Atmospheric Corrosion of Al-Zn Coated Steel Sheets Exposed under Marine Environments in Kenya

ABSTRACT

Corrosion contributes to multibillion USA dollar loses due to deterioration, weakening and ultimate failure of engineering infrastructure globally necessitating further research to build more corrosion resistant materials. The aim of this study was to investigate atmospheric corrosion ofaluminium-zinc coated steelroofing sheets exposed tooutdoor marine environment in Kenya atDiani and Mariakani sites, representing severe marine and urban marine environments respectively. Al-Zn coated sheets measuring 130 mm x 190 mm coated with masses ranging from 60-150gm^{2}were exposed for 2 years. The specimens were collected at periodic intervals following ASTM G1-90 standard method and corrosion products analyzed by Raman spectroscopy, while corrosion rate was determined by weight loss method.Corrosion rate ranged from 0.03 to 0.05mmpyand increased with decreasing masses coatingmaterials from 150 to 60 (gm^2).Diani siterecorded higher corrosion due tosevere marine conditions characterized by high chlorides, RH of 81%, UV of 12mW/cm^2 and a temperature of 27℃.Dominant rust constituents were goethite (a-FeOOH) and lepidocrocite (g-FeOOH), while ferrihydrite and maghemite (a-Fe_2O_3)were measured at low levels suggesting the influence of suphur dioxide and chloride pollution on corrosion rate at both sites.Corossion rates < 0.15 mmpy at both sites suggest excellent protection by the formulated coating media. The results of this contribute to improving the quality of the AZ metal coating media under marine environments.

Keywords*: Atmospheric corrosion, Al-Zn coated steel,Marine environment, Environmental factors.*

1. INTRODUCTION

Corrosion results into massive globalinfrastructure failurethreatening human safety(Alemayehu and Birahane, 2014). In addition, studies by Li and coworkers(2020) found that corrosion products affect both the environment and human health by leaching unprecedented amounts of metallic ions such as aluminium, manganese, iron, copper and zinc from coating materials into drinking water (Li *et al*., 2020).Corrosion processes are driven by either dry or wet deposition of materials in the environment (Hodoroaba, 2020; Lindström and Odnevall , 2011). The major environmental factors that influence the corrosion of metallic roofing sheets include rainfall, temperature, relative humidity, wind and sunshine (Morcillo *et al*., 2013). In tropical regions, the availability of hot and humid climatic conditions constitute the predisposing factors that accelerate corrosion of materials in construction industry. This leads to the need of coming up with alternative materials that are less susceptible to corrosion. Steel, aluminium and iron have been extensively applied in the industry due to characteristic malleability, durability and high strength. Hencealuminium and steel roofing materials are the most preferred in the world (Ooko, 2019)as base metals together with zinc and copper or sometimes as a combination. However, despite steel is prone to corrosion necessitating further research on protectionmeasures against environmental deterioration(Cole *et al*., 2003; Hebbar *et al*., 2014; Morcillo *et al*., 2013).

The environmental factors constitute the major corrosion drivers, with the major classification of the environment into rural, urban, industrial, marine, or a combinations of these (Morcillo *et al*., 2013; Natesan *et al*., 2008). Marine environment is characterized by high corrosion rates (Dean, 2000) due to high levels of chlorides from the rich sodium chloride content in sea water. The strong coastal winds drift salt from the sea water up to eight kilometers from the coastline. The high salinityexperienced in the coastal regions contributes to higher atmospheric corrosion rate compared to rural and urban settings, since high levels of dissolved chlorides raise the conductivity of the electrolyte film on the metal destroying the passivating film (Morcillo *et al*., 2015). The presence of atmospheric pollutants such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and chlorides accelerate corrosion of steel roofing sheets.

The rate of corrosion of metals coated with aluminium, copper and zinc have been widely studied. Ting *and co-workers* (2012) reported corrosion rate ranging between 0.0025 and 0.0314 millimeter per year (mmpy) for galvanized steel, and 0 to 0.0014 mmpy for aluminiumunder marine conditions in Kochi-India suggesting better performance of non-ferrous metals. The process was mainly driven by air pollutants namely chloride, and sulphur dioxide. Further studies in Cuba by Mendoza and Corvo, (2000)on atmospheric corrosion rate of both aluminium and copper found that chloride deposition had a significant influence on corrosion rate, coupled with rainfall, temperature and wetness.

Coating is one of the protective methods used to secure steel sheet from atmospheric corrosion (Raj, 2013). Metallic coatings provide a protective layer on the surface of steel. Commonly applied metals for coating include zinc, aluminium and copper. Zinc has mostly been used because of its higher position on the electrochemical series relative to iron, whereas alloys of aluminium have also been given much attention (Haque*et al*., 2014). Aluminium-Zinc alloy at composition of 55% aluminium and 45% zinc has been used widely as sacrificial and barrier coating, where zinc provides protection on scratches or exposed edges while aluminium provides a barrier to corrosive media (Vargas *et al*., 2009; Natesan *et al*., 2008). This study investigated atmospheric corrosion of aluminium-zinc coated steel roofing sheets under severe marine and urban marine environments.

2. MATERIALS AND METHODS

The study was designed to investigate the influence of environmental factors on the rate of corrosion under severe marine environment 100 m from the Indian Ocean, and marine industrial environment in Mariakani located 40 km from the Indian Ocean. Figure 1 shows the locations of the study sites.

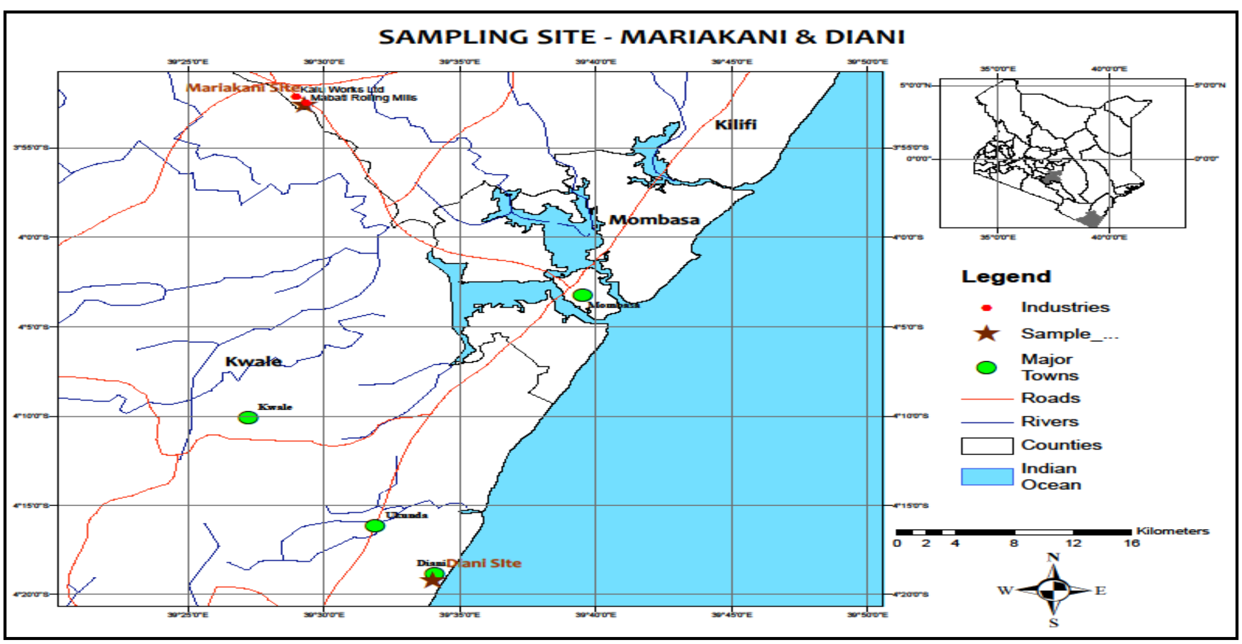

Figure 1*: The map of the sampling sites in Diani and Mariakani*

2.1 Experimental procedure

Experiments werecarried out for a period of 2 yearsfrom July 2019 to September 2021. Metallic coated iron sheets (Al-Zn 55%)had mass composition of 55% aluminium, 1.6% silicon and 43% zinc(East African Standard Committee, 2019).The sheets were sheared into 130 mm x 190 –mm coupons, punched with coded holes identification and cleaned according to ASTM G1-90 method (ASTM, 1999). The initial coating mass was recorded before exposure to the atmosphere, then the racks were inclined at an angle of 45^{o}facing the sea for a period of 2 years according to ASTM G50-76 (ASTM, 2003).Figure 2 illustrates the racks exposed during experimental period. Representative samples of exposed specimen were collected at intervals of 3 monthsover the experimental period and analysedto determine losses in coating mass.

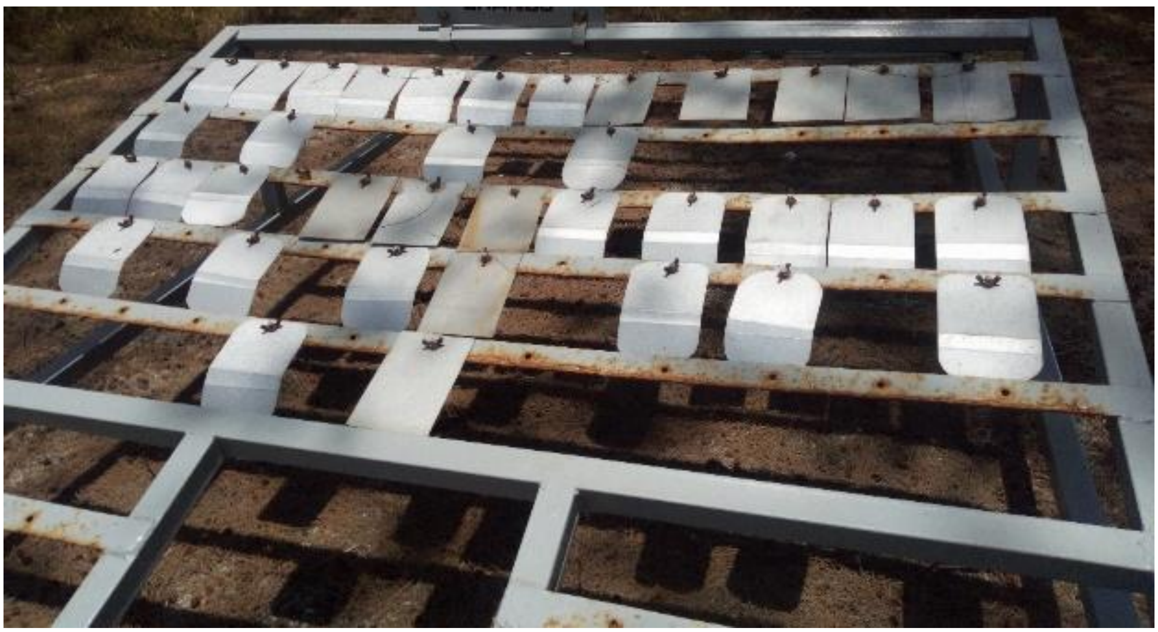

Figure 2: *A set-up for outdoor exposure of 55% Al-Zn metallic coated sheets at Diani site.*

2.2 Determination of corrosion rates of the samples

The samples were collected and cleaned in respective pickling solutions according to the ASTM G1-90 guidelines (ASTM, 1999).Cleaned specimens were dried and the final mass of the coating determined byenergy dispersive X-ray (EDX) Model: 7000 ROHS ASSY for analysis of Al-Zn by comparing the differences in the masses of the coating on the specimen before and after the exposure period.Corrosion rateswere determined in triplicate following Equation 1:

Corrosion rate (C_R) (mmpy) = (ΔW.K)/ (A.T.D) Equation……………….…1

Where ΔW is change in mass of coating material (g), K is a constant (8.76 $x10^4$ mm/y), A is the exposed area of the steel sheet (cm^2), T is time in hours and D is density of the coating in g/cm^3.

2.3Determination of corrosion products by Raman spectroscopy

The corrosion by-products fromexposed metallic coated roofing sheets were analyzed using Notch filter based micro spectrometer Model EZ Raman-NP-785-BISwith 1800 lines/mm grating, 300 mm local length, with thermoelectric cooler (TEC) cooled charged-coupled device (CCD)equipped with a double laser at a frequency of 785 nm. The equipment spectral resolution was of 0.7 cm^{-1}.Sample calibration was conducted before taking measurements. Sample spectralanalysis was carried out using EZ-Raman software.

2.4 Quality assurance and Quality control (QA/QC)

All experiments were conducted in triplicate to verify the results obtained. Blank samples were included in the setup for quality control. All reagents used were analytical grade. All glassware was cleaned, rinsed and dried at 110 ^oC for 12 hours before use. The EDX and Raman Spectrometer were calibrated before use to ensure accuracy of results. Microsoft Excel 2010 and Statistical Package for the Social Science (SPSS) version 20 for windows were used in data analysis.

3. RESULTS AND DISCUSSION

3.1 Corrosion results at Mariakani site

The results revealed strong influence of the mass of coating on the rate of corrosion. Corrosion rate increased from AZ150<AZ85<AZ70<AZ60 suggesting increasing protection of the metallic surface with coating masses (Figure 3).Mariakani site is characterized by industrial marine environment with high sulphur dioxide and nitrogen dioxide levels which could have influenced rate of corrosion. Despite longer distance of the site from the ocean, the site experienced high moisture content which could have enhanced corrosion (Syed, 2006). Corrosion rate was highest during the first year for all the coating

masses, and decreased in subsequent years. The trend could be attributed to formation of a protective film slowing down corrosion(Kamimura *et a*l., 2006; Tamura, 2008).

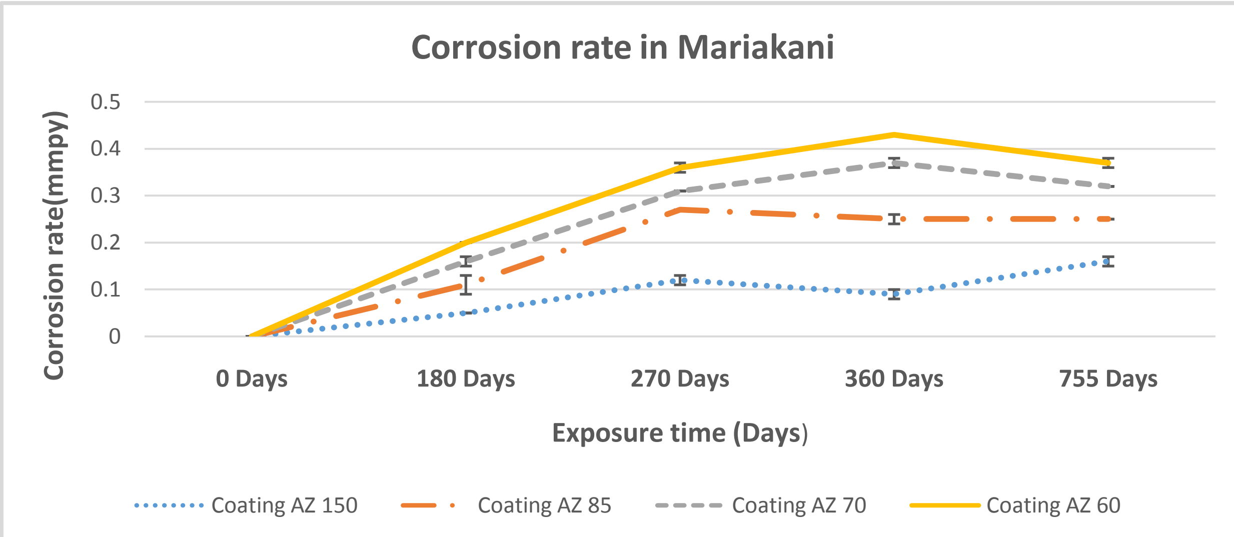

Figure 3*: Corrosion rate of AZ metallic coated iron sheets in Mariakani*

3.2 Corrosion results at Diani site

All the specimen exposed at Diani site experienced high corrosion rates compared to Mariakani site. Corrosion rate increased from AZ150<AZ85<AZ70<AZ60 suggesting a reduction of the rate of corrosion with increasing mass of coating materials. In addition, the high rate of corrosion at Diani was attributed to high levels of chlorides in the atmosphere compared to Mariakani which was located over 40km away. The findings agree with the earlier studies by Zhao and coworkers (2008) who found corrosion rate up to 80 times due to presence of chlorides.Chloride ions getadsorbedon the protective oxide layer and reacts with the metal surface to form intermediate soluble complexesthat accelerate corrosion. The observed fluctuating rate of corrosion at different stages of the experiment could be attributed to the formation and removal of corrosion film productsfrom the surface of the iron sheetswhich agrees with the findings of (Natesan and coworkers (2008). Figure 4 illustrates corrosion of AZ iron sheets covered with different degrees of coating materials that were exposed at Diani site.

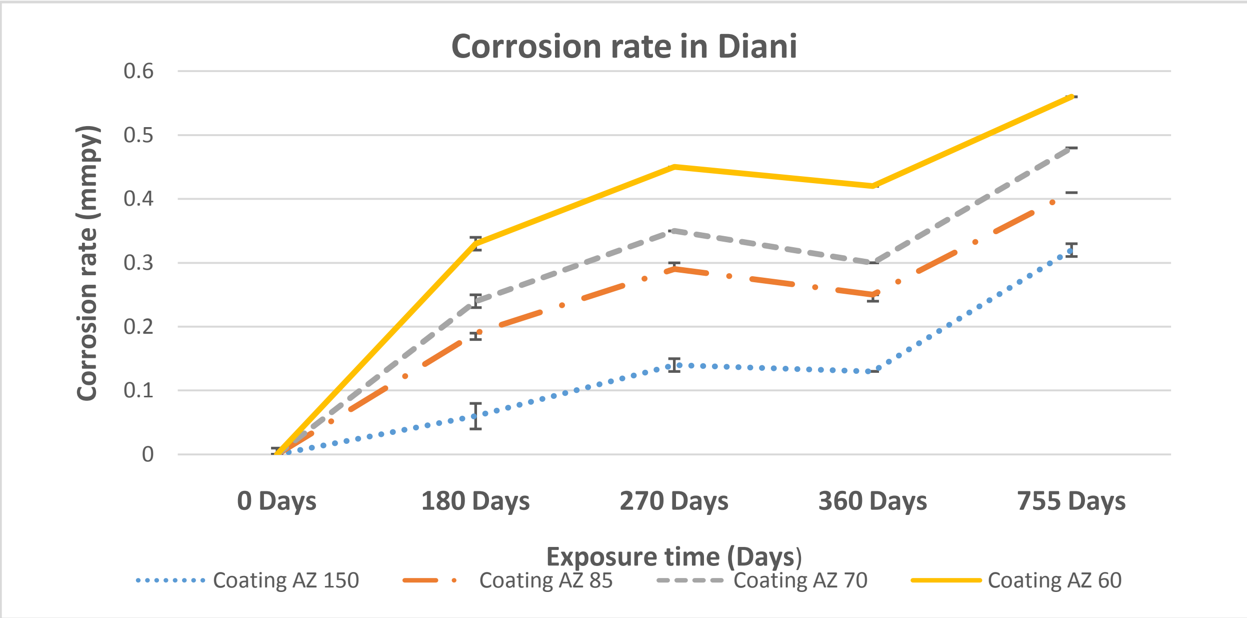

***Figure 4**: Corrosion rate of AZ metallic coated iron sheets at Diani*

Diani site due to its proximity to the ocean experienced higherlevels of relative humidity (81%), UV radiation (12 mW/cm^2), temperature (27 ^{o}C) that accelerated corrosion.Similar findings were reported by Syed (2010), Vashi and Kadiya(2009) andWallinder and Leygraf (2002).

The relatively lowercorrosion rates were experienced at Mariakanithat were attributed to lowchloride levels.Nevertheless Mariakanisite experienced relatively high levels of SO_2(635 µg/m^3) attributable to its location along the Nairobi-Mombasa high way. Sulphur dioxide has been reported to have less effect on stainless steel (H. E. Townsend, 2002)since iron is passivated by sulphate ions and upon saturation the accumulated film of sulphate corrosion products preventfurther corrosion.Furthermore, higher rainfall experienced at Mariakanisite (114 mm) compared to Diani (96 mm) reduced corrosion rate by washing away the pollutants from the surface(Angel *et al*., 2015).

Comparison of corrosion rates measured in the current study to other studies elsewhere revealed lower rates than those reported in Kenya (Ooko, 2019) as illustrated in Table 1.The effect of Covid-19 could have resulted in reduced production in most industries leading to reduction of the $NO_2$and SO_2 levels which are the agents of corrosion(Kumari and Toshniwal, 2020).

***Table 1**: Corrosion rate of various countries in different times*

Country	Corrosion rate	Study Period	Source
South Africa/ Johannesburg	0.500 mm/y	2 years	(Foax *et al*., 2008)
Sri Lanka/Battaramula	0.873 mm/y	1 year	(Foax *et al*., 2008)
Maldives/Hanimadhoo	0.526 mm/y	2 year	(Foax *et al*., 2008)
Mozambique/ Maputo	0.007 mm/y	18 months	(Foax *et al*., 2008)
Kenya/Mariakani	0.033 mm/y	180 days	(Ooko, 2019)
Cuban/Havana	0.005 mm/y	1year	(Hernández, 2018)
Nigeria/Finima	0.0003 mm/y	1 year	(Ekuma & Ogunyemi, 2023)

Figure5illustrates the visual impression of the sampled specimens A, B and C after a 2-year exposure at Diani and Mariakani sites.The specimen exposed at Mariakanisite were darker dueto exposure to vehicular emissions. The specimen exposed to the environment recorded greyish colourationon the

surface.

***Figure 5:** A photograph showing comparison of corroded specimen (AZ 150) at Mariakani andDiani test sites* A *ontrol specimen, (B) -Mariakani specime* B *d (C)- Diani site specimen).* C

3.2 Raman spectroscopy

S1 S2 S3

Raman spectra of corrosion products after a 2 yearof exposure to severe marine environment at Diani revealed the presence of goethite (α-FeOOH), maghemite (γ- Fe_2O_3), akaganeite (β-FeOOH), lepidocrocite (γ –FeOOH) and hemitite (α-Fe_2O_3) (Figure 6). The Raman spectra bands at 480, 1116, 1176, and 1508 cm^{-1} were associated with Goethite. Maghemite presented strong spectra at 346 and 766 cm^{-1} at Diani and Mariakani, respectively. Lepidocrocite γ -FeOOH spectra were at bands 392 and 1098 cm^{-1}. Formation of lepidocrocite γ -FeOOH in both sites indicated it was a key composition of the corrosion product (Zhang *et al*., 2003).

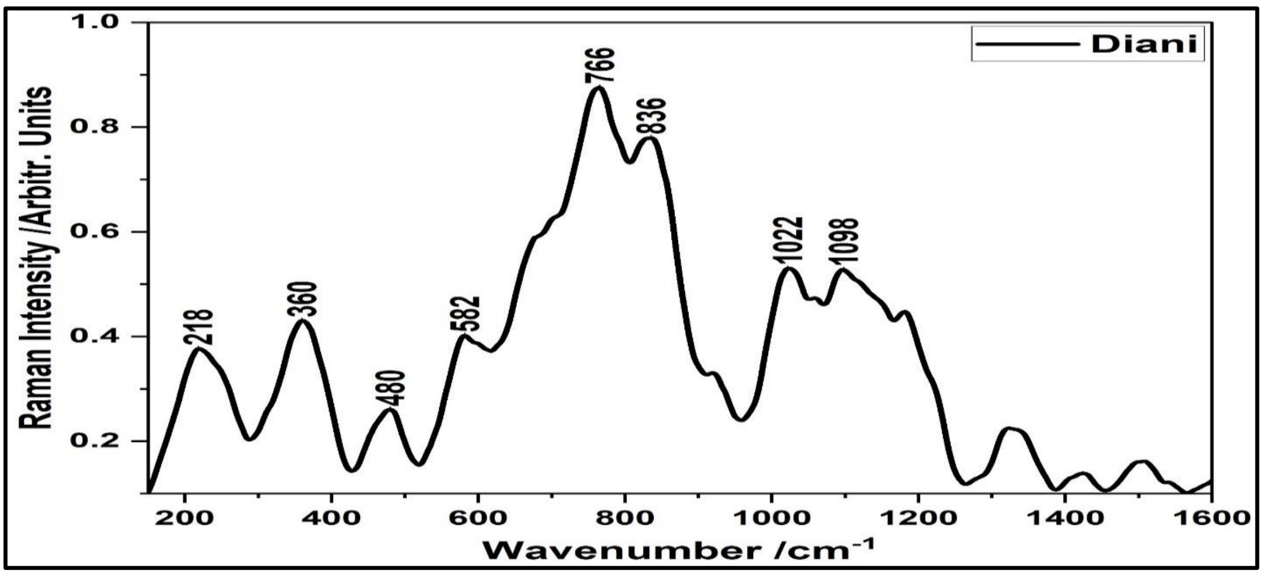

Figure 6. *Raman spectra of AZ metallic coated steel exposed at Diani site*

The sheets exposed displayed phases of goethite, akaganeite, magnetite, maghemite, lepidocrocite and hemitite (Figure 7). Magnetite (Fe_3O_4) band was observed only at Mariakani at a band of 676 cm^{-1}. Formation of (Fe_3O_4) is more likely when there is limited oxygen supply which leads to the environment becoming more reducing (Zhang *et al*., 2003).

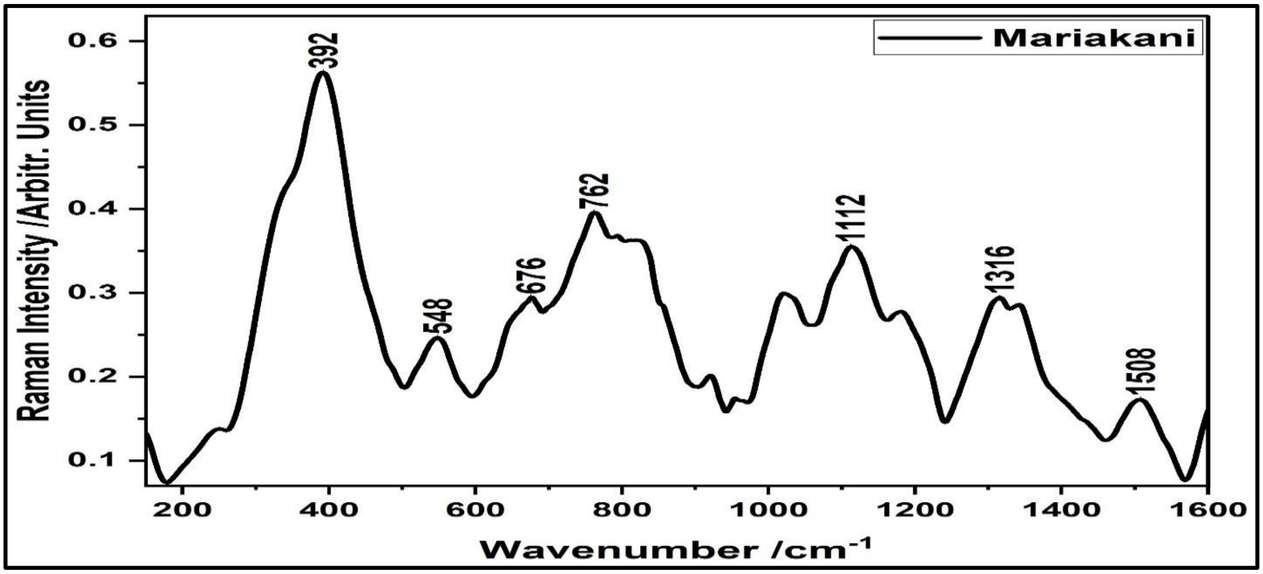

***Figure 7**. Raman spectra of AZ metallic coated steel exposed at Mariakani site*

Akaganeite (β-FeOOH) had a spectrum at 582 and 548 cm^{-1} forDiani and Mariakani, respectively. Maghemite and Akaganeite are considered as the primary corrosion products at marine environment. The presence of Akaganeite is as a result of chlorinated compounds (oxyhydroxideAkaganeite) hence the influence from the sea salt. However, the presence of SO_2 in the atmosphere forms mildly acidic environment which makes $Fe(OH)_2$not to precipitate (Abd-Elmomen, 2015).Due to the distance from the Indian Ocean, reduction of oxygen could have led to formation of magnetite at Mariakani site.

4. CONCLUSION

The extent of corrosion of Al-Zn coated sheets atMariakani and Dianiafter 2 years of exposure were < 0.15 mmpy except for AZ 150 (0.32 mmpy). The findings revealed low corrosivityaccording to the ISO 9223classification of C2 which was attributed to passivation by aluminium and chromium on the steel. AZ 85 and 70 coated steel sheets displayed similar corrosion rate with related performance under marine environment. Higher corrosion rates observed for coating mass lowerthan 70 was attributed to poor adherence of the coating on the substrate during the coating process. The dominant corrosion productsfor Al-Zn coated steel were α-FeOOH, γ- Fe_2O_3, β-FeOOH and α-Fe_2O_3.Chloride and sulphur dioxide enhanced corrosion of AZ coated roofing sheets with the highest resistance to corrosion experienced in the order of AZ150>AZ85>AZ70>AZ60.

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AUTHORS' CONTRIBUTIONS

All authors read and approved the final manuscript.

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