Iron Calcium Carbonate Instability: Structural Modification of Siderite Corrosion Films

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ABSTRACT: Corrosion research related to CO2-containing environments has focused over the past few decades on siderite formation (FeCO3) as a main corrosion product on carbon steel, yet the influence of Ca and other ions on its chemical and structural characteristics is not fully understood. Metal-localized corrosion is the biggest industrial challenge because of the unknown and unpredictable character of this phenomenon that frequently leads to failure. We report here the role of Ca and formation of iron-calcium carbonate (Fe_xCa_yCO_3) through a spiral growth model as in the calcite system and quantify the replacement of Fe^{2+} by Ca^{2+} ions in the structure of FeCO_3 to form Fe_xCa_yCO_3. The incorporation of Ca^{2+} inhibits the completion of spiral segments on the growth of the rhombohedral crystals of FeCO_3, promoting an enlargement of its structure along the c-axis. This leads to distortions in the chemical structure and morphology affecting the chemical and mechanical properties. Under flow conditions over time in an undersaturated environment, Ca is leached out from the expanded structure of Fe_xCa_yCO_3 increasing the solubility of the crystals, weakening the mechanical properties of the resulting corrosion films and stimulating localized corrosion.

KEYWORDS: corrosion, siderite, Fe_xCa_yCO_3, iron carbonate, iron calcium carbonate

INTRODUCTION

Many industries use carbon steel (C-steel) for the construction of pipes, tanks, and pumps for transportation and distribution of bulk gas and liquids demanding an annual steel production of 1.8 billion tonnes.1 The major safety and costly problem for industries using C-steel is because of corrosion costing not only lives but capital up to a total of US$2.5 trillion per year globally.1,2 In oil and gas transport pipelines, corrosion is produced by the chemical interaction between the fluids (i.e., CO_2-saturated brine, hydrocarbons, and chemicals) and steel but similar problems are faced in CO_2 storage and transport industries.3 General corrosion progressively degrades steel materials but the higher risk for pipeline failure is localized corrosion.

Most of the experimental studies regarding corrosion in CO_2 environments point out siderite (FeCO_3) as the main corrosion product although other Fe oxides coexist.4,5 The focus on FeCO_3 is in part because of the fact that the majority of the studies aim to investigate the formation of this product alone but in most of the cases it seems that the purpose is to simplify the system. Real applications have more complex chemistries with the presence of other ions (e.g., Mg, K, Ba, and Sr) in the fluids that cannot only modify the corrosion products but also change the pathway of the reactions, the mechanisms, and kinetics associated. Calcium as an additional ion (Ca^{2+}) in the brine solution has been marginally studied in the corrosion field with only a few works published. These works lack of consensus regarding the effect of calcium on corrosion rates. For example, some authors have reported the increase of corrosion rates when Ca^{2+} is present,6-8 while others have documented reduction instead.9,10 These discrepancies can be because of the use of different experimental conditions and lack of detail or control of them in the experiments.

Nevertheless, most of these works consistently agree in three main points. First, the presence of Ca^{2+} leads to the formation of an iron-calcium carbonate (Fe_xCa_yCO_3) with different morphology and crystallinity in comparison to the extensively studied FeCO_3 crystals.8-12 Second, the solubility of the as-formed Fe_xCa_yCO_3 film increases when compared to a film composed of pure FeCO_3 crystals and it has been suggested that this increase relates to a greater porosity of the Fe_xCa_yCO_3 film.11-14 Third, localized corrosion has often been observed when the brine solution contains Ca^{2+},7,8,10,13,15,16 however, some authors have attributed this effect to the migration of Cl^{-} through the porous film.15,16 Overall, these common observations indicate that the presence of Ca^{2+} induces changes in siderite crystals, which in turn modify the characteristics of the corrosion films, and their further role in steel degradation.

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Furthermore, despite siderite being the most studied corrosion product, the habit (external shape) has just recently described to adopt a rhombohedral geometry comprising of a microfaceted cylinder with trigonal-pyramidal caps. It is well known that habits can change depending on growth conditions and kinetics, leading to specific growth of crystal faces that exhibit different surface chemistries, and hence different interaction with the fluids. Now, we know that introducing Ca\(^{2+}\) into the growth of siderite produces different morphologies, but we do not know whether the only change is the habit or if structural changes are also taking place. Therefore, this work aims to elucidate and quantify the effect of Ca\(^{2+}\) in the structure of siderite to form an iron calcium carbonate (Fe\(_x\)Ca\(_{1-x}\)CO\(_3\)) corrosion product using molecular approaches. We also investigate the behavior of films formed with this product under reference operating conditions to evaluate their role in the conservation of the underlying steel.

## RESULTS AND DISCUSSION

Initial observations of the crystals grown on C-steel in brine solutions containing Ca\(^{2+}\) showed a rounded morphology in comparison to FeCO\(_3\) crystals and evidenced a growth mode in kink sites along steps as reported to occur in calcite (Figure 1). The morphology of these crystals resembles a distorted version of the FeCO\(_3\) morphology. They have rough and smooth surfaces in different directions indicating large anisotropy in bonding. This also suggests that different rates of growth occurred in each direction when compared to siderite, in which smooth crystal faces grow at a slower rate than kinked faces (Figure 1). Figure 1b shows that the growth of Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) crystals occurred in spiral dislocations similar to the growth of calcite. The circle in this figure points at the development of a new spiral segment while the arrow shows that the spiral has been cut off. This was observed in various crystals as presented in Figure S1. The presence of Ca\(^{2+}\) induces distortions in the normal rhombohedral geometry of FeCO\(_3\), enlarging the step along the c-axis and changing its normal progression. This likely increases the formation rate resulting in a disorganized geometry. Certainly, the step enlargement is because of the replacement of Fe\(^{2+}\) with an ionic radii of 0.92 Å by Ca\(^{2+}\) with that of 1.14 Å, which is the opposite phenomenon when Fe\(^{2+}\) is incorporated as an impurity in the structure of calcite. In comparison to the growth of siderite, the incorporation of Ca in the structure does not allow the normal progression of the steps as the steps forming the spiral in Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) have been cut off indicating an inhibition effect (Figure 1b). As expected, this new faster growth geometry introduces stacking faults, strain, and influences the crystal packing, affecting also their arrangement to form a film. This negative effect was evidenced in the inefficient packing of the new formed crystals with gaps between them exposing the bare steel (Figure 1a). Indeed, all these changes have further implications in the chemical (dissolution) and mechanical properties of the iron calcium carbonate and in the developed film.

Diffraction data from the Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) corrosion film showed a shift in the peaks to lower 2\(\theta\) degrees in comparison to that of FeCO\(_3\). For example, the 104 peak of Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) shifted to 31.62 2\(\theta\) in comparison to 32.04 2\(\theta\) of FeCO\(_3\) confirming a modification of the lattice parameters of pure FeCO\(_3\) when Ca\(^{2+}\) replaces Fe\(^{2+}\) in the structure (Figure 2a,b). Calculations yielded an atomic composition of Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) using the formula for a hexagonal lattice that defines the rhombohedral crystal structure of FeCO\(_3\), and also using the unit cell volume in combination to the linear equation that relates volume to a mole fraction of Ca\(^{2+}\) as previously reported. Furthermore, diffraction peaks of Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) are noticeably broader than those of siderite resulting from the lattice distortions and dislocations in the crystal structure induced by the incorporation of Ca\(^{2+}\).

To further understand the changes in the structure of siderite when Ca\(^{2+}\) is present, we quantified the geometrical changes in the structure of Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) compared to FeCO\(_3\) through XANES analyses. As previously reported, the Fe K-edge XANES spectra of FeCO\(_3\) corrosion films, grown under the same conditions of iron calcium carbonate films, have a fingerprint consisting of three peaks between 7110 and 7140 eV as observed in Figure 2c. Although both spectra are very similar, there are clear differences in the pre-edge and in the feature after the white line (peak 3) (Figure 2c). For Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\), the pre-edge (1s-3d) is a flatterened curve in comparison to that of FeCO\(_3\). Taking into account that the shape and the centroid of this feature is sensitive to the oxidation state and coordination environment, our results indicate that Fe as the absorber atom in Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) has a different local chemistry of Fe (e.g., neighbors and distances) than Fe in FeCO\(_3\). We observed similar results from a region of interest (ROI) of a XANES map corresponding to a cross section of a Fe\(_{0.66}\)Ca\(_{0.33}\)CO\(_3\) film (Figures 3a–d). Also, three Fe environments were identified on the cross section, I, II, and III regions (Figures 3a–c). Spectra I and III represent the chemical environment of Fe in the steel, while spectrum II
represents a combination of the fingerprints for the FeCO3 and FeC spectra. However, all the spectra showed clear alteration in the Fe site symmetry (pre-edge) with respect to the spectra of pure siderite and cementite (Figure 3b,d).

To investigate further the structural changes in the local environment of Fe in the Fe0.66Ca0.33CO3 crystals, we quantified interatomic distances of Fe in the structure compared to siderite through extended XAS fine structure (EXAFS) analyses. Initial comparison of the EXAFS data between Fe0.66Ca0.33CO3 and FeCO3 obtained from their respective films showed out-of-phase oscillations in k-space above 5 Å⁻¹ pointing out that Fe0.66Ca0.33CO3 and FeCO3 consist of two different structures (Figure 3). Such differences were quantified through the comparison of Fe–Fe interatomic distances in both Fe0.66Ca0.33CO3 and FeCO3 with the theoretical model of siderite. Our EXAFS data from these two types of films were collected in a small k-space range (3.0–7.0 Å⁻¹) and have some amount of noise; however, in our case these data are useful to provide a good estimation of the changes in the distances between Fe and neighboring atoms as they are not affected by noise in the data. First, we obtained a reasonable fit for the FeCO3 data collected from a film grown using the same conditions for Fe0.66Ca0.33CO3 growth (Table S1). The fit was achieved with a reduced χ² = 28 and an R-factor of 0.03 despite the limitations of our data (Figure 4a–c).

ΔR and ΔE₀ were below 0.1 Å and 10 eV, respectively, and σ² were within expected values (0.003–0.020 Å²). Interatomic distances for Fe–O₁ of 2.13 Å, Fe–C of 3.06 Å, Fe–O₂ of 3.24 Å, and Fe–O₃ of 3.42 Å were similar between FeCO3 and Fe0.66Ca0.33CO3 after 24 h flow. These results suggest that the incorporation of Ca in the structure (i.e., Fe–O of 1.99 Å in Fe0.66Ca0.33CO3 is shorter than 2.13 Å in siderite).
Å, and Fe–Fe$_1$ of 3.70 Å in the FeCO$_3$ crystals were in good agreement with the reported data (Fe–O$_1$ = 2.14 Å, Fe–C = 3.00 Å, Fe–O$_2$ = 3.26 Å, and Fe–Fe$_2$ = 3.73 Å for siderite). Using a k-space range between 3.0 and 7.0 Å$^{-1}$, we achieved a consistent fit for the Fe$_{0.66}$Ca$_{0.33}$CO$_3$ data using the siderite model but created with a substitution of two Fe positions by Ca (Table S1). Fitting values for $\Delta R$, $\Delta E_0$, and $\sigma^2$ were satisfactory with $\chi^2 = 35$ and an R-factor of 0.05 (Figure 4a–c).

Changes in the interatomic distances with respect to siderite (in brackets) were evident, for Fe–O$_1$ of 1.99 Å (2.13 Å), Fe–O$_2$ of 3.32 Å (3.26 Å), and Fe–Fe$_2$ of 3.80 Å (3.70 Å) confirming the bonding distortion identified with our XANES, scanning electron microscopy (SEM), and X-ray diffraction (XRD) data. Figure 5a,b illustrates how these distortions in bonding affect the geometry of the siderite crystals when Ca$^{2+}$ replaces Fe$^{2+}$ in the structure using the interatomic distances from our EXAFS data; and also the subsequent changes in the structure and morphology as evidenced by SEM. Furthermore, crystal packing for film development requires a modification to fit the new rounded morphology and piling up these crystals leaves gaps between the crystals (Figures 1a and S1). This in turn will affect the porosity and mechanical characteristics of the corrosion films conforming by these modified types of structures, and demonstrates how the introduction of another cation in the structure of siderite can change the characteristics of the material composing the corrosion film.

According to molecular dynamic simulations, the incorporation of Fe in the growth of calcite is initially an energetically very favorable (exothermic) process at the initial formation of calcite steps; however, subsequent incorporation of Fe becomes increasingly endothermic inhibiting further growth of the calcite crystals. The similarity in the spiral growth mode of siderite to the calcite system is not surprising but to understand this is the first time that the experimental data demonstrate the spiral growth of siderite in kink steps. In this growth mode, the birth of new faces along the c-axis intersects at obtuse and acute angles resulting in the equivalent kink site along step edges, and it has been demonstrated that this inequivalence plays an important role in the incorporation of ions. Furthermore, spiral growth occurs around dislocation defects in steps that coil to form a spiral pyramid. In our iron calcium carbonate system, Ca$^{2+}$ has a bigger ionic radius compared to Fe$^{2+}$ and the incorporation of Ca$^{2+}$ could be limited to obtuse steps to fit the bigger ion; however, the incorporation of Ca in the siderite structure inhibits its normal growth as observed in our SEM observations, and also demonstrated in the calcite system.

Focusing on testing the behavior of a Fe$_{0.66}$Ca$_{0.33}$CO$_3$ corrosion film, we performed flow experiments as described in the Methods section (i.e., pH 3.6 and 7.0, flow velocity of 1 m/s of 1% NaCl solution at 80 °C for 24 h) using the same conditions as previously reported for FeCO$_3$ films. Initial observations evidenced the severe effect of low pH (3.6) and flow on the dissolution of the Fe$_{0.66}$Ca$_{0.33}$CO$_3$ crystals provoking substantial breakage and leaving behind a porous material (Figure 6a,b). The damage is more severe than films consisting of pure FeCO$_3$ in experiments performed under the same conditions. This points out that the incorporation of Ca$^{2+}$ in the structure of FeCO$_3$ increases the dissolution of the iron calcium carbonate crystals in comparison to the film composed of pure siderite. The situation is more favorable for the Fe$_{0.66}$Ca$_{0.33}$CO$_3$ crystals at pH 7.0 as their morphology is still visible but they show signs of erosion and higher porosity expressed as rougher faces and deteriorated materials along the steps (Figure 6c,d). In addition, substantial dissolution of the Fe$_{0.66}$Ca$_{0.33}$CO$_3$ film at low pH led to the transformation of 65% of FeCO$_3$ from the top surface (~10 nm) to Fe$_2$O$_3$, indicating higher chemical transformation than FeCO$_3$ films; in which under the same experimental conditions, 88% of FeCO$_3$ was preserved (Figure 7b). At neutral pH, Fe$^6$ from the steel was detected probably from the gaps between the crystals but nevertheless showing that the film is not protecting the steel (Figure 7c).

Surprisingly, the incorporation of Ca$^{2+}$ in FeCO$_3$ films is reversible as this element was not detected in X-ray photoelectron spectroscopy (XPS) analyses after flow experiments under both pH conditions (Figure 7d–f). This was further confirmed through energy-dispersive X-ray (EDX) mapping as the direct correlations found between O and Ca in Fe$_{0.66}$Ca$_{0.33}$CO$_3$ films prior flow experiments were not found...
afterward, indicating that both elements were initially part of the crystals but Ca was not present after flow, at least in detectable concentrations (Figure S2).

Moreover, the interatomic distances in the structure of the Fe$_{0.66}$Ca$_{0.33}$CO$_3$ crystals after flow experiments were different to those in the initial Fe$_{0.66}$Ca$_{0.33}$CO$_3$ crystals but closer to the interatomic distances in FeCO$_3$ (Table S1). We were able to quantify them through the fit of the EXAFS data from a Fe$_{0.66}$Ca$_{0.33}$CO$_3$ film after a flow experiment at pH 7.0. The fit was achieved by finding $S_0^2$ to 0.90 for the first path and fixing it for the other three paths included. $\Delta E_0$ was 1.89 ± 1.52. Interatomic distances were consistent to the siderite model without the need of including Ca into the structure Fe−O$_1$ = 2.08 Å, Fe−C$_1$ Å = 2.94 Å, Fe−O$_2$ = 3.20 Å, and Fe−Fe$_1$ = 3.65 Å as the lixiviation of Ca$^{2+}$ from the Fe$_{0.66}$Ca$_{0.33}$CO$_3$ structure was also confirmed through XRD analyses (Figure 2a,c).

### CONCLUSIONS

Overall, our results indicate that Ca$^{2+}$ readily incorporates into the siderite structure under static conditions to form an iron calcium carbonate product, that in our case consisted of Fe$_{0.66}$Ca$_{0.33}$CO$_3$. The growth of the as-formed carbonate, a crystalline matrix of siderite with Ca$^{2+}$ incorporated into the structure, occurs in steps and spiral dislocations following a similar growth mode to the described for the calcite system; however, the incorporation of Ca$^{2+}$ inhibits the completion of spiral segments in the normal growth process of siderite. As a result, a new modified structure of the carbonate (Fe$_3$Ca$_2$CO$_3$) is formed with larger steps along the c-axis to allocate the bigger Ca$^{2+}$ ions, expanding in turn the geometry and modifying the interatomic distances. As a consequence, a rounded type of the siderite crystal morphology is developed leading to the formation of a nonuniform corrosion film with different properties to FeCO$_3$ causing adverse effects for the preservation of steel; (1) inefficient packing of the modified crystal morphology promotes localized corrosion; (2) the open structure of the formed Fe$_3$Ca$_2$CO$_3$ along the c-axis allows the fast hydration of Ca$^{2+}$ into the solution increasing the solubility of the film and exposing the steel to the fluids; and (3) these two effects weaken the mechanical properties of the corrosion films.

### METHODS

Growth of corrosion products on X65 C-steel cylinders (10 mm $\phi$ and 6.25 mm thickness) was performed in an autoclave reactor. First, the specimens were wet ground using silicon carbide (SiC) grit paper sizes of 120, 320, and 600, then rinsed with deionized water and acetone and finally dried with air. A CO$_2$-saturated brine solution composed of 1% NaCl and 220 mg/L Ca was placed in the autoclave and the pH was adjusted to 7.0 at 80°C using NaHCO$_3$. Corrosion films were grown at 80°C under a total pressure CO$_2$ of 30 bar for 72 h. Corrosion films without the presence of Ca in the brine were also produced using the same conditions in the absence of 220 mg/L Ca.

Flow experiments were conducted in an airtight experimental rig built to transfer a brine solution in a closed loop between a glass reactor (fitted with a pH electrode and a condenser) and a flow cell described in Matamoros-Veloza et al. 2020. A CO$_2$-saturated brine solution composed of 1% NaCl and 220 mg/L Ca was placed in the autoclave and the pH was adjusted to 7.0 at 80°C using NaHCO$_3$. Corrosion films were grown at 80°C under a total pressure CO$_2$ of 30 bar for 72 h. Corrosion films without the presence of Ca in the brine were also produced using the same conditions in the absence of 220 mg/L Ca.

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Dissolved oxygen concentration was measured using a DO probe (Intellical LDO101) and only when readings were below 50 ppb, the
experiment was started. Experiments were performed at pH 3.6 and pH 7.0 (adjusted with NaHCO₃) for 24 h. We monitored pH using a Mettler Toledo S213 pH/conductivity meter. We used NaCl (Fluka/Honeywell CAS 7647-14-5 99%), NaHCO₃ (Alfa Aesar 99% CAS 144-55-8), and CaCl₂·2H₂O (VWR CAS 10035-04-08 99.5%). Specimens were carefully transferred for experiments and analyses (i.e., autoclave, flow cell rig, and instruments for analyses), and they were always kept dried in vacuum sealed bags in a vacuum desiccator.

XRD analyses were conducted directly on rinsed and air-dried specimens mounted onto a holder and scanned from 15 to 80° 2θ at 1.55°/min using a Bruker D8 X-ray diffractometer. Our diffraction data were compared to that of the structures of siderite, calcite, and α-Fe₃O₄.70-32 References of the International Centre for Diffraction Data (ICDD) were used for siderite (ICDD 8-0133), calcite (ICDD 5-0586), and α-Fe (ICDD 6-0696). SEM imaging was performed on specimens fixed onto stubs using high-purity double-sided conductive adhesive carbon tabs and mounted on the sample stage of the instrument (TM3000Plus microscope), which was operated at 15 kV. XPS analyses were performed on the surface of the specimens (300 μm × 300 μm, ~10 nm depth) using an EnviroESCA instrument equipped with a monochromatic Al Kα (1.487 keV) X-ray source. For the analyses, the specimens were mounted onto stubs using high-purity double-sided conductive adhesive carbon tabs. The instrument was operated at 3.3 mbar and 40 Ar gas was used for charge compensation. First, we collected survey spectra between 15 and 1500 eV with a pass energy of 100 eV; then high-resolution spectra were collected at 285 eV using the carbon 1s peak. For XPS data analyses, CasaXPS software was used following the procedure described in Biesinger et al. 2011.33 Fe 2p½/high-resolution spectra were fitted using multiple peaks and Shirley background subtraction.

In order to obtain information about the local chemistry of Fe in the corrosion films and to quantify any changes in the structure when Ca is present, Fe K-edge X-ray absorption (XAS) analyses were performed at Diamond Light Source on I18 beamline. For the analyses, a Si(111) monochromator with an energy resolution (ΔE/E) of 1.4 × 10⁻⁶ was calibrated using a Fe-foil at 7111.99 eV. We analyzed Fe₀.₆₆Ca₀.₃₃CO₃ and FeCO₃ corrosion films (initial and after flow) at pH 7.0 and with a flow velocity of 1 m/s. Immediately after the experiments, the films were removed from the flow and prepared as focused ion beam (FIB) lamellae (~500–1000 nm thick). For this, we embedded the specimens in resin and finished polishing them using 600 SiC grit paper to expose the cross section and dried with air.

To prepare the lamellae, a coat of 20 μm of Ir was applied using an Agar Scientific sputter coater to reduce the charge effects and transferred into a FIB FEI Helios G4 CX Dual Beam microscope. A 1 μm thick Pt layer was applied on an area of 20 μm length and a 2 μm width using a Ga⁺ ion beam, then a beam current of 21 nA was applied to remove the material from either side of the lamella, which was subsequently thinned using progressively smaller beam current (9 nA to 40 pA) until achieving the desired thickness. This preparation process yielded lamellae with areas between 280 and 800 μm², which were kept in vacuum until analysis.

For the acquisition of the μ-XANES data for mapping, the lamellae were placed at 45° to the incident beam and the energy-dispersive silicon drift 4-element Vortex ME-4 detector with a Cube preamplifier was positioned normal to the beam direction. Fe foil was used to calibrate the monochromator at 7112 eV. 150 Fe fluorescence maps were collected at discrete energies between 7000 and 7250 eV in the raster mode with a pixel size of 2 μm × 2 μm using 0.1 s per pixel. Mn fluorescence maps were also acquired to identify the areas corresponding to the steel. It was necessary to use an aluminum filter of 0.25 mm to attenuate the incident X-ray beam and to ensure the linear response of the detector. In addition, XANES spectra were collected from FeO, Fe₂O₃, Fe₃O₄, and FeCO₃ as references for linear combination fitting (LCF). In addition, μ-XANES and μ-EXAFS spectra of the Fe₀.₆₆Ca₀.₃₃CO₃ films were collected between 7000 and 7400 eV while spectra of a FeCO₃ film were collected between 6911 and 7580 eV. A step size of ~0.5 eV was used for the measurements.

To produce the XANES maps, a python script was used to stack and convert the fluorescence maps to a single file, they were aligned and analyzed using principal component analysis (PCA) and then cluster analysis in Mantis.35 First, the number of spectral components from PCA was determined and then it was used in iterations to find the number of clusters until reaching a local minimum with no further changes on the map.35 Individual spectra were also obtained from regions of interest (ROI) from the maps to find spectra representative of the films.

The raw XANES data were aligned, averaged prior to normalization, and the background was subtracted using Athena software.65 The spectra were analyzed by comparing the FeCO₃ and Fe₀.₆₆Ca₀.₃₃CO₃ spectra among themselves and with references. We compared the normalized Fe K-edge XANES spectra of the clusters and ROI to the spectra of the Fe references both experimental and from databases.35,36 We performed LCF analysis between 20 eV below and 30 eV above the edge.

The EXAFS region from the spectra was analyzed with Artemis.36 The EXAFS spectra were fitted to a theoretical model generated using the siterite structure in FEFF6 and ATOMS.66 Four single-scattering paths were considered in the fit, Fe–O (first shell) and Fe–Ca–O and Fe–Fe (second shell). We used a shell by shell-fitting approach, finding the amplitude parameter (S₂) for the first shell to be 0.89 that was later used as a fixed value for the four paths. Coordination numbers (N) were used as generated from the theoretical model. The energy shift (ΔE₀) was floated as a fitting parameter and it was constrained to be the same for the four paths. The disorder parameter in the distribution of interatomic distances (σ²) was also allowed to float in the fits. The quality of the fits was assessed against the reduced χ² and the R-factor.65 Intergalactic distance (R), disorder (σ²), and inner potential corrections (ΔE) were extracted from the fits. It is worth noting that despite fitting all our data within a short k-space range, the number of independent points used for the fitting was twice the number of variables following the Stern’s rule.66 All fits were achieved using least squares multiple k-weight fitting. Further details of the fitting process for Fe₀.₆₆Ca₀.₃₃CO₃ before and after flow are presented in Supporting Information.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c14513.

SEM images of the as-formed Fe₀.₆₆Ca₀.₃₃CO₃ corrosion products on C-steel; EDX maps of O and Ca of Fe₀.₆₆Ca₀.₃₃CO₃ corrosion products before and after flow experiments; O 1s XPS spectra collected from Fe₀.₆₆Ca₀.₃₃CO₃ EXAFS data; EXAFS fitting parameters derived from fitting the spectra of Fe₀.₆₆Ca₀.₃₃CO₃ (initial and after flow) films; further details of the fitting process of Fe₀.₆₆Ca₀.₃₃CO₃ EXAFS data; EXAFS fitting parameters derived from fitting the spectra of Fe₀.₆₆Ca₀.₃₃CO₃ (initial and after flow) films; and Fe 2p½/h Ca 2p½/h and O 1s spectral fitting parameters (PDF)

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