Data analysis of the corrosion protection performance of aminobenzene concentrations on 1070 aluminum alloy in dilute HCl solution

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Abstract. Gravimetric and statistical analysis was used to assess the protection performance of aminobenzene compound on 1070 aluminum alloy in 1 M HCl solution in volumetric concentrations of 2.5%, 5%, 7.5%, 10%, 12.5% and 15%. Data output shows aminobenzene performed poorly at lower concentrations (2.5% to 10% aminobenzene concentrations) with highest value of 61.3% at 10% concentration and 480 h of exposure time. However, at higher concentrations the corrosion and oxidation of the aluminium surface was effectively suppressed with peak value of 81.7% at 480 h of exposure. Aminobenzene inhibition performance was determined to be highly concentration dependent with limited variation with respect to observation time. Standard deviation data showed significant variation of protection performance data at lower aminobenzene concentrations due to variation of the protection performance data with respect to observation time and thermodynamic instability of the inhibition mechanism. At 12.5% and 15% aminobenzene concentration the standard deviation values visibly decreased due to improved inhibition performance. Data also showed that only 31.67% of the protection performance data is above 70% inhibition efficiency at margin of error of +8.32%. Data from analysis of variance shows inhibitor concentration is the only statistical relevant factor at 75.57% responsible inhibition output of aminobenzene on the aluminium alloy compared to observation time with statistical relevance value of 12.28%.

1. Introduction

Aluminum is an important structural engineering material whose extensive utilization ranks behind carbon steels. The production and application of aluminum has continued to expand geometrically for applications such as in aerospace, electrical conduction, energy generation, automotive parts, consumer products, shipping and marine etc. [1-3]. This is due to their relatively low density compared to ferrous alloys, light weight and corrosion resistance [4-7]. The mechanical, metallurgical and physical properties of aluminum can be altered and optimized for extreme structural applications [8]. The corrosion resistance of aluminum is due to the formation of an impenetrable, inert oxide layer which is self-healing and enables its extensive utilization in a variety of industrial environments and service conditions. This invariably extends their operational lifespan. However, aluminum being an amphoteric metal can be highly reactive in aqueous acid and alkaline solutions especially in the presence of Cl⁻ anions which accelerates the surface deterioration of the metal. The deterioration appears in the form of white discolorations and precipitates on the metal [9, 10]. The economic and industrial relevance of aluminum enables extensive scientific study of the metal in corrosive...
conditions to optimize their productivity and applications. The study is centered on the electrochemical and corrosion reaction mechanisms occurring the metal surface [11-15]. According to Solange et al [16], localized deterioration of aluminum alloy in chloride solution is strongly related to the particles intermetallic phase and composition. 1xxx series of aluminum are strain hardenable and utilized in applications where structural strength is not an important factor but corrosion resistance is of utmost importance. The corrosion resistance of aluminum can be augmented with the used of fluid derivatives known as corrosion inhibitors. These compounds act by forming a protective barrier on the metal, modification of the corrosive medium and formation of complexes with the corrosive anions [17-25]. Research on appropriate corrosion inhibitors for aluminum is ongoing. However, data analysis of the protection performance corrosion inhibitors is highly relevant to evaluate the advantage and possible limitation of the applied chemical compounds analogous to observation time and inhibitor concentration. Appropriate substantiation of their peak performance with to concentration, storage life, durability and observation time is extremely important. The manuscript focusses on the gravimetric analysis of the inhibition action of aminobenzene on 1070 aluminum in 1 M HCl solution.

2. Material and methods

2.1 Materials preparation

1070 aluminium alloy (A70) rod secured in Lagos, Nigeria was analysed in the Materials Characterization Laboratory at Covenant University, Ota, Ogun State, Nigeria. The elemental components of A70 are outlaid in Table 1. A70 was cut and machined into 7 independent exhibits. The exhibits were grinded and smoothened with emery papers. Aminobenzene (ANZ), a brownish solution was bought from Sigma Aldrich, USA. AZN was deposited into to 1 M HCl in cubic values of 2.5%, 5%, 7.5%, 10%, 12.5% and 15% per 400 mL of the acid.

| Table 1. Atomic components of (wt. %) of A70 |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Element   | Cu        | V         | Mn        | Si        | Fe        | Zn        | Ti        |
| Wt.%      | 0.04%     | 0.05%     | 0.03%     | 0.2%      | 0.25%     | 0.04%     | 0.03%     |
|           | Mg        | Al        |           |           |           |           |           |
| Wt.%      | 0.03%     | 99.7%     |           |           |           |           |           |

2.2 Gravimetric analysis

Gravimetric analysis of ANZ inhibition on A70 was executed at 24 h hiatus for a total of 480 h of exposure. Corrosion rate, \( C_R \) (mm/y) was enumerated from the equation below;

\[
C_R = \left[ \frac{87.6W}{DA} \right] \tag{1}
\]

\( W \) illustrates weight loss (g), \( D \) illustrates density (g/cm\(^3\)), \( A \) illustrates total surface area of A70 exhibit (cm\(^2\)), 87.6 illustrates corrosion rate constant and \( t \) illustrates time (h). Protection performance \( (P_P) \) of the ANZ was enumerated from the equation below;

\[
P_P = \left[ \frac{W_1 - W_2}{W_1} \right] \times 100 \tag{2}
\]

\( W_1 \) and \( W_2 \) illustrates weight loss of A70 at specific ANZ concentrations.

2.3 Statistical analysis

Binary-factor single level anova analysis (F - test) was applied to calculated the statistical importance of ANZ concentrates and observation time on ANZ performance output. The test was done at confidence level of 95% (significance level of \( \alpha = 0.05 \)) according to the equations below. The summation of column squares (observation time) was enumerated as follows;

\[
SS_c = \frac{\sum T_r^2}{nr} - \frac{T^2}{N} \tag{3}
\]

The summation of row squares (ANZ concentration) was enumerated from the equation below;

\[
SS_r = \frac{\sum T_c^2}{nc} - \frac{T^2}{N} \tag{4}
\]

Total summation of squares equals

\[
SS_{Total} = \sum x^2 - \frac{T^2}{N} \tag{5}
\]
3. Results and discussion

3.1 Gravimetric analysis

Table 2 and 3 shows A70 corrosion rate and ANZ protection performance data with respect to observation time. A70 corrosion rate data at 0% ANZ concentration varied from 1.104 mm/y at 24 h to 18.471 mm/y. Between 24 h and 120 h of exposure, progressive increase in corrosion rate occurred to peak value of 37.798 mm/y (120 h) due to electrochemical oxidation of A70 surface according to the equation below;

$$2Al(s)+6HCl(aq)\rightarrow 2AlCl_3(aq)+3H_2(g)$$

The Cl- anions weakens the protective Al2O3 oxide on A70 exposing the substrate alloy to accelerated corrosion. Beyond 120 h, decrease in carrion rate occurred due to weaken of the acid electrolyte. It must be noted that addition of ANZ compound at 2.5% and 5% concentration substantially increased A70 corrosion as shown in Table 2. At 24 h, corrosion rate of A70 has increased to 1.262 mm/y and 1.854 mm/y from 1.104 mm/y at 0% ANZ concentration. Instantaneous increase in corrosion rate results in values to 29.343 mm/y and 47.614 mm/y occurred at 48 h of exposure before gradually decrease with respect to observation time till 16.847 mm/y and 16.835 mm/y at 480 h. This shows ANZ is completely ineffective in suppressing the corrosion of A70. At 7.5% ANZ concentration and 24 h of exposure, the corrosion rate of A70 is negligibly below the value obtained at 0% ANZ. Peak value was attained at 120 h (20.919 mm/y) before gradual decrease to 9.253 mm/y at 480 h. This observation confirms ANZ compound at 7.5% concentration has strong electrochemical influence on A70 corrosion. The final corrosion rate value of 9.253 mm/y is lower than 16.847 mm/y and 16.835 mm/y at 2.5% and 5% ANZ concentration, and 18.471 mm/y. Further increase in ANZ concentration i.e. from 10% to 15% ANZ concentration decreases A70 corrosion. At 24 h, the corrosion rate values are 0.651 mm/y, 0.434 mm/y and 0.631 mm/y compared to 1.104 mm/y at 0% ANZ while at 480 h, A70 corrosion rate values from 10% to 12.5% ANZ concentration are 5.539 mm/y, 7.368 mm/y and 3.419 mm/y. The corrosion rate values at 480 h decreased proportionately with increase in ANZ concentration. The lowest value obtained is 3.419 mm/y at 15% ANZ concentration.

Further insight to the electrochemical behaviour of ANZ is shown in Table 3. The inhibition protection performance of ANZ varied significantly with its concentration as shown in the change in protection performance data with respect to ANZ concentration. At 24 h, poor protection performance data occurred from 2.5% to 7.5% ANZ concentration (-14.3%, -67.9% and 8.9%) due to inability of protonated ANZ molecules to stifle the redox reaction processes. As a result, the molecules are involved in accelerating the corrosion process. The corrosion rate values at this concentration varied with observation time to attain final values of 8.8%, 8.9% and 49.9% at 480 h. At 10%, 12.5% and 15% ANZ concentration, significant improvement in ANZ protection performance is observed with values of 60.7%, 41.1% and 42.9% at 24 h while at 480 h the values are 61.3%, 70.8% and 81.7%. The protection performance data shows ANZ compared effectively inhibited A70 corrosion at higher concentrations from 10% to 15% ANZ concentration while at lower concentrations ANZ performance is significantly poor signifying concentration dependent performance. Secondly, it was noted that ANZ protection performance data varied differentially with exposure time due to delayed inhibition effect on A70 and relative instability with respect to observation time. Comparative plots of ANZ concentration at 2.5% and 15% are shown in Fig. 1. The plot configurations shows ANZ attained relative corrosion inhibition stability at 120 h and 48 h of observation time (2.5% and 15% ANZ concentration) till 480 h. This shows variation in performance output is limited with respect to observation time as the inhibition effect of ANZ exhibits thermodynamic stability. However, the significant difference/variation between the plot configurations shows ANZ concentration strongly influences its performance output. Hence effective utilization of ANZ is possible at higher concentrations of 12.5% and 15% ANZ concentration.
Table 2. A70 corrosion rate data at specific ANZ concentration with respect to observation time

| ANZ Concentration (%) | 0% ANZ | 2.5% ANZ | 5% ANZ | 7.5% ANZ | 10% ANZ | 12.5% ANZ | 15% ANZ |
|-----------------------|--------|----------|--------|----------|---------|-----------|--------|
| Observation Time (h)  |        |          |        |          |         |           |        |
| 0                     | 0      | 0        | 0      | 0        | 0       | 0         | 0      |
| 24                    | 1.104  | 1.262    | 1.854  | 1.006    | 0.651   | 0.434     | 0.631  |
| 48                    | 26.947 | 29.343   | 47.614 | 19.651   | 0.434   | 27.016    | 0.434  |
| 72                    | 20.785 | 33.32    | 44.422 | 20.403   | 3.379   | 18.405    | 0.368  |
| 96                    | 29.654 | 27.292   | 36.132 | 20.164   | 4.792   | 14.223    | 0.325  |
| 120                   | 37.798 | 33.954   | 35.038 | 20.919   | 4.613   | 13.686    | 1.743  |
| 144                   | 33.994 | 32.571   | 34.506 | 18.839   | 4.868   | 13.278    | 2.557  |
| 168                   | 32.935 | 31.563   | 32.636 | 17.201   | 5.206   | 12.328    | 3.175  |
| 192                   | 31.818 | 30.38    | 30.913 | 15.48    | 5.098   | 11.393    | 3.032  |
| 216                   | 31.578 | 29.218   | 29.494 | 14.108   | 4.991   | 10.802    | 3.607  |
| 240                   | 30.783 | 27.91    | 28.154 | 13.335   | 5.113   | 10.004    | 3.589  |
| 264                   | 29.228 | 26.265   | 26.491 | 12.37    | 5.036   | 9.392     | 3.48   |
| 288                   | 27.767 | 24.734   | 24.929 | 11.523   | 4.951   | 8.853     | 3.392  |
| 312                   | 26.412 | 23.438   | 23.541 | 11.134   | 5.044   | 8.463     | 3.463  |
| 336                   | 25.078 | 22.113   | 22.222 | 10.58    | 5.033   | 8.154     | 3.428  |
| 360                   | 23.672 | 20.802   | 20.891 | 10.053   | 4.994   | 7.813     | 3.331  |
| 384                   | 22.302 | 19.636   | 19.971 | 10.097   | 5.387   | 7.535     | 3.471  |
| 408                   | 21.114 | 18.814   | 19.087 | 10.061   | 5.428   | 7.644     | 3.412  |
| 432                   | 20.053 | 18.062   | 18.297 | 9.515    | 5.477   | 7.511     | 3.421  |
| 456                   | 19.083 | 17.352   | 17.626 | 9.356    | 5.539   | 7.368     | 3.419  |
| 480                   | 18.471 | 16.847   | 16.835 | 9.253    | 5.398   | 7.143     | 3.386  |

Table 3. A70 protection performance data at specific ANZ concentration with respect to observation time

| ANZ Concentration (%) | 2.5% ANZ | 5% ANZ | 7.5% ANZ | 10% ANZ | 12.5% ANZ | 15% ANZ |
|-----------------------|----------|--------|----------|---------|-----------|--------|
| Observation Time (h)  |          |        |          |         |           |        |
| 0                     | 0        | 0      | 0        | 0       | 0         | 0      |
| 24                    | -14.3    | -67.9  | 8.9      | 60.7    | 41.1      | 42.9   |
| 48                    | -8.9     | -76.7  | 27.1     | -0.3    | 98.4      | 98.4   |
| 72                    | -60.3    | -113.7 | 1.8      | 11.5    | 83.7      | 98.2   |
| 96                    | -30.2    | -21.9  | 32       | 52      | 83.8      | 98.9   |
| 120                   | 8        | -0.7   | 39.9     | 60.7    | 86.7      | 95     |
| 144                   | 2.4      | -1.5   | 42.1     | 60.9    | 85.7      | 92.5   |
| 168                   | 4.2      | 0.9    | 44.6     | 62.6    | 84.2      | 90.4   |
| 192                   | 4.5      | 3.7    | 47.8     | 62.2    | 84.2      | 90.5   |
| 216                   | 7.4      | 6.6    | 51.3     | 65.8    | 83.4      | 88.6   |
| 240                   | 9.3      | 8.5    | 55.3     | 86.2    | 82.8      | 88.3   |
| 264                   | 10.1     | 9.4    | 56.7     | 67.5    | 82.2      | 88.1   |
| 288                   | 10.9     | 10.2   | 57.7     | 68.1    | 81.3      | 87.8   |
| 312                   | 11.3     | 10.9   | 58.5     | 68      | 80.9      | 86.9   |
| 336                   | 11.8     | 11.4   | 57.9     | 67.5    | 79.9      | 86.3   |
| 360                   | 12.1     | 11.8   | 57.5     | 67      | 79.8      | 85.9   |
| 384                   | 12       | 10.5   | 54.7     | 66.2    | 75.8      | 84.3   |
| 408                   | 10.9     | 9.6    | 52.4     | 63.8    | 74.3      | 83.8   |
3.2 Statistical analysis

The mean, standard deviation (SD) and margin of error for ANZ inhibition performance on A70 are shown in Table 4. The mean data shows the average protection performance data with respect to observation time. The mean values shown in Table 3 vary with ANZ concentration. From 2.5% to 10% ANZ concentration, the mean values are significantly below the data for effective corrosion inhibition with respect to observation time. However, at 12.5% and 15% ANZ concentration the mean values in Table 3 depict effective corrosion inhibition with respect to exposure time. SD shows the extent of variation of ANZ protection performance data from mean value. The greater the variation of protection performance data; the greater the instability of ANZ performance with respect to observation time. This is disadvantageous to the overall inhibition performance of ANZ. The SD values from 2.5% ANZ to 10% ANZ are generally high signifying high variation. However, the values at 12.5% and 15% ANZ concentration are relatively lower with values of 14.88 and 16.48. The lower SD values signify ANZ inhibition performance is relatively stable with respect to observation time and presents a reliable concentration in industrial operating conditions. Table 3 also shows only 31.67% of ANZ protection performance data have values greater than 70% inhibition efficiency at margin of error of ±8.32%.

Table 4. Mean, standard deviation and margin of error for ANZ protection performance on A70 in 1 M HCl electrolyte

| HCl Conc. (%) | 2.5 | 5 | 7.5 | 10 | 12.5 | 15 |
|---------------|-----|---|-----|----|------|----|
| SD            | 22.30 | 43.63 | 17.84 | 26.21 | 14.88 | 16.48 |
| Mean          | -7.79 | -26.27 | 35.08 | 52.23 | 81.40 | 88.37 |
| Margin of Error | +8.32% | Data above 70% Protection Performance | 31.67% |

Statistical estimation by analysis of variance (ANOVA) was used to assess the statistical pertinence of ANZ concentration and observation time on the protection performance values of ANZ in HCl media. The statistical figures are laid out in Table 5 where the statistical relevance factor illustrates the
valuated relevance of the origin of variation (ANZ Conc. and observation time) on the performance output of the ANZ compound. The mean square ratio illustrates the numerical value that must be greater than the theoretical significance factor in order to validate the dominance of the statistical relevance factor. The mean square ratio associated with ANZ concentration and observation time in HCl media exceeds the analogous theoretical significance factor. Hence ANZ concentration and observation time are both numerically relevant, significantly influencing the protection performance values of ANZ on A70. However, ANZ concentration dominates the performance output at 75.57% while the influence of observation time is minimal but relevant at 12.28%.

Table 5. ANOVA data for statistical importance of ANZ concentration and observation time on ANZ protection performance values

| HCl Origin of Variation | Mean Square Ratio (F) | Theoretical Significance Factor | Statistical Relevance Factor, F (%) |
|-------------------------|-----------------------|---------------------------------|------------------------------------|
| ANZ Conc.               | 55.99                 | 2.42                            | 75.57                              |
| Observation Time        | 5.06                  | 2.1                             | 12.28                              |

4. Conclusion
Aminobenzene effectively inhibited the corrosion of 1070 aluminum alloy at higher concentrations. Its inhibition performance was determined to be strongly dependent on its concentration. Data from statistical analysis shows significant variation from standard deviation at lower inhibitor concentration due to instability of the inhibition mechanism and subsequent poor inhibition performance. This contrasts the corresponding low variation at higher aminobenzene concentrations. The protection performance data exhibiting values above 70% inhibition efficiency is however less than 30% signifying concentration dependent inhibition performance. The effect of inhibitor concentration is above 70% from statistical analysis.

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