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Discoloration of Aluminum Roofing Sheets in Uyo, Nigeria: the Physicochemical Factors

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Abstract- Apart from protecting the inside of a building from wind, weather and other potential hazards, the roof, particularly when designed properly, adds to the overall aesthetics of a building. However, in Uyo, Nigeria, aluminium roofing sheets that should otherwise be largely free from corrosion have been observed to, overtime, develop dark patches and permanent stains that is as unsightly as it is stubborn. To characterise these dark patches, nine parameters were studied in a physicochemical analysis including, total dissolved solids, total suspended solids, sulphates, phosphates, nitrates, biochemical oxygen demand, chemical oxygen demand, salinity and dissolved oxygen. The results point to the fact that organic and inorganic material settle on the roofs and breed algae. About 5.12 – 5.42 mg/kg of phosphates and 2.48 – 2.62 mg/kg nitrates recorded present sufficient nutrient base for simple green plants and algae to thrive on. Further, the measured chloride ion content of the sample from the roofs reveal a salinity level of up to 17.55 mg/l. This level of salinity is sufficient to induce a gradual deterioration of the roof surfaces preventing efficient run-off of rain thereby allowing water to clog in some areas and further attracting organic and inorganic matter.

Keywords- *characterisation, roof, discoloration*

I. INTRODUCTION

The topmost part of a building may be covered by roofing sheets fitted onto a roof-supporting truss, a structure composed of wooden or metallic slender members pinned together at their end points. The surface of most roofs are corrugated to enable efficient run-off of water, snow and so on. Materials for roofing sheets range from non-metals like thatches, concrete tiles, asbestos and asphalt shingles to iron, zinc, steel and aluminium in the metallic domain. As roofing materials, the performance of asbestos has been studied by [1]; concrete tiles by [2] and [3]; the nature of run-offs from roofs clad with asphalt shingles is elaborated in [4], [5] and [6]. It is found that non-metallic roof tops deteriorate over time and some of the products of their degradation are well-known pollutants. With the advent of superior material processing techniques like roll-forming, and to offer better structural integrity as well as to tackle the problem of leaching harmful contaminants with run-off, metallic roofing materials were introduced [7]. A lot of knowledge has also been published in the realm of metal roofing materials. Oxygen, acidity of solutions, biological activities, pollution, temperature, and salinity being the major factors that affect the corrosion behavior of metallic roofing sheets [8]. For example, steel has long been known to corrode when exposed to oxygen and moisture hence for use as roofing material, it is often galvanized. However, the added layer of zinc in galvanized steel provides only sacrificial protection: over time, the zinc layer dissolves [9,10]. With the dissolution of the zinc the steel is left exposed and, once again, is susceptible to corrosion. To tackle this problem, aluminum – a metal that resists corrosion by forming an impenetrable oxide layer when exposed to oxygen and moisture – is added to the alloy. The aluminum “barrier” prevents exposure of the steel base even when the zinc protection has been sacrificed [1]. Barring cost, even better performance is obtained if the roofing material is made entirely of aluminum. The metal therefore enjoys wide application in both commercial buildings and residential dwellings even in Uyo, Nigeria [11]. There are three main reasons for the widespread utilization of aluminum for roofing. First, aluminum can be fabricated easily into corrugated forms. Second, it has one-third the weight of steel thereby reducing the self-weight of large structures and lastly, as earlier noted, it displays excellent resistance to corrosion. These advantages of aluminum as well as the fact that it is available as roofing material in bright colors, adding to the overall aesthetics of a building, has made it hugely popular in Nigeria.

Over time however, aluminum roofs in the study area – Uyo, Nigeria – have been observed to show increasing patches of dark coloration. Such ugly discoloration as seen in Fig. 1 and Fig. 2 only serves to detract from the aesthetics of the entire building. It has been established by [12] that rainwater roof run-offs are known to contain chemical contaminants. Following on from that, this paper aims at characterizing the dark stains observed on aluminum roofing sheets in Uyo, Nigeria. Wet weather is experienced in Uyo between April and October whereas the dry season generally begins in November and carries on to March. Consequently, the physical and chemical properties of the material found in the spots on the roofs are examined and discussed in a so-called physicochemical analysis of both wet and dry samples.

Figure 1. Gas Station roof in Uyo (Site 1)

Figure 2. University of Uyo Male Hostel (Site 2)

II. SAMPLING AND TECHNIQUES

The methodology adopted for this work is the laboratory analysis of the wet and dry samples from the affected roofs. Dry samples were collected in January 2015 during the dry season from the University of Uyo Male Hostel Roof and the Nigerian National Petroleum Corporation, (Gas Station) Uyo. The wet samples were collected between April and June 2015 from the affected roofs as well as direct rainfall from the atmosphere in the study area. The tests and analysis were conducted according to the standard methods for examination of wet and dry samples in the Research and Development Laboratory of the Ministry of Science and Technology in Uyo, Nigeria. Physicochemical analysis is very important in extracting ideas about the quality of water and solid substances and for the comparison of the results of different physiochemical parameter values to the standard values. A physicochemical analysis investigates both the physical and the chemical properties of the sample which will aid in the determination of their peculiar nature. The investigation involved consideration of pH, electrical conductivity, turbidity and several other parameters (Table I) of samples of the material constituting the dark stains on the aluminum roofs. The procedure followed to determine the quantity of the various parameters is elaborated in [13,14] but summarized in Table I.

TABLE I. PHYSICOCHEMICAL ANALYSIS PROCEDURE

Property	**Determination procedure**
Total Dissolved Solids (TDS)	i. Dry sample (5.0 g) was air dried and weighed in a 250 ml beaker. 100 ml of distilled water was added and stirred for three minutes. ii. The sample was allowed to stand for thirty minutes. Oven and desiccators-cooled beakers were weighed and recorded as W_1. iii. The sample (50 mg) each was filtered using filter paper into the different beakers. iv. The samples were completely evaporated from the beakers using water bath and the beakers were taken into desiccators and allowed for thirty minutes to cool. v. The beakers were there after re-weighed and recorded as W_2. TDS $= \frac{(W_2-W_1)X10^3}{Volume\ of\ Sample}$
Total Suspended Solids (TSS)	i. The filter papers were oven dried at (105 °C) for two hours and allowed to cool in a desiccator for thirty minutes before weighing and the result recorded as W_1. ii. The sample (50 ml) with suspension only were filtered through the filter paper using filtration apparatus and allowed to dry in the oven at the same temperature and time. iii. At the expiration of the period, the filter papers were removed from the oven using thong and allowed to cool in a desiccator for same period stated above and were re-weighed and recorded as W_2. TSS $= \frac{(W_2-W_1)X10^3}{\text{Volume of sample}}$

Phosphates (PO_4^{3-})	i. To 50ml of the filtered sample, 4ml of ammonium molybdate reagent and about four - five drops of stannous chloride reagent was added. ii. After about ten minutes the colour developed was measured using the ultra violet spectrophotometer at 690nm. iii. A blank reagent is run with same treatment with distilled water as sample. iv. The value of phosphate is obtained by comparing absorbance of sample with the standard curve and expressed as milligram per kilogram and milligram per litre for the dry and wet sample respectively. $\text{Phosphates} = \frac{\text{Absorbance of sample x Concentration of Standard x 1000}}{\text{Absorbance of Std. x Sample taken}}$
Sulphates	i. 100ml of the sample was filtered into a Nessler's tube containing 5ml of conditioning reagent. ii. 0.2g of barium chloride crystals was added with continued stirring. iii. A working standard was prepared by taking 1ml of the standard, 5ml of conditioning reagent and made up to 100ml, to give 100 NTU. iv. The turbidity developed by the sample and the standards were measured using a Nephelometer and the results were tabulated thus. Sulphate = Nephlometric reading x 0.4 x Dilution Factor
Nitrates (NO_3^-)	i. A known volume (50ml) of the sample is pipette into a porcelain dish and evaporated to dryness on a hot water bath. ii. About 2ml of phenol di-sulphonic acid is added to dissolve the residue by constant stirring with a glass rod. iii. Concentrated solution of sodium hydroxide or concentrated ammonium hydroxide and distilled water was added with stirring to make it alkaline. iv. This was filtered into a Nessler's tube and made up to 50ml with distilled water. v. The absorbance was read at 410nm using the UV Spectrophotometer after the development of colour. vii. The value of nitrate was found by comparing absorbance of sample with the standard curve and expressed in milligram per kilogram and milligram per litre for the dry and wet samples respectively. $\text{Nitrates} = \frac{\text{Absorbance of sample x Concentration of Standard x 1000}}{\text{Absorbance of Standard x Sample taken}}$
Salinity (Cl^-)	i. A known volume of sample (50ml) was taken into the 250ml Erlemyer flask. ii. Three drops of the indicator were added and shaken iii. The mixture was titrated with 0.01N $AgNO_3$ to a brick red $\text{Salinity} = \frac{\text{V2 x E x N x 1000}}{\text{V}}$ Where V = Volume of Sample, V_2= Volume of $AgNO_3$, E = Equivalent weight of NaCl N = Normality of $AgNO_3$
Dissolved Oxygen	i. Using the membrane electrode method which has a sensing element protected by an oxygen-permeable plastic membrane that serves as a diffusion barrier against impurities. ii. The calibrations are carried out following the manufacturer's calibration procedure. The electrode was dipped into the sample. iii. Under steady conditions the electric current read was directly proportional to the dissolve oxygen concentrations (electric current is directly proportional to the activity of molecular oxygen) and the readings were recorded.
Biochemical Oxygen Demand (BOD)	i. The sample was determined for first day D.O (D_1). ii. Various dilutions (at least three) were prepared to obtain about 50 % depletion of D.O. using sample and dilution water. iii. The samples were incubated at 20 °C for five days and the fifth day D.O (D_5) is noted using the oximeter. iv. A reagent blank was also prepared in a similar manner. $\text{BOD} = \frac{(D1 - D5)}{P}$ P - Decimal factor of prepared sample
Chemical Oxygen Demand (COD)	i. 15 ml of concentrated sulphuric acid with 0.3 g of mercuric sulphate and a pinch of silver sulphate along with 5 ml of 0.025 M potassium dichromate was taken into a Nessler's tube. ii. 10 ml of sample (thoroughly shaken) is pipetted out into this mixture and kept for about ninety minutes on the hot plate for digestion. iii. 40 ml of distilled water was added to the cooled mixture (to make up to 50 ml) and titrated against 0.25 M FAS using ferrous indicator, till the colour turns from blue green to wine red indicating the end point. iv. A reagent blank was also carried out using 10 ml of distilled water. $\text{COD} = \frac{\text{(Blank reading − Sample reading) x N x F x 1000}}{\text{Sample taken}}$

III. RESULTS AND DISCUSSION

Rainfall is known to be significantly polluted, although this usually depends on the location, industrial density, traffic intensity, prevailing winds, season, previous dry periods, etc. Consequently, the first chemical and physical parameters measured were pH, temperature and electrical conductivity. The pH plays an important role in all chemical reactions associated with formation, alteration and dissolution of minerals in water. Temperature influences the chemical and bio-chemical characteristics of the samples. Average temperature in both sites was recorded as 28°C. Electrical conductivity gives an indication of the extent to which free ions are present in the roof run-off samples collected. The results shown in Fig.3 show that samples were near-neutral as the pH values range from 6.65 – 7.09. Fig. 4 displays the level of conductivity measured in the samples. This trend is indicative of possible dissolution of deposited aerosols and leaching of roofing materials.

The analysis of the physicochemical parameters for dry samples from sites 1 and site 2 indicate the presence, at times in copious amounts, of nutrients favourable for microorganism growth, algae inclusive. For instance, nitrates which represent the final product of the biochemical oxidation of ammonia, were observed to be present in the samples within a range of 2.48 – 2.62 mg/kg (Fig. 5). Also, the phosphate content in the samples was found to range from 5.12 – 5.42 mg/kg. In these quantities, both nitrates and phosphates are known to promote eutrophication (excessive plants and algae growth). The roof samples, rich in nitrates and phosphates, lower the dissolved oxygen content especially in the dry sample. The increasingly anaerobic conditions together with sufficient nutrients results in a favourable growing and thriving environment for algae. Possibly for good measure and to complete a near-perfect environment for microbial growth, the samples presented with organic as well as inorganic matter in the form of total dissolved solids (55.0 – 66.0 mg/kg); total suspended particles (51.0 – 96.0 mg/kg); and turbidity levels of between 127.0 – 248.0 mg/kg (Fig. 5). The organic and inorganic materials probably emanate from decomposed vegetation deposited by wind action on the roofs or droppings from birds, reptiles and other animals which are not drained off the roof as a consequence of little or no rainwater run-off in the dry season. Some level of salinity was measured in both roof dirt samples – 219 mg/kg in site 1 and 234 mg/kg in site 2 (Fig. 4) – indicative of the presence of chloride ions and hence the strong possibility of corrosion attack on the roof surface.

For the wet samples shown in Fig. 6, it was observed that total dissolved solids – consisting of inorganic and organic substances – ranged from 8.0 to 35.0 mg/l. The inorganic substances include clay, silt, minerals, metals etc., which settled on the surfaces of roofs and creates corrosion and scaling problems on the roof coatings.

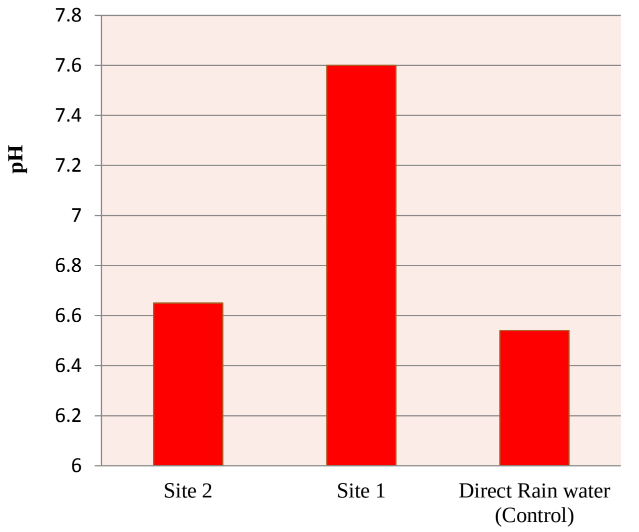

Figure 3. pH of samples

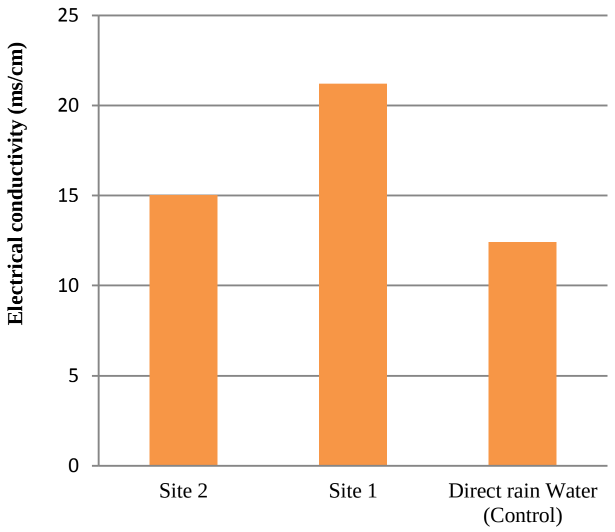

Figure 4. Electrical conductivity of samples

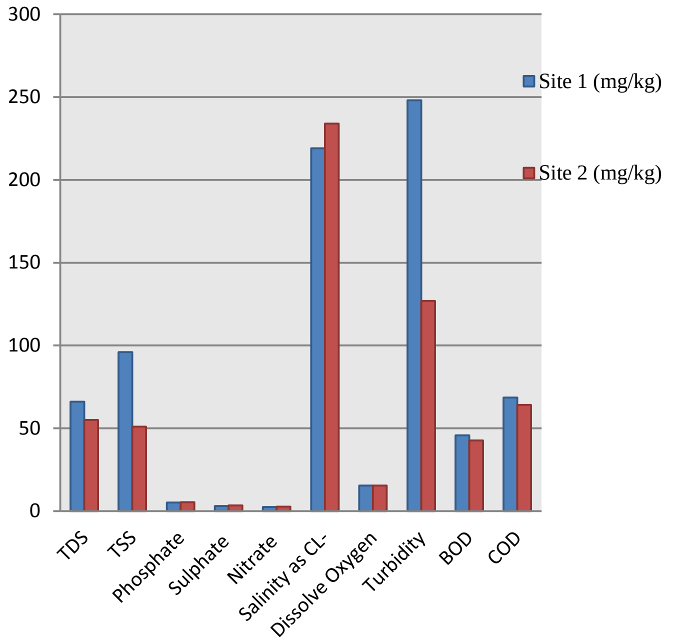

Figure 5. Physicochemical parameters of wet sample

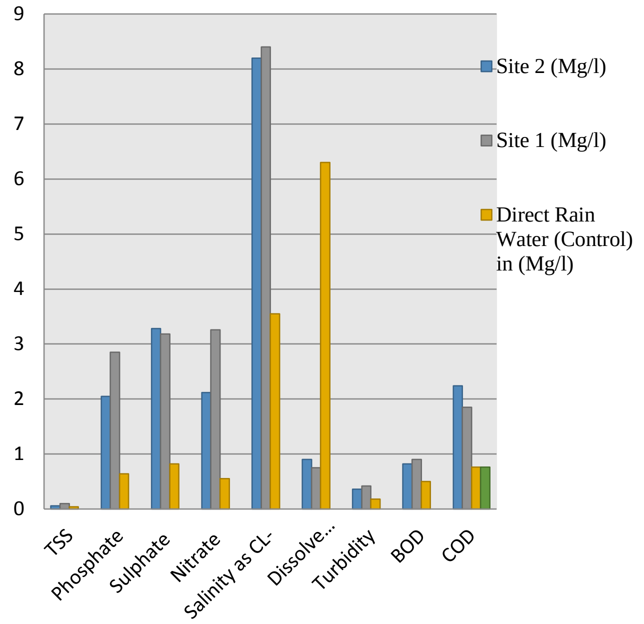

Figure 6. Physicochemical parameters of dry sample

The total suspended solids (TSS), measured by the fine particles of sediment and the pollutant that are attached to them ranged from 0.04 – 0.10 mg/kg. The particles suspended serve as a place of attachment for bacteria.

Phosphate and nitrate which support the growth of algae were found to be present in the wet samples up to 2.85 mg/l and 3.26 mg/l respectively. Further, the rainwater samples from the affected roofs were found to have salinity values ranging between 3.55 mg/l and 17.55 mg/l. Salinity (measured as chloride ions) in the rainwater samples from the affected roofs causes chemical reaction that deteriorate the roof by softening and peeling the roof coating for corrosion to take place. The slight pitting of the roofs together with the slope of the roof allows water to clog in some areas which gives rise to humid conditions that favour algae growth.

The turbidity value of the study area for the wet sample ranged between 0.18 – 4.05 NTU. Turbidity in rain water may be due to the presence of inorganic particulate matter in the atmosphere from vehicle exhaust soot, incineration, bush burning etc. High turbidity values protect microorganisms from the effects of disinfection thereby stimulating bacterial growth. It is deemed as the cloudiness of a liquid as a result of particulate matter being suspended within it. Its importance is highlighted by the fact that suspended solids interfere with effective chlorination/disinfection and helps to shield bacteria [15].

Chemical oxygen demand (COD) determines the oxygen required for chemical oxidation of organic matter. COD values convey the amount of dissolved oxidized organic matter including the non-biodegradable matters present in it. The values of COD in the water samples ranged from 0.76 mg/l to 3.09 mg/l due to high concentration of pollutants and organic matter.

Biochemical Oxygen Demand (BOD) is used to measure oxygen used and equate it to the amount of organic matter within the water sample. BOD measures the amount of oxygen used by microorganisms, in this case bacterium, to oxidize organic matter present within the water sample. BOD in the wet samples ranged from 0.50 mg/l to 2.02 mg/l. COD and BOD tracks the overall organic content of the rain water.

IV. CONCLUSION

This study investigated the qualitative factors responsible for the dark stains on aluminum roofs in Uyo. Data from the analysis of the affected roofs were collected which indicated the presence of algae and conditions favorable for algae growth as the major cause of the dark stains on colored aluminum roofs after few years of installation. Roof rainwater run-off samples as well as dry samples from the roof surfaces were analyzed and found to contain organic materials, inorganic types as well as substantial amounts of nitrates and phosphorous. This combination, together with the level of BOD and COD measured, offers a favorable condition for algae to grow and nutrients that ensure it thrives. Also, an appreciable level of salinity measured by chloride ion concentration was noted in analyzed samples. The effect of such salinity is to induce a chemical reaction that gradually deteriorates the roof allowing water to clog in some areas and further attracting organic and inorganic matter. Therefore, from the physicochemical point of view, the discoloration of aluminum roofing sheets is the result of a combination of factors all favorable to algae formation and sustenance.

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