

Galvanic Interactions between Surface Layers and Bare Carbon Steel in Aqueous CO₂ Environments

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ABSTRACT

Iron carbonate (FeCO₃), magnetite (Fe₃O₄) and iron carbide (Fe₃C) layers are able to form on carbon steel surfaces in aqueous carbon dioxide (CO₂) environments, and suspected to play a critical role in uniform and localized corrosion of the underlying steel. Fe₃C and Fe₃O₄ are known to establish micro-galvanic cells with uncovered regions of the steel surface, due to their conductive and semi-conductive nature respectively, enhancing corrosion rates. To evaluate the significance of the layers' galvanic corrosion in an aqueous CO₂ environment, layers of Fe₃C, Fe₃O₄ and FeCO₃ were formed on X65 carbon steel surfaces. The coupons were then galvanically coupled to a bare X65 carbon steel coupon at different area ratios (AR = 1 and 10) in a pH 5, 1 wt.% NaCl, CO₂-saturated solution at 50°C. Galvanic currents were measured using zero resistance ammetry over 24 h, with similarly high galvanic currents measured for the Fe₃C-bare steel and Fe₃O₄-bare steel couples, enhancing the bare steel corrosion rates. The galvanic current was significantly smaller and reversed for the FeCO₃-bare steel couple, enhancing rather the corrosion rate of the FeCO₃-covered coupon.

Key words: galvanic corrosion, carbon steel, zero resistance ammetry, magnetite, iron carbide, iron carbonate

INTRODUCTION

In aqueous carbon dioxide (CO₂)-saturated environments, such as those found in geothermal energy, oil and gas and carbon abatement industries, various naturally occurring layers can be found on the internal surface of carbon steel infrastructure, such as pipelines, as they corrode in the mildly acidic conditions. Amongst the most commonly found layers are iron carbonate (FeCO₃)¹⁻⁷, iron carbide (Fe₃C)^{8, 9} and magnetite (Fe₃O₄).^{10, 11} FeCO₃ can offer corrosion protection to the underlying steel when formed under certain conditions, as too can Fe₃O₄. Fe₃C is typically associated with enhancement of electrochemical activity of carbon steel and is revealed due to preferential dissolution of ferrite in the steel microstructure – through the formation of a porous network at the steel surface. Each of these layers play a fundamental role in the uniform and localized corrosion of the underlying carbon steel.

One key property of the surface layer is its surface and bulk conductivity, and ability to establish a galvanic couple with bare regions (i.e. not covered by the layer) of the carbon steel surface. A galvanic couple comprises two distinct regions that are *net cathodic* and *net anodic*, which are electrically (through solid conductive pathways) and ionically (through aqueous solution) connected. Such naturally formed galvanic couples at the steel surface can be particularly problematic when only partial coverage of a layer on the surface is achieved^{12, 13} or when conditions are not favorable to achieve full surface coverage.² Fe₃C, for example, is a metallic conductor and readily establishes a galvanic couple with the bare steel, whilst Fe₃O₄ is a semi-conductor, with both layers able to sustain the cathodic reaction.^{14, 15} In an aqueous CO₂ environment, the cathodic reaction, Equation (1), occurs as a result of CO_{2(g)} dissolving in water to form carbonic acid (H₂CO₃), which then partially dissociates to provide a source of hydrogen ions (H⁺) that are consumed in the cathodic reaction:



Once a galvanic couple is established, the bare carbon steel acts as the net anode, enhancing the anodic dissolution of iron:



Fe₃C layers are widely reported to be revealed on the surface of corroding carbon steel, experimentally observed as a gradual increase in corrosion rate over time through sustained galvanic interaction between the layer and the steel surface.^{8, 9, 14-16} In the galvanic cell that forms, Fe₃C is proposed to act as the net cathode whilst the ferrite phases in the steel microstructure perform as the net anode. Fe₃C forms a porous (high surface area) layer on the carbon steel surface, and it has been proposed that acidification within the Fe₃C porous structure can also synergistically contribute to enhancing the corrosion rate.^{9, 17} Rather low electrical resistivity values of the order of 10⁻⁵ - 10⁻⁴ Ω·cm across a range of temperatures up to 100 °C have been reported for Fe₃C.¹⁸

Fe₃O₄ layers are also found on carbon steel surfaces in aqueous CO₂ environments, generally at temperatures above 100 °C and neutral-alkaline pH.^{10, 19} Fe₃O₄ is a semi-conductor with an inverse spinel crystal structure, and produces a galvanic interaction when coupled to carbon steel.²⁰ Electrical resistivity values of Fe₃O₄ are strongly influenced by temperature and stoichiometry (i.e. the ratio of Fe³⁺ to Fe²⁺ ions in the Fe₃O₄ crystal structure), with reported values of the order 10⁻² to 10⁻¹ Ω·cm.²¹ Fe₃O₄ layers have been shown to reduce corrosion rates when covering the carbon steel. Nonetheless, due to the galvanic interaction that can occur between magnetite and iron, localized corrosion of the underlying ferrite metal is possible.⁹

Depending on environmental conditions, most notably solution chemistry, pH, and temperature, FeCO₃ (siderite) crystals can nucleate and grow on the carbon steel surface and reduce CO₂ corrosion rates by several orders of magnitude.^{1, 2} FeCO₃ is almost certainly an electrical insulator and therefore is not expected to readily establish a galvanic couple with the bare carbon steel surface. Schmitt et al.²² measured the electrical properties of FeCO₃ layers formed on different grades of carbon steel surfaces,

reporting resistivity values in the range of $10^3 - 10^5 \Omega\cdot\text{cm}$ at 80°C , confirming the insulating nature of FeCO_3 . Hence, any driven galvanic interaction is likely attributable to a change in surface chemistry at the steel- FeCO_3 interface, which initiates a potential difference between any nearby bare steel surface.^{9, 22, 23} However, the role of FeCO_3 in this context and the link to the initiation of localized corrosion is unclear. Galvanic measurements, using a zero resistance ammeter (ZRA), between FeCO_3 -covered carbon steel coupons and bare carbon steel coupons at net cathode to net anode surface area ratios ranging from 1:1 to 200:1, demonstrated that a small galvanic current (less than $20 \mu\text{A}/\text{cm}^2$ at an equal anode to cathode surface area ratio) was measurable.²⁴ Galvanic interactions between bare carbon steel and FeCO_3 -covered carbon steel have also been suggested in other studies.^{25, 26} However, it has not been clearly established why galvanic interaction between FeCO_3 layers and bare carbon steel occurs. FeCO_3 is an insulator,²² therefore, galvanic interaction on FeCO_3 -layered coupons may be caused by the widely reported co-existence of Fe_3C and FeCO_3 on carbon steel surfaces.^{1, 8, 9} Surface coverage of FeCO_3 is typically considerably lower than 100%, even when corrosion rates of carbon steel have dropped significantly,^{3, 7} suggesting the presence of other layers on the surface have contributed to galvanic corrosion. The stage of FeCO_3 growth, plus the ability of the layer to re-establish (or 'heal') are critical surface coverage parameters that have influenced galvanic current measurements.^{25, 26}

In aqueous CO_2 environments, it is quite possible for Fe_3O_4 , Fe_3C and FeCO_3 layers to co-exist on the carbon steel surface.^{10, 11} The involvement of each layer in the galvanic corrosion of carbon steel has been acknowledged in literature, but relatively few studies have investigated the mechanistic effects of galvanic interaction with surface layers or quantitatively compared the different layers. In this study, Fe_3C , Fe_3O_4 and FeCO_3 layers formed on X65 carbon steel coupons were galvanically coupled to bare carbon steel coupons in a CO_2 -saturated solution and compared. To establish the effects of galvanic corrosion caused by the different layers, electrochemical and surface analysis techniques were employed.

EXPERIMENTAL PROCEDURE

Material Preparation

American Petroleum Institute (API)¹ 5L X65 carbon steel, which has a ferritic-pearlitic microstructure and the chemical composition shown in Table 1, was machined into disc coupons with a thickness of 6 mm. The microstructure of this particular X65 grade and composition has been shown using an optical microscope in a previous study related to corrosion in CO_2 environments.²⁷ To enable electrochemical measurements, a copper wire was soldered to the reverse side of a carbon steel coupon before embedding in a non-conductive epoxy resin, resulting in exposed surface areas of 0.49 cm^2 and 4.9 cm^2 for the two different diameter coupons used. Prior to all experiments, coupons were wet ground to the required surface finish for the intended experiment (detailed in the following sections), degreased with acetone, rinsed with deionized water and dried using compressed air.

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	bal.

Experimental Methods

Two types of experiments were completed in this study, firstly to form corrosion layers on carbon steel surfaces and secondly to conduct galvanic corrosion experiments in which the layered coupons were galvanically coupled to a bare carbon steel surface using a ZRA. All experiments were carried out in a glass beaker setup, shown in Figure 1, with some minor differences between the experimental conditions,

¹ American Petroleum Institute, 200 Massachusetts Avenue NW, Washington, DC 20001-5571, USA

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detailed in the following sections. In all experiments, the glass beaker was placed on a hot plate to control the temperature and the solutions was gently stirred. An immersed thermocouple ensured appropriate regulation between the hotplate and the solution temperature.

Fe₃C Layer Formation (50 °C, pH 3.8, 24h, PCO₂=0.87 atm, P_{tot}=1 atm)

The formation of an Fe₃C layer was achieved by simply exposing the X65 carbon steel to conditions conducive to uniform corrosion in the absence of other surface films, such as FeCO₃. Experiments were conducted in 1 L of deionized water containing 1 wt.% of sodium chloride (NaCl) heated to a temperature of 50 °C. CO₂ (>99.8% purity) was bubbled into the solution for a minimum period of 12 h prior to starting the experiment, and bubbled continuously throughout the experiment to achieve and maintain CO₂ saturation, reducing the pH of the solution to pH 3.8 (confirmed using a pH probe). Two carbon steel coupons with a surface area of 4.9 cm² were wet ground progressively using 180, 600, 800 and 1200 grit silicon carbide (SiC) grinding paper, before being immersed in the solution for a period of 24 h.

FeCO₃ Layer Growth (80 °C, pH 6.8, 20h, PCO₂=0.54 atm, P_{tot}=1 atm)

The growth of FeCO₃ layers has been widely reported on carbon steel surfaces in aqueous CO₂ environments.^{1, 3, 10, 24, 25} Conditions in this study were chosen that replicated experiments in which a wide surface coverage of FeCO₃ was achieved on carbon steel at ambient pressure.^{2, 7} These experiments were carried out in a CO₂-saturated, 1 L, 3.5 wt.% NaCl solution maintained at a temperature of 80 °C. To increase the pH, thus creating favorable conditions for FeCO₃ growth, sodium hydrogen carbonate (NaHCO₃) was added, resulting in a pH 6.8 solution. Two carbon steel coupons, with a surface area of 4.9 cm², were wet ground using 180, 400 and 600 grit SiC grinding paper and immersed in the solution for a period of 20 h. A higher surface roughness was chosen to promote FeCO₃ growth.

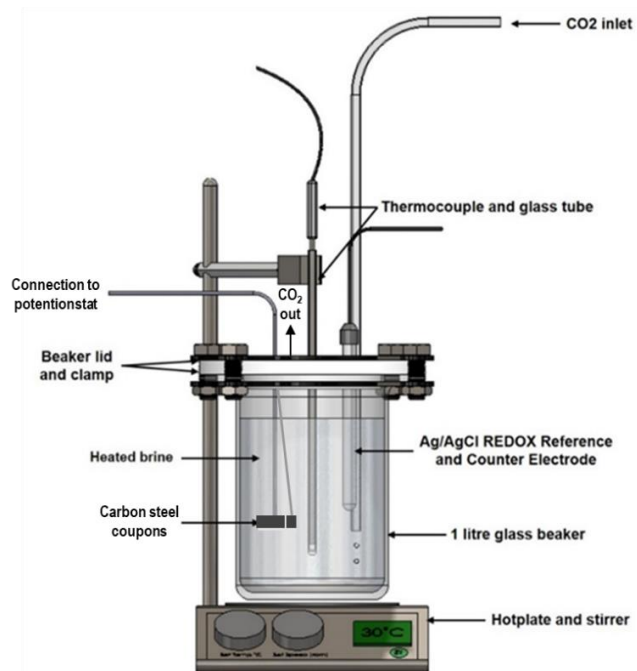


Figure 1: Experimental apparatus used for growing corrosion layers on carbon steel

Fe₃O₄ Layer Deposition (80 °C, pH~14, PCO₂=0.00 atm, P_{tot}=1 atm)

Whilst Fe₃O₄ layers on carbon steel surfaces have been observed in CO₂ environments, it is often found in combination with other surface layers, such as FeCO₃.^{3, 10} Therefore, establishing an understanding of