Evaluation and Modeling of Corrosion Rate of Selected Roofing Sheets Using Tetraoxosulphate (vi) Acid and Trioxonitrate (v) Acid as Simulated Acid Rain

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Authors’ contributions
This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

ABSTRACT
The study focuses on the evaluation of the impact of acid rain on some common roofing sheets, including; Stone Coated, Galvanized, 0.55 m and 0.45 mm Long Span, Aluminum/Zinc sheet using simulated acid rain. The simulated acid rain was from four different molar concentrated $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$. The parameter used for the evaluation was a weight loss of the roofing sheet over the study period. Gravimetric analysis technique was adopted for the study. At the end of the study, the result obtained showed that for 1 mole solution $\text{H}_2\text{SO}_4$, 0.45 mm Long Span recorded the lowest weight loss of 0.43 g, followed by Cameroon zinc with loss of 0.46 g while 0.55 mm long Span recorded 0.63 g. Stone-coated and galvanized sheet melted up before the end of the experiment. 1 mole solution of $\text{HNO}_3$ recorded a similar trend with 0.46 g, 0.36 g, 0.47 g and 3.95 g weight loss for 0.55 mm long Span, Cameroon Zinc, 0.45 mm Long Span and stone Coated sheet respectively while Galvanized sheet melted up before the experiment ends. Stone Coated and Galvanized sheet melted up before the end of the experiment in 0.5 mole $\text{H}_2\text{SO}_4$ while 0.45 mm Long Span, 0.55 mm long span and Cameroon Zinc recorded 0.47 g, 0.5 g and 0.35 g weight loss respectively. Only Galvanized sheet melted up in 0.5 mole of $\text{HNO}_3$, 3.5 g, 0.28 g, 0.38 g and 0.3 g weight loss was...
1. INTRODUCTION

It is a well-known phenomenon that after a period of time the roofing-sheets on buildings turn reddish or brownish, the trend continues until the roofs start having holes on its surfaces. This occurrence is attributed to corrosion. Corrosion is one of the major causes of material loss in structures, automobile and everything that has to do with metals. It is a spontaneous process that converts relatively unstable metals and metals products into chemically stable compound such as oxide, hydroxide or sulfide. It is a gradual denaturing or destruction of metallic materials when it chemically reacts with its environment. Ujam et al. [1] defined corrosion as an attack on metallic materials due to reaction with its environment. In other words, it is electrochemical oxidation of metal with strong oxidation agents such as oxygen and sulfate [2,3]. A typical example of this type of reaction is the formation of iron oxide which is as a result of electrochemical oxidation. Researchers described corrosion as the extractive metallurgy in reverse. In simple term corrosion can be considered as the return of materials to a lower energy level (initial state) after been excited to a higher energy level during processing [4,5].

Corrosion is a natural phenomenon; thermodynamics and kinetic are the major fundamentals in which corrosion is investigated, [6]. Thermodynamic gives the possibilities of certain types of corrosion occurring in a given material while kinetic explain the mechanism and the rate in which this occurrence can take place. In nature, most metallic elements (apart from noble metals) appeared majorly as an oxide of the metal which are at very stable state exhibiting low energy level; for it to be useful for different purposes, it has to be refined and modify to sue such purpose and this involves excitation of the low energy and stable oxide to high energy metal with increase in energy level.

Thus, these metals which are in higher energy levels are in a constant quest for favourable conditions to return to a lower energy level which are the oxides of the metals. As a consequence, whenever environmental conditions and other parameters are favorable, the metals return to their initial nature. This is corrosion [5].

Corrosion also takes place in non-metallic materials like ceramic and polymers, although in this case it is termed “degradation”. In degradation the essential properties of the material are loss (strength, appearance, permeability etc.).

Many materials corrode due to exposure to wet or moist condition, but there are some substances that increase the rate of corrosion when in contact with the metallic material. Some compounds speed up the rate of reaction (oxidation) within the surface of the materials and this make the material to corrode faster.

Over the years, the rate of corrosion of roofing sheets in heavy industrial areas like Niger delta is alarming; this is caused by the emission of toxic gases like \( \text{SO}_x \) and \( \text{NO}_x \) into the atmosphere which give rise to acid rain.

When \( \text{SO}_x \) and \( \text{NO}_x \) combine with \( \text{O}_2 \) in the atmosphere and dissolved in rain, solutionsa solution of \( \text{H}_2\text{SO}_x \) and \( \text{HNO}_x \) are formed. These, which when deposited on roofing sheets speed up corrosion. The reaction between the roofing sheets and the acid rain is a complex one. It involves variables such as the concentration of the pollutants, climate condition and the nature of the exposed surface. When once the polluted water gets to the surface of the roofing sheet the reactivity depends on the duration of contact, type of material involve and the presence of other substances. Other factors considered as the cause of corrosion are the quality of the roofing sheets. It has been observed that most of the roofing sheets are not up to specifications and the manner in which it has been handled before installation also a contributing factor that promotes corrosion, [7].

| Keywords: Roofing sheets; modeling; evaluation; concentration; pollutants; acid rain and simulate. |  
|---|---|
Acid rain is a serious environmental problem in the industrial area whose effect is so devastating especially during the raining season when the relative humidity is very high, [8].

In the quest to curtail the effect of the acid rain on roofing sheets, metallurgy researchers have developed different types of roofing sheets that can withstand corrosion effects of acid rain; some are alloy of high tensile strain while some are galvanized. Hence, in view to ascertain the quality and durability of some commonly used roofing sheets, it becomes imperative for a mathematical model to be developed to assist in validating the best roofing material for pollutants in the environment, especially, industrial areas. In this work, the corrosion rate of some roofing sheets was modelled after subjecting them to simulated acid rain environments.

2. MATERIALS AND METHODS

The roofing sheets used for the experiment were 0.45mm long span (Alumaco brand), 0.55 mm long span (First Aluminum brand), Galvanized steel, Cameroon Zinc and stone coated sheet. These were sourced from different building material shops in Choba and Aluu, Rivers State, Nigeria. Samples of these were made to the same sizes of 5 cm x 4 cm. Specimen coupons were washed with ethanol to remove any surface dirt, grease and any foreign substances. This was to ensure that secondary reaction does not occur during the experiment and also for ease of interaction between the metal surfaces and the solutions with regards to ASTM GI Standard, (Cole et al, 1999). The coupons were then weighed in digital weighing balance to obtain the initial weight of the samples. The samples were then immersed in a prepared solution of simulated acid rain (solutions of 0.5 mole and 1mole of HNO₃ and H₂SO₄). The samples were removed and dried to check for loss in weight on a daily bases for a period of 30 days.

Regression analysis was applied after data collection to model the weight loss and the rates of corrosion of the roofing sheets in the different media. Polynomial equation of the fourth order was used because of its high degree of accuracy in order statistical analysis.

The weight loss equations according to fourth order polynomial are of the form below;

\[ y = at^4 + bt^3 + ct^2 + dt + e \]  \hspace{1cm} 3.1

Where y is the loss in weight.

To obtain the rate of corrosion, the weight loss equations were differentiated. The equation obtained is of the form below;

\[ R = 4at^3 + 3bt^2 + 2ct + d \]  \hspace{1cm} 3.2

Where R is the rate of material loss and a, b, c, d. are constant.

To validate the model, coefficient of Regression R was used.

3. RESULTS

The plot results obtained from the research are as shown from Fig.1 to Fig 4. The plots depicts the loss in weight against time of the roofing sheets sample in different media.

4. MATHEMATICAL MODEL OBTAINED FROM THE STUDY

The mathematical models of weight loss and corrosion rate of the research study are shown below. Polynomial fourth order regression model was adopted. The models show a good fit to the data with R²'s of 0.9 and above.

5. DISCUSSION

The roofing sheets samples responded responses were slightly different when immersed in the different media. The observed trends are discussed below.

5.1 Observed Effect When Immerging Samples in 1mole Solution of H₂SO₄

1. Stone-coated roofing sheet: Stone-coated sheet showed a drastic loss in weight in the first two days when immersed in the solution. Reason being that the acid attacks the interface between the metallic part and the coated part and weaken the adhesive; this makes the coated part to separate from the metallic part. Thus, because of exposure of both surfaces of the metal, rapid loss in weight was observed until the metal part melted up on the 16th day.

2. Galvanized steel: Rapid attack of galvanized steel was observed in the first
two days until it melted up on the third day. This is due to the aggressive effect of the concentrated acid on Zinc.

3. **0.45 mm Long Span (Alumaco Brand):** A slow rate of corrosion was recorded with intermittent constant weight in day 2 and 3, 6 and 7, 11 and 12, 15 and 16, 25 and 26. This is due to the formation of passivation layer on the surface of the metal which inert acid attacks temporary. Total weight loss of 0.43 g was recorded.

4. **0.55 mm Long Span (First Aluminum Brand):** A very slow rate of weight loss as recorded for 0.45 mm long span was also recorded for 0.55 mm Long Span with intermittent constant weight for some consecutive days. Overall weight loss of 0.63 g was recorded.

5. **Aluminum/Zinc (Cameroon Zinc):** The observed trend for Al/Zn roofing sheet is similar to the last two roofing sheets mentioned above, with weight loss of 0.46 g. Thus, in 1 mole solution of H$_2$SO$_4$ Galvanized steel has the highest corrosion rate, while 0.45 mm Long Span showed the highest resistance in the solution.

![Fig. 1. Weight loss of samples against time in 1mole solution of H$_2$SO$_4$](image1)

![Fig. 2. weight loss of samples against time in 1mole solution of HNO$_3$](image2)
5.2 Observed Effect when Immersing Samples in 1mole Solution of HNO₃

1. **Stone Coated.** Stone-coated roofing sheet showed a rapid but steady loss in weight from initial value of 6.93g to final value of 2.98g (total weight loss 3.95g) within the period of study. The coated surface remained attached to the metallic surface till the end of the study. The rapid decrease in weight was due to the aggressive nature of the acid on the metallic surface, no much effect was observed on the coated part which entail that the coated surface protects the sheet from corrosion when NOx gas is the major pollutant.

2. **Galvanized steel.** Cloudy bubble was observed when Galvanized steel was immersed in HNO₃ solution. This continues until it melted up on the second day of the experiment.

3. **0.45 mm Long Span (Alumaco Brand).** It showed very high resistant in the solution with total loss in weight of 0.47g within the period of study. The weight remained constant within the first three days of study. It gradually losses weight from the fourth day with intermittent constant weight recorded in some consecutive days.

4. **0.55 mm Long Span (First Aluminum).** Although it showed good resistant to the acid attack, a steady but minimal weight loss was recorded with total loss in weight
### Table 1. Model equation for weight loss and rate of corrosion for 1mole solution of H₂SO₄

<table>
<thead>
<tr>
<th>S/N</th>
<th>Name of roofing sheet</th>
<th>Weight loss equation</th>
<th>Equation for rate of corrosion</th>
<th>R² square value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stone Coated</td>
<td>( y = -6 \times 10^{-6} x^4 + 0.0002x^3 + 0.031x^2 - 0.8595x + 6.9997 )</td>
<td>( R = 2.4 \times 10^{-4} t - 0.0006t^2 + 0.062t - 0.8595 )</td>
<td>0.9912</td>
</tr>
<tr>
<td>2</td>
<td>Galvanized Steel</td>
<td>( y = 5 \times 10^{-5} x^4 - 0.0031x^3 + 0.0697x^2 - 0.6147x + 1.6542 )</td>
<td>( R = 2 \times 10^{-4} t^3 - 0.0093t^2 + 0.1394t - 0.6147 )</td>
<td>0.8295</td>
</tr>
<tr>
<td>3</td>
<td>0.45 mm Long Span (Alumaco)</td>
<td>( y = 2 \times 10^{-7} x^4 - 7 \times 10^{-6}x^3 - 0.0002x^2 - 0.01x + 0.9326 )</td>
<td>( R = 8 \times 10^{-7} t - 2.1 \times 10^{-5}t^2 - 0.0004t - 0.01 )</td>
<td>0.9947</td>
</tr>
<tr>
<td>4</td>
<td>0.55 mm Long Span (First Aluminum)</td>
<td>( y = 8 \times 10^{-7} x^4 - 3 \times 10^{-5}x^3 - 0.0002x^2 - 0.0233x + 2.1183 )</td>
<td>( R = 3.2 \times 10^{-5} t^3 - 9 \times 10^{-5}t^2 + 0.0004t - 0.0233 )</td>
<td>0.9968</td>
</tr>
<tr>
<td>5</td>
<td>Aluminum/Zinc Alloy (Cameroon Zinc)</td>
<td>( y = 1 \times 10^{-5} x^4 - 9 \times 10^{-6}x^3 + 0.003x^2 - 0.0192x + 0.96 )</td>
<td>( R = 4 \times 10^{-7} t^3 - 2.7 \times 10^{-5}t^2 + 0.0009t - 0.0192 )</td>
<td>0.9963</td>
</tr>
</tbody>
</table>

### Table 2. Model equation for weight loss and rate of corrosion for 1mole solution of HNO₃

<table>
<thead>
<tr>
<th>S/N</th>
<th>Name of roofing sheet</th>
<th>Weight loss equation</th>
<th>Equation for rate of corrosion</th>
<th>R² square value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stone Coated</td>
<td>( y = 3 \times 10^{-5} x^4 - 0.002x^3 + 0.0504x^2 - 0.5656x + 6.0934 )</td>
<td>( R = 1.2 \times 10^{-4} t^4 - 0.006t^3 + 0.3t^2 - 0.5656 )</td>
<td>0.8904</td>
</tr>
<tr>
<td>2</td>
<td>Galvanized Steel</td>
<td>( y = 4 \times 10^{-5} x^4 - 0.0028x^3 + 0.0627x^2 - 0.5386x + 1.3804 )</td>
<td>( R = 1.6 \times 10^{-4} t^4 - 0.0084t^3 + 0.1254t^2 - 0.5386 )</td>
<td>0.7038</td>
</tr>
<tr>
<td>3</td>
<td>0.45 mm Long Span (Alumaco)</td>
<td>( y = -2 \times 10^{-6} x^4 + 0.0002x^3 - 0.0041x^2 + 0.0144x + 0.9182 )</td>
<td>( R = -8 \times 10^{-6} t^4 + 0.0006t^3 - 0.0082t^2 + 0.0144 )</td>
<td>0.9906</td>
</tr>
<tr>
<td>4</td>
<td>0.55 mm Long Span (First Aluminum)</td>
<td>( y = 8 \times 10^{-7} x^4 - 5 \times 10^{-5}x^3 + 0.0013x^2 - 0.0279x + 2.1131 )</td>
<td>( R = 3.2 \times 10^{-5} t^3 - 1.5 \times 10^{-4}t^2 + 0.0026t - 0.0279 )</td>
<td>0.9974</td>
</tr>
<tr>
<td>5</td>
<td>Aluminum/Zinc Alloy (Cameroon Zinc)</td>
<td>( y = 4 \times 10^{-7} x^4 - 2 \times 10^{-5}x^3 + 0.0003x^2 - 0.0114x + 0.9346 )</td>
<td>( R = 1.6 \times 10^{-6} t^3 - 6 \times 10^{-5}t^2 + 0.0006t - 0.0114 )</td>
<td>0.9949</td>
</tr>
</tbody>
</table>
### Table 3. Model equation for weight loss and rate of corrosion for 0.5mole solution of H$_2$SO$_4$

<table>
<thead>
<tr>
<th>S/N</th>
<th>Name of roofing sheet</th>
<th>Weight loss equation</th>
<th>Equation for rate of corrosion</th>
<th>$R^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stone Coated</td>
<td>$y = -8E-06x^4 + 0.0005x^3 + 0.0007x^2 - 0.5009x + 6.6976$</td>
<td>$R = -3.2E-05t^3 + 0.0015t^2 + 0.0014t - 0.500$</td>
<td>$R^2 = 0.9628$</td>
</tr>
<tr>
<td>2</td>
<td>Galvanized Steel</td>
<td>$y = 4E-05x^3 - 0.003x^2 + 0.0695x^2 - 0.6374x + 1.8419$</td>
<td>$R = 1.2E-04t^3 - 0.009t^2 + 0.139t - 0.6374$</td>
<td>$R^2 = 0.9263$</td>
</tr>
<tr>
<td>3</td>
<td>0.45 mm Long Span</td>
<td>$y = 6E-07x^4 - 3E-05x^3 + 0.0002x^2 - 0.0093x + 0.9373$</td>
<td>$R = 2.4E-06t^3 - 9E-04t^2 + 0.0006t - 0.0093$</td>
<td>$R^2 = 0.9954$</td>
</tr>
<tr>
<td></td>
<td>(Alumaco)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.55 mm Long Span</td>
<td>$y = -1E-06x^4 + 8E-05x^3 - 0.0021x^2 - 0.0001x + 2.1002$</td>
<td>$R = -4E-06t^3 + 2.4E-04t^2 - 0.0042t - 0.0001$</td>
<td>$R^2 = 0.9951$</td>
</tr>
<tr>
<td></td>
<td>(First Aluminum)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Aluminum/Zinc Alloy</td>
<td>$y = 8E-07x^4 - 6E-05x^3 + 0.0013x^2 - 0.0214x + 0.9543$</td>
<td>$R = 3.2E-06t^3 - 1.8E-04t^2 + 0.0026t - 0.0214$</td>
<td>$R^2 = 0.9948$</td>
</tr>
<tr>
<td></td>
<td>(Cameroon Zinc)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 4. Model equation for weight loss and rate of corrosion for 0.5mole solution of HNO$_3$

<table>
<thead>
<tr>
<th>S/N</th>
<th>Name of roofing sheet</th>
<th>Weight loss equation</th>
<th>Equation for rate of corrosion</th>
<th>$R^2$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Stone Coated</td>
<td>$y = 3E-05x^3 - 0.002x^2 + 0.0504x^2 - 0.5656x + 6.0934$</td>
<td>$R = 1.2E-04t^3 - 0.006t^2 + 0.100t - 0.5656$</td>
<td>$R^2 = 0.8904$</td>
</tr>
<tr>
<td>2</td>
<td>Galvanized Steel</td>
<td>$y = 4E-05x^3 - 0.0028x^3 + 0.0627x^2 - 0.5386x + 1.3804$</td>
<td>$R = 1.6E-04t^3 - 0.0084t^2 + 0.125t + 0.5386$</td>
<td>$R^2 = 0.7038$</td>
</tr>
<tr>
<td>3</td>
<td>0.45 mm Long Span</td>
<td>$y = -2E-06x^4 + 0.0002x^3 - 0.0041x^2 + 0.0144x + 0.9182$</td>
<td>$R = -8E-06t^3 + 0.0006t^2 - 0.0082t + 0.0144$</td>
<td>$R^2 = 0.9906$</td>
</tr>
<tr>
<td></td>
<td>(Alumaco)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.55 mm Long Span</td>
<td>$y = 8E-07x^4 - 5E-05x^3 + 0.0013x^2 - 0.0279x + 2.1131$</td>
<td>$R = 3.2E-06t^3 - 1.5E-04t^2 + 0.0026t - 0.0279$</td>
<td>$R^2 = 0.9974$</td>
</tr>
<tr>
<td></td>
<td>(First Aluminum)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Aluminum/Zinc Alloy</td>
<td>$y = 4E-07x^4 - 2E-05x^3 + 0.0003x^2 - 0.0114x + 0.9346$</td>
<td>$R = 1.6E-06 -6E-05t^2 + 0.0003t - 0.0114$</td>
<td>$R^2 = 0.9949$</td>
</tr>
<tr>
<td></td>
<td>(Cameroon Zinc)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
of 0.46 g during the period of study. Constant weight was recorded for some consecutive days due to formation of oxide layer on the surface.

5. **Aluminum/Zinc Sheet (Cameroon Zinc).** Cameroon Zinc showed a steady decrease in weight for the first four days. A total weight loss of 0.36 g was recorded during the study period, which makes it the best sheet for HNO₃ embedded environment.

5.3 Observed Effect when Immersing Sample in 0.5 mole solution of H₂SO₄

1. **Stone coated Roofing Sheet:** Stone coated roofing sheet immersed in 0.5mole solution of H₂SO₄ showed the trend as observed in 1mole solution of the acid. The sample melted up during the second week of the studied.
2. **Galvanized Steel:** A rapid cloudy bubble was observed when the coupon was immersed in the solution. The bubble continues steadily until the sheet decayed up on third day.
3. **0.45 mm Long Span (Alumaco Brand):** The rate of decrease in weight of the sheet in the first five days is insignificant; a total loss in weight of 0.47 g was recorded during the studied period.
4. **0.55 mm Long Span (First Aluminum Brand):** The sheet showed a gradual and steady decreased in weight over the period of study, with weight total loss of 0.5g. Constant weight in some consecutive days was recorded due to the formation of passivation on the surface.
5. **Aluminum/Zinc Roofing Sheet (Cameroon Zinc):** Steady but insignificant weight loss was recorded for the sheet during the period of study. The weight of the coupon changed from 0.93 g to 0.63 g (total weight loss of 0.3 g). Intermittent constant weights were also recorded due to formation of oxide at the surface of the metal.

5.4 Observed Effect When Immersing Sample in 0.5 mole Solution of HNO₃

1. **Stone Coated Roofing Sheet:** The stone coated sheet showed a steady and significant decrease in weight throughout the period of study. Total loss in weight of 3.51 g was recorded. The weight decrease is due to attack of the acid on the metallic surface while the coated part remained unattached
2. **Galvanized Steel:** Galvanized steel showed a rapid weight loss in the solution. The decrease continues steadily until the sheet melted up on the 9th of the experiment.

3. **0.45 mm Long Span (Alumaco Brand):** The sheet showed high resistant to corrosion in the solution. Overall weight loss of 0.28g was recorded at the end of the study. It has the highest resistant in the solution.
4. **0.55 mm Long Span (First Aluminum Brand):** Total loss in weight of 0.38g was recorded over the period of studied. Formation of oxide was noted due to constant weight recorded in some consecutive days.
5. **Aluminum/Zinc Roofing Sheet (Cameroon Zinc):** Steady but insignificant weight loss was recorded for the sheet during the period of study. The weight of the coupon changed from 0.93 g to 0.63 g (total weight loss of 0.3 g). Intermittent constant weights were also recorded due to formation of oxide at the surface of the metal.

6. **CONCLUSION**

Generally, the formation of passivation layer in on Aluminum coated products proved to be effective in reducing the rate of corrosion of the roofing sheet. The extents of attack of the roofing sheet depended majorly on the concentration level of the pollutant. H₂SO₄ solution has showed more aggressive attack on the sheets than HNO₃ solution. The rates in at which the sheets corroded is determined by the level of pollutant, type of pollutant and the exposure time.

From the regression models tested for corrosion rate and weight loss of the sheets, fourth order Polynomial (Quartic equation) regression model gives the best fit to the data. Sodiki, [9] used regression model of a second order to model some metals, this also attest to the fact that regression model can give a good fit to corrosion analysis.

**COMPETING INTERESTS**

Authors have declared that no competing interests exist.

**REFERENCES**

1. Oji and Okon; CSIJ, 28(4): 1-9, 2019; Article no.CSIJ.53598


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