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Atmospheric corrosion of hot dip galvanized structural steel exposed to the tropical climate of Thailand

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Abstract

Hot dip galvanized steels were tested in the atmospheric tropical climate environments of Thailand for 12 month from March 2021 to March 2022. Three locations were studied, i.e. a rural area at Saraburi in the central part, an industrial area at Chonburi in the eastern part, and a coastal/urban area at Songkhla in the southern part of Thailand. The thickness loss of the galvanized steel samples was measured by the weight loss method. Types of corrosion products observed on the samples were zincite, wulfingite, hydrozincite, and simonkolleite. All of them were found on the sample at Songkhla. Three of them, except simonkolleite, were found on the sample at Chonburi. Only two of them, zincite and wulfingite were found on the sample at Saraburi. In addition, pit corrosion was found to be severe on the sample at Songkhla in the shape of a meteor crater.

1. Introduction

Hot dip galvanized steel is made of carbon steel that is coated with zinc. Prior to the galvanization, carbon steel is pickled with caustic cleaning chemicals, dipped in a flux solution, and bathed in molten zinc. During the bathing process, zinc is bonded thermodynamically to the carbon steel surface and the steel becomes hot dip galvanized steel. It is used mainly for outdoor steel structures such as light poles, road view signboards, and transmission towers.

Atmospheric corrosion is the degradation of metal surfaces due to the electrochemical reactions between environments and itself in the presence of a thin-film electrolyte. Through the reactions, the metal loses its thickness as it transforms into corrosion products. For galvanized steel, types of corrosion products were reported differently worldwide. Usually, they were zincite, zinc hydroxide, hydrozincite, simonkolleite, and godaite [1,2,3]. Depending on the characteristics of environments, their formation depends on factors such as wetness, temperature, humidity, and deposition rates of gases and ions such as SO_2, CO_2, Cl^-, etc.

Thailand is located in the tropical climate zone near the equator. Its climate is controlled by two seasonal monsoons: the northeast and the southwest monsoon. The northeast monsoon is active between November and January while the southwest monsoon is active between May and October. These major winds control the temperature and rainfall of the country in their directions of passing. The northeast monsoon brings cold air from China to parts of Thailand that are located above the Gulf of Thailand while it brings moisture from the gulf to precipitate in the southern part of Thailand. In the case of the southwest monsoon, it brings hot air and moisture from the Indian Ocean and Andaman Sea to precipitate in the southern part of Thailand and it brings hot air and moisture from the Gulf of Thailand to precipitate in parts of Thailand that are located above the gulf. The unique feature of monsoons makes Thailand's climate unique from the others.

In Thailand, hot dip galvanization is a popular method for protecting structural carbon steel from atmospheric corrosion. Nevertheless, not much research has been done on its performance and corrosion behavior in the country except for the official corrosion map website application introduced by the National Metal and Materials Technology Center (MTEC) [4]. Rather, the majority of the research had been done on carbon steel and weathering steel [5,6,7,8]. Thus, there is still a lack of knowledge about galvanized steel in the country. During March 2021 and March 2022, an atmospheric exposure test was conducted in 19 different locations. The test program covered the corrosion rates of carbon steel, painted steel, and hot dip galvanized steel. For galvanized steel, the corrosion rate data had already been delivered in a thesis [9]. However, it still lacked data on its corrosion products and micro surface appearances. This research paper focused on these two aspects as they might affect the steel service life. Corroded galvanized steel samples from Saraburi, Chonburi, and Songkhla stations were used in this study as environmental parameters could be monitored at these stations. Results from this research are useful for the durability design of hot dip galvanized steel structures in the tropical climate of Thailand.

2. Materials and methods

Galvanized steel samples of 100 mm × 150 mm × 4.5 mm with zinc coating, having a purity of 99.995% from SHG-grade zinc, were atmospherically exposed in Saraburi, Chonburi, and Songkhla provinces in Thailand from March 2021 to March 2022. Their base steel was carbon structural steel grade SM490A with its chemical composition listed in Table 1 from the spark emission spectroscopy. Their galvanized coating thickness was measured between 90 µm to 100 µm. At Saraburi station, the test was conducted on the ground in a private residential area near rice fields (rural area) in the central part of Thailand. At Chonburi station, the test was conducted on the ground at a galvanizing factory in the WHA industrial estate (industrial area) in the eastern part of Thailand. Lastly, at Songkhla station, the test was conducted on top of a building at Rajamangala University in the city of Songkhla, near Samila Beach (urban/coastal area) in the southern part of Thailand. The distances from the sea (the Gulf of Thailand) to each station are 110 km, 18 km, and 0.3 km for Saraburi, Chonburi, and Songkhla, respectively. Temperature, relative humidity, and rainfall at the stations were monitored monthly using a weather station. The Cl^- dry deposition rate and SO_2 dry deposition rate were monitored every 6 month using the dry gauze and the lead cylinder according to ISO 9225. The surface of the galvanized steel samples was prepared according to ASTM G1. Before the exposure test, the samples were dry polished with silicon carbide paper number 120 followed by 600, rinsed with distilled water followed by acetone, dried by a blower, weighed, and put inside a desiccator. During the exposure test, the samples were mounted on the 30° exposure racks that were set facing toward the closest sea direction. Figure 1 shows examples of the test setup at the three stations together with the weather station, dry gauze, and lead cylinder. Environmental conditions at the stations during the exposure test are shown in Figure 2. In the figure, the Cl^- values from the dry gauze were converted into the standard Cl^- values by a multiplication factor of 2.4 [10]. Moreover, the SO_2 value at Saraburi was missing for the second 6 month due to technical difficulties. After 3, 6, and 12 month, four samples were collected back from each station and sent to the laboratory for analysis. For each period, in each location, three collected samples were used immediately for the thickness loss analysis, and one collected sample was stored separately for later corrosion product and surface analysis. For thickness loss analysis, the thickness loss of the samples was calculated by the weight loss method. For corrosion products and surface analysis, the corrosion products were characterized using XRD technique with BRUKER diffractometer, and the micro surface appearances were studied using SEM and EDS with JEOL scanning electron microscope and Oxford Instrument energy dispersive spectroscopy.

3. Results and discussion

3.1 Corrosion

Figure 3 shows examples of the surface appearances of the galvanized steel sample before and after 3, 6, and 12 month for the exposure tests at Saraburi, Chonburi, and Songkhla, respectively. Before the exposure tests, the galvanized steel was bright and shiny. After the exposure test, the galvanized steel was blunt and dull. Corrosion products were visible in local areas rather than the entire surface. The 12th-month sample at Saraburi shows a darker surface appearance compared to the other two stations. This is due to dark depositions that covered the surface of the sample which can be removed mechanically. They possibly came from the seasonal burning of rice fields from local farmers near the station.

Figure 1. the test setup at Saraburi a), Chonburi b), and Songkhla c) together with the weather station d), dry gauze e) and lead cylinder f).

Table 1. Compositions of the base carbon steel as a % by weight.

Base Steel	%C	%Mn	%Cu	%Cr	%Si	%P	%Ni
SM490A	0.1991	1.2525	0.0080	0.0290	0.0105	0.0135	0.0107

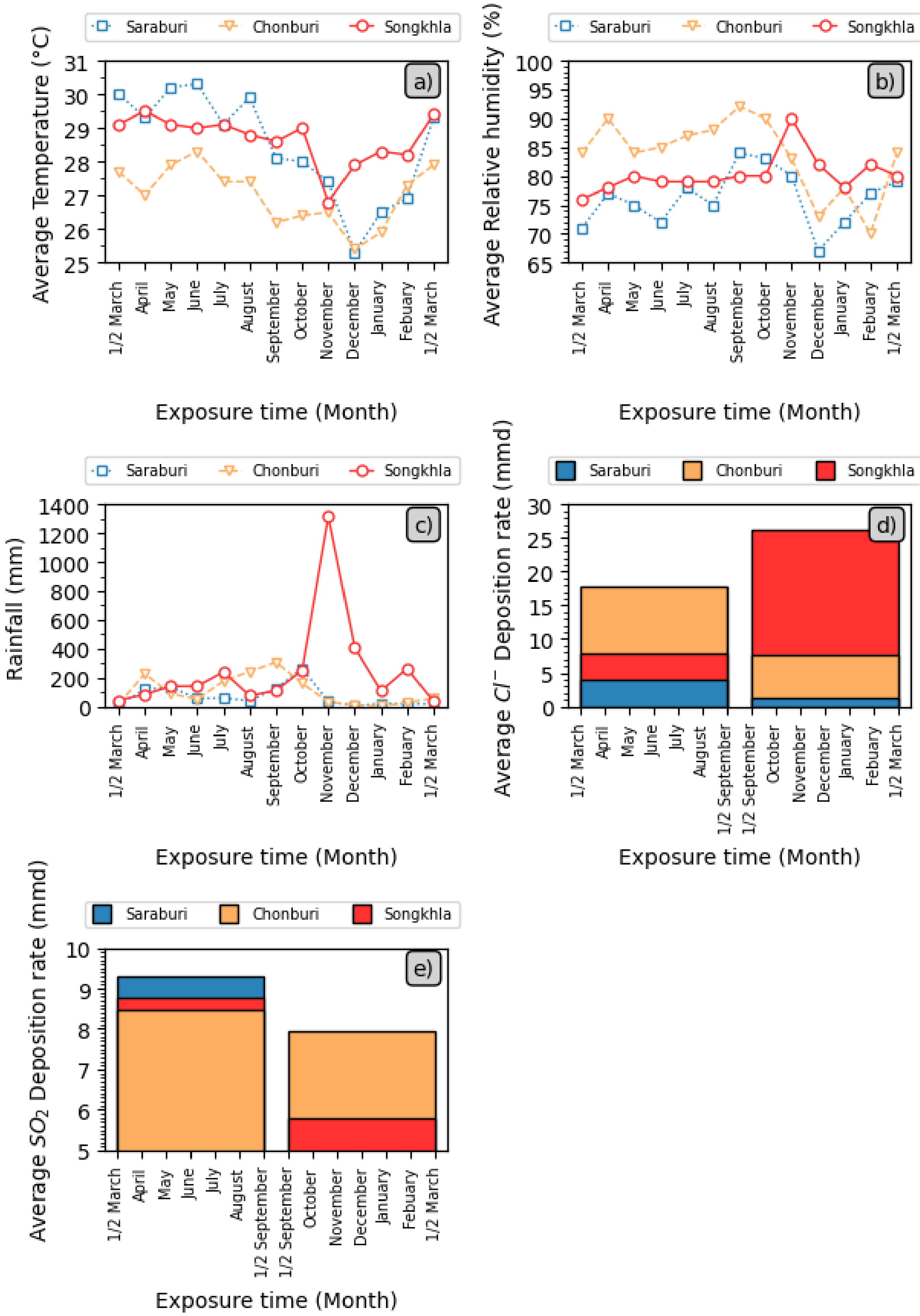

Figure 2. Evironmental conditions at the stations; Average temperature (a), Average relative humidity (b), Rainfall (c), Average Cl^- deposition rate (d), and Average SO_2 deposition rate (e).

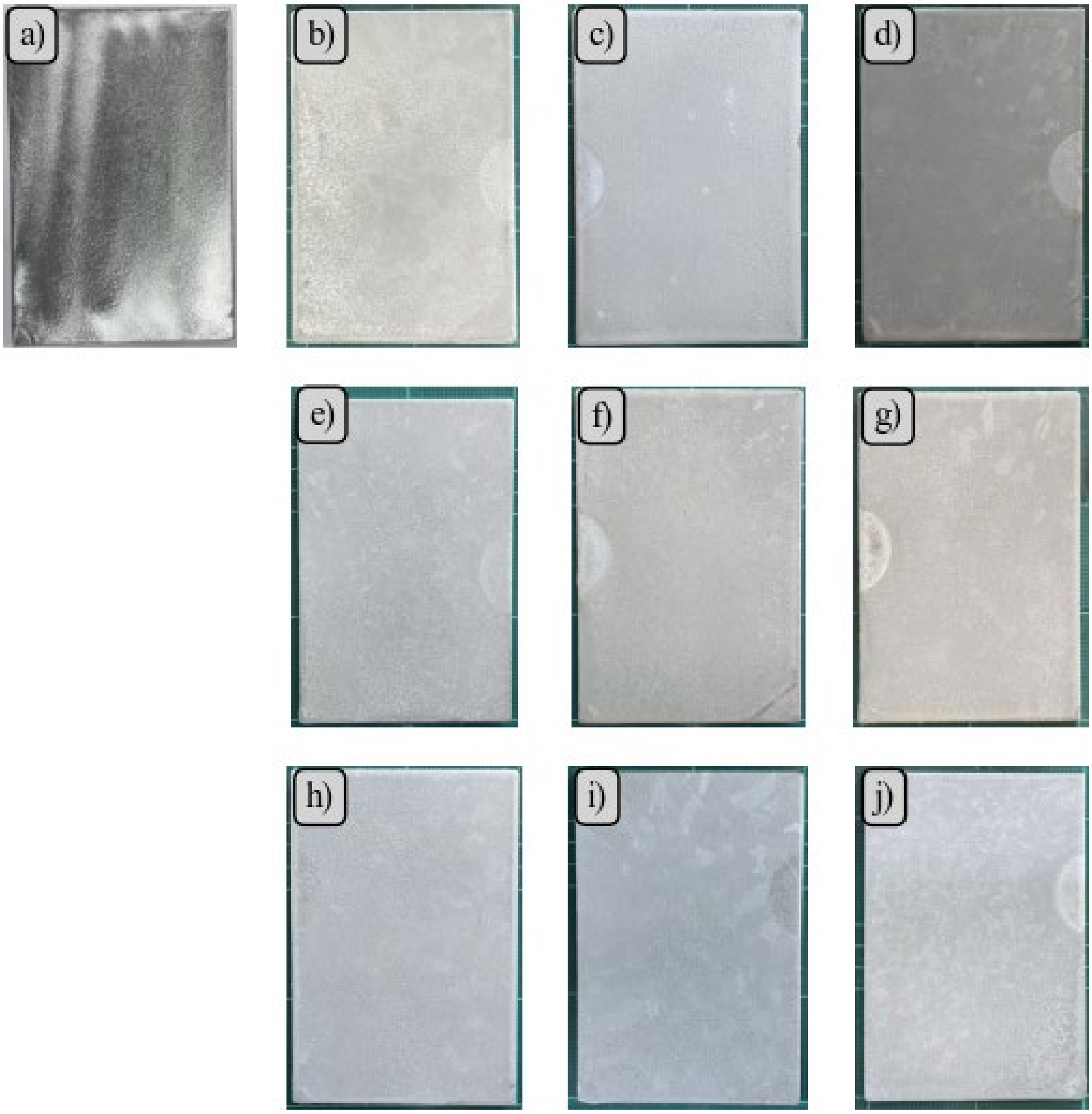

Figure 3. Surface appearances of galvanized steel samples; (a) before the exposure test, (b) to (d) after 3, 6, and 12 month of exposure at Saraburi, (e) to (g) after 3, 6, and 12 month of exposure at Chonburi, and (h) to (j) after 3, 6, and 12 month of exposure at Songkhla.

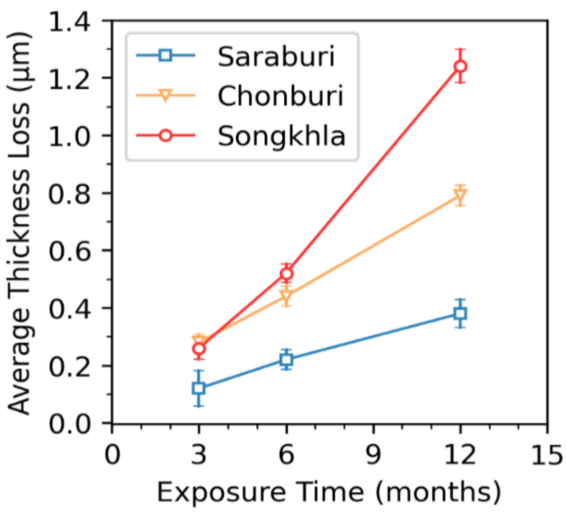

Figure 4. Average thickness loss of the galvanized steel samples exposed at Saraburi, Chonburi, and Songkhla.

Prior to evaluating the thickness loss, the corroded samples were pickled using chromic acid at 80°C according to ISO 8407. After the pickling, they were rinsed with distilled water followed by acetone, dried by a blower, and weighed. These processes were repeated several times until the weight loss became stable. Thickness loss in micron of the tested galvanized steel can be calculated by the following Equation:

$$C = \frac{W}{\rho A} \times 10^4 \quad (1)$$

where C is the thickness loss (μm), W is the sample weight loss (g), ρ is the density of zinc (7.14 g·cm^{-3}), and A is the sample exposure surface area (cm^2). The results are shown in Figure 4. It can be seen that Songkhla has the highest thickness loss, followed by Chonburi and then Saraburi. This is because the rainfall and Cl^-deposition rate were found to be the highest at Songkhla and the lowest at Saraburi, where Chonburi was in the middle as shown in Table 2. The thickness loss at Chonburi and Saraburi showed a similar pattern compared to

Songkhla, which is related to the country's seasonal monsoon. Both stations received the maximum amount of rainfall from July to October, which corresponds to the 4th to 7th month of the exposure test. In this period, the southwest monsoon carried moisture from the Gulf of Thailand to precipitate on lands in the central, eastern, and potentially northeastern parts of Thailand. Following this interval, the stations remained dry most of the time until March, which corresponds to the 12th month of the exposure test. During this dry period, the thickness loss at the stations increased at a slow rate. In the case of Songkhla, the station received the maximum amount of rainfall from October to February, which corresponds to the 7th to 11th month of the exposure test. In this period, the northeast monsoon carried moisture from the Gulf of Thailand to precipitate on lands in the southern part of Thailand, causing the thickness loss at the station to increase at a drastic rate. Furthermore, the monsoons possibly brought more airborne salt to the stations as the Cl^- deposition rates were recorded higher during the first six months compared to the second six months at Chonburi and Saraburi, while the rates were recorded higher during the second six months compared to the first six months at Songkhla. Such an observation where rainfall is a contributor to thickness loss of the galvanized steel was reported in Mexico due to the zinc runoff effect [11]. Zinc ions are released and dispersed into the environment from the corrosion product film and the coating surface bulk. Especially during the first rain event after some dry periods, the first flush, the ions get released significantly [11,12]. Velva et al also reported that 63% to 87% of the total corrosion weight loss of the galvanized steel was due to this effect in Mexico [13]. In this research, SO_2 was found to be insignificantly related to thickness loss. Normally, SO_2 is the cause of acid rain in the environment. However, it was found in particular that acid rain in Thailand is not likely to occur due to the neutralizing effect of the NH_4:SO_4 ratio found in the rainwater [14]. Temperature and relative humidity were also observed to be insignificant to the thickness loss. Comparing the 12th-month thickness loss result of each station in this research, which is the first-year corrosion rate to the first-year corrosion rate predicted by the existing corrosion map introduced by MTEC, the map provides 50% greater corrosion magnitude at Saraburi and Chonburi and 80% greater corrosion magnitude at Songkhla [4]. Despite the large differences in the corrosion magnitude, the map still provides an agreeable result based on two reasons. The first reason is primarily due to large historical data of environmental parameters that are averaged and used as a source for the mathematical model to predict corrosion. It is possible that environmental parameters such as rainfall, temperature, and relative humidity might deviate significantly from the average during the exposure test period of this research. The second reason is the elevation related to the chloride deposition rate. This can be seen in the case of the exposure test at Songkhla. The test was conducted on top of a building later than on the ground near the beach. It is possibly due to the fact that the chloride deposition rate is much greater on the ground compared to on top of a building. Sea salt aerosol particles, SSA cannot possibly travel much high from the ground elevation. Bongochgetsakul *et al.* report this behavior of SSA using water-sensitive paper. Particle size and particle distribution are larger and denser at 1 m from the ground compared to 4 m at a sand beach [15].

The thickness loss of metals over time is usually described by the logarithmic Equation as follows:

$$\log C = \log A + B \log t \;\text{ or }\; C = At^B \tag{1}$$

where C is the thickness loss (μm), t is time (year), A is constant and B is the diffusion coefficient. The diffusion coefficient can refer to two meanings: the protectiveness of corrosion products on the metal surface or the aggressiveness of the atmosphere on the metal surface. For a metal that has a thick film of corrosion products characteristic like carbon steel, it usually refers to the protectiveness of those corrosion products to the steel. On the other hand, for metals that have a thin film of corrosion products characteristic like galvanized steel, it usually refers to the aggressiveness of the atmosphere to the steel. Table 3. shows a summary of the values A and B, which were determined using a linear regression between thickness loss and exposure time in log-log coordinates. Typically, the B value is around 0.55 for carbon steel and 0.84 for zinc and galvanized steel [16]. Additionally, the B values of 0.5 to 0.8 were observed for the galvanized steel in the rural and coastal areas, respectively in Vietnam, which has the same tropical climate as Thailand [2]. From the findings, the corrosion behavior of the galvanized steels was found to be normal at Saraburi and Chonburi and severe at Songkhla. Since the B value is greater than 1.0 at Songkhla, it indicates that the thickness loss is expected to increase in the acceleration rather than linear manner over time, which highly shortens the galvanized steel service life.

Table 2. Environmental conditions of the stations recorded from March 2021 to March 2022.

Abbreviations: Avg. = average, RH = relative humidity, mmd = mg/(m^2·day)

Exposure stations	Avg. Temperature (°C)	Avg. RH (%)	Rainfall (mm/year)	Avg. Cl (mmd)	Avg. SO_2 (mmd)
Saraburi	28.5	76.2	927	2.64	9.3
Chonburi	27.0	83.7	1813	12.72	8.5
Songkhla	28.7	80.2	3288	16.80	8.8

Table 3. Calculated A and B values for galvanized steel samples at Saraburi, Chonburi, and Songkhla.

Exposure stations	*A* Constant	*B* Coefficient
Saraburi	0.38	0.83
Chonburi	0.77	0.75
Songkhla	1.20	1.11

3.2 Corrosion products and surface appearance

Figure 5. shows the characterization of corrosion products on the samples at Saraburi, Chonburi, and Songkhla. Because the samples were too big to fit inside the equipment, they were cut into smaller samples of 20 mm × 20 mm from the center of the original corroded samples. Before cutting, they were covered with a plastic wrapper to prevent dust contamination. The figure only shows the 12th-month results, as it was unable to conduct the test in the 3rd month and 6th month because the samples still had a low amount of corrosion products. Due to the lower amount of corrosion products, their peak sets were only found near the base of the original zinc peaks, which are definitely from the zinc coating bulk itself. Also, a single unknown peak set was detected on the sample at Chonburi. Some of its peaks might be located inside other corrosion product peaks, which made the total peak set unidentifiable. Beside the unidentifiable peak set, peak sets of ZnO (Zincite), ε-$Zn(OH)_2$ (Wulfingite), $Zn_5(CO)_3(OH)_6$ (Hydrozincite), and $Zn_5(OH)_8(Cl)_2{\cdot}H_2O$ (Simonkolleite) were detected on the samples. The summary is presented in Table 4. These corrosion products appear to be common for the galvanized steel exposed in tropical climate countries, in which they are known for hot and humid features [2,3]. Based on the results, the progression of corrosion products together with environmental parameters is expected as Zincite → Wulfingite → Hydrozincite, or Simonkolleite. Zincite is likely to be the initial corrosion product that develops on the samples as it requires only zinc and some oxygen in the atmosphere to be formed. When the oxide is exposed to moisture, it can transform into several types of $Zn(OH)_2$ (Zinc Hydroxide). In this study, it was found to be ε-$Zn(OH)_2$. The hydroxide is later used as a seed crystal to form other hydrozincite and simonkolleite as follows [17]:

$$Zn(OH)_{2(S)}+4Zn^{2+}+4(OH^{-})+2\left(CO_3^{2-}\right)\rightarrow Zn_5(CO_3)_2(OH)_6 \quad (3)$$

$$Zn(OH)_{2(S)}+4Zn^{2+}+6(OH^{-})+2\left(Cl^{2-}\right)\rightarrow Zn_5(OH_8)Cl_2{\cdot}H_2O \quad (4)$$

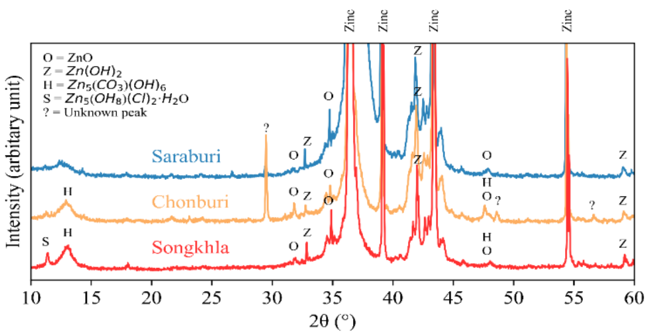

Figure 5. X-ray diffractogram of corrosion products on the galvanized steel samples exposed at Saraburi, Chonburi, and Songkhla for 12 month..

Hydrozincite is created in the presence of carbonic acid. As carbon dioxide gas diffuses into moisture on the galvanized steel surface, it forms the acid and reacts with the previously formed hydroxide to create hydrozincite. Likewise, simonkolleite is created in the high chloride environment. As airborne salt is dissolved in the moisture on the galvanized steel surface, chloride ions react with the previously formed hydroxide to create simonkolleite. In marine environments, simonkolleite predominates the surface of galvanized steel. It forms an island of platelets with a lamellar shape. Once it experiences rainfall, it can reshape into globular morphology [18]. In addition, hydrozincite and simonkolleite are popular in coastal areas as they require a relative humidity of 85% to 100% to be created [19]. Due to the similarity in the structure between hydrozincite and simonkolleite, hydrozincite can also transform into simonkolleite through the replacement of chloride ions in its lactic [17].

Figure 6 shows the representatives of SEM images of the surfaces of the sample at Saraburi, Chonburi, and Songkhla together with EDS results in Table 5. The samples used were another cut of 20 mm × 20 mm samples near the center of the original samples used for XRD experiments. Before cutting, the corroded samples were also covered with a plastic wrapper. According to the result, the sample exposed at Songkhla is the rustiest, followed by Chonburi and Saraburi. Conversely, the sample at Chonburi is the dirtiest as it is covered with a lot of pollutant particles. In the figure, EDS revealed the presence of the Fe element in them. Presumably, they are waste products released from factories and deposited on the sample surface. Dark patches were observed on the sample at Chonburi and Songkhla. EDS usually detects them containing high percentages of C compared to the general area. These areas have the potential to be the region of hydrozincite. Furthermore, XRD only detected hydrozincite as the only carbonate corrosion product on the samples. However, those areas are non-uniform, possibly because carbon dioxide gas diffused into droplet-shaped moisture. At Songkhla, the sample was heavily pitted. Figure 7 provides a closer look at some pits on the sample surface. Judging from SEM images, they resemble a meteor crater of 100 µm in diameter. The structure of the pits was observed to be swelling on top of the coating surface first and later on sinking down in the middle and creating a meteor crater shape. In this research, the pit depth was not measured. Furthermore, they contained some spike ball structures in them. According to EDS, these spike ball structures are more likely to be pure zinc than a corrosion product due to a very high percentage of Zn. This evidence confirms that the pits are actually deep into the zinc coating surface rather than stopping at the corrosion product layer. However, the mechanism of the pit corrosion could not be discussed in this research as samples were not monitored often. Based on the result, the galvanized steel at Songkhla will undergo a local failure from the pit corrosion first rather than run out of the zinc coating.

Table 4. Corrosion products found on the galvanized steel samples.

Saraburi	Chonburi	Songkhla
Zincite	Zincite	Zincite
Wulfingite	Wulfingite	Wulfingite
-	Hydrozincite	Hydrozincite
-	-	Simonkolleite

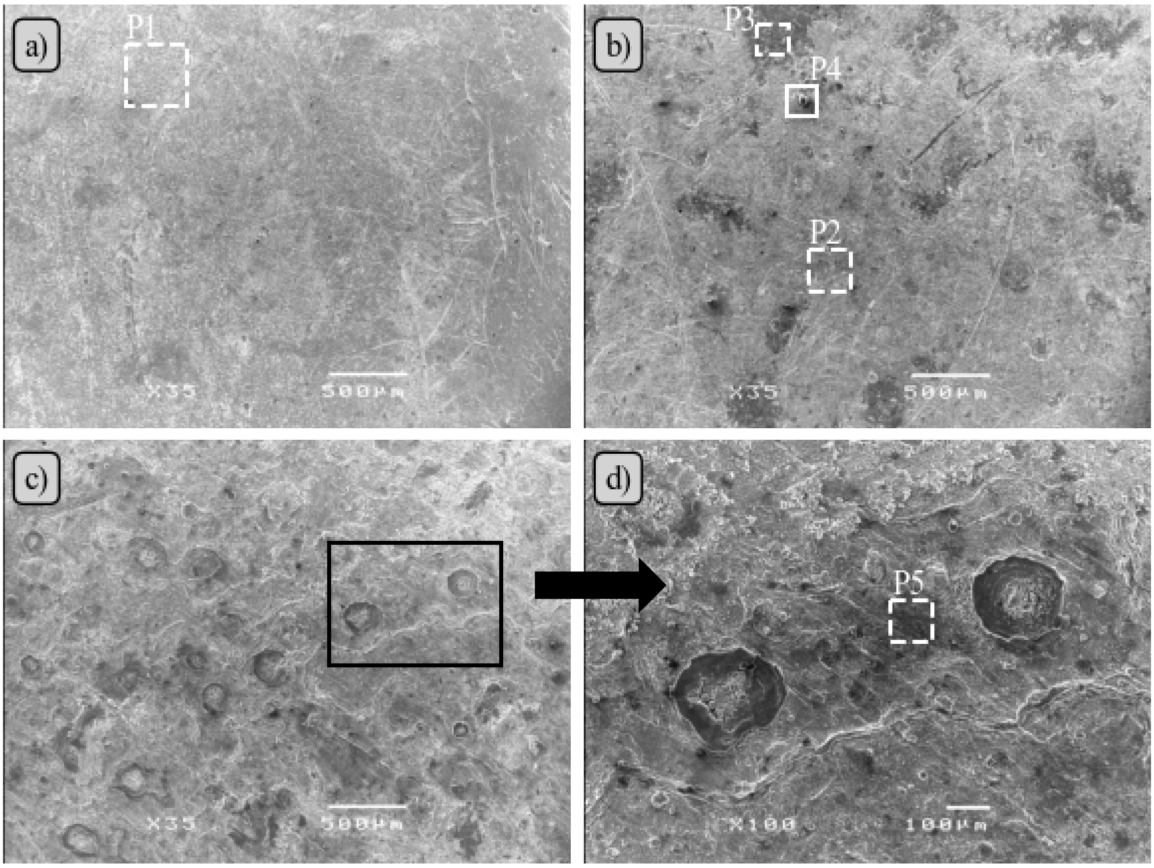

Figure 6. SEM images of surfaces of the galvanized steel samples exposed for 12 month at Saraburi (a), Chonburi, (b), and Songkhla (c), and (d).

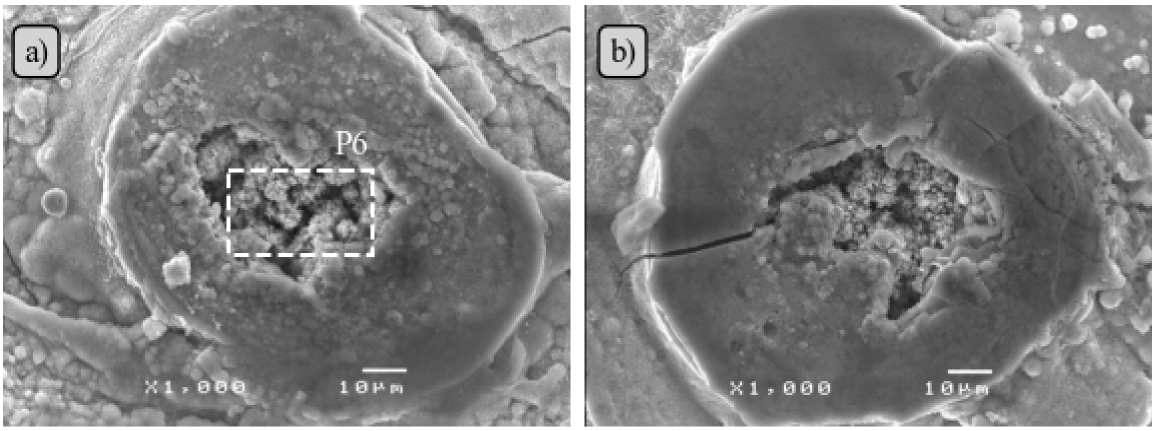

Figure 7. Meteor craters like pits on the surface of the galvanized steel sample exposed at Songkhla for 12 months.

Table 5. Results of EDS as element weight by % on the measurement areas.

Point area	Description	EDS, element weight by %					
		C	O	S	Cl	Zn	Fe
P1	General area	4.34	13.58	0.95	0.46	80.67	-
P2	General area	3.33	13.95	0.29	0.45	81.97	-
P3	Dark patch	23.46	23.32	0.80	0.27	52.15	-
P4	Particle	6.12	13.76	0.28	0.51	70.81	8.52
P5	Dark patch	30.35	12.94	0.39	1.50	54.82	-
P6	Spike balls	0.37	2.91	-	0.17	96.55	-

Table 6. Minimum galvanized coating thickness according to ASTM A123/A123M [20].

Abbreviation: t = Thickness of the base carbon structural steel (mm)

Category	t < 1.6	1.6 ≤ t < 3.2	3.2 ≤ t < 4.8	4.8 ≤ t < 6.4	6.4 ≤ t < 16	≥ 16
Structural shape	45 µm	65 µm	75 µm	75 µm	100 µm	100 µm

Table 7. Theoretical service life of hot dip galvanized steel made of common construction pipe and tube with a wall thickness of 3.2 mm.

Exposure station	Area type	Coating thickness	First-year corrosion rate	Service life
Saraburi	Rural area	75 µm	0.38 $\mu m \cdot year^{-1}$	197 year
Chonburi	Industrial area	75 µm	0.79 $\mu m \cdot year^{-1}$	95 year
Songkhla	Coastal area	75 µm	1.24 $\mu m \cdot year^{-1}$	60 year

3.3 Service life of hot dip galvanized structural steel

The zinc coating thickness of galvanized steel based on the thickness of carbon structural steel can be estimated according to Table 6 according to ASTM A123/A123M [20]. Corrosion of zinc under atmospheric corrosion is usually calculated as a linear behavior over time [21]. This means the service life of the galvanized steel can be obtained by dividing the coating thickness by the first-year corrosion rate. The theoretical service life of hot dip galvanized steel made of common construction pipe and tube with a wall thickness of 3.2 mm at Saraburi, Chonburi, and Songkhla can be calculated in Table 7. The table shows that the galvanized steel can last almost 200 year in Saraburi, 100 year in Chonburi, and 60 year in Songkhla, respectively, before losing all of the coating. This calculation assumes that the corrosion is uniform over the entire exposure surface. Furthermore, the calculation can only be applied to nearby galvanized steel structures not too far from the exposure test site. Nevertheless, it proves that galvanized steel structures might be durable in the tropical climate of Thailand, except for coastal areas, where they need more service life design considerations due to pit corrosion. The galvanized steel structures in this area will likely undergo local failure due to pit corrosion first before losing all of the coating. Therefore, the service life might potentially be shorter than the value calculated. To extend the galvanized steel structure's service life, several solutions can be taken, such as applying additional paint layers on top of the galvanized coating or increasing the thickness of the base carbon structural steel so that it can achieve more coating thickness during the galvanization.

4. Conclusions

Conclusions can be drawn as follows:

1. The thickness loss of galvanized steel was mainly dependent on the rainfall and Cl^- deposition rate in the tropical climate of Thailand. These parameters were affected by the seasonal monsoon of the country.
2. The corrosion products on the galvanized steel samples were zincite, wulfingite, hydrozincite, and simonkolleite. Zincite and wulfingite were found at the three stations. Hydrozincite was found only at Chonburi and Songkhla. Simonkolleite was found only at Songkhla due to the presence of high chloride deposition rates.
3. Pits were observed only at Songkhla. They resembled a meteor crater. Moreover, they contained some spike ball structures, which appeared to be pure zinc.
4. Galvanized steel structures are durable in Thailand, except for the coastal area due to pit corrosion.

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