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Functional-Group-Directed Occlusion of Polystyrene Microspheres within FeCO₃ Layers: Long-Term Corrosion Protection and Mechanical Stability of Carbon Steel

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Abstract

FeCO₃ corrosion-product layers can suppress CO₂ corrosion of Carbon Steel (CS), but their long-term protectiveness is limited by dissolution, structural defects and mechanical breakdown that can promote localized corrosion of the underlying CS. Here, carboxyl- or amino-functionalized polystyrene microspheres (PS-COOH or PS-NH₂, 10 ppm) were added once after 2 h immersion to engineer PS-FeCO₃ polymer–mineral composite layers during 900 h exposure. In-situ electrochemical monitoring showed that the PS-FeCO₃ composite layers provided long-term uniform corrosion inhibition comparable to that of the unmodified FeCO₃ layer. The composite layers effectively suppressed localized pitting damage and improved mechanical performance; among them, the PS-NH₂-FeCO₃ composite layer gave the best corrosion-mechanical response, reducing the deepest-pit depth and total pit count by 50.8% and 84.4%, respectively, while increasing hardness, reduced modulus and full-delamination load to 7.1 GPa, 313.5 GPa and 34.7 N, respectively. PS occlusion therefore offers a route to durable FeCO₃-based corrosion protection for CS.

Introduction

CS remains widely used in oil and gas production, transport and processing

infrastructure because of its low cost, mechanical reliability and ease of fabrication.¹ In aqueous environments containing dissolved CO₂, CS is susceptible to internal corrosion as CO₂ hydration promotes electrochemical steel dissolution.²⁻⁴ This degradation can cause wall thinning, localized attack, leakage and loss of structural integrity, creating safety risks, and substantial economic costs.⁴⁻⁶ As CO₂ handling expands from conventional hydrocarbon systems to transport and storage infrastructure, mitigating CO₂ corrosion of CS remains an important challenge.⁷⁻¹⁰

Corrosion control in CO₂-containing service environments typically combines materials selection, coatings or liners, pH and water management, inhibitor treatment and monitoring.¹¹⁻¹³ Film-forming organic inhibitors are widely used because they adsorb onto CS and create interfacial barriers that limit the transport of corrosive-species and suppress electrochemical reactions.^{5,14-16} However, their effectiveness depends on maintaining sufficient surface coverage, which is sensitive to inhibitor concentration, adsorption/desorption behavior, fluid chemistry, temperature and flow conditions.¹⁵⁻¹⁸ In practice, this often requires continuous injection or periodic batch treatment, adding chemical demand, operational complexity, and environmental concerns.^{19,20} These limitations motivate strategies that reduce repeated inhibitor replenishment by engineering more durable protective layers formed in-situ.^{21,22}

FeCO₃ corrosion-product layers can form naturally on CS in CO₂-saturated brine when pH, temperature and Fe²⁺/CO₃²⁻ supersaturation favor FeCO₃ precipitation.^{3,23,24} Once established, FeCO₃ can cover active sites, restrict mass transport and reduce CR, in favorable cases to below 0.1 mm year⁻¹.^{3,25} These layers are nevertheless not intrinsically stable. Changes in pH, temperature or solution chemistry can disturb FeCO₃ saturation and promote dissolution or dissolution-reprecipitation, while shear, erosion, strain and mechanical loading can remove or fracture the layer.^{21,24,26,27} Heterogeneous or damaged FeCO₃ may lose protection and promote localized corrosion.^{3,25} Enhancing the compactness, continuity, interfacial adhesion and mechanical durability of FeCO₃ while retaining its in-situ formation advantage therefore remains a central challenge in CO₂ corrosion control.

Recent studies have begun to engineer FeCO₃ corrosion-product layers. Taleb et al.²¹ introduced FeCO₃ micro-modification using a silicon-rich nanofiller to accelerate FeCO₃ growth and improve layer density, protectiveness and mechanical durability. Shaikhah et al.²² demonstrated that poly (allylamine hydrochloride) (PAH) can interact with both FeCO₃ and bare CS to form FeCO₃–PAH hybrid layers, thereby reducing general and localized corrosion while improving adhesion, elasticity, and delamination resistance.

Biomimetic-inspired crystal engineering provides a conceptual basis for modifying FeCO_3 corrosion-product layers, because polymers and functional nanoparticles can be occluded within growing inorganic crystals to form organic–inorganic nanocomposites.²⁸ In carbonate model systems, occlusion efficiency and guest distribution are controlled by nanoparticle surface chemistry, charge and stabilizer-chain architecture, which govern interactions with growing calcite surfaces.^{29–31} These design rules have enabled spatially patterned and functional host–guest crystals and have recently been translated to electrochemically formed FeCO_3 corrosion-product layers.^{28,32} Shaikhah et al.³³ introduced PS-COOH and PS-NH₂ during in-situ FeCO_3 formation on CS in CO₂-saturated brine. Their 48 h study showed that both PS can be incorporated into FeCO_3 to form polymer–mineral composite corrosion-product layers, with functional-group identity controlling occlusion mode, film microstructure and barrier performance. Both composite layers achieved higher general-corrosion inhibition efficiencies and reduced localized-pitting damage compared with unmodified FeCO_3 . Although this 48 h study established the short-term feasibility of PS- FeCO_3 composite layers formation, it did not resolve the long-term stability and evolution of the composite layer. Whether PS remains embedded in FeCO_3 during prolonged exposure, how its functional-group-dependent distribution evolves, and how it affects continued corrosion-product-layer growth remain unresolved. It is also unclear whether the short-term suppression of uniform corrosion and localized pitting persists after long-term immersion, and what mechanical properties the resulting composite layers retain.

To address these questions, 10 ppm PS-COOH or PS-NH₂ was introduced once into a CO₂-saturated brine corrosion system after 2 h of immersion. In-situ electrochemical measurements were used to track interfacial electrochemical and corrosion rate (CR) evolution and cumulative average thickness loss (P_u) over 0–900 h. After exposure, scanning electron microscopy (SEM) was used to examine the surface and cross-sectional morphologies of the FeCO_3 -based layers and the distribution of PS within composite layers. X-ray diffraction (XRD) and Raman spectroscopy were used to analyse corrosion-product composition. Surface profilometry was used to quantify localized pitting damage. Nanoindentation measured the hardness and reduced modulus of the corrosion-product layers, while progressive-load scratch testing evaluated their resistance to scratch-induced failure.

Results

In-situ electrochemical measurements

Figure 1 presents the time-dependent open-circuit potential (OCP) and reciprocal polarization resistance (R_p^{-1}) responses of the blank, PS-COOH-, and PS-NH₂-enriched systems during 900 h of immersion in CO₂-saturated brine.

The measured OCP values of all systems were initially around -735 mV vs. Ag/AgCl (sat. KCl) and shifted progressively toward more positive potential with increasing immersion time. Meanwhile, all systems exhibited high initial R_p^{-1} values, followed by a rapid decrease during the early stage of exposure. Within the first approximately 250 h, the R_p^{-1} responses of the three systems were broadly similar, after which system-dependent differences became more evident.

The blank system showed a slow OCP evolution, remaining close to -700 mV for most of the exposure before becoming more positive at later times; correspondingly, its R_p^{-1} decrease became more gradual after approximately 250 h. The PS-NH₂-enriched system reached a relatively stable OCP range of approximately -680 to -690 mV at an earlier stage and maintained this response during prolonged immersion, while its R_p^{-1} values also became relatively stable after approximately 250 h and remained close to those of the blank system. In contrast, the PS-COOH-enriched system displayed a delayed, but more pronounced positive OCP shift after approximately 150 h, followed by sustained fluctuations mainly between -550 and -600 mV during the intermediate and later stages. Its R_p^{-1} continued to decrease after approximately 250 h and stabilized after approximately 400 h, remaining the lowest among the three systems for much of the later exposure.

The coupled evolution of OCP and R_p^{-1} indicates a progressive change in the interfacial electrochemical state during immersion.^{34,35} In CO₂-containing environments, a positive shift in OCP has commonly been associated with the development of a corrosion-product-covered or pseudo-passive interface, while the concurrent decrease in R_p^{-1} reflects a reduction in electrochemical corrosion activity.^{26,35,36} This behavior is consistent with the progressive formation and consolidation of FeCO₃-rich corrosion product layers, which can reduce the active steel area and increasingly restrict charge transfer and/or mass transport.³⁴⁻³⁶ The subsequent stabilization of both OCP and R_p^{-1} suggests that the interface reached a relatively stable electrochemical state, consistent with a transition from active steel dissolution toward a more stable corrosion-product-

covered interface.³⁵

Shaikhah et al.³³ showed that, after 48 h, the blank FeCO₃, 10 ppm PS-COOH, and 10 ppm PS-NH₂ systems reached broadly comparable R_p values of approximately 5.0–7.0, 5.0–6.0, and 4.0–5.0 $\times 10^3 \Omega \text{ cm}^2$, respectively, although the PS modified the preceding R_p development profiles. Because the 48 h study used a solution-volume-to-steel-area ratio (V/S) of approximately 222 mL cm⁻², whereas the present work used a higher V/S ratio of 500 mL cm⁻², the 0–48 h R_p values from the two datasets should not be directly compared quantitatively.^{34,37} In contrast, the present 900 h dataset reveals a clearer long-term divergence: the PS-COOH-enriched system maintained a lower R_p^{-1} response during the middle and later stages, while the PS-NH₂-enriched system remained comparable to, or slightly lower than, the blank system over much of the exposure.^{34,38}

The P_u over 0–900 h, estimated from R_p using a fixed Stern–Geary coefficient based on the assumed β_a and β_c values, was 7.2, 5.0, and 4.4 μm for the blank, PS-COOH-, and PS-NH₂-enriched systems, respectively (**Figure 3**), corresponding to reductions of 30.9% and 39.9% for the two PS-enriched systems relative to the blank. Although the PS-COOH-enriched system showed the lowest R_p^{-1} , during much of the middle and later exposure, the lowest P_u was obtained for the PS-NH₂-enriched system. This difference reflects the time-integrated nature of the R_p -derived calculation, in which early-stage R_p differences can strongly influence P_u .

Overall, a single PS addition after 2 h of immersion maintained the previously reported short-term corrosion-control performance, which was comparable to that of the unmodified FeCO₃ layer, while providing modestly enhanced and sustained inhibition of uniform corrosion relative to the unmodified FeCO₃ layer as the PS-FeCO₃ composite layers continued to evolve during long-term immersion.

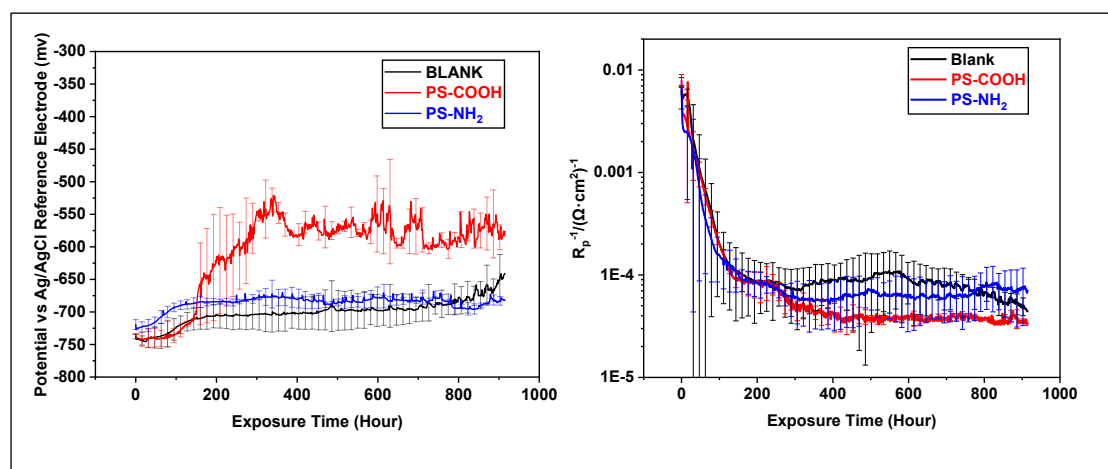


Figure 1. Mean OCP and R_p^{-1} evolution of the blank, PS-COOH-, and PS-NH₂-enriched systems during 900 h immersion in CO₂-saturated brine. Error bars represent standard deviations and are shown at every 15th data point for clarity.

Microscopic Characterization

Figure 2 shows the surface and cross-sectional SEM morphologies of the corrosion-product layers formed after 900 h of immersion. In the blank system, the CS surface was covered by an unmodified FeCO₃ layer composed of coarse, faceted rhombohedral crystals, with representative crystal dimensions of approximately 12.5-14.8 μm . Many crystals displayed surface depressions or local defects, and cross-sectional SEM revealed an uneven FeCO₃ layer with local thicknesses of approximately 5.1-6.9 μm . In the PS-COOH-enriched system, the surface morphology changed to a more compact PS-FeCO₃ composite layer consisting of smaller crystal dimensions of approximately 3.8-5.0 μm , while the cross-section showed a thicker layer of approximately 11.4-13.1 μm . PS-associated features were visible across the surface and cross-section, indicating broad retention of PS-COOH throughout the FeCO₃-based layer. In the PS-NH₂-enriched system, the surface also showed refined FeCO₃ crystals relative to the blank system, with representative dimensions of approximately 5.1-7.5 μm , and the cross-sectional layer thickness was approximately 9.1-11.8 μm . Compared with PS-COOH, fewer PS-associated features were observed on the outer surface, whereas PS-NH₂-associated regions were mainly located near the inner corrosion-product layer adjacent to the steel substrate.

Shaikhah et al.³³ reported that, after 48 h, the unmodified system formed a continuous FeCO₃ layer composed of well-defined rhombohedral crystals with smooth facets and sharp edges, with a thickness of approximately 7.2-9.3 μm . In the presence of 10 ppm PS-COOH, the rhombohedral FeCO₃ morphology was retained, but the crystals became smaller, more closely packed, and rougher, while PS-COOH was embedded in the FeCO₃ layer and mainly concentrated near the outer region and crystal surfaces; this approximately 7.8-9.4 μm -thick layer appeared denser, with tighter grain packing. By contrast, 10 ppm PS-NH₂ produced smaller, denser, and rougher FeCO₃ crystals, forming a thinner layer of approximately 4-7.5 μm that was more uniform, fine-grained, and showed very low visible porosity through the layer depth.

Compared with the 48 h morphologies, prolonged immersion to 900 h produced clear time-dependent evolution of the FeCO₃-based layers. In the blank system, the initially well-defined and smooth rhombohedral FeCO₃ crystals became coarser and more defective, while the cross-section became locally thinner and less uniform. In the PS-

COOH-enriched system, the refined crystal morphology was retained, but the layer thickened markedly, and PS-associated features became more broadly distributed across both the surface and cross-section. In the PS-NH₂-enriched system, the compact fine-grained morphology also persisted, but the layer became thicker than that reported after 48 h, with PS-NH₂-associated regions mainly concentrated near the inner corrosion-product layer adjacent to the CS substrate.

The morphological differences observed after 900 h are consistent with functional-group-dependent interactions between PS and the growing FeCO₃ layer.^{28,33,39} In the blank system, FeCO₃ precipitation is governed by local surface chemistry and coupled nucleation-growth processes. Prolonged immersion in the present work led to crystal coarsening, surface defects, and local cross-sectional non-uniformity.^{27,40} In the PS-enriched systems, PS could interact with FeCO₃ growth fronts and become incorporated as organic inclusions, thereby perturbing crystal growth and promoting smaller, more compact FeCO₃-based morphologies.^{32,33,41} For PS-COOH, carboxylate-bearing surfaces can interact with carbonate growth sites and modify crystal growth, supporting broader PS-COOH retention during continued FeCO₃ precipitation.^{28,29} By contrast, the inner enrichment of PS-NH₂ may reflect preferential early immobilization of amine-functionalized particles at the exposed CS/developing-FeCO₃ layer interface, consistent with reports that amine-containing polymers can interact with both bare CS and FeCO₃.^{22,42} Subsequent outward FeCO₃ growth would then be consistent with burial of this initial PS-NH₂-rich region and less extensive capture within the outer growth region.²⁹

The SEM morphology results provide structural context for interpreting electrochemical responses. FeCO₃ corrosion-product layers with high surface coverage, compact and continuous growth, and interfacial integrity can more effectively reduce the electrochemically active steel area, constrain charge-transfer and mass-transport pathways, thereby improving corrosion inhibition.^{34,35,37} Within this framework, the PS-FeCO₃ composite layers displayed more favorable barrier-forming characteristics than unmodified FeCO₃ layer, including refined FeCO₃ crystals, fewer visible defects, more compact and continuous layer growth, and increased layer thickness. These morphological features are consistent with the more protective electrochemical behavior of the PS-enriched systems, expressed as a more positive OCP, reduced R_p^{-1} responses during key exposure intervals, and lower P_u .^{34,35,37}

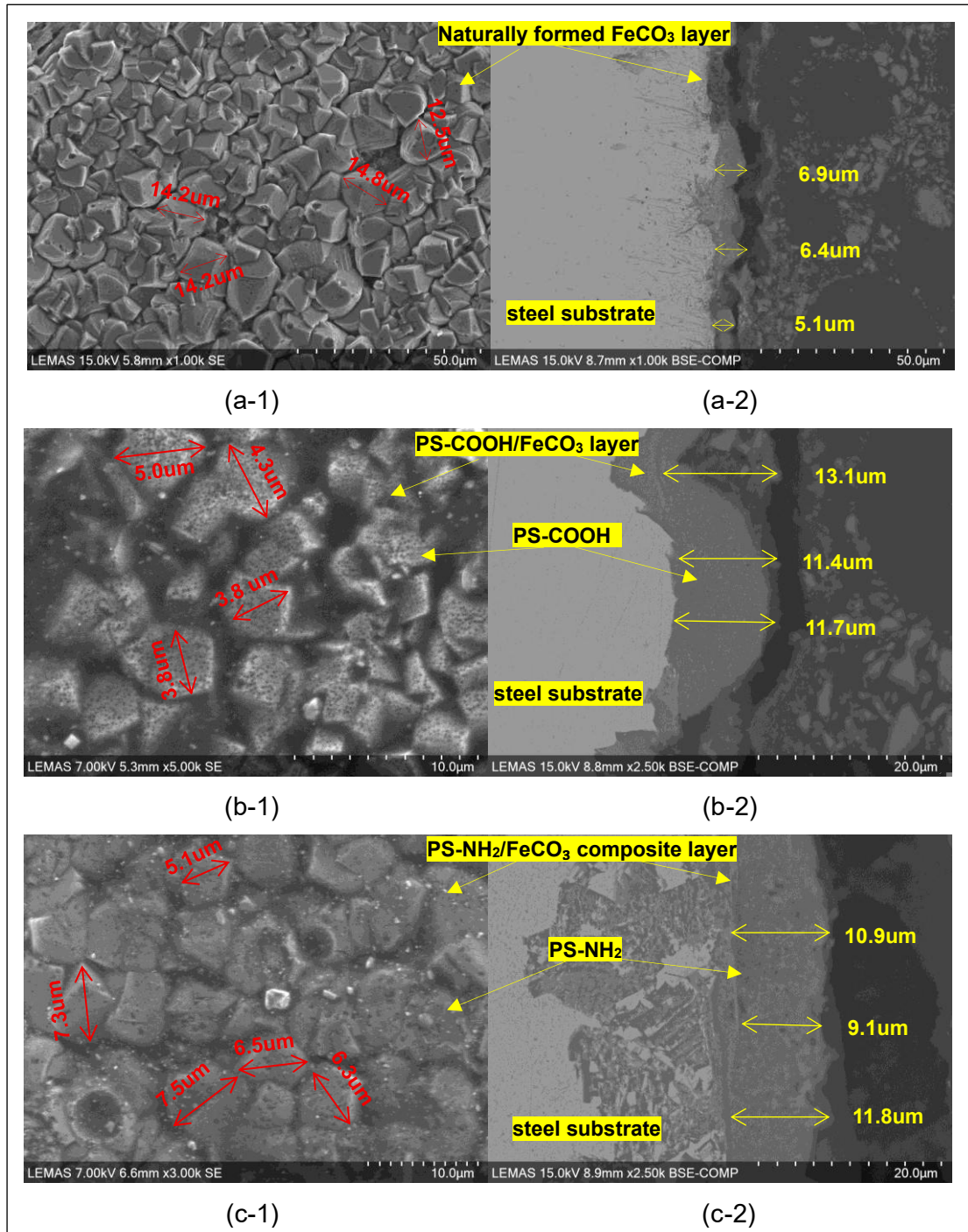


Figure 2. Surface and cross-sectional SEM morphologies of corrosion product layers formed on steel surfaces after 900 h of immersion: (a) naturally formed FeCO_3 layer, (b) PS-COOH- FeCO_3 composite layer, and (c) PS-NH₂- FeCO_3 composite layer. Subpanels (a-1–c-1) show the surface morphologies, with red arrows indicating representative positions for crystal-diameter measurements; subpanels (a-2–c-2) show the corresponding cross-sectional morphologies, with yellow arrows indicating representative positions for corrosion-product-layer thickness measurements.

Pitting corrosion behavior

Surface profilometry of the underlying CS substrates after corrosion-product removal was used to quantify pitting damage severity after 900 h of exposure.^{43,44} **Figure 3** compares the P_u with average pit depth, average pit diameter, deepest-pit depth, d_{max} , and total pit count, to distinguish uniform corrosion from localized pitting damage after 900 h of exposure.²² **Figure 4** compares the d_{max} , deepest-pit diameter, D_{max} , and the diameter-to-depth aspect ratio of the deepest-pit to characterize the geometry and penetration tendency of the most severe localized corrosion feature. The aspect ratio was used to distinguish whether pit development was dominated by lateral broadening or vertical penetration into the steel substrate.^{45,46}

As shown in **Figures 3 and 4**, the PS-COOH- and PS-NH₂-enriched systems reduced the total pit count by 71.4% and 84.4%, respectively, relative to the blank system. The corresponding reductions in average pit depth, average pit diameter, and d_{max} were 3.2% and 18.8%, 7.0% and 62.8%, and 2.8% and 50.8%, respectively. The D_{max} decreased by 5.6% in the PS-COOH-enriched system but increased by 20.4% in the PS-NH₂-enriched system. In addition, the aspect ratios of the blank, PS-COOH-, and PS-NH₂-enriched systems were 0.78, 0.76, and 1.91, respectively.

Together with the lower P_u , these results indicate that the composite layers, particularly the PS-NH₂-FeCO₃ composite layer, reduced both uniform corrosion and localized pitting damage. The aspect ratios of the PS-COOH-enriched and blank systems were both below 1 and closely comparable, indicating similar penetration-dominated pit development. In contrast, the aspect ratio above 1 in the PS-NH₂-enriched system indicates a shallower pit with greater lateral development.

In the 48 h study by Shaikhah et al.³³ both composite layers reduced the total pit count by 96.0% relative to the unmodified FeCO₃ layer, while the average pit depth decreased by 40.0% and 50.0%, respectively. The average pit diameter remained comparable to that of the unmodified FeCO₃ layer for the PS-COOH-FeCO₃ composite layer but increased by 27.9% for the PS-NH₂-FeCO₃ composite layer. The present dataset and the study by Shaikhah et al. were obtained under different pitting-analysis conditions; therefore, the pitting parameters obtained from the two studies should not be directly compared quantitatively. Rather, the comparison is used to examine the evolution of the pitting characteristics observed in the short-term study after prolonged exposure.

Overall, after 900 h, the composite layers, particularly the PS-NH₂-FeCO₃ layer, retained stronger suppression of localized pitting damage than the unmodified FeCO₃

layer. The pit-development characteristics observed after 48 h were broadly preserved after extending the exposure to 900 h. Both datasets indicate that the PS-NH₂-FeCO₃ layer favors shallower pits with greater lateral development, whereas the unmodified FeCO₃ and PS-COOH-FeCO₃ layers remain more closely associated with penetration-dominated pit development.

In the blank system, the unmodified FeCO₃ layer was relatively coarse, locally non-uniform, and defect-containing, which could promote confined electrolyte pockets and localized galvanic or crevice-like conditions beneath or between FeCO₃ crystals. Such localized environments favor concentrated anodic dissolution over a small area, thereby promoting penetration-dominated pit growth.^{25,47,48}

For the PS-NH₂-enriched system, the lowest P_u and strongest localized-pitting suppression can be attributed to the preferential stabilization of the CS/layer interface. This system reached a stable OCP earlier, maintained a more positive OCP than the blank system over much of the exposure period, and showed a consistent trend in R_p^{-1} evolution, suggesting earlier formation and greater long-term stability of a protective corrosion-product-covered surface. SEM characterization showed that PS-NH₂-associated features were mainly enriched near the CS/layer interface; compared with the unmodified FeCO₃ layer, the PS-NH₂-FeCO₃ layer exhibited refined crystals, increased thickness, improved continuity, and fewer apparent defects. This interfacial incorporation may have stabilized active pit-base regions and limited further downward dissolution. Once vertical penetration was restricted, the residual attack could be expressed mainly through pit-wall or peripheral dissolution, or through the coalescence of neighboring shallow defects, producing a shallower but relatively wider deepest-pit geometry.^{22,25,44,49} Although the present data cannot confirm the role of PS spatial distribution in controlling uniform corrosion, localized corrosion, this incorporation mode may have promoted earlier nucleation, growth, and stabilization of the composite layer and may also be relevant to the enhanced mechanical integrity discussed in the following section.

By contrast, the PS-COOH-enriched system showed a delayed but more positive shift in OCP, and a later decrease in R_p^{-1} during the middle and later stages. This response suggests that the protective corrosion-product-covered surface developed later than in the PS-NH₂-enriched system but exhibited a stronger resistive response once the PS-COOH-FeCO₃ layer was established. SEM observations showed that the PS-COOH-FeCO₃ layer was thicker, finer-grained, and more continuous than the unmodified FeCO₃ layer. PS-COOH-associated features also appeared to be more broadly distributed throughout the composite layer, while Raman analysis indicated a higher

relative abundance of PS within the composite layer. This incorporation pattern may have contributed to a stronger through-layer barrier effect and greater restriction of mass transport during prolonged exposure. However, compared with the PS–NH₂-enriched system, the PS–COOH-enriched system exhibited a higher P_u , weaker localized-pitting suppression, and a lower aspect ratio. This may reflect the later development of the protective layer, allowing greater early-stage metal loss and pit initiation or propagation before the barrier became fully effective, while the aspect ratio remained close to that of the blank system.

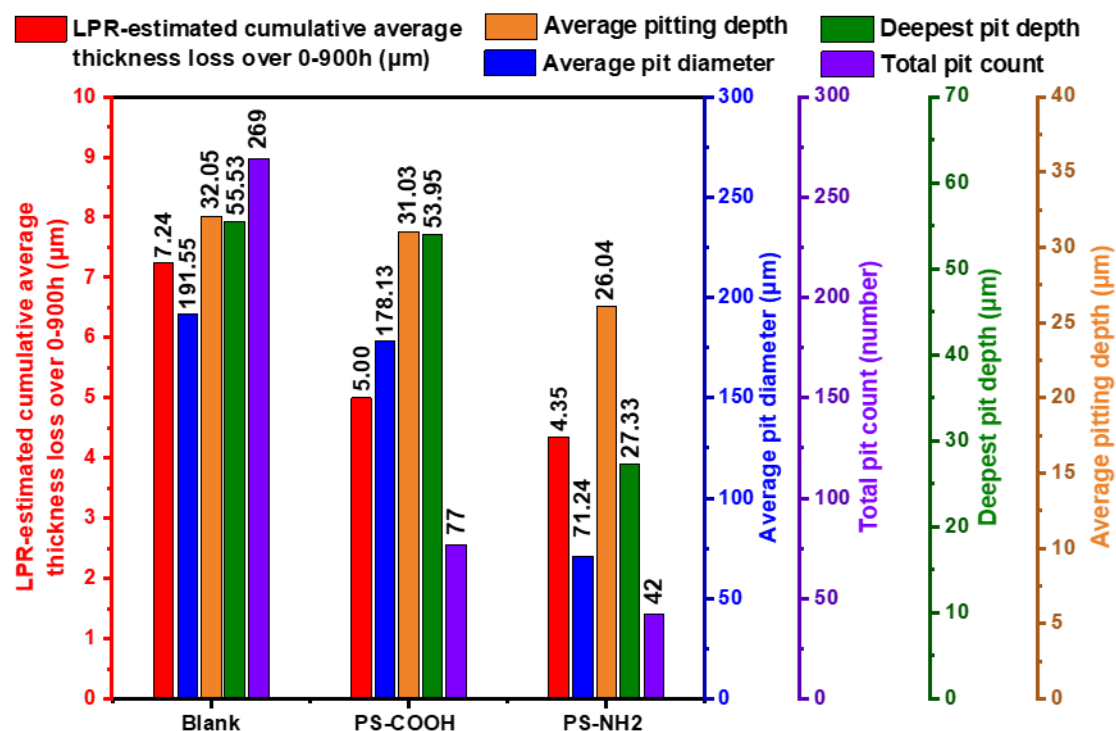


Figure 3. Comparison of P_u and pitting parameters after 900 h exposure.

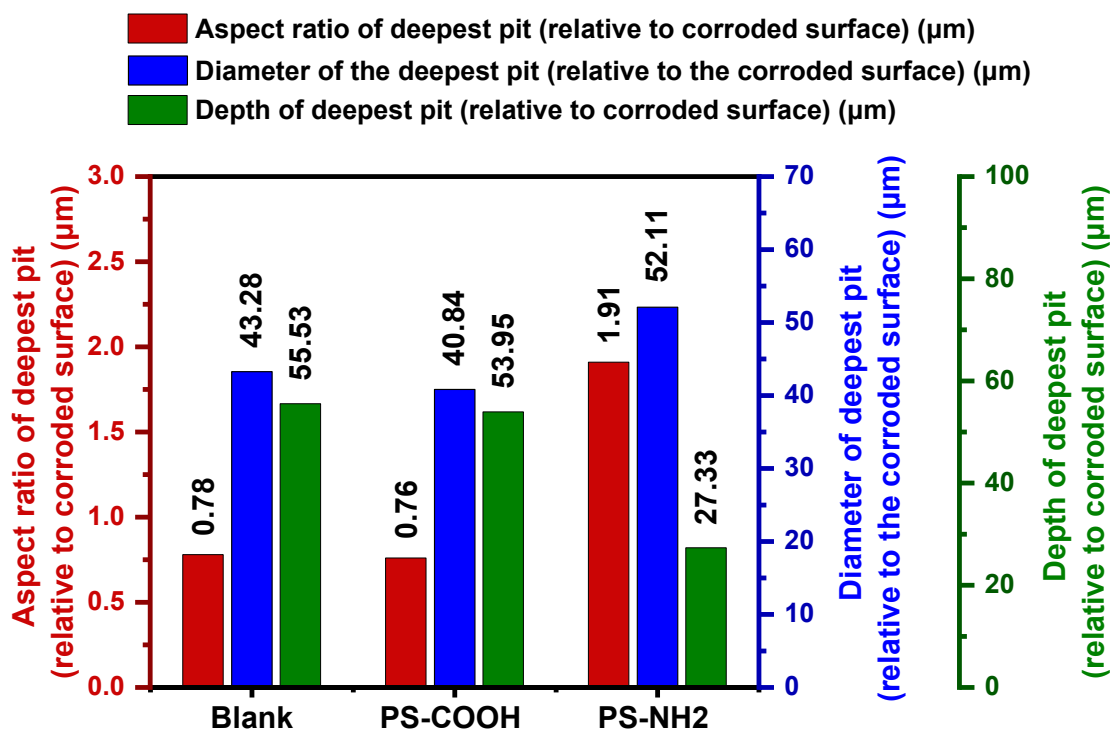


Figure 4. Comparison of D_{max} , d_{max} , and aspect ratio after 900 h exposure.

Chemical characterization

Figure 5 presents the XRD patterns of the corrosion-product layers formed after 900 h of immersion. In all systems, the principal diffraction peaks were indexed to rhombohedral FeCO_3 (ICDD 01-080-2673), together with reflections from the underlying $\alpha\text{-Fe}$ substrate (ICDD 04-002-1061). Similarly, in the 48 h study by Shaikhah et al.³³ rhombohedral FeCO_3 (R-3c) was identified as the dominant crystalline phase in all films, with $\alpha\text{-Fe}$ substrate reflections also observed.

900 h SEM observations showed that PS were incorporated into the FeCO_3 matrix with functional-group-dependent spatial distributions, while the rhombohedral FeCO_3 morphology was retained. This interpretation is consistent with carbonate occlusion studies showing that colloidal or polymeric particles can be engulfed by growing carbonate crystals without significantly disturbing the host lattice or the diffraction-resolved crystal structure.^{39,50,51} Therefore, the incorporated PS acted as organic inclusions within an FeCO_3 -rich framework, rather than forming a new crystalline corrosion product.

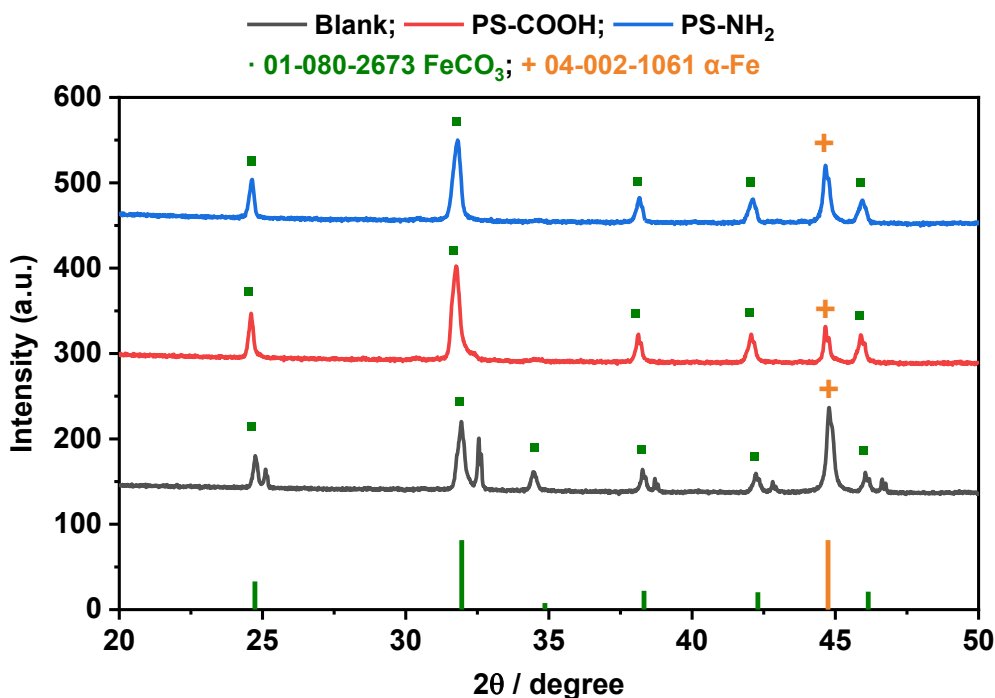


Figure 5. XRD patterns of corrosion product layers formed in the blank, PS-COOH-, and PS-NH₂-enriched systems after 900 h of corrosion immersion.

Figure 6 presents the Raman spectra of the corrosion-product layers. The spectrum of the blank system contained Raman bands characteristic of FeCO₃, with bands at 180 and 281 cm⁻¹ assigned to the translational and librational lattice modes of FeCO₃, respectively, and bands at 730 and 1084 cm⁻¹ assigned to the in-plane bending and symmetric stretching vibrations of CO₃²⁻, respectively.⁵² The PS-COOH- and PS-NH₂-enriched systems retained these FeCO₃-related Raman bands and additionally exhibited polystyrene bands mainly located at 1001, 1031, and 1602 cm⁻¹, which correspond to the aromatic ring-breathing mode, in-plane C–H deformation, and aromatic ring skeletal stretching vibration, respectively.^{53,54}

To compare the relative retention of PS within the composite layers, the Raman spectra were analyzed using a semi-quantitative peak-height comparison. Mayorga et al.⁵⁵ identified the ~1001 cm⁻¹ Raman band as a semi-quantitative marker of Raman-detectable polystyrene abundance in aqueous suspensions. In the present work, the height of this PS band was normalized to the height of the carbonate stretching band at ~1084 cm⁻¹ to obtain a PS-to-FeCO₃ Raman peak-height ratio. This ratio was 0.46 for the PS-COOH-FeCO₃ layer and 0.26 for the PS-NH₂-FeCO₃ layer.

Overall, after 900 h, only FeCO₃ Raman signature was detected in the blank system, whereas both FeCO₃ and PS signatures were detected in the PS-enriched systems. The higher PS-to-FeCO₃ peak-height ratio for PS-COOH suggests a greater relative

abundance of Raman-detectable PS within the composite layer compared with PS-NH₂. This interpretation is consistent with the SEM observations, where PS-COOH-associated features were more broadly and abundantly distributed across both the FeCO₃ crystal surfaces and cross-section, whereas PS-NH₂-associated features were less numerous on the outer crystal surfaces and were mainly concentrated near the inner layer/CS interface.

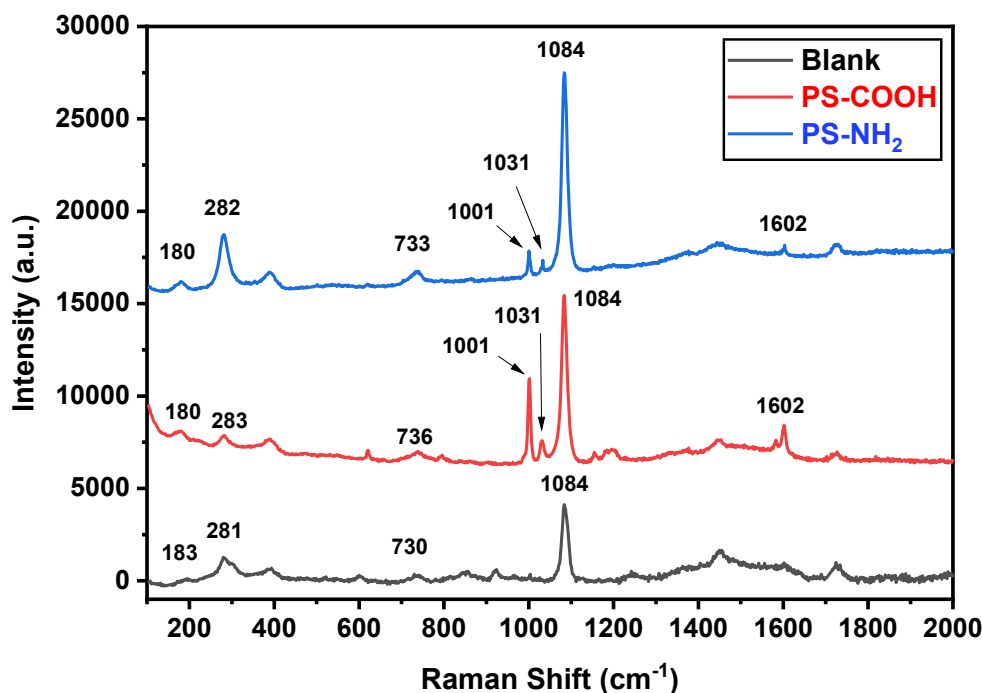


Figure 6. Raman spectra of corrosion product layers formed in the blank, PS-COOH-, and PS-NH₂-enriched systems after 900 h of corrosion immersion

Mechanical characterization

Figure 7 shows the nanoindentation-derived hardness and reduced modules of the corrosion-product layers formed after 900 h of exposure. The unmodified FeCO₃ layer exhibited a hardness of 3.2 ± 0.3 GPa and a reduced modulus of 216.6 ± 17.6 GPa. The corresponding values were 6.4 ± 3.0 GPa and 223.6 ± 36.6 GPa for the PS-COOH-FeCO₃ layer, and 7.1 ± 2.2 GPa and 313.5 ± 89.7 GPa for the PS-NH₂-FeCO₃ layer. Relative to the unmodified FeCO₃ layer, the hardness increased by 100.0% and 121.9% in the PS-COOH- and PS-NH₂-FeCO₃ layers, respectively, while the reduced modulus increased by 3.2% and 44.7%, respectively.

Figure 8 summarizes the critical loads and calculated shear stresses associated with cohesive failure, adhesive failure, and full delamination of the corrosion-product layers; the corresponding scratch-track morphologies and test parameters are provided in

Appendices II & III. Compared with the unmodified FeCO_3 layer, the composite layers showed higher critical loads and calculated shear stresses at all three failure stages. The increases in critical load/corresponding shear stress were 16.4%/7.5% and 33.6%/7.7% for cohesive failure, 38.5%/20.6% and 52.7%/19.2% for adhesive failure, and 8.7%/4.0% and 30.9%/9.7% for full delamination in the PS-COOH- and PS-NH₂- FeCO_3 layers, respectively.

Composite layers exhibited higher hardness, reduced modulus, and scratch-failure resistance than unmodified FeCO_3 layer, with the PS-NH₂- FeCO_3 layer showing the best mechanical responses. XRD and Raman characterization confirmed that FeCO_3 remained the principal crystalline corrosion product in all systems and that PS was retained within the composite layers in the PS-enriched systems. SEM observations showed that PS incorporation refined the FeCO_3 crystals, suppressed visible crystal-surface defects, increased layer thickness, and improved layer compactness and continuity, with functional-group-dependent PS distributions. Together, these results suggest that the enhanced mechanical response of the composite layers arises mainly from changes in layer architecture and PS incorporation mode.

This interpretation is consistent with previous FeCO_3 studies linking layer protectiveness to coverage, continuity, density, porosity, thickness, and resistance to localized chemical or mechanical breakdown.^{3,27} Engineered- FeCO_3 studies have shown that microstructural modification or polymer-assisted hybridization can improve FeCO_3 layer density, adhesion, elasticity, and delamination resistance.^{21,22} Accordingly, the finer FeCO_3 crystals, fewer visible defects, greater thickness, and improved compactness observed here likely reduced defect-assisted stress concentration and compliant pore/void space, thereby improving the effective load-bearing continuity of the composite layers.^{27,56}

Differences between the composite layers can be attributed to their distinct PS incorporation modes. In the PS-COOH- FeCO_3 layer, PS was distributed more uniformly and extensively throughout the composite layer. This may improve compactness and barrier continuity but may also introduce a larger fraction of mechanically compliant polymer into the load bearing FeCO_3 framework. Carbonate-polymer composite studies have shown that extensive occlusion of polystyrene or other polymeric inclusions can reduce hardness and modulus, depending on inclusion content, distribution, and interfacial coupling.^{41,50} Thus, extensive PS-COOH incorporation may partially offset the mechanical benefits of FeCO_3 refinement and densification. By contrast, PS-NH₂ was mainly enriched near the CS/layer interface, with lower overall through-layer incorporation. Shaikhah et al.²² showed that PAH

adsorbs onto both bare CS and FeCO_3 , forming an FeCO_3 -PAH hybrid layer with higher Young's modulus, adhesion force, and shear-induced delamination resistance than unmodified FeCO_3 layer. Therefore, PS- NH_2 enrichment near the CS/layer interface may enhance interfacial integrity while limiting compliant-polymer incorporation within the load-bearing FeCO_3 framework,^{41,50} explaining the higher nanoindentation hardness, reduced modulus, and delamination resistance of the PS- NH_2 - FeCO_3 layer.

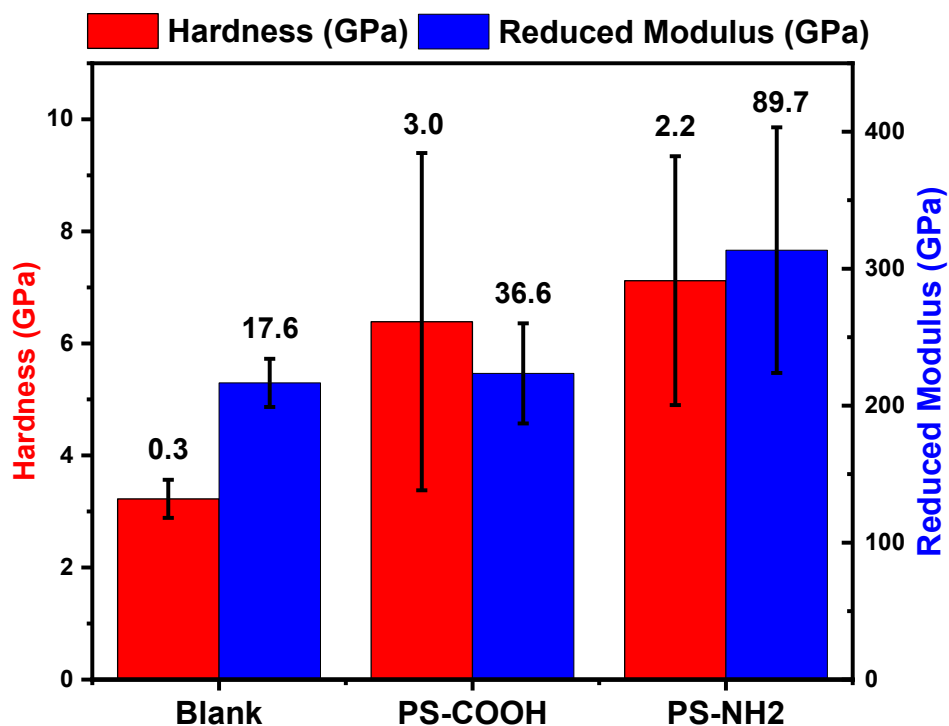


Figure 7. Hardness and reduced modulus of the corrosion product layers formed in the blank, PS-COOH-, and PS- NH_2 -enriched systems after 900 h of corrosion exposure. Data are presented as mean $\pm$ standard deviation.

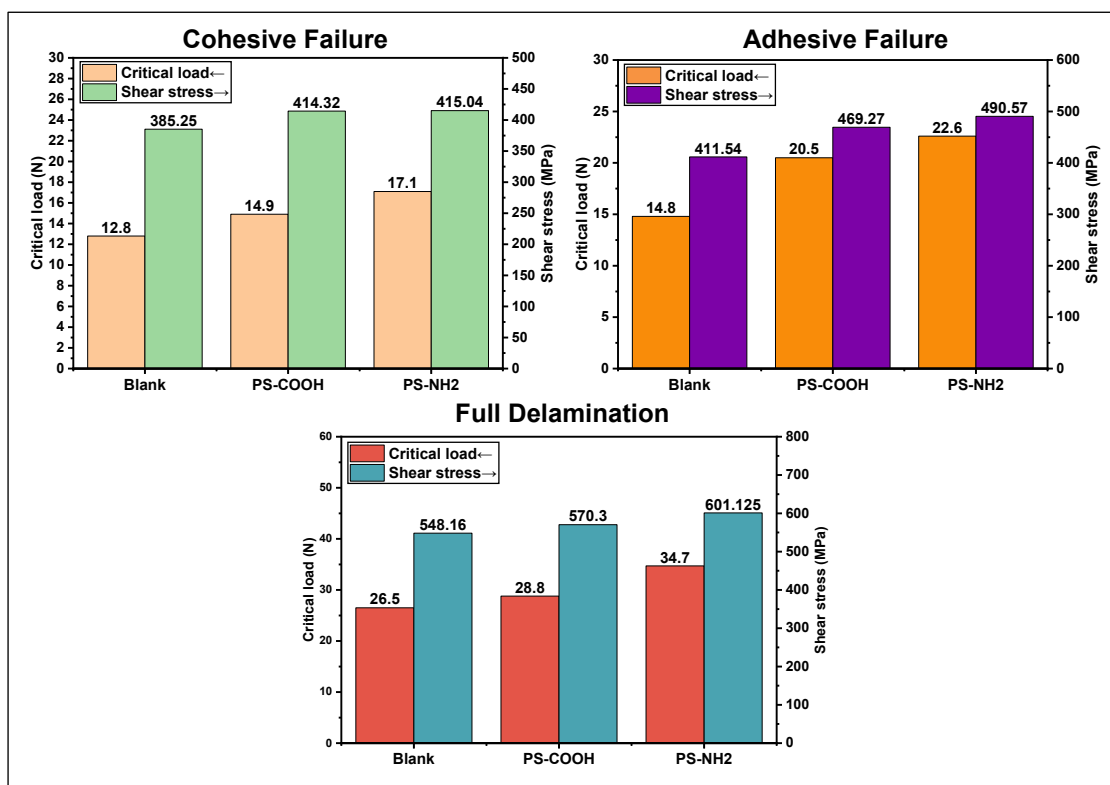


Figure 8. Critical loads and calculated shear stresses of corrosion product layers formed in the blank, PS-COOH-enriched, and PS-NH₂-enriched systems at different scratch-induced failure stages.

Methods

In-situ electrochemical measurements

900 h immersion tests were conducted in 1 L of CO₂-saturated 3.5 wt.% NaCl brine buffered to pH 6.6 with anhydrous NaHCO₃. The CO₂ partial pressure was maintained at 0.8 bar throughout the experiment. The temperature was maintained at 60 °C using a calibrated hot-plate stirrer, and the solution was continuously stirred at 100 rpm with a magnetic stir bar. Periodic measurements confirmed that the solution pH remained within 6.6 ± 0.15 throughout the exposure. Three systems were investigated: a blank system without PS addition, and two PS-enriched systems in which 10 ppm PS-COOH or PS-NH₂ was introduced once after an initial 2 h corrosion period. No further PS addition was made during the remaining exposure.

API 5L X65 CS specimens were machined into 10 mm × 10 mm × 5 mm cuboids and used as working electrodes. A copper wire was soldered to the rear surface of each

specimen, which was then embedded in non-conductive resin to expose a 1 cm² surface area. Before immersion, the exposed surfaces were sequentially wet ground with 60, 120, and 600 grit SiC papers, rinsed with deionized water and acetone, dried under nitrogen.

PS-COOH and PS-NH₂ with an average diameter of 200 nm were obtained from Stratech-Bangs Laboratories, USA, and used as received.

In-situ electrochemical measurements were performed using ACM Instruments Gill 8 Channel potentiostat controlled by ACM Sequencer software. The potentiostat was connected to a conventional three-electrode cell comprising the CS working electrode, an Ag/AgCl reference electrode saturated with KCl (+0.197 V vs. SHE at 25 °C), and a platinum counter electrode. During Linear polarization resistance (LPR) monitoring, the OCP was continuously recorded, and LPR measurements were taken every 1 h. For each scan, the working electrode was polarized from -15 mV to +15 mV relative to the measured OCP at a scan rate of 10 mV min⁻¹.

Apparent CR estimates were derived from the LPR-measured R_p values using the Stern–Geary relationship. The apparent corrosion current density, i_{corr} , was calculated as:^{44,57}

$$i_{corr} = \frac{B}{R_p} = \frac{1}{R_p} \times \frac{\beta_a \times \beta_c}{2.303(\beta_a + \beta_c)}$$

Where B is the Stern–Geary coefficient, and β_a and β_c are the anodic and cathodic Tafel slopes, respectively.⁵⁷ Because potentiodynamic polarization measurements were not performed during the long-term experiments, a fixed Stern–Geary coefficient was applied consistently to all systems; therefore, the resulting values are treated as R_p -derived apparent CR estimates. The anodic and cathodic Tafel slope magnitudes were both assumed to be 120 mV dec⁻¹; therefore, B was calculated as 26 mV and used to convert R_p into i_{corr} .^{58,59}

The CR, in mm year⁻¹, was then calculated using:²²

$$CR = \frac{K \times i_{corr} \times M_{Fe}}{n \times F \times \rho}$$

Where i_{corr} is expressed in mA cm⁻², ($K=3.16 \times 10^5$) is the unit conversion factor, ($M_{Fe}=55.8$ g mol⁻¹) is the molar mass of iron, ($n=2$) is the number of electrons released during iron dissolution to Fe²⁺, ($F=96485$ C mol⁻¹) is Faraday's constant, and ($\rho=7.87$ g cm⁻³) is the density of CS.²²

The P_u was calculated by trapezoidal integration of the CR curve over the 0–900 h

exposure period:⁵⁹

$$P_u(\mu m) = \frac{1000}{24 * 365} \sum_{i=1}^{n-1} \frac{CR_i + CR_{i+1}}{2} (t_{i+1} - t_i)$$

Where CR_i and CR_{i+1} are the CR measured at two adjacent time points; t_i and t_{i+1} are the corresponding exposure times.

Morphological Characterization of Corrosion Products

Surface and cross-sectional morphologies of the corrosion-product layers formed on the CS specimens were examined using a Hitachi SU3900 large-chamber variable-pressure SEM. All micrographs were collected at an accelerating voltage of 15 kV and a working distance of 8–10 mm.

Chemical Characterization of Corrosion Products

XRD analysis was performed using a PANalytical X'Pert multipurpose diffractometer equipped with dual Cu $K\alpha_{1+2}$ radiation sources and 10×10 mm programmable divergence slits. The instrument was operated at 40 kV and 40 mA. All measurements were carried out at room temperature in continuous scan mode over a 2θ range of 20° – 50° . Phase identification was performed using PANalytical HighScore Plus software associated with the X'Pert system.

Raman spectra were acquired using a confocal Raman spectrometer (Renishaw inVia). A 488 nm laser (Nano Mater Edge) was used at 50% laser power, corresponding to 150 mW. Spectra were collected using a $2400 \text{ lines mm}^{-1}$ grating, with an exposure time of 10 s and 3 accumulations for each measurement. The spectral range was 100 – 3200 cm^{-1} , and the spectral resolution was 1 cm^{-1} .

Characterization of Pitting Corrosion Damage

Before pitting analysis, corrosion product was removed using a Clarke's solution prepared according to ASTM G1-03 (20 g Sb_2O_3 and 50 g SnCl_2 in 1 L concentrated HCl, specific gravity 1.19), with ultrasonication for 10 min at room temperature.^{60,61} The specimens were then rinsed with deionized water and acetone and dried under nitrogen. Pitting damage was quantified following ASTM G46-94 using an NPFLEX 3D optical interferometer (Bruker). Nine $3 \text{ mm} \times 3 \text{ mm}$ scans were stitched to cover approximately 81% of the 1 cm^2 exposed surface. Pits were identified using an operational depth threshold of $\geq 20 \mu\text{m}$ relative to the corroded surface; for diameter

analysis, only pits with an equivalent diameter $\geq 30 \mu\text{m}$ were included. Pitting damage was reported as the average depth and diameter of the ten deepest pits, d_{max} , and total pit count.^{44,62}

The aspect ratio was calculated as:

$$\text{Aspect ratio} = \frac{D_{\text{max}}}{d_{\text{max}}}$$

Mechanical Properties Determination

Nanoindentation tests were performed using a Nano Test platform (Micro Materials Ltd., UK) equipped with a Berkovich diamond tip to evaluate the mechanical properties of the corrosion product layer. Each test consisted of 20 loading–unloading cycles, with a spacing of 0.1 mm between adjacent indents to improve statistical robustness. A constant loading and unloading rate of 0.2 mN s^{-1} was applied, and the maximum load was set to 1 mN. A dwell period of 20 s was applied at the peak load to ensure mechanical equilibrium. To reduce the influence of thermal drift, 80% of the unloading force was maintained for an additional 60 s before completing unloading.²² Hardness and reduced modulus were obtained from the unloading portion of the load–displacement curves using the Oliver–Pharr method.⁶³

Progressive-load scratch tests were performed using a TriboTechnic Millennium 200 scratch tester with a Rockwell C diamond indenter (120° sphero-conical geometry, 200 μm tip radius). The normal load was progressively increased from 0 to 50 N over a 5 mm scratch length at a scratching speed of 10 mm min^{-1} , following ASTM G171-03 and the procedure previously applied to corrosion-product layers.^{22,64} Critical loads were determined from the load-distance profile by measuring the distance from the scratch origin to the corresponding damage or removal region.⁶⁵ Scratch tracks were examined by optical microscopy (Leica DM6000) to identify the failure modes, including cohesive failure, adhesive failure, and full delamination.

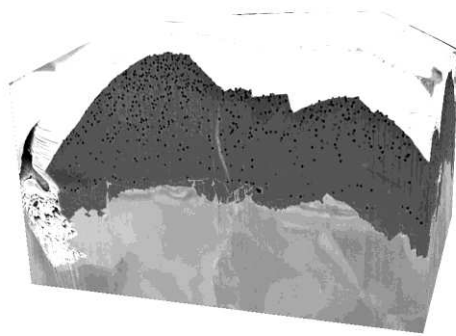
The corresponding shear stresses were calculated from the critical loads using the adhesive-film model of Olivier and Bull:^{66,67}

$$\tau = \frac{L_c}{\pi * a * \sqrt{R^2 - a^2}}$$

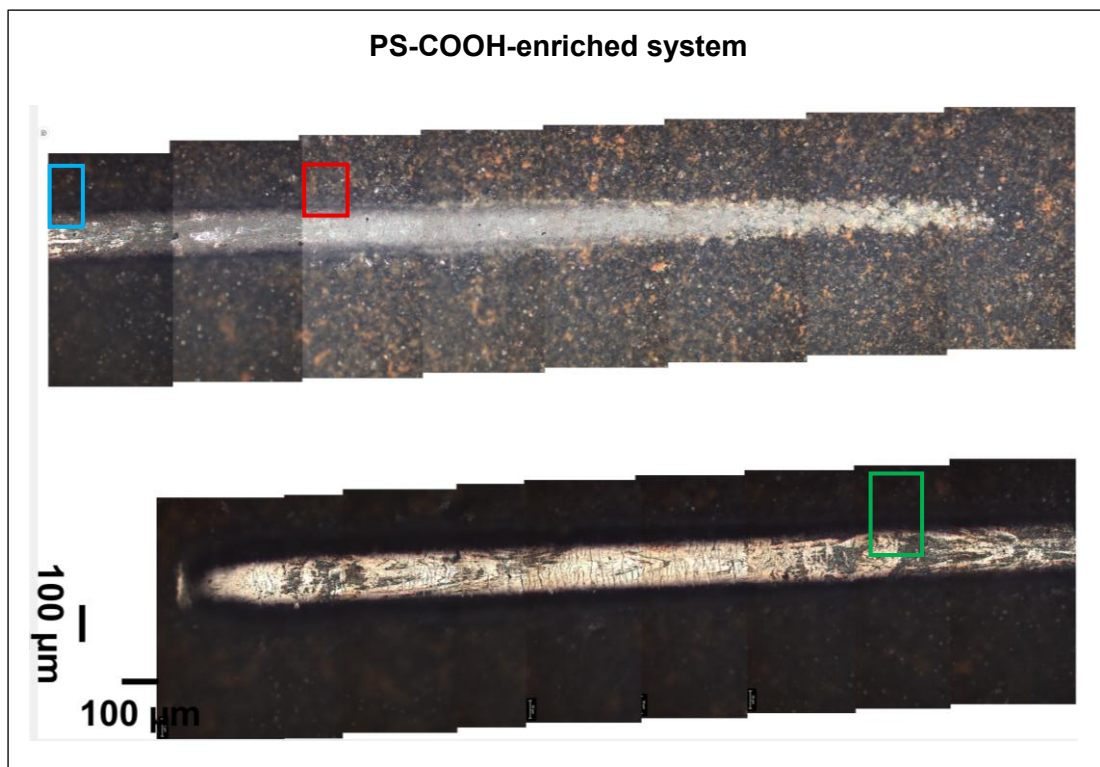
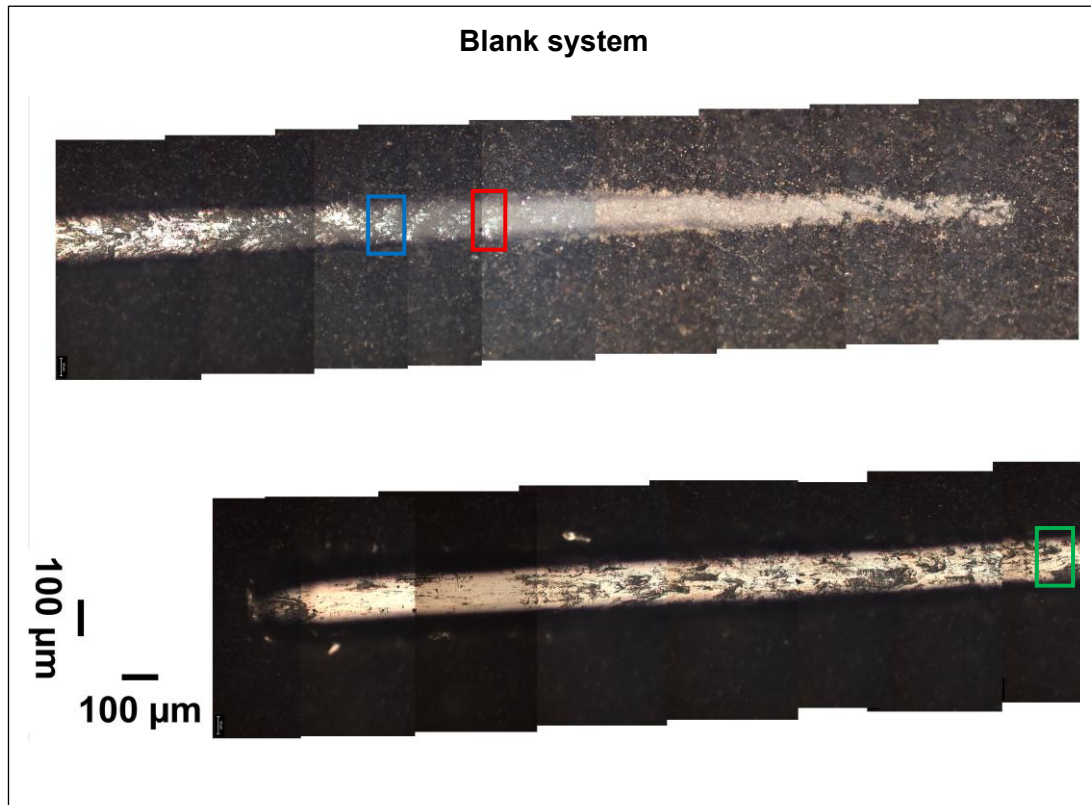
Where τ is the shear stress (Pa), L_c is the critical load (N), R is the indenter radius (m), and a is the radius of the projected contact area (m).

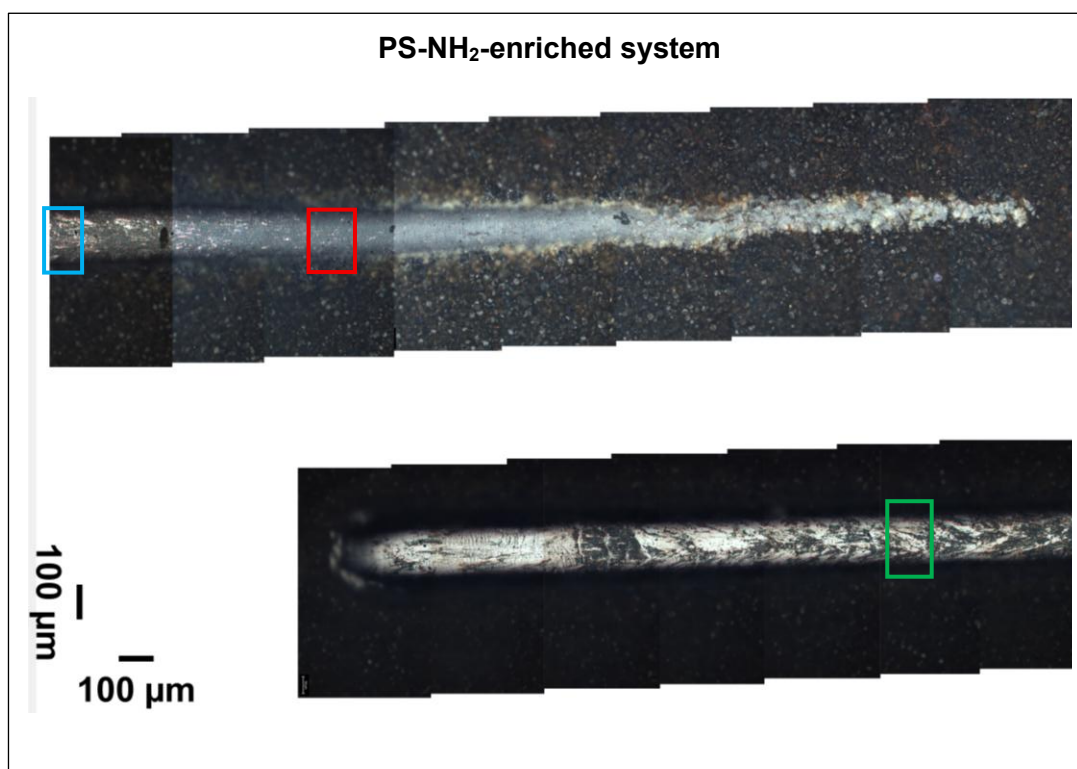
Appendix:

I. Slice-and-view focused ion beam-scanning electron microscopy reconstruction of X65 CS with FeCO_3 crystals and PS-COOH after 48 h of corrosion immersion.



II. Optical microscopy images of progressive-load scratch tracks on corrosion product layers





Where Red, blue, and green boxes indicate the locations corresponding to the critical loads for cohesive failure, adhesive failure, and full delamination, respectively.

III. Sliding Distance, Critical Load, Scratch Area Radius, and Shear Stress Corresponding to Different Scratch-induced Failure Modes of Pure FeCO₃ and PS-FeCO₃ Composite Corrosion Product Layers

Failure Mode	Parameter	Unit	PS-COOH-FeCO ₃	PS-NH ₂ -FeCO ₃	Pure FeCO ₃
Noticeable Damage / Cohesive Failure	Sliding Distance	(mm)	1.7	1.9	1.4
	Critical Load	(N)	14.9	17.1	12.8
	Scratch Area Radius	(m)	6×10^{-5}	7×10^{-5}	5.5×10^{-5}
	Shear stress	(MPa)	414.32	415.04	385.25
Buckling Failure	Sliding Distance	(mm)	2.3	2.5	1.7

/ Adhesive Failure	Critical load	(N)	20.5	22.6	14.8
	Scratch area radius	(m)	7.5×10^{-5}	8×10^{-5}	6×10^{-5}
	Shear stress	(MPa)	469.27	490.57	411.54
Total Delamination / Full Delamination	Sliding Distance	(mm)	3.1	3.7	2.9
	Critical load	(N)	28.8	34.7	26.5
	Scratch area radius	(m)	9×10^{-5}	11×10^{-5}	8.5×10^{-5}
	Shear stress	(MPa)	570.3	601.15	548.16

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Author Contributions Statement

M.Z. performed the experiments, analyzed the data, prepared the figures and wrote the original manuscript. F.P., D.S., C.W. and W.T. contributed to data interpretation and reviewed and edited the manuscript. W.T. supervised the project. All authors approved the final version of the manuscript.

Data availability

The data supporting the findings of this study are not publicly available in a repository but are available from the corresponding author, Mingzhe Zheng (ml21mz@leeds.ac.uk), upon reasonable request for academic and research purposes.

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