

Assessment of Hybrid Amino Acid Iron Carbonate Corrosion Layer Protective Properties in a CO₂-containing Aqueous Environment

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ABSTRACT

Iron carbonate (FeCO₃) is a carbon dioxide (CO₂) corrosion by-product known to provide corrosion resistance to carbon steel in specific environmental conditions. Nonetheless, it suffers from both chemical dissolution and mechanical damage when the pH is low and when subjected to particle impingement, respectively. This work aims at understanding whether incorporating two amino acids, mainly cysteine and glycine help improve either the reduction in corrosion rate or the mechanical properties of FeCO₃. In addition to their corrosion inhibition properties, it is anticipated that incorporating such organic moieties directly into the FeCO₃ layer as it grows should have a positive effect on properties such as the modulus, in turn making the layer less prone to internal stresses and disbandment. Our results show that both amino acids incorporate within the FeCO₃ matrix and affect the hardness and modulus of the hybrid layer. Moreover, cysteine is able to reduce localized corrosion attack in such environments.

Key words: iron carbonate, carbon steel, cysteine, glycine, hardness, modulus, CO₂ corrosion

INTRODUCTION

Oil and gas production in a CO₂ saturated environment is known to lead to corrosion due to dissolved carbonic acid. However, when the conditions are favorable, a protective FeCO₃ layer can also form which reduces the material degradation of the underlying steel by up to ten or a hundred times.¹ The formation of FeCO₃ is possible via the reaction shown in equation 1.



FeCO₃ can be removed as a result of many detrimental effects such as chemical dissolution due to pH fluctuations (especially when the acidity increases) but also from internal stresses that lead to its cohesive disbandment and erosion attack due to silica sand particles.² Once partially damaged, the beneficial material mitigation effect offered by FeCO₃ will on the contrary lead to a higher risk of localized corrosion attack.

Engineering a more resilient FeCO₃ has been successfully carried out in our laboratories and a hybrid organic-inorganic FeCO₃ has shown improved electrochemical and mechanical properties.³ Many researchers have studied the effect of amino acids on various engineering materials including mild steel, which is one of the main materials of choice in oil and gas sector.⁴

Ituen et al. have showed that N-acetyl cysteine behaves as a mixed-type inhibitor in an acidic environment when checking its effect on X80 mild steel.⁵ Similarly, Mobin et al. studied the direct effect of L-cysteine as an environmentally safe corrosion inhibitor for mild steel by relying on mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy.⁶ The Inhibition efficiency varied between 50 to 98% depending on the amino acid initial concentration. Farahati et al. also analyzed the behavior of L-Cysteine as a green corrosion inhibitor for mild steel in 1 M HCl solution and achieved an inhibition efficiency as high as 91% after 4 hours of immersion.⁷ Amin et al. studied both L-cysteine and S-methyl cysteine alongside alanine as an environmentally friendly corrosion inhibitor for iron in 1M HCl and cysteine appeared to be the best candidate with an inhibitor efficiency reaching 93% with 75% being reached in the case of alanine.⁸ Moreover, Oguzie et al. inspected the behavior of cysteine in a sulfuric acid solution with low carbon steel. Impedance measurements showed an inhibition efficiency as high as 92%.⁹ Other groups such as Abdul Rahiman et al. engineered a polymer composite cysteine known as polyvinyl alcohol cysteine and studied its adsorption and thermodynamic properties in an acidic environment with an inhibitor efficiency reaching 90%.¹⁰ More recently, Kokalj et al. compared the adsorption behavior of Cysteine and Penicillamine on the Fe(110) with the aim of linking the bonding energy to the corrosion mitigation potential.¹¹

On the other hand, Lima *et al.* studied the behavior of glycine, relying on glycine max meal extracts to analyze its corrosion inhibitor abilities in a sulfuric acid medium and the inhibitor efficiency depending on loadings varied between 50 and 98%.¹² Zeinali et al. analyzed the effect of glycine-based dithiocarbamates as corrosion inhibitors for cold rolled carbon steel in HCl solutions and their results showed that inhibitor efficiencies as high as 95% can be reached in specific conditions.¹³ Another group that studied the effect of a bespoke glycine derivative on mild steel in concentrated sulfuric acid medium was Amin et al. and the inhibitor efficiency reached 64%.¹⁴ More recently, Verma et al. analyzed the performance of a plant extract known as glycine max leaves as a green corrosion inhibitor for mild steel in 1M HCl and an inhibition efficiency as high as 68% was established.¹⁵

While most of the findings focused on the direct effect of adsorbing the amino acids on the steel surface, the current work aims at studying the behavior of the *in situ* developed hybrid FeCO₃-Cysteine and FeCO₃-Glycine in CO₂ saturated environments to assess the electrochemical, chemical, and mechanical properties of these corrosion layers.

EXPERIMENTAL PROCEDURE

Material Preparation

The material of choice serving as the working electrode in the electrochemical three electrode test setup was API-5L-X65 which has a ferritic-pearlitic microstructure and the chemical composition as shown in Table 1. The steel coupons were 15×15×5 mm samples that have been wet-ground in sequence of 120, 320 and 600 grit emery papers, degreased in acetone and rinsed with ethanol after being cast in resin and dried with compressed air. To enable the completion of electrochemical measurements, a copper wire was soldered to the reverse side of a carbon steel coupon and the active surface area is estimated at 2.25 cm².

Table 1: Chemical composition (wt.%) of X65 carbon steel

C	Mn	Ni	Nb	Mo	Si	V	P	S	Fe
0.15	1.422	0.09	0.054	0.17	0.22	0.06	0.025	0.002	97.81

Glycine and L-Cysteine were purchased from Sigma Aldrichⁱ.

Experimental Methods

Electrochemical linear polarization resistance (LPR) was implemented to study the corrosion mechanism. Morphological changes and layer composition were analyzed with microscopy with both Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) coupled with Electron Diffraction Spectroscopy (EDS) to obtain the chemical signature of the cross-sections. The nature of the corrosion layer was further confirmed by running X-ray Diffraction (XRD) and the mechanical properties for both hardness and modulus of the hybrid system extracted from nano-indentation analysis.

Electrochemical tests

Bubble tests (Figure 1) were run at 60°C in static conditions and at atmospheric pressure with and without addition of Cysteine and Glycine in order to assess the amino acid effect on the corrosion rate evolution. A three-electrode cell setup was used, where the reference electrode was a silver-silver chloride and the counter electrode was made of platinum. The brine was composed of 3.5 wt.% sodium chloride (NaCl) with a total volume of one liter, and the desired pH of 6.6 was adjusted at the start via addition of Sodium Hydrogen Carbonate (NaHCO₃). The brine was saturated with CO₂ which was bubbled continuously until the end of the test.

Electrochemical LPR and EIS experiments were carried out using an ACM Gill 12ⁱⁱ potentiostat with a cell settle times of 5 min allowing for the Open Circuit Potential (OCP) to stabilize between recurrent measurements.

Tafel constants at the test start of uninhibited and amino acids enriched environments were computed by sweeping ± 300 mV from OCP at a scan rate of 10 mV/ min. Linear polarization resistances used to extract general corrosion rates were set up as LPR sweeps between ± 15 mV from OCP at a sweep rate of 10 mV/min. EIS tests were set at an excitation voltage of 10 mV by scanning a frequency range comprised between 10 MHz and 4 mHz. All experiments were 48 hours long and ex situ analysis was carried out on coupons after that time duration.

ⁱ Trade name

ⁱⁱ Trade name

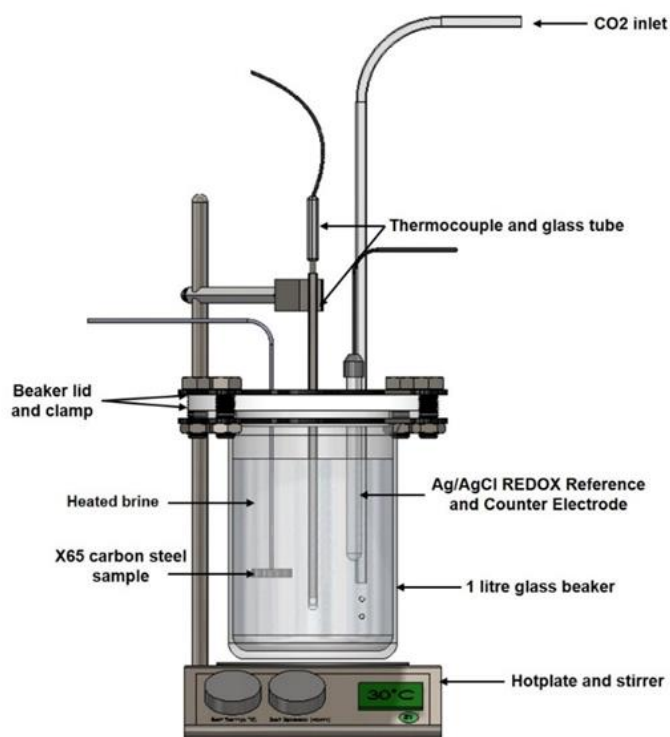


Figure 1: Glass beaker experimental apparatus for analysis of pure and hybrid FeCO_3 corrosion layer in aqueous CO_2 environments

Microscopic analysis

Scanning electron microscopy was carried out on the carbon steel samples using a Carl Zeiss EVOⁱⁱⁱ MA15 to assess coverage and topography of the pure and hybrid FeCO_3 corrosion layer growth. All micrographs were collected at an accelerating voltage of 20 kV and at a working distance between 8 and 10 mm. Cross sections of the coupons were prepared using an FEI Helios G4 CX^{iv} DualBeam Focused Ion Beam (FIB)-SEM to image the steel/layer interface. Coupons were removed from an experiment and carbon coated before mounting in the FIB instrument and orientating at 52°. SEM images of the layers were obtained in secondary electron mode at an operating voltage of 5 kV prior to depositing a Pt layer and milling a 15 μm wide, 10 μm deep cross-section using a gallium ion beam at an operating current of 21 nA. A series of cross-section cleaning procedures followed at an operating current of 2.5 nA. After preparation, gallium beam images were obtained of the cross sections at an operating current of 7.7 pA.

XRD analysis

X-ray diffraction (XRD) measurements were performed on a Panalytical X'pert^v multipurpose diffractometers with a voltage of 40 kV and an intensity of 40 mA using dual copper $\text{Cu K}\alpha_{1+2}$ radiations with 10×10 mm programmable divergence slits. The diffractograms were registered on iron carbonate films in the angular region of $2\theta = 20\text{--}80^\circ$ at room temperature and all scans were carried out in continuous mode. Phase identification was accomplished via the X'pert related software, Panalytical high score plus^{vi}.

ⁱⁱⁱ Trade name

^{iv} Trade name

^v Trade name

^{vi} Trade name

Mechanical properties determination via nano-indentation

Nano-indentation tests were performed using the Nano Test (Micro Materials Limited, UK)^{vii}, with a Berkovich^{viii} diamond indenter. For the purpose of statistics and reliability, 100 loading/unloading curves were made in each experiment to find the average results. All experiments were performed at a constant loading and unloading rate equal to 0.2 mN/s and to a maximum load of 1 mN (controlled maximum load). The hold time at maximum load was 20 s, and thermal drift correction was set at 60 s of holding period at 80% unloading. The unloading curves were used to derive the hardness and modulus values by analytical technique developed by Oliver and Pharr.¹⁶

Surface Profilometry analysis and localized corrosion measurement

The extent of localized corrosion on the X65 carbon steel surface was evaluated via a surface profilometry approach relying on the 3D surface profilometer Bruker NPFlexTM^{ix}. Before analysis, the post-test specimens were prepared by cleaning the surface using Clarke's solution in accordance with ASTM Standard G 1-03.¹⁷ For each experimental condition, two square regions were scanned with a total area of 100 mm² (10 x 10 mm²) on each specimen. The raw data was analyzed in Vision64^x software package by carefully applying selected thresholds with distinct pit depths, diameters and areas being quantified, in alignment with previous work.³

RESULTS

Hybrid Layer Formation and electrochemical mechanism

The corrosion rate variation with regard to time in the presence and absence of amino acids is plotted in Figure 2. When no amino acid is added, the corrosion rate gradually drops to below 0.1 millimeter/year (mm/year), which is consistent with what is achieved in previous studies.¹ Introducing cysteine at 2 h pre-corrosion tends to reduce the corrosion rate drastically to values below 0.07 mm/year, slightly higher than the uninhibited condition. Interestingly, the corrosion rate stays constant (0.06 mm/year) during the rest of 46 h of immersion time indicating the high performance of cysteine in blocking active corrosion sites available on steel surface. Offering a constant corrosion rate after injection would provide the potential beneficial impact of a non-renewed medium in ensuring a stable corrosion product on steel surface altering the saturation ratio. From this finding, it is suggested that cysteine is adsorbing uniformly on preformed corrosion product FeCO₃ and bare steel surface as a protective film against the bulk corrosive medium. When injected in the later stage of pre-corrosion at 34 h, cysteine decreases the corrosion rate further from 0.15 mm/year to 0.004 mm/year cooperating with the pre-evolved corrosion product FeCO₃ to offer a more efficient hybrid layer against corrosion, which confirms the corrosion product stability impact that the amino acid is able to provide. This suggests that cysteine exhibit a synergistic inhibition impact via positive interaction with the preformed corrosion product FeCO₃ to suppress the degradation of the steel surface. In the other hand, the administration of glycine at 2 and 34 h pre-corrosion time show no impact on the corrosion rate values (see Figure 2), which is contrary with the findings observed in a previous study conducted by Lima *et al.*¹² This is due to the difference between the corrosion condition (such as pH value) glycine is employed in, for instance the current study pH is 6.6 while the pH used in Lima *et al.*¹² is below 4. In general, the corrosion rate is relatively stable which means that no pseudo-passivation layers are formed, and thus the corrosion rates evolution is to be related mainly to the formed pure FeCO₃ or hybrid Amino Acid- FeCO₃ layer.

^{vii} Trade name

^{viii} Trade name

^{ix} Trade name

^x Trade name