Synergistic Effect of NaCl and SO₂ on the Initial Atmospheric Corrosion of Zinc Under Wet–Dry Cyclic Conditions

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Abstract

The synergistic effect of NaCl and SO₂ on the atmospheric corrosion of zinc has been studied at equivalent total but different ratios of molar deposition rate under wet–dry cyclic conditions. The results show that the corrosion rates, corrosion morphologies and the composition of the corrosion products are strongly influenced by the molar deposition rate ratio of NaCl and SO₂ (NaCl/SO₂). The corrosivity of NaCl and SO₂ toward zinc increases in order of SO₂ < 1:3 < 3:1 < NaCl < 1:1. The corrosion morphology is patchy corrosion for Group 1:1, while it is pocking corrosion for the other four experimental groups. The corrosion product containing sulfur and chlorine detected on zinc is Gordaite (NaZn₄SO₄(OH)₆Cl·6H₂O), which has quite porous structure and was supposed to cause the patchy corrosion tendency of zinc in Group 1:1. In addition, soluble zinc corrosion products, which can inhibit the atmospheric corrosion process of zinc, were found on zinc samples in Groups 1:3 and SO₂ and connected to the lower corrosion rates of zinc in these two groups.

Keywords Atmospheric corrosion · Zinc · Synergistic effect · Corrosivity · Corrosion morphology · Gordaite

1 Introduction

Zinc is an important structural metal and has been extensively used in many applications, such as buildings, electrical engineering and automobile industry, due to its good corrosion resistance and relatively low price [1–3]. As one of the metals regularly exposed to the indoor and outdoor atmosphere, a significant body of work has been performed to explore the atmospheric corrosion behavior and mechanism on zinc in both field exposures and controlled laboratory environments [4–8]. Besides the strong humidity dependence [9], it is generally agreed that the atmospheric

corrosion of zinc is accelerated by chloride and gaseous pollutants [10–12].

Ocean is one source for chloride in the form of marine aerosols, which is produced by the turbulent ocean states and surf actions and transported inland primarily by coastal winds [13]. Sodium chloride (NaCl) is a main accelerator of zinc atmospheric corrosion. The corrosive nature of NaCl to metal zinc is mainly due to its deliquescence characteristics, which can produce a strong electrolyte film on the surface of zinc. Compared with other common chloride, such as magnesium and calcium chloride (MgCl₂ and CaCl₂), NaCl shows the most corrosive to zinc [14]. However, the atmospheric corrosion of zinc is a complicated process that other factors must be taken into account as well.

Sulfur dioxide (SO₂) is known as a stimulator of the zinc atmospheric corrosion, and the corrosion rate of zinc is related to the concentration of SO₂ in the air [3]. It is widely accepted that the oxidation of SO₂ to produce sulfate ions (SO₄^{2−}) decreases the local pH and therefore increases the corrosion rate of zinc [15]. In addition, the oxidation of SO₂ is enhanced by some gaseous species such as NO₂ and O₃, which have a synergistic effect with SO₂ and can increase the corrosion rate several times [16]. An interesting phenomenon about zinc atmospheric corrosion in the presence of SO₂ is that the corrosion rate was inversely proportion

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to the temperature, and it was attributed to the formation of insoluble zinc hydroxysulfate which slows down the deposition of SO₂ on the surface at higher temperature [10].

Despite NaCl and SO₂, which have well-known corrosive effects toward zinc, are both present in notable amounts in many outdoor environments, only a few laboratory studies have been carried on about the synergistic effect of these two factors. The first systematic laboratory investigation reporting on the effects of SO₂ and NaCl with realistic concentration of SO₂ on zinc was investigated by Sevansson and Johansson [17]. They found that SO₂ could slow down the corrosion rate of zinc somewhat in the presence of moderate to high surface concentration of NaCl, which was attributed to the formation of NaZn₄SO₄(OH)₆Cl·6H₂O. The regularities of initial atmospheric corrosion of zinc in the presence of different amount of NaCl deposition with and without SO₂ were investigated by Qu et al. [2] using quartz crystal microbalance (QCM). They found that the combined effect of NaCl and SO₂ on the corrosion of zinc was greater than that caused by each single component. And it was suggested to be caused by the acidification of the surface electrolyte caused by SO₂. Despite the works discussed above, there is still a lack of understanding of the synergistic corrosion mechanism of these two factors toward zinc.

It has been reported that the deposition rate ratio of these two corrosive media varies with territories in the outdoor environments [6, 18]. However, its effect has been discussed in few studies. In present work, different molar deposition rate ratios of SO₂ and NaCl with the same total molar deposition rate were applied on the zinc surface to further investigate the synergistic effect of the two corrosive species on the atmospheric corrosion of zinc. Abnormal phenomenon of zinc was observed in this experiment, and a possible corrosion mechanism has been proposed in Sect. 4.

2 Experimental

2.1 Sample Preparation and the Wet–Dry Cyclic Exposure

The zinc samples (99.9% purity) with dimensions of 50 × 25 × 2 mm³ were used for gravimetric measurement and morphology observation, and 10 × 10 × 2 mm³ were for the XRD analysis in the laboratory experiment. The samples were ground down to 400 mesh using SiC emery papers, rinsed with ethanol and finally dried by cold air. After stored in a desiccator for 24 h, the gravimetric samples were weighed using analytic balance (The precision is 0.1 mg.)

The deposition rate of SO₂ on zinc was controlled by the amounts of NaHSO₃ added on the samples. Pure NaCl (Group NaCl), NaHSO₃ (Group SO₂) and mixtures of NaCl and NaHSO₃ at molar deposition rate ratios (NaCl/NaHSO₃)

of 3:1 (Group 3:1), 1:1 (Group 1:1) and 1:3 (Group 1:3) were used to contaminate the zinc surfaces. The deposition rates of the two salts for each experimental group are summarized in Table 1.

The wet–dry cycles were conducted by using a Weiss–Voetsch temperature and climatic test system. The test involves the following steps within a 24-h period: (1) wetting the samples with 10 μL cm^{−2} of 0.2 mol L^{−1} electrolyte (the solvent is the mixture of water and alcohol in volume ratio of 1:1); (2) drying the samples in an oven at 30 °C; (3) wetting the samples in the corrosion chamber maintained at 30 °C and 90% relative humidity (RH) for 1 h; (4) drying the samples in the chamber maintained at 30 °C and 60% RH for 2 h; (5) repeating the steps (3) to (4) 7 times. The samples were retrieved for analysis after 336 h.

2.2 Gravimetric Measurement

Corrosion products generated on the zinc surface after laboratory exposure were removed by immersing the samples in a specific solution (prepared by putting 100 g NH₄Cl in distilled water to make 1000 mL solution) at 70 °C for 5 min according to ISO 8407 [19]. After removal of corrosion products, the specimens were rinsed with distilled water by ultrasound, dried in warm air and put into the desiccator. After 24 h, they were weighed to determine their mass loss.

2.3 Corrosion Product Analysis

The corrosion products were analyzed by X-ray diffraction (XRD) and Fourier transformed infrared spectroscopy (FTIR). The XRD measurements were carried out by using a Rigaku-D/Max-2500PC diffractometer complying a Cu target under 40 kV–40 A with a range of 10°–90° and a scanning rate of 2° min^{−1}. The examination area was approximately 15 × 15 mm². The results were analyzed by Jade 5.0 software. Samples for FTIR measurements were measured using KBr pellet method. Spectra were obtained by adding 64 scans at 4 cm^{−1} resolution in the range from 400 to 4000 cm^{−1}. The background spectrum was obtained from a pure KBr pellet.

Table 1 Deposition rates of the salts in each experimental group

Salts	NaCl	3:1	1:1	1:3	SO ₂
NaCl Deposition rate (mg m ^{−2} d ^{−1})	1170	877.5	585	292.5	0
NaHSO ₃ Deposition rate (mg m ^{−2} d ^{−1})	0	520.5	1141	1561.5	2082
Molar deposition rate ratio	–	3:1	1:1	1:3	–

2.4 Corrosion Morphology Analysis

The samples for morphology analysis were cut into the size of approximately $20 \times 20 \text{ mm}^2$ and were observed by a XL30-EFG scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). The cross section samples were mounted in epoxy resin, mechanically ground down to 2000 mesh with SiC paper and then polished with 1.5- μm diamond paste.

3 Results

3.1 Mass Loss After Laboratory Exposure

The corrosion kinetics of zinc can be determined by the mass loss. In order to have a clearer view of the corrosion damage, the mass loss of the zinc specimens was converted to the thickness loss. The thickness loss of the Zinc specimens can be calculated by the following equation (Eq. 1) [20]:

$$D = \frac{W_t}{\rho S} \times 10^4, \quad (1)$$

where D is the thickness loss (μm), W_t is the weight loss (g), ρ is the density of zinc (7.14 g cm^{-3}), and S is the exposed area (cm^2) of the specimen.

Figure 1 shows the thickness loss of zinc specimens as a function of the deposition rate ratio of NaCl/SO₂ after 336-h exposure. It can be seen from Fig. 1 that the thickness loss of Group NaCl is approximately twice as much as that of Group SO₂. That is to say, NaCl is much more corrosive to zinc than SO₂ under the simulated environment. It is also found that the thickness loss decreases as the ratio of NaCl/SO₂ decreases in all

Fig. 1 Thickness loss of the zinc samples in various groups

experimental groups except the Group 1:1, the value in which is, however, the highest. In summary, the corrosivity of NaCl and SO₂ toward zinc increases in order of $\text{SO}_2 < 1:3 < 3:1 < \text{NaCl} < 1:1$.

SO₂ was known to decrease the pH of the electrolyte film on metal surface to accelerate its corrosion rate [15]. However, its lower corrosive effects on zinc than NaCl and highest corrosion rate of zinc observed in Group 1:1 indicate that the corrosion mechanisms of zinc induced by these two salts are more complicated.

3.2 Characterization of Corrosion Products by XRD and FTIR

3.2.1 Phase Analysis with XRD

The analysis with XRD of corrosion products on zinc samples in all groups is shown in Fig. 2. Simonkolleite ($\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$), which has the strongest peak at 11.2° , is found on zinc samples where the deposition rate of NaCl is higher than SO₂ (Groups NaCl and 3:1). Gordaite ($\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$), which has the second strongest peak at 13.6° (the strongest peak of Gordaite is at 6.8° which is out of the XRD measure range in this experiment), occurs on all zinc samples where both NaCl and SO₂ are present (Groups 3:1, 1:1 and 1:3). Zinc sulfate hydroxide hydrate ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$) with the strongest peak at 16.2° and Gunningite ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) with the strongest peak at 26.2° were only detected in Group SO₂. Changoite ($\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), which has the strongest peak at 27.1° , exists on zinc samples where the deposition rate of NaCl is lower than SO₂ (Groups 1:3 and SO₂). In addition, there were some small peaks from zinc hydroxide ($\text{Zn}(\text{OH})_2$) found in the XRD spectroscopies of Groups NaCl, 3:1 and 1:1. Obviously, all peaks of the corrosion products detected above are quite sharp, indicating that they are well-defined crystals.

3.2.2 FTIR Spectroscopy

The transmission FTIR spectra of corrosion products on the samples of all experimental groups are shown in Fig. 3. The analysis of the results indicates that the bands and peaks are mainly assigned to three species of ion groups—hydroxyl (or crystal water) groups, carbonate ions and sulfate ions.

The broad bands in the region from 3300 to 3600 cm^{-1} with several peaks are due to the stretching vibration of hydroxyl groups [2, 11, 21–23]. The strong bands in the region from 1600 to 1700 cm^{-1} are caused by deformation vibration of crystal water [21]. There are also peaks at 785 – 795 cm^{-1} , 905 cm^{-1} and 1024 cm^{-1} attributed to the vibration of Zn–O–H from zinc hydroxy corrosion products [11]. $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ has strong bands at 3450 cm^{-1}

Fig. 2 XRD patterns of the corroded zinc samples: **a** Group NaCl; **b** Group 3:1; **c** Group 1:1; **d** Group 1:3; **e** Group SO₂

and peaks at 1620 cm^{-1} , 905 cm^{-1} and 460 cm^{-1} [14]. The FTIR results for Groups NaCl and 3:1 support the existence of $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ in the corrosion products. The

intense peaks at 3507 , 3401 , 3342 cm^{-1} in the FTIR spectra for Groups 1:1 and 1:3 (Fig. 3c, d) correspond to the characteristic absorbance peaks for $\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl}\cdot 6\text{H}_2\text{O}$

Fig. 3 FTIR spectroscopies of the corrosion products on zinc samples: **a** Group NaCl; **b** Group 3:1; **c** Group 1:1; **d** Group 1:3; **e** Group SO₂

well [21], which is consistent with the analysis of the XRD patterns.

The strong bands in the region from 1300 to 1600 cm⁻¹ are due to the asymmetric stretching vibration of carbonate

ions, while the out-of-plane and in-plane bending vibrations from carbonate ions have peaks at 835 cm⁻¹ and 710 cm⁻¹ [22, 24, 25]. It was reported that the carbonate ions from hydrozincite (Zn₅(CO₃)₂(OH)₆) have peaks

around at 1500 cm⁻¹, 1390 cm⁻¹, 835 cm⁻¹ and 705 cm⁻¹. The FTIR results indicate the existence of Zn₅(CO₃)₂(OH)₆ on samples in Groups NaCl, 3:1, 1:1 and 1:3. In addition, the peak at 1427 cm⁻¹ may be due to the carbonate ions from sodium carbonate (Na₂CO₃) [26].

The strong bands from 1100 to 1200 cm⁻¹ are due to the asymmetric stretching vibration of sulfate ions. The peaks at 985–990 cm⁻¹ are attributed to the symmetric stretching vibration of sulfate ions. The peaks at 615–620 cm⁻¹ are due to the deformation vibration of sulfate ions [2, 11, 25]. Combined with the XRD results, these peaks are mainly caused by the sulfate compounds—NaZn₄SO₄(OH)₆Cl·6H₂O, ZnSO₄·H₂O, Zn₄SO₄(OH)₆·5H₂O and Na₂Zn(SO₄)₂·4H₂O.

The final results of the corrosion products by XRD and FTIR analysis in this work are summarized in Table 2. It can be seen from Table 2 that the composition of corrosion products on zinc samples varies with the deposition rate ratio of NaCl and SO₂. In groups where both NaCl and SO₂ are present, NaZn₄SO₄(OH)₆Cl·6H₂O formed. Zn₅(OH)₈Cl₂·H₂O was generated in groups where the deposition rate of NaCl is higher than SO₂, while soluble corrosion products, ZnSO₄·H₂O and Na₂Zn(SO₄)₂·4H₂O formed in groups where the deposition of NaCl is lower than SO₂. Zn₅(CO₃)₂(OH)₆ was generated in the form of amorphous state in all groups except Group SO₂. In addition, trace amount of Zn(OH)₂ was found in groups where the deposition rate of NaCl is no lower than SO₂.

Table 2 Corrosion products detected by XRD and FTIR on the corroded zinc samples

Groups	Corrosion products
NaCl	Zn ₅ (OH) ₈ Cl ₂ ·H ₂ O Zn(OH) ₂ Zn ₅ (CO ₃) ₂ (OH) ₆
3:1	NaZn ₄ SO ₄ (OH) ₆ Cl·6H ₂ O Zn ₅ (OH) ₈ Cl ₂ ·H ₂ O Zn(OH) ₂ Zn ₅ (CO ₃) ₂ (OH) ₆
1:1	NaZn ₄ SO ₄ (OH) ₆ Cl·6H ₂ O Zn(OH) ₂ Zn ₅ (CO ₃) ₂ (OH) ₆
1:3	NaZn ₄ SO ₄ Cl(OH) ₆ ·6H ₂ O Na ₂ Zn(SO ₄) ₂ ·4H ₂ O ^a Zn ₅ (CO ₃) ₂ (OH) ₆
SO ₂	Na ₂ Zn(SO ₄) ₂ ·4H ₂ O ^a ZnSO ₄ ·H ₂ O ^a Zn ₄ SO ₄ (OH) ₆ ·H ₂ O

^aSoluble substances

3.3 Morphologies of the Corroded Samples

3.3.1 Macro-Morphologies of the Corroded Surfaces

The differences in performance of the two salts and their mixtures toward zinc are well visible, and the appearances of the samples in a 48-h dry state after exposure are shown in Fig. 4. For all experimental groups except Group 1:1, the corrosion products are distributed uniformly on the surface of the samples. It can be seen from Fig. 4c that there are several white island-like protuberances located randomly on the surface and the length of some is over 5 mm. It is a typical morphology for patchy corrosion attack.

3.3.2 Corrosion Morphologies of the Samples After Removal of Corrosion Products

Figure 5 shows the second electron images of the sample surfaces after removal of corrosion products. It can be seen that there are numerous small pits (the length is less than 50 μm) generated on the sample surfaces uniformly in all groups except Group 1:1. In contrast, the overall scan of the sample surfaces in Group 1:1 found large amounts of big pits (the length is more than 500 μm) on the zinc surface. Figure 5e shows the morphology of one big pit. Combination with the macro-morphology of the corroded sample surfaces, it can be concluded that the corrosion attack of zinc is pocking corrosion in Groups NaCl, 3:1, 1:3, SO₂, while it is patchy corrosion in Group 1:1. Noticeably, traces of intergranular corrosion were discovered on the zinc surfaces as illustrated in Fig. 5b, d, f, h, j. It indicated that the grain boundary of zinc samples may be a susceptible structure to pitting when contacting with the corrosive species such as Cl⁻ and SO₄²⁻. Similar interesting appearance was also observed by Cole et al. [23], who indicated that crystalline product decorated grain boundaries in the secondary spread region under a micro-droplet. In addition, the corrosion morphologies of the pits in this investigation have crystallographic features as shown in Fig. 5b, d, f, h, j, which indicates that the electrochemical dissolution of zinc may preferentially occurs on some certain crystalline planes. Alvarez and Galvele found the similar phenomenon and concluded that pitting of zinc in NaCl solutions developed along {0001} and {10 $\bar{1}$ 0} planes [27]. This may explain why the crystallographic features were found on zinc exposed to simulated atmosphere in this work.

3.3.3 SEM-EDS Results of the Corroded Samples

SEM and EDS were applied to examine the corrosion product morphology and chemical compositions on the corroded samples. Combination with the results of XRD and FTIR, the distribution of the corrosion products was analyzed by EDS. As EDS does not permit a

Fig. 4 Surface photographs of the corroded zinc samples: **a** Group NaCl; **b** Group 3:1; **c** Group 1:1; **d** Group 1:3; **e** Group SO₂

separation of the primarily Zn and Na peaks, the contents of Zn, O, Cl, S were recorded in the EDS measurements. In addition, the soluble corrosion products (ZnSO_4 and $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) were not observed in the cross section images due to the polishing process with water.

3.3.3.1 SEM-EDS Results of Corroded Samples in Groups NaCl and SO₂ Figures 6 and 7 show the surface and the cross section morphologies of the corrosion products on samples in Group NaCl and Group SO₂. The chemical compositions of the points marked by the arrows are listed in Table 3.

Fig. 5 Surface morphologies of the zinc samples after removal of the corrosion products: **a, b** Group NaCl; **c, d** Group 3:1; **e, f** Group 1:1; **g, h** Group 1:3; **i, j** Group SO₂

Fig. 6 Corrosion products morphologies on corroded zinc samples in Group NaCl: **a–c** the surface morphologies, **d** the cross section morphology

Fig. 7 Corrosion products morphologies on corroded zinc samples in Group SO_2 : **a–c** the surface morphologies, **d** the cross section morphology

Table 3 Element composition of the points marked in Figs. 6 and 7 examined by EDS

Points	Zn (at%)	O (at%)	Cl (at%)	S (at%)
A	15.4	81.8	2.80	—
B	29.9	56.3	13.8	—
C	27.2	72.2	0.540	—
D	30.3	64.6	5.08	—
E	7.31	79.7	—	13.0
F	28.2	66.6	—	5.21
G	28.7	63.7	—	7.60

In Group NaCl (Fig. 6), it can be seen from the surface images that amorphous sponge-like corrosion products (Fig. 6b) cover most of the surface and a certain amount of laminar crystals (Fig. 6c) were observed at the remaining areas. The EDS results show that the primary elements of the laminar crystals (Table 3, Point B) are Zn, O, Cl with a very close ratio to that of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Table 5). While the sponge-like products (Table 3, Point A) have the same chemical species but much lower content of Cl. Combination with the XRD and FTIR results that $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ is well-defined crystal compound and the carbonate corrosion products are amorphous, the laminar crystals should be consisting of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, and the sponge-like products are mainly comprised of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. The cross section image (Fig. 6d) exhibits two different layers of corrosion products—a dark gray outer layer with lower content of Cl (Table 3, Point C) and a bright gray inner layer with much higher content of Cl (Table 3, Point D). It suggests that $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ is primarily distributed in the inner layer and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ or $\text{Zn}(\text{OH})_2$ is mainly distributed in the outer layer.

In Group SO₂ (Fig. 7), it is shown that there is a thin layer of flake-like corrosion products (Fig. 7c, d) with some volcano-like crystals (Fig. 7a) located on the corroded sample surface. The EDS results show that the flakes (Table 3, Point F, G) and volcano-like crystals (Table 3, Point E) have a similar S content with $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Table 5), respectively. It indicates that a thin layer of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ with some volcano-like crystals consists mainly of $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ on the sample surfaces.

3.3.3.2 SEM-EDS Results of Corroded Samples in Groups 3:1, 1:1, 1:3 The overall scan of the corroded surface of the sample in Group 3:1 indicates that most of the surface is covered by the platelet-like corrosion products (Fig. 8a, b). The EDS results (Table 4, Point A, B) suggest that two different platelet-like corrosion products exist on the surface. The element contents of the platelets assembling like a “network” (Fig. 8b, Point A) are quite close to that of

$\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$ (Table 5), which indicates they consist of $\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$. While the analysis of the elemental composition of the larger platelets (Fig. 8b, Point B) distributed on the “network” implies that they are primarily Zn-Cl-O containing compounds which is supposed to be $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. Figure 9 shows the SEM-EDS mapping of the cross section of the corroded zinc samples in Group 3:1. The SEM image exhibits two different structures alternative precipitating in the corrosion product layer—the laminar structure adhered to the substrate and in the mediate layer (Region I) and the relatively compact structure in the mediate and surface layers (Region II). The EDS mapping indicates that the Zn, O and Cl are distributed throughout the corrosion product layer, while S enriches only in Region II. Combination with the XRD and FTIR results, it can be speculated that $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ is present in Region I and $\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$ is distributed in Region II.

The macro-photograph reveals that there are plenty of white island-like protuberances on the corroded surface of sample in Group 1:1. Figure 8c shows the SEM image of one of the protuberances. The higher magnification images reveal that clusters of pine needle-like crystalline phase are located at the central region of the protuberance (Fig. 8d) and cellular-like corrosion products are distributed around the protuberance (Fig. 8e). The analysis of the EDS results (Table 4, Point C, D) indicates that the former is predominantly composed of $\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$ (Table 5) and the latter is supposed to be mainly consisting of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ or $\text{Zn}(\text{OH})_2$. Figure 10 shows the SEM-EDS mapping of the cross section of the corroded zinc sample in Group 1:1 (Approximately half of a protuberance is exhibited in the SEM image.) It can be seen that the structure of the protuberance is quite porous with several holes are in it. The EDS mapping shows that Zn and O are distributed throughout the corrosion product layer, while Cl and S enrich in the central part of the protuberance. It suggests that $\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$ is primarily distributed in the patchy pit with $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ or $\text{Zn}(\text{OH})_2$ around it, which is in accordance with the surface SEM-EDS analysis.

The observation of the corroded surface of the sample in Group 1:3 (Fig. 8f–h) shows that the surface is covered by randomly assembling platelet-like corrosion products (Fig. 8f) with some bulk crystals (Fig. 8g) on them. The elemental composition analysis of these corrosion products with two shapes (Table 4, Point E, F) indicates that the platelets are composed of $\text{NaZn}_4\text{SO}_4(\text{OH})_6\text{Cl} \cdot 6\text{H}_2\text{O}$ and the bulk crystals are consisting of $\text{Na}_2\text{Zn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Table 5). The SEM-EDS mapping of the cross section of the corroded zinc sample in Group 1:3 is shown in Fig. 11. There are two structures—a relatively compact layer comprising of vertical oriented platelets adhered to substrate and a porous outer layer composed by disordered oriented small platelets

Fig. 8 SEM images of the surface morphologies on corroded zinc samples: **a, b** Group 3:1; **c–e** Group 1:1; **f–h** Group 1:3

Table 4 Element composition of the points marked in Fig. 8 examined by EDS

Points	Zn (at%)	O (at%)	Cl (at%)	S (at%)
A	15.7	74.6	4.87	4.79
B	24.2	64.5	9.75	1.62
C	16.4	73.4	4.88	5.34
D	17.4	81.3	0.310	1.03
E	7.20	78.8	–	14.0
F	19.2	69.7	5.09	5.95

Table 5 Element composition of zinc corrosion products

Compounds	Zn (at%)	O (at%)	Cl (at%)	S (at%)
Zn ₅ (OH) ₈ Cl ₂ ·H ₂ O	31.2	56.2	12.5	–
NaZn ₄ SO ₄ (OH) ₆ Cl·6H ₂ O	18.2	72.7	4.54	4.54
Zn ₄ SO ₄ (OH) ₆ ·5H ₂ O	20.0	75.0	–	5.00
Na ₂ Zn(SO ₄) ₂ ·4H ₂ O	6.67	80.0	–	13.3
ZnSO ₄ ·H ₂ O	14.3	71.4	–	14.3

The values were calculated based on the chemical formula given above, and only Zn, O, Cl, S were taken into account

exhibited in the SEM image. The EDS mapping indicates that both of the structures in the corrosion product layer are mainly consisting of Zn–O–Cl–S compounds, which is supposed to be NaZn₄SO₄(OH)₆Cl·6H₂O.

4 Discussion

The atmospheric corrosion of zinc is generally considered as an electrochemical process [28], involving the anodic dissolution of zinc (Eq. 2).

The cathodic process is either hydrogen evolution or oxygen reduction. In order to estimate the corrosion damage caused by the hydrogen reduction in Group SO₂, it could be roughly assumed that the entire hydrogen ions in HSO₃[–] were released in the form of H₂ eventually. Thus, the thickness loss of zinc caused by the hydrogen reduction was calculated to be approximately 1.27 μm, which was only 35% of the total thickness loss in Group SO₂. In fact, a proportion of H⁺ ions were neutralized by OH[–] ions produced by the reduction of O₂. Therefore, the corrosion damages in all groups were dominantly caused by oxygen reduction (Eq. 3).

It can be seen from Table 2 that the composition of the corrosion products varies with the deposition rate ratio of

NaCl and SO₂. NaZn₄SO₄(OH)₆Cl·6H₂O is the only compound which containing sulfate and chlorine detected on zinc samples, and formed in all groups where NaCl and SO₂ are present. In contrast, Zn₅(OH)₈Cl₂·H₂O was merely generated in groups where the deposition of NaCl is higher than SO₂. It indicated that NaZn₄SO₄(OH)₆Cl·6H₂O is more thermodynamically stable than Zn₅(OH)₈Cl₂·H₂O in the presence of SO₂. Table 2 also shows that soluble zinc corrosion products, ZnSO₄·H₂O and Na₂Zn(SO₄)₂·4H₂O formed in groups where the deposition rate of NaCl is lower than SO₂. It is very likely that the lower corrosion rate of zinc (Fig. 1) was caused by these two substances. This will be elaborated in detail later in this section (Paragraph 5 and 6 of Sect. 4).

Zn₅(CO₃)₂(OH)₆ is a disordered non-stoichiometric compound with a variable ratio of OH/CO₃ [29]. The fact that the peaks of Zn₅(CO₃)₂(OH)₆ are missing in the XRD patterns (Fig. 2a–d) but discovered in the FTIR spectra (Table 2) implies the formation of amorphous carbonate compounds during exposure. This phenomenon was also found in the investigation by Zhu et al. [22]. It is notable that carbonate compounds were generated in the form of amorphous state in all groups except Group SO₂. CO₂ was responsible for the formation of carbonate corrosion products on the zinc surface. It is suggested that the absorption of CO₂ tended to occur in the cathodic region to neutralize the alkali [5] produced by the reduction of O₂ and insoluble Zn₅(CO₃)₂(OH)₆ would participate as one species of the corrosion products at that region. However, no carbonate compound was detected on zinc samples in Group SO₂ (Table 2). It can be explained that HSO₃[–] deposition and SO₄^{2–} formation acidified the surface electrolyte more strongly than CO₂ deposition, and consequently, CO₂ deposition was inhibited [11].

It is worth noting that insoluble zinc corrosion products as well as soluble zinc corrosion products generated on zinc samples in this work (Table 2). Limstrom et al. [28] have studied the influence of salt deposits on the atmospheric corrosion of zinc. The chloride-containing salts, NaCl and ZnCl₂, and the sulfate-containing salts, Na₂SO₄ and ZnSO₄, were investigated. It was found that Na⁺ was by far more corrosive toward zinc than Zn²⁺. Simultaneously, the corrosion rate of zinc was directly correlated with the amount of Na⁺ and did not depend on whether Na₂SO₄ or NaCl was added. The mechanism they proposed to explain the different corrosivity of Na⁺ and Zn²⁺ toward zinc was: the comparatively rapid corrosion caused by the sodium salts was suggested to be due to the absence of insoluble sodium compounds; in contrast, the Zn²⁺ ions precipitated as zinc hydroxy products in the cathodic areas due to the high pH values produced, resulting the blocking of the cathodic sites.

The corrosion kinetic results of zinc (Fig. 1) show that the corrosivity of NaCl and SO₂ toward zinc increases in order of SO₂ < 1:3 < 3:1 < NaCl < 1:1. The lower thickness loss of zinc in Groups SO₂ and 1:3 can be attributed to the

Fig. 9 SEM-EDS mapping in the frame area of the cross section of the corroded zinc sample in Group 3:1

Fig. 10 SEM–EDS mapping in the frame area of the cross section of the corroded zinc sample in Group 1:1

Fig. 11 SEM-EDS mapping in the frame area of the cross section of the corroded zinc sample in Group 1:3

Fig. 12 Higher magnification SEM images of cross section in Group 1:1 marked in Fig. 10

formation of soluble zinc corrosion products. In Groups 1:3 and SO₂ of present work, the formation of soluble ZnSO₄·H₂O and Na₂Zn(SO₄)₂·4H₂O (Table 2) could result in the Zn²⁺ ion electrolyte being present in large region on the sample surface (Figs. 7a, b, 8f, g) during the wet period. Therefore, the according hydroxy products would tend to precipitate directly on the cathodic sites where the soluble substances presented as soon as the electrochemical corrosion commenced and inhibited the cathodic reaction process. It may be noted that zinc hydroxy products formed in Group NaCl as well. However, in this case the precipitation is expected to occur close to the anodic sites and the precipitation would therefore interfere the cathodic reaction less significantly.

As analyzed previously, the corrosion attack on zinc samples in Group 1:1 shows patchy corrosion and the corrosion products distribution is dramatically inhomogeneous (Figs. 4c, 5e). The SEM–EDS results reveal that NaZn₄SO₄(OH)₆Cl·6H₂O is located in the central regions of the patchy pits, while Zn₅(CO₃)₂(OH)₆ or Zn(OH)₂ is distributed around the pits. It can be explained [30] that the inhibition effect of NaZn₄SO₄(OH)₆Cl·6H₂O to zinc dissolution is much weaker than that of Zn₅(CO₃)₂(OH)₆ or Zn(OH)₂. Thus, the zinc dissolution in the regions which is covered by NaZn₄SO₄(OH)₆Cl·6H₂O tended to be faster and would act as anodes. As corrosion progressed, Cl[−] and SO₄^{2−} ions migrated to the anodic sites and more NaZn₄SO₄(OH)₆Cl·6H₂O would precipitate in the anode sites. As a result, protuberances formed and patchy corrosion occurred. Figure 12 shows the enlarged SEM images of the regions marked in Fig. 10. It can be seen that there are numerous lathy pores in the protuberance (Region I). In contrast, the structure of the corrosion products around the protuberance (Region II) is much more compact. Therefore, it is reasonable to speculate that the less protectiveness of the compound NaZn₄SO₄(OH)₆Cl·6H₂O

is due to the porous structure which can provide a passage of the corrosive species toward the metal surface and migration of the Zn²⁺ ions away from the metal surface.

However, in Groups 3:1 and 1:3, NaZn₄SO₄(OH)₆Cl·6H₂O formed, but no patchy pits were found. In Group 3:1, it was observed that layers of Zn₅(OH)₈Cl₂·H₂O (Fig. 9, Region I) are intercalated in the corrosion product layers and their structures are relatively more compact. It is suggested that the formation of Zn₅(OH)₈Cl₂·H₂O promotes the protectiveness of the corrosion product layer where NaZn₄SO₄(OH)₆Cl·6H₂O precipitated [5] (Fig. 9, Region II) and the dissolution of the zinc were inhibited; in Group 1:3, it was found that the distribution of NaZn₄SO₄(OH)₆Cl·6H₂O in the corrosion product layer is quite uniform and no obvious region for carbonate compounds in the layer was observed. Thus, there was no obvious effect induced by the corrosion products on the dissolution process of zinc in Groups 3:1 and 1:3, and only small pits penetrated in the samples due to micro different chemical distribution.

5 Conclusion

The synergistic effect of NaCl and SO₂ toward the atmospheric corrosion of zinc was investigated with different molar deposition rate ratios. The following conclusions can be drawn with the analysis of the corrosion kinetics, corrosion products and corrosion morphologies:

1. The corrosion rate of zinc is dramatically influenced by the molar deposition rate ratio of NaCl and SO₂ under wet–dry conditions. The corrosivity of NaCl and SO₂ toward zinc increases in the order of SO₂ < 1:3 < 3:1 < NaCl < 1:1.

2. The composition of corrosion products on zinc samples varies with the deposition rate ratio of NaCl and SO₂. NaZn₄SO₄(OH)₆Cl·6H₂O formed in groups where both NaCl and SO₂ are present. Zn₅(OH)₈Cl₂·H₂O was generated in groups where the deposition rate of NaCl is higher than SO₂, while soluble corrosion products, ZnSO₄·H₂O and Na₂Zn(SO₄)₂·4H₂O formed in groups where the deposition of NaCl is lower than SO₂. Zn₅(CO₃)₂(OH)₆ was generated in the form of amorphous state in all groups except Group SO₂. In addition, trace amount of Zn(OH)₂ was found in groups where the deposition rate of NaCl is no lower than SO₂.
3. The corrosion is pocking corrosion in all groups except Group 1:1, where the corrosion is patchy corrosion. The patchy corrosion in Group 1:1 is suggested to be caused by the formation of NaZn₄SO₄(OH)₆Cl·6H₂O.

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