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Role of Chloride on the Environmental Degradation of Micro-Alloyed Steel in Simulated Fuel Grade Ethanol Environment

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Reference

ABSTRACT
In this study, micro-alloyed steel (MAS) material commonly used in the manufacture of auto parts and pipes was immersed in simulated fuel grade ethanol (SFGE) blends and its performance was evaluated. In order to determine the role of chloride on corrosion behavior, electrochemical measurement was conducted in low-conductivity ethanolic solutions in the absence of supporting electrolyte; also mass loss test was performed. Consistent with the mass loss and electrochemical test results, the effect of chloride on the degradation of MAS in the fuel ethanol environments can be classified from the least corrosive concentration to the highest as follows: 0 mg/L < 32 mg/L < 64 mg/L NaCl. Chloride increased the pitting tendency of MAS in E20, E40, and E80 blends.

Keywords
micro-alloyed steel, fuel-grade ethanol, polarization, chloride, pitting
Introduction

Over the last ten years, many governments have commenced looking for a way to combat the impact of fuel emissions on the environment. Consequently, the use of fuel ethanol by blending it with gasoline has become prevalent in a number of countries. In so doing, fewer emissions are released into the environment, contributing significantly to greenhouse gas (GHG) mitigation. E10 (10% bioethanol – 90% gasoline), which is one of the most prevalent biofuel blends, is used as a substitute for gasoline. Ethanol is one of the core components of impending reformulated fuels and suggests limitless advantages due to its physical and chemical characteristics, low production costs, and environmental friendliness, amongst many others [1]. Such advantages include a thriving farm industry, reduced dependence on foreign oil, lower emissions, and valuable use of by-products. However, fuel ethanol has some downsides regarding material compatibility. Its chemical composition can have a degrading effect on materials that are typically compatible with gasoline [2–4].

Incidents of corrosion attack have been found in some fuel ethanol system materials such as castings in fuel pumps and fuel tanks, steel, and aluminum alloys [1,5]. The presence of components such as chlorides, water, methanol, dissolved oxygen, and acetic acid within the established limits by the American Society for Testing and Materials (ASTM) in ASTM D4806-16a [6] might increase the susceptibility of steel to corrosion and stress corrosion cracking (SCC) [7]. When dissolved oxygen was minimized through nitrogen purging, there was no SCC in the presence of all additional species at their maximum levels. However, on introducing oxygen, SCC occurred [7]. In addition, a study carried out by the American Petroleum Institute [8] involved the use of corrosion potential technique for evaluating SCC susceptibility of steel when exposed to ethanol. The results revealed increased proneness to SCC with increasing corrosion potential. Further studies include the addition of chemical additives to SFGE to provide scavenging of oxygen in solution as well as inhibition of SCC in fuel grade ethanol (FGE) using slow strain rate (SSR) techniques [9], besides examination of pitting corrosion in SFGE solutions on carbon steel [10]. The results obtained by scavenging oxygen showed a dependence of ethanol SCC on corrosion potential that was consistent with observations from previous American Petroleum Institute (API) studies.

The effect of inorganic chloride in ethanolic solutions on the SCC behavior of carbon steels has also been investigated by varying the inorganic chloride concentrations between 0 and 70 mg/L [11], and a much wider concentration from 0 to 0.1 M [12] in SFGE. Lou et al. [11] reported that chloride disrupts surface film and enhances pitting corrosion. Cao et al. [12] found that chloride is required for ethanol SCC but is not the governing influence for crack growth. Besides, significant information has been collected from reviews, reports, and summaries of studies investigating the compatibility of fuel ethanol with certain metallic materials [13–15]. All of the findings point to the fact that SCC of metals do occur in fuel grade ethanol (FGE) environment, whether simulated or field FGE due to several factors that have been mentioned.

In this study, micro-alloyed steel is analyzed for failure in simulated E20, E40, and E80 fuel ethanol environments under aerated conditions. Micro-alloyed steel is
a cost-effective high strength steel, which has favorable application in the automotive industry. Nonetheless, there is sparse information in literature regarding the corrosion behavior of micro-alloyed steel in fuel ethanol blends.

Experimental

MATERIALS AND TEST ENVIRONMENTS

The metal specimens used for this study were machined from new micro-alloyed steel plates in as-received condition. The chemical composition of this steel is presented in Table 1. The fuels used for immersion and electrochemical tests were E20, E40, and E80 blends. The simulated fuel ethanol test environments were prepared partly in consistence with ASTM Standard D4806 [6] for fuel grade ethanol. The reagents used include: 195 proof ethanol, glacial acetic acid, pure methanol, pure sodium chloride (NaCl) with purity >99%, and ultra-pure water (~18 MΩ-cm). NaCl was first dissolved in water, and then added to ethanol to reach the specified NaCl and water concentrations, respectively, for each of the fuel blends. The concentration of chloride was methodically altered to study its influence on the corrosion and fracture behavior of micro-alloyed steel. This was achieved by using 0, 32, and 64 mg/L chloride ion (Cl⁻) concentrations [16]. The denaturant used was unleaded gasoline. The baseline composition for the simulated fuel-grade ethanol used in this study is shown in Table 2. All reagents used were of analytical grade. The corrosion tests were carried out in aerated conditions at room temperature of 27°C. To study the influence of chloride, reference tests were carried out in the absence of chloride for all the ethanol concentrations.

IMMERSION TEST

Flat square coupons of dimensions 30 by 30 by 11 mm were machined from micro-alloyed steel plates for mass loss tests. The specimens were dry-abraded up to 800 grit, degreased with acetone, and used immediately for testing. The area as well as weight of each specimen was measured before exposure to the test environments for the purpose of post-calculation. Immersion of duplicate samples for each test condition was carried out for 60 days’ duration. A total of 18 samples were used for the test. Each sample was suspended in 300 ml of the test solution using airtight plastic containers. For E20 blend, the test solution of 300 ml was obtained by adding 240 ml unleaded gasoline to 60 ml SFGE. E40 and E80 blends were also prepared by the

| TABLE 1 |
| Chemical composition of micro-alloyed steel in as-received condition. |
| Element | C | Mn | Si | Cr | Ni | Al | Ti | Mo | Cu | Fe |
| Micro-alloyed | 0.13 | 0.77 | 0.012 | 0.027 | 0.015 | 0.042 | 0.0025 | 0.0017 | 0.006 | balance |

| TABLE 2 |
| Baseline composition of simulated fuel grade ethanol used for the tests. |
| 195 Proof Ethanol (vol. %) | Methanol (vol. %) | Water (vol. %) | NaCl (mg/L) | Acetic Acid (mg/L) |
| 98.5 | 0.5 | 1 | 32 | 56 |
addition of 180 ml unleaded gasoline to 120 ml SFGE and 60 ml unleaded gasoline to 240 ml SFGE, respectively. The solution was replenished fortnightly to diminish changes in solution composition, replace the ionic impurities, and to compensate for evaporation. After the immersion tests, thick oxide films formed on the samples’ surfaces were removed by mechanical and chemical means, in accordance with ASTM G1-03(2011) [17] for preparing, cleaning, and evaluating corrosion test specimens. The surfaces of the corroded samples were further characterized using a FEI-430 NOVA NANO FEG-SEM and a Jeol scanning electron microscope.

ELECTROCHEMICAL MEASUREMENTS

A Gamry reference 600 Potentiostat/Galvanostat/ZRA was used for open circuit potential (OCP) and anodic polarization measurements. The test setup comprises of a three electrode glass cell with saturated calomel electrode (SCE) as the reference electrode and platinum electrode as a counter electrode (Fig. 1).

The platinum electrode was constructed by using a glass frit to isolate platinum wire from the working electrode. To minimize the effect of high solution resistance associated with ethanolic solutions [12,18], the electrochemical cell was designed in such a way as to ensure minimal distance between the working electrode and the lugin capillary of the reference electrode. Each experiment was carried out in duplicate so as to determine the reproducibility of the experiments. Eighteen rectangular samples with dimensions 14 by 10 by 5 mm were used for the electrochemical tests. The samples were dry-abraded up to 2000 grit, degreased with acetone, and dried. The test samples were further mounted with bakelite, in this manner decreasing contact area. The mounted samples were threaded to a carbon steel rod (working electrode) and suspended in solution. The working electrode was also insulated from the test solution by means of a Teflon® tape. All the polarization tests began with cathodic polarization at −0.75 V versus SCE in order to ensure similar reduced metal surfaces for the tests. A potential scan rate of 2 mV/s was used to lessen the influence of chloride leakage from high-silica glass as described elsewhere [9,18].

FIG. 1
Schematic of the electrochemical cell design for anodic polarization tests.
VISUAL EXAMINATION AND DETERMINATION OF CORROSION RATES

Visual examination was carried out to verify existence of pits, discoloration at the completion of exposure, or alteration of surface texture. Weight measurements were taken to record the mass loss of each specimen exposed to the test environment. The corrosion rate was computed in mils per year (mpy) using equation (1) in accordance with ASTM Standard G1-03 [17]:

\[
\text{Corrosion rate} = \frac{K}{C^2} \cdot \frac{W}{A} \cdot \frac{T}{D} 
\]

where:

- \( K \) = a constant (534),
- \( T \) = the exposure time in hours,
- \( A \) = the sample area in square inches,
- \( W \) is the mass loss in miligrams, and
- \( D \) is the density in g/cm³.

MICROSTRUCTURE AND RAMAN SPECTROSCOPY ANALYSIS

Characterization of surface morphology after corrosion was carried out using a FEG-SEM, coupled with energy dispersive spectrometer (EDS). The corrosion products from immersion tests were analyzed with Nicolet Almega XR Dispersive Raman spectrometer having a wavelength of 530 nm.

Results and Discussion

ROLE OF CHLORIDE ON MASS LOSS TESTS

For each ethanol concentration, the effect of chloride was investigated via 32 and 64 mg/L NaCl and with respect to a reference test in the absence of chloride. The effect of NaCl additions on the corrosion behaviour of micro-alloyed steel in E20, E40 and E80 is shown in Fig. 2.

In E20, corrosion rate is seen to increase from 8.17E-03 mpy in the absence of chloride to 1.25E-02 mpy upon addition of 32 mg/L chloride concentration. When

FIG. 2

Effect of chloride on the corrosion rate of MAS in simulated E20, E40 and E80 fuel ethanol environments (average values).
chloride was increased to 64 mg/L, a higher corrosion rate of 1.96E-02 mpy was observed. This implies that with chloride addition and increasing chloride concentration, the material deteriorates in E20 with respect to the reference test in the absence of chloride. Similarly, in both E40 and E80 with 32 mg/L NaCl, there was an increase in corrosion rate with respect to the reference test from 1.62E-02 to 2.21E-02 mpy in E40 and 4.99E-02 to 6.03E-02 mpy in E80. However, the addition of 64 mg/L NaCl caused a drop in corrosion rate of MAS in E40 (2.01E-02 mpy) and E80 (5.88E-02 mpy). This behavior was unexpected as chloride products formed are not expected to improve corrosion behavior [19].

Generally, the presence of chloride ions in solution initiates breakdown of passivity and the reaction is known to be diffusion controlled. Nevertheless, in sodium chloride solutions at certain concentrations (dependent on material-environment system), the film thickening rate can increase with increasing concentration of sodium chloride [20,21]. In this work, the adsorption of chloride ions in micro-alloyed steel, up to a threshold concentration of 32 mg/L from E40 and E80 fuel ethanol environments, resulted in degradation of the material. At higher chloride concentration of 64 mg/L, corrosive actions at the grain boundaries have been slowed down, thereby reducing corrosion rate. The margin of reduction in corrosion rate of MAS in E40 and E80 in the presence of 64 mg/L NaCl is very small, approximately 9 % in the case of E40 and 2 % in the case of E80. Consequently, the low margin of reduction suggests that increasing chloride concentration does not have any significant effect on the corrosion rate of MAS in E40 and E80 simulated fuel ethanol blends. However, an assessment of all the test conditions reveals that, the reference test carried out in the absence of chloride, displays the lowest corrosion rate. Therefore, the presence of chloride in fuel ethanol either in low or high concentrations can be said to be a potential problem in the life cycle of MAS.

Figs. 3–5 show the morphology of MAS samples after 60 days of immersion in the presence and absence of chloride, taken at identical magnification of 1000x. Pitting (localized) corrosion is obvious on the SEM images of the samples, which were immersed in E20, E40, and E80 with 32 mg/L NaCl (Fig. 4). The existence of pits is attributed to the action of chloride since no pitting was detected on the samples tested in the absence of chloride. This finding is in agreement with published literature regarding the role of chloride on corrosion of carbon steel in simulated fuel grade ethanol environment [18]. It must also be pointed out that for micro-alloyed steel samples immersed in E20, both pit size and pit density increased as chloride concentration increased from 32 to 64 mg/L as shown by the SEM images in Fig. 5.

ROLE OF CHLORIDE ON ELECTROCHEMICAL TESTS
Anodic polarization was used to investigate the polarization behavior of MAS. Reference electrochemical tests were carried out in the absence of chloride and used as a basis for investigating the effect of chloride on polarization behavior of MAS. The effects of chloride and increasing chloride concentration on the polarization behavior of MAS in the presence and absence of chloride are shown in Fig. 6. In order to mimic a parallel outcome of potential disruption from equilibrium in the fuel ethanol environments, MAS samples were anodically polarized with identical potential difference (1.5VSCE) from their preliminary OCPs. The result in Fig. 6 shows that MAS does not exhibit distinct passivation behavior as well as pitting potential with
anodic polarization in the range of ethanol-chloride ratio. Poor passivity was exhibited by MAS in the fuel ethanol environments, which is consistent with the behavior of metals in alcoholic environments as reported in literature [18]. To permit a number of corrosion kinetics and elimination of chloride seepage from the salt bridge, the polarization experiments were carried out at a scan rate of 2 mV/s. The $E_{corr}$ and $i_{corr-estimate}$ as observed for each test condition are shown in Table 3. For all the samples tested in E20, E40, and E80, the evaluated current density ($I_{corr-estimate}$)

FIG. 3 Post-corrosion SEM images of MAS at 1000x after 60 days immersion in (a) E20, (b) E40, and (c) E80 in the absence of NaCl showing presence of cracks and absence of pits.

FIG. 4 Post-corrosion SEM images of MAS at 500x after 60 days immersion in (a) E40 and (b) E80 with additions of 32 mg/L NaCl showing pitting due to presence of chloride.
measured from the polarization curves increased with increasing chloride concentration up to 64 mg/L chloride. It is important to state that the corrosion rates obtained by immersion tests in E40 and E80 do not entirely agree with the polarization test results. From the mass loss tests, a decrease in corrosion rate of MAS was observed with 64 mg/L chloride concentration in E40 and E80. The poor correlation seen between the 60 days’ mass loss corrosion rates and the electrochemical corrosion rates is probably caused by the protective action of thick corrosion products formed on the samples with longer exposure time during the mass loss tests. The polarization measurement gave a picture of the corrosion rate, while the mass loss measurement integrated the corrosion rate over the time of immersion.

However, consistent with the mass loss and electrochemical test results, the effect of chloride on the degradation of MAS in the fuel ethanol environments can be classified from the least corrosive concentration to the highest as follows: 0 mg/L < 32 mg/L < 64 mg/L NaCl.

CHARACTERIZATION OF THE OXIDE LAYERS FORMED ON MAS EXPOSED TO E20, E40, AND E80

Analyses of the corroded steels after 60 days of immersion in E20, E40, and E80 at 27°C were carried out by Raman spectroscopy. Fig. 7 shows the results of Raman spectroscopy of the corrosion products. It reveals the presence of iron oxyhydroxides such as iron hydroxide [Fe(OH)$_2$], goethite [$\alpha$-FeOOH], and maghemite [$\gamma$-Fe$_2$O$_3$] [22–24]. A strong band at 549 cm$^{-1}$ is found, signifying the presence of hematite. The existence of water in the simulated fuel ethanol environments stimulates the formation of iron hydroxide as reported elsewhere [18]. A broad and stronger band at 1423 cm$^{-1}$ present in the Raman spectroscopy of corrosion products obtained from samples immersed in the presence and absence of NaCl indicates the presence of maghemite. A strong band of Goethite is also present at 550 cm$^{-1}$.

Conclusion

The role of chloride in the environmental degradation of micro-alloyed steel in simulated E20, E40, and E80 fuel ethanol blends has been studied with 0–64 mg/L NaCl concentration. The specific conclusions arrived at are as follows:
FIG. 6
Effect of chloride on anodic polarization of MAS in (a) E20, (b) E40, and (c) E80 showing lower current density measured for MAS in E20 in all the tested conditions.
1. Chloride increased the pitting tendency of MAS in E20, E40, and E80 blends. In the absence of chloride, no pitting was observed.

2. The mass loss of MAS increased in E20 with increase in chloride concentration up to 64 mg/L.

3. In E40 and E80, mass loss of MAS increased with the presence of chloride up to a concentration of 32 mg/L; beyond that threshold, the effect of increasing chloride was insignificant.

4. The correlation between mass loss corrosion rates and electrochemical corrosion rates is poor. The lack of agreement is probably caused by the protective action of thick corrosion products formed on the samples with longer exposure time during the mass loss tests.

5. Consistent with the mass loss and electrochemical test results, the effect of chloride on the degradation of MAS in the fuel ethanol environments can be classified from the least corrosive concentration to the highest as follows: 0 mg/L < 32 mg/L < 64 mg/L NaCl.

### TABLE 3
Anodic polarization data showing the influence of chloride in E20, E40, and E80 environments.

<table>
<thead>
<tr>
<th>Test Environment</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr-estimate}$ (A/cm²)</th>
<th>CR (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E20 + 0 mg/L NaCl</td>
<td>-4.45E+02</td>
<td>4.64E-07</td>
<td>2.07E-01</td>
</tr>
<tr>
<td>E20 + 32 mg/L NaCl</td>
<td>-4.40E+02</td>
<td>2.41E-06</td>
<td>1.07E+00</td>
</tr>
<tr>
<td>E20 + 64 mg/L NaCl</td>
<td>-4.73E+02</td>
<td>7.14E-06</td>
<td>3.18E+00</td>
</tr>
<tr>
<td>E40 + 0 mg/L NaCl</td>
<td>-4.86E+02</td>
<td>1.73E-05</td>
<td>7.73E+00</td>
</tr>
<tr>
<td>E40 + 32 mg/L NaCl</td>
<td>-4.19E+02</td>
<td>1.87E-05</td>
<td>8.33E+00</td>
</tr>
<tr>
<td>E40 + 64 mg/L NaCl</td>
<td>-4.40E+02</td>
<td>5.51E-05</td>
<td>2.46E+01</td>
</tr>
<tr>
<td>E80 + 0 mg/L NaCl</td>
<td>-3.93E+02</td>
<td>7.99E-05</td>
<td>3.56E+01</td>
</tr>
<tr>
<td>E80 + 32 mg/L NaCl</td>
<td>-4.13E+02</td>
<td>8.27E-05</td>
<td>3.69E+01</td>
</tr>
<tr>
<td>E80 + 64 mg/L NaCl</td>
<td>-4.27E+02</td>
<td>9.92E-05</td>
<td>4.42E+01</td>
</tr>
</tbody>
</table>

### FIG. 7
Raman shift of corrosion products from MAS in simulated fuel ethanol showing the presence of iron hydroxide, maghemite, and goethite.
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