Steel corrosion inhibition by calcium nitrate in halide-enriched completion fluid environments

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Calcium nitrate (Ca(NO₃)₂) has been suggested to inhibit steel corrosion. However, the effectiveness of corrosion inhibition offered by calcium nitrate in highly halide-enriched environments, for example, completion fluids, is not well known. To better understand this, the inhibition of corrosion of API P110 steel by Ca(NO₃)₂ was studied using vertical scanning interferometry in solutions consisting of 10 mass % calcium chloride (CaCl₂) or 10 mass % calcium bromide (CaBr₂), for example, to simulate the contact of completion fluids with the steel sheath in downhole (oil and gas) applications. The evolution of the surface topography resulting from the initiation and growth of corrosion pits, and general corrosion was examined from the nano-scale to micron-scale using vertical scanning interferometry. Special focus was paid to quantify surface evolution in the presence of Ca(NO₃)₂. The results indicate that, at low concentrations (≈1 mass %), Ca(NO₃)₂ successfully inhibited steel corrosion in the presence of both CaCl₂ and CaBr₂. Statistical analysis of surface topography data reveals that such inhibition results from suppression of corrosion at fast corroding pitting sites. However, at higher concentrations, calcium nitrate’s effectiveness as a corrosion inhibitor is far less substantial. These results provide a means to rationalize surface topography evolution against the electrochemical origin of corrosion inhibition by NO₃⁻ species, and provide guidance regarding the kinetics, and susceptibility to degradation of the steel sheath during exposure to halide-enriched completion fluids.

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INTRODUCTION

High-density brines have long been used during drilling, completion, and workover operations during oil and gas production.¹ Concentrated aqueous solutions of halide salts of alkali and alkaline earth metals, which provide high fluid density while minimizing cost, are commonly used in these applications.¹ However, such high concentrations of halides, particularly chloride (Cl⁻) and bromide (Br⁻), are likely to result in significant corrosion of the steel pipe (sheath) that conveys fluid hydrocarbons to the surface.²–⁴ Halides induce steel corrosion by a variety of processes including: break down of the airborne oxidation film, accelerating pit formation, and facilitating pit growth.⁵–⁷ Chloride ions are considered to be more aggressive than Br⁻ due to their higher electron affinity and stronger adsorption on the oxidation film surface.⁸

Inhibitors such as calcium nitrite (Ca(NO₂)₂) and calcium nitrate (Ca(NO₃)₂) are known to retard the corrosion of reinforcing steel.⁹–¹¹ While Ca(NO₃)₂ is cheap and abundant, its ability to inhibit corrosion in highly concentrated halide environments is not known. Nevertheless, it has been suggested that nitrate inhibits corrosion by facilitating the formation of ferric hydroxide (Fe(OH)₃) in the anodic corrosion region, decreasing the extent of iron migration as aqueous ferrous/ferric chlorocomplexes, and thereby reducing iron dissolution.⁹,¹² While corrosion inhibition by Ca(NO₃)₂ has been studied using electrochemical methods¹³,¹⁴ — direct observations of corroding surfaces from the nano-scale to micron-scale, which can be rationalized against electrochemical studies, have remained broadly unavailable.

Vertical scanning interferometry (VSI) can be used to study the kinetics of reactions at solid–liquid interfaces, including mineral dissolution, precipitation, and metallic corrosion at unparalleled resolution.¹⁵–¹⁷ The high lateral and vertical resolution¹⁸ of VSI makes it ideally suited to monitor small changes in the topography of steel surfaces, due to processes such as the dissolution of steel,¹⁵ precipitation of corrosion products,²⁰ and the growth of the passive films,²¹ from the nano-scale to micron-scale. This capability offers significant advantages over electrochemical methods which, most often, can only measure bulk behavior.¹³,¹⁴ Furthermore, the capability to probe spatially localized corrosion over large sample areas (10 s of mm²) presents advantages over scanning probe techniques, which are most often restricted to examining small, very localized surface areas.²²,²³

Herein, the retarding effect of Ca(NO₃)₂ on the corrosion of American Petroleum Institute (API) P110 steel is examined in the presence of brines composed using calcium chloride (CaCl₂) or calcium bromide (CaBr₂).²⁴,²⁵ VSI is used to quantitatively and statistically analyze three-dimensional (3D) surface topographies, and their evolution, in time to reveal the mechanisms by which Ca(NO₃)₂ alters and suppresses halide-induced corrosion. The outcomes support the use of Ca(NO₃)₂-based brines in completion...
and workover fluid environments and provide insights into its behavior as a corrosion inhibitor.

RESULTS AND DISCUSSION

Corrosion inhibition by calcium nitrate in the presence of halide-containing brines

Figure 1 shows representative height change maps of the steel surfaces following immersion in brines consisting of 10 mass % CaCl₂ and 10 mass % CaBr₂ solutions for 0, 1, 3, and 7 days. Expectedly, characteristic general corrosion features are observed following exposure to halide brines. This includes processes encompassing the initiation, propagation, and accumulation of corrosion pits. Quantitative evolutions of the average surface height change of API P110 steel over time as a function of Ca(NO₃)₂ dosage in the presence of 10% CaCl₂ and 10% CaBr₂ brines are shown in Fig. 2a, b. A linear function fitted to the data set reveals the net reaction rate, that is, including steel dissolution and corrosion. The uncertainty in rates is estimated to be around 15% based on replicate experiments. The relative corrosion rates in the presence of various dosages of Ca(NO₃)₂, RCRᵥ, were calculated as:

$$\text{RCR}_\text{CN} = \frac{\text{CR}_\text{CN}}{\text{CR}_0},$$

where CRₐ and CR₀ refer to corrosion rates in the presence and absence of Ca(NO₃)₂, respectively.

The average height change and corrosion rate data reveals that, in general, lower concentrations of Ca(NO₃)₂ are more effective at inhibiting corrosion than higher concentrations. Also, at low nitrate concentrations (≤1 mass %), the extent of inhibition enhances with increasing Ca(NO₃)₂ concentration. Indeed, a minimum in the corrosion rate is observed at a Ca(NO₃)₂ concentration of 1 mass % following exposure to both CaCl₂ and CaBr₂ brines. This result is consistent with previous findings which indicate that lower concentrations of Ca(NO₃)₂ are suited for ensuring inhibition. Increasing the dosage of Ca(NO₃)₂ to 10 mass % decreased the effectiveness for inhibition in both halide-containing solutions.

The mechanism of corrosion inhibition by Ca(NO₃)₂ is revealed by statistical analysis of surface height evolutions and microstructural observations.

Statistical analysis of corroding surface topographies was carried out for steel samples exposed to CaCl₂ brines—both in the absence of and in the presence of Ca(NO₃)₂. The representative frequency distributions of surface height change of steel surfaces containing 10 mass % CaCl₂ are shown in Fig. 3a-d. The frequency values in the distribution plots are normalized to the total number of pixels—thereby indicative of the percentage of the total surface area that is occupied by a given corrosion feature.

To offer quantitative analysis and the significance of the (height change) frequency distributions, first, the data were fitted using a two-term Gaussian function of the form:

$$f(x) = a_1 \cdot \exp\left(-\left(\frac{x - b_1}{c_1}\right)^2\right) + a_2 \cdot \exp\left(-\left(\frac{x - b_2}{c_2}\right)^2\right).$$

where $x$, $a$, $b$, and $c$ denote height change, a scaling factor for frequency, mean height change, and the spread in height change, respectively. The subscripts 1 and 2 denote the main peak and secondary peak, respectively. The fitting exercise revealed main peaks, centered at $-0.53$, $-0.88$, $-1.52$, and $-1.86$ μm for reaction conditions...
times of 1, 3, 5, and 7 days, respectively. These peak values are smaller than the average surface height change, that is, \(-1.04\), \(-2.72\), \(-4.44\), and \(-6.10\) μm (Fig. 2a) at the corresponding reaction times. Indeed, the main peaks represent slowly corroding areas (lighter brown shade) shown in Fig. 1a–d. The areas identified by the main peak encompass 40–60% of all pixels—indicating that a majority of the steel surface is only slightly affected by corrosion. A broader distribution to the left (i.e., more negative values of height change) of the main peak is observed that is labeled by dashed lines in Fig. 3a. The secondary peaks correspond to height changes in the range of \(-8\) to \(-20\) μm, consistent with localized regions undergoing much higher surface retreat (darker brown in color scale) as compared to the bulk surface seen in Fig. 1a–d. As time elapsed, the positions of the secondary peaks shifted by around 5 μm to more negative values as denoted by the horizontal orange arrow, suggesting that localized sites—for example, pits—serve as fast reaction zones that recess at a rate that is much higher than the bulk alloy surface. In addition, it should be noted that the normalized frequency of pixels increased (as marked by vertical green arrows; see Fig. 3a) implying that the extent of the surface affected by corrosion increased due to growth and coalescence of existing pitted areas, and the formation of new pits. As such, section loss due to corrosion results from both: (1) general recession of the steel surface to a small extent (by <2 μm after 7 days) and (2) fast localized corrosion that manifests by the deepening and lateral growth of pitting sites.

Figure 3b–d illustrates the effects of Ca(NO₃)₂ dosage on corrosion rates for API P110 steel exposed to 10 mass % CaCl₂ brine. Foremost, at low dosages of Ca(NO₃)₂ (i.e., 0.1 mass % and 1 mass %), the frequency distribution curves differ from the case with no nitrate in several significant ways. First, both the main and secondary peaks are shifted to less negative values upon Ca(NO₃)₂ addition, consistent with the decrease in average height change shown in Fig. 2a. Based on analysis of the fitting parameters \(b_1\) and \(b_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. In addition, peak widths given by the parameters \(c_1\) and \(c_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. In addition, peak widths given by the parameters \(c_1\) and \(c_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. In addition, peak widths given by the parameters \(c_1\) and \(c_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. In addition, peak widths given by the parameters \(c_1\) and \(c_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. In addition, peak widths given by the parameters \(c_1\) and \(c_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced. In addition, peak widths given by the parameters \(c_1\) and \(c_2\)(see Fig. 4a), it is suggested that Ca(NO₃)₂ reduces corrosion rates by suppressing both general recession (i.e., bulk dissolution) and fast localized corrosion at pitting sites, although the influence on localized corrosion is more pronounced.
evidencing that increasing [NO$_3^-$] beyond an optimal value is detrimental.

To better elucidate the functions of Ca(NO$_3$)$_2$ as a corrosion inhibitor, the VSI observations were augmented by SEM visualizations of corroding surfaces. First, as shown in Fig. 5a, API P110 steel presents a single-phase martensitic microstructure with a grain size of around 10 μm. Visualization of corroded microstructures reveals that pits are localized at pre-austenite grain boundaries, for example, as shown in Fig. 5b and S2, consistent with previous observations. It is generally thought that in the presence of Cl$^-$ ions, surface defect sites, for example, grain boundaries, and secondary-phase inclusions are most vulnerable to pitting. As pitting initiates, the release of iron in the form of Fe$^{2+}$ promotes local acidification within the pit following the reaction: (1) Fe$^2$ + 2H$^+$ → Fe$^{2+}$ + H$_2$, and (2) Fe$^{2+}$ + H$_2$O → Fe(OH)$^+$ + H$.\textsuperscript{38-41}$ The high local pH and Fe$^{2+}$ activities at the bottom of the pit—and the corresponding gradient that develops—results in the transport of anions towards the pitted area. The concentration gradient of ions induces the development of an electrochemical potential difference between the pit bottom and the surface of the steel that can be as high as hundreds of millivolts.\textsuperscript{42,43}

The pit morphologies observed in Fig. 5 are significantly smaller than stable pits that form on surface of passivated steels.\textsuperscript{44} Further, as shown in Fig. 5b, herein, a rapidly corroding zone is noted to form around a central pit whose radius is several times larger than that of the pit itself, that is, in terms of its radial dimension. A line profile (Fig.5e) drawn through the center of the pit—using the VSI topography image (Fig. 5c)—shows that the surrounding radial area (“basin”) encompasses a radius of 80 μm, whereas the central pit only achieves a maximum radius of 17 μm (and a depth of around 3.5 μm). It is the formation of such radial basins that explains the secondary peaks evident in the frequency distribution curves (Fig. 3).

By simulating the effects of anodic corrosion on the evolution of the pit geometry, we attribute the formation of these radial basins as being the result of near-surficial, lateral expansion of the pit mouth (e.g., see Fig. 5b-f), for example, as observed in the corrosion of AISI 1045 steel by Guo et al.\textsuperscript{30} As such, Fig. 6 shows the simulated local potential distribution and resulting electric field strength distribution and the implications on the formation...
As such, in closing this paper has comprehensively examined the corrosion of API P110 steel in concentrated halide environments in the presence of Ca(NO$_3$)$_2$ as a corrosion inhibitor. Special focus is placed on examining the evolution of corroding topographies—at unparalleled resolution—across a large field of view (FOV) using VSI for samples reacted in a controlled environment under isothermal conditions. Careful analysis of
surface topographies, pixel-by-pixel, indicates that while moderate concentrations of Ca(NO₃)₂ can effectively inhibit corrosion in the presence of Cl⁻ and Br⁻, such inhibition is compromised at higher dosages due to the significant oxidizing potential of the bulk solution. By statistical analysis of surface height data ("frequency distributions"), it is highlighted that Ca(NO₃)₂ suppresses localized corrosion primarily, although a measurable effect on general corrosion was also observed. Localized corrosion is manifested by a fast dissolution zone (i.e., basin), which forms in the vicinity of central pitting sites. Simulations of the electrochemical evolutions within a pit suggest that these features arise from the fast expansion of the pit mouth whose local curvature results in the concentration of an electric field distribution. The mechanism of NO₃⁻ inhibition is consistent with this model such in the presence of nitrate the oxidation of Fe²⁺ to Fe³⁺ leads to the precipitation and deposition of Fe oxides and hydroxides, hindering further pit expansion. To the best of our knowledge, this is the first time that the inhibition effect of Ca(NO₃)₂ has been evidenced from quantitative and statistical analysis of corroding surfaces. These findings provide new insights regarding the role of the water chemistry and inhibitor dosage to suppress steel corrosion evolutions in aggressive halide-rich environments.

**METHODS**

**Materials: Preparation of steel surfaces and brines**

Commercially available API P110 steel (McMahon Steel Supply) with a nominal composition of C (0.25%), Si (0.36%), Mn (1.24%), P (0.013%), S (0.004%), Cr (0.50%), Al (0.03%), and Fe (97.6%) was used. During its processing, this steel is quenched, giving rise to a microstructure that is characterized as monophasic martensite. The steel was machined into coupons having dimensions of 6 mm × 6 mm × 4 mm (length × width × height) and then embedded in epoxy resin to facilitate handling, while leaving only the top surface of the steel exposed. The steel surface was
then polished successively using SiC sand paper and diamond paste until it featured a surface roughness ($S_z$) of 1 µm. Thereafter, the sample was ultrasonically rinsed with ethanol and deionized (DI) water for 3 min, and stored in a desiccator after being dried under an air stream. The epoxy-mounted samples were secured on kinematic mounts (Thorlabs) to maintain imaging positions within ±3 µm and ±1 µm over the course of the experiments.

Brines were prepared by adding ACS reagent grade CaCl$_2$, CaBr$_2$, and Ca(NO$_3$)$_2$ to DI water to produce 10% CaCl$_2$ or 10% CaBr$_2$ solutions that contain 0%, 0.1%, 1%, and 10% Ca(NO$_3$)$_2$ (mass basis). The measured pHs of these solutions are listed in Table 1. These concentrations were chosen to encompass a wide range of Ca(NO$_3$)$_2$ concentrations to assess the effect(s) of a diversity of dosage levels, and potential changes in inhibition mechanisms and the resulting effects on corrosion evolutions.

Methods: Surface topography evolutions captured using VSI
Corrosion behavior under brine immersion was monitored for up to 7 days at 25 ± 0.2 °C in a temperature-controlled environment. The surfaces of the steel samples were exposed to brine volumes on the order of 135 ± 2 mL resulting in a nominal surface-to-volume ratio (mm$^{-1}$) of 1/9000. Prior to immersion, approximately half of the sample surface was covered with a peelable silicone mask (Silicone Solutions SS-380) to preserve a portion of the steel surface in a pristine state, which serves as the reference surface. As a result, absolute height changes can be ascertained by comparing the reference surface with the reacted (i.e., exposed to brine) surface. The effectiveness of this procedure is illustrated in Fig. 7, which shows VSI images of a steel surface before and following immersion. To assess the chemical stability of the silicone mask, concentrations of dissolved silicon in contact with brine were measured using a Perkin-Elmer Avio 200 inductively coupled plasma optical emission spectrometer. Measured Si concentrations ranged from 0.13 to 1.14 ppm, with an average value of 0.64 ppm. This level of silicon abundance and negligible changes in the silicon mask’s surface topography following immersion indicate that it is inert up on exposure to the brine environment.

The steel’s surface topography was monitored following its contact with the brines at time intervals of 0, 1, 3, 5, and 7 days. At each time point (except 0 days), any corrosion products that may have formed on the steel surface were removed following ASTM G1. Thereafter, the silicon adhesive was peeled cleanly and the surface topography was examined using VSI. The VSI used a Zygo NewView 8200 fitted with a 5× Mirau objective having a numerical aperture of 0.13 and offering a lateral (in the x and y directions) resolution of 1.63 µm. The lateral resolution is determined by both the objective and the spatial sampling of the camera (1024 pixel × 1024 pixel in one FOV, that is, 1.67 mm × 1.67 mm). The resolution in the z-direction is estimated to be on the order of ±2 nm based on analysis of a NIST traceable step-height standard. Imaging of the steel surface that encompassed an area on the order of 12–15 mm$^2$ was carried out by stitching multiple overlapping sub-images that were acquired sequentially along a grid map. It should be noted that the use of kinematic mounts as described above enabled repeatability in lateral positioning on the order of ±3 µm which is similar to the resolution of images acquired using this specific (5×) Mirau objective.
Analysis of 3D surface topography data
The 3D surface topography images (i.e., height maps) obtained using VSI were processed and analyzed using Matlab® R2017b and rendered using Gwyddion.27

Quantification of corrosion rates from average height change: The absolute surface height change at time $t$, $\Delta z_t$, was determined from the difference in average heights of the reacted ($z_t$) and reference ($z_r$) surfaces, $z_t^r$ and $z_r^r$, respectively, at time $t$, as compared to that at time 0, as given by:

$$\Delta z_t = (z_t^r - z_0^r) - (z_r^r - z_0^r). \tag{4}$$

Hence, at time $t = 0$, the absolute height change, $\Delta z_0 = 0$, whereas a negative $\Delta z_t$ would imply a net decrease in surface height at a given pixel location, that is, loss of metal due to corrosion. Although corrosion is expected to result in the deposition of corrosion products which have a higher molar volume compared to the native alloy, and hence result in a height increase, the removal of corrosion products before each imaging sequence eliminates ambiguities in the interpretation of height change—resulting in a height decrease, in time.

Frequency distribution of height change: In addition to surface height changes, the spatial distribution of height change was assessed—pixel by pixel—across a given surface. This offers insights into the frequency distributions of reaction (corrosion) rates. The 3D images, following alignment in the vertical direction using the known reference surface, were each subtracted pixel-by-pixel from that obtained at $t = 0$, to give the **height change map**. The frequency distribution of height changes, normalized to the total number of pixels—which is on the order of $10^7$ pixels—is then plotted for each time interval.

**Fig. 7** Representative VSI topography maps of API P110 steel surface obtained a as-polished, and b following immersion in 10 mass % CaCl$_2$ brine for 7 days. The boundary between the unreacted (“masked”) surface and reacted surface is labeled by the dashed line. The scale bars represent a length of 2 mm
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