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Atmospheric Corrosion Studies in Kenya: Past, Present and Future

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Despite the regular inspections and current contingencies made in the HF plant at Key words: Atmospheric Necsa, an isolated case where two mild steel vessels leaked HF during operation corrosion, occurred without warning. The failure of both these vessels necessitated their environmental premature decommissioning, and showed that better understanding the corrosion pollutants, ISO of mild steel used in the HF industry was needed. The failure of the mild steel was standards, Centre of traced to nitric acid (HNO3) contamination in the sulphuric acid (H2SO4) feedstock excellence which eventually concentrated in the technical grade HF product downstream. A study to simulate the industry corrosion conditions in a laboratory was required to better estimate the service life of the steels used in the HF plant because understanding the effect of HNO3 contamination on the plant's steels and the determination of corrosion inhibition strategies was essential. Unfortunately, HF is an extremely hazardous chemical and concentrations above 70% HF have a fuming capacity, making it a potentially lethal chemical for corrosion experiments. *Therefore, to safely work with HF, the safety risk for working with the chemical first* had to be categorised and assessed. This entailed determining the internal hazards of handling HF and its consequences, the probability of exposure and then mitigating actions that would lower the risk to a point that corrosion experiments could safely be conducted. A regular safety risk assessment, a process description, a "what if" analysis, as well as an external hazard and operability study (HAZOP) was completed. This lead to the implementation of a specialized experimental setup that proved to be prepared for any HF exposure contingencies while still producing HF corrosion data comparable to literature. Moreover, preventative measures including the use of HF resistant PPE (Personal Protective Equipment), well ventilated facilities and HF resistant Teflon containers were put in place which eventually resulted in the safe execution of corrosion tests completed there.

1. Introduction

Corrosion is a phenomenon that results in the destruction of materials due to chemical or electrochemical action arising from the surrounding environment. Thermodynamically corrosion is a spontaneous process that cannot be stopped but can be reduced (Syed, 2006). Atmospheric corrosion refers to corrosion in the air as opposed to corrosion that occurs in aqueous media. It is one of the most visible of all corrosion processes that is often seen on rusty bridges, flag poles, buildings and outdoor monuments. The large segment of the paint industry is committed to the manufacture and application of products for the protection of metals, as well as the large-scale operations of the galvanizing industry attest to the importance of controlling atmospheric corrosion (Roberge, 2008).

The exposure of a metal to the natural ambient atmosphere can vary considerably in terms of moisture content, temperature, and the amount of pollutants in air. Atmospheres are usually classified as rural, urban, industrial, marine, or a combination of these. According to Naixin et al., (2002) atmospheric corrosion is the most prevalent type of corrosion for common metals. In Tanzania Potgieter-Vermaak et al. (2011) found that degree of degradation of galvanized roof sheets was highest at the coastal site, followed by urban site sample, and the rural sample recorded the lowest degradation. Studies by (Haberecht et al. (1999) showed that corrosion rate in New Zealand decreased as one moved from the hinterland to the coastline. While there have been studies on corrosion of materials under different environmental conditions, little attention has been paid to atmospheric corrosion of roofing steel sheets in Kenva despite steel sheets being the common roofing materials. It is for this reason that the University of Nairobi and the Mabati Rolling Mills are collaborating on a corrosion project. The main objective of this study was to investigate the effect of atmospheric corrosion on metallic coated and pre-painted steel roofing materials in selected sites in Kenva.

2. Past Corrosion studies in Kenya

This section discusses some of the corrosion studies that have been conducted in Kenya in the

past years. Karuu (1989), investigated the corrosive properties of the soils in which underground pipes were laid. The study involved the laying of domestic water pipes both in the laboratory and in the field. The laboratory pipes showed a decrease in mass with time which was attributed to the formation of corrosion products on the surface of the corroding pipe. The field pipes progressively deteriorated with time which was mainly due to washing away of the corrosion products from the surface of the pipe by rain.

In 1979, Nthurima conducted an electrochemical study of the factors affecting underground corrosion of steel in soils. The factors of concern were: oxygen diffusion rates, soil moisture content, soil resistivity, salt concentrations, pH and bacterial activity. The corrosion rates of steel were determined by polarization and weight loss measurements. The study revealed that the corrosion rate was influenced by the dissolved oxygen content at the surface of the metal and any factor that affected the diffusion of oxygen had a marked effect on corrosion rate.

3. Factors Affecting Atmospheric Corrosion The key factors that affect atmospheric corrosion

The key factors that affect atmospheric corrosion include:

3.1 Moisture

In a completely dry atmosphere, oxygen and carbon dioxide do not cause corrosion (Roberge, 2008) indicating that some moisture is necessary. Salts of sulfur and chlorine can aggravate corrosion by forming electrolytes in industrial atmospheres. The presence of rain may have a beneficial effect by washing away the atmospheric pollutants that have settled on exposed surfaces, however, if rain collects on the surface, it may enhance corrosion by ensuring continuous wetness on the surface as illustrated in Figure 1.



Figure 1. An installed panel showing rainfall droplets on a brick red sample at Mariakani corrosion test site, near the coastal region of Kenya

3.2 Temperature

The role of temperature on corrosion can be considered in terms of the normal increase in corrosion activity which theoretically doubles for each ten-degree increase in temperature and in the effect of temperature lag of metallic objects that is due to their heat capacity. As the ambient temperature drops in the evening, metallic surfaces tend to remain warmer than the humid air surrounding them and do not begin to collect condensation until sometime after the dew point has been reached. According Uhlig and Revie (1984), as the temperature begins to rise in the surrounding air, the lagging temperature of the metal structures will tend to make them act as condensers thereby maintaining a film of moisture on their surfaces. Studies by Angel et al., (2015), on atmospheric corrosion of galvanized steel in different environments in Chile and Mexico, showed that there was a trend in the decreased corrosion with increase in temperature when the weather data between the two countries were compared.

Cycling temperatures could produce severe corrosion on metal objects in the Tropics and on metal tools. Since Kenya lies within the tropics, the roofing materials are likely to experience severe corrosion. The dew point of an atmosphere indicates the equilibrium condition of condensation and evaporation from a surface hence it is usually advisable to maintain the temperature at 10 to 15°C above the dew point to ensure that no corrosion occurs due to condensation on the surface that could be colder than the ambient environment (Shreir, 1994).

3.3 Relative Humidity (RH)

Relative humidity is the ratio of the quantity of water vapor present in the atmosphere to the saturation quantity at a given temperature, and it is expressed as %. A fundamental requirement for atmospheric corrosion processes is the presence of a thin film of an electrolyte that can form on metallic surfaces when exposed to a critical level of humidity. While this film is almost invisible, the corrosive contaminants it contains are known to reach relatively high concentrations, especially under conditions of alternate wetting and drying. The critical humidity level would vary depending on the nature of the corroding material, the tendency of corrosion of products and surface deposits to absorb moisture, and the presence of atmospheric pollutants. Most atmospheric corrosion can be prevented by maintaining RH below 60%.

3.4 Pollutants

Sulfur dioxide (SO₂), which is the gaseous product of the combustion of fuels that contain sulfur such as coal, diesel fuel, gasoline and natural gas, has been identified as one of the most important air pollutants which contribute to the corrosion of metals (Ovri and Iroh, 2013). Angel et al (2015) used XRD to confirm the presence of sulfate in corrosion products and hence concluded that sulfur dioxide played an important role in the galvanized-steel corrosion. SO₂ would therefore play a great role in the industrial sites chosen for study in Kenya. Nitrogen oxides (NO_x) are also known to be promoters of corrosion. In urban areas, the major source of nitrogen oxides is the exhaust fumes from vehicles. Hence, sulfur dioxide, NOx and airborne aerosol particles can react with moisture and UV light to form new chemicals that can be transported as aerosols.

3.5 Aerosol particles

The aerosol particles are usually present in outdoor atmospheres and their concentrations depend upon a number of factors that include location, time of the day or year, atmospheric conditions, presence of local sources, altitude and wind velocity. Urban areas usually contain the highest concentrations that reach up to 108 and 109 particles per cm³, with particle size ranging from around 100 µm to a few nm. Size is normally used to classify aerosol because it is the most readily measured property and other properties can be inferred from size information. Studies have indicated that there is a strong correlation between wind speed and the deposition of aerosols. Saline winds have shown very good correlation between chloride deposition rates and wind speeds up to above a threshold of 3 m s⁻¹ or 11 km h⁻¹(Alcala and Custodio, 2008). Generally,

air pollutants such as sulphur dioxide, hydrogen sulphide, oxides of nitrogen and chlorides have been found to contribute to atmospheric corrosion (Brown and Master, 1982).

Studies in Taiwan by Luo (2016) on atmospheric corrosion of galvanized steel showed that increased humidity, chlorides and SO_2 concentration resulted in the increased corrosion rate of the metals. He also found that not only did northeastern monsoon have a lot of effect on chloride deposition inland, but it also increased corrosion rate in the autumn and winter.

4. Effects of Atmospheric Corrosion

Atmospheric corrosion effects in Kenya are evident under various environmental conditions. In the marine environment which is typical of the coastal region of Kenya (Mombasa), corroded roofs are commonly observed (Figure 2). The exposed parts such as roofs have the tendency to corrode however, the enclosed spaces will show low corrosion rates.



Figure 2. One of the many corroded roofing sheets at Mariakani market, 36 km from Indian Ocean, Kenya

In an industrial environment the causes of corrosion would be the sulfur oxide (SO_X) and nitrogen oxide (NO_X) produced by the burning of automotive fuels and domestic fuel emissions as in the case observed in an industrial area in Nairobi (Figure 3). A number of roofs are being painted in the country to reduce corrosion.



Figure 3. Brown rust formed on a roof of an office in Nairobi's industrial area

Galvanized roofs are known to corrode in bands of rust seen in parts of the galvanized iron sheet. In the rural parts of Kenya, such structures are common. The popular use of galvanized iron as a roofing material in Tanzania has also been reported by Potgieter-Vermaak et al. (2011). kind Whatever the of atmosphere, the environmental conditions will vary over a period. Metrological conditions in Kenya are quite variable considering the existence of an ocean along the coast of the country. As one moves upcountry, plains and mountains are encountered. A typical climatic data for Mariakani site at the Kenyan coast is presented in Table 1.

> Table 1. Mariakani Annual Climatic Data (Source: climatemps.com, 23-01-2016)

Months	Temp.ºC	Precipitation mm	Relative humidity,%	
Jan	27.1	32.4	69	
Feb	27.6	18.6	66.9	
Mar	27.9	62.1	68.5	
Apr	27.1	148.1	73.6	
Мау	25.7	217.1	76.2	
Jun	24.4	81.1	73.1	
Jul	23.7	65.5	74	
Aug	24.3	57.2	73.1	
Sep	25.4	61.5	71.3	
Oct	25.4	81.1	71	
Nov	26.5	100.8	72.5	
Dec	26.9	71.6	72.2	
Ave	26.0	83.1	71.8	

Air temperature is one of the most important factors that affect corrosion of metallic coated roofing materials. Time of wetness (TOW) which is the time during which the metal surface is covered with thin film of electrolyte will determine the duration of the electrochemical corrosion process and is an important environmental factor that would affect the atmospheric corrosion (Veleva and Alpuche-Aviles, 2002). The increased corrosion rate of carbon steel that occurs at night and in rainy day than in the daytime and sunny day represents the influence of the time of wetness.

(https://www.researchgate.net/publication/2630 85899, May 10, 2016).

Sea-salt deposition is very important а environmental factor since deposited salts decrease the eventual protective properties of corrosion products formed on the metal surface and act as centers of water vapor condensation that facilitate electrochemical reactions. Therefore the variation in temperature, humidity and rainfall will form favorable atmospheric environments for atmospheric corrosion. The atmosphere can vary considerably with respect to moisture content, time of wetness, temperature, and the amount of pollution and other contaminants present. Climatic data hence provide useful information on atmospheric corrosion of roofing materials.

Galvanized roofing sheets

There is a large scale use of galvanized roofing sheets to try and control atmospheric corrosion in Kenya. However, cases of corroded galvanized sheets are still common in the country (Figure 4).



Figure 4. Corroded galvanized roofing sheet near a highway in Nairobi, Kenya

This is probably the effect of sulfur dioxide and nitrogen oxide from moving vehicles. The paint industry which is committed to the manufacture and application of paint products for the protection of metals and the large-scale operations of the galvanizing industry attest to the importance of controlling atmospheric corrosion. Economic losses caused by atmospheric corrosion cannot be ignored since they account for significant disappearance of the metals used in construction. A large number of metallic parts are discarded because of atmospheric corrosion. The corroding material does not necessarily require a large amount of electrolyte but the nature of the electrolyte is important. The quality of metallic coated and pre-painted roofing products can be improved if their response towards atmospheric corrosion under various environmental conditions is understood.

5. Corrosion research methodology

Study sites

The study sites for the atmospheric corrosion of the roofing materials were: Kisii, Athi River, Mariakani and Mombasa as indicated in Figure 5.



Figure 5. Map of Kenya showing the sites for the atmospheric corrosion study. The sites are marked with the sign Δ

The corrosion study sites were chosen to represent different corrosion environments. These sites can be described as severe marine (Mombasa), marine industrial (Mariakani), inland industrial (Athi River) and industrial rural (Kisii). This paper provides results for pre-painted roofing materials for Mariakani test site only.

Experimental procedure

Pre-painted roofing materials were obtained from selected manufacturers and given code numbers for purposes of the experiment. The samples (190 mm x 130 mm) were placed on the racks (Figure 6) and exposed to corrosive environment at the Mariakani test site for ninety days.



Figure 6. The setup of exposure rack at Mariakani site

At the end of the ninety days, the samples were analyzed for change in fade and gloss using Spectroguide (BYK Gardner GMGH) that measures fade and gloss. Fade refers to the gradual loss of brightness while gloss refers to percentage of light that reflects rather than diffuses from a surface, painted or not.

6. Results and Discussion

The values of parameters used to provide information on fade and gloss after 90 days exposure of the pre-painted steel sheets at the Mariakani test site are presented in Table 2.

Table 2. Exposure results for the pre-painted samples at Mariakani Site

Sample ID	Color	Parameters				
Manufacturer 1		dL	da	db	ΔΕ	ΔG
MK01/CP/16/MBA- PP/01	Red	0.93 ± 0.32	-1.31±0.61	-2.03 ±0.39	2.62 ± 0.54	-0.73±0.27
MK01/CP/16/MBA- PP/02	Green	-1.95 ±0.22	6.14 ± 0.60	-3.00 ±0.22	3.92 ±2.53	14.7 ± 6.0
MK01/CP/16/MBA- PP/03	Blue	0.47 ± 0.13	-0.33±0.11	0.43 ± 0.14	0.70 ± 0.19	-5.80 ± 0.69
Manufacturer 2		dL	da	db	ΔE	ΔG
MK01/CP/16/CHI- PP/01	Red	0.46 ± 007	-0.69 ± 0.69	-1.07 ± 0.20	1.39 ± 0.44	-5.33 ± 2.15
MK01/CP/16/CHI- PP/02	Green	1.27 ± 0.14	1.14 ± 0.18	-1.01 ± 1.03	1.78± 0.22	12.5 ± 9.1
MK01/CP/16/CHI- PP/03	Blue	0.47 ± 0.13	-0.26 ± 0.11	0.43 ± 0.14	0.70 ± 0.19	-5.80 ± 0.69

Key:

dl –change in lightness; da – change in color; dbchange in intensity of the color; ΔG – change in gloss; and ΔE - color difference.

In measuring fade, the color was considered in terms of three factors that described color. The factors were: the lightness, the hue and the chroma. The value of lightness indicated the degree of the lightness or darkness of the color. The hue indicated "what" color it was while the chroma described how intense the color was. The color is commonly measured on a color meter with three values: L, a, and b. The overall color change was given as ΔE which provided

information on the fading of the sample, and it was calculated using the following expression:

$$\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$
(1)

where, L – The lightness on a scale of 100=white, 0=black; a- Negative values are green, positive values are red. Intensity increases as the value is far from 0; b- Negative values are blue, positive values are yellow. Intensity increases as the value is far from 0.

Discussion

In Table 2, it was observed that the pre-painted red coating from manufacturer 1 had a greater color loss (fade variation) of $\Delta E= 2.63\pm0.54$ Hunter units compared to the red coating from manufacturer 2 which registered $\Delta E = 1.39 \pm 0.44$ Hunter units. This revealed that red coated sheet from manufacturer 2 was a superior product for roofing applications. The superiority of the red coat from manufacturer 2 was further supported by its gloss retention. It exhibited a higher reflectivity of light (both UV and visible portion of sunlight) with an enhanced gloss improvement of 5.33**±2.15** Hunter units over the red coating from manufacturer 1 which was 0.73±0.27. UV light is known to decompose paint pigments, making them permanently lighter. The degree of color loss depends on the amount of UV exposure, the type of pigment, the type of resin, and the color.

The green coating for manufacturer 1 had a $\Delta E=3.92\pm2.53$ Hunter's unit (color difference) while manufacturer 2, $\Delta E=1.78\pm0.22$ Hunters units. These values were not so significantly different to decide on the best product from either of the two manufacturers. However in terms of change in gloss (ΔG), (manufacturer 1, $\Delta G = 14.7 \pm 6.0$; manufacturer 2 $\Delta G = 12.5 \pm 9.1$), the green coating from manufacturer 2 could be considered a better roofing product.

The study showed that the blue roofing sheets from manufacturer 1 and 2 had similar properties in terms of fade variation and gloss retentions ΔE = 0.70±0.19 Hunter units and ΔG = 5.80±0.69 respectively.

The loss of gloss could be attributed to natural weathering over time which roughens the paint

surface. This type of gloss loss could be considered as permanent. The loss of gloss could also result from the buildup of dirt on the paint. However, washing off the dirt would restore the gloss.

The current study showed that blue coating is the best product in retaining the color among the three products tested while green coating is the worst. None the less, green coating reflects much of the incident sunlight hence the best for the cool roofing technology applications.

5. Conclusion

The roofing materials used in this study were coated red, green and blue. In terms of color loss gloss retention, red materials from and manufacturer 2 were found to be more superior products than those from manufacturer 1. Green products produced by both manufacturers 1 and 2 gave the best product that showed the lowest color loss. The fading and gloss of the steel sheets varied with the source (manufacturer). The study has provided preliminary information on the fading and gloss properties of the pre-painted steel roofing sheets that were obtained from two manufactures when tested under the corrosive atmospheres of Mariakani test site (marine industrial environment). The investigation on the atmospheric corrosion of pre-painted metallic substances could provide means for prevention of atmospheric corrosion and improving the quality of the products so long as the conditions of exposure are specified and considered during the design of the experiment.

6. Future corrosion research

It is expected that the data obtained from other research sites (Mombasa, Athi River and Kisii) would be useful in producing the first corrosion map of Kenya. The project is of significance since would provide national reference information on atmospheric corrosion for metal coated and prepainted steel roofing products in the Kenyan market. The atmospheric corrosion studies could also provide the Kenyan building industry with guidelines on the selection of quality roofing products and structural steel for application that could withstand corrosion.

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