Synergistic effect of essential oil distillates on the corrosion protection of GX4CrNiMo16-5-1 stainless in acid-chloride electrolyte

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Abstract. The inhibition capability of admixed rosemary oil with cinnamon cassia oil (RC), and grapefruit oil with lemongrass oil (GL) on GX4CrNiMo16-5-1 martensitic stainless steel (GX4ST) corrosion was studied in 6 M H_2SO_4/3.5% NaCl electrolyte by potentiodynamic polarization and optical microscopy characterization. Results show both admixed distillates performed effectively on GX4ST. The corrosion rate of GX4ST without the distillates at 2.82 mm/y significantly decreased to average value of 0.04 mm/y and 0.05 mm/y analogous to average inhibition efficiency of 98.64% and 98.23% for RC and GL compound. The oil distillates exhibit consistent anodic corrosion inhibition behavior at all concentrations studied. Corrosion thermodynamic calculations showed the distillates chemisorbed on the martensitic steel with Gibbs free energy values greater than -46.01 KJmol\(^{-1}\) with respect to Langmuir isotherm equation which indicates negligible of lateral interaction effect among inhibitor molecules and surface coverage protection mechanism. Optical image representations of GX4ST after corrosion without the distillates showed severe surface degradation of general and localized corrosion. This contrast the images of the inhibited steel surface which were closely similar to the steel image before corrosion.

1. Introduction
The consequences of corrosion of metallic alloys is enormous [1]. The most widely used metallic alloys are ferrous based especially stainless steels. Significant number of manufactured products consists of stainless steel. Stainless steels are recyclable, exhibits excellent mechanical properties, interfacial equilibrium, and thermal deformation resistance [2-4]. The steels are extensively utilized for structural application in nuclear, chemical processing, desalination, fertilizer production and petrochemical industries by reason of their extraordinary resilience against corrosion compared to carbon steels [5, 6]. The resilience of stainless steels against corrosion is due to the evolution of an insulating and inert oxide film on the steel. The oxide results from the presence of alloying elements within the steel metallurgical structure especially Cr and Ni which chemically combines with dissolved O\(_2\) to passivate the steel surface. Electrochemical reaction of stainless steels with anions such as SO_4^{2-}, Cl\(^{-}\), S_2O_3^{2-}, NO_3^{-} etc reacts with the outer electrons on the steel’s exterior destabilizing the protective film especial at regions with flaws and discontinuities. Circumstances resulting in the disintegration of the protective oxide on stainless steels are prevalent in astringent industrial conditions couples with extreme temperature and high velocity fluid movement. Sequel to the collapse of passive films localized corrosion degradation majorly responsible for failure of stainless steels iniciates and progresses [7, 8]. Pitting corrosion occurs
due to the evolution and increase in microscopic holes on stainless steel exterior which is significantly destructive to the operational lifespan of the steel in service especially in aqueous environments [9, 10]. The existence of $\text{SO}_4^{2-}$ and $\text{Cl}^-$ anions in aqueous environments causes instability of the protective oxide on steels leading to selective deterioration i.e. pitting corrosion [11]. The electrochemical performance of stainless steels analogous to the evolution, resilience and disintegration of their passive film is fundamental to the comprehension of the pitting corrosion resilience of these alloys. Mitigation against pitting corrosion is affiliated with cost consequences due to repair of metallic structures and components, and sustainability of their lifespan and reliability. Pitting corrosion is acute, insidious and undetectable which increases the difficulty to predict and design against [12]. Research on pitting corrosion evolution and progression on stainless steels have provided insight to the present understanding of its phenomena and have contributed to appropriate material selection for industrial application [13-18]. Yi et al [19] evaluated the pitting resistance of type 316 steel in specific chloride solutions and established that the critical pitting potential of the steel substantially depends on induced electrochemical factors. Hodge and Wilde [20] ascertained that Ni-Cr alloys (10% Cr content) exhibited passivation coupled with adequate resilience against pitting in sulphate-chloride solution. Piron et al [21] also ascertained correlating behavior between Ni 200 and Inconel 600 steel in sulphate solution. Friend [22] studied the disintegration of the insulating film on alloy 22 at critical chloride concentration. Investigation on metastable and stable pit propagation coupled with the influence of electrochemical factors have seen considerable progress with several mechanisms proposed to explain collapse of the passive film [23-27]. The resilience of these alloys against the damaging effect anionic species largely depends on the attributes and composition of their insulating film, repassivation tendency, metastable pitting behaviour and resilience to pitting corrosion. The ability of the protective oxide on stainless steels to with stand collapse and/or repassivate after breakdown in aqueous corrosive environments strongly influences the resilience of the steels to pitting corrosion. This can be significantly improved upon through the utilization of chemical fluids identified as corrosion inhibitors. Corrosion inhibitors substantially decrease the corrosion rate of metallic alloys in corrosive fluids [28, 29]. Inhibitors exhibit definite reaction behaviour analogous to specific alloys, industrial condition, concentration range etc. which influences their effectiveness. Traditional corrosion inhibitors (e.g. chromates, nitrates, nitrites, arsenic, phosphates etc.) are toxic [30-32]. Compounds of organic origin are proven alternatives but expensive and slightly toxic [33-39]. The relevance of sustainable, safe and cost-effective compounds cannot be overemphasized. Plants distillates have shown in previous research to be promising [40-42]. However, their inhibition performance against localized corrosion reaction phenomena needs to be ascertained. This manuscript focusses on the effect of plant distillates on the pitting corrosion evaluation and inhibition of GX4CrNiMo16-5-1 martensitic stainless steel.

2 Experimental methods

GX4CrNiMo16-5-1 martensitic stainless-steel plate (GX4ST) was acquired from Vienna University of Technology, Austria with average nominal (wt.%) content laid out in Table 1. The steel plate was cut to 12 test pieces with average dimension of 1 cm$^3$. They were subsequently smoothened with emery papers with 120, 240, 320, 600, 800, 1200 and 2500 grit before being washed with deionized H$_2$O and acetone. Grapefruit and lemon oil distillates were combined in ratio 1:1 and concocted in cubic concentrates of 1%, 2%, 3%, 4% and 5% in 200ml of 6M H$_2$SO$_4$/3.5% NaCl electrolyte while rosemary and cinnamon cassia were combined in ratio 1:1 and similarly prepared.

| Element | C  | Si | Mn | P  | S  | Cr | Mo | Ni | Ti | N  | Cu | V  | Fe |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Content | 0.06 | 0.8 | 1 | 0.04 | 0 | 17 | 1.5 | 6 | 0 | 0 | 0.3 | 0.1 | 73.21 |

Potentiodynamic polarization investigations were executed with a triple electrode cable design inside a beaker filled with 200 mL of the electrolyte and joined to Digi-Ivy 2311 potentiostatic device. GX4ST
electrodes encased in solidified resin with visible surface area of 1 cm$^2$. Polarization plots were observed at sweep rate of 0.0015 V/s from set potential of $-0.5V$ and $+1.5V$. Pt wire was engaged as the counter electrode and Ag/AgCl as the standard electrode. Corrosion current density, $J_c$ (A/cm$^2$) and corrosion potential, $E_c$ (V) data were gotten from Tafel estimation approach. The corrosion rate $C_R$, (mm/y) and the inhibition efficiency, $\eta$ (%) were computed from the numerical formula;

$$C_R = \frac{0.00327 \times J_c \times E_q}{D}$$  

(1)

$D$ represents density (g/cm$^3$) $E_q$ represents equivalent of GX4ST. 0.00327 represents corrosion rate constant for computations in mm/y. Optical microscopy analysis was done with Omax trinocular metallurgical microscope for morphological analysis of the steel surface.

3 Results and discussion

3.1 Potentiodynamic polarization studies

Potentiodynamic polarization plots of GX4ST corrosion in 6M H$_2$SO$_4$/3.5% NaCl solution at 1-5% RC and GL concentration are laid out in Fig. 1(a) and (b). Table 2 exhibits the polarization data obtained. The corrosion rate of GX4ST at 0% RC and GL concentration (2.82 mm/y relating to corrosion current density of $2.62 \times 10^{-4}$ A/cm$^2$) significantly differs from the values obtained at 1-5% concentration of the inhibitors preceding from oxidation of the steel surface by SO$_4^{2-}$ and Cl$^-$ anions. The anions are responsible for the release of Fe$^{2+}$ ions into the acid-chloride electrolyte coupled with Cr depletion on the steel’s protective film. Consequently, the chemical fusion of H$_2$ atoms leads to evolution of H$_2$ gas and O$_2$ reduction reactions which are also responsible for selective degradation of the steel.

Observation of GX4ST polarization plots at 0% inhibitor concentration in Fig. 1(a) and (b) shows the anodic-cathodic polarization slopes are substantially greater than the slopes at other inhibitor concentration due to action redox reaction mechanism during potential scanning. At 1% RC concentration in Fig. 1(a), significant decrease in the anodic-cathodic plot configuration are visible due to interference and suppression of the redox reaction mechanism. This observation coincides with corrosion rate of 0.03 mm/y and corrosion current density of $3.04 \times 10^{-6}$ A/cm$^2$. RC concentration had negligible effect on its inhibition performance with inhibition efficiency result remaining generally similar. This proves the inhibition performance of RC is concentration dependent. This claim is proven from the similarities in configuration of the anodic polarization plots at 1-5% RC concentration and the cathodic plots at 2-5% RC concentration. It signifies the inhibition performance of RC is under activation control due to stability of the inhibition action and behaviour of RC analogous to concentration. Corrosion rate of GX4ST varies between 0.03 mm/y and 0.04 mm/y while the inhibition efficiency varies between 98.84% and 98.53%. The corrosion potential of the polarization plots at specific RC concentration tends to electropositive values due to dominant anodic inhibition behaviour. However, the optimal difference between the corrosion potential of GX4ST polarization plot at 0% RC and specific RC concentration is 103 mV signifying RC exhibits anodic inhibition behaviour. This shows that protection of the steel by protonated RC molecules occurred through adsorption. This is further confirmed from the pseudo passivation behaviour of the anodic polarization plots.

The performance of GL inhibitor is generally similar to RC with respect to corrosion rate and inhibition efficiency values, which varied between values of 0.06 mm/y – 0.04 mm/y and 97.94% - 98.71%. However, variation of the anodic-cathodic plots with respect to GL concentration shows GL inhibition behaviour steers significantly away from activation control mechanism. The slopes of the plot configuration show the mechanism of GL inhibition is significantly influenced by the redox reactions taking place on the steel surface. The deviation in corrosion potential to electropositive values shows GL inhibits GX4ST surface through surface coverage with optimal difference in corrosion potential between GL inhibited steel and the steel at 0% GL concentration is 90 mV which shows GL is also an anodic type inhibitor. Comparing the performance of the inhibitor compounds it’s clearly visible that the performance of the inhibitors is generally similar and highly effective.
Table 2. Potentiodynamic polarization output of GX4ST corrosion in 6 M H$_2$SO$_4$/3.5% NaCl solution at 1-5% RC and GL concentration

| RC Inhibitor | Sample | RC Conc. (%) | LCS $C_R$ (mm/y) | RC $\xi_F$ (%) | $C_i$ (A) | $C_P$ (V) | $R_P$ (Ω) | $B_c$ (V/dec) | $B_a$ (V/dec) |
|--------------|--------|--------------|------------------|----------------|-----------|-----------|-----------|-------------|-------------|
| A            | 0      | 2.82         | 0                | 2.96E-04       | 2.62E-04  | 0.364     | 86.73     | -9.115      | 12.490      |
| B            | 0.5    | 0.03         | 98.84            | 3.44E-06       | 3.04E-06  | 0.261     | 7479.00   | -8.635      | 13.370      |
| C            | 1      | 0.04         | 98.53            | 4.36E-06       | 3.86E-06  | 0.328     | 5894.00   | -7.056      | 9.081       |
| D            | 1.5    | 0.03         | 98.91            | 3.23E-06       | 2.86E-06  | 0.310     | 7961.00   | -5.662      | 9.139       |
| E            | 2      | 0.04         | 98.41            | 4.71E-06       | 4.17E-06  | 0.285     | 5450.70   | -7.698      | 13.167      |
| F            | 2.5    | 0.04         | 98.53            | 4.37E-06       | 3.86E-06  | 0.285     | 5886.00   | -7.149      | 11.300      |

| GL Inhibitor | Sample | RCC Conc. (%) | LCS $C_R$ (mm/y) | RCC $\xi_F$ (%) | $C_i$ (A) | $C_P$ (V) | $R_P$ (Ω) | $B_c$ (V/dec) | $B_a$ (V/dec) |
|--------------|--------|--------------|------------------|----------------|-----------|-----------|-----------|-------------|-------------|
| A            | 0      | 2.82         | 0                | 2.96E-04       | 2.62E-04  | 0.364     | 86.73     | -9.115      | 12.490      |
| B            | 0.5    | 0.06         | 97.94            | 5.74E-06       | 5.08E-06  | 0.274     | 4477.00   | -10.660     | 28.710      |
| C            | 1      | 0.05         | 98.06            | 5.42E-06       | 4.79E-06  | 0.282     | 4815.00   | -11.550     | 14.290      |
| D            | 1.5    | 0.06         | 97.99            | 5.63E-06       | 4.98E-06  | 0.324     | 5387.80   | -9.321      | 12.600      |
| E            | 2      | 0.04         | 98.43            | 4.38E-06       | 3.88E-06  | 0.342     | 6078.00   | -10.290     | 14.000      |
| F            | 2.5    | 0.04         | 98.71            | 3.59E-06       | 3.18E-06  | 0.274     | 7158.00   | -9.496      | 25.270      |

Figure 1. Potentiodynamic polarization plots of GX4ST corrosion in 6 M H$_2$SO$_4$/3.5% NaCl solution at 1-5% (a) RC concentration and (b) GL concentration
3.2 Corrosion thermodynamic studies

Adsorption isotherms provide insight into the mechanism of inhibitor-metal interaction leading to stifling of the redox reactions identified with corrosion. Inhibitor protection of metallic alloys occurs through electrostatic attraction between protonated inhibitor molecules in the electrolyte solution and valence electrons on the ionized steel surface. Strong electrostatic attraction culminates in effective corrosion inhibition. However, this assertion is subject to the ionic behaviour of corrosive species as most organic corrosion inhibitors depends on preadsorption of the corrosive species onto the steel before electrostatic attraction of the inhibitor onto the steel surface. Secondly, the organo-metallic complexation is also an important factor i.e. covalent bonding between the RC/GL molecules and the ionized steel surface stifles the corrosion reaction mechanisms. This reaction mechanism is termed chemisorption. In cases where the bonding is weak, it falls under Van der Waals interaction termed physisorption [43]. Data obtained from potentiodynamic polarization was evaluated with conventional adsorption isotherms. Only Langmuir isotherm models prove to be most applicable with interaction coefficients greater than 0.9 for RC and GL inhibitors. The interaction coefficient values are laid out in Table 3 below;

| Adsorption Isotherm | RC Inhibitor | GL Inhibitor |
|--------------------|--------------|--------------|
| Langmuir           | 1            | 0.9999       |

The Langmuir isotherm plots obtained from the fluid electrolyte in the presence of the inhibitors are presented in Figs. 2(a) and (b). Langmuir isotherm indicates that adsorption of inhibitor molecules occurs at the same definite reaction sites in the absence lateral interaction among inhibitor molecules with respect to mono layer adsorption according to the equation below;

\[ \theta = \frac{K_{ads}C_{inh}}{1 + K_{ads}C_{inh}} \]  

(2)

\( K_{ads} \) represents equilibrium constant of adsorption and \( C_{inh} \) represents molar concentration of inhibitor compound [44].

Data output of Gibbs free energy (\( \Delta G \)) calculated from equation 5 are displayed in Table 4. The data indicates the nature, potency and stability of adsorption mechanism of RC and GL inhibitor on GX4ST in the acid-chloride solution. The equilibrium constant of adsorption (\( K_{ads} \)) was computed from Langmuir isotherm equation.

\[ \Delta G_{ads} = - 2.303RT \log [55.5K_{ads}] \]  

(3)
55.5 indicate molar concentration of $\text{H}_2\text{O}$ in the acid solution, $R$ indicates universal gas constant and $T$ indicates absolute temperature. The $\Delta G$ data from the acid solutions in the presence of RC and GL inhibitors shows the inhibitor interaction mechanism occur through chemisorption adsorption [45]. The $\Delta G$ values associated with RC inhibition action are slightly higher than the corresponding values for GL inhibitor which signifying higher adsorption strength. The general slight decrease in value in the presence of both inhibitors results from lateral repulsion effect between protonated inhibitor molecules which in effect is negligible.

### Table 4. Data output for Gibbs free energy ($\Delta G$) and equilibrium constant of adsorption ($K_{\text{ads}}$) for RC and GL adsorption on GX4ST in 6 M $\text{H}_2\text{SO}_4$/3.5% NaCl

| Sample | RC Inhibitor | GL Inhibitor |
|--------|--------------|--------------|
|        | Inhibitor Conc. (%) | Inhibitor Conc. (M) | Surface Coverage ($\theta$) | Equilibrium Constant of adsorption ($K$) | Gibbs Free Energy, $\Delta G$ (Kjmol$^{-1}$) | Equilibrium Constant of adsorption ($K$) | Gibbs Free Energy, $\Delta G$ (Kjmol$^{-1}$) |
| A      | 0             | 0            | 0                           | 0                        | 0                        | 0                        | 0                        |
| B      | 0.5           | 1.77E-03     | 3.53E-03                    | 0.988                    | 5                        | -53.79                   | 971                      | 4291032.0                | -47.80 |
| C      | 1             | 5.30E-03     | 7.07E-03                    | 0.985                    | 5                        | -51.48                   | 990                      | 6149334.6                | -48.69 |
| D      | 1.5           | 0.989        | 8.84E-03                    | 0.984                    | 5                        | -51.23                   | 988                      | 3468913.5                | -47.27 |
| E      | 2             | 7576552.8    | -49.21                      | 0                        | 0                        | 0                        | 0                        | 2087012.9                | -46.01 |

#### 3.3 Optical image analysis

Optical images of GX4ST prior to and after corrosion assessment are exhibited from Fig. 3(a) to 5(b). Fig. 3(a) presents the image after metallographic preparation prior to corrosion test. Fig. 3(b) shows the morphology of GX4ST after corrosion in 6M $\text{H}_2\text{SO}_4$/3.5% NaCl. Extensive surface degradation is clearly visible due to oxidation of the steel exterior by the corrosive action of $\text{SO}_4^{2-}$ and $\text{Cl}^{-}$ anions. Corrosion pits are also visible due to localized electrochemical deterioration at definite areas on the steel where the passive protective film weakened. Fig. 4(a) to 5(b) exhibits the morphology of GX4ST after corrosion in the presence of 1% and 5% RC and GL concentrations respectively. The morphologies show effective inhibitor protection as they contrast the degraded morphology in Fig. 3(b). The corrosive anions where hindered from diffusing unto and reacting with the steel surface. However, miniature surface degradation and corrosion pits are still partially visible due to preadsorbed corrosive anions which aided the electrostatic attraction of the protonated inhibitor molecules. However, the surface morphology of the inhibited steels is well protected and assents with the results from potentiodynamic polarization.
4. Conclusion
Admixture of rosemary oil with cinnamon cassia oil, and grapefruit oil with lemongrass oil effectively inhibited the corrosion of GX4CrNiMo16-5-1 martensitic stainless steel in chloride-sulphate solution. Both admixed oil distillates performed adequately at specific concentrations with inhibition efficiency values generally signifying stability of the inhibitive electrochemical behavior of the oil distillates in the electrolyte. The admixed oil distillates exhibited anodic type inhibition effect resulting in surface coverage over the entire steel. The oil distillates adsorbed onto the steel by chemisorption reaction process through covalent bonding and strong electrostatic attraction. Optical images of the inhibited steel significantly differ from the non-inhibited and corroded steel due to absence of protonated oil distillates to counterbalance the combined destructive effect of chlorides and sulphates in the electrolyte.

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