



	<b>Experiment title:</b> <b>In Situ Characterization of Sweet Oilfield Corrosion Scaling as a Function of Salinity: Further Measurements</b>	<b>Experiment number:</b> 28-01-1196
<b>Beamline:</b> BM28	<b>Date of experiment:</b> from: 24/01/2018 to: 29/01/2018	<b>Date of report:</b> 27/05/2016
<b>Shifts:</b> 15	<b>Local contact(s):</b> Oier Bikondoa	<i>Received at ESRF:</i>
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## Report:

Affordable, secure, net-zero energy is possibly the greatest challenge of the age. One issue that plagues this industry is infrastructure degradation through corrosion, which can undermine economic viability, as well as increase the probability of failure. On this basis, immense effort is being applied to explore routes to control this phenomenon with an increasing emphasis on lower environmental impact solutions, such as harnessing naturally formed corrosion scales. For instance, it is proposed that the barrier properties of scales formed on carbon steel in aqueous CO<sub>2</sub>-saturated (sweet) environments, encountered in geothermal power plants, carbon capture facilities, and oil production, can mitigate corrosion. In this experiment, we have tested this hypothesis, providing evidence to suggest that even *intact* sweet corrosion scales may be undermined by spatially localised corrosion, so that they cannot be relied upon alone for structural integrity.

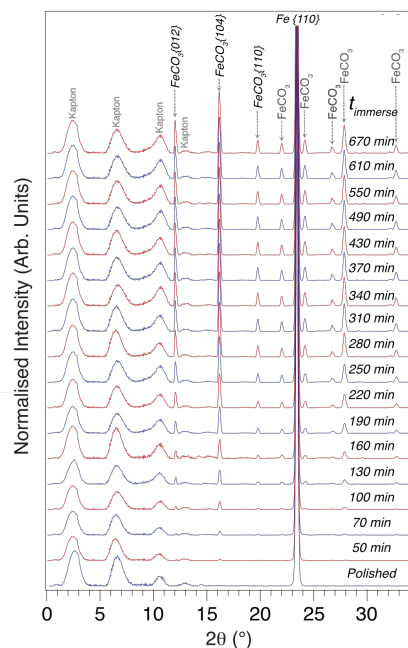
Sweet corrosion of carbon steel results from the presence of carbonic acid (H<sub>2</sub>CO<sub>3</sub>(aq)), which is formed through reaction of H<sub>2</sub>O with dissolved CO<sub>2</sub>. This aqueous species underpins the cathodic corrosion reaction (H<sub>2</sub>(g) evolution), driving anodic dissolution of the metal atoms (Fe(s) to Fe<sup>2+</sup>(aq)). Concurrent with substrate dissolution, precipitation of surface adhered siderite (FeCO<sub>3</sub>) crystallites also often occurs, which has been shown to significantly modify the rate of corrosion. In particular, *operando* studies, where X-ray scattering data are acquired in tandem with electrochemical measurements, have reported that FeCO<sub>3</sub> reduces corrosion, offering substantial substrate protection.

One potential deficiency of the *operando* studies of sweet corrosion scaling is the surface area used for calculation of the corrosion rate. It has been assumed to be equal to the initial geometric area of the sample that is exposed to solution, and not to vary as a function of immersion time ( $t_{immerse}$ ). In reality, an increasingly smaller proportion of the surface will be electrochemically active as the insulating FeCO<sub>3</sub> scale grows across the substrate. Consequently, the anodic dissolution rate of the remaining active area may be significantly underestimated in previous *operando* studies, leading one to misjudge the degree of scale-induced protection.

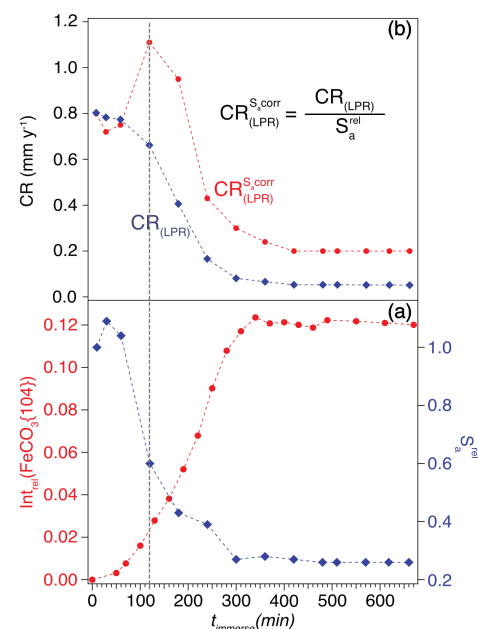
We have examined this important topic through combining grazing incidence X-ray diffraction (GIXRD) with electrochemical measurements, i.e., linear polarisation resistance (LPR) and electrochemical impedance spectroscopy (EIS). *Operando* data were acquired as a function of  $t_{immerse}$ , with the electrochemically active surface area being obtained from EIS. For these measurements, which were undertaken on the XMaS beamline (BM28), a custom-made electrochemical cell, allowing both GIXRD and electrochemical monitoring, was employed. A photon energy of  $h\nu = 15$  keV, and an incidence angle ( $\alpha_i$ ) of 3° were used for data acquisition.

Figure 1 displays a series of GIXRD diffractograms, acquired as a function of immersion time from a Fe sample submerged in the sweet solution of interest, i.e., pH = 6.80 ± 0.05, T = 80 ± 3°C, [O<sub>2</sub>(aq)] < 20 ppb, P<sub>tot</sub> = 1.01 bar, and P<sub>CO<sub>2</sub></sub> = 0.54 bar. Immersion results in the appearance of a number of peaks, all assigned to FeCO<sub>3</sub>, which initially increase in intensity with time.

The relative FeCO<sub>3</sub>{104} diffraction peak intensity (Int<sub>rel</sub>(FeCO<sub>3</sub>{104})) and the relative electrochemically active surface area (S<sub>a</sub><sup>rel</sup>) as a function of t<sub>immerse</sub> are compared in Figure 2 (a); the latter has been extracted from EIS data. The profiles are consistent with electrochemically inert FeCO<sub>3</sub> scale blocking corrosion sites.



**Figure 1** A series of diffractograms, displayed as a function of immersion time, from a Fe sample submerged in a sweet solution at pH = 6.80 ± 0.05, T = 80 ± 3°C, and [O<sub>2</sub>(aq)] < 20 ppb. The bottommost diffractogram is of a polished substrate, acquired prior to immersion.



**Figure 2** (a) Plots of Int<sub>rel</sub>(FeCO<sub>3</sub>{104}) (red circles) and S<sub>a</sub><sup>rel</sup> (blue diamonds) as a function of t<sub>immerse</sub>. (b) Plots of CR<sub>(LPR)</sub><sup>S<sub>a</sub><sup>corr</sup></sup> (red circles) and CR<sub>(LPR)</sub> (blue diamonds) as a function of t<sub>immerse</sub>. The vertical dashed grey line indicates the CR<sub>(LPR)</sub><sup>S<sub>a</sub><sup>corr</sup></sup> profile maximum.

The impact of the variation in S<sub>a</sub><sup>rel</sup> on calculated corrosion rate is illustrated in Figure 2 (b), which shows the temporal evolution of corrosion rate determined from LPR measurements both with (CR<sub>(LPR)</sub><sup>S<sub>a</sub><sup>corr</sup></sup>) and without (CR<sub>(LPR)</sub>) correction for S<sub>a</sub><sup>rel</sup>. Clear differences are apparent, indicating the importance of considering S<sub>a</sub><sup>rel</sup> for assessing the protection offered by electrochemically inert corrosion scale. Most notably, CR<sub>(LPR)</sub><sup>S<sub>a</sub><sup>corr</sup></sup> stabilises at a value of ~ 0.2 mm y<sup>-1</sup>, which is almost half an order of magnitude greater than the uncorrected corrosion rate (CR<sub>(LPR)</sub> ~ 0.05 mm y<sup>-1</sup>). Furthermore, in contrast to the CR<sub>(LPR)</sub> data, CR<sub>(LPR)</sub><sup>S<sub>a</sub><sup>corr</sup></sup> exhibits a peak at t<sub>immerse</sub> ~ 120 min. A previous *operando* study, where measurements were made with the sample anodically polarised, has attributed a similar peak in current density to *direct electrochemical formation* of FeCO<sub>3</sub>, as the peak maximum coincides with the highest scale growth rate. Here, as indicated by the vertical dashed grey line superimposed on Figure 2, the CR<sub>(LPR)</sub><sup>S<sub>a</sub><sup>corr</sup></sup> peak maximum (t<sub>immerse</sub> ~ 120 min) occurs somewhat prior to the maximum in scale growth kinetics at t<sub>immerse</sub> ~ 220 min. This observation suggests another source for the peak at t<sub>immerse</sub> ~ 120 min in the current case, e.g., local variation in interfacial chemistry as scale grows.

In summary, through combined *operando* GIXRD/LPR/EIS measurements, the temporal evolution of the growth and corrosion control properties of a FeCO<sub>3</sub> scale formed on high purity iron in sweet solution has been elucidated. It is demonstrated that estimation of the relative electrochemically active surface area with electrochemical impedance spectroscopy has enabled more robust calculation of localised corrosion rates, demonstrating that such scales are less protective than often perceived previously. These results have key implications for the use of naturally occurring FeCO<sub>3</sub>, and other surface scales, as a barrier to corrosion. In our opinion, even in their *intact* state (i.e., ignoring local physical/chemical breakdown), these scales are highly likely to be, at best, semi-protective, and *in situ* chemical treatment and/or surface pre-treatment is required to guarantee their reliability.

A manuscript based on these results has been submitted to *ACS Applied Materials and Interfaces*.