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Atmospheric Corrosion of Hot Dip Zinc Coated Steel in Coastal and Rural Areas of Vietnam

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The comparative results of corrosion testing in humid tropical atmosphere in rural and coastal areas for hot dipped zinc coatings are presented below. The test was conducted in outdoor conditions over a period of five years. The mass loss and other performance characteristics of two types of zinc coatings were evaluated, analysed and discussed in relation to the climatic and environmental parameters. The corrosion rates of the coatings exposed to coastal conditions were about three times higher than the corrosion rates appreciated in rural conditions. The data demonstrates that the corrosion process obeys an equation of the form $M=At^n$, where M is the loss of metal and t is the time of exposure. A and n are constants which values depend on the environmental characteristics and the physicochemical behavior of the corrosion products respectively. Corrosion is strongly influenced by atmospheric time of wetness (TOW) and airborne salinity. The nature and composition of corrosion products are also considered. Simonkolleite, a major crystalline phase, was found in the zinc corrosion products exposed to coastal conditions, while zinc hydroxide and zinc hydrosulfate are easily found in rural settings.

Keywords: *zinc coating, corrosion rate, corrosion product, airborne salinity*

1. Introduction

Corrosion in natural environments has long been a subject of great interest for materials development and application. In Vietnam, the issue has been paid special attention due to its typical humid tropical climate with high temperature, humidity and prolonged time of wetness. The situation is more severe due to high concentration of airborne salinity coming from the sea and corrosive pollutants caused by growing industries. For decades, many weathering test programs have been conducted in different climatic regions of the country to evaluate corrosion performance of various metals and alloys [1-6].

According to Le Thi Hong Lien [2], in Vietnam's atmosphere, corrosion process obeys an equation of the form $M=At^n$ and zinc corrosion tends to be predominantly determined by the chloride ion concentration in the air. However, crystalline composition of corrosion products formed with specific features under humid tropical conditions, such as the appearance of zinc hydroxycarbonate or hydrozincite in the initial stage. Besides, simonkolleite appears to be formed under low chloride content which is different from results obtained by Almeyda E. and al. [7,8].

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The paper aims to update the corrosion database and compare data with recent researches. As such, the results of outdoor exposure testing for hot dip zinc coatings at two sites, representing a coastal marine and a rural atmosphere, are summarized and discussed in this paper. The differences of corrosion rates, behaviors and corrosion products nature in coastal and rural humid tropical areas are also discussed.

2. Experimental Procedure

2.1 Description of exposure sites and environmental characterization

Locations of the exposure sites are described in Table 1. Nhatrang site is traditionally considered as a coastal marine climate with high airborne salinity; meanwhile, Mytho site is commonly considered as a rural tropical climatic zone with moderately low chlorides and another industrial pollutants concentrations.

The data of various climatic parameters, airborne salinity and sulfur dioxide contents during testing were recorded and reported. The average temperature, relative humidity and precipitation values were calculated from daily measurements by common meteorological methods. TOW values were calculated by empirical equation proposed by

Table 1 Locations of testing sites

Parameter / Site	Mytho	Nhatrang
Latitude/longitude	10°22'N, 106°24'E	12°12N, 109°12E
Distance from the sea, km	~ 50	0.1
Classification	Rural	Coastal

Le Thi Hong Lien [2], based on linear regression treatment of the data collected from more than 150 meteorological stations during period of 10 years (TOW = -14.09T + 228.63RH -13050 with R^2= 0.93, where T is average air temperature and RH is relative humidity).

The pH of rain water is the average value of daily collection data measured by Jenway 3150 pH meter. The airborne salinity and atmospheric sulfur dioxide contents were determined by standardized wet candle and passive specimen methods respectively.

2.2 Test samples and testing procedure

Three types of hot dip zinc coatings were taken for outdoor exposure testing. The carbon steel substrates with dimension 100x150x1-3 (mm) were prepared and coated. All samples have coating weights of 50 g/m^2 approximately. Three parallel samples of each coating were taken for outdoor exposure and were checked annually during five years of exposure testing. The samples were exposed facing south under an angle 45^o in unsheltered condition.

The sample surfaces were pretreated following common standards before and after testing. Corrosion rates were determined by mass loss method according to ASTM G1.

The surface appearance of samples was observed visually and recorded by scanner images. The surface morphology was detected by metallographic method by Leica 2500 Microscope with X200 magnification. Crystalline phases of corrosion products were identified by XRD method with Brucker D8 Advance X-ray Diffractometer

3. Results and Discussion

3.1 Corrosion Rate and Corrosivity of the Atmosphere

Environmental characteristics of the sites and the corrosion losses of zinc samples after five years of testing are presented in Table 2 and Table 3.

At first glance, both environments can be classified according to ISO 9223 as τ_4 category according to TOW criteria falls predominantly between 2500 ÷ 5500 h. These values were changed from 4768 h to 5415 h for Nhatrang

Table 2 Environmental Characteristics and Corrosion Loss of Zinc at Nhatrang Test Site (Coastal Conditions)

Test Year	Environmental Characteristics							Corrosion loss (g/m^2)
	Temperature (°C)	Relative humidity (%)	TOW (hours)	Precipitation (mm)	pH of rain water	Salinity (mg/m^2.d)	Sulfur dioxide (μg/m^3)	
0.5	26.2	79.9	4851	186.4	5.9	58.0	0.85	22.39
1	27.0	79.6	4768	819.4	5.9	79.31	0.85	21.65
2	26.5	80.3	4935	1902	6.1	56.18	< 1.0	42.32
3	24.9	82.3	5415	2073	6.3	41.93	< 1.0	45.77
4	27.3	81.1	5107	940.7	5.9	39.45	< 1.0	35.98
5	27.0	78.8	4585	1031	5.8	68.43	< 1.0	43.76

Table 3 Environmental Characteristics and Corrosion Loss of Zinc at Mytho Test Site (Rural Conditions)

Test Year	Environmental Characteristics							Corrosion loss (g/m^2)
	Temperature (°C)	Relative humidity (%)	TOW (hours)	Precipitation (mm)	pH of rain water	Salinity (mg/m^2.d)	Sulfur dioxide (μg/m^3)	
0.5	26.5	81.6	5233	350.5	5.1	12.0	5.4	2.470
1	26.9	82.6	5455	1510	5.6	17.4	5.2	3.668
2	26.8	81.7	5251	1522	5.5	12	5.2	9.066
3	26.9	80.8	5044	1572	5.7	10.1	5.3	-
4	27.2	81.1	5108	1654	5.9	11.8	4.3	12.08
5	26.6	83.3	5620	1616	5.6	13.2	4.2	15.65

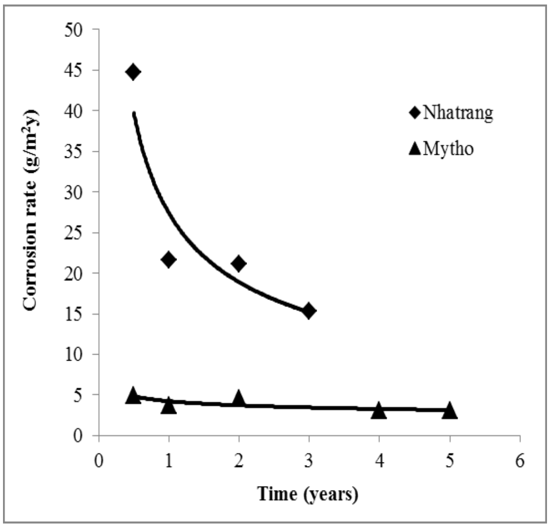


Fig. 1 Time dependence of corrosion rate for zinc coatings.

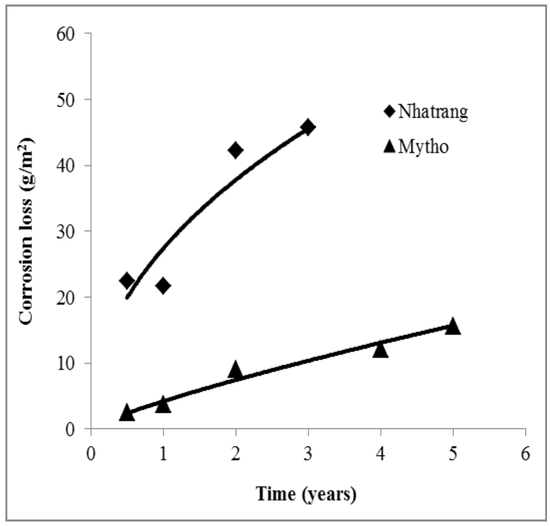


Fig. 2 Time dependence of mass loss for zinc coatings.

site and from 5044 h to 5620 h for Mytho site (an exception is the value 5620 h at Mytho, was insignificantly higher than τ_4 top limit 5500 h). Nhatrang site is characterized by very high airborne salinity ranging from 39.45 to 79.31 mg/m^2.d (S_2 class by ISO 9223) due to its proximity to the sea. Meanwhile, the airborne salinity in Mytho site is 20.0 mg/m^2.d (S_1 class by ISO 9223). Both sites appeared to be low polluted areas with weak to neutral pH values of rain water and very low sulfur dioxide concentrations (P_0 class with < 1.0 μg/m^3).

The corrosion losses of Nhatang specimen had high values. After the first year of exposure, the mass loss reached a significant value of 21.65 g/m^2 and showed increasing tendency while exposure period. The red rust of specimen was found at the edge side in three years, which explains the exceeding initial coating weigh of zinc (50g/m^2). The corrosion loss amount of steel substrate is clearly included in the total weight loss. Therefore, the interpretation of corrosion loss weight depending on the exposure time is limited in three years.

Another situation has been revealed for zinc corrosion mass loss in Mytho rural conditions. After first year of exposure testing, this value was about six times lower in comparison to those exposed in Nhatrang site (3.668 to 21.65 g/m^2) and steadily increased from year to year. The predominant cause can be attributed to small chlorides deposition on the samples surface from airborne salinity, because other characteristics such as average air temperature, relative humidity, TOW, precipitation, pH of rain water and sulfur dioxide content, were approximately similar to Nhatrang coastal conditions.

Time dependence of corrosion rate and mass loss for the coatings are presented in Fig. 1 and Fig. 2. From the Fig. 2, that the dependence of mass loss on exposure time shows that the corrosion process of zinc coatings mostly obeys the law of power model $M = At^n$ with the values of *A, t* and *n* given in Table 4.

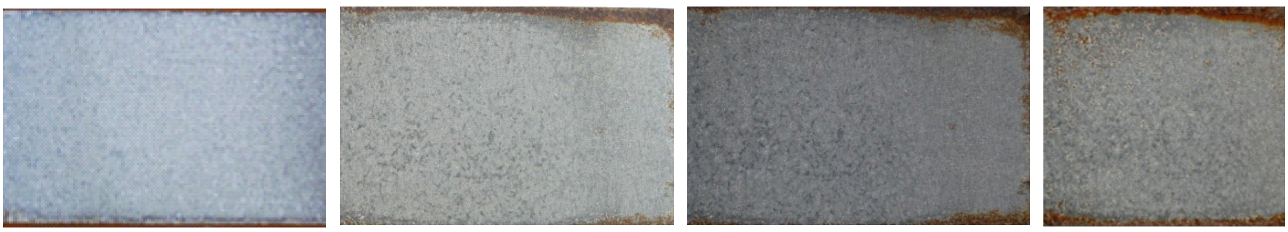
The values n < 0.5 at Nhatrang exposure site indicate that the diffusion process of the aggressive agents from environment decreases with time due to some protective abilities of the corrosion products. Meanwhile, n > 0.5 values at Mytho site indicate that due to the porous corrosion product layers, the environmental agents are easy to penetrate to the substrate. Similar findings have been revealed by Benarie M. [9] and Feliu S. [10]. Corrosion of zinc coating has been effectively retarded by the corrosion products formed on the surface during the exposure as proven by many authors [11].

Table 4 The fitted *A, n* values of model $M = At^n$ for zinc coatings

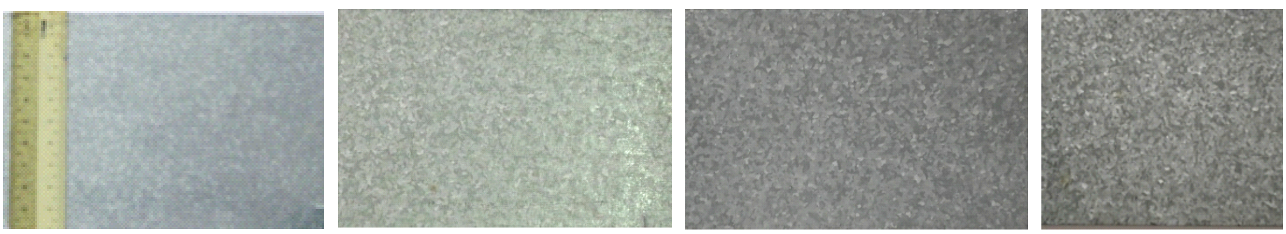
Site	A	n	R^2
Nhatrang	27.41	0.46	0.83
Mytho	4.23	0.81	0.97

Table 5 Description of surface appearance in Nhatrang atmosphere after exposure

Site	Time	Appearance
Nhatrang	After 3rd year	Grey corrosion products on coating. Surface is roughly corroded forming a group of grey spots throughout the sample surface. Brown corrosion appeared on the edges
	After 4th year	Grey corrosion products on coating. Surface is roughly corroded forming a group of grey spots throughout the sample surface. More brown corrosion appeared on the edges
	After 5th year	Surface became bared with thin white zinc oxide layer. Severe brown corrosion on surface edges, especially on bottom area of the coatings
Mytho	After 3rd year	White coating surface remained in good conditions. Slight corrosion was detected on surface
	After 4th year	Grey corrosion products were revealed on coating surface. No brown corrosion has been detected
	After 5th year	Grey corrosion products widely distributed on coating surface. No brown corrosion has been detected

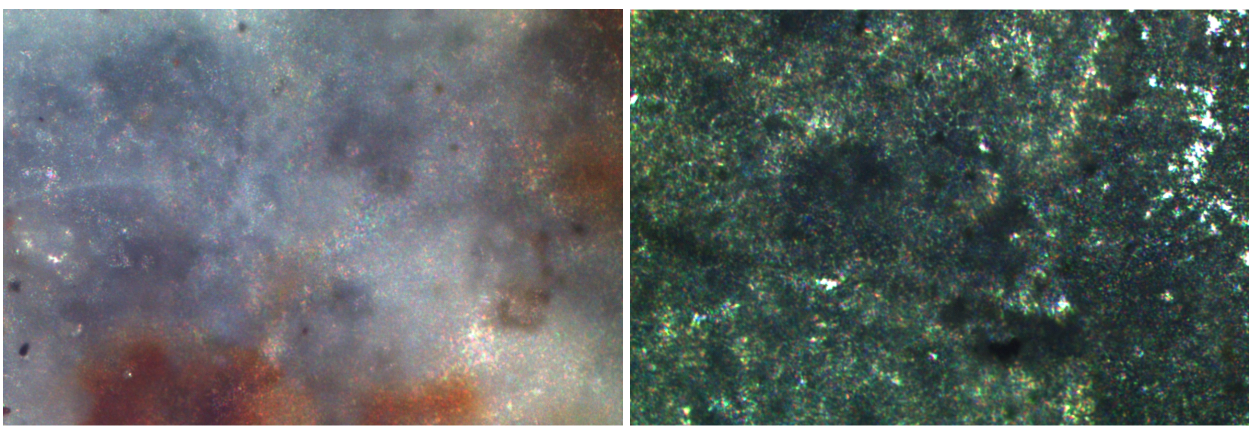


Nhatrang



Mytho

Fig. 3 Surface appearance of the tested samples after first, third, fourth and fifth year of exposure.



Nhatrang *Mytho*

Fig. 4 Metallographic images of the tested samples after fifth year of exposure.

3.2 Surface Appearance and Corrosion Products

Surface appearance of the zinc coatings, exposed in Nhatrang and Mytho conditions are described in Table 5 and presented in Fig. 3. The samples images from

Nhatrang site show visible influence of marine climate on the corrosion behavior of the coatings after five years of outdoor exposure testing. The signs of brown steel substrate corrosion were revealed after third year of testing. These behaviors are very similar to the results reported by the authors [2] and [3] for zinc. Meanwhile, comparative results for surface appearance of the zinc coatings exposed in Mytho conditions show much better protective quality after five years of outdoor exposure test. No brown corrosion signs were detected for all tested samples.

More detailed pictures for the tested samples after fifth year of exposure were presented in Fig. 4 taken by metal-

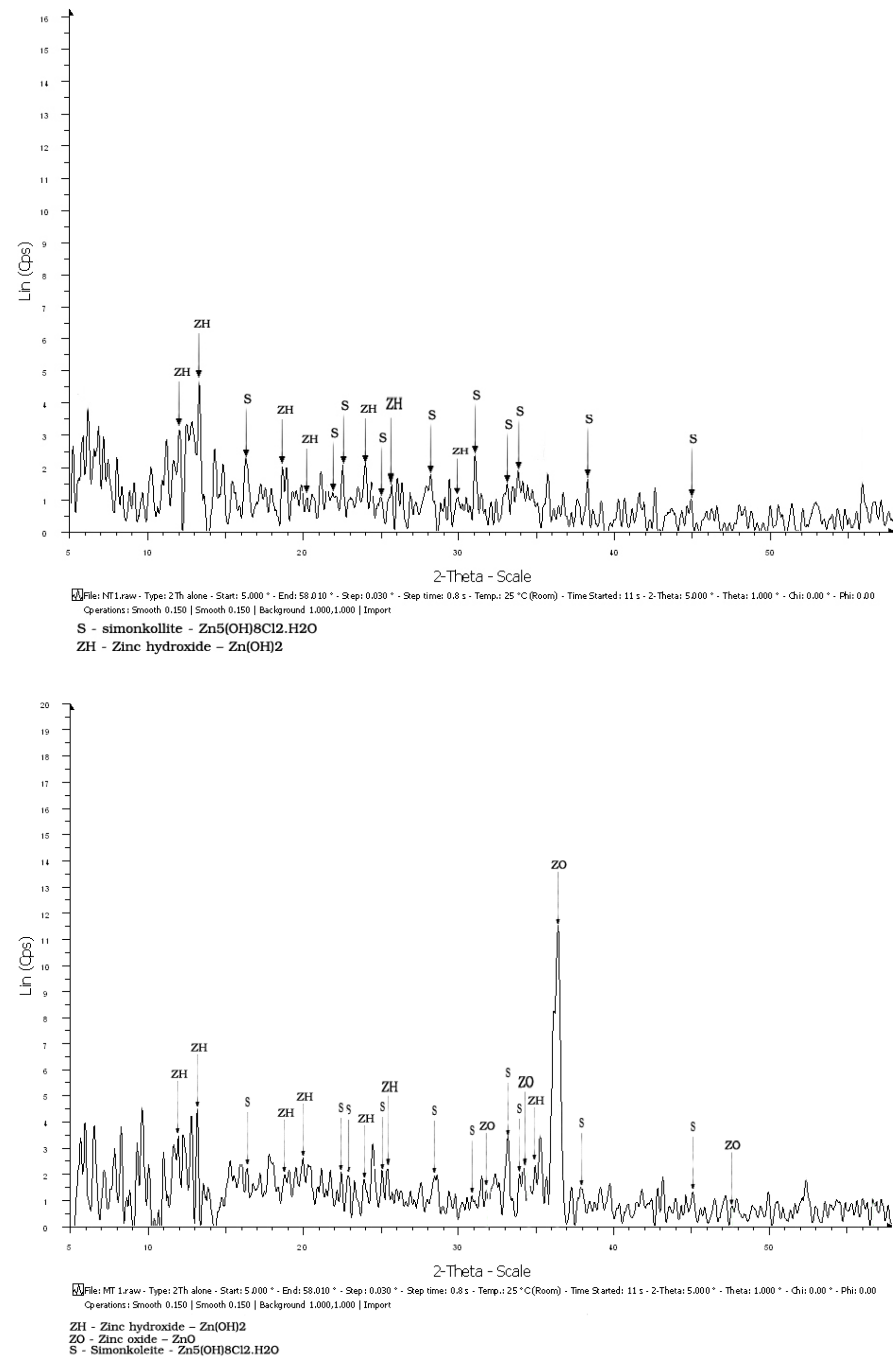


Fig. 5 XRD diagram of the samples after five years of exposure testing. (upper: Nhatrang; lower:Mytho)

Table 6 The crystal phases in corrosion products

Materials	Crystal phases in corrosion products	
	Nhatrang coastal	Mytho rural
Zinc coating	Simonkolleitte, Zinc hydroxide, maghemite, rokuehnite	Zinc hydroxide, zincite, simokolleite

lographic method. Very clear deteriorations are noticed on coating surface with bared exposed steel substrate for sample tested in Nhatrang site.

Reasons for color changes at the surface are due to complicated process of corrosion product transformation during exposure period. Different crystal or amorphous phases of these products forming on the specimen surfaces would be very specific indicators for corrosive atmospheres (Fig. 5).

Influences of airborne salinity and other environmental characteristics are more clearly shown considering the chemical composition of corrosion products in Table 6 after five years of exposure. Some conclusions can be drawn from analysing the crystal phases of specimens exposed at different sites of Nhatrang and Mytho.

Table 6 shows that the main compounds are zincite - ZnO, zinc hydroxide - $Zn(OH)_2$, zinc hydroxychloride - $Zn_5(OH)_8Cl_2.H_2O$ in corrosion products of the samples exposed at Mytho site. Among them the stable phase such as zinc hydroxychloride- $Zn_5(OH)_8Cl_2.H_2O$ was identified early on samples exposed in coastal areas, which could be attributed to the high air humidity favouring the formation of this phase that contributes to protectiveness of corrosion products on zinc coatings. At Nhatrang site, some iron compounds such as maghemite, rokuehnite were detected in coating surface due to substrate corrosion.

Simonkolleite is a major crystal phase in zinc corrosion product formed in marine conditions while zinc hydroxide is very popular for urban environments. Simonkolleite has also been detected for the samples exposed at Mytho rural site, where airborne salinity is lower than 20 mg/m^2.d. According to Morcillo M. et al., this compound can be detected in corrosion products of zinc at airborne salinity higher than this value [12]. It is specific case for the humid tropical conditions, when zinc hydroxychloride formation occurs at both rural and coastal testing sites. As previously informed, simonkolleite presents on tested zinc only at sites with higher 55 mg/m^2.d of chloride ions [7, 8].

4. Conclusion

● Corrosion rates of hot dip zinc coatings at Nhatrang coastal site are about six times higher than the values obtained for Mytho rural atmosphere. Airborne salinity is a main factor in accelerating corrosion of zinc coatings in Nhatrang conditions.

● The corrosion process obeys an equation of the form $M=At^n$, where M is the loss of metal and t is the time of exposure. A and n coefficients are constants which values depend on the environmental characteristics and the physicochemical behavior of the corrosion products respectively.

● Simonkolleitte is a major crystal phase in zinc corrosion product formed in marine conditions. However, it can also appear when airborne salinity is under 20 mg/m^2.d in specific humid tropical conditions.

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