Effect of Molybdate on the Passivation of Carbon Steel in Alkaline Solutions under Open-Circuit Conditions

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The effect of molybdate on the passivation of AISI 1020 carbon steel under open-circuit conditions in pH 12.5 calcium hydroxide solutions containing chloride was investigated via electrochemical tests and surface characterization techniques. In the early stage, molybdate increased the rate of passivation, with inhibition efficiency being positive. During the later stage, after the carbon steel has passivated, precipitation of calcium molybdate over parts of the sample surface resulted in slight negative inhibition efficiency and the passive film was found to have a higher proportion of ferrous cations and a smaller thickness. However, the precipitation of a thick calcium molybdate film over the entire surface can reverse this situation, increasing the polarization resistance through a cathodic inhibition mechanism. The electrochemical and XPS results showed that regardless of its effect on the final polarization resistance, the presence of calcium molybdate precipitates led to a decrease in the total extent of carbon steel oxidation, indicating an overall beneficial effect. Molybdate was also shown to be effective against localized corrosion, with 14.6 mM molybdate sufficient in preventing passivity breakdown in pH 12.5 solution containing 564 mM chloride.

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Carbon steel is not a corrosion resistant alloy. However, in highly alkaline environments such as concrete, the formation of a passive oxide film on the surface reduces the corrosion rate to a very low level.1 In such environments, corrosion of carbon steel occurs mostly through two mechanisms: chloride contamination and carbonation by atmospheric CO2 resulting in a pH drop.2–10 To counter the corrosion of carbon steel in highly alkaline environments, corrosion inhibitors can be added. Currently, calcium nitrite is being used in the construction industry as an admixed inhibitor for its set-accelerating and corrosion inhibition properties.11

Considerable research has been conducted on the inhibition of carbon steel corrosion in alkaline solutions by nitrite anions.8,13–19 Nitrite, being an oxidizing anodic inhibitor, oxidizes ferrous cations to ferric cations rapidly at anodic sites, which then precipitate out as ferric oxyhydroxides to repair defects in the passive film.11 Calcium nitrite works well for concrete with water to cement ratio less than 0.5 ratio for effective corrosion inhibition.17 From use in immersed reinforced concrete structures due to toxicity much evidence attesting to its success in this role.23,27–29 Molybdate is a non-oxidizing anodic inhibitor of corrosion inhibitor in neutral solutions such as cooling water systems, with be added. Currently, calcium nitrite is being used in the construction industry as an admixed inhibitor for its set-accelerating and corrosion inhibition properties.11

In one of the earliest works on the use of sodium molybdate as an inhibitor in alkaline solutions, Thomas and Egan showed that 50 mM MoO42− was able to inhibit pitting corrosion caused by 25 mM Cl− in a saturated calcium hydroxide solution.20 Hope and Ip showed that the combination of calcium nitrite (4.5 parts) and sodium molybdate (1 part) protected steel samples effectively when the ratio of the inhibitors (nitrite and molybdate) to chloride ions was around 1:1; according to these authors, the combination of nitrite and molybdate appeared to be more effective than just using calcium nitrite alone.31

Tang et al. showed that in a pH 8 solution, sodium molybdate at a low concentration of 0.013 wt% was effective in conferring a degree of passivity to carbon steel that would otherwise be absent.33 At higher concentrations, the pitting potential increased while the anodic current density decreased significantly when the molybdate concentration was 2 wt%; Raman spectroscopy indicated the presence of molybdate on the surface of the steel, supporting the adsorption inhibition hypothesis.35 Tommasselli et al. showed that sodium molybdate was more effective than sodium nitrite at low concentrations (0.013 wt%) in corrosion inhibition for carbon steel in pH 8 solution.36 Deyab and El-Rehim showed that molybdate is better than nitrite but not as good as tungstate (which is more costly than molybdate) in inhibiting pitting corrosion in a pH 10 solution.

As the existing literature on corrosion inhibition by molybdate for carbon steel under alkaline conditions focuses mostly on the inhibition of localized corrosion, there is a gap regarding its effect on passivation. In this work the effects of molybdate on the rate of passivation and the passive film were studied in pH 12.5 alkaline solutions over a period of 20 hours under open-circuit conditions. The corrosion potential was monitored along with EIS experiments at regular time intervals to obtain the polarization resistance for a measure of the corrosion current density. Furthermore, the total extent of Fe oxidation was estimated from the electrochemical data. The effects of calcium molybdate precipitation (characterized by SEM, EDX and XRD) on the passive film (characterized by XPS) and the passivation rate are reported and analyzed.

**Experimental**

*M*aterials and sample preparation.—Flat AISI 1020 carbon steel specimens (20 mm × 20 mm × 2 mm) with a nominal composition (in wt%): 0.20 C; 0.25 Si; 0.45 Mn; 0.04 P; 0.04 S; balance Fe were used in this work. Each sample was abraded with SiC papers from grade P180 to P600 prior to the electrochemical experiments. After grinding, the sample was degreased with ethanol, washed with deionized water.
and blown dry with compressed air at room temperature. The clean surface was then covered with an electrochemical mask cut from 3 M Electroplating Tape 470 that exposed a circular area of 1 cm² to the electrolyte.

For each experiment, 100 ml of electrolyte was prepared with deionized water and reagent-grade chemicals (calcium hydroxide, sodium chloride and anhydrous sodium molybdate). The electrolyte was quiescent during the experiment, but was purged with compressed N₂ gas for at least 30 minutes prior to the immersion of the carbon steel electrode. The pH value of the electrolyte was measured with an electronic pH meter (Eutech PC 700) before and after each experiment to ensure that the pH of the electrolyte did not drop significantly (<0.3 pH unit) over the duration of the experiment (20 h) due to corrosion by atmospheric carbon dioxide. For ease of discussion, the solution conditions were divided into three sets, as shown in Table 1, which were designed to analyze the effect of chloride and molybdate.

In pH 12.5 Ca(OH)₂ solutions containing 48.6 mM MoO₄²⁻, a thick calcium molybdate layer precipitated on the carbon steel surface. Therefore, additional tests were conducted in a pH 12.5 NaOH solution to identify the effect of the precipitation products on the corrosion behavior. The pH 12.5 solutions mentioned in this work all refer to the pH value of the electrolyte measured with an electronic pH meter (Eutech PC 700) before and after each experiment.

Results and Discussion

**OCP results.**—Figure 1a shows that in pH 12.5 solutions with varying chloride concentrations and no molybdate (Set A), the OCP was not strongly influenced by Cl⁻ levels up to 282 mM, becoming more positive over time from −0.49 V vs. SCE at 0.5 h to −0.34 V vs. SCE at 20 h, indicating that the carbon steel samples were undergoing passivation. For [Cl⁻] = 564 mM, the OCP initially increased abnormally fast before becoming more negative due to passivity breakdown arising from crevice corrosion. Figure 1b shows that when 14.6 mM MoO₄²⁻ inhibitor was present (Set B), carbon steel was observed to passivate in all the solutions tested, with the OCP at 20 h generally around −0.35 V vs. SCE regardless of the chloride concentration.

The OCP-time profiles for Set C (564 mM Cl⁻ and varying molybdate concentrations) are shown in Figure 1c. As mentioned above, localized corrosion occurred in the absence of molybdate. For the two experiments conducted with 4.9 mM MoO₄²⁻, one passivated while the other experienced passivity breakdown. Consistent passivation was achieved when [MoO₄²⁻] ≥ 14.6 mM. For [MoO₄²⁻] = 48.6 mM, a thick precipitated CaMoO₄ film formed that led to a negative shift in OCP, observable as a hump in the OCP-time profile at 3.5 h. To confirm that the observed negative shift in OCP can be attributed to this CaMoO₄ film, the 48.6 mM MoO₄²⁻ experiment was also conducted in pH 12.5 NaOH solution and now no such hump was observed in the OCP-time profile. The precipitation of CaMoO₄ on the carbon steel surface increased with molybdate concentration (for [MoO₄²⁻] ≥ 48.6 mM), causing the OCP to be more and more negative. However, for the 146 mM MoO₄²⁻ solution, no visible CaMoO₄ film formed in the test cell during the electrochemical experiment; due to the high molybdate concentration, most of the calcium cations precipitated out as CaMoO₄ during preparation of the sample electrolyte. The most positive OCP-time profile observed in Set C was for 146 mM MoO₄²⁻, with OCP being ~0.27 V vs. SCE at 20 h.

Note that the initial OCP values of the carbon steel samples were always more positive than the hydrogen equilibrium potential (~0.98 V vs. SCE at pH 12.5). Figure 1 shows that the most negative OCP recorded for each experiment was more positive than ~0.6 V vs. SCE for all experiments except the 282 mM Cl⁻ experiment in Figure 1a. This indicates that oxygen reduction was the main cathodic reaction supporting the anodic reaction at all times and that the Ni₃ purg before the electrochemical experiment did not remove all the dissolved oxygen.

**EIS results.**—Figure 2 shows Bode plots for carbon steel at pH 12.5 with 564 mM Cl⁻ and 48.6 mM MoO₄²⁻, with Figure 2a being for Ca(OH)₂ solution and Figure 2b for NaOH solution. The only distinct difference between the two Nyquist plots (not shown) is a high frequency kink in the spectrum for the Ca(OH)₂ solution that became noticeable after 6 h, indicating a second time constant associated with the precipitated CaMoO₄ film. The effect of the precipitated CaMoO₄ film shows up clearly in the Bode phase angle plot between 10² Hz and 10⁴ Hz when comparing Figures 2a and 2b.

The Rₑ was obtained via fitting of an equivalent electrical circuit (EEC) to the impedance data. Two different EECs (Figure 3) were used in this work. When CaMoO₄ precipitates were absent or only partially covered the surface, a single-time constant Randles circuit was used (Figure 3a), with the space charge capacitance (Cₑ) modulated by a constant phase element (CPEₑ = Z = 1/(Tωⁿ), where T and P are the magnitude and exponent of the CPE unit respectively). The CPEₑ unit exhibited near-ideal capacitance behavior (P > 0.9). The Rₑ represents mostly the resistance of the passive oxide film

| Table I. Solution conditions of experimental sets used in this work. |
|-------------------|-------------------|-------------------|-------------------|
| Set | pH | [OH⁻] (mM) | [Cl⁻] (mM) | [MoO₄²⁻] (mM) |
| A   | 12.5 | 31.6 | 0, 28.2, 113, 282, 564 | 0 |
| B   | 12.5 | 31.6 | 0, 28.2, 113, 282, 564 | 14.6 |
| C   | 12.5 | 31.6 | 0, 4.9, 14.6, 48.6, 146 | 564 |

were analyzed in CasaXPS software and were calibrated with respect to the C 1 s peak at 284.6 eV.

X-Ray Diffraction (XRD) experiments were carried out with a Bruker D8 Advance diffractometer using Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 10° to 80°, using a step size of 0.1° and time per step of 0.5 s.
compensated resistance (the impedance spectrum. The resistance in series represents the un-
tances are not resolved since only one time constant was observed in
the impedance spectrum. The resistance in series represents the un-
compensated resistance (Rc), which comprises the solution resistance
between the working electrode and the reference electrode, contact
resistances and cable resistances.

When a CaMoO₄ film was precipitated over the entire exposed
carbon steel surface, a two-time constants EEC is required (Figure 3b). This two-time constants EEC is commonly used to model non-
conducting and porous paint coatings on metals and contains a
CPEc element which here represents the capacitance of the precipitated
film. The Rc in this EEC represents the solution resistance between
the reference electrode and the CaMoO₄ film, while Rpore represents
the resistance of the pores in the CaMoO₄ film. Note that
Rc, Rpore and Rs are negligible compared to Rp, Table II gives typical fitting results
from the two EECs used in this work.

Figure 4a shows the average Rp for Set A (no molybdate) and Set
B (14.6 mM MoO₄²⁻) against the chloride concentration. The Rp was
generally on the order of 10⁵ Ω cm² and 10⁶ Ω cm² at 0.5 h and 20 h
respectively, with the order of magnitude increase in Rp indicating that
the carbon steel was undergoing passivation during this time period.
The presence of molybdate in Set B resulted in Rp being higher at 0.5 h but lower at 20 h when compared to Set A. This implies that
molybdate increases the rate of passivation (higher Rp at earlier times)
but may have a slight detrimental effect at longer times. For 564 mM
Cl⁻ but no molybdate, sustained localized corrosion occurred so that
Rp dropped by almost two orders of magnitude from the value before
passivity breakdown; the addition of 14.6 mM MoO₄²⁻ was sufficient
to maintain passivity.

Figure 4b shows the average Rp for Set C against the molybdate
concentration. The Rp at 0.5 h and 20 h in pH 12.5 Ca(OH)₂ solu-
sions generally increased with molybdate concentration. Note that
consistent passivation was achieved only when [MoO₄²⁻] = 14.6 mM. For [MoO₄²⁻] = 48.6 mM, the Rp in the Ca(OH)₂ solution where a
complete CaMoO₄ film precipitated was approximately 0.5 MΩ cm²
higher than that in the NaOH solution (where no such CaMoO₄ film
formed). This suggests that the CaMoO₄ film is contributing to Rp
through another mechanism besides a barrier effect since the small
Rpore value of 50 Ω cm² (Table II) does not contribute significantly to
the overall resistance of the system. The mechanism of this in-
crease will be discussed further in a later section, Effect of CaMoO₄
precipitates on passivation.

Figure 4c shows the Rp over time for selected samples, to illustrate
the influence of the solution composition and molybdate addition on
the passivation behavior of the carbon steel in pH 12.5 solutions as a
function of time.

SEM and EDX results.—Some of the carbon steel samples in pH
12.5 Ca(OH)₂ solutions containing molybdate had white and powdery
precipitates on the surface after the electrochemical experiment. These
precipitates were not washed off when rinsing with deionized water,
although they could be scraped off with a gloved finger. SEM images
(Figure 5a) shows that the precipitates exist as spherulites (spherical
objects having a radiating structure) with a diameter ranging from 4
μm to 9 μm. EDX showed that the chemical composition of these
precipitates is consistent with CaMoO₄ (Figure 5b). For [MoO₄²⁻] ≤
14.6 mM, CaMoO₄ clusters formed when individual spherulites grew
into each other. For [MoO₄²⁻] = 48.6 mM, a continuous film covered

\[ R_{cp} \] rather than the charge transfer resistance (Rct). These two resis-
tances are not resolved since only one time constant was observed in
the impedance spectrum. The resistance in series represents the un-
compensated resistance (Rc), which comprises the solution resistance
between the working electrode and the reference electrode, contact
resistances and cable resistances.

The presence of molybdate in Set B resulted in Rp indicating that
carbon steel was undergoing passivation during this time period.
Note that consistent passivation was achieved only when [MoO₄²⁻] = 14.6 mM. For [MoO₄²⁻] = 48.6 mM, the Rp in the Ca(OH)₂ solution where a
complete CaMoO₄ film precipitated was approximately 0.5 MΩ cm²
higher than that in the NaOH solution (where no such CaMoO₄ film
formed). This suggests that the CaMoO₄ film is contributing to Rp
through another mechanism besides a barrier effect since the small
Rpore value of 50 Ω cm² (Table II) does not contribute significantly to
the overall resistance of the system. The mechanism of this in-
crease will be discussed further in a later section, Effect of CaMoO₄
precipitates on passivation.

Figure 4b shows the average Rp for Set C against the molybdate
concentration. The Rp at 0.5 h and 20 h in pH 12.5 Ca(OH)₂ solu-
sions generally increased with molybdate concentration. Note that
consistent passivation was achieved only when [MoO₄²⁻] = 14.6 mM. For [MoO₄²⁻] = 48.6 mM, the Rp in the Ca(OH)₂ solution where a
complete CaMoO₄ film precipitated was approximately 0.5 MΩ cm²
higher than that in the NaOH solution (where no such CaMoO₄ film
formed). This suggests that the CaMoO₄ film is contributing to Rp
through another mechanism besides a barrier effect since the small
Rpore value of 50 Ω cm² (Table II) does not contribute significantly to
the overall resistance of the system. The mechanism of this in-
crease will be discussed further in a later section, Effect of CaMoO₄
precipitates on passivation.

Figure 4c shows the Rp over time for selected samples, to illustrate
the influence of the solution composition and molybdate addition on
the passivation behavior of the carbon steel in pH 12.5 solutions as a
function of time.
the entire steel surface when CaMoO₄ spherulites stacked upon each other, around three layers deep (Figure 5c). The bonds between individual spherulites are quite strong, since the drying shrinkage cracks other, around three layers deep (Figure 5c). The bonds between individual spherulites are quite strong, since the drying shrinkage cracks were transgranular in nature rather than intergranular (Figure 5d).

**XRD results.**—Only the sample in pH 12.5 Ca(OH)₂ solution containing 48.6 mM MoO₄²⁻ had a sufficiently thick precipitated film for XRD to be performed successfully. The XRD pattern (Figure 6) indicates a tetragonal structure in the space group I₄₁/a, consistent with JCPDS 29–0351 (CaMoO₄) with all of the expected diffraction peaks observed. Two of the peaks observed within the 20 scan range belongs to the carbon steel substrate and corresponds to α-Fe phase (ferrite), consistent with JCPDS 06–0696.

**XPS results.**—XPS experiments were conducted for selected samples. Calcium molybdate precipitates present on the sample surface (for solutions containing 14.6 mM MoO₄²⁻) were removed from the surface prior to the XPS experiment by scraping. Figure 7a shows the Mo 3d spectrum for carbon steel in pH 12.5 solution with 564 mM Cl⁻ and 146 mM MoO₄²⁻. Note that no CaMoO₄ precipitates formed on the carbon steel surface for this electrochemical experiment as Ca²⁺ cations precipitated out during preparation of the sample electrolyte. The Mo 3d spectrum is consistent with those reported in literature for Mo (VI), suggesting that molybdate anions are incorporated into or adsorbs on the outer surface of the passive oxide film without undergoing reduction. However, as the Mo 3d peaks are slightly asymmetrical with a very faint shoulder on the lower binding energy side of both peaks, the presence of a small amount of Mo (IV) cannot be ruled out.

Four peaks from possible iron compounds were considered for fitting of the Fe 2p½ spectra (Figure 7b). Table III shows the known peak positions and the full width at half maximum (FWHM) of the compounds used for the fits. The average fractional intensity from the fitting results, the Fe³⁺/Fe²⁺ ratio and Feoxide/Fe metal ratio (as a measure of the passive film thickness) are given in Table IV.

In pH 12.5 solutions without molybdate, the ratio of ferric to ferrous cations was more than 3 (indicating that ferric cations were the majority in the passive oxide film), while the ratio of Fe oxides/Femetal ratio (as a measure of the passive film thickness) are given in Table IV.

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**Figure 2.** (a) Bode plot for carbon steel in pH 12.5 solution constituted by Ca(OH)₂ with 564 mM Cl⁻ and 48.6 mM MoO₄²⁻; (b) Bode plot for carbon steel in AISI 1020 carbon steel in pH 12.5 solution constituted by NaOH with 564 mM Cl⁻ and 48.6 mM MoO₄²⁻.

**Figure 3.** Equivalent electrical circuits used in this work for fitting impedance data with (a) one time constant and (b) two time constants. RE and WE stand for reference electrode and working electrode respectively.

<table>
<thead>
<tr>
<th>Solution conditions</th>
<th>Time (h)</th>
<th>Rs (Ω cm²)</th>
<th>Rpo2 (Ω cm²)</th>
<th>Rp (Ω cm²)</th>
<th>T (F cm⁻² s⁻¹)</th>
<th>P</th>
<th>CPEf</th>
<th>T (F cm⁻² s⁻¹)</th>
<th>P</th>
<th>CPEic</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 12.5, 564 mM Cl⁻, 0 mM MoO₄²⁻</td>
<td>0.5</td>
<td>27</td>
<td>-</td>
<td>2.4 × 10⁵</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.0 × 10⁻⁵</td>
<td>0.91</td>
<td>3.8 × 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>27</td>
<td>-</td>
<td>4.8 × 10⁵</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.0 × 10⁻⁵</td>
<td>0.89</td>
<td>3.3 × 10⁻⁵</td>
</tr>
<tr>
<td>pH 12.5, 564 mM Cl⁻, 48.6 mM MoO₄²⁻</td>
<td>0.5</td>
<td>25</td>
<td>51</td>
<td>3.5 × 10⁵</td>
<td>1.7 × 10⁻⁵</td>
<td>0.86</td>
<td>5.0 × 10⁻⁵</td>
<td>0.91</td>
<td>3.8 × 10⁻⁵</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>25</td>
<td>51</td>
<td>4.2 × 10⁵</td>
<td>1.7 × 10⁻⁵</td>
<td>0.86</td>
<td>6.0 × 10⁻⁵</td>
<td>0.89</td>
<td>3.3 × 10⁻⁵</td>
<td>0.95</td>
</tr>
</tbody>
</table>
Figure 4. The average $R_p$ at 0.5 h and at 20 h for (a) Set A (no molybdate) and Set B (with 14.6 mM MoO$_4^{2-}$) against the chloride concentration; (b) Set C (pH 12.5, 564 mM Cl$^-$) against the molybdate concentration. (c) $R_p$ against time for selected samples.

Figure 5. Results from SEM and EDX showing (a) precipitated spherulites in pH 12.5 Ca(OH)$_2$ solution containing 113 mM Cl$^-$ and 14.6 mM MoO$_4^{2-}$, (b) EDX spectrum of the precipitated spherulites is consistent with CaMoO$_4$, (c) thick precipitated CaMoO$_4$ film in pH 12.5 Ca(OH)$_2$ solution containing 564 mM Cl$^-$ and 48.6 mM MoO$_4^{2-}$, and (d) transgranular cracks in the precipitated CaMoO$_4$ film.

Inhibition efficiency of molybdate at early and later stages of passivation.—The inhibition efficiency ($\eta$) is defined as:

$$\eta = \frac{i_{\text{corr, no inh}} - i_{\text{corr, inh}}}{i_{\text{corr, no inh}}}$$

Figure 6. XRD pattern of the white powdery film precipitated on AISI 1020 carbon steel exposed to pH 12.5 Ca(OH)$_2$ solution containing 564 mM Cl$^-$ and 48.6 mM MoO$_4^{2-}$. The diffraction peaks are consistent with JCPDS 29-0351 (CaMoO$_4$) and JCPDS 06-0696 ($\alpha$-Fe).
Since the Stern-Geary equation can be used to convert $R_i$ into passive film thickness.

where $i_{corr, no inh}$ and $i_{corr, inh}$ represent the corrosion current density in the absence and presence of the inhibitor (molybdate) respectively. Since the Stern-Geary equation can be used to convert $R_i$ into passive film thickness.

Figure 7. (a) Mo 3d high resolution XPS spectrum of AISI 1020 carbon steel surface (sample in pH 12.5 solution containing 564 mM Cl$^-$ and 146 mM MoO$_4^{2-}$), and (b) curve fitting performed for Fe 2p$_{3/2}$ high resolution XPS spectrum (sample in pH 12.5 solution containing 113 mM Cl$^-$ and 0 mM MoO$_4^{2-}$).

$R_B$ where $B$ is the Stern-Geary coefficient, the inhibitor efficiency can also be expressed as:

$$\eta = \frac{\left(\frac{R_B}{R}\right)_{inh}}{\left(\frac{R_B}{R}\right)_{no inh}}$$

Table III. Peak parameters of XPS spectra used for fitting iron compounds.

<table>
<thead>
<tr>
<th>Element (photoelectron core level)</th>
<th>Peak number</th>
<th>Assignment</th>
<th>Peak position ($\pm 0.5$ eV)</th>
<th>FWHM ($\pm 0.2$ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 2p$_{3/2}$</td>
<td>Fe-1</td>
<td>Fe metal</td>
<td>707.0</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>Fe-2</td>
<td>Fe$_3$O$_4$ (Fe$^{2+}$)</td>
<td>708.5</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Fe-3</td>
<td>Fe$_2$O$_4$ (Fe$^{3+}$) / Fe$_2$O$_3$/FeOOH</td>
<td>711.0</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Fe-4</td>
<td>Fe$_2$O$_3$-satellite</td>
<td>712.7</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table IV. Average fractional intensity from fitting of Fe 2p$_{3/2}$ XPS spectrum. Sample standard deviation in brackets. The Fe$^{2+}$/Fe$^{3+}$ ratio is calculated from ((Fe-3) + (Fe-4))/(Fe-2). The Fe$_{oxides}$/Fe$_{metal}$ ratio is calculated from ((Fe-2) + (Fe-3) + (Fe-4))/((Fe-1) and is proportional to the passive film thickness.

<table>
<thead>
<tr>
<th>[Cl$^-$] (mM)</th>
<th>[MoO$_4^{2-}$] (mM)</th>
<th>Fe-1</th>
<th>Fe-2</th>
<th>Fe-3</th>
<th>Fe-4</th>
<th>$\frac{Fe^{2+}}{Fe^{3+}}$ Ratio</th>
<th>$\frac{Fe_{oxides}}{Fe_{metal}}$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>113</td>
<td>0</td>
<td>0.17 (&lt;0.01)</td>
<td>0.18 (0.05)</td>
<td>0.55 (0.03)</td>
<td>0.10 (0.01)</td>
<td>3.6</td>
<td>4.7</td>
</tr>
<tr>
<td>113</td>
<td>14.6</td>
<td>0.21 (&lt;0.01)</td>
<td>0.24 (0.01)</td>
<td>0.47 (0.02)</td>
<td>0.08 (0.03)</td>
<td>2.3</td>
<td>3.8</td>
</tr>
<tr>
<td>564</td>
<td>0</td>
<td>0.17 (&lt;0.01)</td>
<td>0.19 (0.05)</td>
<td>0.53 (0.06)</td>
<td>0.11 (0.01)</td>
<td>3.3</td>
<td>5.0</td>
</tr>
<tr>
<td>564</td>
<td>14.6</td>
<td>0.23 (0.01)</td>
<td>0.26 (0.01)</td>
<td>0.45 (0.01)</td>
<td>0.06 (&lt;0.01)</td>
<td>1.9</td>
<td>3.4</td>
</tr>
<tr>
<td>564</td>
<td>146</td>
<td>0.16 (0.01)</td>
<td>0.21 (0.02)</td>
<td>0.51 (0.01)</td>
<td>0.12 (0.01)</td>
<td>3.0</td>
<td>5.2</td>
</tr>
</tbody>
</table>
In order to analyze the effect of molybdate on the passivation of the carbon steel as a function of time, Table V gives the \( \eta \) values for the early stage (0.5 h) and later stage (20 h) of passivation. In Set B (14.6 mM \( \text{MoO}_4^{2-} \)), using Set A (no molybdate) as the baseline, \( \eta \) at 0.5 h ranged from 2% to 31% while \( \eta \) at 20 h ranged from −17% to −4% for all chloride concentrations except 564 mM \( \text{Cl}^- \). The \( \eta \) values at 20 h ranged from 2% to 31% while \( \eta \) at 0.5 h ranged from 2% to 31% for all chloride concentrations except 564 mM \( \text{Cl}^- \). The \( \eta \) values at 20 h were near 100% due to the successful prevention of localized corrosion by molybdate.

The positive and relatively high \( \eta \) values at 0.5 h indicate that molybdate results in a faster passivation rate during the early stage of passivation. This is most likely due to the adsorption of molybdate anions on the outer surface of the growing passive oxide film (as indicated by XPS results). The competitive adsorption of molybdate against chloride would have allowed the passive film to thicken faster by reducing the dissolution rate of the passive oxide film at the oxide/solution interface.

The very high \( \eta \) values observed at 20 h from the prevention of spontaneous localized corrosion by molybdate is due to the large difference in \( R_p \) for active and passive carbon steel. However, for samples that would have remained passive even in the absence of molybdate, the negative \( \eta \) observed at 0.5 h indicates that molybdate’s presence at a late passivation stage did not lead to a decrease in the passive current density and may even increase it slightly. Nonetheless the absolute corrosion rates remained very low (at insignificant levels for most industrial applications) as the carbon steel samples were already passivated. Possible explanations related to the precipitation of CaMoO₄ are discussed in a later section regarding this phenomenon.

**Reduction of total extent of carbon steel oxidation due to inhibition by molybdate.**—Comparison of \( \eta \) values for a corrosion inhibitor at specific times provides useful information but offers only a snapshot of the corrosion situation at a particular time. To obtain a better understanding of the overall corrosion situation, it is valuable to estimate the total extent of carbon steel oxidation during the passivation process.

At moderate temperatures, the thermal oxidation of iron follows a parabolic law and during passivation under potentiostatic conditions the current density declines with time following an inverse power law. Thus \( \eta \) values during passivation under open-circuit conditions in this work (obtained from \( R_p \) via the Stern-Geary equation) were fitted with a power law equation as a function of time (\( t \)):

\[
\frac{1}{R_p} = kt^{-\alpha}
\]

where \( k, k_t \), and \( \alpha \) are constants. Most of the \( \alpha \) values ranged from −0.9 to −0.6 in this work. Figure 8 (with \( B \) assumed to be 52 mV) shows that the power law relationship in Equation 5 fits the experimental data well, with \( R^2 > 0.99 \). Note that the actual value of \( B \) affects only the value of \( k_t \) but not the nature of the (power law) relationship between \( i_{corr} \) and \( t \).

Integration of \( i_{corr} \) over the corrosion time duration gives the charge density passed \( (Q) \) which is then converted using Faraday’s law into an estimated thickness of carbon steel oxidized \( (d_{Fe}) \). The charge density passed is a measure of the extent of oxidation of the metal, regardless of whether this leads to active dissolution or passive film formation.

For experiments in which the carbon steel specimen subsequently experienced passivity breakdown, the \( d_{Fe} \) value given is the projected value at 20 h based on the behavior before passivity breakdown, i.e. the thickness of steel that would have been oxidized during passivation if localized corrosion had not initiated.

\[
Q = \frac{Bk}{\alpha + 1} \left[ t^{\alpha+1} - t_i^{\alpha+1} \right]
\]

where \( t_i \) and \( t_f \) are the initial and final time (taken to be 0 h and 20 h respectively in this work).

\[
d_{Fe} = \frac{MQ}{nF\rho}
\]

where \( M \) is the molecular weight, \( \rho \) is the density, \( F \) is Faraday’s constant, and \( n \) is the number of electrons transferred per unit chemical species. For simplicity, values of pure iron are used,

![Figure 8. Corrosion current density \( (i_{corr}) \) vs. time (\( t \)) for Set A (pH 12.5 solutions with various chloride concentrations and no molybdate), showing a power law relationship between \( i_{corr} \) and \( t \) under open-circuit conditions.](image)

<table>
<thead>
<tr>
<th>Solution</th>
<th>[Cl(^-)] (mM)</th>
<th>[MoO(_4^{2-})] (mM)</th>
<th>State at 0.5 h (without MoO(_4^{2-}))</th>
<th>State at 0.5 h (with MoO(_4^{2-}))</th>
<th>( \eta ) at 0.5 h (%)</th>
<th>State at 20 h (without MoO(_4^{2-}))</th>
<th>State at 20 h (with MoO(_4^{2-}))</th>
<th>( \eta ) at 20 h (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 12.5</td>
<td>0</td>
<td>14.6</td>
<td>Passive</td>
<td>Passive</td>
<td>Passive</td>
<td>Passive</td>
<td>Passive</td>
<td>Passive</td>
</tr>
</tbody>
</table>

Set B (using Set A as baseline)

| pH 12.5  | 564             | 0                   | Passive                         | Passive                         | Passive           | Passive                         | Passive                         | Passive           |

Set C

| pH 12.5  | 564             | 0                   | Passive                         | Passive                         | Passive           | Passive                         | Passive                         | Passive           |
Effect of CaMoO₄ precipitates on passivation.—Molybdate anions adsorbed on the passive film surface most likely served as the nucleation sites for the subsequent precipitation of the first layer of calcium molybdate spherulites, which explains the adherence of these spherulites to the sample surface. Calcium molybdate spherulites that precipitated in the bulk of the solution before settling on the passive film are unlikely to have adhered as well to the passive film surface.

Figure 4a showed that at 20 h, the \( R_p \) for passivated systems in Set B is marginally lower (indicating a slightly higher \( i_{corr} \)) than Set A. Furthermore, comparing Set B to Set A, the total extent of oxidation (Figure 9a) and the thickness of the passive film were reduced while the proportion of ferrous cations in the passive film (Table IV) increased. These results observed in the presence of CaMoO₄ precipitates may be due to one or more of the following reasons, related to the fact that the precipitated CaMoO₄ acts as a porous insulator which blocks the diffusion of oxygen to and/or corrosion products away from the steel’s surface.

Firstly, a higher dissolution rate for the passive oxide film (containing a higher proportion of ferrous cations) formed in the presence of CaMoO₄ precipitates since ferrous cations are more soluble than ferric cations. The higher proportion of ferrous cations may be due to less dissolved oxygen reaching the steel surface, which makes it unavailable to chemically oxidize the ferrous cations to ferric cations. At steady state, for the passive film to be maintained at a constant thickness, the passive current density (rate of oxidation at the metal/film interface) has to be equal to the dissolution current at the film/solution interface. A higher dissolution current requires a higher passive current (hence lower \( R_p \)), which is also consistent with a lower passive film thickness. However, the faster increase in \( R_p \) during the early passivation stage in the presence of molybdate implies a lower dissolution rate due to molybdate stabilizing ferrous cations in the passive film, as supported by the XPS analysis in Table IV. This explanation is plausible only if the dissolution rate at the film/solution interface varies with time. That is to say, in the presence of molybdate the dissolution rate is a low and relatively constant value while in the absence of molybdate the dissolution rate is higher at first and then subsequently drops to a lower value.

Secondly, the higher current density at a late passivation stage may be a result of the oxidation of ferrous cations into ferric cations. Due to obstruction by CaMoO₄ spherulites on the surface, the oxidation of ferrous cations within the passive film by dissolved oxygen in the solution was held up in the early passivation period, resulting in a slow and ongoing oxidation of ferrous cations into ferric cations in the later period of passivation. This is aided by the restricted diffusion of ferrous cations away from the steel surface by the precipitated CaMoO₄, which means they are more likely to be electrochemically oxidized to ferric cations given sufficient time.

Thirdly, an increase in the electrical conductivity of the passive oxide film facilitates the cathodic reduction reaction despite a decrease in the effective surface area caused by the adsorbed CaMoO₄ spherulites. This is due to either an increase in donor density (oxygen vacancies) from the hindered entry of oxygen atoms into the passive film or the passive film behaving more like Fe₃O₄ (which is the most conductive among iron oxides) rather than Fe₂O₃ due to the higher proportion of ferrous cations that were found in the XPS analysis (Table IV).

The conditions necessary for coverage of the entire carbon steel surface by CaMoO₄ were fulfilled in this work only by the pH 12.5 solution constituted by Ca(OH)₂ containing 48.6 mM MoO₄²⁻. Only in the case of complete surface coverage was the CaMoO₄ film’s effect detectable within the EIS impedance data as a second time constant (Figure 2); the EIS impedance data exhibited only one time constant when the surface coverage by CaMoO₄ spherulites was not complete. The presence of a complete CaMoO₄ film precipitated on the carbon steel surface resulted in a more negative OCP and higher \( R_p \) compared to that observed in the absence or incomplete coverage by such a precipitate film. This implies a decrease in the cathodic reaction rate, i.e. cathodic inhibition due to a significant reduction in the effective surface area available for the oxygen reduction reaction.

\[
d_{Fe} = c_{Fe}Q
\]

where \( M = 55.85 \text{ g mol}^{-1}, \rho = 7.87 \text{ g cm}^{-3} \text{ and } n = 3; \]

\[
d_{Fe} = 2.45 \times 10^{-5} \text{ cm}^{3}\text{ mol}^{-1}.
\]

Comparing Sets A and B in Figure 9a, if \( B \) is 52 mV, 14.6 mM MoO₄²⁻ decreased the \( d_{Fe} \) by as much as 0.2 nm (one monolayer) in pH 12.5 solutions (representing a 20% drop). Figure 9b shows the \( d_{Fe} \) against the molybdate concentration for Set C, where \( d_{Fe} \) decreased with increasing molybdate concentration before increasing at 146 mM MoO₄²⁻ to a value that is lower than in the absence of molybdate. For 48.6 mM MoO₄²⁻, the presence of a complete CaMoO₄ precipitate film in the pH 12.5 Ca(OH)₂ solution resulted in the \( d_{Fe} \) being lower by 0.1 nm compared to carbon steel samples in pH 12.5 NaOH solution.

If it is assumed that all the Fe atoms oxidized contribute toward passive film growth, then the electrochemical results are consistent with the XPS results presented in Table IV, where the presence of 14.6 mM MoO₄²⁻ decreased the \( \text{Fe}_{\text{oxide}}/\text{Fe}_{\text{metal}} \) ratio, indicating a thinner oxide film. The increase in \( d_{Fe} \) at 146 mM MoO₄²⁻ in Set C is also reflected in the increase in the \( \text{Fe}_{\text{oxide}}/\text{Fe}_{\text{metal}} \) ratio in Table IV.

These results indicate that regarding the addition of molybdate, the faster increase in \( R_p \) during the early passivation stage (where the corrosion rate is higher) outweighs the slightly higher corrosion rate of passivated systems, such that the overall extent of metal oxidized during passivation is lower. This may also be interpreted as molybdate reducing the extent of oxidation necessary (thinner passive film) for the carbon steel to achieve passivation in alkaline solutions.

**Figure 9.** (a) Comparison of \( d_{Fe} \) against chloride concentration for Set A (0 mM MoO₄²⁻) vs. Set B (14.6 mM MoO₄²⁻), and (b) comparison of \( d_{Fe} \) against molybdate concentration for Set C (pH 12.5 solutions with 564 mM Cl⁻).
SEM imaging (Figure 5c) showed that this complete precipitate film has a thickness of a few microns, significantly thicker than the passive oxide film thickness of around 5 nm. 37 The small $R_{pore}$ value (Table II) is consistent with a porous CaMoO$_4$ film that permits access by the sample electrolyte to the passive oxide film surface; $R_{pore}$ is in fact the net resistance of two parallel resistances: the resistance of the mesh formed by CaMoO$_4$ particles and the solution resistance through the pores of the CaMoO$_4$ film, with the former being much higher than the latter. Hence oxygen reduction still occurs mainly on the passive film surface.

Calculations of the expected volume and the apparent volume of the precipitates present on the carbon steel surface show that the porosity of the CaMoO$_4$ film is around 60% if the precipitated film is assumed to be stacked three layers thick, with each layer having an average thickness of 6.7 μm (values from SEM imaging). Note that precipitation of CaMoO$_4$ occurred on all wetted areas (around 100 cm$^2$) within the electrochemical test cell and not just the exposed carbon steel area (1 cm$^2$). As precipitation of CaMoO$_4$ could occur during N$_2$ purging when [MoO$_4$] = 146 mM, prior to the immersion of the carbon steel electrode, the mechanism of precipitation is likely simply exceeding the solubility limit of CaMoO$_4$ and does not involve the carbon steel. Also note that the calcium concentration of the pH 12.5 solution (0.5 × 31.6 mM = 15.8 mM) is the limiting factor when [MoO$_4$] = 48.6 mM. The values for the molecular weight and density of CaMoO$_4$ used in calculations are 200.02 g mol$^{-1}$ and 4.35 g cm$^{-3}$ respectively. 38 By taking the square of the cube root of the proportion for the dense CaMoO$_4$ phase, this implies that around 50% of the carbon steel’s surface area is unavailable for the oxygen reduction reaction.

The discrepancy between the reduction in the effective surface area (50%) of the working electrode due to adsorption by CaMoO$_4$ particles and the increase in $R_p$ (<20%) in the presence of this thick precipitated CaMoO$_4$ film indicates that a more refined model may be needed to estimate the decrease in effective surface area. It could also imply that some reduction of oxygen occurs on the CaMoO$_4$ precipitate mesh before reaching the passive film surface. Nonetheless, it is clear that a thick CaMoO$_4$ film precipitated over the entire surface provides a cathodic inhibition mechanism for reducing the passive current density.

In this work, the addition of molybdate results in an overall reduction in the extent of oxidation (smaller $d_{ca}$) regardless of whether the CaMoO$_4$ precipitates form a complete film. However, the analysis here suggests that for good long-term corrosion protection (higher $R_p$ for passivated systems), a complete CaMoO$_4$ film is better than a bare surface (no CaMoO$_4$ film) which in turn is better than an incomplete precipitate film where parts of the passive oxide film are still exposed. This is important in cases where the corrosion time duration is long such that the slightly lower $R_p$ may eventually nullify the decrease in oxidation achieved during the early stage of passivation. This also illustrates the usefulness of estimating the overall extent of carbon steel oxidation as a parameter to complement the measurement of $R_p$ in assessing the effectiveness of a corrosion inhibitor.

Note that the precipitation of CaMoO$_4$ on the carbon steel surface also helps to reduce the susceptibility of the carbon steel toward localized corrosion by shifting the OCP in the negative direction up to 80 mV (Figure 1c). This increases the passive potential range between the corrosion potential and the pitting potential.

**Effect of molybdate on passivation without precipitation of CaMoO$_4$**—In the absence of precipitated CaMoO$_4$, such as 146 mM MoO$_4^{2−}$ or when NaOH is used in place of Ca(OH)$_2$, the OCP is more positive by up to 70 mV (Figure 1c) compared to passive systems in Set A without molybdate inhibitor (Figure 1a). In addition, XPS results (Table IV) showed that the thickness and the proportion of ferric cations of the passive film increased back to levels comparable to that observed without addition of molybdate.

To explain these observations, a likely mechanism is the competitive adsorption of molybdate against chloride anions on the surface of the passive oxide film. As chloride anions complex ferrous cations and promote the dissolution of the passive film at the film/solution interface, molybdate competes with chloride for adsorption on the passive film surface and stabilizes the ferrous cations within the passive film, at active sites of passive film defects. This prevents pit nucleation and/or propagation in a sort of pore-plugging mechanism, promoting passivation and avoiding passivity breakdown. 49

The slightly more positive OCP in the presence of relatively high concentrations of molybdate may indicate that molybdate either has a catalytic effect on oxygen reduction or that molybdate is itself a weakly oxidizing agent. The latter explanation is counter to the common view of molybdate as a non-oxidizing anodic inhibitor and that molybdate should be redox inactive in moderately alkaline solutions. 49 Nevertheless, some support for this latter explanation is provided by the work of Lopez-Garrity and Frankel who observed that for aluminum alloy (AA2024-T3) in NaCl solution, molybdate may be reduced over the intermetallic particles and then subsequently re-oxidized by dissolved oxygen to form polyomolybdate species. 26 They estimated the reversible potential in neutral NaCl solution for the reduction of MoO$_4^{2−}$ to Mo(OH)$_4^{−}$ at 0.1 M MoO$_4^{2−}$ to be around −0.64 V vs. SCE. Considering that localized acidification may occur at active sites, this reversible potential should range from −0.40 V to −0.88 V vs. SCE for pH 5 to pH 9.

Thus, it may be that molybdate is reduced to a lower oxidation state at nascent sites of localized corrosion where the potential is sufficiently negative for molybdate to be redox active, supported by the oxidation of the carbon steel. The Mo (IV) species is subsequently re-oxidized to a higher oxidation state supported by the reduction of oxygen, which explains why Mo (IV) was not detected in the XPS experiments, although as noted the Mo 3d peaks in Figure 7a are slightly asymmetrical with a very faint shoulder on the lower binding energy side of both peaks that could be due to a small amount of Mo (IV).

**Conclusions**

The effect of molybdate on the passivation of AISI 1020 carbon steel under open-circuit conditions in pH 12.5 solutions containing chloride was investigated via electrochemical tests and surface characterization techniques.

During the early stage, molybdate increased the rate of passivation, with the inhibition efficiency being positive. The most likely mechanism is the competitive adsorption of molybdate against chloride on the passive film surface, resulting in a stabilization of the ferrous cations against complexing by chloride. This reduces the dissolution rate during the early stage of passivation such that the passive film growth is faster.

During the later stage when the carbon steel has passivated, the presence of molybdate in Ca(OH)$_2$ solutions resulted in slightly lower $R_p$ values (negative inhibition efficiency), most likely associated with the effects of CaMoO$_4$ precipitation over parts of the sample surface, such as the passive film having a higher proportion of ferrous cations and a smaller thickness. However, the precipitation of a complete CaMoO$_4$ film over the entire carbon steel surface can increase the $R_p$ by up to 0.5 M2 cm$^{-2}$ (compared to a bare surface) through a cathodic inhibition mechanism, due to a significant reduction in the effective surface area available for oxygen reduction. Therefore, careful control of the solution conditions such that a complete CaMoO$_4$ film precipitates over the entire carbon steel surface is important as partial coverage leads to $R_p$ values lower than that on bare surfaces.

The total extent of Fe oxidation was estimated from the electrochemical data and showed that regardless of its effect on the final $R_p$, the presence of CaMoO$_4$ precipitates led to a decrease in the total extent of Fe oxidation in pH 12.5 solutions containing chloride, indicating an overall beneficial effect. The slightly lower long-term $R_p$ will be an issue only when the corrosion time duration is long, such that the advantage of the decrease in Fe oxidation in the early passivation period is negated. This illustrates the usefulness of the overall extent of Fe oxidation as a parameter to complement the measurement of $R_p$ at a specific time in assessing the effectiveness of a corrosion inhibitor.
For cases where CaMoO₄ precipitation did not occur, the passive films formed in the absence and presence of molybdate have similar thickness and ferric/ferrous cations ratio, except that the latter has molybdate anions adsorbed on the surface. The more positive OCP values in the presence of molybdate (by around 70 mV) may indicate that molybdate is acting as a weak oxidizing agent, possibly at active sites of passive film defects.

Finally, molybdate was also shown to be an effective corrosion inhibitor against localized corrosion, with 14.6 mM MoO₄²⁻ being sufficient to prevent passivity breakdown in pH 12.5 solution containing 564 mM Cl⁻.

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References