Corrosion resistance study of UNS A96110 aluminum alloy in chloride-sulphate solution

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Abstract. Electrochemical analysis of the corrosion resistance of UNS A96110 aluminum alloy (UN6110) in neutral chloride media at 0.5%, 1%, 1.5%, 2%, 2.5%, 3% and 3.5% NaCl concentration, and 3.5% NaCl/sulphuric acid solution at concentrations of 0.00625 M and 0.1 M by potentiodynamic polarization method. UN6110 exhibited lower corrosion in the acid chloride solution compared to the results obtained from the neutral chloride media. The lowest corrosion rate (0.097 mm/y) was obtained from the neutral chloride solution at 0.5% NaCl corresponding to corrosion current density of 8.78 x 10^-6 A/cm² and polarization resistance of 2927 Ω while the highest value 0.344 mm/y was obtained at 3.5% NaCl concentration. Polarization plot showed significant variation at the anodic portion of the polarization plots with visible potential transients on the passivation portion of the plot. The aluminium alloy exhibited passivation reaction mechanisms due to formation and breakdown of the inert protective oxide. Variation of the cathodic polarization plots shows activation controlled reduction reactions. In sulphate-chloride solution, corrosion rate UN6110 significantly increased to 15.855 mm/y at 0.00625 M and 20.017 mm/y 0.1 M. Optical images obtained from the neutral chloride solution showed the presence of large micro corrosion pits and grooves due to the electrochemical action of chlorides. This differs from the images obtained from the acid chloride solution which showed general surface deterioration couple with well-defined micro and macro corrosion pits.

1. Introduction
Aluminum has important industrial applications due to its exceptional toughness, corrosion resistance, and proportion of strength to weight, formability, good weldability, recyclability and impact resistance [1, 2]. The mechanical and physical properties attributed to aluminium can be modified to meet the specific demands of application conditions. The sole purpose of aluminium application in the automotive industry is to reduce vehicle mass without compromising specific strength, design and fuel efficiency requirements [3]. The corrosion resistance of aluminum is due to the formation of Al₂O₃ on the metal surface which self-heals when slightly abraded or placed in mildly corrosive environments [4]. The presence of alloying elements within the aluminium substrate matrix is responsible for its extensive structural application. However, the alloying element cause discontinuities in the aluminium matrix and creates heterogeneous metallurgical structure which results in the formation of microscopic voids, flaws and in most cases impurities. This increases the vulnerability of the alloy to localized corrosion deterioration [5-9]. In environments with threshold chloride concentrations, the passive film on aluminium alloy tends to breakdown exposing the steel to continuous corrosion deterioration [10]. Marine environments with its extensive structural architecture are highly corrosive to aluminium alloys due to the presence of chlorides, sulphates [11, 12]. Proper documentation of the threshold corrosion resistance of aluminium alloys is important for material selection purposes. UN6110 aluminum is a 6000-series aluminium alloy with silicon as the main alloy addition. They are extensively applied in automobile vehicle due to their high strength, stiffness to
weight ratio, formability and weldability. This article focuses on the corrosion resistance of UN 6110 aluminium alloy in neutral chloride and sulphate contaminated artificial seawater.

2. Material and methods

UNS A96110 aluminium alloys (UN6110) procured disposable vehicular part was analysed with PhenomWorld scanning electron microscope (Model No. MVE0224651193) at the Materials Characterization Laboratory, Covenant University, Ota, Ogun State, Nigeria. The elemental composition of 0.5% Fe, 0.22% Cu, 0.15% Mn, 0.043% Mg, 0.2% Zn, 0.1%, 1.5% Si, 0.052% trace elements with the balance being Al was determined. UN6110 sample was cut, sectioned and placed in pre-hardened resin mounts with surface areas of 1 cm². The exposed surface underwent metallographic preparation with coarse emery papers (120, 240, 400, 600, 800, 1000, 1500, 2000, 2500 and 3000 grits), and 6 µm diamond polishing solution before cleaning with distilled H₂O and C₃H₆O. Standard grade NaCl procured from Qualikems, India was formulated in volumetric concentrations of 0.5%, 1%, 1.5%, 2%, 2.5%, 3% and 3.5% NaCl in 200 mL of distilled H₂O. Standard grade H₂SO₄ at 98% purity was formulated in molar concentration of 0.00625 M, 0.0125 M, 0.025 M, 0.05 M and 0.1 in neutral chloride solution (3.5% NaCl concentration). Polarization test of UN6110 was performed with Digi-Ivy potentiostat. The potentiostat configuration consists of triple electrode system (mounted UN6110), Ag/AgCl reference electrode and Pt wire counter electrode. The electrodes were immersed in 200 mL of the neutral chloride and acid chloride media a cell container interfaced with the potentiostat and computer. Plots were obtained at scan rate of 0.0015 V/s between potentials of -1.75 V to +0.5 V. Corrosion current density, \( C_J (\text{A/cm}^2) \) and corrosion potential, \( C_P (\text{V}) \) were obtained from the plots by Tafel extrapolation method. Corrosion rate \( C_R (\text{mm/y}) \) was calculated from the equation below;

\[
C_R = \frac{0.00327 \times C_P \times E_Q}{D}
\]

\( E_Q \) is the equivalent weight (g) of UN6110, 0.00327 is a corrosion rate constant and \( D \) is the aluminum alloy density (g).

3. Results and discussion

3.1 Electrodeposition results

Results from potentiodynamic polarization test for UN6110 in the neutral chloride and acid chloride electrolyte are presented in Tables 1 and 2. Fig. 1 and 2 shows the corresponding polarization curves for UN6110 corrosion in neutral and acid chloride solution. The rate of deterioration of UN6110 in the acid chloride media was significantly higher compared to the neutral chloride solution from observation of the corrosion rate results. This is as a result of the oxidation of alloy surface by the combined effect of sulphates and chloride anions in the acid chloride solution compared to the effect of chloride anions from the neutral chloride solution. Corrosion rate results from both solutions increased with concentration due to the increased oxidation strength of the electrolyte. The corrosion rate obtained at 0.5% chloride concentration is 0.097 mm/y at corrosion current density of 2.29 x 10⁻⁵ A/cm² and polarization resistance of 1121 Ω. At 3.5% chloride concentration, the rate of corrosion has increased to 0.344 mm/y. The cathodic polarization curves in Fig. 1 are closely aligned with similar slopes which signifies the \( O_2 \) reduction and \( H_2 \) evolution mechanism are under activation control with respect to increase in chloride concentration. However, significant variations are visible on the anodic polarization curves signifying the deteriorating effect of the chloride anions. Miniature current transients are occurred on the anodic polarization curves at 0.5% and 1% chloride concentration resulting from the formation, breakdown and reformation of the passive film on UN6110. After 1% chloride concentration the passivated region of the anodic polarization curves visibly reduced as a result of collapse of the protective film coupled with increase in corrosion rate. This is also evident on the anodic polarization curves. The corrosion potential values shown in Table 1 differ with chloride concentration. At 0.5% chloride concentration, the corrosion potential initiated at -1.011 V and increased (with respect to concentration) to -1.047 V at 3.5% chloride concentration signifying the strong effect of cathodic reaction mechanism under activation control as earlier mentioned.
The polarization curves in Fig. 2 significantly differ from the curves in Fig. 1 due to the presence of sulphates in the electrolyte solution. The passivated region present in Fig. 1 is completely absent (excluding 0M sulphate solution) due to destruction of the passive film on the metallic alloy. The combined effect of sulphates and chlorides caused breakages on the protective film at rates faster than its ability to reform; hence the resulting accelerated corrosion compared to the values obtained in the neutral chloride solution. The corrosion rate results obtained increased with increase in sulphate concentration. At 0.00625 M concentration the corrosion rate of UN6110 to 15.855 mm/y (corrosion current density of $1.44 \times 10^{-3}$ A/cm² and $4.46 \times 10^{-4}$ A/cm², and polarization resistance of 18.60 $\Omega$). The corrosion potential for UN6110 shifts from -0.677 V to -0.657 V due to dominant anodic reaction mechanism related to accelerated oxidation of UN6110 surface and increased corrosion though visible changes in cathodic polarization slope with respect to sulphate concentration shows cathodic reaction mechanisms counterbalanced the anodic counterparts.

Table 1. Polarization data of UN6110 corrosion in neutral chloride solution from 0.5% to 3.5% chloride concentration

| Sample | NaCl Conc. (%) | Corrosion Rate, $C_r$ (mm/y) | Corrosion Current, $C_i$ (A) | Corrosion Current Density, $C_j$ (A/cm²) | Corrosion Potential, $C_p$ (V) | Polarization Resistance, $R_p$ ($\Omega$) | Cathodic Tafel Slope, $B_c$ (V/dec) | Anodic Tafel Slope, $B_a$ (V/dec) |
|--------|----------------|-----------------------------|-----------------------------|------------------------------------------|-------------------------------|-------------------------------------------|----------------------------------|----------------------------------|
| A      | 0.5            | 0.097                       | 8.78E-06                    | 8.78E-06                                 | -1.011                        | 2927.00                                   | -10.590                          | -5.024                           |
| B      | 1              | 0.128                       | 1.17E-05                    | 1.17E-05                                 | -1.010                        | 2203.00                                   | -10.630                          | 3.915                            |
| C      | 1.5            | 0.284                       | 2.58E-05                    | 2.58E-05                                 | -1.043                        | 1223.00                                   | -8.889                           | 3.479                            |
| D      | 2              | 0.318                       | 2.88E-05                    | 2.88E-05                                 | -1.048                        | 897.20                                    | -10.010                          | 2.923                            |
| E      | 2.5            | 0.319                       | 2.90E-05                    | 2.90E-05                                 | -1.031                        | 893.30                                    | -8.593                           | 1.958                            |
| F      | 3              | 0.326                       | 2.97E-05                    | 2.97E-05                                 | -1.045                        | 864.11                                    | -9.321                           | 1.796                            |
| G      | 3.5            | 0.344                       | 3.12E-05                    | 3.12E-05                                 | -1.047                        | 823.2                                    | -9.202                           | 1.786                            |

Table 2. Polarization data for UN6110 corrosion in neutral chloride solution (3.5% NaCl concentration) at 0 M to 0.1 M sulphate concentration

| Sample | H₂SO₄ Conc. (%) | Corrosion Rate, $C_r$ (mm/y) | Corrosion Current, $C_i$ (A) | Corrosion Current Density, $C_j$ (A/cm²) | Corrosion Potential, $C_p$ (V) | Polarization Resistance, $R_p$ ($\Omega$) | Cathodic Tafel Slope, $B_c$ (V/dec) | Anodic Tafel Slope, $B_a$ (V/dec) |
|--------|----------------|-----------------------------|-----------------------------|------------------------------------------|-------------------------------|-------------------------------------------|----------------------------------|----------------------------------|
| A      | 0              | 0.344                       | 3.12E-05                    | 3.12E-05                                 | -1.047                        | 823.20                                   | -9.202                           | 1.786                            |
| B      | 0.00625        | 15.855                      | 1.44E-03                    | 1.44E-03                                 | -0.677                        | 18.60                                    | -3.315                           | 5.635                            |
| C      | 0.0125         | 13.693                      | 1.24E-03                    | 1.24E-03                                 | -0.653                        | 20.78                                    | -3.774                           | 1.419                            |
| D      | 0.025          | 13.148                      | 1.19E-03                    | 1.19E-03                                 | -0.652                        | 23.24                                    | -5.805                           | 4.272                            |
| E      | 0.05           | 13.432                      | 1.22E-03                    | 1.22E-03                                 | -0.662                        | 20.04                                    | -6.274                           | 5.597                            |
| F      | 0.1            | 20.017                      | 1.82E-03                    | 1.82E-03                                 | -0.657                        | 14.13                                    | -6.323                           | 2.647                            |
Fig. 1 Potentiodynamic polarization plots of Al6110 corrosion in neutral chloride solution at 0.5% to 3.5% NaCl concentration

Fig. 2 Potentiodynamic polarization plots of Al6110 corrosion in acid chloride solution at 0 M to 0.1 M sulphate concentration

3.2 Optical microscopy studies

Optical images for UN6110 corrosion in neutral and acid chloride solution are shown Fig. 3 to Fig. 5(b) at mag. x100. Fig. 3 shows the optical image before corrosion. Fig. 4(a) and (b) shows the optical images of UN6110 after corrosion from 0.5% and 3.5% chloride solution. Fig. 4(a) and (b) significantly contrast Fig. 3 due to the debilitating effect of chlorides on the alloy surface. The image in Fig. 4(a) shows extensive surface deterioration with micro-pits resulting from corrosion. Comparing the image to Fig. 4(b), the extent of corrosion damage is much higher with enlarged pits and connecting grooves due to higher degree of surface oxidation resulting increase chloride concentration. The images shown in Fig. 5(a) and (b) significantly differs from Fig. 4(a) and (b) due to differences in the constituents of the electrolyte where corrosion occurred. The deterioration mode
in Fig. 5(a) is that of general surface deterioration at 0.00625 M sulphate concentration. However, at 0.1M sulphate concentration well defined micro and macro corrosion pits are visible on the alloy surface.

![Image](image1.png)

**Fig. 3** Optical image of UN6110 before corrosion

![Image](image2.png)

**Fig. 4** Optical images of UN6110 after corrosion in neutral chloride solution (a) at 0.5% chloride concentration and (b) at 3.5% chloride concentration

![Image](image3.png)

**Fig. 5** Optical images of UN6110 after corrosion in acid chloride solution (a) at 0.00625M sulphate concentration and (b) at 0.1M sulphate concentration

4. **Conclusion**

Electrochemical studies were performed on UN6110 aluminium alloy in neutral chloride and sulphate contaminated artificial seawater solution to assess its corrosion resistance. The corrosion resistance of
the alloy in the acid chloride media was significantly lower compared to values obtained in the neutral chloride media. Corrosion rate increased with increase in chloride and sulphate concentration. Passivated regions on the polarization plots from the neutral chloride solution shows localized deterioration of the alloy dominated the corrosion reaction mechanism compared to the plots from the acid chloride media were passivation completely disappeared due to extensive anodic dissolution over the aluminium surface. Images from optical microscopy showed the extent and mode of corrosion damage on UN6110 from both solutions differ from each other.

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