

Corrosion protection through naturally occurring films: New insights from iron carbonate

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Abstract:

Despite intensive study over many years, the chemistry and physics of the atomic level mechanisms that govern corrosion are not fully understood. In particular, the occurrence and severity of highly localised metal degradation cannot currently be predicted and often cannot be rationalised in failure analysis. We report a first principles model of the nature of protective iron carbonate films coupled with a detailed chemical and physical characterisation of such a film in a carefully controlled environment. The fundamental building blocks of the protective film, siderite (FeCO_3) crystallites, are found to be very sensitive to the growth environment. In iron-rich conditions, cylindrical crystallites form that are highly likely to be more susceptible to chemical attack and dissolution than the rhombohedral crystallites formed in iron-poor conditions. This suggests that local degradation of metal surfaces is influenced by structures that form during early growth and provides new avenues for the prevention, detection and mitigation of carbon steel corrosion.

Introduction:

Corrosion is a persistent problem across many industries and public services, costing \$2.5 trillion dollars per annum globally while also risking individual safety and environment harm¹. Much of this cost arises due to the ubiquitous use of carbon steel as an engineering material, despite its inherently weak resistance to corrosion. Oil and gas transmission pipelines, for example, undergo chemical attack due to the dissolution of CO₂ into the brine that flows along with hydrocarbons^{2,3}. Similarly, the transport of hydrogen, as proposed in a renewable energy future, leads to pipeline breakdown due to the diffusion of hydrogen into the metal⁴. In such systems, localised degradation is the most difficult to prevent, as it often arises from the local breakdown of protective films formed from inhibitors, coatings or natural corrosion products, which is difficult to predict, monitor, or control⁵. This vulnerability exposes facilities to the risk of sudden and catastrophic equipment failure, and so a mechanistic understanding of the process is highly desirable.

A key impediment to the identification of drivers for such localized corrosion is the absence of studies focusing on the molecular structure and reactivity of naturally-forming protective films, which are commonly referred to as corrosion scales. In the dissolved CO₂ regime, it is well known^{6–8} that these scales are composed of densely packed siderite (FeCO₃) crystallites (Fig. 1), but further details of these building blocks are scarce, **despite being observed widely in the recent literature**^{8–11}. Only in the past year has the habit, namely the characteristic external shape, of these FeCO₃ crystallites been explicitly described, and even then only qualitatively¹². In contrast to the anticipated rhombohedral geometry, a more complex 3D shape was reported, comprising a micro-facetted cylinder with trigonal-pyramidal caps, as illustrated in the inset in Fig. 1 (b).

To reveal the origin of the FeCO₃ habit, which is likely to play a central role in the protective properties of the scale, we have developed a theoretical model using first principles thermodynamics based on density functional theory (DFT). The model predicts a crystallite habit in excellent agreement with that observed experimentally and provides a detailed description of the

atomistic and electronic structure of the exposed surfaces. The occurrence of this distinctive habit is likely to be sensitive to many environmental factors and here we demonstrate, with the support of experimental measurements, that it can be controlled by the local concentration of Fe^{2+} cations. This development may prove to be critical towards the design of new corrosion protection strategies as each habit possesses specific surface chemistries which, as we will discuss below, offer different levels of corrosion protection.

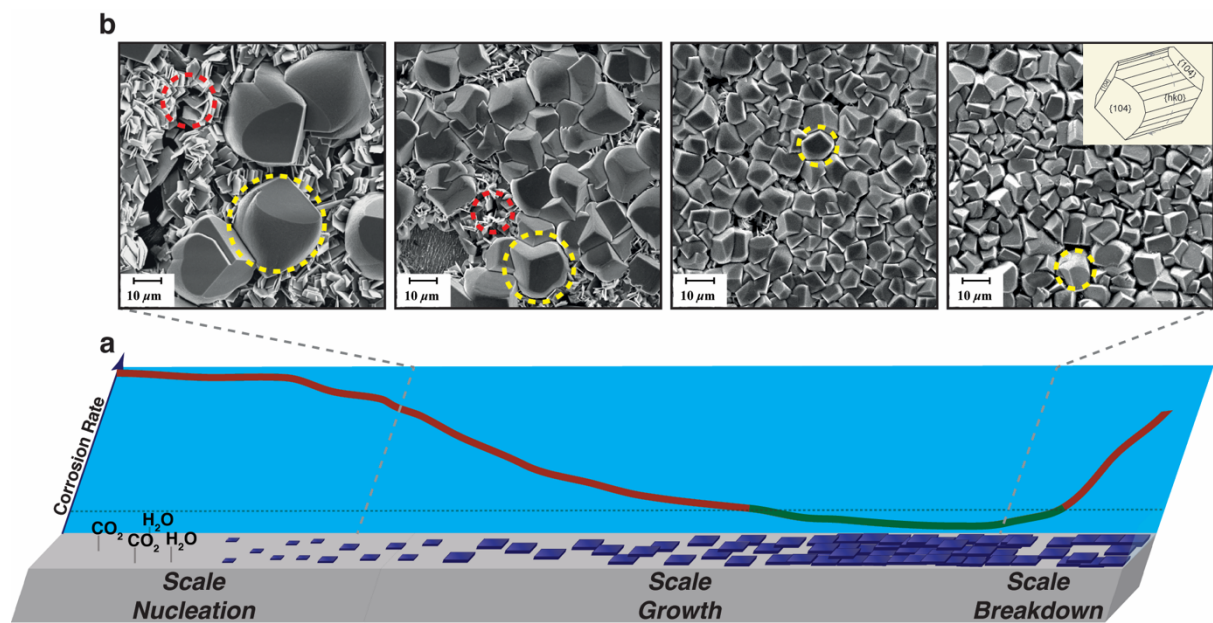


Fig. 1. Evolution of a CO_2 corrosion product film. (a) Illustration of the lifecycle of a CO_2 corrosion product film, and the accompanying corrosion rate. For long-term structural integrity, the corrosion rate should be maintained in the green zone, i.e. a protective film is required to form and remain. (b) Scanning electron microscopy (SEM) images showing the growth of a densely packed, protective corrosion product film on iron in CO_2 -saturated water at 80°C and pH 6.8. Primarily, the film consists of siderite crystallites (highlighted by broken yellow circles), which are micro-faceted cylinders with trigonal-pyramidal caps; the inset in the right hand SEM image shows a schematic of the habit, including orientation of exposed facets, as indicated previously¹². Plate-like crystallites (highlighted by broken red circles), observed during the earlier stages of film growth, have been identified as chukanovite ($\text{Fe}_2(\text{OH})_2\text{CO}_3$)¹².

Results and Discussion:

Following initial validation of the modelling approach through application to bulk FeCO_3 , a hierarchical methodology was applied to select a number of likely low energy FeCO_3 surfaces^{13,14}. Both stoichiometric (S) and non-stoichiometric (NS) terminations were identified as candidate surfaces, where S (NS) surfaces retain (lose) bulk atomic ratios in the topmost layers. For each candidate, DFT calculations were employed to identify the most stable atomic configuration, allowing determination of the surface free energy of formation; details of surface selection and atomic structure are provided in the Supporting Information and Tables S1-S7. A plot of the surface free energies of formation as a function of the relative chemical potential of iron ($\Delta\mu_{\text{Fe}}$) is displayed in Fig. 2; the range of $\Delta\mu_{\text{Fe}}$ displayed corresponds to a variation from Fe-poor to Fe-rich conditions (as detailed in the Supporting Information). The surface free energies of S-terminations are invariant, whereas those of NS-terminations depend strongly on $\Delta\mu_{\text{Fe}}$. It is, therefore, expected that the crystal habit also varies with $\Delta\mu_{\text{Fe}}$.

The *ab initio* predicted crystal habits, generated using a Wulff construction¹⁵, are shown at the top of Fig. 2 for two distinct values of $\Delta\mu_{\text{Fe}}$. In iron poor conditions ($\Delta\mu_{\text{Fe}} = -5.95$ eV), a near perfect rhombohedral habit, dominated by S{104} surfaces, is predicted, with a minor contribution from NS{001} surfaces at opposing corners. Moving to iron rich conditions ($\Delta\mu_{\text{Fe}}$ to -4.95 eV), a significantly different habit is predicted, comprising a hexagonal cylinder of NS{110} surfaces capped top and bottom with trigonal pyramids of S{104} surfaces. This change is driven by NS{110} becoming the most thermodynamically favoured surface under more Fe-rich conditions (Fig. 2), which is itself a result of this surface being able to incorporate an excess of iron as Fe coordination drops to Fe-O_4 from the Fe-O_5 of the S{104} surface.

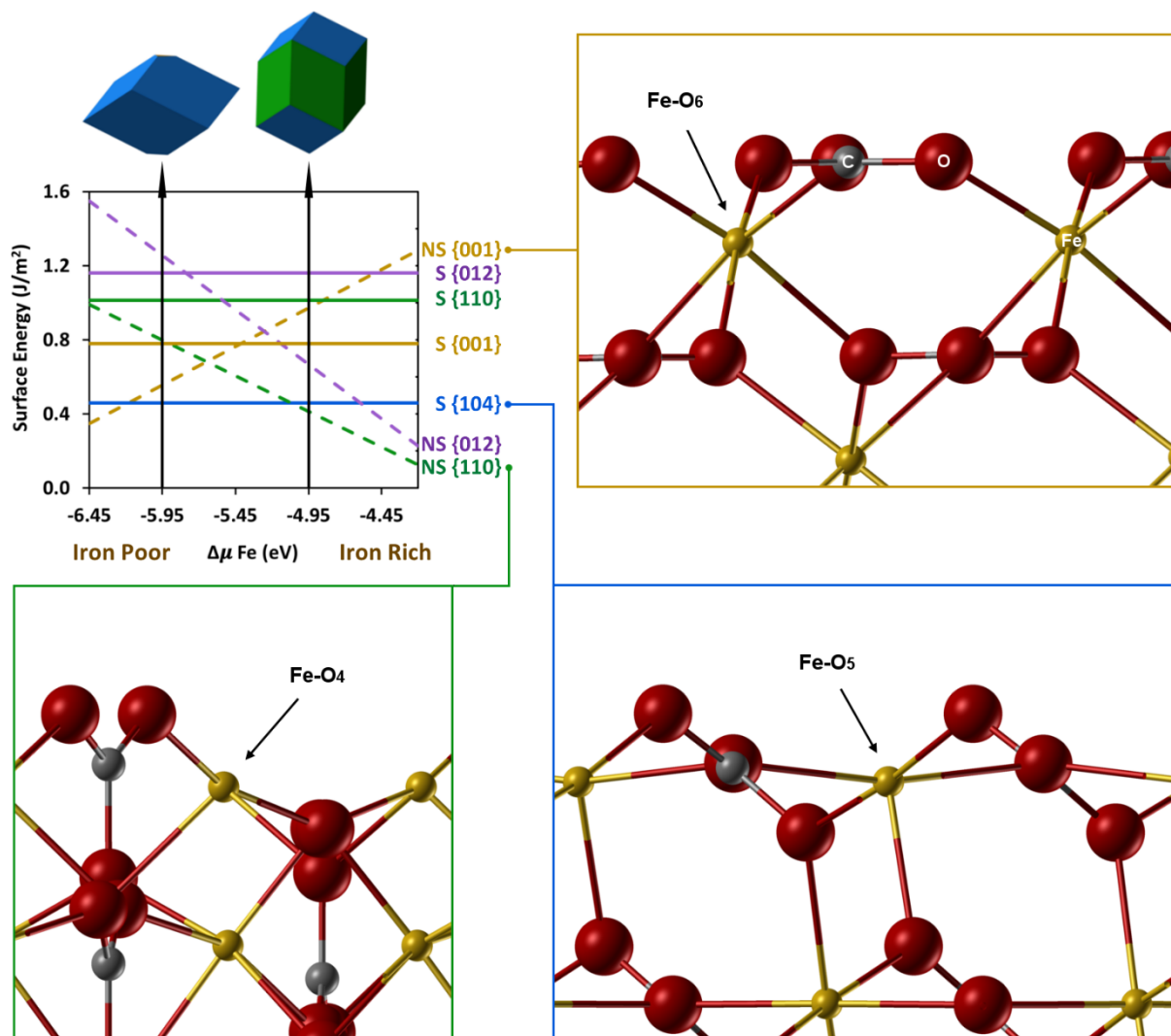


Fig. 2. Ab initio Modelling. The computed surface free energies of formation of stoichiometric (S) and non-stoichiometric (NS) FeCO_3 surfaces plotted as a function of $\Delta\mu_{Fe}$, with $\Delta\mu_{O_2} = -0.46$ eV (equivalent to $O_2(aq) < 10$ ppb to mimic an oilfield solution environment¹²). Predicted FeCO_3 equilibrium crystal habits, at $\Delta\mu_{Fe} = -5.95$ eV and $\Delta\mu_{Fe} = -4.95$ eV, are depicted at the top-left of the figure with facet colours representing the crystallographic directions indicated in the surface energy plot. The surface structures that manifest in the predicted habits are provided for comparison, highlighting the change in Fe coordination at the terminations.

At $\Delta\mu\text{Fe} = -4.95$ eV, the predicted habit closely resembles that typically observed (Fig. 1); the difference in cylindrical curvature is almost certainly simply attributable to only considering one of the many possible $\{hk0\}$ -type surface (NS{110}) in the calculations. Hence, DFT modelling, even though it is conducted *in vacuo*, reproduces the in-solution habit remarkably well. Moreover, the coincidence of the *ab initio* habit with experiment at this iron-rich value of $\Delta\mu\text{Fe}$ is seemingly consistent with there being a significant concentration of $\text{Fe}^{2+}(\text{aq})$ in the vicinity of a corroding substrate; $\Delta\mu\text{Fe}$ can be considered to be equivalent to the concentration of Fe^{2+} ions in solution, i.e. the $\text{Fe}^{2+}(\text{aq})$ concentration increases with $\Delta\mu\text{Fe}$ from left ($\text{Fe}^{2+}(\text{aq})$ -poor) to right ($\text{Fe}^{2+}(\text{aq})$ -rich) in Fig. 2.

The predicted change in habit with the local concentration of $\text{Fe}^{2+}(\text{aq})$ suggests that there will be a significant difference in the FeCO_3 crystallites growing on a corroding (iron) and a non-corroding polytetrafluoroethylene (PTFE) substrate. Such precipitates were formed by immersion in CO_2 -saturated ($\text{O}_2(\text{aq}) < 10$ ppb) deionized H_2O at 80°C and pH 6.8 for 24 h. 10 mM $\text{FeCl}_2(\text{aq})$ was added to the solution to provide an extrinsic source of $\text{Fe}^{2+}(\text{aq})$. The resulting crystallite habits are compared in Fig. 3. For the non-corroding PTFE substrate, where the only source of $\text{Fe}^{2+}(\text{aq})$ is the $\text{FeCl}_2(\text{aq})$, rhombohedra are observed. In contrast, the habit in Fig. 1, a micro-faceted cylinder with trigonal pyramidal caps, is maintained on the corroding iron. Given that these two scenarios represent $\text{Fe}^{2+}(\text{aq})$ -poor and $\text{Fe}^{2+}(\text{aq})$ -rich environments, respectively, these images strongly suggest that the *ab initio* model has correctly identified the S{104} and NS{110} surfaces and their contributions to the crystal habit. It also confirms that the habit can be controlled by the local $\text{Fe}^{2+}(\text{aq})$ concentration.

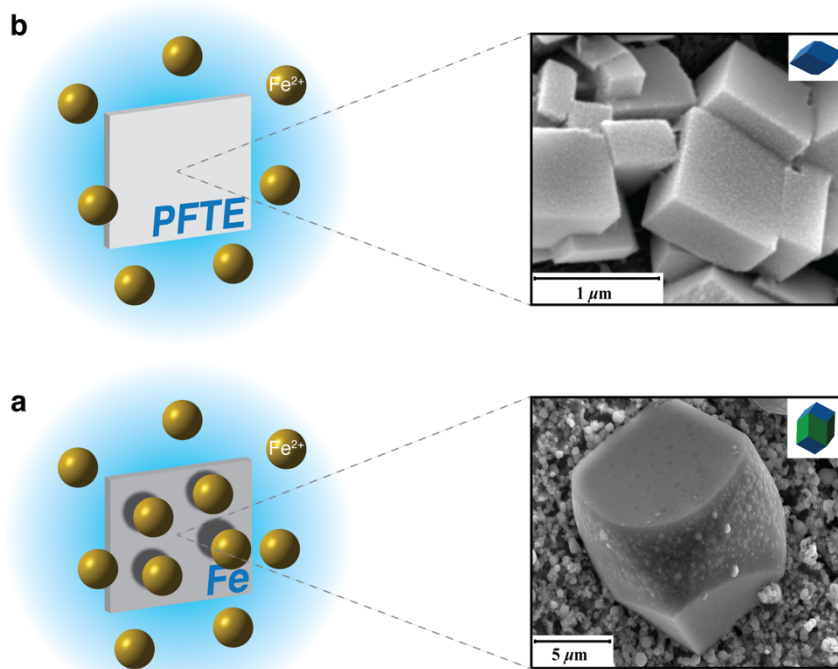


Fig. 3. Impact of substrate on FeCO_3 habit. SEM of FeCO_3 crystallites formed on (a) iron and (b) PTFE after 24 hours of immersion in CO_2 -saturated 10 mM FeCl_2 solution at 80°C and pH 6.8. For the iron, as shown in the illustrations to the left, $\text{Fe}^{2+}(\text{aq})$ cations are derived from both $\text{FeCl}_2(\text{aq})$ and substrate corrosion. Insets in SEM images display the corresponding predicted crystallite habits for iron poor (top) and iron rich (bottom) conditions.

This variation in crystallite habit from the iron-rich to iron-poor conditions is likely to be a critical factor in determining the corrosion protection properties of a scale, as it strongly influences crystallite packing and grain boundary energetics. In addition, the atomistic and electronic structure of the exposed surfaces will underpin chemical reactivity, e.g. interactions with other solutes and chemical inhibitor species. As such, it is important to examine the predicted surface structures involved in more detail. The chemical reactivity of the individual surfaces towards any chemical inhibitor or scale stabilizing species can be inferred from analysis of their computed electronic structure and 3D charge density. The former reveals the energy alignment of surface localized states that relates to the tendency of the surface reaction sites towards oxidation or reduction. The latter

allows one to visualize the spatial distribution of the states, revealing both their availability for hybridization and any steric hindrance for potential reactants.

Focusing on the S{104} and NS{110} surfaces of FeCO_3 , it is found that the former is likely to be relatively unreactive due to a lack of surface localized electronic states (Fig. 4). In contrast, the NS{110} surface (Fig. 4) shows the presence of several surface localized states below the bulk conduction band minimum (bCBM, 3.7 eV). These electronic states, which lie at 2.4 eV, 2.8 eV and 3.15 eV above the Fermi level (E_f), may be characterized as electron acceptor states, which increase the likelihood of the reaction site undergoing reduction. From the atomic structure of the surface (Fig. 4) it is evident that among these states only the O electron acceptor states centred at 2.8 eV are easily accessible to reactants as they originate from the exposed bi-coordinate O ions located in the surface troughs. The 3D charge density of these acceptor states (Fig. 4) is characteristic of a combination of O-2p orbitals, and form a π overlap interaction with the acceptor states of the adjacent subsurface Fe ion, which are themselves characteristic of a combination of Fe-3d orbitals (Fig. 4). It is likely that this interaction will weaken upon the attack of electron donor species that can form strong σ type bonds with the O-2p orbitals. This termination of the NS{110} surface could therefore readily become decorated by reducing species such as electron donor inhibitors, or otherwise be easily reconstructed or destabilized through strong surface-molecule reactions.

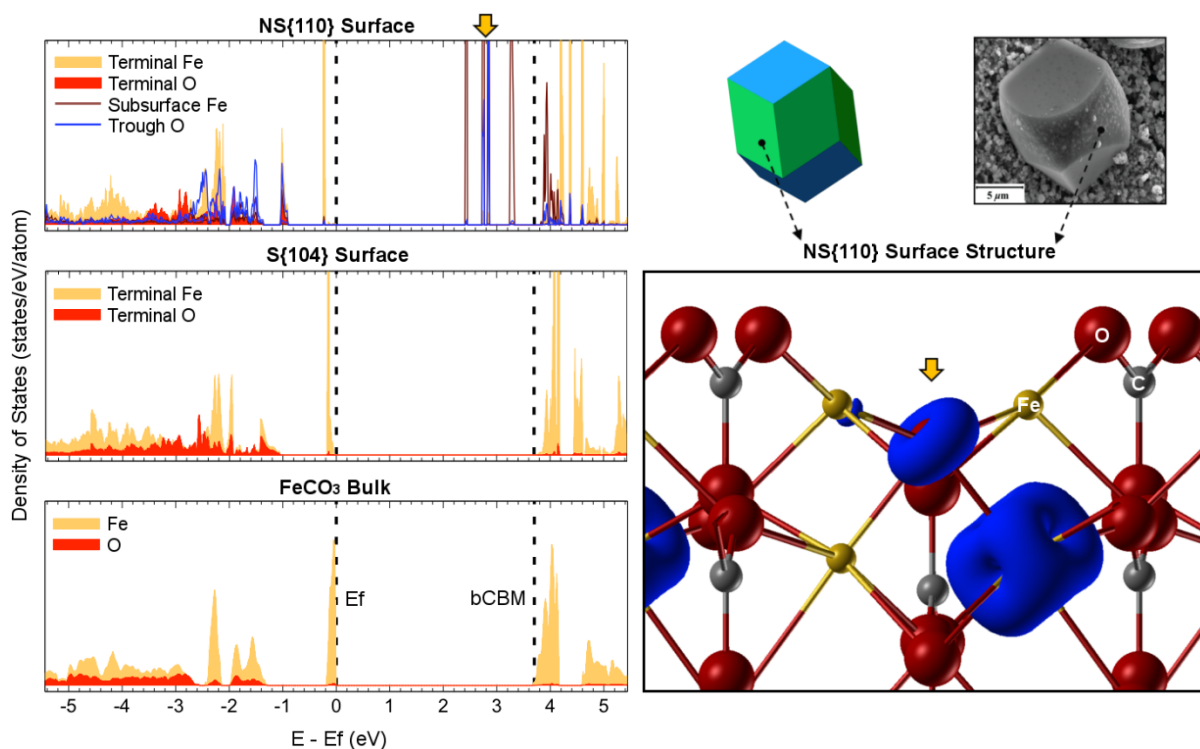


Fig. 4. Analysis of surface chemistry. Projected density of electronic states (DOS) of FeCO_3 bulk, the stoichiometric (S) {104} surface and the non-stoichiometric (NS) {110} surface with its terminating atomic structure. E_f and bCBM represent the energies (E) of the Fermi level and bulk conduction band minimum respectively, indicated by dashed lines. The 3D charge density of the surface states centred at 2.8 eV is visualized with a blue isosurface (iso level = 0.02 electron/bohr³). Yellow arrows indicate the bi-coordinated O atom located in the surface trough from which the characteristic O-2p electron acceptor states at 2.8 eV originate.

Conclusions:

Based on a first principles model of corrosion film growth we suggest that the local degradation of metal surfaces in corroding conditions is influenced by structures that form during the early stages of growth. In an iron-rich environment, thermodynamically favoured cylindrical FeCO_3 crystallites grow, which are likely to be significantly more susceptible to chemical attack and dissolution than the rhombohedral crystals forming in iron poor environments. This offers a new insight into the tendency for breakdown of protective FeCO_3 films and subsequent localized corrosion. $\text{Fe}^{2+}(\text{aq})$

released during corrosion encourages the growth of cylindrical FeCO_3 crystallites that are likely to form less-protective areas of the film. Natural variations in the concentration of $\text{Fe}^{2+}(\text{aq})$ during scale growth may thus lead to areas of the film that are more susceptible to degradation. This insight also suggests new avenues for corrosion control. For instance, localized corrosion could be reduced by engineering the protective films to ensure formation of the comparatively more stable rhombohedral crystallites as building blocks. Alternatively, if cylindrical crystals have already formed, it may be possible to enhance protection through targeting the $\text{NS}\{\text{hk}0\}$ terminated facets with customized inhibitors or stabilizing species, to minimize crystallite dissolution or enhance inter-crystallite binding. Chemical labels that specifically target these facets might also be used to identify regions of the film susceptible to localised degradation.

Overall, we conclude that the combination of first principles modelling with detailed structural and chemical characterisation is a powerful methodology for exploring new avenues in the prediction, detection and mitigation of localised corrosion.

Methods:

All calculations have been performed using the CRYSTAL17 program^{16,17}, based on the expansion of the crystalline orbitals as a linear combination of a local basis set consisting of atom centred Gaussian orbitals. For iron atoms, the pob-TZVP basis set is adopted¹⁸. For carbon and oxygen atoms the 6-311G* and 8-411G* basis sets published by Valenzano *et al.* which have been validated in studies of the isoelectronic compound CaCO_3 are adopted¹⁹.

Electron exchange and correlation are approximated using the B3LYP hybrid-exchange functional incorporating 20% Hartree-Fock exchange, which is expected to be more reliable than the local density approximation or GGA approaches in systems containing open d-shell Fe, where electronic self-interaction must be compensated^{20–22}. B3LYP was introduced to condensed matter theory in 2000 for this purpose and has consistently proven to provide a qualitatively correct description of a range of open *d*-shell transition metal compounds^{23–27}.

The exchange and correlation potentials and energy functional are integrated numerically on an atom-centred grid of points. The integration over radial and angular coordinates is performed using Gauss-Legendre and Lebedev schemes, respectively. A pruned grid consisting of 99 radial points and 5 subintervals with (146,302,590,1454,590) angular points has been used for all calculations (the XXLGRID option implemented in CRYSTAL¹⁶). This grid converges the integrated charge density to an accuracy of about $\times 10^{-6}$ electrons per unit cell. The Coulomb and exchange series are summed directly and truncated using overlap criteria with thresholds of 10^{-7} , 10^{-7} , 10^{-7} , 10^{-7} , and 10^{-14} as described previously^{16,28}. Reciprocal space sampling was performed on a Pack-Monkhorst net with a shrinking factor of 8. The self-consistent field procedure was converged up to a tolerance in the total energy of $\Delta E = 1 \times 10^{-7}$ Eh per unit cell.

The cell parameters and the internal coordinates were determined by minimization of the total energy within an iterative procedure based on the total-energy gradient calculated analytically with respect to the cell parameters and nuclear coordinates. Convergence was determined from the root mean square (rms) and the absolute value of the largest component of the forces. The thresholds for the maximum and the rms forces (the maximum and the rms atomic displacements) were set to 0.00045 and 0.00030 (0.00180 and 0.0012) in atomic units. Geometry optimization was terminated when all four conditions were satisfied simultaneously.

The FeCO₃ bulk geometry was optimized in the trigonal R-3c (167) space group, obtaining the parameters $a = 4.714$ and $c = 15.323$. Symmetry constraints were removed for calculation of the bulk electronic structure. The surface geometry optimization (for the slabs cut from the optimized bulk geometry) was carried out for the internal atomic coordinates only. The convergence of surface

energy was verified by plotting both unrelaxed and relaxed surface energies of each surface as a function of slab thickness, whereby the minimum requirement of slab thickness in terms of surface energy convergence to $1 \times 10^{-2} \text{ J/m}^2$ is 16 Å.

Concerning experimental work, high purity Fe samples (99.99+%) were cut from a rod (10 mm diameter, Goodfellow). These samples were 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 ethanol, and dried under a flow of nitrogen gas. To facilitate submersion of a Fe sample in CO₂-saturated solution, the back face of the sample was secured to a glass capillary tube and then the back and sides were painted with lacquer so that only one face of the Fe sample was exposed to solution. PTFE samples (20 mm x 15 mm x 3 mm) were cut from a block of PTFE (Direct Plastics). A small hole was bored through each sample, allowing it to be suspended from a loop of PTFE thread tape during immersion. Prior to immersion PTFE samples were washed with deionized-H₂O, ethanol, and then dried.

Immersion experiments were performed in a jacketed 1 L glass cell (Pine Instruments), located in a glove box. 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. Besides allowing sample introduction, another four of these ports were used for a thermometer, dual gas inlet, liquid in/out fittings, and a Liebig condenser to minimize solution loss during immersion experiments.

Prior to insertion of either a Fe or PTFE sample into the cell, the required CO₂-saturated solution was prepared. Initially, either 0.9 L or 1.0 L (see below) of deionised water (de-H₂O, resistivity 15 MΩ.cm) was introduced into the cell. Following sealing of the cell (a ground glass bung was used in place of the Fe or PTFE sample at this point), high purity CO₂ (99.995%, BOC gases) was bubbled through the solution. 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. This procedure enabled O₂ dissolution into the solution in the cell to be minimized, i.e. [O₂(aq)] < 10 µg/L. [O₂(aq)] was measured with an electrochemical oxygen sensor (Orbisphere A1100, Hach Lange).

For experiments conducted in 10 mM FeCl₂ solution, sufficient reagent (99+%, ACROS Organics) was added to produce 0.1 L of FeCl₂, and then bubbled with nitrogen for 18-24 h prior to addition to 0.9 L of CO₂ saturated solution. The solution in the cell was then 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 pH determination.

Once [O₂(aq)] was < 10 µg/L, 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; 18-24 h of CO₂ bubbling was required to reliably achieve [O₂(aq)] < 10 µg/L. Subsequently, the Fe or PTFE sample was inserted into the cell, and immersed for a pre-determined period. After this time, the sample was removed from the cell, and dried inside the N₂ glove box. Finally, the sample was removed from the glove box and stored under vacuum to minimize degradation prior to *ex situ* characterization. A FEI Quanta 650 SEM was employed to acquire the images (secondary electron) shown in Fig. 1 and Fig. 3.

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Author contributions:

Conceptualization: Ehsan A Ahmad, Robert Lindsay and Nicholas M Harrison. Funding acquisition: Robert Lindsay and Nicholas M Harrison. Investigation: Ehsan A Ahmad, Hao-Yeh Chang, Karyn Cooper, Mohammed Al-Kindi and Gaurav R. Joshi. Writing – original draft: Ehsan A Ahmad, Writing – review & editing: Ehsan A Ahmad, Robert Lindsay, Nicholas M Harrison .

Competing interests:

Authors declare no competing interests.

References:

- (1) Koch, G.; Varney, J.; Thompson, N.; Moghissi, O.; Gould, M.; Payer, J. *NACE 2016 Impact Study*; 2016.
- (2) Kermani, M. B.; Morshed, A. Carbon Dioxide Corrosion in Oil and Gas Production - A Compendium. *Corrosion* **2003**, 59 (8), 659–683. <https://doi.org/10.5006/1.3277596>.
- (3) Moiseeva, L. S. Carbon Dioxide Corrosion of Oil and Gas Field Equipment. *Protection of Metals*. 2005, pp 76–83. <https://doi.org/10.1007/s11124-005-0011-6>.
- (4) Haeseldonckx, D.; D'haeseleer, W. The Use of the Natural-Gas Pipeline Infrastructure for Hydrogen Transport in a Changing Market Structure. *Int. J. Hydrogen Energy* **2007**, 32 (10), 1381–1386. <https://doi.org/https://doi.org/10.1016/j.ijhydene.2006.10.018>.
- (5) Papavinasam, S.; Doiron, A.; Revie, R. W. Effect of Surface Layers on the Initiation of Internal Pitting Corrosion in Oil and Gas Pipelines. *Corrosion* **2009**, 65 (10), 663–673. <https://doi.org/10.5006/1.3319093>.
- (6) Dugstad, A. (IFE). Mechanism of Protective Film Formation during CO₂ Corrosion of Carbon Steel. In *NACE Conference*; 1998; pp 1–11.
- (7) Sun, W.; Nesic, S. Basics Revisited: Kinetics of Iron Carbonate Scale Precipitation in CO₂ Corrosion. In *Corrosion*; Texas, 2006; p Paper No. 365.
- (8) Gao, M.; Pang, X.; Gao, K. The Growth Mechanism of CO₂ Corrosion Product Films. *Corros. Sci.* **2011**, 53 (2), 557–568. <https://doi.org/10.1016/j.corsci.2010.09.060>.
- (9) Esmaeely, S. N.; Young, D.; Brown, B.; Nešić, S. Effect of Incorporation of Calcium into Iron Carbonate Protective Layers in CO₂ Corrosion of Mild Steel. *CORROSION* **2017**. <https://doi.org/10.5006/2261>.
- (10) De Motte, R.; Mingant, R.; Kittel, J.; Ropital, F.; Combrade, P.; Necib, S.; Deydier, V.; Crusset, D. Near Surface PH Measurements in Aqueous CO₂ Corrosion. *Electrochim. Acta* **2018**, 290, 605–615.
- (11) Barker, R.; Al Shaaili, I.; De Motte, R. A.; Burkle, D.; Charpentier, T.; Vargas, S. M.; Neville, A. Iron Carbonate Formation Kinetics onto Corroding and Pre-Filmed Carbon Steel Surfaces in Carbon Dioxide Corrosion Environments. *Appl. Surf. Sci.* **2019**, 469, 135–145. <https://doi.org/10.1016/J.APSUSC.2018.10.238>.
- (12) Joshi, G. R.; Cooper, K.; Zhong, X.; Cook, A. B.; Ahmad, E. A.; Harrison, N. M.; Engelberg, D. L.; Lindsay, R. Temporal Evolution of Sweet Oilfield Corrosion Scale: Phases, Morphologies, Habits, and Protection. *Corros. Sci.* **2018**, 142, 110–118. <https://doi.org/10.1016/j.corsci.2018.07.009>.
- (13) Kramer, D.; Ceder, G. Tailoring the Morphology of LiCoO₂: A First Principles Study. *Chem. Mater.* **2009**, 21 (16), 3799–3809. <https://doi.org/10.1021/cm9008943>.
- (14) Ahmad, E. A.; Mallia, G.; Kramer, D.; Kucernak, A. R.; Harrison, N. M. The Stability of LaMnO₃ Surfaces: A Hybrid Exchange Density Functional Theory Study of an Alkaline Fuel Cell Catalyst. *J. Mater. Chem. A* **2013**, 1 (37), 11152–11162. <https://doi.org/10.1039/c3ta11382e>.
- (15) Wulff, G. XXV. Zur Frage Der Geschwindigkeit Des Wachstums Und Der Auflösung Der Krystallflächen. *Zeitschrift für Krist. - Cryst. Mater.* **1901**, 34 (1–6), 449. <https://doi.org/10.1524/zkri.1901.34.1.449>.
- (16) Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C. M.; Civalieri, B.; Maschio, L.; Rerat, M.; Casassa, S.; Baima, J.; Salustro, Kirtman B. *CRYSTAL17 User Manual*; University of Torino: Torino, 2014; Vol. 114.

- (17) Dovesi, R.; Erba, A.; Orlando, R.; Zicovich-Wilson, C. M.; Civalleri, B.; Maschio, L.; Rérat, M.; Casassa, S.; Baima, J.; Salustro, S.; Kirtman, B. Quantum-Mechanical Condensed Matter Simulations with CRYSTAL. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8* (4), e1360. <https://doi.org/10.1002/wcms.1360>.
- (18) Laun, J.; Vilela Oliveira, D.; Bredow, T. Consistent Gaussian Basis Sets of Double- and Triple-Zeta Valence with Polarization Quality of the Fifth Period for Solid-State Calculations. *J. Comput. Chem.* **2018**, *39* (19), 1285–1290. <https://doi.org/10.1002/jcc.25195>.
- (19) Valenzano, L.; Torres, F. J.; Doll, K.; Pascale, F.; Zicovich-Wilson, C. M.; Dovesi, R. Ab Initio Study of the Vibrational Spectrum and Related Properties of Crystalline Compounds; the Case of CaCO₃ Calcite. *Zeitschrift für Phys. Chemie* **2006**, *220* (7), 893–912. <https://doi.org/10.1524/zpch.2006.220.7.893>.
- (20) Pereira, L. L.; Santos, L. M. P.; Santos, W.; Oliveira, A.; Rattner, D. Mais Médicos Program: Provision of Medical Doctors in Rural, Remote and Socially Vulnerable Areas of Brazil, 2013–2014. *Rural Remote Health* **2016**, *16* (1), 3616. <https://doi.org/10.1002/qua>.
- (21) Corà, F. *The Performance of Hybrid Density Functionals in Solid State Chemistry: The Case of BaTiO₃*; Kaltsoyannis, N., McGrady, J. E., Eds.; Structure & Bonding; Springer Berlin / Heidelberg, 2005; Vol. 103. <https://doi.org/10.1080/00268970500179651>.
- (22) Mallia, G.; Orlando, R.; Llunell, M.; Dovesi, R. On the Performance of Various Hamiltonians in the Study of Crystalline Compounds. The Case of Open Shell Systems. In *Computational Materials Science*; Catlow, C. R. A., Kotomin, E. A., Eds.; NATO SCIENCE SERIES, III: Computer and Systems Sciences; IOS Press, Amsterdam, 2003; Vol. 187, pp 102–121.
- (23) Bailey, C. L.; Liborio, L.; Mallia, G.; Tomić, S.; Harrison, N. M. Defect Physics of CuGaS₂. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2010**, *81* (20), 205214. <https://doi.org/10.1103/PhysRevB.81.205214>.
- (24) Boeglin, C.; Ersen, O.; Pilard, M.; Speisser, V.; Kronast, F. Temperature Dependence of Magnetic Coupling in Ultrathin NiO/Fe₃O₄ (001) Films. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2009**, *80* (3), 035409. <https://doi.org/10.1103/PhysRevB.80.035409>.
- (25) Muscat, J.; Wander, A.; Harrison, N. M. On the Prediction of Band Gaps from Hybrid Functional Theory. *Chem. Phys. Lett.* **2001**, *342* (3–4), 397–401. [https://doi.org/10.1016/S0009-2614\(01\)00616-9](https://doi.org/10.1016/S0009-2614(01)00616-9).
- (26) Cai, X. F.; Gu, Y. S.; Wu, L. Y. New Considerations in Studies on Uplift of the Qinghai-Tibet Plateau. *Bull. Mineral. Petrol. Geochemistry* **2012**, *31* (2), 152–159. <https://doi.org/10.1103/PhysRevB.75.165201>.
- (27) Ahmad, E. A.; Liborio, L.; Kramer, D.; Mallia, G.; Kucernak, A. R.; Harrison, N. M. Thermodynamic Stability of LaMnO₃ and Its Competing Oxides: A Hybrid Density Functional Study of an Alkaline Fuel Cell Catalyst. *Phys. Rev. B* **2011**, *84* (8), 085137. <https://doi.org/10.1103/PhysRevB.84.085137>.
- (28) Pisani, C.; Dovesi, R.; Roetti, C. *Hartree-Fock Ab Initio Treatment of Crystalline Systems*; Lecture Notes in Chemistry; Springer Verlag: Heidelberg, 1988; Vol. 48. <https://doi.org/10.1007/978-3-642-93385-1>.