

***In-situ* synthesis of corrosion product-polymer composites on carbon steel for enhanced erosion-corrosion protection in CO₂ corrosion environments**

Dilshad Shaikhah
Institute of Functional Surfaces, School of
Mechanical Engineering, University of Leeds
Leeds, LS2 9JT
United Kingdom

Bruce Cowe
TotalEnergies, OneTech
CSTJF Avenue Larribau,
F-64018 Pau
France

Wassim Taleb
Institute of Functional Surfaces, School of
Mechanical Engineering, University of Leeds
Leeds, LS2 9JT
United Kingdom

Anne Neville
Institute of Functional Surfaces, School of
Mechanical Engineering, University of Leeds
Leeds, LS2 9JT
United Kingdom

Maalek Mohamed-Said
TotalEnergies, OneTech
CSTJF Avenue Larribau,
F-64018 Pau
France

Richard Barker
Institute of Functional Surfaces, School of
Mechanical Engineering, University of Leeds
Leeds, LS2 9JT
United Kingdom

ABSTRACT

Iron carbonate (FeCO₃) is a common corrosion product found on steel surfaces in carbon dioxide (CO₂)-containing aqueous environments. The formation of this corrosion product on the internal walls of carbon steel pipelines can suppress material dissolution by over an order of magnitude, providing an effective form of corrosion inhibition. One significant limitation associated with relying upon solely FeCO₃ to suppress material dissolution is its propensity to be locally removed by chemical or mechanical mechanisms. Here we report a novel strategy, implemented to generate a mineral-polymer nanocomposite layer *in situ* on an X65 steel surface in a CO₂ corrosion environment. The formation of the layer is achieved through the intercalation of functionalized polystyrene nanospheres into the developing FeCO₃ corrosion product. We demonstrate the feasibility of microsphere intercalation into the FeCO₃ crystal layer through appropriate functionalization. Such intercalation produces a composite structure that affords excellent corrosion protection analogous to ‘natural’ FeCO₃. Additionally, the composite FeCO₃ layer offers unique, enhanced physical-mechanical properties compared with naturally formed FeCO₃ layer. The process provides a potential means of improving the resistance of corrosion product layers to mechanical removal, and hence, the initiation of localized corrosion.

Key words: CO₂ corrosion, carbon steel, iron carbonate, corrosion products, polystyrene microspheres, composite layer

INTRODUCTION

Hydrocarbons still remain as a fundamental contributor towards meeting the worldwide demand for energy, despite the growth of other alternative sources such as renewable and nuclear options.¹ Due to low cost and availability, carbon steel, remains as the most commonly used material for pipelines in down and upstream activities within the oil and gas industry.² However, carbon steel is not an exceptional metal alloy from the perspective of internal corrosion resistance. The economical cost for its degradation and related failures represent 10% to 30% of the maintenance budget in petroleum industry.³ It is therefore crucial that the corrosion of such a susceptible steel is managed and controlled accordingly.

Approximately, half of pipeline failures are attributed to either carbon dioxide (CO_2), so called 'sweet' corrosion, or hydrogen sulfide (H_2S), known as 'sour' corrosion.⁴ Controlling corrosion is an expensive protocol based on various strategies proposed by materials and/or corrosion engineers, for instance: modification of materials or solutions⁵⁻¹⁰, coatings^{11,12}, corrosion inhibitors^{13,14} and improvements of operations¹⁵. Among the aforementioned strategies, arguably the most efficient and certified method to control corrosion is using corrosion inhibitors owing to the general cost and returns on investments.²

In sweet and sour corrosion environment, such as those found in geothermal energy, oil and gas and carbon abatement industries, various naturally formed corrosion products can be found and may play a key factor in corrosion control behaving as a corrosion inhibitor in blocking active sites. Amongst the most commonly found layers are magnetite (Fe_3O_4)¹⁶, iron carbonate (FeCO_3 - which develops predominantly in CO_2 -containing environments)¹⁷ and iron sulfides (FeS)¹⁸. All these corrosion products are capable of significantly inhibiting general corrosion under certain conditions, so it is arguably beneficial to maintain them for potential corrosion mitigation. Once the films of the corrosion product cover the inner surface of pipeline, they act as physical barriers protecting from further corrosion.¹⁷ Nonetheless, their protection efficiency is limited due to local heterogeneity or discontinuities in the layer that can cause localized corrosion; moreover, the corrosion products can be removed with a mechanical force or chemical dissolution.¹⁹⁻²⁷

To control the composition, structure, size and morphology of crystalline minerals in nature, living organisms intercalate organic additives into the inorganic matrix through a process known as biomineralization, resulting in the formation of composite materials. These composites are hybrid materials composed of inorganic and organic constituents on a nano and microscale, holding distinctive and fascinating physico-mechanical properties which strongly contradict those properties observed by any constituent working independently.²⁸ In artificial biomineralization systems, biopolymers have attracted significant attention in synthesis of mineral composites (mainly mineral carbonates) owing to their exceptional properties, high compatibility, cost, and adsorption affinity.^{29,30} Among the polymers, block copolymer micelles and surface functionalized polymers are the most promising organic additives owing to their solubility in aqueous medium, versatile size and capability of intercalation with metal carbonates during crystallization.³¹

An important example of a surface functionalized polymers is carboxyl polystyrene particles (PSCOOH), a polymer consisting of polystyrene in the core of the sphere and carboxylic groups on the surface. This polymer has displayed strong intercalation affinity in the synthesis of single calcite crystals, producing a calcite composite which holds distinctive physico-mechanical properties, i.e. enhancing fracture toughness, when compared with the pure calcite crystal.³² Herein, this study in CO_2 corrosion aims to *in-situ* engineer a nanocomposite corrosion product layer consisting of the inorganic crystal layer matrix, the FeCO_3 corrosion product (inorganic) and the organic intercalant, carboxyl polystyrene microsphere, on X65 carbon steel.

To compare the corrosion protection of the newly formed composite micro-layer with pure FeCO_3 , the surface of the X65 carbon steel coupons was monitored electrochemically. This work also assesses the crystal structure and morphology of the layers as well as the degree of incorporated PSCOOH into FeCO_3

crystals through the application of various surface analysis techniques. Ultimately, the mechanical properties of FeCO₃–PSCOOH composite layer and pure FeCO₃ layer are characterised via nano-indentation.

EXPERIMENTAL PROCEDURE

Material Preparation

Based on its widespread use within the oil and gas industry, carbon steel (API 5L X65) was selected as the substrate material and formed the working electrode for the electrochemical experiments. The elemental composition of carbon steel is shown in Table 1³³, with the steel possessing a ferritic-pearlitic microstructure.

Table 1: Chemical composition (wt.%) of X65 carbon steel³³

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

The carboxyl polystyrene microspheres (average diameter 200 nm) were purchased from Bangs Lab (US) and used without further purification. The carbon steel test specimens, (used as working electrodes for electrochemical studies), were cut into cuboids (15 mm x 15 mm x 5 mm). Electrical connections to working electrodes were achieved by soldering a copper wire to the reverse side, before embedding in a non-conductive resin, producing an exposed area of 2.25 cm² for corrosion measurements. The exposed test surface of each embedded specimen was subsequently wet ground up to 600 grit silicon carbide papers, followed by rinsing with de-ionized water and acetone before drying with nitrogen gas and placing in the aqueous test environment.

Experimental Methods

Two types of experiments were conducted in this work, firstly to form a FeCO₃ corrosion layer on carbon steel surfaces and secondly, synthesis of corrosion product-polymer composite layer in the presence of various dosages of PSCOOH microspheres into the aqueous phase. All experiments were conducted in a glass cell setup, similar to the setup shown in Figure 1, with some minor differences between each experimental conditions, as detailed in the following sections. In all experiments, the glass beaker was placed on a hot plate to control the temperature and was gently stirred using a magnetic stirrer at 100 rpm.

FeCO₃ Layer Growth

The evolution of FeCO₃ layers has been widely reported on carbon steel surfaces in aqueous CO₂ environments. Conditions in this study were chosen that replicated experiments in which a high surface coverage of FeCO₃ was achieved on carbon steel at ambient pressure.¹⁷ These tests were conducted using a conventional glass (or bubble) cell setup integrated with a three-electrode electrochemical cell. A liter of brine solution was prepared with dissolving 35g sodium chloride (NaCl) (99% analytical grade - Sigma Aldrich) in 1 L deionized water for each experiment. The 1 L 3.5 wt.% NaCl brine solution was saturated with CO₂ overnight for at least 12 h by bubbling CO₂ gas through the solution continuously. Prior to the start of each experiment, the brine solution was heated to desired temperature (60°C) and the pH was adjusted to 6.7 via the addition of sodium bicarbonate (NaHCO₃). Two carbon steel coupons, with a surface area of 4.9 cm², were wet ground using 180, 400 and 600 grit SiC grinding paper. The test conditions are summarized in Table 2 and were selected as literature and previous experience of the researchers identified such conditions were highly conducive to the formation of a FeCO₃ layer on carbon steel within a 48 h test period.

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FeCO₃-PSCOOH Composite Layer Growth

In order to investigate the intercalation degree of PSCOOH into the corrosion product on the carbon steel surface and the composite corrosion protection efficiency to inhibit the electrochemical reactions in a CO₂-containing aqueous environment, a series of *in-situ* synthesis of corrosion product tests monitored with electrochemical analysis were performed. The PSCOOH microspheres are soluble in aqueous solution due to the presence of carboxylic groups on the surface of the spheres and originally stored in 10 wt.% distilled water solution. Initially, the intercalation degree of PSCOOH was assessed via injecting the (10, 100, 1000 micL) PSCOOH into the 1 L brine solution using a micro-pipette at a fixed pre-corrosion period of 2 h to achieve (1, 10 and 100 ppm) PSCOOH in the 1 L brine solution.

Table 2. Operational conditions and polymer loadings used in the electrochemical experiments

Parameter	Values
Temperature	60°C
CO ₂ partial pressure	~0.8 bar
Substrate material	Carbon Steel (API 5L X65 Steel)
Working solution	3.5 wt.% NaCl
pH	6.6 ± 0.20
PSCOOH concentration	1, 10 and 100 ppm
Time when PSCOOH introduced to solution	2 h
Test duration	48 h

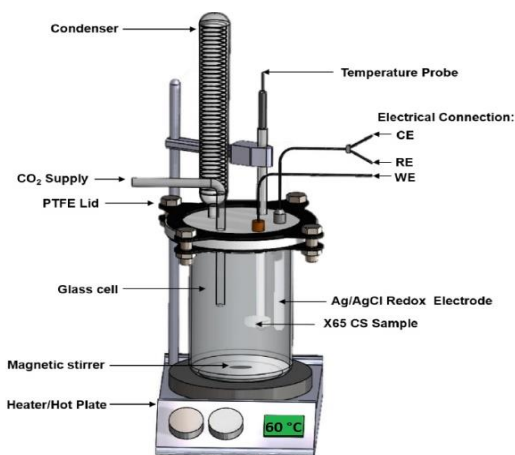


Figure 1: Three-electrode glass (bubble) cell apparatus for growth of layers and electrochemical analysis in aqueous CO₂ environments

Electrochemical Techniques

Linear Polarization Resistance and Tafel Polarization

Linear polarization resistance (LPR) measurements were completed to determine the corrosion rates of the carbon steel specimens in FeCO₃ and corrosion product-polymer composite layer formation experiments. For LPR measurements, a three-electrode cell was employed, with the carbon steel coupon acting as the working electrode and a combination electrode containing a silver/silver chloride (Ag/AgCl) reference and platinum (Pt) counter electrode completing the three-electrode cell. The open circuit potential (OCP) was monitored in between LPR measurements completed every 15 min, in which the carbon steel coupon was polarized from -15 mV to +15 mV relative to OCP at a scan rate of 0.25 mV/s.

To determine the corrosion rate, the polarization resistance (R_p) in $\Omega\cdot\text{cm}^2$ obtained from the LPR measurements was used to calculate a corrosion current density (i_{corr}) in mA/cm^2 :

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

where B is the Stern-Geary coefficient (mV) and β_a and β_c are the anodic and cathodic Tafel constants (mV) respectively. The corrosion rate (V_c) in mm/year is then calculated:

$$V_c = \frac{K i_{\text{corr}} M_{\text{Fe}}}{n F \rho} \quad (2)$$

where K is a conversion factor to convert the corrosion rate into mm/yr ($K = 3.16 \times 10^5$), M_{Fe} is the molecular mass of iron (55.8 g/mol), n is the number of electrons liberated in the anodic reaction ($n = 2$), F is the Faraday constant (96,485 C/mol) and ρ is the density of the steel ($\rho = 7.87 \text{ g}/\text{cm}^3$).

Potentiodynamic polarization measurements were performed at strategic times (2 and 48 h corrosion time), where significant modification on steel surface occurred. It should be stressed that each test was carried out in completely separate cells. The scans for the formation of a 'pure' FeCO_3 layer were collected at 2 h (before formation) and at end of the immersion test (48 h) once the film had fully formed. In a separate test, after the addition of 10 ppm PSCOOH at 2 h of exposure time, the polarization scan (2 h) was conducted (within 15 minutes to allow OCP to stabilize). The scan at 48 h for FeCO_3 -PSCOOH was taken in a separate experiment, 46 h after PSCOOH microspheres were introduced at 2 h pre-corrosion. Anodic and cathodic Tafel polarization was conducted by polarizing up to ± 500 mV vs OCP at a scan rate 15 mV/min. Furthermore, each branch of the Tafel plot (anodic and cathodic) were collected on separate test specimens in separate test vessels. Equation (5) was used to calculate the inhibition efficiency (IE%) where i_0 and i_{corr} are the corrosion current density values without and with inhibitor, respectively:

$$\text{IE}\% = \frac{i_0 - i_{\text{corr}}}{i_0} \times 100 \quad (5)$$

Surface Analysis

The layers formed on the carbon steel coupons were imaged using a Hitachi SU8230 Scanning Electron Microscope (SEM) in secondary electron mode at an operating voltage of 20 kV. After the corrosion experiments, coupons were removed from the epoxy resin and carbon coated for SEM analysis. A top view image was obtained of the coupons to analyze the formed layers.

To determine the intercalation of PSCOOH microspheres inside the FeCO_3 crystal layer, the specimens with FeCO_3 and FeCO_3 – PSCOOH layers were cross-sectioned. The cross-sections of the specimens were prepared using an FEI Helios G4 CX 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. The images taken from FIB analysis were used to analyze the intercalation degree of PSCOOH microspheres inside the crystals using ImageJ software.

To identify the crystalline composition of the layers, X-ray diffraction (XRD) measurements were completed using a Bruker D8 diffractometer. A 10 x 10 mm area in the center of the coupon from a 2θ range from 20° to 80° . The total scan time was approximately 45 min.

Mechanical Property Characterization

Nano-indentation tests were implemented employing the Nano Test (Micro Materials Limited, UK), with a Berkovich diamond indenter. For reliable analysis, 100 loading/unloading curves were computed in each experiment to find the average results. All experiments were carried out 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.³⁴

RESULTS

Synthesis and Corrosion Behavior of FeCO_3 layer and FeCO_3 -PSCOOH Composite Layer

The corrosion rates measured in the experiments in which either an FeCO_3 layer or FeCO_3 -PSCOOH composite layer were produced on the carbon steel surface are shown in Figure 2. The average corrosion rates are reported from a minimum of three repeat experiments, with error bars showing the standard deviation of three measurements. To investigate the intercalation efficiency of PSCOOH microspheres into the corrosion product FeCO_3 , three different concentrations were selected (1, 10 and 100 ppm) and added to the solution at 2 h pre-corrosion in separate cells for two days. Figure 2 shows that, in the absence of PSCOOH microspheres, the corrosion rate progressively drops to around 0.1 millimetre/year (mm/year) after 20 h of corrosion and continue to decrease to 0.01 mm/year by the end of the experiment, suggesting the corrosion active sites of the steel surface are blocked due to the formation and coverage of the FeCO_3 layer, as reported by numerous other authors.¹⁷ The presence of 1 and 10 ppm PSCOOH microspheres show no significant effect on the corrosion rate response vs. time which remains very similar to the transient response in the absence of the spheres. This indicates that the carbon steel surface continues to corrode which permits the continued formation of FeCO_3 layer. Consequently, the crystal growth of FeCO_3 on the surface of carbon steel remains unaffected, despite the presence of PSCOOH microspheres. However, introducing 100 ppm PSCOOH microspheres into the solution decreases the corrosion rate rapidly from 1.5 to 0.7 mm/year (within 15 mins). The corrosion rate then gradually decreases to below 0.2 mm/year by the end of two days. The corrosion rates' results imply that the PSCOOH microspheres below a concentration of 10 ppm present no/very low effect on corrosion inhibition initially upon their addition to the system and no intervention on the crystal growth of corrosion product layer. The latter observation is confirmed with topographical analysis, which is discussed in the following section. The threshold of 10 ppm on one side and 100 ppm on another side will need to be finetuned indeed, as it is assessed in static condition (100 rpm). this threshold might evolve under dynamic condition, for instance, 10 ppm under 100 rpm could be equivalent to 50 ppm under higher dynamic conditions (500 rpm or 700 rpm). Thus, it can be concluded that there is a requirement to generalize the threshold dosage aspect to wider conditions.