 1 h immersion is visualized using a polar bar plot of R_p and $|Z|_{0.01 \text{ Hz}}$ values. Furthermore, long-term performance of the inhibitors was assessed by monitoring R_p and $|Z|_{0.01 \text{ Hz}}$ at 24-hour intervals until 120 h, providing insight into their stability. According to [Eq. 1](#), R_p and $|Z|_{0.01 \text{ Hz}}$ can be converted to P_{inh} , which could construct the time-dependent heat map of all alloys with different inhibitors in [Fig. 4](#).

3.1.1. Short-term measurements (1 h immersion)

In a 3 wt% NaCl solution, all three Cu-based alloys—excluding Ni metal—exhibited clear improvements in both R_p and $|Z|_{0.01 \text{ Hz}}$ upon the addition of most organic compounds, indicating their general effectiveness for Cu-containing alloys. While Ni metal displayed negligible interaction with most inhibitors—and in some cases even accelerated corrosion—the inhibitors effective for Cu generally maintained their performance with CuNi alloys. However, the inhibition power did not decline consistently with increasing Ni content. Among these alloys, CuNi₁₈Zn₂₀ showed the strongest corrosion resistance in the presence of inhibitors. However, since its Blank sample already had the highest R_p and $|Z|_{0.01 \text{ Hz}}$ values, further assessment using P_{inh} is required to distinguish and quantify its true inhibition behavior. The best-performing inhibitors varied across the different alloys, highlighting

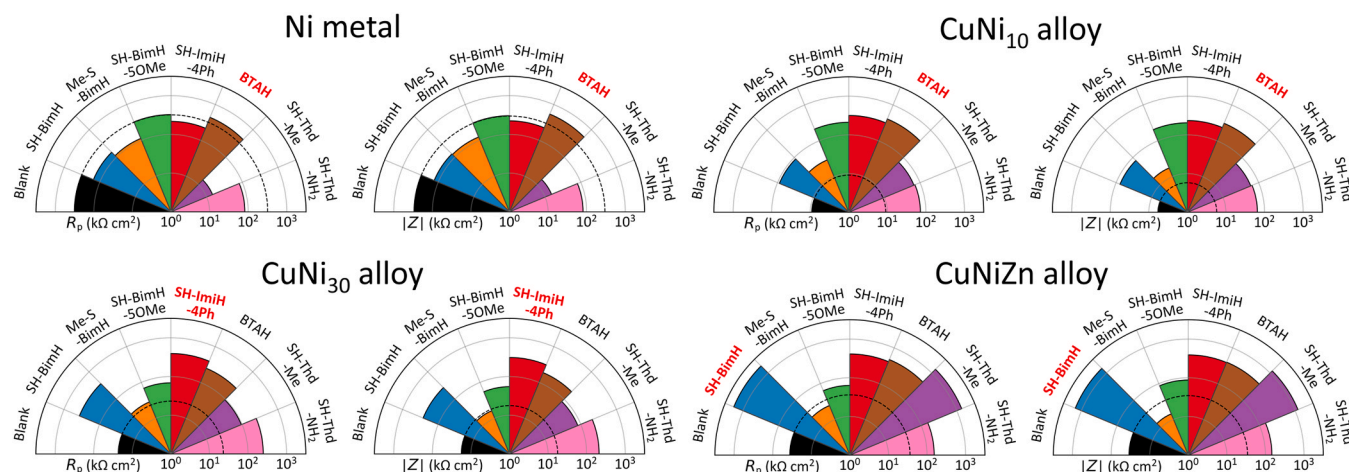


Fig. 3. Polar bar plots of R_p (left) and $|Z|_{0.01 \text{ Hz}}$ (right) for Ni metal, CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀ alloys. Values are presented on a logarithmic scale, with the dashed black half-circle lines indicating the results of the Blank (uninhibited) samples. The most effective inhibitor for each alloy is highlighted in red and bold. The corresponding fitted curves for R_p are provided in the [Supporting Information \(Figs. S1–S4\)](#), and the EIS plots used to extract $|Z|_{0.01 \text{ Hz}}$ are shown in [Figs. S5–S8](#).

that alloying elements significantly influence the surface interactions with inhibitors.

For Ni metal, only BTAA showed a weak inhibition, while the others showed no meaningful suppression. Several inhibitors (SH-BimH, Me-S-BimH, SH-ImiH-4Ph, SH-Thd-Me, and SH-Thd-NH₂) appeared to promote corrosion. Nonetheless, the R_p and $|Z|_{0.01 \text{ Hz}}$ values of the Blank Ni sample were 1–2 orders of magnitude higher than those of the Blank of the other alloys, suggesting that Ni possesses superior intrinsic corrosion resistance under chloride exposure. But effective inhibitors can further elevate the R_p and $|Z|_{0.01 \text{ Hz}}$ values for alloys, thereby surpassing the resistance of Ni metal.

For CuNi₁₀, all inhibitors led to marked increases in R_p and $|Z|_{0.01 \text{ Hz}}$, indicating that minor Ni addition did not compromise the inhibition of the Cu component. The results followed the trend that inhibitors effective for Cu were also effective for CuNi₁₀. Among these, BTAA showed the best performance, followed by SH-ImiH-4Ph and SH-BimH-50Me, while Me-S-BimH was the least effective.

For CuNi₃₀, the increased Ni content led to higher R_p and $|Z|_{0.01 \text{ Hz}}$ in the Blank sample, indicating enhanced corrosion resistance. Although most inhibitors failed to inhibit Ni metal, they remained effective on CuNi₃₀, which contained ~70 wt% Cu. SH-ImiH-4Ph, SH-BimH, and SH-BimH-50Me showed strong inhibition, while Me-S-BimH remained ineffective.

In CuNi₁₈Zn₂₀, with ~18 wt% Ni and an additional 20 wt% Zn, the Blank sample showed the highest intrinsic resistance after 1-h immersion compared to other alloys. Inhibitors such as SH-BimH and SH-Thd-Me provided strong corrosion protection, followed by SH-ImiH-4Ph and BTAA. Conversely, Me-S-BimH accelerated corrosion in this alloy.

The EIS phase-angle profiles differed substantially among the investigated inhibitor–alloy systems ([Figs. S5–S8](#)), indicating variations in the number and degree of overlap of the apparent interfacial relaxation processes. These profiles also evolved during the 120 h immersion period ([Figs. S32–S38](#)). Consequently, condition-specific equivalent circuits would be required to fit different inhibitors, alloys, and immersion times, and the resulting circuit parameters would not necessarily retain directly comparable physical meanings across the complete dataset. For this reason, no circuit-derived R_f , R_{ct} , or C_{dl} values are compared in this study. Instead, $|Z|_{0.01 \text{ Hz}}$ is used only as a directly measured low-frequency impedance descriptor to complement the R_p trends under identical experimental conditions, whereas XPS provides independent information about the chemical composition and probable bonding environments of the inhibitor-derived surface layers.

3.1.2. 120-h electrochemical measurements

Heat maps in [Fig. 4](#) illustrating the 120-h evolution of P_{inh} for Ni metal and three CuNi alloys in 3 wt% NaCl solutions containing organic inhibitors are selected based on 1-h results ([Fig. 3](#)). The left and right panels correspond to P_{inh} values calculated from R_p and $|Z|_{0.01 \text{ Hz}}$, respectively. P_{inh} values are labeled on the maps and represent measurements obtained after immersion times of 1 h, 24 h, 48 h, 72 h, 96 h, and 120 h. Actual testing times may deviate by ± 2 h from the nominal values. A blue-to-red color gradient indicates increasing P_{inh} values. The corresponding fitting curves and values of R_p as well as EIS spectra used for $|Z|_{0.01 \text{ Hz}}$ are provided in the [Supporting Information \(Figs. S9–S38\)](#). The three most effective inhibitors for each alloy are outlined in red boxes. Both electrochemical techniques yielded consistent trends in P_{inh} evolution over time.

All selected inhibitors exhibited $P_{inh} > 0$ during the 1 h immersion, confirming their initial inhibition effect. Over prolonged immersion periods, BTAA showed negligible or even adverse effects on Ni, indicating limited corrosion inhibition. In contrast, all inhibitors maintained significant effectiveness on the three CuNi alloys, except for SH-BimH-50Me on CuNi₁₀, which exhibited a decline in P_{inh} beyond 1 h. The rest displayed stable or increasing P_{inh} values over time.

In the case of CuNi₁₀, both SH-BimH and SH-ImiH-4Ph reached the high inhibition range (~14–21 dB) between 24 and 120 h, indicating that, over time, an effective inhibitive film formed. BTAA maintained relatively high P_{inh} values (mostly ≥ 15 dB) throughout the full duration, demonstrating rapid and stable protection. SH-BimH-50Me, while initially effective at 1 h, rapidly lost its inhibition and remained in a low P_{inh} range (~2–4 dB), indicating it cannot form a stable film. SH-Thd-Me and SH-Thd-NH₂ showed considerable time-dependent variation: SH-Thd-Me peaked at 24 h and then declined, whereas SH-Thd-NH₂ exhibited a delayed response near 96 h but failed to sustain at high levels, suggesting limited film durability and long-term effectiveness.

On CuNi₃₀, SH-BimH, SH-ImiH-4Ph, and SH-Thd-Me demonstrated the most promising inhibition performance. SH-BimH quickly reached a high P_{inh} and maintained around 16–20 dB from 24 to 120 h, indicating fast film formation and strong stability. SH-Thd-Me displayed a distinct time-dependent improvement: starting with moderate P_{inh} (~10–13 dB), during the first 24 h, it surged to ~24 dB at 48 h, then stabilized at a high level (~17–21.6 dB) through to 120 h, suggesting the formation of a durable protective film. SH-ImiH-4Ph mostly maintained a strong inhibition threshold (~15–16.5 dB). SH-BimH-50Me exhibited only moderate protection; despite a short-lived increase (~17.2 dB at 48 h, LPR), P_{inh} declined to ~12–13 dB thereafter, indicating worse long-term film stability than the best ones. SH-Thd-NH₂

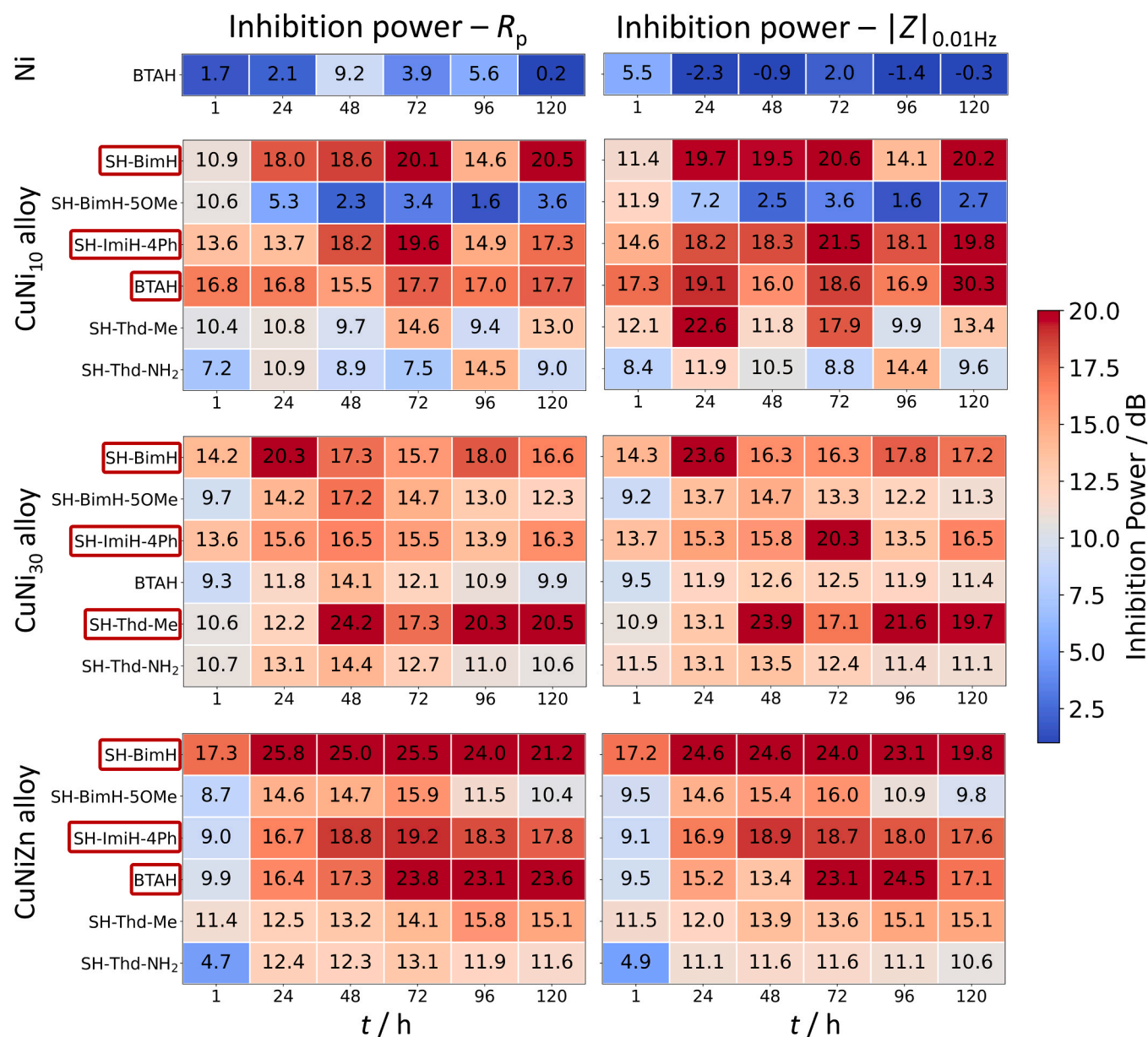


Fig. 4. Time-resolved heat maps of 120-h P_{inh} evolution for Ni metal and CuNi alloys in 3 wt% NaCl with organic inhibitors selected based on short-term electrochemical results (Fig. 3). Left and right panels show P_{inh} values calculated from R_p and $|Z|_{0.01\text{ Hz}}$, respectively. Labeled P_{inh} values correspond to immersion times of 1, 24, 48, 72, 96, and 120 h (± 2 h). A blue-to-red gradient reflects increasing inhibition power. R_p fitting curves and EIS data used for these calculations are available in the [Supporting Information](#) (Figs. S9–S38). The three most effective inhibitors for each alloy are highlighted with red boxes.

and BTAH remained low (~ 9 – 13 dB) throughout the tests, with occasional values approaching 14 dB, suggesting limited protective capability on CuNi₃₀.

In the CuNi₁₈Zn₂₀ system, SH-BimH consistently achieved the highest inhibition across all measured periods, starting at ~ 17 dB (1 h), remaining exceptionally high (~ 25 – 26 dB) from 24 to 72 h, and sustaining ~ 20 – 24 dB through 96–120 h, suggesting rapid and durable formation of a dense protective film. SH-ImiH-4Ph showed a P_{inh} of ~ 9 dB at 1 h, stabilizing at ~ 17 – 19 dB at 24 h, maintaining strong inhibition through 120 h. BTAH showed significant time-dependent enhancement: initially low (~ 9 – 10 dB), it improved by 24–48 h (~ 16 – 17 dB), and then surged during 72–120 h (~ 23 – 24 dB), suggesting substantial thickening or structural optimization of the inhibitor film over time. SH-Thd-Me showed a gradual improvement from moderate levels, reaching ~ 15 dB only at 96–120 h, indicating slow inhibition kinetics. SH-BimH-5OMe also showed moderate performance, briefly

nearing ~ 15 – 16 dB during 24–72 h but later declined to ~ 10 – 12 dB.

3.2. Potentiodynamic polarization curves

Potentiodynamic polarization measurements provide complementary information on the anodic and cathodic current responses, the stability of the surface films under applied polarization, and their evolution with immersion time. In this study, potentiodynamic polarization curves were recorded on metal and alloy samples immersed in a 3 wt% NaCl solution with and without a 1 mM inhibitor for 1 h, 24 h, and 120 h. The potential range was -0.25 – 0.65 V_{Ag/AgCl} with a scan rate of 1 mV s^{-1} , as shown in Figs. 5–8. The corresponding parameters were displayed in Tables 1–4. It should be noted that the immersion durations refer to nominal times; the actual deviations were within ± 3 h. For the 120-h condition, the tested inhibitors correspond to those selected in the P_{inh} analysis at 120 h. The figure is divided into eight subplots, one for

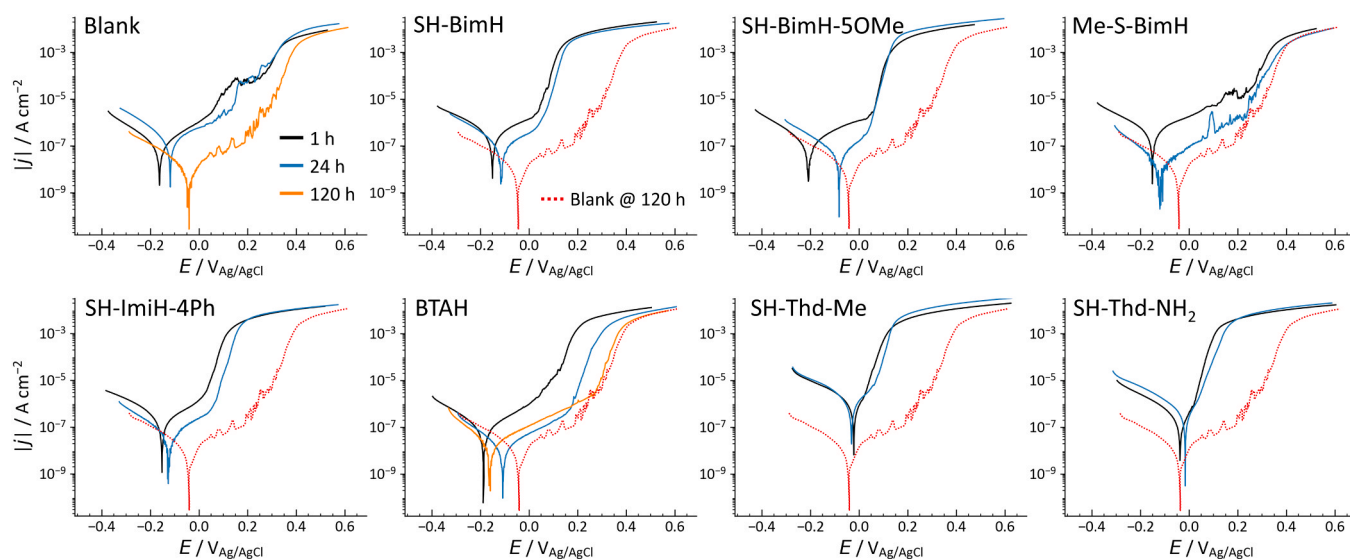


Fig. 5. Potentiodynamic polarization curves of Ni metal in 3 wt% NaCl solution without (Blank) and with 1 mM organic inhibitors after immersion for 1 h, 24 h, and 120 h (the latter for selected inhibitors only). The potential range was -0.25 – 0.65 $V_{Ag/AgCl}$, with a scan rate of 1 mV s^{-1} . The data are presented in eight subfigures, with a specific inhibitor condition in the top-left corner. For all inhibitor-containing curves, the polarization curve of the Blank sample after 120 h immersion is included as a red dashed line.

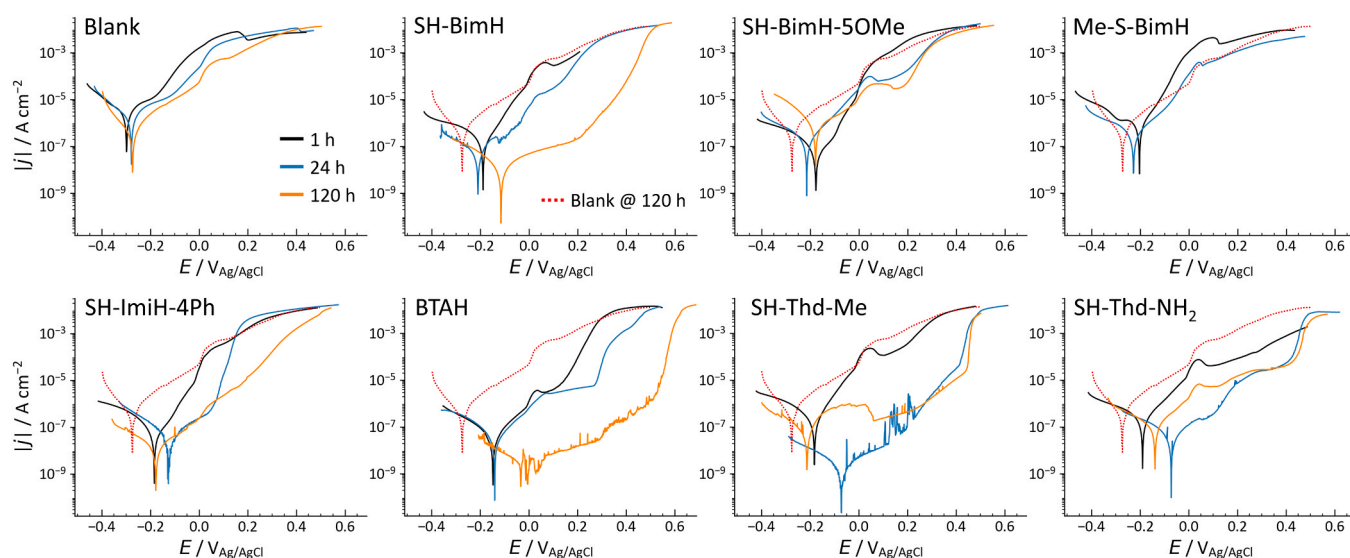


Fig. 6. Potentiodynamic polarization curves of CuNi₁₀ in 3 wt% NaCl solution without (Blank) and with 1 mM organic inhibitors after immersion for 1 h, 24 h, and 120 h (the latter for selected inhibitors only). The potential range was -0.25 – 0.65 $V_{Ag/AgCl}$, with a scan rate of 1 mV s^{-1} . The data are presented in eight subfigures, with a specific inhibitor condition in the top-left corner. For all inhibitor-containing curves, the polarization curve of the Blank sample after 120 h immersion is included as a red dashed line.

Blank and seven for inhibitor-containing samples. In each subplot, curves recorded after 1 h, 24 h and 120 h of immersion are shown. For all inhibitor-containing subplots, an additional polarization curve (dashed red line) recorded for the inhibitor-free solution after 120 h immersion is overlaid to compare the corrosion resistance of the film formed naturally with that formed in the presence of the inhibitor. The PDP curves depicting the electrochemical response of the various alloys as a function of immersion time are presented in Figs. S39–S42, and the comparative performances of different materials within a single environment are detailed in Figs. S43–S44 of the Supporting Information.

Well-defined linear Tafel regions were not observed for several inhibited systems. Therefore, conventional anodic and cathodic Tafel slopes were not shown in Tables 1–4. The apparent j_{corr} values obtained by non-linear fitting are retained only as model-dependent, semi-

quantitative descriptors and are not used to determine absolute corrosion rates or infer elementary reaction mechanisms. Hereafter, j_{corr} refers to the apparent value obtained from non-linear fitting and is used only for semi-quantitative comparison. The PDP curves are primarily interpreted through the directly measured changes in anodic and cathodic current response, the stability of the surface films under polarization, and their evolution with immersion time. The principal evaluation of inhibitor performance is based on the replicated LPR measurements, complemented by the low-frequency impedance modulus, whereas the probable surface coordination environments are evaluated using XPS.

Ni metal displayed the lowest j_{corr} , about one order of magnitude lower than that of CuNi alloys without the addition of inhibitors. Among the alloys, CuNi₁₀—due to its low Ni content—displays the highest j_{corr} ,

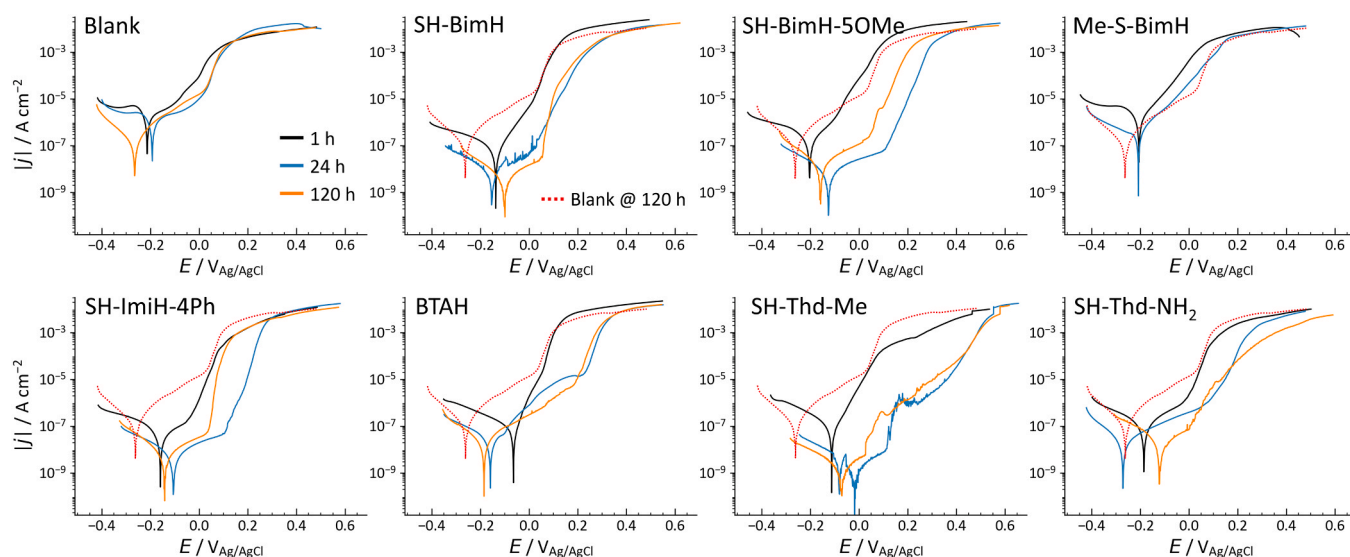


Fig. 7. Potentiodynamic polarization curves of CuNi₃₀ in 3 wt% NaCl solution without (Blank) and with 1 mM organic inhibitors after immersion for 1 h, 24 h, and 120 h (the latter for selected inhibitors only). The potential range was -0.25 – 0.65 V_{Ag/AgCl}, with a scan rate of 1 mV s⁻¹. The data are presented in eight subfigures, with a specific inhibitor condition in the top-left corner. For all inhibitor-containing curves, the polarization curve of the Blank sample after 120 h immersion is included as a red dashed line.

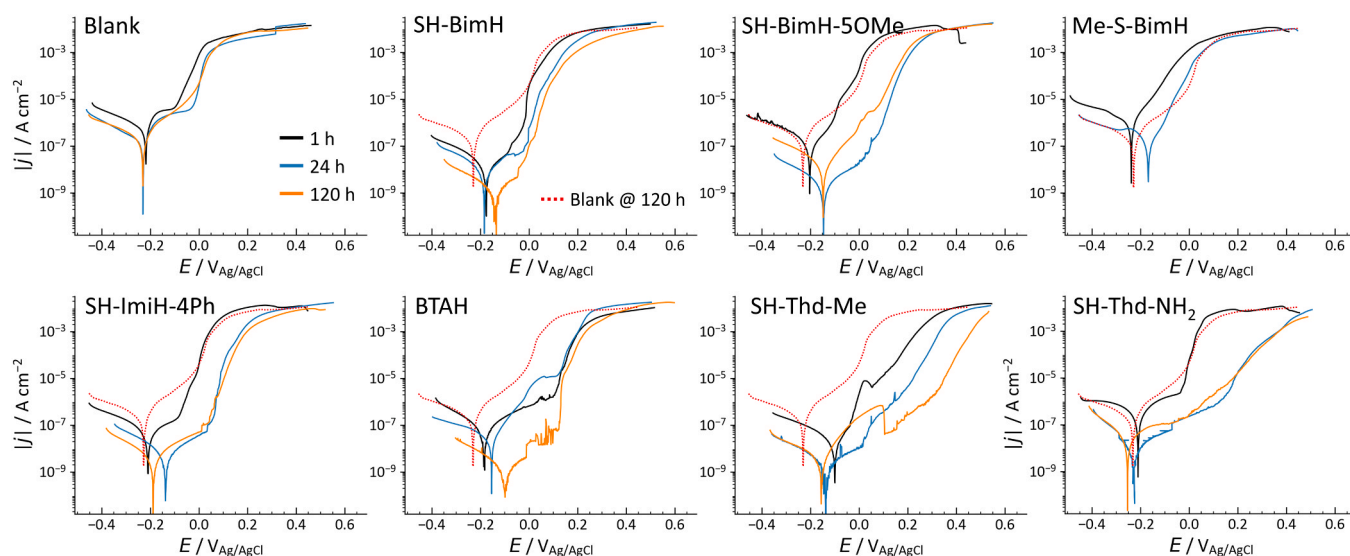


Fig. 8. Potentiodynamic polarization curves of CuNi₁₈Zn₂₀ in 3 wt% NaCl solution without (Blank) and with 1 mM organic inhibitors after immersion for 1 h, 24 h, and 120 h (the latter for selected inhibitors only). The potential range was -0.25 – 0.65 V_{Ag/AgCl}, with a scan rate of 1 mV s⁻¹. The data are presented in eight subfigures, with a specific inhibitor condition in the top-left corner. For all inhibitor-containing curves, the polarization curve of the Blank sample after 120 h immersion is included as a red dashed line.

while CuNi₃₀ shows slightly higher values than CuNi₁₈Zn₂₀. However, after the introduction of inhibitors, the alloys exhibited significantly reduced j_{corr} , with values at least one order of magnitude lower than that of Ni metal. Notable examples include BTAH-treated CuNi₁₀, SH-Thd-Me-treated CuNi₃₀, and SH-BimH-treated CuNi₁₈Zn₂₀ after 120 h. A detailed analysis of the PDP curves for Ni metal and the CuNi alloys will be presented in the following discussion.

3.2.1. Ni metal

As shown in Fig. 5, the PDP curves of Ni metal after immersion for 1, 24, and 120 h in various electrolyte solutions are presented, with the corresponding electrochemical parameters summarized in Table 1. Based on the j_{corr} values and anodic current densities at identical potentials, none of the inhibitors exhibited anodic currents lower than that

of uninhibited Ni after 120 h, indicating that immersion in the inhibitor-containing solutions for 1 or 24 h did not lead to the formation of a more protective surface film than that developed by Ni in the Blank solution after 120 h. Although BTAH showed some reduction in anodic current at 24 h, it still failed to achieve lower anodic reactivity than the 120 h Blank sample. In the absence of inhibitors, a passive film composed of NiO and Ni(OH)₂ could form on the Ni surface [41], which contributes to the improved corrosion resistance of Ni in this electrolyte (j_{corr} reduced to 0.011 $\mu\text{A cm}^{-2}$ after 120 h and passive range extending to ~ 0.2 V_{Ag/AgCl}). However, at higher potentials, the film tends to convert into Ni(OH)₂, resulting in decreased passivation stability and increased anodic current [42].

Several S-containing inhibitors (SH-BimH, Me-S-BimH, SH-ImiH-4Ph, SH-Thd-Me, and SH-Thd-NH₂) appeared to promote corrosion. As

Table 1

Apparent Tafel parameters for Ni metal in 3 wt% NaCl with and without 1 mM inhibitor (derived from Fig. 5).

Electrolyte	Duration / h	$E_{\text{corr}} / \text{V}_{\text{Ag/AgCl}}$	$j_{\text{corr}} / \mu\text{A cm}^{-2}$
Blank	1	−0.162	0.098
	24	−0.118	0.182
	120	−0.042	0.011
SH-BimH	1	−0.150	0.319
	24	−0.116	0.105
SH-BimH-5OMe	1	−0.207	0.126
	24	−0.082	0.043
SH-ImiH-4Ph	1	−0.152	0.222
	24	−0.124	0.043
Me-S-BimH	1	−0.151	0.383
	24	−0.120	0.014
BTAH	1	−0.188	0.079
	24	−0.108	0.012
	120	−0.165	0.013
SH-Thd-Me	1	−0.021	1.111
	24	−0.031	1.158
SH-Thd-NH ₂	1	−0.037	0.220
	24	−0.015	0.374

Table 2Apparent Tafel parameters for CuNi₁₀ in 3 wt% NaCl with and without 1 mM inhibitor (derived from Fig. 6).

Electrolyte	Duration / h	$E_{\text{corr}} / \text{V}_{\text{Ag/AgCl}}$	$j_{\text{corr}} / \mu\text{A cm}^{-2}$
Blank	1	−0.298	2.083
	24	−0.278	1.959
	120	−0.273	0.420
SH-BimH	1	−0.189	0.330
	24	−0.209	0.046
	120	−0.115	0.017
SH-BimH-5OMe	1	−0.177	0.118
	24	−0.214	0.158
	120	−0.178	0.944
SH-ImiH-4Ph	1	−0.184	0.114
	24	−0.124	0.043
	120	−0.177	0.012
Me-S-BimH	1	−0.203	0.391
	24	−0.228	0.252
BTAH	1	−0.147	0.046
	24	−0.140	0.062
	120	−0.033	0.0019
SH-Thd-Me	1	−0.182	0.358
	24	−0.071	0.0024
	120	−0.213	0.102
SH-Thd-NH ₂	1	−0.189	0.251
	24	−0.072	0.059
	120	−0.138	0.079

extensively demonstrated in classical surface science studies on sulfur-Ni interaction [43,44], sulfur exhibits an exceptionally high thermodynamic affinity for Ni. These strongly adsorbed sulfur-containing species occupy the surface active sites and block the adsorption of OH[−]. The presence of multiple sulfur anchoring sites in molecules like SH-Thd-Me and SH-Thd-NH₂ intensifies this competitive adsorption. Consequently, this specific blocking effect completely suppresses the nucleation and growth of the protective Ni(OH)₂ layer, maintaining the Ni surface in an active dissolution state. This mechanism is directly corroborated by the potentiodynamic polarization results (Fig. 5). For instance, Ni treated with SH-Thd-Me and SH-Thd-NH₂ exhibits an immediate, sharp increase in anodic current density and a complete absence of passivation behavior in the anodic region. The presence of dual reactive sulfur atoms in these molecules severely exacerbates the disruption of the passive film, causing the most detrimental "passivation disruption" effect among all tested compounds.

Furthermore, while some literature indicates that azole derivatives can inhibit Ni corrosion in highly acidic environments (e.g., 4% HNO₃) [45], their protective efficiency is not promising in neutral chloride solutions. As demonstrated by Cao et al. using in-situ SERS in a neutral

medium [46], azole molecules (such as 10 mM BTAH) coordinate with Ni merely as neutral molecules rather than forming dense polymeric networks, resulting in a highly defective and non-compact surface layer. This weak interaction perfectly explains the time-dependent electrochemical behavior observed on Ni. During the initial immersion (1 h), this sparse molecular layer acts as a temporary, weak physical barrier, leading to the minor improvement in R_p and $|Z|_{0.01 \text{ Hz}}$ values (Figs. 3 and 4). However, during prolonged exposure (120 h), this non-compact film fails to resist continuous chloride penetration. For inhibitors relying solely on N-coordination (such as BTAH), their sparse adsorption does not aggressively disrupt the passive film like the S-containing compounds; nevertheless, the absence of strong interfacial bonds and a dense cross-linked network results in a negligible long-term inhibition enhancement. Consequently, the initial weak protection gradually fades, and the polarization curve after 120 h (Fig. 5) shows no significant difference compared to the inhibitor-free Ni blank.

3.2.2. CuNi₁₀ alloy

The potentiodynamic polarization curves and associated electrochemical parameters of the CuNi₁₀ alloy after immersion in 3 wt% NaCl

Table 3Apparent Tafel parameters for CuNi₃₀ in 3 wt% NaCl with and without 1 mM inhibitor (derived from Fig. 7).

Electrolyte	Duration / h	$E_{\text{corr}} / \text{V}_{\text{Ag/AgCl}}$	$j_{\text{corr}} / \mu\text{A cm}^{-2}$
Blank	1	−0.213	0.614
	24	−0.192	1.706
	120	−0.264	0.167
SH-BimH	1	−0.137	0.110
	24	−0.153	0.0059
	120	−0.099	0.0041
SH-BimH-5OMe	1	−0.203	0.193
	24	−0.125	0.0067
	120	−0.158	0.016
SH-ImiH-4Ph	1	−0.159	0.059
	24	−0.105	0.0059
	120	−0.141	0.0050
Me-S-BimH	1	−0.205	0.899
	24	−0.208	0.272
	1	−0.064	0.091
BTAH	24	−0.159	0.015
	120	−0.185	0.025
SH-Thd-Me	1	−0.112	0.176
	24	−0.018	0.0018
	120	−0.071	0.0012
SH-Thd-NH ₂	1	−0.185	0.111
	24	−0.271	0.019
	120	−0.121	0.012

Table 4Apparent Tafel parameters for CuNi₁₈Zn₂₀ in 3 wt% NaCl with and without 1 mM inhibitor (derived from Fig. 8).

Electrolyte	Duration / h	$E_{\text{corr}} / \text{V}_{\text{Ag/AgCl}}$	$j_{\text{corr}} / \mu\text{A cm}^{-2}$
Blank	1	−0.218	0.510
	24	−0.230	0.312
	120	−0.230	0.244
SH-BimH	1	−0.175	0.014
	24	−0.184	0.008
	120	−0.137	0.0005
SH-BimH-5OMe	1	−0.203	0.123
	24	−0.146	0.0018
	120	−0.147	0.018
SH-ImiH-4Ph	1	−0.209	0.040
	24	−0.138	0.0056
	120	−0.188	0.0032
Me-S-BimH	1	−0.238	0.876
	24	−0.168	0.138
	1	−0.184	0.053
BTAH	24	−0.154	0.035
	120	−0.099	0.0009
SH-Thd-Me	1	−0.100	0.026
	24	−0.137	0.0019
	120	−0.156	0.0024
SH-Thd-NH ₂	1	−0.210	0.483
	24	−0.227	0.010
	120	−0.253	0.0015

solutions, with and without various organic inhibitors, for 1, 24, and 120 h are presented in Fig. 6 and Table 2, respectively.

After 1 h of immersion, all inhibitor-treated samples exhibited a marked reduction in corrosion j_{corr} relative to the Blank, showing the early-stage inhibition effect. Notably, SH-BimH, SH-ImiH-4Ph, and BTAH demonstrated a progressive decline in j_{corr} with increasing immersion time, indicating that the protective film either adsorbed more strongly or thickened over time. However, SH-BimH-5OMe, SH-Thd-Me, and SH-Thd-NH₂ exhibited fluctuating or stable current densities over time, suggesting limited durability of the protective films or weak interfacial interactions.

SH-BimH and BTAH showed similar anodic responses at 1 h and 24 h, followed by a significant reduction—by 1–2 orders of magnitude—in anodic current density at 120 h, reflecting enhanced anodic inhibition over time. SH-ImiH-4Ph displayed notable current suppression after 24 h, which remained stable at $\sim +300$ mV vs. E_{corr} through 120 h, with a further reduction at higher overpotentials,

indicating robust film formation.

SH-Thd-Me and SH-Thd-NH₂ initially reduced anodic currents at 24 h, but inhibition performance deteriorated by 120 h, indicating film degradation or instability, consistent with P_{inh} trends shown in Fig. 4.

In summary, SH-BimH, SH-ImiH-4Ph, and BTAH provided time-enhanced anodic inhibition on CuNi₁₀, characterized by sustained j_{corr} suppression and reduced anodic current. Other inhibitors exhibited lower efficiency, with limited long-term stability likely due to weak adsorption or film structures.

3.2.3. CuNi₃₀ alloy

The PDP curves and fitted electrochemical parameters of the CuNi₃₀ alloy after 1, 24, and 120 h immersion in 3 wt% NaCl solution, with and without organic inhibitors, are shown in Fig. 7 and Table 3, respectively.

In the Blank, j_{corr} initially increased from 0.614 $\mu\text{A cm}^{-2}$ (1 h) to 1.706 $\mu\text{A cm}^{-2}$ (24 h), then significantly dropped to 0.167 $\mu\text{A cm}^{-2}$ after 120 h. This behavior is consistent with the formation of a native passive

layer over prolonged immersion [5]. Among the inhibitors, SH-BimH, SH-ImiH-4Ph, and SH-Thd-Me demonstrated the greatest reductions in j_{corr} over time and a stable passive range.

Notably, SH-BimH showed a steady decrease in j_{corr} from $0.110 \mu\text{A cm}^{-2}$ (1 h) to $0.0041 \mu\text{A cm}^{-2}$ (120 h), corresponding to a two-order-of-magnitude improvement relative to the 120 h immersion result of Blank. The anodic current density also exhibited significant suppression at all immersion times, indicating stable and effective anodic inhibition. SH-ImiH-4Ph followed a similar trend, with j_{corr} dropping from $0.059 \mu\text{A cm}^{-2}$ (1 h) to $0.0050 \mu\text{A cm}^{-2}$ (120 h). Its anodic polarization behavior also remained stable over time, with particularly lower current densities at overpotentials up to $+0.15 \text{ V}$ vs. E_{corr} , suggesting good film stability under electrochemical stress.

SH-Thd-Me displayed strong time-dependent improvement, with j_{corr} sharply decreasing from $0.176 \mu\text{A cm}^{-2}$ (1 h) to $0.0012 \mu\text{A cm}^{-2}$ (120 h)—the lowest among all inhibitors tested. Moreover, compared to SH-BimH and SH-ImiH-4Ph, its anodic curves at high potentials showed lower current density at 120 h, indicating a more robust inhibitor film.

In contrast, SH-BimH-5OMe showed relatively high j_{corr} at 1 h ($0.193 \mu\text{A cm}^{-2}$), but decreased significantly by 24 h ($0.0067 \mu\text{A cm}^{-2}$). However, this trend did not persist; j_{corr} increased slightly to $0.016 \mu\text{A cm}^{-2}$ at 120 h, and the anodic curve showed an increasing current density, implying that the protective film may be unstable or undergo partial breakdown over longer immersion.

BTAH and SH-Thd-NH₂ demonstrated moderate inhibition: while j_{corr} declined from 1 h to 120 h, their anodic current remained higher than that of SH-BimH, SH-Thd-Me or SH-ImiH-4Ph, particularly at overpotentials about $+0.15 \text{ V}_{\text{Ag/AgCl}}$, suggesting a less compact or less strongly bonded film. Me-S-BimH failed to provide effective corrosion protection for CuNi₃₀.

In summary, SH-BimH, SH-ImiH-4Ph, and SH-Thd-Me exhibited the most effective and stable corrosion inhibition on CuNi₃₀, as evidenced by consistent reductions in j_{corr} and suppressed anodic currents over

time. Other inhibitors showed either limited or unstable performance, highlighting the importance of both film formation kinetics and long-term stability in determining inhibitor efficiency.

3.2.4. CuNi₁₈Zn₂₀ alloy

The polarization curves and fitted electrochemical parameters of the CuNi₁₈Zn₂₀ alloy immersed in 3 wt% NaCl solution, with and without inhibitors, for 1, 24, and 120 h are presented in Fig. 8 and Table 4, respectively. In the Blank, j_{corr} gradually decreased over time (from $0.510 \mu\text{A cm}^{-2}$ at 1 h to $0.244 \mu\text{A cm}^{-2}$ at 120 h), reflecting the intrinsic passivation behavior of CuNi₁₈Zn₂₀ and the formation of a native surface film [47]. The passive region extends only $\sim 0.1 \text{ V}$ above E_{corr} at 1 h and $\sim 0.2 \text{ V}$ at 24 and 120 h, beyond which the current density increases rapidly, suggesting breakdown of the passive film.

Among all tested inhibitors, SH-BimH showed the most remarkable inhibition performance based on j_{corr} . Its j_{corr} steadily declined from $0.053 \mu\text{A cm}^{-2}$ (1 h) to $0.0009 \mu\text{A cm}^{-2}$ (120 h), reaching a value two orders of magnitude lower than the Blank (120 h). However, the current density increased rapidly as the potential became more anodic, indicating that the protective film is less resistant to higher overpotentials.

For SH-ImiH-4Ph, the j_{corr} was relatively high at 1 h ($0.040 \mu\text{A cm}^{-2}$), but dropped significantly to $0.0032 \mu\text{A cm}^{-2}$ at 24 h and remained stable through 120 h. The anodic polarization curve at 120 h remained suppressed until $+0.2 \text{ V}$ (E_{corr}), which shows a larger passive range than that of SH-BimH.

The j_{corr} of BTAH reduced from $0.053 \mu\text{A cm}^{-2}$ (1 h) to $0.0009 \mu\text{A cm}^{-2}$ (120 h), with a pronounced anodic current suppression especially evident at higher potentials ($+0.1\text{--}0.2 \text{ V}$ vs E_{corr}). This suggests progressive thickening or reorganization of the inhibitor film over time, resulting in enhanced anodic inhibition.

SH-Thd-Me presented moderate inhibition performance. While j_{corr} decreased from $0.026 \mu\text{A cm}^{-2}$ (1 h) to $0.0024 \mu\text{A cm}^{-2}$ (120 h), the anodic polarization behavior at high overpotentials showed sustained

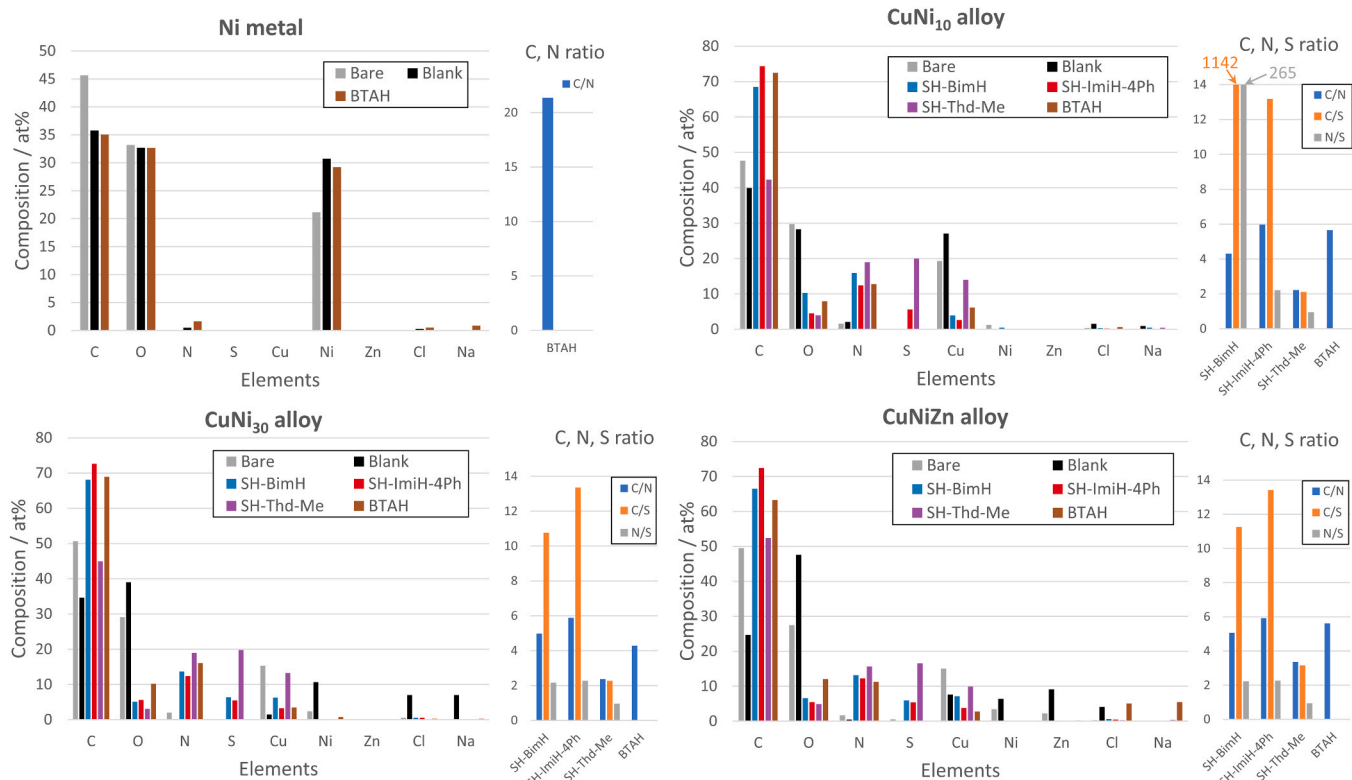


Fig. 9. High-resolution XPS-derived surface composition of Ni metal and CuNi alloys after polishing (Bare) and 120 h immersion in 3 wt% NaCl, either in the absence of inhibitors (Blank) or with 1 mM SH-BimH, SH-ImiH-4Ph, BTAH, or SH-Thd-Me (Ni only tested in BTAH). On the right side of each subplot, the ratios of C/N, C/S and N/S were displayed. Na was also included in the analysis to evaluate possible surface contamination from residual NaCl after rinsing.

current density suppression up to + 0.65 V vs E_{corr} , indicating that a strongly bonded and compact film had formed across the surface after 120 h of immersion.

SH-Thd-NH₂ was a moderate inhibitor. Although the j_{corr} at 120 h (0.0015 $\mu\text{A cm}^{-2}$) was not as low as that of other inhibitors, the anodic current density remained lower up to + 0.65 V compared to those of all others except SH-Thd-Me. The overall polarization behavior closely resembled that of SH-Thd-Me at 120 h, suggesting either strong interfacial bonding of the inhibitor film or that these two structurally related organic molecules promote the formation of a distinct passive film on the alloy at higher potentials.

In summary, SH-BimH, SH-ImiH-4Ph, and BTAH showed strong, time-enhanced inhibition effects on CuNi₁₈Zn₂₀, with suppressed j_{corr} values and well-maintained anodic passivation after long-term immersion. In contrast, inhibitors such as SH-BimH-5OMe and Me-S-BimH exhibited inferior or unstable behavior, limiting their practical application for long-term corrosion protection of CuNi₁₈Zn₂₀ alloys. SH-Thd-Me and SH-Thd-NH₂ displayed enhanced inhibition at elevated potential.

3.3. X-ray photoelectron spectroscopy analysis

High-resolution XPS spectra were used to evaluate the surface composition of Ni metal and CuNi alloys after mechanical polishing (Bare) and subsequent 120 h immersion in 3 wt% NaCl solutions, without (Blank) or with 1 mM organic inhibitors added (SH-BimH, SH-ImiH-4Ph, BTAH, or SH-Thd-Me), as shown in Fig. 9. In the case of Ni, only BTAH is applied, as it was the sole compound demonstrated to be effective. These four inhibitors were selected from seven compounds investigated electrochemically based on their high inhibition efficiencies (Fig. 4). The elemental surface compositions are given in Supporting Information, Table S3. The detection of N and/or S elements indicates the formation of inhibitor films. The C/N, C/S and N/S ratios were calculated to assess differences between the experimental and molecular compositions of organic compounds at the surface (Table S4 and Fig. 9). The presence of Cl after subtracting the Na content indicates the formation of Cl-containing corrosion products. The Na spectra are also presented to check for the presence of residual NaCl after rinsing.

3.3.1. Surface composition analysis

The Bare (as-polished) surfaces consist mainly of metal and oxygen signals, i.e., the surface of Cu is covered with copper oxide, that of Ni with Ni oxide, whereas the alloy surfaces contain also contributions from Cu, Ni and Zn oxides (Fig. 9). Among all analyzed samples, the Bare specimens exhibited higher carbon content than the Blank samples, likely due to residual polishing compounds or solvent contamination (e. g., ethanol or acetone) from the cleaning process.

Comparative measurements for Blank samples immersed for 120 h in 3 wt% NaCl reveal that the surface film formed during immersion in NaCl differs depending on the alloy composition (Fig. 9 and Table S3); it changes from Ni oxide for Ni metal, over predominantly Cu oxide layer for CuNi₁₀, a predominantly Ni oxide for CuNi₃₀, and a mixed Cu/Ni/Zn oxide layer for CuNi₁₈Zn₂₀.

The situation changes, however, when the samples were immersed in NaCl containing inhibitors. For all alloys, the Ni or Zn surface content in inhibitor-treated samples remained below 1.0 at%, and Cu was the only metal detected among metal signals (Fig. 9 and Table S3). This indicates that the surface layer is selectively enriched in Cu, which preferentially reacts with the added inhibitors.

In our previous studies, we have shown that macroscopic selective dissolution (dealloying) of Ni and Zn occurs for binary CuNi, CuZn, and ternary CuNiZn alloys in various uninhibited environments, such as slightly alkaline 0.5 M NaCl (pH = 9.2) [48], simulated physiological solution (pH = 7.4), chloride containing borate buffer solution [49] and artificial sweat (pH = 6.5) [30], increasing with prolonged immersion time [29, 30, 48]. Given these past findings, one might assume a similar

macroscopic dealloying process causes the Cu enrichment observed here. However, it is critical to clarify that the Cu enrichment observed here in the presence of highly effective inhibitors does not imply a continuous, macroscopic selective dissolution of the bulk matrix.

Rather, it points to a nanoscale transient process during the initial stage of immersion. Initially, the native surface oxides or loosely bound metallic sites containing Ni and Zn are susceptible to Cl[−] attack and undergo a rapid, nanoscale transient dissolution. As this initial dissolution exposes the underlying stable Cu sites (the primary component of the matrix), the inhibitor molecules physis/chemisorb onto these exposed Cu sites, forming a highly protective Cu–inhibitor layer. This dense film ceases further dissolution, leaving the remaining Ni and Zn safely buried below the thin Cu-rich surface layer.

This mechanism is supported by the counter-example of the BTAH/CuNi₃₀ system. In this specific case, where the simple single-dentate inhibitor failed to provide complete and dense coverage on the highly alloyed matrix, localized corrosion proceeded, leading to the distinct detection of typical corrosion products such as NiOOH and Cu(II) species (see below Fig. 12). The complete absence of such Ni or Zn signals on surfaces protected by other optimal inhibitors confirms that the preferential dissolution is strictly limited to the initial transient conditioning of the topmost nanoscale layer, which is immediately followed by robust inhibitor protection.

For Ni metal, the addition of BTAH did not result in significant changes in surface elemental composition after 120 h of immersion compared to the Blank. The measured O and Ni content remained almost equal. The slight increase in N content was attributed to trace amounts of BTAH adsorbed on the surface, providing direct evidence that no dense or continuous inhibitor layer was formed, which agrees with the *in-situ* SERS observations by Cao et al. [46] demonstrating the sparse adsorption of neutral BTAH molecules on Ni. Consequently, the presence of these trace BTAH molecules exhibited no significant influence on the passivation process. The low Cl content (~0.3 at%) further confirms the good intrinsic resistance of Ni to Cl[−]-induced corrosion.

Table 5

The BE values of relevant elemental compounds used in this study. Those values are indicated as dashed lines in Figs. 10–13 to assist in the interpretation of XPS spectra. Reference values for Ni-related species were obtained from the references [50–52]. The BE for other reference species were adopted from [33,35, 53–55]. * Values refer to the apparent BE (BE = $h\nu - \text{KE}$, kinetic energy).

Element	No.	Assignment / Species	BE / eV
C 1 s	1	C–C / C–H (Adventitious)	284.8
	2	C–N / C–O	286.1–286.5
	3	C–S	286.9
	4	C=O	288.4
O 1-s	1	O ^{2−}	530.0
	2	OH [−]	531.0
	3	H ₂ O/OOH [−] /Organic O	532.0
N 1-s	1	=N– (imine-like)	399.0
	2	–NH ⁺ /M–N (protonated/metal-coordinated)	400.4
S 2p	1	Metal–S (2p _{3/2})	162.5
	2	Organic –S– / –SH	164.2
Cl 2p	1	Metal Cl (2p _{3/2})	198.4
Cu 2p	1	Cu(0) / Cu(I) (2p _{3/2})	932.5
	2	Cu(II) (2p _{3/2})	934.8
Cu LMM*	3	Cu(II) Satellite	~943.0
	1,2	Cu(0) (Metal)	568.3, 565.3
	3	Cu ₂ O	570.0
	4	Cu–Inhibitor	571.5
Ni 2p	1	Ni	852.6
	2	NiO	854.6
	3	Ni(OH) ₂	855.2
	4	NiOOH	855.8
Zn 2p	1	Zn	1021.4
	2	ZnO	1022.0
	3	Zn(OH) ₂	1022.7
	4	ZnCl ₂	1023.7
Zn LMM*	1,2	Zn	494.3, 491.2
	3	ZnO/Zn(OH) ₂	499.5

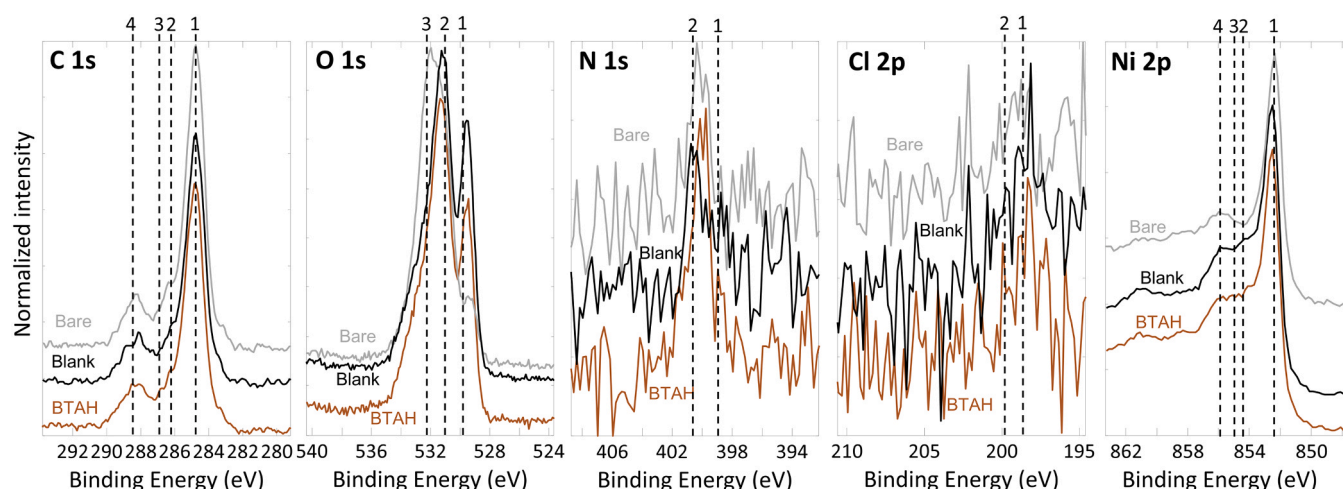


Fig. 10. High-resolution XPS spectra of the Ni metal surface after polishing (Bare), immersion in 3 wt% NaCl (Blank), and immersion in 3 wt% NaCl containing 1 mM BTAH for 120 h, where dashed lines indicate the peak positions of reference compounds. Peak assignments are as follows: **C 1 s**—(1) C-C / C-H (Adventitious), (2) C-N / C-O, (3) C-S, (4) C=O; **O 1 s**—(1) O^{2-} , (2) OH^- , (3) $\text{H}_2\text{O}/\text{OOH}^-$ /organic species; **N 1 s**—(1) C=N-C, (2) C-NH-C; **S 2 p**—(1) Metal-S ($2p_{3/2}$), (2) Organic-S- / -SH (S $2p_{1/2}$); **Cl 2 p**—(1) Cl $2p_{3/2}$, (2) Cl $2p_{1/2}$; **Ni 2 p**—(1) Ni, (2) NiO, (3) $\text{Ni}(\text{OH})_2$, (4) NiOOH.

In contrast, all three CuNi alloys showed increased carbon content and N/S ratio after 120 h immersion in inhibitor-containing solutions compared to their respective Blank samples, indicating surface enrichment of organic species. The Blank samples exhibited elevated oxygen contents (30–50 at%), suggesting the formation of oxide or hydroxide corrosion products, while these values dropped below 10 at% on inhibitor-treated surfaces, reflecting both corrosion inhibition and organic film coverage. The experimental N/S ratios of 2 for SH-ImiH-4Ph for all three alloys and SH-BimH for CuNi_{30} and $\text{CuNi}_{18}\text{Zn}_{20}$ equal the theoretical ratio of 2 (Table S4). For C/N ratios, the highest experimental values are obtained for SH-ImiH-4Ph, aligned with its molecular structure, followed by BTAH and SH-BimH. SH-Thd-Me showed the smallest C/N ratio, aligned with the theoretical ratio of 1.5. All experimental values are somewhat larger than those calculated from the molecular structure (Table S4), suggesting a surface enrichment with carbon. The C/S experimental ratios also follow theoretical values, but are somewhat higher due to carbon enrichment. The exception is SH-BimH for CuNi_{10} , where the sulphur concentration was negligible.

Cl contents also corroborated the inhibition effect. For CuNi_{10} , the Cl^- -related content remained below 1 at%, for CuNi_{30} and can be regarded as negligible (equal Na and Cl), while $\text{CuNi}_{18}\text{Zn}_{20}$ showed a markedly higher Cl level (~ 4 at%), indicating reduced Cl^- resistance upon Zn addition. These results suggest that increasing Ni content enhances Cl^- tolerance, while Zn alloying may promote Cl-induced corrosion product formation.

In CuNi_{10} , SH-BimH treatment yielded no detectable S, along with the presence of N, suggesting detachment of the -SH group and surface interaction via an N-containing bond during film formation. However, the SH-BimH yielded similar S (~ 5 –6 at%) and N (~ 12 –13 at%) levels for CuNi_{30} and $\text{CuNi}_{18}\text{Zn}_{20}$, with N/S theoretical ratios near 2:1, indicating S and N were stable in the molecular structure after film formation. The alloy composition thus affects the bonding mechanism of this inhibitor.

SH-ImiH-4Ph led to pronounced N and S enrichment ($\sim 2 \times$ higher N than SH-BimH) among all alloys, suggesting both N and S groups contribute to stable film formation. The Cu content is the lowest among all inhibitor-treated alloys, which could be attributed to the thicker surface film, which allows limited interaction between the Cu substrate and the incident X-ray.

Across all alloys, SH-Thd-Me yielded high and nearly equivalent contents of N and S (~ 15 –19 at% each), consistent with its molecular structure. Interestingly, these samples' surfaces also retained relatively high Cu content, implying a thinner film, possibly due to horizontal

molecular orientation.

BTAH treatment samples produced high N content (~ 16 at%) with suppressed Cu (~ 3 –4 at%), reflecting a comparatively thick and protective organic layer, as well as for SH-BimH and SH-ImiH-4Ph.

In summary, XPS surface composition analysis confirmed that N- and/or S-containing inhibitors form surface films on CuNi alloys, with varying degrees of thickness and elemental enrichment. Higher Ni content improves resistance against chloride ions, whereas Zn alloying may compromise it when used without an inhibitor. Among the inhibitors, based on the low Cu content, SH-ImiH-4Ph displayed a thicker layer while SH-Thd-Me exhibited the highest surface enrichment (highest N content) and tended to form thinner films.

3.3.2. High-resolution XPS spectra of Ni, CuNi_{10} , CuNi_{30} and $\text{CuNi}_{18}\text{Zn}_{20}$

Due to the complexity of the films formed by the interaction between the inhibitor and the metal surface, precise quantitative deconvolution of XPS peaks represents a significant challenge for all elements. To address this, BE values from established literature were utilized as reference species. Table 5 categorizes the characteristic compounds associated with the analyzed elements, assigning peak numbers that are consistently applied to the dashed reference lines in Figs. 10–13 to facilitate spectral interpretation. Reference values for Ni-related species were obtained from refs. [50–52], while those for the remaining elements were adopted from references [33,35,53–55].

Based on the quantitative surface analysis, Cu is identified as the primary metallic element interacting with the inhibitors. The enrichment of N and S on the surface is directly associated with the formation of a protective layer. Consequently, Cu LMM, N 1 s, and S 2p spectra are essential for understanding the bonding mechanism. Upon inhibitor coordination, the Cu LMM BE shifts toward a higher energy state [32,35,56], as indicated in Table 5.

In the N 1 s region, the signal near 400.4 eV assists in identifying metal-coordinated (N-M) or protonated nitrogen ($-\text{NH}^+$), which indicates the N bond to the surface; while imine-like ($=\text{N}-$) species appear at higher BE could indicate the presence of the organic inhibitor itself without bonding on the surface. These assignments are aligned with our previous reports on mercapto-based inhibitors forming two peaks in N 1 s spectra related to pyrrole and pyridine forms of the N atom [35,53]. The coexistence of imine-like and metal-coordinated N can also indicate the formation of thiolate species, as the thione form lacks imine-like N [32,35,57].

For S 2p, the spectra exhibit a doublet feature with a strict $2p_{3/2}$: $2p_{1/2}$ area ratio of 2: 1 and a fixed spin-orbit splitting of ~ 1.18 eV. The peak

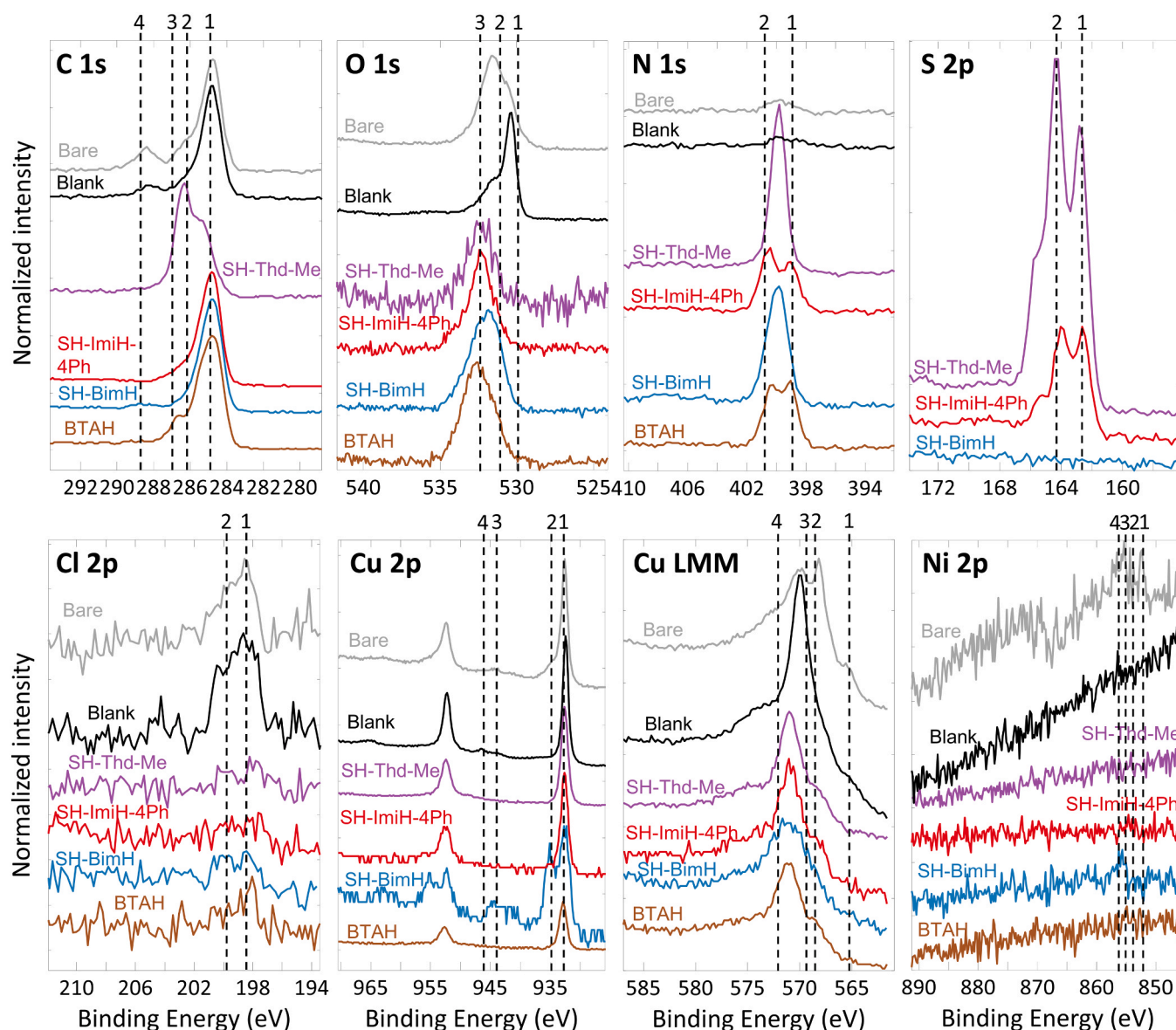


Fig. 11. High-resolution XPS spectra of the CuNi₁₀ surface after polishing (Bare), immersion in 3 wt% NaCl (Blank), and immersion in 3 wt% NaCl containing 1 mM SH-BimH, SH-ImiH-4Ph, BTAH, or SH-Thd-Me for 120 h, where dashed lines indicate the peak positions of reference compounds. Peak assignments are as follows: **C 1 s**—(1) C-C / C-H (Adventitious), (2) C-N / C-O, (3) C-S, (4) C=O; **O 1 s**—(1) O²⁻, (2) OH⁻, (3) H₂O/OOH⁻/organic species; **N 1 s**—(1) C≡N-C, (2) C-NH-C; **S 2p**—(1) Metal-S (2p_{3/2}), (2) Organic -S- / -SH (S 2p_{1/2}); **Cl 2p**—(1) Cl 2p_{3/2}, (2) Cl 2p_{1/2}; **Cu 2p**—(1) Cu/Cu₂O, (2) Cu(OH)₂, (3) Cu(II) satellite peak; **Cu LMM**—(1) Cu, (2) Cu/CuO, (3) Cu₂O, (4) Cu-inhibitor species; **Ni 2p**—(1) Ni, (2) NiO, (3) Ni(OH)₂, (4) NiOOH.

at 162.5 eV confirms S-metal bonding, whereas the component at 164.2 eV represents organic sulfur or -SH groups [58,59]. These peak relationships allow for a definitive assessment of the sulfur bonding state after immersion.

Figs. 10–13 display XPS spectra of polished Ni metal, CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀ surfaces, as well as after immersion in 3 wt% NaCl for 120 h, and in 3 wt% NaCl containing 1 mM SH-BimH, SH-ImiH-4Ph, BTAH, or SH-Thd-Me for 120 h (only BTAH was tested for Ni). Spectra include C 1 s, O 1 s, N 1 s, S 2p, Cl 2p, and Ni 2p for all samples. Cu 2p and Cu LMM spectra were additionally acquired for Cu-containing alloys, while Zn 2p and Zn LMM were collected for the CuNi₁₈Zn₂₀ alloy. As discussed in Section 3.3.1, the compositional analysis was based on the integrated intensities of high-resolution peaks. To enhance clarity of spectral shifts and surface-bonding variations, the XPS curves in Figs. 10–13 were normalized and vertically offset as appropriate on the y-axis. The spectra were not normalized for intensity.

A peak associated with C=O bonds was observed in all polished,

unimmersed samples, and also remained for all Blank samples except CuNi₁₈Zn₂₀. This likely results from residual organics introduced during polishing or solvent cleaning. In contrast, in inhibitor-containing solutions (excluding the Ni metal case), the C=O peak disappeared, suggesting that the inhibitor molecules effectively replaced these surface species through stronger interactions with the alloy surface. Given the susceptibility of the C 1 s signal to adventitious carbon contamination, this study does not attempt detailed quantification of carbon functional groups. Instead, C 1 s spectra are used as supporting evidence to indicate variations in organic or oxygen-containing surface species.

The C 1 s spectra are dominated by the aliphatic C-C/C-H component at ~284.8–285.0 eV, which is commonly observed due to adventitious carbon species on air-exposed surfaces. However, for SH-Thd-Me-treated CuNi alloys, the C 1 s spectra are dominated by a higher-BE peak (~286–288 eV) with a lower-BE shoulder near ~285 eV for CuNi₁₀ and CuNi₃₀. Considering the molecular structure of SH-Thd-Me (containing heteroatom-rich ring carbons), the dominant C 1 s contribution

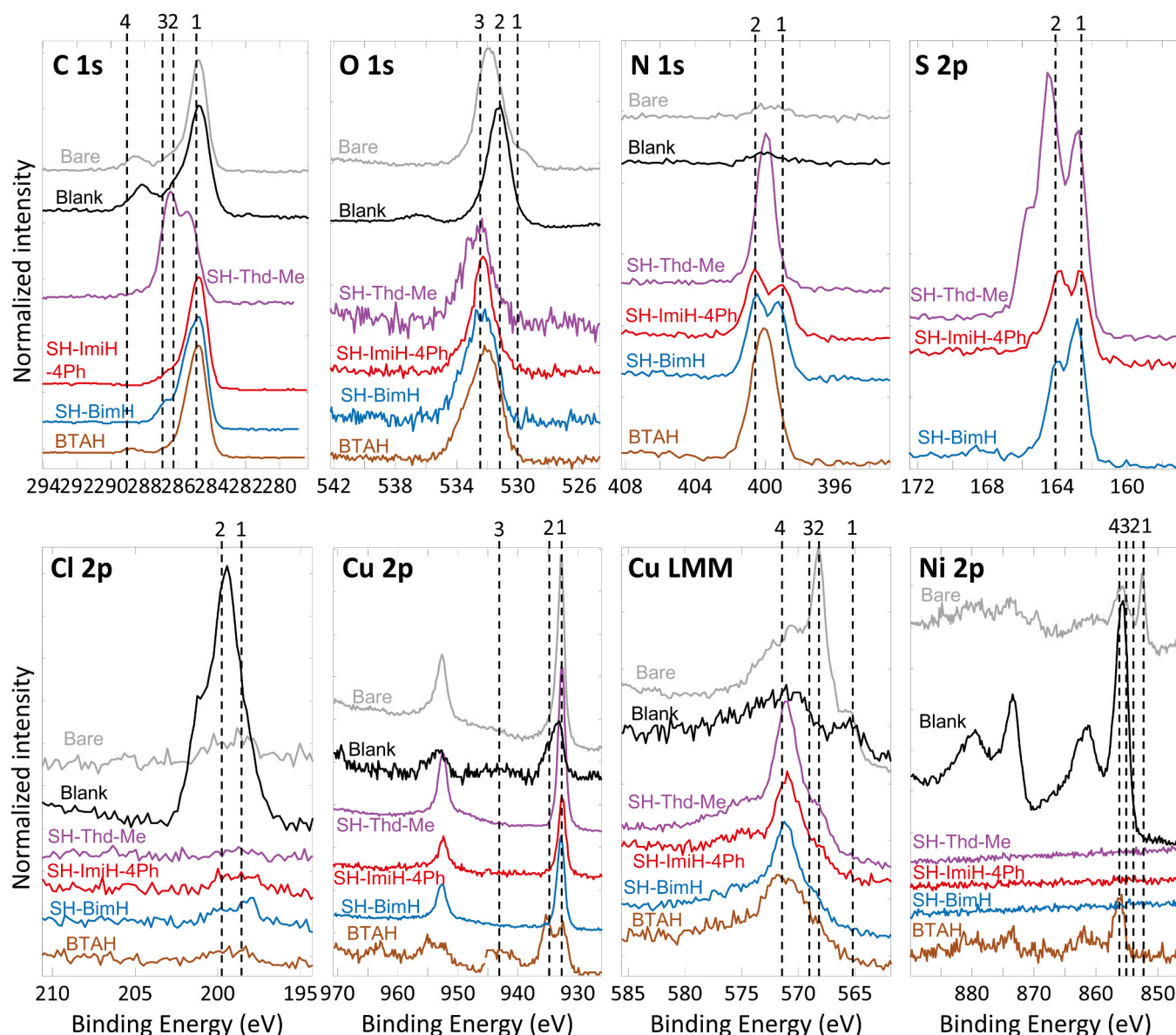


Fig. 12. High-resolution XPS spectra of the CuNi₃₀ surface after polishing (Bare), immersion in 3 wt% NaCl (Blank), and immersion in 3 wt% NaCl containing 1 mM SH-BimH, SH-ImiH-4Ph, BTAH, or SH-Thd-Me for 120 h, where dashed lines indicate the peak positions of reference compounds. Peak assignments are as follows: **C 1 s**—(1) C-C / C-H (Adventitious), (2) C-N / C-O, (3) C-S, (4) C=O; **O 1 s**—(1) O²⁻, (2) OH⁻, (3) H₂O/OOH⁻/organic species; **N 1 s**—(1) C=N-C, (2) C-NH-C; **S 2 p**—(1) Metal-S (2p_{3/2}), (2) Organic -S- / -SH (S 2p_{1/2}); **Cl 2 p**—(1) Cl 2p_{3/2}, (2) Cl 2p_{1/2}; **Cu 2 p**—(1) Cu/Cu₂O, (2) Cu(OH)₂, (3) Cu(II) satellite peak; **Cu LMM**—(1) Cu, (2) Cu/CuO, (3) Cu₂O, (4) Cu-inhibitor species; **Ni 2 p**—(1) Ni, (2) NiO, (3) Ni(OH)₂, (4) NiOOH.

is attributed to heteroatom-bound carbon environments (C-N/C=N/C-S), whereas the ~285 eV shoulder is assigned to the C-C/C-H. Therefore, C 1 s = 284.8 eV was not used as the charge reference for these inhibitor-derived overlayers; instead, spectra were aligned to a Cu core level, which provided consistent energy alignment across the inhibitor-treated samples.

Ni metal

Fig. 10 shows the XPS spectra of Ni metal for the Bare, Blank and BTAH samples. The N 1 s region exhibits poorly resolved peaks, with minimal differences observed among the Bare, Blank, and BTAH-treated samples. Thus, N from BTAH does not form a well-defined adsorption layer or surface film on the Ni surface. Additionally, no distinct Cl 2 p peaks were observed, suggesting negligible chloride-related species on the surface.

The O 1 s spectrum of the Bare sample shows a strong peak at ~532 eV, likely arising from adsorbed H₂O, hydroxyl groups, or oxygen-containing organic residues. After 120 h of immersion, both the Blank

and BTAH-treated samples show a minor low-energy peak (~529–530 eV) corresponding to O²⁻, along with a major peak of OH/oxyhydroxide contribution near 531–532 eV, suggesting the formation or thickening of an oxide/hydroxide surface layer.

A similar trend is observed in the Ni 2 p spectra. While the Bare sample still displays a noticeable metallic Ni signal, a peak around 855.8 eV indicates partial surface oxidation to NiOOH. After immersion, the spectra of both Blank and BTAH samples exhibit stronger shoulder features corresponding to Ni(II) species (e.g., NiO, Ni(OH)₂) and possibly Ni(III) (NiOOH), suggesting enhanced surface oxidation. However, the metallic Ni signal remains prominent, implying that the oxide/hydroxide layer is relatively thin or non-uniform.

CuNi₁₀

The XPS spectra of CuNi₁₀ with Bare, Blank, SH-BimH, SH-ImiH-4Ph, BTAH and SH-Thd-Me samples are shown in Fig. 11. In the polished (Bare) state, the O 1 s spectrum exhibits a broad peak, indicating multiple oxygen-containing species. The dominant high-BE

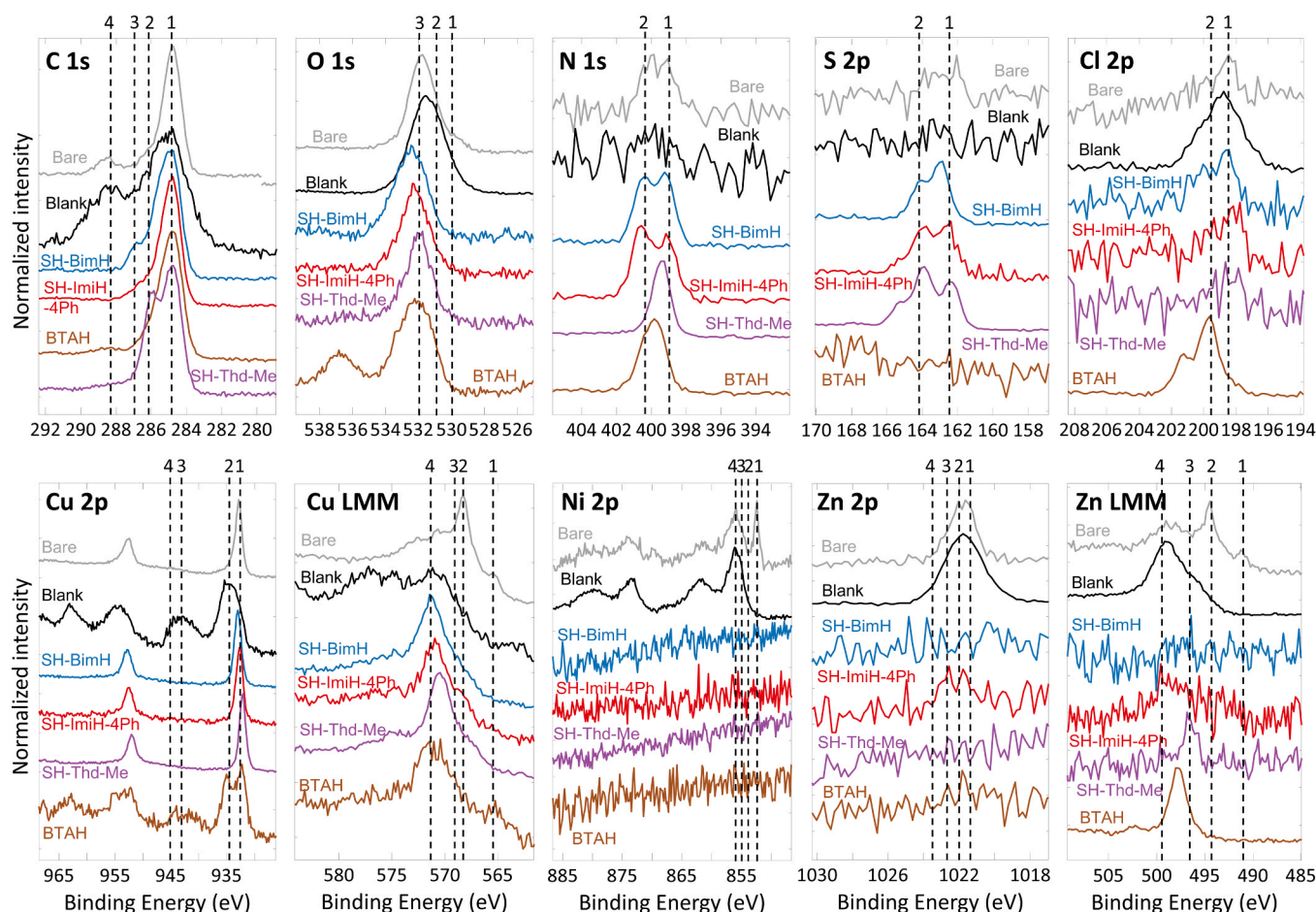


Fig. 13. High-resolution XPS spectra of the CuNi₁₈Zn₂₀ surface after polishing (Bare), immersion in 3 wt% NaCl, and immersion in 3 wt% NaCl containing 1 mM SH-BimH, SH-ImiH-4Ph, BTAH, or SH-Thd-Me for 120 h, where dashed lines indicate the peak positions of reference compounds. Peak assignments are as follows: **C 1 s**—(1) C-C / C-H (Adventitious), (2) C-N / C-O, (3) C-S, (4) C=O; **O 1 s**—(1) O²⁻, (2) OH⁻, (3) H₂O/OOH⁻/organic species; **N 1 s**—(1) C=N-C, (2) C-NH-C; **S 2p**—(1) Metal-S (2p_{3/2}), (2) Organic -S- / -SH (S 2p_{1/2}); **Cl 2p**—(1) Cl 2p_{3/2}, (2) Cl 2p_{1/2}; **Cu 2p**—(1) Cu/Cu₂O, (2) Cu(OH)₂, (3) Cu(II) satellite peak; **Cu LMM**—(1) Cu, (2) Cu/Cu₂O, (3) Cu₂O, (4) Cu-inhibitor species; **Ni 2p**—(1) Ni, (2) NiO, (3) Ni(OH)₂, (4) NiOOH; **Zn 2p**—(1) Zn, (2) ZnO, (3) Zn(OH)₂, (4) ZnCl₂; and **Zn LMM**—(1,2) Zn, (3) Zn(II)-inhibitor species, (4) ZnO/Zn(OH)₂.

contribution (~531–533 eV) is consistent with hydroxyl/water and/or oxygen-containing organic species, while a lower-BE component (~529–530 eV) suggests the presence of O²⁻ in metal oxides. Consistently, the Cu LMM spectrum shows features characteristic of a mixed Cu⁰/Cu⁺ surface, where Cu metal and Cu(I) oxide (Cu₂O) are distinguishable more reliably by Cu LMM than by Cu 2p alone.

After 120 h immersion in 3 wt% NaCl without inhibitors (Blank), the O 1s envelope becomes narrower and the low-BE portion (~529–530 eV) increases, indicating enrichment in the oxide component peak. The corresponding Cu LMM feature sharpens and trends toward the characteristic Cu₂O-like position, suggesting the formation of a Cu(I) oxide film. The Cu 2p_{3/2} peak is centred at 934.8 eV with no satellite peak associated with Cu(II) species. The oxide may contain chloride species, as some Cl was detected. No Ni signal was detected, proving that the surface oxide layer consists predominantly of Cu oxide/hydroxide.

In inhibitor-treated samples, the O 1s spectra show enhanced intensity in the high-BE region (~531–533 eV), consistent with contributions from hydroxyl/organic oxygen associated with the inhibitor-derived overlayer. The Cu LMM features in these cases deviate from the Blank sample, shifting toward reported Cu-inhibitor-related line-shape/position changes. Among the inhibitors, only the SH-BimH-treated sample shows a weak Cu 2p component that may be consistent with trace Cu(II) species (CuO/Cu(OH)₂); however, its low intensity suggests a minor fraction. Given the weak Ni signal in these alloys, Ni

chemical states were not used as a constraint for deconvoluting O 1 s.

After 120 h of immersion, Ni 2p signals were essentially absent in most samples. Only the SH-BimH-treated sample exhibited a very weak feature near 855.2–855.8 eV, tentatively consistent with trace Ni(OH)₂/NiOOH. For Cl 2p, small peaks were detected only in the Bare and Blank samples, suggesting limited Cl adsorption and/or minor Cl-containing surface species in the absence of inhibitor protection. In contrast, Cl 2p was below the detection limit for all inhibitor-treated samples, implying that the inhibitor layers effectively suppress Cl⁻ adsorption/penetration.

For BTAH and SH-ImiH-4Ph, the N 1 s spectra can be described by two components: a lower-BE peak (~398.5–399.6 eV) attributed to imine-like/neutral heterocyclic N, and a higher-BE peak (~399.8–401.5 eV) associated with metal-coordinated and/or protonated N environments. These features support the existence of persistent inhibitor-derived N species at the surface after immersion, with partial coordination to Cu while maintaining heterocyclic character. In contrast, SH-BimH and SH-Thd-Me exhibit a single broadened N 1 s peak (399.0–400.4 eV), suggesting a sum of neutral, coordinated, and partially protonated N states.

The S 2p spectra further display the chemical state of thiol-derived sulfur. Notably, no S 2p signal was detected for SH-BimH within the XPS detection limit, suggesting low surface sulfur coverage. For SH-ImiH-4Ph and SH-Thd-Me, an S 2p_{3/2} peak at ~162.5 eV confirms the presence of metal-thiolate (M-S) bonding. The apparent excess intensity

on the high-BE side beyond the expected S 2p doublet ratio indicates an additional doublet with S 2p_{3/2} near ~163.8–164.0 eV, consistent with unreacted/weakly bound thiol or other organic-sulfur environments (and/or disulfide-like species). For SH-Thd-Me, the relatively stronger ~164 eV contribution is consistent with its heterocycle containing an additional ring sulfur atom, which can increase the fraction of organic-sulfur-type.

CuNi₃₀

Fig. 12 summarizes the high-resolution XPS spectra of the CuNi₃₀ surfaces under Bare, Blank, and inhibitor-treated conditions after 120 h of immersion. On the Bare CuNi₃₀ surface, the O 1 s spectrum displays a broad peak centered around 531–532 eV, indicating the coexistence of various oxygen-containing species, including surface hydroxyls, adsorbed water, and possibly organic O species. The Cu LMM spectrum suggests that Cu mainly exists in its metallic state, with no significant oxidation features. In contrast, the Ni 2p spectrum shows a broad peak between 855.2–855.8 eV, attributed to the presence of Ni(OH)₂ or NiOOH, which is consistent with the O 1 s result.

After 120 h immersion in 3 wt% NaCl (Blank), the O 1 s peak narrows and shifts towards lower BE corresponding to hydroxide regions, suggesting the growth of hydroxide-rich surface films. The Cu LMM signal diminishes significantly, and the Cu 2p peaks broaden and shift toward higher BE, implying the formation of Cu(II)-containing corrosion products. The Ni 2p signal increases, with a single broad peak at ~855.5 eV, indicative of the complete transformation of Ni into Ni(OH)₂/NiOOH. This observation aligns with the O 1 s shift and suggests that, in the absence of inhibitors, the surface film tends to evolve toward Ni-based hydroxides. The elemental composition ratio of Cu and Ni is only 0.13, confirming that the surface layer predominantly contains Ni. The presence of Cl 2p peaks in the Blank condition, in the absence of corresponding NiCl₂ signals [60], points to the likely formation of CuCl₂ as the dominant chloride corrosion product.

In the inhibitor-treated samples, the C 1 s spectra show enhanced high-BE components, indicating the accumulation of organic inhibitor layers. Notably, SH-Thd-Me exhibits dominant peaks at 286–288 eV, with only a weak shoulder at ~285 eV, consistent with results in CuNi₁₀. In all inhibited samples, O 1 s peaks shift towards higher BE (~531–533 eV), suggesting an increased proportion of surface hydroxyls or organic oxygen species within the inhibitor-derived surface layer.

The Cu LMM spectra shift consistently away from the Cu(I) oxide region and toward BE associated with Cu-inhibitor layer formation, further supported by the emergence of clear N 1 s and S 2p peaks. Except for BTAH, no Ni 2p peaks are detected in inhibitor-treated samples. On the BTAH-treated surface, the appearance of the Ni(OH)₂/NiOOH peaks, alongside Cu(II) features in Cu 2p, yet with no detectable Cl 2p signal, suggests localized corrosion and partial failure of surface protection.

N 1 s signals were consistently detected in all inhibitor-treated samples. SH-ImiH-4Ph and SH-BimH both exhibit two well-resolved peaks corresponding to imine-like and M–N/–NH⁺ environments, indicating strong nitrogen coordination to the surface and the probable formation of thiolate bonds. SH-Thd-Me displays a narrower single peak, while BTAH shows a broader single peak leaning towards M–N/–NH⁺, suggesting a less uniform nitrogen environment dominated by metal coordination.

S 2p spectra further differentiate the S-containing inhibitors. As expected, BTAH exhibits no S signal. SH-BimH, SH-ImiH-4Ph, and SH-Thd-Me all show typical S 2p doublets in the 162–164 eV range. In SH-BimH, a small high-BE shoulder raises the high-energy contribution slightly above the ideal 2:1 ratio, suggesting a dominant Cu–S bonding with minor –SH or organic S present. SH-ImiH-4Ph exhibits nearly equal intensities for the two peaks, indicating significant high-energy contributions from surface-enriched organic S species. SH-Thd-Me shows the strongest high-energy peak dominance, suggesting the most prominent organic S character among the three.

Cl 2p signals in all inhibitor-treated samples are suppressed to near

the detection limit, in stark contrast to the Bare and Blank conditions. This highlights the effectiveness of inhibitors in preventing Cl[–] attack on the CuNi₃₀ surface.

CuNi₁₈Zn₂₀

Fig. 13 presents high-resolution XPS spectra of the CuNi₁₈Zn₂₀ alloy under: polished state (Bare), after immersion in 3 wt% NaCl for 120 h (Blank), and after immersion in 3 wt% NaCl containing 1 mM of selected inhibitors (SH-BimH, SH-ImiH-4Ph, BTAH, SH-Thd-Me) for 120 h. In the Bare condition, the O 1 s peak is centered around ~532 eV and shows a broad distribution, indicating the presence of various surface oxygen species introduced during polishing. A distinct Ni 2p signal appears in the NiOOH BE range, and weak Zn LMM peaks associated with ZnO/Zn(OH)₂ are also observed, confirming the presence of initial oxide/hydroxide species. However, metallic-state signals remain detectable in the Cu 2p/Cu LMM, Ni 2p, and Zn 2p/Zn LMM spectra, suggesting that the native oxide layer is relatively thin, allowing significant contributions from the metallic substrate.

Compared to Bare, the Blank sample shows a broader O 1 s peak shifted toward ~531 eV, indicating a more complex surface oxygen chemistry with increased hydroxide/water-related species. The Ni 2p region broadens and overlaps with both NiOOH and Ni(OH)₂ binding energies, suggesting the Ni has primarily converted into mixed nickel oxyhydroxides. In Zn LMM, metallic Zn features diminish significantly, and the spectrum is dominated by Zn(OH)₂-like characteristics, indicating the preferential formation of Zn hydroxide species. Cu 2p spectrum displays enhanced intensity in the Cu(II) region along with a satellite peak, indicating the formation of Cu(II)-based corrosion/hydration products (e.g., CuO or Cu(OH)₂); the presence of Cl 2p would further support the formation of CuCl₂ species. Overall, the surface products in the Blank condition can be described as follows: Cu is primarily present as Cu(II) species, Ni as Ni(OH)₂/NiOOH, and Zn predominantly as Zn(OH)₂. The layer formed contains all three types of oxide/hydroxide, i.e. the ratios Cu/Ni and Cu/Zn are 1.2 and 0.8, respectively, indicating that they are relatively evenly distributed.

For inhibitor-treated samples, the C 1 s behavior is broadly similar to that of other alloy systems. SH-Thd-Me, however, shows a distinct main C 1 s peak around ~284.8 eV with a shoulder at ~286 eV, suggesting differences in the surface carbon environment, likely due to the chemical nature and coverage behavior of the inhibitor layer. All inhibitors induce a shift in the O 1 s peak toward higher BE (~531–533 eV), consistent with increased proportions of hydroxyl/adsorbed oxygen species or oxygen from organic layers. It should be noted that the ~537 eV peak in the BTAH sample originates from Na KLL Auger transitions overlapping the O 1 s region and is excluded from discussions of oxygen species (see Fig. 9).

Both SH-BimH and SH-ImiH-4Ph display two well-defined peaks of comparable intensity attributed to imine-like and M–N/–NH⁺-like structures, suggesting that these inhibitors form Cu–N bound layers involving multiple N environments. SH-Thd-Me exhibits a narrower peak centered closer to the imine-like region, while BTAH presents a broader single peak shifted towards the M–N/–NH⁺ region, indicating a more dispersed coordination environment dominated by M–N interactions. These spectral features correlate with electrochemical results (Fig. 4), where SH-BimH, SH-ImiH-4Ph, and BTAH exhibited superior corrosion inhibition performance, supporting the role of strong nitrogen coordination in forming stable protective layers.

The S 2p spectra are consistent with trends observed in the CuNi₃₀ results. All three S-containing inhibitors (SH-BimH, SH-ImiH-4Ph, SH-Thd-Me) exhibit typical S 2p doublets between 162–164 eV, indicating dominant thiolate-type (M–S) bonding. SH-BimH shows a Cu–S-dominated doublet with a minor organic S contribution. SH-ImiH-4Ph retains a more pronounced high-BE peak, reflecting a higher presence of non-coordinated or free thiol species. SH-Thd-Me exhibits the strongest organic S features, likely due to its unique thioether ring structure that enhances organic S retention on the surface.

Importantly, in the SH-Thd-Me sample, although no pronounced

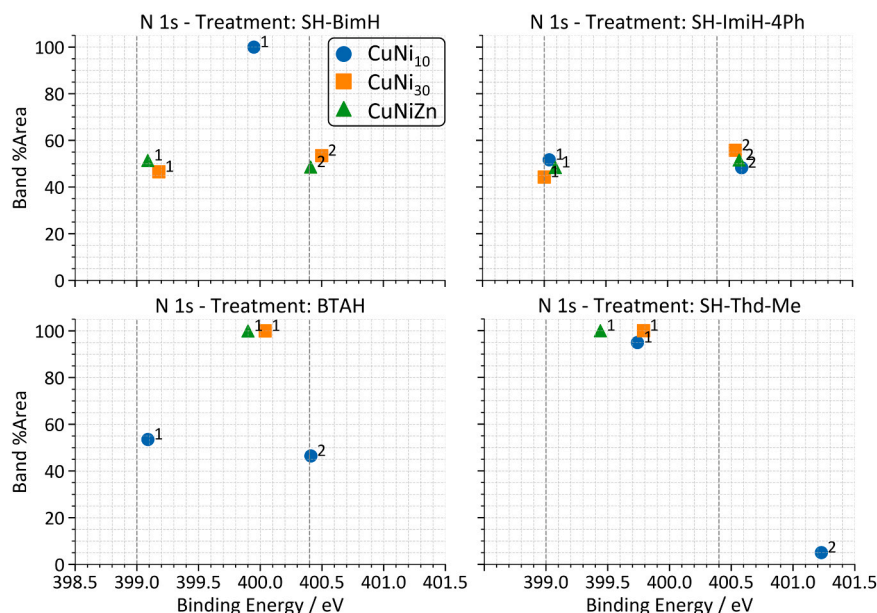


Fig. 14. Summary of the curve-fitting results for N 1s spectra after 120 h immersion in 3 wt% NaCl with selected inhibitors. The four panels show the distribution of fitted component BE and relative band areas for different inhibitor conditions. Colors and marker shapes denote the alloy (CuNi₁₀, CuNi₃₀, CuNi₁₈Zn₂₀). The vertical dashed grey lines are the same reference as in Figs. 10–13 for N 1s. Component indices (1–2) correspond to the position of the fitted peak positions, as described in Table 5. Further details are provided in Table S5 (Supplementary Information).

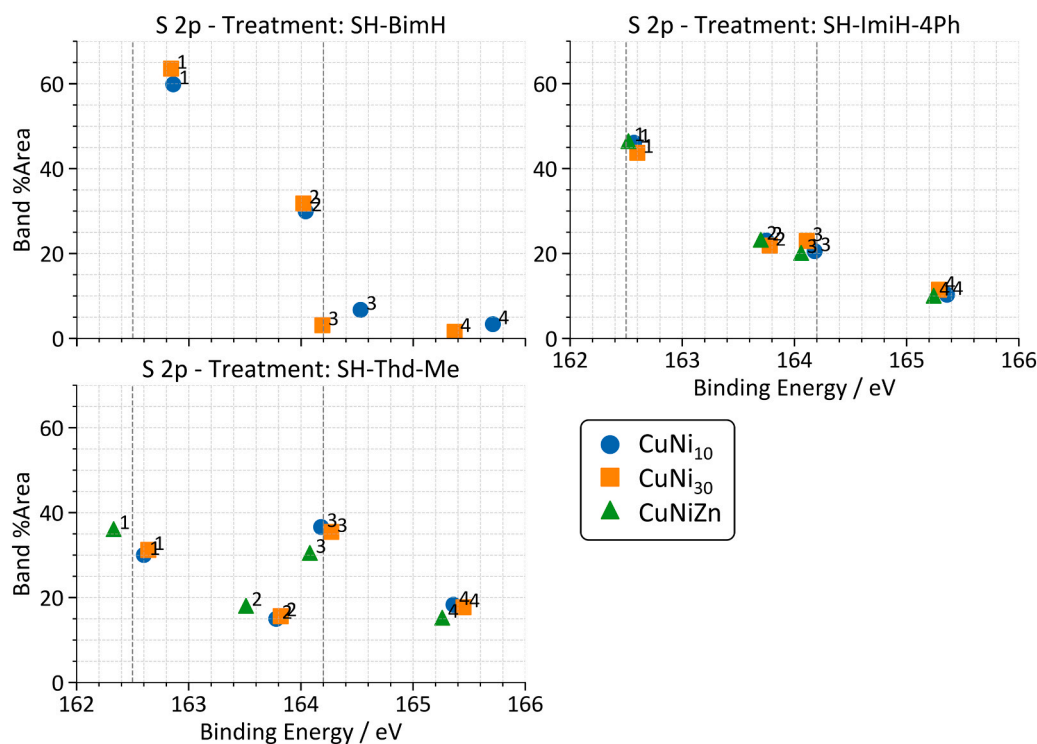


Fig. 15. Summary of the curve-fitting results for S 2p spectra after 120 h immersion in 3 wt% NaCl with selected inhibitors. The three panels show the distribution of fitted component BE and band areas for different inhibitor conditions. Colors and marker shapes denote the alloy (CuNi₁₀, CuNi₃₀, CuNi₁₈Zn₂₀). For S 2p, the deconvolution was performed using 2 spin-orbit doublets with fixed splitting ($\Delta SO \approx 1.18$ eV) and area ratio ($2p_{3/2}:2p_{1/2} = 2:1$). Component indices (1–4) correspond to the position of the fitted peak positions, as described in Table 5. The dashed grey lines are the same reference as in Figs. 10–13 for S 2p. Further details are provided in Table S6 (Supplementary Information).

metal oxide features are observed, Zn 2p and Zn LMM spectra show peaks at BE associated with Zn–S species (e.g., ZnS), suggesting that SH-Thd-Me may react with Zn to form Zn(II)–S–R compounds. In the case of BTAH, despite relatively good corrosion inhibition in electrochemical

tests, Cu(II)-related features are still present in the Cu 2p spectrum, and Zn LMM shows additional peaks near ~ 498 eV. These may indicate the formation of Zn(II) corrosion products or Zn–S–R coordination species, suggesting potential localized corrosion or side reactions at the micro-

scale.

3.3.3. Corrosion inhibition mechanism of organic inhibitors on CuNi alloys

Ni metal and the CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀ alloys show distinct differences in corrosion susceptibility in 3 wt% NaCl, with Ni metal showing the highest corrosion resistance and CuNi₁₈Zn₂₀ the lowest. During polarization and long-term immersion, the composition of the surface oxide layers formed differs: from Ni oxide on Ni metal, to a predominantly Cu oxide layer for CuNi₁₀, a predominantly Ni oxide for CuNi₃₀, and a mixed Cu/Ni/Zn oxide layer for CuNi₁₈Zn₂₀. This observation aligns with our previous studies on Cu–Zn and Cu–Ni alloys and with the prevailing zinc and nickel oxides observed at the surface layer, as the Zn and Ni contents in the alloy increase [5,13,29–33].

In our previous work on Cu–Zr amorphous alloys, a stable ZrO₂ layer spontaneously formed on the surface after preparation [37]. This passive oxide film provided the dominant corrosion protection, leaving little opportunity for inhibitors to interact with the underlying metal. In contrast, in Cu–Zn systems (e.g., Cu₇₀Zn₃₀), inhibitors such as SH-ImiH-4Ph exhibited effective corrosion suppression at both Cu and Zn sites, indicating a mechanism closely aligned with the additive behavior of metal–inhibitor interactions [33]. However, in the present study, most inhibitors showed limited or even negative effects on Ni metal, while exhibiting significant improvement on CuNi and CuNi₁₈Zn₂₀ alloys. This difference suggests that the inhibition mechanism in alloy systems cannot be simply extrapolated from that of metal–inhibitor systems, but is instead governed by surface compositional evolution (e.g., surface segregation or enrichment) and local electronic structure modifications induced by alloying.

High-resolution XPS analysis further supports this hypothesis. After 120 h immersion, all alloy surfaces (within the XPS sampling depth) exhibited strong Cu enrichment and significant attenuation of Ni and Zn signals (not detectable). This observation implies that the principal active binding sites for inhibitor molecules reside on Cu-related surface species. While we cannot exclude the involvement of Ni/Zn, the observed N and S signals associated with inhibitor layers predominantly co-exist with Cu, suggesting that Cu is the primary interaction element within the detection limits and signal-to-noise ratios of our measurements.

Despite the consistent Cu surface enrichment across all samples, the most effective inhibitors varied with alloy composition: BTAH, SH-ImiH-4Ph and SH-BimH for CuNi₁₀, SH-Thd-Me, SH-BimH and SH-ImiH-4Ph for CuNi₃₀, and SH-BimH, BTAH and SH-ImiH-4Ph for CuNi₁₈Zn₂₀, as evidenced by the lowest j_{corr} and highest R_p or $|Z|_{0.01 \text{ Hz}}$ values. This variation indicates that even on Cu-enriched surfaces, inhibitor binding strength and film stability are influenced by the alloying elements—likely due to their effects on the local electronic structure and the atomic environment around Cu atoms. These changes could affect Cu–inhibitor interaction and the evolution of protective films, thereby accounting for the composition-dependent inhibitor efficiency.

In our previous studies, we analysed N 1s and S 2p spectra on mercapto-based inhibitors SH-BimH and SH-BimMe and SH-ImiMe for Cu and CuZn alloys [35,53]. In this study, the choice of mercapto-based inhibitors is broader. The inhibitor adsorption is further affected by the alloying element, i.e. type of substrate. Therefore, to gain deeper insight into the inhibitor film structures, peak deconvolution was performed on N 1s and S 2p spectra (Figs. 14 and 15). The details about the fitting parameters and curves can be found in (Figs. S43–S48). The S 2p region was fitted using 2 doublet pairs with constrained spin–orbit splitting (~1.18 eV) and area ratios (2:1) to prevent overfitting. Notably, SH-ImiH-4Ph showed highly consistent N 1s and S 2p peak positions and area ratios across all alloys (Figs. 11–13 and Table S4), suggesting a stable and reproducible interfacial bonding mode that is not influenced by the alloying elements. The presence of imine-like N and organic S is consistent with literature reports indicating that imidazole/phenyl-containing triazoles can form a Cu–inhibitor layer in 3 wt% NaCl [61]. Besides, the significant attenuation of Cu signals observed in

SH-ImiH-4Ph-treated alloys (Fig. 9) implies a possibly thick multilayer structure.

In contrast, SH-BimH displayed pronounced alloy-dependence. On CuNi₁₀, only N signals were detectable alongside the presence of Cu(II) and NiOOH/Ni(OH)₂ signals, suggesting a more defective film. On CuNi₃₀ and CuNi₁₈Zn₂₀, the S 2p spectra were dominated by Cu–S (thiolate) contributions, with minimal organic S signals (<10%), and the N 1s signal shows the presence of Cu–N coordination, indicating a densely packed interfacial layer with limited inhibitor molecules on the surface. This mixed Cu–S/N coordination is likely responsible for the increasing corrosion resistance observed from CuNi₁₀ to CuNi₃₀/CuNi₁₈Zn₂₀.

For BTAH, the strongest inhibition was observed on CuNi₁₀. Its N 1s spectrum could be deconvoluted into Cu–N and imine-like components, aligning with the classic Cu(I)–BTA complex formation model. This film type is well-known for its stability in chloride-containing environments [62]. However, on CuNi₃₀ and CuNi₁₈Zn₂₀, N 1s showed a broad, single peak with poorly resolved subcomponents, suggesting more heterogeneous N-coordination environments. XPS also revealed increased Cu(II) features in CuNi₃₀ and Cu(II) + Zn(II) features in CuNi₁₈Zn₂₀, indicating that BTAH was less effective in suppressing localized corrosion in these systems—underscoring the need to consider both macroscopic inhibition and potential micro-scale vulnerabilities.

Finally, SH-Thd-Me performed best on CuNi₃₀. Its enhanced effectiveness likely stems from film rearrangement and densification over time (the P_{inh} increased by more than 2 times at 48 h than at 24 h), rather than specific interactions with Ni. Although XPS revealed a minimal decreasing of Cu signals—suggesting a thinner film—the electrochemical data indicated high surface coverage and impedance. A plausible explanation is that SH-Thd-Me forms a lying-down, high in-plane coverage film with limited vertical thickness, a common structure–performance profile for organic inhibitors.

While the XPS results confirm the formation of Cu-enriched surfaces across all tested alloys, the stark differences in inhibitor performance indicate that the chemical reactivity of these surface Cu atoms is not identical. Although in-situ valence band measurements or *ab-initio* calculations were not performed in this experimental study, this phenomenon could be explained through the classical d-band center model [63] and subsequent Density Functional Theory (DFT) studies on bimetallic Cu-alloys [64–66].

When Cu is alloyed with transition metals like Ni, the incorporation of subsurface alloying atoms significantly modifies the electronic structure of the host metal. According to classical DFT calculations by Nørskov and co-workers [64], the presence of subsurface Ni induces both geometric strain and ligand effects (charge transfer), which may broaden the Cu d-band and shift the d-band center of the surface Cu atoms. This shift will alter the chemisorption energetics. The chemisorption of azole inhibitors primarily relies on the donation of lone-pair electrons from the N and S heteroatoms into the empty d-states of the metal, accompanied by back-donation [67]. Because the subsurface Ni modulates the d-band center of the topmost Cu layer, it consequently "tunes" the orbital overlap between the Cu active sites and the inhibitor functional groups.

This electronic modulation provides a theoretical framework for our observations: on low-alloying matrices (e.g., CuNi₁₀), single-dentate N-coordination (e.g., BTAH) exhibits excellent inhibition, indicating promising orbital matching, yielding sufficient adsorption energy; another example is the SH-BimH, which shows solely N-bond on the CuNi₁₀ surface (Fig. 15). Conversely, on highly alloyed matrices (e.g., CuNi₃₀ and CuNi₁₈Zn₂₀), the severe electronic modulation of surface Cu induces an orbital mismatch for simple single-dentate ligands. To compensate for this modulated electronic environment, the system should demand molecules with stronger multi-dentate chelating abilities (such as the synergistic -SH and heterocyclic N anchoring in SH-Thd-Me or SH-ImiH-4Ph). This theoretical deduction is consistent with the *ab-initio* and XPS investigations in previous research [32] on CuZn

systems; this study demonstrated that mercapto-substituted azoles (such as SH-BimH) achieve superior inhibition on highly heterogeneous, Zn-containing surfaces due to the engagement in synergistic multi-dentate bonding, forming exceptionally stable metal-S and metal-N bonds simultaneously across active sites. Therefore, utilizing such multi-dentate spatial configurations to overcome the alloying-induced electronic modulation serves as a fundamental principle for composition-adaptive inhibitor design.

Building upon these mechanistic insights, as well as the intensity of the Cu signal in XPS (Fig. 9 and Table S3), we can link the structural features of the inhibitors (e.g., film thickness, spatial orientation, and denticity) to the "molecular structure" design principles, thereby deducing explicit engineering guidance for specific alloy applications in dynamic marine environments:

- **For highly alloyed Cu alloys (e.g., CuNi₁₈Zn₂₀ and CuNi₃₀):** The severe surface heterogeneity and alloying-induced electronic modulation weaken simple single-dentate chemisorption. Thus, compounds containing multiple synergistic coordination sites (i.e., multi-dentate S and N anchoring, such as SH-BimH) should be strictly preferred for long-term inhibition. The multi-dentate design effectively compensates for the orbital mismatch at individual active sites, locking onto the surface to prevent localized breakdown.
- **For applications requiring ultra-thin but highly efficient protective coatings:** Molecular structures that intrinsically favor a compact, "lying-down" horizontal orientation (e.g., SH-Thd-Me) should be prioritized. This structural design maximizes the in-plane footprint, effectively blocking active dissolution sites even at minimal film thickness, which is highly advantageous in nanoscale precision applications where thick coatings are undesirable. Relatively high intensity of Cu signals in XPS spectra implies the formation of a thin inhibitor layer, but with a high level of protection.
- **For universal Cu-alloys protection:** Molecular designs that promote the formation of thick, stable multilayer networks (e.g., SH-ImiH-4Ph) via robust intermolecular interactions should be selected. The resulting film thickness, as judged by a low intensity of Cu signals in XPS spectra, serves as a powerful, composition-insensitive physical barrier that buffers against the varying local electronic environments of different substrate compositions.

Ultimately, by adaptively matching the molecule's spatial orientation, denticity, and film-forming thickness to the specific alloying-induced electronic environment, the corrosion protection of multinary alloys can be systematically optimized from empirical screening to rational design.

4. Conclusions

In this study, the corrosion inhibition behaviors of a series of organic inhibitors—including SH-BimH, SH-ImiH-4Ph, BTAH, SH-BimH-5OMe, Me-S-BimH, SH-Thd-NH₂ and SH-Thd-Me—were systematically investigated on Ni metal and three Cu-based alloys (CuNi₁₀, CuNi₃₀, and CuNi₁₈Zn₂₀) in 3 wt% NaCl solution. Both short-term (1 h) and long-term (120 h) electrochemical tests were performed, coupled with surface XPS analyses, to elucidate the mechanisms of inhibitor-substrate interactions. The following conclusions can be drawn:

- During polarization or immersion in a NaCl solution, the surface layer changes from Ni oxide on Ni metal to predominantly Cu oxide on CuNi₁₀ and Ni oxide on CuNi₃₀, and finally to a mixed Cu/Ni/Zn oxide on CuNi₁₈Zn₂₀. In NaCl containing an organic inhibitor, however, the surface layer transforms into a predominantly Cu surface layer for all three alloys.
- Inhibitor performance strongly depends on alloy composition. While most inhibitors showed negligible or even adverse effects on Ni metal, they exhibited significant corrosion inhibition on Cu-

containing alloys, with optimal inhibitors varying by alloy (three listed from most efficient downwards): BTAH, SH-ImiH-4Ph and SH-BimH for CuNi₁₀, SH-Thd-Me, SH-BimH and SH-ImiH-4Ph for CuNi₃₀, and SH-BimH, BTAH and SH-ImiH-4Ph for CuNi₁₈Zn₂₀, given based on 120-h immersion and impedance magnitude at 0.01 Hz.

- XPS results revealed that after 120 h immersion, surface Ni and Zn signals were largely absent. The surface enrichment in Cu is driven by an initial nanoscale transient dissolution of the native oxides, which is immediately terminated by rapid inhibitor adsorption. This suggests that inhibitor long-term protection mainly arises from the formation of Cu-inhibitor coordination films.
- Electronic modulation by alloying elements: In addition to surface Cu enrichment, alloy-induced changes in the local electronic environment may contribute to the observed composition-dependent inhibition. Such electronic effects may influence adsorption strength and film stability, although they were not directly measured in the present study.
- The chemical structure of inhibitors must adaptively match the specific surface state:
 - o SH-ImiH-4Ph forms stable, relatively thick organic layers with consistent N/S bonding environments across all alloys, providing broad adaptability.
 - o BTAH, although generally effective electrochemically (especially on mildly alloyed CuNi₁₀), shows signs of localized Cu(II) corrosion products in XPS on highly alloyed matrices (CuNi₃₀), suggesting simple single-dentate N-coordination provides incomplete long-term surface protection on heavily modulated surfaces.
 - o SH-BimH demonstrates enhanced inhibition when both -SH and N groups coordinate with the surface Cu; otherwise, its performance weakens (e.g., on CuNi₁₀).
 - o SH-Thd-Me likely adopts a "lying-down" adsorption configuration, forming a thin yet compact film that results in excellent inhibition even at minimal film thickness.

In summary, the effectiveness of organic inhibitors on Cu-based alloys is jointly determined by the substrate composition, the resulting surface Cu enrichment, the electronic modulation by alloying elements, and the specific multilayer nature/spatial configuration of the inhibitor. These insights move beyond empirical screening to establish the fundamental principles of "composition-adaptive inhibitor design". They provide explicit engineering guidance: understanding how subsurface alloying elements modulate the local electronic environment of surface Cu is the key to adaptively matching molecular structures for optimal long-term corrosion protection in marine environments.

CRedit authorship contribution statement

Ingrid Milošev: Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization. **Chenyang Xie:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, 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.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.corsci.2026.114175](https://doi.org/10.1016/j.corsci.2026.114175).

Data availability

Data will be made available on request.

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