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# Effect of Chloride in The Electrochemical Degradation of Carbon Steel in E40 Fuel Ethanol Applications

O.O. Joseph<sup>1\*</sup>, F.A. Ishola<sup>1</sup>, S.A. Afolalu<sup>1</sup>, S.O. Banjo<sup>1</sup>, A. Busari<sup>2</sup>, C.O. Asagba<sup>1</sup>, A.O. Inegbenebor<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Covenant University, P.M.B. 1023, Ota, Nigeria

<sup>2</sup>Department of Civil Engineering, Covenant University, P.M.B. 1023, Ota, Nigeria

Corresponding Author; funmi.joseph@covenantuniversity.edu.ng

## Abstract

The effect of different chloride concentration on the corrosion rate of carbon steel in E40 is presented in this study. The corrosion rates for each sample were examined using gravimetric method and polarization measurement. The samples were immersed into E40 fuel grade ethanol containing NaCl concentrations of (0, 8, 16, 24 and 32 mg/L) for a minimum of 10 days and a maximum of 40 days. Results obtained from both gravimetric and polarization measurements show that as chloride concentration amplified from 0 mg/L to 32 mg/L, there was an increase in corrosion rate of the carbon steel with the exception of a slight decrease at 24 mg/L on the 30<sup>th</sup> and 40<sup>th</sup> day. Corrosion rate was observed to be dependent on exposure time.

**Keywords:** chloride, fuel ethanol, E40, steel

## 1. Introduction

The production of fuel grade ethanol relentlessly expanded in the course of recent decades. Ethanol is most ordinarily utilized as a gasoline additive. Ethanol is mixed with gasoline to build the octane rating and in addition to enhance the emanation nature of the gasoline engine. Fuel grade ethanol (FGE) has a high-octane rating of 116. Ethanol consumes neatly because of its oxygen content. As of late numerous nations have begun to advance the utilization of biofuels or other sustainable energizes to lessen ozone depleting substance discharge and to expand fuel sources. Because of this purpose, there has been an expansion of the ethanol content in ethanol–gasoline blends of late. On the other hand, ethanol blending in gasoline accelerates corrosion susceptibilities of metals during pipeline transportation, storage, car fuelling systems etc. due to ethanol's hygroscopic nature and impurities present [1-10]. One of these impurities accelerating corrosion is chloride introduced most times during the production process of the fuel grade ethanol and it is recognised to cause SCC (stress corrosion cracking).

The material utilized for taking care of gas is principally carbon steel. Carbon steel is powerless to rust and SCC in ethanol–gasoline mixes containing adequate measure of ethanol. As of now, there have been a few disappointments in the business because most pipes or storage tanks holding (FGE) are made of carbon steel [11]. Being the most extensively used industrial material, carbon steel, accounts for roughly 85%, of the yearly steel manufacture globally. In spite of its somewhat inadequate deterioration resistance, carbon steel is utilised in enormous capacities in nuclear power plants, marine applications, fossil fuel power plants, chemical processing, transportation, petroleum production as well as refining, mining, pipelines, metal-processing equipment and construction [12]. Thus, this study is focused at



examining the effect of varying concentration of chloride, an impurity in E40 fuel ethanol application on carbon steel degradation.

## 2. Experimental

### 2.1 Material and Test Environment

The chemical composition of the as-received steel as seen Table 1 shows that the steel used for this study is a low carbon steel of ASTM specification otherwise referred to as ASTM A106 Grade A steel.

Table 1. Determined chemical composition of carbon steel material

Mea	C	Si	Mn	Cr	Mo	Ni	Nb	Ti	Al	Fe
s.	%	%	%	%	%	%	%	%	%	%
<x>	0.141	0.14	0.28	0.346	<0.001	<0.001	<0.004	<0.001	0.009	98.9
		4	3	0	00	5	0	00	8	

The test environment used for the study was E40 fuel grade ethanol. It contained 40% simulated fuel grade ethanol and 60% gasoline. The reagents used includes: 5% of 800ml Pure methanol, 1% of 800ml Distilled water, 5.6% of 800ml acetic acid with purity of 99.8%, 88.4% of 800ml ethanol. NaCl was liquefied in H<sub>2</sub>O, and at that point added to ethanol to attain the stated NaCl (8, 16, 24 and 32 mg/L) and water concentrations. Reference tests were conducted in the non-appearance of chloride.

### 2.2 Immersion Test

The carbon steel was cut into 40 pieces' specimen, each of 20 mm x 20 mm. 20 pieces of the carbon steel were immersed as experimented samples while the remaining 20 pieces were immersed as replica. Each of these samples and the replica were polished with abrasive paper grades of 60, 150, 400 and 600  $\mu$ m, degreased with acetone and weighed before testing. The test environment was poured in conical flaks of 200ml along with diverse NaCl concentration (0, 8, 16, 24 and 32) mg/L as contaminant. Five (5) samples set up a test frequency. These test period (10, 20, 30 and 40 days), and each test was duplicated to ascertain the reproducibility of the tests.

After exposure to the test environment for each test frequency, the coupons were removed from solution. The Corrosion products were mechanically scraped off, the samples were cleaned and left to dry. Thereafter, the final weight of the specimens was measured. The corrosion rate for each exposure time was also calculated using the formula in Equation 1 [13].

$$\text{Corrosion Rate} = (W \times K) / (T \times A \times D) \quad (1)$$

Where W is mass loss (mg), K is a constant (534), T is exposure time (hours), D is density (g/cm<sup>3</sup>), A is area (square inches).

## 2.3 Polarization Test

Short lengths of copper wires were properly soldered to the samples used for the potentiodynamic polarization test before they were mounted in small cups of epoxy resins and left to cure for some time and then removed from the cups. The mounted samples were grinded to ensure the metal surface was properly exposed and then polished with emery paper up to 1200 grade. An electrochemical cell was setup comprising of the mounted sample as the working electrode, the silver-silver chloride as the reference electrode, the platinum electrode as the counter electrode and the simulated E40 as the electrolyte. The electrochemical cell was connected to the DIGI-VY Potentiostat to cause instantaneous corrosion using current and potential. The instantaneous corrosion rate was determined using linear polarization under aerated conditions of the electrochemical cell. The Open Circuit Potential (OCP) was first determined before conducting Linear Sweep Voltammetry (LSV). Duplicate experiments were carried out so as to determine the repeatability of the tests.

## 3. Results and Discussion

### 3.1 Chloride effect on mass loss corrosion rate

Figure 1 shows the graphical representation of the corrosion rate of all the samples submerged in varying chloride concentration. The figure shows that corrosion rate of carbon steel increased by way of increase in exposure time with the lowest values being obtained on the 10<sup>th</sup> day and the highest values on the 40<sup>th</sup> day. The effect of increasing chloride concentration was also studied and it was observed that on the 10<sup>th</sup> and 20<sup>th</sup> days, corrosion rate sporadically increased as chloride increased up till 32 mg/L. However, the scenario changed on the 30<sup>th</sup> day where a deviation from linearity was observed at 24 mg/L NaCl (a drop in corrosion rate from 2.87E-05 to 2.60E-05 mils per year (mpy)). Similarly, on the 40<sup>th</sup> day, a drop in corrosion rate occurred at 24 mg/L NaCl from 3.72E-05 to 2.06E-05 mpy. The decline in corrosion rate thus observed may be attributable to a passivating effect of the oxide layer formed [14].

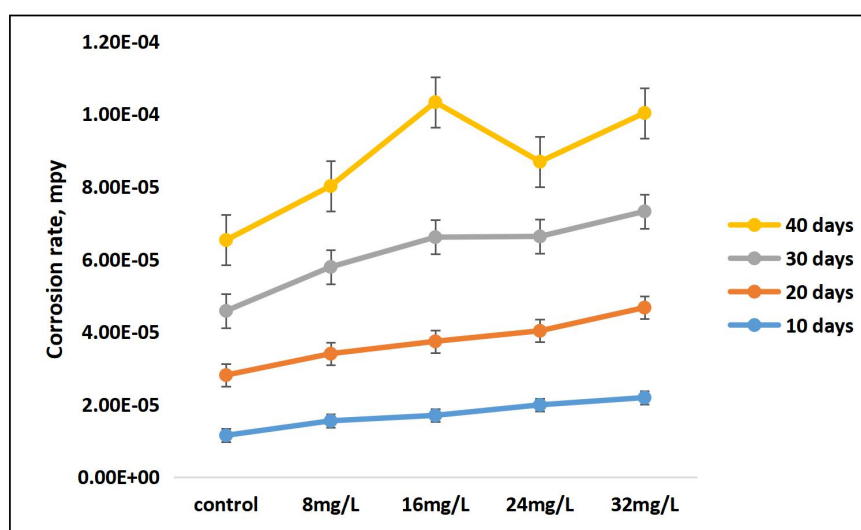


Figure 1. Chart showing chloride effect on corrosion rate of carbon steel for varying exposure times.

### 3.2 Chloride effect on polarisation measurements

The polarization behaviour of carbon steel was investigated using linear sweep voltammetry. Figure 2 shows the control tests used as a foundation designed for investigating chloride effects on polarization behaviour of carbon steel. Linear polarization of the carbon steel samples was ensured with comparable potential difference of 1.5 V<sub>SCE</sub> from their principal open circuit potentials (OCPs). 0.01 V/s was used as scan rate for the tests. Besides, Table 2 shows the estimated current density ( $i_{\text{corr-estimate}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) as detailed for all the test settings. In the presence of chloride at 8, 16, 24, and 32 mg/L, higher current densities were acquired relative to the control test.

Table 2. Linear polarization data showing chloride effects in simulated E40 FGE.

Test Environment	$E_{\text{Corr}}$ (V)	$I_{\text{Corr}}$ (A/cm <sup>2</sup> )	$R_p$ ( $\Omega$ )	CR(mm/yr)	$\beta_c$ (A/V)	$\beta_a$ (A/V)
Control	-0.470	5.851E-07	4.391E+04	6.783E-03	7.668E+00	5.315E+00
E40_8 mg/L NaCl	-0.493	2.316E-06	1.110E+04	2.648E-02	5.815E+00	5.834E+00
E40_16 mg/L NaCl	-0.497	4.018E-06	6.394E+03	4.650E-02	5.629E+00	5.865E+00
E40_24 mg/L NaCl	-0.515	6.256E-06	4.107E+03	7.252E-02	4.973E+00	6.069E+00
E40_32 mg/L NaCl	-0.522	1.403E-05	1.832E+03	1.626E-01	4.750E+00	6.161E+00

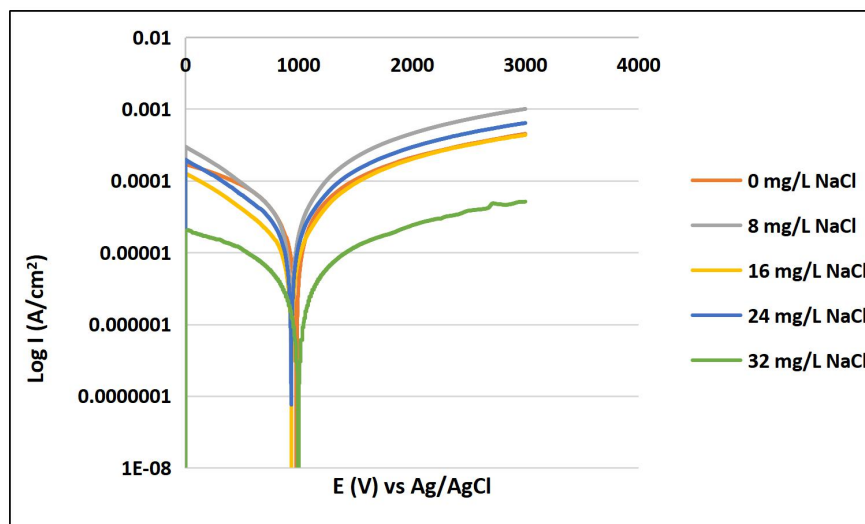


Figure 2. Chloride effect on polarization of carbon steel.

The corrosion rates calculated from Tafel slopes and the  $i_{\text{corr-estimate}}$  increased progressively from 0 mg/L to 8 mg/L up until 32 mg/L NaCl. This result is in line with deductions from immersion tests. It can be seen that carbon steel did not reveal distinctive passivation manner

in addition to pitting potential with linear polarization in the ethanol-chloride proportion range [14]. The corrosion potential ( $E_{corr}$ ) shifted to more negative values suggesting increase in anodic process with increase in chloride.

#### 4. Conclusion

Chloride effect on the deterioration manner of carbon steel in E40 has been studied. Based on the results, it can be concluded that corrosion rate of carbon steel increased by way of increase in exposure time with the lowest values being obtained on the 10<sup>th</sup> day and the highest values on the 40<sup>th</sup> day. Increasing chloride concentration had a linear effect on corrosion rate with up to 16 mg/L NaCl on the 30<sup>th</sup> and 40<sup>th</sup> days, after which a deviation from linearity was noted. Corrosion rate is dependent on exposure time.

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