Temporal evolution of sweet oilfield corrosion scale: Phases, morphologies, habits, and protection

Gaurav R. Joshi, Karyn Cooper, Xiangli Zhong, Anthony B. Cook, Ehsan A. Ahmad, Nicholas M. Harrison, Dirk L. Engelberg, Robert Lindsay

A B S T R A C T

Electrochemical measurements and substrate analysis have been employed to study the corrosion of iron in sweet solution (pH = 6.8, T = 80 °C) over a period of 288 h. Correlated with decreasing corrosion rate, diffraction, microscopy, and spectroscopy data reveal the evolution of adhered sweet corrosion scale. Initially, it is comprised of two phases, siderite and chukanovite, with the latter affording little substrate protection. Subsequently, as the scale becomes highly protective, siderite is the sole component. Notably, siderite crystals are concluded to display a somewhat unexpected habit, which may be a trigger for local breakdown of protective sweet scales.

1. Introduction

Sweet corrosion of the internal walls of oilfield infrastructure (e.g. pipelines) fabricated from carbon-steel is of huge concern in upstream oil and gas production [1,2]. This phenomenon is driven by the dissolution of CO₂(g) in H₂O(l) to form aqueous carbonic acid (H₂CO₃(aq)), supplying reactant(s) for the cathodic process [3–5]; the dissolution of iron (Fe(s) ➝ Fe²⁺(aq)) occurs at anodic sites [6]. In tandem with substrate degradation, adhered solid corrosion products may also form, which can significantly reduce the rate of corrosion and so increase structural integrity [7]. Given such functionality, significant effort has been applied to characterise this scale, including its composition and morphology (see, for example, Ref [8–12]). In an attempt to understand and potentially control, its properties. Here, we extend this work with a detailed study of the formation of a highly protective sweet scale, employing diffraction, microscopy, and spectroscopy techniques to reveal key scale characteristics.

Up until relatively recently, sweet corrosion scale was considered to be composed exclusively of crystalline siderite (FeCO₃), precipitating from solution due to near surface supersaturation of its ionic constituents (Fe²⁺(aq) and CO₂⁻(aq)) [8,9]; studies suggest that this process involves the initial nucleation of amorphous ferrous carbonate (AFC) [10–12] at the corroding surface. Some more contemporary work, however, reveals the existence of more complex multi-component sweet corrosion scales, with chukanovite (Fe₂(OH)₂CO₃) and/or magnetite (Fe₃O₄) coexisting alongside siderite [13–19]. Interestingly, these additional scale components are not always observed, which may simply be a result of the sensitivity of the analytical techniques applied. Alternatively, given the multi-dimensional nature of the parameter space for these experiments, such conflicting results may simply be a result of minor variations in experimental conditions, e.g. solution chemistry, flow and temperature, as well as substrate chemistry and microstructure.

In light of the above, the current study has targeted characterisation of sweet corrosion scale under tightly controlled conditions. Moreover, we have minimised system complexity as far as possible, including employing high purity iron as the substrate, as well as carefully regulating and monitoring solution conditions, e.g. [O₂(aq)]. Specifically, we have studied the corrosion scale formed on iron in CO₂-saturated aqueous solution (pH = 6.8, T = 80 °C) over a period of 288 h, using complementary characterisation techniques, i.e. grazing incidence X-ray diffraction (GIXRD) and Raman μ-spectroscopy to determine scale composition, and scanning electron microscopy (SEM), including focused ion beam (FIB) SEM, to determine scale morphology; corrosion rates were determined with linear polarisation resistance (LPR). Besides identifying the scale components formed under the current experimental conditions, thorough analysis of acquired data also provides fresh insight into the habits of scale crystallites, as well as their

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2. Experimental details

Discs (≈ 5 mm in depth) cut from high purity Fe rod (10 mm diameter, 99.99% C., Goodfellow; see Table S1 in Supplementary Material for a list of impurities) were employed as substrates (working electrodes) for this study. These samples were mounted in epoxy resin so as to expose one flat face (area ∼ 0.785 cm²), ground with a series of SiC papers (80 grit, 240 grit, 600 grit, 1200 grit, 2400 grit and 4000 grit), and stored in a desiccator until required. Immediately prior to employing a sample, it was once again ground with 4000 grit SiC paper, washed with deaerated ethanol, and dried under a flow of nitrogen gas. Electron microscopy confirmed that following this preparation procedure, the Fe surfaces were flat and largely featureless (see Fig. S1(a) in Supplementary Material). Surface etching, following 1-hour immersion in CO2-saturated deionised water (80 °C, pH 8.0), revealed the substrate microstructure. It consists of irregular shaped grains of ferrite with dimensions ranging from ∼ 50 μm to ∼ 500 μm (see Fig. S1(b) in Supplementary Material).

Electrochemical measurements were performed in a jacketed 1 L glass cell (Pine Instruments). The cell has seven entrance/exit ports located atop; the ports are ground glass sockets to allow the cell to be hermetically sealed during operation through the use of appropriate cone fittings. Three of these ports were used for the Fe working electrode (WE), platinum counter electrode (CE) and a silver/silver chloride reference electrode (RE); the latter was located in a separate vessel containing saturated KCl solution, and connected to the primary cell by means of a polymer gel electrolytical salt bridge (cotton thread soaked in KCl and coated with Agar gel, purchased from Labtec Corrosion Workshop Ltd) situated within a Luggin probe. A thermometer, dual gas inlet, and liquid in/out fittings were inserted into three other ports. The remaining port was used to accommodate a Liebig condenser to minimise solution loss during immersion experiments. A schematic diagram of this setup is displayed in Fig. 1(a).

Before inserting the Fe sample (WE) into the cell, the CO2-saturated solution was prepared. Initially, the jacketed cell was transferred into a glove box. Next, the glove box was sealed, and N2 (99.998% purity, BOC gases) was bubbled through the de-H2O. The CO2 was exhausted via the Liebig condenser through a Drechsel bottle inside the glove box. Next, the glove box was sealed, and N2 (99.998% purity, BOC gases) was flowed through it; the N2 (+ CO2) was vented to the laboratory through another Drechsel bottle. This procedure enabled CO2 dissolution into the solution in the cell to be minimised; empirically, we found that it was not possible to reproducibly achieve low [O2(aq)], i.e. < 10 μg/L, without the N2 atmosphere provided by the glove box.

[O2(aq)] was measured with an electrochemical oxygen sensor (Orbisphere A1100, Hach Lange).

Following optimisation of the CO2/N2 flows in/out of the cell/glove box, the solution in the cell was heated to, and maintained at, 80 ± 1 °C by circulating hot water through the cell’s jacket using a thermostatically controlled water bath (Grant Optima TC120) located outside of the glove box. Once this temperature had been achieved, NaHCO3 (Analytical Reagent Grade, Fisher Scientific) was added to the CO2-saturated solution to increase the pH to 6.80; a pH electrode (1043B, Hanna Instruments) was used for in situ pH determination. Subsequently, the CO2 bubbling was continued until measured [O2(aq)] became < 10 μg/L. At this juncture, the CO2 flow was switched from bubbling to blanket, i.e. the CO2 gas is simply flowed over the solution surface rather than bubbled through it. In accordance with a publication on the topic [20], we found 18–24 h of CO2 bubbling was required to reliably achieve [O2(aq)] < 10 μg/L.

Once the targeted [O2(aq)] (< 10 μg/L), pH (6.80), and temperature (80 °C) had all become stable, ∼ 5 mL aliquot of cell solution was withdrawn for determination of dissolved Fe2⁺ concentration ([Fe2⁺(aq)]) with inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300, Perkin Elmer, calibrated to provide a precision of ± 2.0 × 10⁻⁷ M). Subsequently, the Fe working electrode was inserted into the cell and electrochemical measurements were initiated, employing a computed controlled potentialstat (Modulab, Solartron Analytical). LPR (scan range ± 10 mV vs. open circuit potential (OCP), scan rate 1 mVs⁻¹) data were acquired each hour throughout the immersion; outside of these measurements the sample was allowed to remain at OCP.

At the end of the pre-determined immersion period, the iron sample was removed from the cell, and dried inside the N2 glove box. In addition, [O2(aq)] and pH were measured, and subsequent to stirring, ∼ 5 mL of solution was removed for [Fe2⁺(aq)] determination. Subsequently, the sample was removed from the glove box and stored under vacuum to minimise degradation (e.g. oxidation) prior to ex situ characterisation. To ascertain the temporal evolution of the substrate, a number of such immersion experiments were undertaken for a systematic series immersion times, i.e. 24 h, 72 h, 144 h, 216 h, and 288 h. For each immersion time, the experiment was repeated 2 or 3 times (except 216 h) using freshly prepared Fe samples, resulting in 11 independent immersion experiments, i.e. 2 × 24 h, 3 × 72 h, 3 × 144 h,
we have used this approach to obtain relative corrosion rates, working on similar sweet corrosion systems (see, for example, Ref. However, as other researchers have done previously including those statements is strictly only possible if both reactions obey Tafel kinetics. It should be noted that employment of the Stern-Geary relationship to derive corrosion rates from LPR measurements is accompanied by an uncertainty in the corrosion rate calculation. On this basis, we conclude that our approach is suitable for the purpose of the current study, i.e. it does not significantly impact on the reported corrosion rate trend and subsequently drawn conclusions.

Extracting values from Fig. 2, the corrosion rate decreases from

Table 1

<table>
<thead>
<tr>
<th>[O2(aq)] (μg/L)</th>
<th>pH</th>
<th>[Fe2+(aq)] (x 10⁻⁷ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start</td>
<td>7.0 ± 0.7</td>
<td>2.0 ± 1.4</td>
</tr>
<tr>
<td>End</td>
<td>8.0 ± 1.0</td>
<td>2.0 ± 1.5</td>
</tr>
<tr>
<td>[O2(aq)] (μg/L)</td>
<td>6.0 ± 3.3</td>
<td>7.0 ± 3.0</td>
</tr>
<tr>
<td>pH</td>
<td>8.0 ± 0.1</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>[Fe2+(aq)] (x 10⁻⁷ M)</td>
<td>7.5 ± 0.7</td>
<td>1.0 ± 0.1</td>
</tr>
</tbody>
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1 × 216 h, and 2 × 288 h).

Regarding ex situ substrate characterisation, composition was investigated with GIXRD on a Phillips X-pert diffractometer, using a Cu Kα (λ = 0.154 nm) source at an incidence angle of αi = 6°. This measurement geometry was employed to acquire data more sensitive to the near surface region of the substrates. Raman μ-spectroscopy was also used as a probe of surface phases. It was undertaken on a Renishaw 100 system μ-spectrometer, with a HeNe laser (λ = 633 nm) being employed as the radiation source (~ 2 mW power at the sample). The diameter of the beam at the sample was ~ 5 μm. Surface structure/morphology was imaged with a FEI Quanta 650 SEM. Cross-sectional SEM images perpendicular to the substrate surface were obtained through focused ion beam (FIB) milling (Ga ions), using a FEI Quanta 3D FIB-SEM.

3. Results and discussion

The values obtained for [O2(aq)], pH and [Fe2+(aq)] at the start and end point of each immersion time are listed in Table 1. From these data, it is clear that the target [O2(aq)] (< 10 μg/L) was consistently achieved. Concerning [Fe2+(aq)], this always increases by at least one order of magnitude from the start to the end of the immersion period. Given the corrosion exhibited by the substrate (see below), this is to be expected. As for pH, a starting value (pHstart) of 6.80 ± 0.02 was invariably obtained, but as the immersion time increased so too did the end pH (e.g. pHend = 6.91 ± 0.01 after 288 h of immersion). The origin of this small increase in bulk solution pH is most likely due to the concurrent increase in [Fe2+(aq)], as the maintenance of solution electroneutrality requires a simultaneous decrease in [H+(aq)] [21].

Lin-lin and log-lin plots in Fig. 2 show the corrosion rate of high purity iron as a function of immersion time in the CO2-saturated solution (T = 80 °C, pHstart = 6.80 ± 0.02) over 288 h. These corrosion rates and standard deviation errors have been determined from polarisation resistance (Rp) values extracted from LPR data acquired during the 11 independent immersion experiments. To obtain these corrosion rate values, a Stern-Geary coefficient (B) of 38 mV/decade was employed, which was determined from potentiodynamic polarisation (PDP) data (see Supplementary Material). Solution resistance (Rs), extracted from complementary high frequency EIS measurements, was also taken into account. It should be noted that employment of the Stern-Geary relationship to derive corrosion rates from LPR measurements is strictly only possible if both reactions obey Tafel kinetics. However, as other researchers have done previously including those working on similar sweet corrosion systems (see, for example, Ref. [22]), we have used this approach to obtain relative corrosion rates, and so a trend, as a function of time, accepting that there may be some systematic error in the corrosion rate calculation. On this basis, we conclude that our approach is sufficient for the purpose of the current study, i.e. it does not significantly impact on the reported corrosion rate trend and subsequently drawn conclusions.

Extracting values from Fig. 2, the corrosion rate decreases from 1.64 ± 0.35 mm/y at the start of immersion to 0.019 ± 0.002 mm/y at the end (288 h), which equates to a ~ 99% decrease in overall corrosion rate. Examining the lin-lin plot (Fig. 2(a)), the rate of corrosion rate decrease diminishes with time, i.e. the gradient decreases as a function of time. Indeed, towards the end of the 288 h immersion time, the corrosion rate variation becomes almost imperceptible in Fig. 2(a). As demonstrated by the log-lin plot (Fig. 2(b)), however, as 288 h of immersion is approached an absolute minimum in corrosion...
rate is not achieved; rather the corrosion rate is still noticeably decreasing. Accompanying this corrosion rate trend, there is an increase in OCP, as shown in Fig. 2(b). On the basis of previous work on carbon steel in sweet environments, such an increase in OCP may be interpreted as resulting from so-called ‘pseudo-passivation’ [23–25].

Given the observed variation in corrosion rate, together with the increase in OCP, it is almost certain that an increasingly protective corrosion scale is being formed throughout the 288 h of immersion. Direct evidence of the formation of adhered scale is provided by the SEM image displayed in Fig. 3. Acquired from a sample that has been immersed for 24 h (corrosion rate is 0.41 ± 0.10 mm/y), surface bound discrete crystallites are apparent, exhibiting two different habits, i.e. platy and equant. On the basis of earlier work [16,17], it is likely that these platy and equant crystals are chukanovite and siderite, respectively. Supporting evidence for this assignment is derived from Raman μ-spectroscopy data. The inset in Fig. 3 displays such spectra acquired from platy (blue line) and equant (red line) crystallites in the spectral region associated with the CO$_3^{2−}$ symmetric stretch ($ν_3$). Comparing these data with literature [26], the Raman shifts are consistent with the platy ($ν_1$ ~ 1068 cm$^{-1}$) and equant ($ν_1$ ~ 1084 cm$^{-1}$) crystals being chukanovite and siderite, respectively.

To gain insight into the temporal evolution of the adhered corrosion scale, Fig. 4 shows SEM images acquired after 24 h, 72 h, 144 h, 216 h and 288 h of immersion. These data indicate that the scale crystals become more densely packed with time, which is consistent with the decreasing corrosion rate assuming that the scale reduces the electroactive area for Fe corrosion. Moreover, the ratio of siderite (equant) to chukanovite (platy) crystals appears to increase with immersion time, with no chukanovite being detectable at 288 h of immersion. This finding suggests that pseudo-passivation is achieved only upon the formation of a dense interlocking siderite scale.

In addition to increasing packing density, another aspect of the siderite crystal temporal evolution is their variation in size. Inspection of the images in Fig. 4 suggests that they initially grow in size before subsequently becoming smaller. A more quantitative assessment of this trend has been determined from measurements of the size of 125 randomly sampled siderite crystals (5 crystals per SEM image, across 25 separate randomly acquired SEM images from a sample surface) for each immersion time. Fig. 5 shows these results, with both the mean size (circles) and the maximum - minimum size range (error bars) being plotted. Clearly, the mean siderite crystal size decreases to a maximum at 144 h of immersion (~ 15 μm) and then shrinks (~ 5 μm at 288 h).

Focusing on the habits of the scale crystals, a detailed survey of the adhered siderite indicates that it all adopts largely the same shape independent of immersion time. Simply referred to as equant above, a more complete description is a micro-faceted cylinder (diameter:height aspect ratio ~ 1) with trigonal-pyramidal caps. A schematic diagram of this habit is presented in Fig. 6(a). Facet orientations are labelled according to Ref. [27], which discusses isomorphous calcite crystals displaying a similar habit. Turning to the platy chukanovite crystals, Fig. 6(b) illustrates the adopted habit. Based on GIXRD data (see below), we propose that the large flat surfaces are potentially (021) oriented facets.

As demonstrated by the annotated diffractograms displayed in Fig. 7, GIXRD data also indicate the formation of chukanovite and siderite following substrate immersion. In this figure, representative data for each immersion time (i.e. 24 h, 72 h, 144 h, 216 h and 288 h) are shown, along with a diffractogram acquired from a polished sample (top right insert). As expected, the polished sample only exhibits peaks arising from the α-Fe substrate (ICDD-PDF 04-007-9753). In contrast, all of the immersed samples present additional peaks, which are assigned to either siderite (FeCO$_3$, a = 4.626 Å, c = 15.288 Å, γ = 120°; ICDD-PDF 00-029-0696) or chukanovite (Fe$_2$(OH)$_2$CO$_3$ a = 12.396 Å, b = 9.407 Å, c = 3.215 Å, β = 97.78°; ICDD-PDF 00-060-0353). The latter phase is only detected up to 144 h; it should noted that this result is in line with the SEM images (Fig. 4), except that chukanovite is only entirely absent from the scale after 288 h of immersion (Fig. 4(m), (n), (o)), which can be concluded to be simply due to a difference in technique sensitivities. These GIXRD data, which are all normalised to the intensity of the most prominent FeCO$_3$ peak (110) at 2θ = 32.0°, also indicate that the lateral coverage and/or scale thickness generally increases with immersion time, i.e. the signal from the Fe substrate is diminished at longer immersion times.

Concerning the diffraction signal arising from chukanovite in Fig. 7, it is interesting to note that the peak expected to be the most intense ((021) at 2θ = 33.9° [28]) is either absent or very weak. This result agrees with XRD data presented by Tanupabrungsun et al. [16], which show a low intensity (021) peak for a sweet corrosion scale formed after 24 h of immersion at 120°C. We suggest that this profile distortion is likely to be a result of both differential absorption of the X-ray beam and a degree of preferred orientation, arising from the platy habit of the crystals. On this basis, we suggest that the large flat surfaces are likely to be (021) oriented facets (as labelled in Fig. 6(b)).

Having established a comparable qualitative description of scaling from the SEM and GIXRD data (i.e. mixed siderite/chukanovite scale to siderite only at longer immersion times), Fig. 8 shows a more quantitative evaluation of the amount of adhered siderite, chukanovite, and siderite + chukanovite (total) scale as a function of immersion time. More specifically, the plot shows the variation in fractional scale coverage determined from SEM images using the point count method (see Supplementary Material for details of this approach). It is apparent that initially as the total scale coverage increases the corrosion rate decreases, indicating that the scale is offering protection to the substrate. However, even though the total fractional scale coverage is already ~ 1 after 72 h of immersion, the corrosion rate is still 0.21 ± 0.05 mm/y, i.e. it is significantly greater than the value at 288 h (0.019 ± 0.002 mm/y). Therefore, total scale coverage is seemingly not the key parameter in determining substrate protection. Examination of the coverage of individual scale components (siderite and chukanovite) in Fig. 8 offers further insight, as it can be seen that the increase in siderite coverage more or less tracks the decrease in corrosion rate. In contrast, the chukanovite coverage remains approximately constant from 24 h to 144 h of immersion, and subsequently decreases towards
zero. On this basis, it can be concluded that siderite is the primary source of substrate protection (pseudo-passivation), and that chukanovite crystallites do not act as a particularly significant physical/diffusion barrier to corrosion.

One further important aspect of scale morphology is thickness, which has been probed by FIB-SEM. Representative cross-sectional images of the scale for immersion times of 72 h, 144 h, 216 h, and 288 h are shown in Fig. 9, along with plan views of where the cross-sections were acquired. Comparing the various cross sections, it can be observed that the thickness of the scale does not vary greatly. This finding is consistent with the number of siderite layers remaining constant for all immersion periods, with only the lateral surface coverage and crystallite size varying. More explicitly, given the lateral dimensions of these siderite crystals, and their equant habit, the layer thickness, which is similar to the lateral size of the crystallites, indicates that there is always only a single layer of siderite crystals at the surface.

Further understanding of the scale morphology can be gained from more detailed examination of the cross sections in Fig. 9. For the images acquired after 72 h and 144 h of immersion (Fig. 9(b) and (d), respectively), both equant (siderite) and platy (chukanovite) crystallites are visible. Moreover, in the area primarily occupied by chukanovite, there is an associated void at the scale/substrate interface in each image. Assuming that they are not artefacts of sample preparation, such volumes may arise through poor scale adherence and/or corrosion undercutting the scale. This result is consistent with the deduction that chukanovite might not provide a particularly significant barrier to corrosion.

The cross section in Fig. 9(f), which was recorded following 216 h of immersion, again shows equant (siderite) and platy (chukanovite) crystallites. In this case, however, the platy phase appears to be sitting atop a well-adhered continuous layer of scale, which we assign to siderite. One may presume that this compact siderite layer is the source of substrate protection (0.055 ± 0.008 mm/y) at 216 h. After 288 h of immersion, as shown in Fig. 9(h), the scale remains continuous and well adhered to the Fe substrate, consistent with the measured corrosion rate (0.019 ± 0.002 mm/y). It should be noted that although we indicate that there is a continuous layer of siderite after 216 h and 288 h of
immersion, there may still be gaps between the individual crystallites, which cannot be resolved with the FIB-SEM.

Summarising the above results, a cartoon of the temporal evolution of the sweet scale formed in this study and associated corrosion rates is presented in Fig. 10. In brief, the scale is initially composed of both siderite and chukanovite crystallites, which increase in coverage with time. From 72 h onwards the substrate is essentially entirely covered with scale, although the corrosion rate continues to decrease. This phenomenon is correlated with the loss of chukanovite from the scale, leaving siderite as the only protective phase.

In addition to facilitating the snapshots of scale evolution displayed in Fig. 10, a number of topics worthy of further examination emerge from the results described above. Firstly, the reasons for the appearance, and subsequent disappearance, of chukanovite as a sweet scale component deserve consideration. As mentioned in the Introduction, this phase has previously been identified in such scales [13-18], but is not always apparent. Thus it is pertinent to discuss the likely key parameters leading to its precipitation. Previous studies report that low
[O_2(aq)], alkaline pHs, and significant concentrations of dissolved carbonate species (H_2CO_3/HCO_3^-/CO_3^{2-}) tend to favour chukanovite precipitation [26,28,29]. Moreover, Azoulay et al. [30] indicate that the ratios R = [Fe^{2+}(aq)]/[OH^- (aq)] and R' = [CO_3^{2-}(aq)]/[OH^- (aq)] are central to the favourability of a chukanovite formation. Specifically, they conclude that there is a preference for chukanovite precipitation over a range of ratio values in the vicinity of R = 1 and R' = 0.5; R = 1 and R' = 0.5 are ideal ratios in that they match the stoichiometry of chukanovite (Fe_2(OH)_2CO_3).

Given the above, we suggest that the appearance of chukanovite, alongside siderite, in our sweet scale results from corrosion related reactions that drive near surface chemical speciation towards that required for precipitation of this phase. As proposed by Ingham et al. [11], it may be that the presence of sufficient Fe^{2+}(aq) favours the formation of amorphous ferrous hydroxide-carbonate (AFHC), in tandem with AFC, leading to the nucleation of crystalline chukanovite, as well as siderite. Also, variations in interfacial pH may lead to the formation of significant concentrations of specific Fe^{2+}(aq) complexes, such as [Fe(H_2O)_6(OH)]^{+}(aq), favouring the growth of chukanovite, e.g.

\[ n\text{Fe}_2\text{(OH)}_2\text{CO}_3(s) + 2\text{[Fe(H}_2\text{O)}_6\text{(OH)}]\text{]}^{+}(aq) + \text{CO}_3^{2-}(aq) \rightarrow (n+1) \text{Fe}_2\text{(OH)}_2\text{CO}_3(s) + 10\text{H}_2\text{O} \]  

(1)

Such local chemistry may be particularly likely in the current immersion experiments as there is negligible solution flow, favouring the development of near surface chemical speciation gradients, both parallel and perpendicular to the substrate surface. Interestingly, chukanovite has been observed in other sweet corrosion studies, where local interfacial chemistry is almost certainly highly influential, e.g. under a sand deposit [17], at a weld joint [19], and upon anodic polarisation of the substrate [18].

Turning to the subsequent disappearance of chukanovite as the immersion time increases, this phase may simply dissolve as the surrounding solution becomes under-saturated with respect to chukanovite, i.e.

\[ \text{Fe}_2\text{(OH)}_2\text{CO}_3(s) + 10\text{H}_2\text{O} \rightarrow (n+1) \text{Fe}_2\text{(OH)}_2\text{CO}_3(s) + 10\text{H}_2\text{O} \]  

(2)

where SI_{chuk} is the chukanovite saturation index, and K_{sp(chuk)} is the solubility product of chukanovite.

Alternatively, given that chukanovite is thermodynamically metastable with respect to siderite [30], it may be that, even though the solution remains supersaturated with respect to chukanovite (SI_{chuk} > 0), there is a time-dependent transformation to the more stable phase. The feasibility of this route to siderite is supported by studies of the precipitation of the structurally analogous magnesium carbonate, magnesite (MgCO_3) [31,32]. Data from this latter system indicate that, under some conditions, magnesite can form via a metastable hydroxide-carbonate, namely hydromagnesite (Mg_2(OH)_2(CO_3)\_4(4H_2O)); the metastable hydromagnesite is also structurally similar to chukanovite (see Refs [33–35]).

Focusing on the role of chukanovite in substrate protection, as demonstrated above, this phase does not directly impede corrosion to a significant extent. As a result, one could conclude that chukanovite is merely a coincidental transient scale component, i.e. it precipitates and then dissolves due to spatio-temporal variations in interfacial chemistry, without impacting upon the formation of the more protective siderite scale. Conversely, it could be that the chukanovite either hastens or hinders the kinetics of the growth of the ultimate siderite scale, although it is of itself not protective. Based on data presented here, we speculate the latter scenario, i.e. the persistence of metastable chukanovite as a scale component for up to 216 h kinetically impedes the formation of the pseudo-passive siderite-only corrosion scale.

Concerning siderite, both crystal habit and size variation are topics of particular note. With regards to the former, as illustrated in Fig. 6(a), these crystallites are micro-faceted cylinders with trigonal-pyramidal caps. Initially, it was supposed that this crystal shape was perhaps somewhat anomalous, resulting from our particular experimental setup/procedures, as the lowest energy equilibrium shape is anticipated to be rhombohedral with (104) oriented facets [27]. Reviewing previous literature, however, indicates that this habit is apparent in images...
of other sweet scales [36–38], but has simply not been explicitly identified to date, i.e. the micro-faceted cylinder with trigonal-pyramidal caps is quite a typical siderite habit reported in sweet corrosion scales.

As to the origin of this habit, it should be noted that the external geometry exhibited by a crystallite can be understood either as an approximation to an equilibrium morphology determined by the surface formation free energy of each facet, or as the result of differences in the growth velocity of facets in the attachment energy model; in growth from a supersaturated solution of the crystallite ions in perfect equilibrium the two models predict the same habit. Additional species at the growth interface, however, can alter surface free energies and thus kinetically accelerate or inhibit the growth of particular facets. Assuming the validity of the facet assignments in Fig. 6(a), the presence of the (hk0) micro-facets, which are expected to have high surface energies [27], most likely results from surface adsorption of dissolved species, e.g. HCO$_3^-$ (aq) or CO$_2$(aq). We speculate that subsequent destabilisation of these micro-facets through surface desorption, due to changes in solution chemistry, could be a trigger for local breakdown of a pseudo-passive siderite scale.

Turning to the variation in the size of the siderite crystallites with immersion time, as shown in Fig. 5, following an increase in mean size up to 144 h, there is significant shrinkage. Again, similar behaviour has been observed in some previous sweet corrosion studies [36,39], but has not been the subject of much discussion. Initial coarsening is consistent with classical Ostwald ripening [40], where smaller crystals are essentially consumed through dissolution and re-deposition onto larger crystals. The origin of the subsequent size decrease is less clear, although this phenomenon is not unprecedented, as there are examples of so-called reverse coarsening (or reverse Ostwald ripening), where smaller crystals grow at the expense of larger ones [41–43]. Assuming that thermodynamics govern this process, the growth in the population of small crystallites must be driven by a significant reduction in their surface (interface) energy relative to the bulk energy, leading to small sizes with larger surface area/bulk crystal volume ratios [42]. Previously, it has been concluded that such changes in stability can be induced by surface adsorbates [43]. Here, given that the siderite scale is substrate adhered and densely-packed after 288 h (Fig. 4), we speculate that the reverse coarsening is induced due to variations in substrate-crystallite or inter-crystallite interface energies as a function of size. We note that, as well as established crystallites undergoing reverse coarsening, there must also be nucleation of additional siderite to achieve the full substrate coverage that we observe after 288 h of immersion.

4. Conclusions

In summary, the temporal evolution, over 288 h of immersion, of a sweet corrosion scale formed in CO$_2$-saturated water (pH = 6.8, T = 80 °C) is characterised in terms of composition, morphology, and protection. Electrochemical measurements indicate the gradual formation of a pseudo-passive surface, displaying a very low corrosion rate. GIXRD, Raman μ-spectroscopy, and (FIB) SEM data demonstrate that this pseudo-passivation is a result of the formation of a densely packed scale, comprising of a single layer of siderite crystallites. For shorter immersion times, the scale is found to also contain chukanovite, which provides little direct substrate protection. One particularly notable insight is the explicit identification of the habits of the chukanovite and siderite crystallites, with the latter forming micro-faceted cylinders with trigonal-pyramidal caps. Of further note is the size evolution of the siderite crystallites, which display reverse coarsening (i.e. they shrink) with longer immersion times, after initially undergoing classical Ostwald ripening.

Data availability

The raw and processed data required to reproduce these findings are available to download from https://doi.org/10.17632/3fbzkp6fvc.2 [44].
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