Fundamental insights into the stabilisation and chemical degradation of the corrosion product scales

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Carbonate stability plays a crucial role in clarifying the evolution and protection of the naturally formed corrosion scales on the steel surface in the application of geothermal production. In this paper, the stability of the corrosion scales from both micro and atomic level are studied via a combination of electrochemistry, surface analysis and first-principle calculation. The chemical and physical characterisation of various iron–calcium mixed carbonates are experimentally analysed and results are compared with the first-principle calculation. In the presence of Ca2+, the preferential loss of Ca during the dissolution experiments was observed, the interactions within the crystal weaken where Ca2+ co-precipitation, confirmed by a faster degradation rate for Ca0.51Fe0.49CO3 than FeCO3. This work reveals the degradation and protection performance of the naturally formed carbonate layers and provides insights into understanding the corrosion product stability and chemical breakdown of the corrosion scales.

INTRODUCTION

Ensuring engineering integrity while reducing the cost is the eternal topic for all industries such as oil and gas, geothermal, and nuclear. The research and development of corrosion-resistant alloys (CRAs) can achieve the material integrity aspect while the rise in cost restricted the applications1. Carbon steel was widely used in the industry such as oil and gas or geothermal productions based on its low cost and excellent mechanical performance2–6. However, carbon steel was subject to corrosion in the presence of CO2, resulting in the fast iron dissolution, and followed by the development of the corrosion products gradually covering the surface and effectively reduce the corrosion behaviour2–5,7–6.

Iron carbonate (FeCO3), for example, formed on the surface was considered as a natural protective scale to prolong the lifetime of carbon steel2,5,7,10. A large amount of previous research has adverted the FeCO3 protection to the surface through forming FeCO3 scales under amorphous or crystalline state5,11,12. The coverage and compactness for the development of FeCO3 scales were fully discussed in the literature in terms of crystal sizes13–15, orientation16, solution pH12,17, and other factors12,18. Recent studies found that simplified corrosion products such as FeCO3 can misestimate the corrosion product protection to the steel19–22. Esmaeely et al.20 revealed that the presence of high concentration Ca2+ to be responsible for the growth of Ca1-x Fe2+CO3 on the surface. Similar work done by Hua et al.21 indicated that the associated effects of Cl–, Ca2+, Mg2+, and CO3− within brine solution on the growth of the corrosion scales, they reported that the presence of Ca2+ prefers to co-precipitation within the crystalline FeCO3 and accentuates the total penetration rate of carbon steel. Shamsa et al.22 verified the addition of Ca2+ led to the growth of a less protective Ca1−xFe2+CO3 scale which not only accelerated the pit growth but also increased the general corrosion rate.

The structures for various carbonates FeCO3(siderite), MgCO3 (magnesite) and CaCO3 (calcite) have been studied for decades since they are extensively present in Earth’s crust3,23. Faruque et al.24 reported the electronic and bonding properties of rhombohedral CaCO3 and found the indirect energy gap to be 5.07 eV. Brik25 revealed that the calcite conduction band is much narrower than the one of magnesite. Elizabeth et al.26 investigated the dolomite (CaMg(CO3)2) (1 0 4) phase and showed the Mg and Ca atoms have different bond distances with oxygen atoms and the main Ca–O interatomic distances turned to be greater after optimization of the surface. The analysis from Golosova et al.27 demonstrated that the anisotropic lattice compression of siderite was mainly contributed by the Fe–O bonds. Han et al.28 calculated the interactions of iron in Mg1−xFexCO3 from the iron-poor (x = 0.125) to the iron-rich (x = 1, FeCO3 siderite) and found that the volume difference concerning MgCO3 changes with Fe doping and resulted in the difference in relative enthalpy. Numerous studies reported that the effects of pressure, temperature, and metal ion doping concerning structure optimization and electron distribution for carbonates. However, rare results regarded the mixture carbonates as corrosion products and focused on their corrosion protection to the surface as well as their electron distribution changes during the corrosion reactions.

To reveal the protective nature of the corrosion scales, samples covered by FeCO3 layers, iron-calcium carbonate layers, and calcium-containing corrosion product layers were prepared by high temperature and high-pressure corrosion tests. The dissolution of these complex compounds was established through exposed them to a CO2-saturated solution at and pH of 3.75. Linear polarisation resistance (LPR) and electrochemical impedance spectroscopy (EIS) methods were used for tracking the degradation of the corrosion scales. In addition, first-principle thermodynamics based on the density functional theory (DFT) were used to provide a detailed theoretical investigation on the required calcium effects of bond energy, atomistic and electronic structure of the crystals, and was associated with the corrosion product protection to the surface. It is crucial to study these effects on the true protective performance of the corrosion products and reveal the stability of the naturally formed corrosion...
scales to be effective in corrosion protection for carbon steel under geothermal applications.

RESULTS
Stability properties of corrosion products caused by Ca doping

Supercells of Ca$_{1-x}$Fe$_x$CO$_3$ doping with various Ca mole fractions were calculated and compared with pure siderite (FeCO$_3$, $x = 1$) and pure calcite (CaCO$_3$, $x = 0$), with the preferred orientation along the plane (1 0 4), as shown in Fig. 1a–e. The results summarised in Fig. 2 represent the characteristics of various Ca$_{1-x}$Fe$_x$CO$_3$. Ca mole fraction contains from Ca-poor ($x = 0$) to Ca-rich ($x = 1$) and found the average Fe–O distance for FeCO$_3$ is 2.1 Å, while the average bond length between Ca and O turns to be 2.4 Å for CaCO$_3$ at the top surface. The replaced sites by Ca results in the weakening of interaction between Ca cations and C–O$_3$ for Ca$_{1-x}$Fe$_x$CO$_3$ ($x > 0$), the length for Ca–O bonds in Ca$_{0.25}$Fe$_{0.75}$CO$_3$ and Ca$_{0.5}$Fe$_{0.5}$CO$_3$ increased by compressing the bond length of Fe–O, which suggests the non-uniform bond energy within Ca$_{1-x}$Fe$_x$CO$_3$. As the co-precipitation of Ca$^{2+}$ approached 75%, the increase in the bond length of Ca–O dominated the lattice parameter and resulting in the total volume expansion and leading to the increase in the bond length of Fe–O as well, which suggests that the stability for both Ca–O and Fe–O bonds decreased for Ca$_{1-x}$Fe$_x$CO$_3$ compared with pure FeCO$_3$.

Since Fe atoms were replaced by Ca atoms within the crystal, the unit-cell volume of Ca$_{1-x}$Fe$_x$CO$_3$ expends to a looser arrangement than FeCO$_3$, and the unit-cell approaches the volume of CaCO$_3$ as the increase in the mole fraction of Ca within the unit-cell.

The electron density for FeCO$_3$ and Ca$_{1-x}$Fe$_x$CO$_3$ structures are provided to visualize the effect of Ca$^{2+}$ co-precipitation. It can be seen that C and O atoms join via high electron density and form a molecular structural unit connected by strong covalent bonds for FeCO$_3$. In the regions around Fe ions in Fig. 3a, there are electrons overlaps to the adjacent oxygen, indicating the covalent contribution is seen between Fe and O atoms with the predominant of the ionic bond.

After the co-precipitation of Ca$^{2+}$ as shown in Fig. 3b, no electron interaction is observed between Ca and O considering the relatively longer distance than that of Fe–O. However, the constraint bond exists between Fe and O atoms and enhances with the increase of Ca$^{2+}$ co-precipitation level from 25 to 50%, accompanied by the rotation of the plane of C–O$_3$ molecular structural units due to the repulsion of the calcium atoms (Fig. 3c). When the Ca contents approach 75%, the expanded volume resulted in a decrease in the interactions between cations and oxygen, such as Ca–O and Fe–O bonds (Fig. 3d). The difference of electron density between Ca–O bonds and Fe–O bonds suggests the preferential for Ca–O bonds break during the dissolution of iron–calcium mixed carbonate into ions.

Many studies have proved the growth of the carbonated corrosion scales by the precipitation/dissolution processes. The steel substrate beneath the carbonates suffered localised corrosion since the naturally formed corrosion scales are porous and local dissolution of the corrosion scales can occur at the material interface. Figure 4 provides examples of Ca$_{0.5}$Fe$_{0.5}$CO$_3$ dissolution by losing Ca$^{2+}$ and Fe$^{3+}$, respectively, which yields the
dissolution pathway as follows:

\[
Ca_{1-x}Fe_xCO_3 \rightarrow Ca_{1-x}Fe_xCO_3(Ca_{\text{vac}}) + Ca^{2+}
\]  

\[
Ca_{1-x}Fe_xCO_3 \rightarrow Ca_{1-x}Fe_xCO_3(Fe_{\text{vac}}) + Fe^{2+}
\]

where \(Ca_{1-x}Fe_xCO_3(Ca_{\text{vac}})\) and \(Ca_{1-x}Fe_xCO_3(Fe_{\text{vac}})\) are shown as Fig. 4a, b, and the dissolution energy is expressed as follows:

\[
E_{\text{dissolution}} = E_{Ca_{1-x}Fe_xCO_3(Ca_{\text{vac}})} + E_{\text{ions}} - E_{Ca_{1-x}Fe_xCO_3}
\]

The change in energy of dissolution by losing \(Ca^{2+}\) ion (785.5 kcal/mol) is smaller compared with that by losing \(Fe^{2+}\) ion (832.0 kcal/mol), suggesting the degradation of corrosion products by preferential breaking Ca–O bonds.

**Effect of time on the dissolution of corrosion product scales**

Once the presence of \(Ca^{2+}\) ions was found in the fluids of geological formation, the precipitation of calcium-enriched carbonates was proposed to influence the morphology and structure, as well as affecting corrosion protection to the steel surface compared with the naturally formed FeCO₃. To confirm the DFT calculation described above, revealing the degradation mechanisms of pure FeCO₃ and iron-calcium mixed carbonates, carbon steel covered by various corrosion products were prepared.
in a simulated geothermal environment without the presence of Ca\(^{2+}\).

Figure 5 shows the SEM images and XRD patterns of the prepared corrosion products formed in 60 °C conditions without the addition of Ca salts, and Supplementary Figs 3b and 4 illustrate the thickness of the corrosion scales prior to dissolution experiments. The presence of Ca\(^{2+}\) in the solution resulted in the peaks for naturally formed corrosion products shifted to the left from FeCO\(_3\) (purple dash lines) and toward a mixture of Fe–Ca carbonates (green dash lines), which consistent with our previous studies\(^{21,22}\). The shifted peaks from XRD measurement correspond with the increase of d-spacing for the plane (1 0 4) for iron-calcium mixed carbonate according to Bragg’s law as shown in Eq. (4):

\[
d = \frac{n \lambda}{2 \sin \theta}
\]

where \(n\) is a positive integer and \(\lambda\) is the wavelength of the incident X-ray wave. The mole fraction of calcium in the iron-calcium mixed carbonate was 0.51 according to the relationship between d-spacing and calcium proportion, the calculations are shown in Supplementary Eq. (7).

Polarisation resistance (\(R_p\)) can reflect the dissolution speed of the corrosion scales with time. The obtained in situ \(R_p\) measurements by the LPR technique are plotted in Fig. 6. The recorded \(R_p\) during the corrosion scale dissolution were determined from the slope of the line:

\[
R_p = \frac{\Delta E}{\Delta t}
\]

Purple and green symbols represent \(R_p\) for carbon steels covered by pure FeCO\(_3\) and Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) scales exposed to the CO\(_2\)-saturated 3 wt.% NaCl solution at 15 °C respectively. For both FeCO\(_3\) and Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) scales covered samples, high \(R_p\) values were measured at the beginning. The initial \(R_p\) for naturally formed FeCO\(_3\) was higher than that of Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\), suggesting that the sample covered with FeCO\(_3\) has a lower initial corrosion rate. For stage 2, a sharp \(R_p\) reduction was recorded for the sample covered with Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) due to the scale dissolved fast with immersion time in comparison with the sample covered with FeCO\(_3\). A relatively stable \(R_p\) was recorded at stage 3 after 1000 mins for the sample covered by Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) and similar values were measured after 6000 mins for sample surface covering FeCO\(_3\), suggesting the dissolution of the corrosion scales consisted of Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) was easier compared with pure FeCO\(_3\) under the same experimental conditions.

Figure 7 presents the EIS measurements of samples exposed to the solution at each dissolution stage. The impedance measured in stage 1 during the dissolution process, smaller semicircle and higher corrosion rate were obtained compared to that of sample covered with FeCO\(_3\) as shown in Fig. 7.

Figures 8b and d represent the dissolved corrosion products after 120 hrs which correspond to stage 3 in Figs 6 and 7. The morphology in Fig. 8b indicates that the gaps appeared and were revealed as a result of the preferential dissolution occurring at the boundaries between FeCO\(_3\) crystals. For the dissolution experiment of Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\), the surface as shown in Fig. 8d illustrates porous corrosion products. The high magnification SEM images show the crystals were partially dissolved on the surface and resulted in porous characteristics and poor protection which agree with the EIS measurements as shown in Fig. 7d and f.

Supplementary Fig. 3 indicates the detected elemental compounds of Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) scales before and after dissolution by using EDS. The EDS results indicate that the proportion of Ca within the corrosion products was about 48.7% before the dissolution, this value decreased to 3.5% after dissolution experiments. The results are supported by DFT calculation which suggests the weak bonds between Ca\(^{2+}\) and CO\(_2\) and the degradation of Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) by preferential breaking Ca-O bonds. It is interesting to note that the presence of Ca-rich areas was detected locally and mainly found in the pores after 120 h of dissolution (Supplementary Fig. 3e), suggesting that the growth of Fe\(_{0.51}\)Ca\(_{0.49}\)CO\(_3\) scales contains ununiform Ca mole fraction and results in the preferential dissolution occurred locally on the surface.

**DISCUSSION**

The present study helps fill the current knowledge gaps that the degradation processes of naturally formed corrosion scales occur from the micro-level to the molecular level on the surface. Combining the first-principle DFT calculations and experimental validation is an effective way that can be used to elucidate the dissolution of corrosion product scales and protection performance to the steel surface. Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) with a complex structure that considers the preferential orientation, composition, and interactions that yield insights into the molecular mechanisms of sensitive sites for degradation. The results of our first-principle calculations reveal that the degradation of Ca\(_{0.51}\)Fe\(_{0.49}\)CO\(_3\) by preferential breaking Ca-O bonds and the required breaking...
energy to lose Ca is smaller than Fe in FeCO₃ structure (Fig. 4). The propensity of Ca dissolution within the Fe–Ca mixed carbonates accelerates with the increase of Ca²⁺ co-precipitation (Supplementary Fig. 5) and the obtained results are validated with experimental measurements. In the absence of Ca²⁺, the results suggest that the preferential dissolution occurs at the grain boundary, indicating the weak sites for a protective FeCO₃ layer. During the dissolution process of the sample was covered by dense FeCO₃ crystals, the aggressive ions such as CO₃²⁻, Cl⁻ can penetrate through the weak sites, reaching the steel substrate as shown in Fig. 8. In the presence of H⁺, the fast dissolution occurs at Ca²⁺ co-precipitation sites and acts as pathways for the penetration of aggressive ions, which promotes the subsequent local corrosion processes and develops into pores/gaps on the surface. In both cases, the preferential dissolution occurs at the grain boundary or locally, indicating a high risk of potential to induce localised corrosion on the surface, resulting in a major threat to the pipeline integrity. The current study yields atomistic insights into the interactions and weak spots involved in complex corrosion products and can serve as the input data to guide the corrosion prediction of carbon steel used in geothermal production applications.

In summary, we compare the characteristics of the naturally formed corrosion product layer in CO₂-saturated formation water in the presence or absence of Ca²⁺ ions, and focus on the degradation mechanism for iron-calcium mixed carbonates layers and compared with pure iron carbonate scale in acidification conditions. The following main conclusions can be made:

1. The co-precipitation of Ca²⁺ into iron carbonate increases the bond length between cation and oxygen and expands the lattice volume.

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**Fig. 5** Surface morphology and composition of the corrosion products. The formation of the corrosion products in 60 °C conditions with/without the addition of Ca. a SEM-FeCO₃, b SEM-Ca₀.₅₁Fe₀.₄₉CO₃, and c XRD patterns.

**Fig. 6** In situ Rₚ measurements. Dissolution measurements of carbon steel covered with (purple) FeCO₃ or (green) Ca₀.₅₁Fe₀.₄₉CO₃ scale over time in a CO₂-saturated 3 wt.% NaCl solution at 15 °C.
2. The Ca$^{2+}$ co-precipitated position acts as weak sites and is favourable to breakdown, leading to local dissolution and accelerating the penetration rate of carbon steel.

3. Although both Fe–O and C–O bonds within Ca$_{1-x}$Fe$_x$CO$_3$ can be broken in a condition at a lower pH, FeCO$_3$ presents better stability than Ca$_{0.51}$Fe$_{0.49}$CO$_3$. The weak bonds between Ca$^{2+}$ and CO$_3^{2-}$ promote the preferential dissolution in Ca-containing region, leaving a porous corrosion product layer consist of a high proportion of Fe.

4. The experimental results indicated that the presence of Ca-rich areas was detected locally and mainly found in the pores after the dissolution experiments, suggesting that the growth of Ca$_{1-x}$Fe$_x$CO$_3$ scales contains ununiform Ca mole fraction and results in the preferential dissolution occurred locally on the surface.

METHODS

Preparation of naturally formed corrosion scales

Carbon steel specimens (API SL X65) were cut from a bar (15-mm diameter, BAO steel) and the thickness is 6 mm. The elemental composition of carbon steel specimens consisted of 0.260 wt.% C, 0.32 wt.% Si, 0.43 wt.% Mn, 0.008 wt.% P, 0.005 wt.% S, 0.490 wt.% Cr, 0.8 wt.% Mo, 0.037 wt.% Ni, 0.080 wt.% V, ≤0.010 wt.% Ti, and balance with Fe. The specimens used for the electrochemical testing were sealed in resin to leave one surface with an exposure area of 1.77 cm$^2$ to the solution. All these specimens were ground the entire surface from 120 to 800 grit SiC papers, rinsed with distilled water, acetone, and ethanol, then dried with compressed nitrogen gas. Prepared specimens were stored in a vacuum desiccator and used within 10 min. The in situ autoclave setup is provided in Supplementary Fig. 1. Three immersion specimens and three electrochemical specimens were placed within the autoclave separately for each test, generating a volume to surface ratio of 33 ml/cm$^2$. The autoclave sealed at ambient temperature and the whole system was flushed with high-pressure CO$_2$ to remove the remaining O$_2$, then pumping in the prepared solutions (solution 1: CO$_2$-saturated 3 wt.% NaCl, 0.08 wt.% NaHCO$_3$ solution; solution 2: CO$_2$-saturated 1.54 wt.% NaCl, 1.83 wt.% CaCl$_2$·2H$_2$O, 0.08 wt.% NaHCO$_3$ solution, maintained Cl$^-$ concentration constant and O$_2$ < 10 ppb), followed by pressurising the autoclave to 20 bar with CO$_2$, then heated to 60 °C and the test duration is 72 h of exposure test to generate pure FeCO$_3$ layer or a mixture of Ca$_{1-x}$Fe$_x$CO$_3$ layer on the sample surface.

The naturally formed corrosion products were observed by scanning electron microscope (SEM, Hitachi, Regulus 8100). All images were collected at an accelerating voltage of 15 kV and a working distance of ~15.3 mm. The total composition of naturally formed corrosion scales was collected using X-Ray Diffraction (XRD, Bruker D8 ADVANCE) over a range of 2$\theta$ = 20–70° at a step size of 0.033° per second. The compositions of corrosion scales provided with a HORIBA EX-350 AZtecEnergy energy dispersive spectroscopy (EDS) system using spot scanning and mapping.

Dissolution of the naturally formed corrosion scales

The prepared specimens covered by corrosion scales were exposed to a CO$_2$-saturated 3 wt.% NaCl solution at 15°C and pH 3.75. During the dissolution process, LPR was employed for tracking the dissolution of the corrosion scales and performed at −10 to 10 mV vs OCP at a scanning rate of 0.167 mV/s by Gamry workstation in a conventional three-electrode
cell. The prepared specimens were used as working electrode, platinum foil as the counter, and saturated calomel electrode (SCE) as a reference electrode, respectively. The EIS measurements at various dissolution stages were performed, which were monitored in the CO2-saturated solution at OCP over a frequency range of 100 kHz to 10 mHz using 10 mV sinusoidal potential modulation. The electrochemistry data was analysed with surface morphology and corrosion product compositions at various dissolution stages via SEM, XRD, and EDS.

First-principle calculation

First-principles thermodynamics based on DFT were used to calculate the optimised atomistic and electronic structure of the naturally formed corrosion products. To simplify the model, typical corrosion products were selected, which are FeCO3 (siderite), Ca0.25Fe0.75CO3, Ca0.5Fe0.5CO3, and CaCO3 (calcite) based on the experimental results via XRD, more details calculation of Ca and Fe mole fraction within the crystals can be found in our previous publications21,22. For siderite and calcite (inorganic crystal structure database, ICSD), supercells were constructed in (1 0 4) cleave surface. The Ca0.25Fe0.75CO3, Ca0.5Fe0.5CO3, and Ca0.75Fe0.25CO3 supercells were constructed by replacing the Fe atoms in the interlayers with Ca atoms. Based on the geometry optimization model proposed by CASTEP, the generalized gradient approximation (GGA) exchange-correlation energy functional was used with the Perdew-Burke-Ernzerhof (PBE) method and the Kurdjumov-Sachs (KS) relationship. For the Fe-containing systems, a Hubbard U of 4.5 eV was employed for the correction of Fe 3d-electrons. The ultrasoft pseudopotential (USPP) was performed to describe the effective parameter of interaction between electrons and ion core, the cutoff energy is 380 eV for a plane-wave basis with a k-point set of 33334. The ionic relaxation was considered as convergence when the total energies below 10−5 eV and the force on every atom is less than 0.03 eV/Å.

Figure 8: The surface morphology of before/after dissolution experiment. a Crystalline FeCO3 before dissolution experiment, b crystalline FeCO3 after the dissolution experiment at 15 °C; c Ca-containing corrosion scales before dissolution experiment, d Ca-containing corrosion scales after the dissolution experiment at 15 °C.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.

Received: 6 October 2020; Accepted: 14 January 2021; Published online: 15 February 2021

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ACKNOWLEDGEMENTS
This work is supported by the Postdoctor Research Foundation of Shunde Graduate School of University of Science and Technology Beijing (No. 2020BH013).

AUTHOR CONTRIBUTIONS
X.Y. performed the density functional theory calculations and analyzed the results with the help of Y.H. and L.Z. X.Y. and Y.H. wrote the manuscript and performed the experiments. Data interpretation was discussed among all authors.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41529-021-00152-x.

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