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Characterization of the Corrosion Products Formed on Zinc in Archipelagic Subtropical Environments

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The atmospheric corrosion of zinc samples exposed at 25 test sites with different climatic and pollution conditions was investigated during a two-year exposure program carried out in three of the Canary Islands (Spain) as to cover the typical range of subtropical environmental conditions. The composition and distribution of the corrosion products of zinc were analyzed qualitatively by X-ray diffraction (XRD). Simonkolleite ($Zn_5(OH)_8Cl_2$) and hydrozincite ($Zn_4CO_3(OH)_6 \cdot H_2O$) were the corrosion products more frequently observed, revealing that chloride and carbon dioxide are the most aggressive pollutants present in the atmosphere. Sulphate-containing species, namely Zinc oxysulfate ($Zn_3O(SO_4)_2$), Zinc hydroxysulfate ($Zn_4SO_4(OH)_6$), Zinc diamminehydroxynitrate ($Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$) and zinc chlorohydroxysulfate ($NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$), were also found though in smaller amounts.

Keywords: Atmospheric corrosion; Zinc; Sodium chloride; Carbon dioxide; Sulphur dioxide; X-Ray diffraction.

1. INTRODUCTION

Atmospheric corrosion is an electrochemically-driven process with large economic impact in industrialized societies [1]. It has been estimated that the cost of protection against atmospheric corrosion is about 50% of the total costs of all corrosion measures [2]. Atmospheric corrosion occurs in the presence of an aqueous layer developed on the oxidized metal under environment exposures.

The electrolyte layer is usually quite thin, leading to the formation of highly localized corrosion cells. Additionally, the corrosion products resulting from the atmospheric action may eventually protect a metal against further corrosive action. Indeed, it is the formation of corrosion products during exposure of zinc in the atmosphere that is responsible for the rather high corrosion resistance of this metal. These surface films effectively protect the metal from the aggressive attack of the environment. The list of corrosion products formed on zinc after natural weathering conditions is quite large, and it includes hydroxides, oxides, carbonates, sulphates, chlorides, and complex mixtures of these anionic species [3-13]. Interestingly enough, some corrosion products have been found to be identical to minerals occurring in nature despite the very different formation mechanisms involved [7,14]. But the technological interest in the identification [15-19] of the layer of corrosion products formed originates from their own chemical reactivity [20,21] and their role on the corrosion process [22]. That is, the kinetics and extension of the corrosion reactions are influenced by the physicochemical characteristics of the resulting corrosion products, namely composition, morphology, structure, compactness, adherence to the underlying metal substrate, etc. Additionally, weather factors such as the duration and frequency of wet-dry cycles, rain, temperature and wind regimes, and the presence in the atmosphere of typical pollutants (SO_2, Cl^-, NO_x, etc.), may modify the characteristics of the corrosion products [6,8,10,14,16]. In fact, the combination of weather factors, moisture and the distribution of pollutants existing at the beginning of the exposure greatly determine the onset and advancement of corrosion processes even at significantly later stages [20,22].

Atmospheres are usually classified, as for the characterization of material degradation, into four main classes, namely rural, urban, industrial and marine environments [23]. They are established from the combination of weathering factors and concentrations of chemical species, which may also result from anthropogenic activities. In this way, it is customary to classify atmospheric corrosivity in the following groups [24]: (i) Rural atmospheres, which do not contain aggressive chemical contaminants (deposition rate of SO_2 and NaCl lower than mg m^{-2} day^{-1}), where main corrosive agents are moisture, organic and inorganic dusts, and gaseous components such as oxygen and carbon dioxide. (ii) Urban and industrial atmospheres, characterized by pollution composed principally by sulphur compounds; in a humid ambient, these compounds generate a highly corrosive acid layer on exposed surfaces (deposition rate of SO_2 higher than 15 mg m^{-2} day^{-1}, whereas that of NaCl lower than this value). (iii) Marine atmospheres, usually an aerosol carried by the wind that contains NaCl particles and settles on exposed surfaces (deposition rate of NaCl higher than 15 mg m^{-2} day^{-1}). In addition, grades are made within each class to further characterize them with somewhat greater detail. Despite the extended use of this procedure, its applicability is at least limited in the case of tropical and subtropical regions, and can even be of no use in the case of disrupted territories such as oceanic archipelagos. In the latest case, the wind regimes are strong enough to produce marine environments at locations situated at big distances from the coastline, even at rather high altitudes. This is the situation occurring at the Canary Islands in the Atlantic Ocean, which present a big variety of environments comprised in a rather small geographical region. The Canary Islands is an archipelago of seven islands and six islets with a total area of 7499 km^2 located in the Atlantic Ocean close to the African continent. They have a climate characterised by the atmospheric dynamics typical of subtropical latitudes, the cold oceanic draft action, and the effect of the so called Trade Winds. These winds blow in Northeast direction, carrying a great amount of salinity. Among the three Eastern islands of the archipelago, which constitute the province of Las Palmas de Gran Canaria, big climatic differences are observed due to their different orography. The rough relief of Gran Canaria induces the stagnation of clouds which are swept by the Trade Winds originating a very humid environment and drop condensations half-way of the mountainside (from 500 to 1100 m), a feature not present in Lanzarote and Fuerteventura. In this way, a wide variety of microclimates are developed in the islands (i.e., industrial-marine, marine, rural, and humid-rural), thus allowing for the different corrosive environments to be distributed in a rather small territory [25-28]. The current study is directed to the characterization of the corrosion products formed on zinc during 2 years of atmospheric exposure in 25 test sites distributed in these three islands. The main objective of this work was to derive correlations between atmospheric parameters and the corrosion processes for this metal.

2. EXPERIMENTAL

Table 1. Chemical composition of zinc plates.

Element	Zn	Cu	Ti	Al
Content (wt%)	99.5	0.1-0.2	0.02-0.2	< 0.006

Table 2. Geographic coordinates and type of atmospheres of the test sites

Test site			Elevation (m)	Geographic coordinate		Atmosphere / Corrosivity index according to ISO 9223
				West longitude	North latitude	
Gran Canaria	1	FEDEX. Muelle de la Luz	15	28º 08' 59"	15º 24' 10"	Industrial / C3
	2	Cabildo Insular de Gran Canaria	40	28º 06' 16"	15º 24' 20"	Urban / C3
	3	Central Térmica de Jinámar	30	28º 02' 35"	15º 23' 43"	Industrial / C4
	4	Instituto Canario de Ciencias Marinas	20	27º 59' 27"	15º 21' 34"	Industrial / C5
	5	Colegio Plácido Fleitas (Telde)	200	28º 00' 00"	15º 24' 20"	Rural / C3
	6	Aeropuerto de Gran Canaria	50	27º 55' 54"	15º 22' 30"	Industrial / C3
	7	Central Térmica Juan Grande	30	27º 48' 16"	15º 25' 33"	Industrial / C3
	8	Planta Desal. ELMASA (San Agustín)	40	27º 46' 21"	15º 31' 50"	Rural / C3
	9	Colegio Público de Mogán	280	27º 53' 10"	15º 43' 09"	Rural / C3
	10	Ayuntamiento San Nicolás de Tolentino	70	27º 59' 10"	15º 46' 40"	Rural / C3
	11	Colegio Público Valle de Agaete	255	28º 05' 19"	15º 39' 38"	Rural / C3
	12	Ayuntamiento de Agaete	50	28º 06' 24"	15º 42' 05"	Rural / C3
	13	Colegio Público Sardina del Norte	50	28º 09' 10"	15º 41' 10"	Rural / C3
	14	Ayuntamiento de Guía	185	28º 08' 27"	15º 37' 12"	Rural / C3
	15	Ayuntamiento de Teror	600	28º 03' 40"	15º 32' 08"	Rural / C3
	16	Colegio Público de San Mateo	850	28º 00' 48"	15º 31' 00"	Rural / C3
Fuerteventura	17	Corralejo	50	28º 42' 13"	13º 54' 02"	Rural / C3
	18	Ayuntamiento de Puerto del Rosario	23	28º 30' 00"	13º 51' 06"	Rural / C3-C4
	19	Tenencia de alcaldía de Gran Tarajal	10	28º 12' 49"	14º 01' 13"	Rural / C3
	20	Subestación UNELCO Costa Calma	100	28º 09' 42"	14º 13' 55"	Rural / C3
	21	Central Térmica Las Salinas	38	28º 32' 01"	13º 50' 22"	Industrial marine / C5
	22	El Cotillo	35	28º 40' 54"	14º 00' 45"	Marine / C3
Lanzarote	23	Ayuntamiento de Haría	278	29º 08' 51"	13º 30' 02"	Rural / C3
	24	Central Térmica Punta Grande	25	28º 59' 20"	13º 30' 00"	Industrial / C3
	25	Aeropuerto de Lanzarote	15	28º 56' 51"	13º 35' 58"	Rural / C3

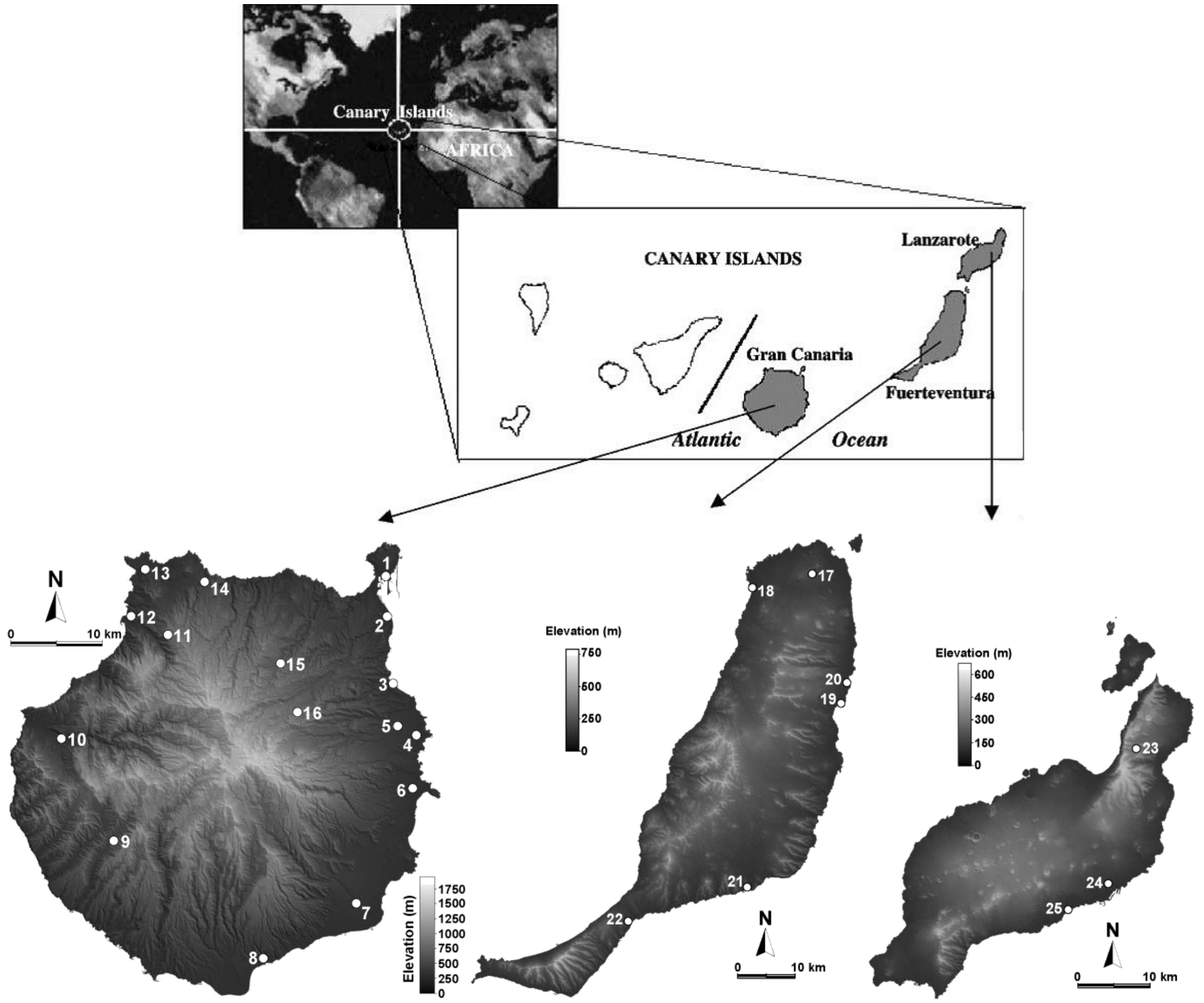

Figure 1. Locations of corrosion test sites in the three Eastern Canary Islands.

Specimens of 100 mm x 40 mm x 2 mm were cut from zinc plates of composition given in Table 1. All the specimens were prepared uniformly. A 12 mm dia. hole was made on each plate to fix them on the rack and they were first cleaned, one at a time, with water and soap and later with acetone. Next, the oxide layer was eliminated according to the ASTM G1-90 norm [29]. Once the plates were cleaned and dried, they were weighed using precision scales (Sartorius BP 210 S) and stored in plastic bags until they were placed in the test sites. The 25 different locations chosen in the islands of Gran Canaria, Fuerteventura and Lanzarote are shown in Figure 1, whereas the corrosion categories of the testing stations estimated from the pollution levels and weather factors according to ISO standards 9223 and 9224 [23,24] are listed in Table 2. ISO/TC 156 N 250 norm (also named the Husy's method) [30] was employed for the determination of SO_2 pollution. In brief, sulphur dioxide of the atmosphere was absorbed by the PbO_2 of the sulphur dioxide capturer and was transformed into $PbSO_4$, which was determined by a turbidimetric method [31]. Salinity was determined following the ISO/DP 9225 norm (also called the wet candle method) [32]. The amount of chloride captured in the candles was determined by titration [33]. Plates were exposed at 45º from the horizontal according to the ISO/DIS 8565 norm [31], and they were oriented NNE to face the predominant direction of the Trade Winds.

Zinc corrosion products were identified by X-ray diffraction (XRD), using a Siemens D-5000 diffractometer equipped with a Cu Kα1 5406⊕ anode. The XRD patterns were scanned in the $5^o \leq 2\theta \leq 35^o$ range at a rate of 1.5º min^{-1}. XRD characterization was either performed on the retrieved samples or on the powder scrapped-off the zinc plates. Non scrapped samples were investigated because the corrosion products were often tightly adhered to the remaining metal surface and constituted a very thin layer, thus making product removal rather difficult. In this case, the diffractograms exhibited the peaks corresponding to the base metal in addition to those of the corrosion products [34].

3. RESULTS AND DISCUSSION

Table 3. Corrosion products and main climatic characteristics for the exposures. ToW and pollutants data are given as accumulated values over the given exposure period.

Island	Test site	Corrosion products		Cl$^-$ (mg m^{-2} day^{-1})		SO_4^{2-} (mg m^{-2} day^{-1})		ToW (hours year^{-1})	
		1st year	2nd year	1st year	2nd year	1st year	2nd year	1st year	2nd year
Gran Canaria	1 Muelle de La Luz	HS,G	O,G	34.44	26.98	9.72	7.31	3723	8410
	2 Cabildo de Gran Canaria	HC,S,O,HS,G	S,O,HS	18.90	15.43	0.70	0.56	1257	2941
	3 C. T. de Jinámar	S,CS,N	S,CS,N	168.94	105.88	12.30	10.24	3824	9689
	4 Taliarte	HC,S,HS,CS	HC,S,HS,CS	933.75	548.36	12.90	9.02	7215	14440
	5 Telde	HC	-	30.53	23.14	8.01	7.86	1515	6976
	6 Aeropuerto de Gando	S,N	S,N	53.16	33.74	6.40	7.01	3651	11388
	7 C.T. Barranco de Tirajana	S,N,CS	S,N,CS	133.04	79.69	18.47	14.63	1021	2055
	8 San Agustín	HC,S	HC,S,HS	22.15	16.40	3.27	3.10	2675	7070
	9 Mogán	HC,S,G	HC,S	38.65	27.74	0.21	0.26	1391	2949
	10 San Nicolás de Tolentino	HC,S	HC,S,HS	23.88	18.49	0.15	0.19	1324	2521
	11 Valle de Agaete	S	HC,S,G	20.27	15.76	0.08	0.09	1574	4208
	12 Agaete	HC,S,O,HS,G	S,G	21.56	20.91	0.35	0.35	274	2908
	13 Sardina del Norte	HC,S,O,HS,G	HC,S,O,HS,G	51.64	46.78	0.11	0.13	2213	3155
	14 Santa María de Guía	HC,S,HS	HC,S,HS	28.58	22.17	0.27	0.26	1936	5575
	15 Teror	HC,S	HC,S	13.25	11.33	0.22	0.35	2403	9570
	16 San Mateo	HC	HC	14.42	10.07	0.13	0.14	2510	6117
Fuerteventura	17 Corralejo	S,HC	S,HC	39.06	36.35	0.26	0.92	2901	6741
	18 Puerto del Rosario	S,O	S,CS	29.61	32.37	0.34	0.57	5713	12821
	19 Gran Tarajal	HC,S,O,HS	HC,S,HS	59.50	55.78	0.37	1.47	2315	3273
	20 Costa Calma	HC,S	HC,S	56.36	40.94	0.18	0.66	2628	5800
	21 Central Térmica Las Salinas	HC, S, N	HC,S,N	138.13	105.76	3.50	4.93	5543	12651
	22 El Cotillo	S, HC	S, HC	158.69	119.53	0.38	0.92	1245	2767
Lanzarote	23 Haría	HC,S,O,HS	HC,S,O,HS	32.45	22.58	0.21	0.20	3109	5468
	24 C. T. Punta Grande	HC,S,N	HC,S,N	42.35	32.54	2.81	3.13	3714	7137
	25 Aeropuerto de Lanzarote	HC,S	S,O	61.87	42.51	0.31	0.70	2265	7018

Names and chemical formulas of corrosion products:

G: $NaZn_4Cl(OH)_6SO_4\cdot 6H_2O$ (Gordaite or zinc chlorohydroxysulfate)
O: $Zn_3O(SO_4)_2$ (Zinc oxysulfate)
HC: $Zn_4CO_3(OH)_6\cdot H_2O$ (Hydrozincite or zinc hydrocarbonate)
HS: $Zn_4SO_4(OH)_6\cdot 4H_2O$ (Zinc hydroxysulfate)
N: $Zn_5(OH)_8(NO_3)_2\cdot 2NH_3$ (Zinc diamminehydroxynitrate)
S: $Zn_5(OH)_8Cl_2$ (Simonkolleite or zinc hydroxychloride)
CS: $Zn_{12}(SO_4)_3Cl_3(OH)_{15}\cdot 5H_2O$ (Zinc(I) chlorohydroxysulfate)

The chemical composition and structure of the corrosion products formed on zinc exposed to the environment in different geographical locations in the Canary Islands up to 2 years were established from the analysis of X-ray diffractograms. Atmospheric conditions at the test sites were characterized in terms of mean pollutant concentrations and time of wetness (ToW), i.e., accumulated values were determined for the exposure times considered. A compilation of the data obtained by XRD analysis and the weather and pollution characteristics from the 25 test sites is given in Table 3. It is clear that the composition of the corrosion product layers developed on the zinc specimens greatly vary depending on the test sites at which they were retrieved, thus supporting that the atmospheric conditions occurring at each location conform a specific corrosion environment. In the following paragraphs, identification of the chemical characteristics of the different surface layers formed on zinc will be performed, and correlations with the local weathering conditions will be attempted.

Hydrozincite (zinc hydrocarbonate, $Zn_4CO_3(OH)_6{\cdot}H_2O$) has been the zinc corrosion product of greatest occurrence in this investigation. It was found after both 1 and 2 year exposures. Generally speaking, this compound exhibits some anticorrosion protection properties [5], and it is thermodynamically stable in both neutral and close to neutrality aqueous solutions [35]. This compound has been frequently reported for zinc exposed to marine atmospheres [16], which certainly is the main environment in an archipelagic location as the Canary Islands. In brief, zinc reacts in a marine environment to form a layer of hydrozincite, though the actual protective characteristics of a given layer may vary from one place to another depending on the amount of pollutants deposited on the metal during the exposure, and the length of time the metal surface remained wet. Furthermore, hydrozincite is an intermediate in the formation of other zinc corrosion products, particularly simonkolleite (zinc hydroxychloride, $Zn_5(OH)_8Cl_2$).

Despite the wide occurrence of hydrozincite among the test sites, there were a few locations at which the formation of this compound did not occur. They exhibited high ToW values as their characteristic factor. As the surface of the metal remains with an aqueous film for rather extended periods, dissolution of hydrozincite, a relatively soluble species in water, is favoured, and chloride ions can replace carbonate ions, resulting in the precipitation of simonkolleite [16,17]. A rather fast phase transformation from hydrozincite into simonkolleite occurs to such extent that hydrozincite may not even be detected in the surface layers formed over the corroded zinc samples. This was the case for the samples retrieved from test sites 1, 3, 5, 6, 7, 11, 12, and 18. Furthermore, hydrozincite was not longer observed after 2-year exposure in test sites 2, 12, and 25 (see Figure 2). In the former case, hydrozincite dissolution might have occurred due to the synergistic combination of high chloride (Cl^-) and sulphate (SO_4^{2-}) ion concentrations, and long ToW, resulting in the enhancement of the anodic half reaction responsible of zinc corrosion. The simultaneous occurrence of these 3 atmospheric conditions has a detrimental effect on the protection of the zinc metal by the surface layer of corrosion products, which become thermodynamically unstable and dissolve in slightly acidic environments. An alternate explanation is that the corrosive atmosphere may be sufficiently aggressive to promote transformations in the precipitated hydrozincite phase. They would be induced by the chloride ions deposited at the interface between the surface layer and the atmosphere. The net effect is that carbonate ions (CO_3^{2-}) are replaced by chloride ions.

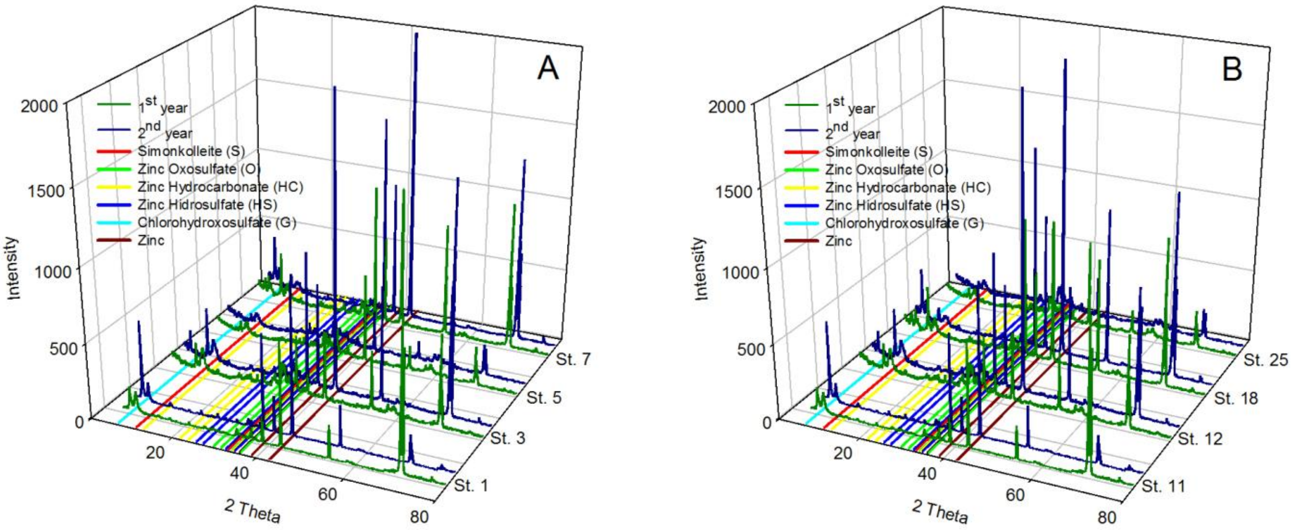

Figure 2. XRD patterns of the zinc samples retrieved after 1 and 2 years exposure in: (A) test sites 1, 3, 5, and 7; (B) test sites 11, 12, 18 and 25.

Neither hydrozincite was detected in the surface layers of the samples retrieved from test site 11 after 1 year, nor from test site 12 after 2 years, nor from test site 2 both after 1 and 2 years. In these locations, weather factors and the amount of pollutants were not high enough as to produce long wetting periods. Rather, drying cycles of the metal surface would be predominant instead. This condition may lead to compactness of the corrosion products, and pollutants might then be incorporated to them when a thin electrolyte layer eventually wets the surface. Complete transformation of hydrozincite to simonkolleite is thus envisaged.

Formation of simonkolleite during the atmospheric corrosion of zinc in rural, marine and industrial environments has already been reported [16-19]. This compound becomes thermodynamically stable when high chloride concentrations are attained in neutral environments [17], and it is formed quickly as result of chloride ion adsorption on the metal surface. Due to the small ionic radius and the elasticity of the chloride ions, they are able to penetrate the hydrozincite layer through pores and defects, where they replace carbonate ions (CO_3^{2-}) to form simonkolleite. The resulting surface layers exert a poor anticorrosion protection to the metal due to their contents in the aggressive chloride ions, as well as their solubility in slightly acidic electrolytes. That is, ionic transport between the anodic and cathodic half cells distributed on the metal surface is enhanced, and the corrosive process is effectively favoured.

The strong influence of the marine environments on the atmospheric corrosion of zinc is indicated by the fact that simonkolleite is found in almost all the test sites after 2 years exposure, the only exceptions being locations 1, 5, and 16. Therefore, chloride ions must be regarded as the main aggressive agent in archipelagic subtropical environments [36]. Yet, the reported exceptions may support the idea of a threshold value for chloride concentration to be overcome for the corrosive attack to be initiated on zinc, likewise to what happens with some other materials [37]. Low chloride deposition rates and ToW values were measured at stations 5 and 16. The situation at test site 1 is somewhat different. In this case, the proposed metastability of simonkolleite proposed by Graedel may hold [7], and this compound might be gradually transformed into less soluble zinc hydroxysulfates.

Zinc oxysulfate ($Zn_3O(SO_4)_2$) was also identified as corrosion product for zinc. Zinc oxysulfates result by decomposition of the metal sulfates. They occur when zinc oxides are acidified by sulfuric acid, and they have also been observed as a secondary reaction of zinc sulphate with existing zinc oxide (ZnO) [38]. Thus, zinc oxysulfate might be an intermediate in the reaction leading to the formation of zinc hydroxysulfate. Zinc oxysulfate was found in the corrosion product layer retrieved from test sites 12, 18, and 19 after 1 year exposure, in locations 2, 13, and 23 both in the first and the second year, and only after 2 years exposure at stations 1 and 25 (cf. Figure 2). Though rather low sulphur dioxide depositions occurred in those locations, excepted sites 1 and 13, the high ToW values may have facilitated the dissolution of the reactive gas SO_2 in the electrolyte and its subsequent transformation to the more stable sulphate ion (SO_4^{2-}). Sulphate ions can thus become the priority electron acceptor leading to an acceleration of the dissolution-precipitation mechanism [17]. Furthermore, nucleation of sulphur-containing corrosion products should be favoured.

Zinc hydroxysulfate ($Zn_4SO_4(OH)_6$) was found in the samples taken from test sites 2, 4, 13, 14, 19, and 23 both years. It was also found in station 12 after 1 year, and in location 8 at the second year. It is known that nucleation of this corrosion product is supported by high ToW values. Yet, the duration of wetness is very small during the first year at station 12 (namely, 274 hours), a fact directly affecting the occurrence of drying and wetting cycles. Precipitation of corrosion products is favoured, which may explain the variety of corrosion products observed in this case. Zinc oxysulfate and zinc hydroxysulfate are both found, though moisture layers are formed on the metal less frequently. On the other hand, zinc hydroxysulfate was observed in the absence of zinc oxysulfate for test site 1 after 1 year, for stations 8, 10, and 19 after 2 years, and for location 14 after 1 and 2 years. An explanation for this observation can be given on the basis of SO_2 occurrence simultaneously to high ToW values and chloride contents. In this way, the dissolution-precipitation mechanism is enhanced, leading to the direct and fast formation of zinc hydroxysulfate.

A mixed chloride-sulphate ionic compound, gordaite (zinc chlorohydroxysulfate, $NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$)) [17,39] was found at test sites 9 and 18 after 1 year, at location 11 after 2 years, and at stations 1 and 12 after both 1 and 2 years. This compound has been reported as the final corrosion product in some long duration atmospheric exposures [40]. Since the metal remains wet for long periods at test sites 1, 11, 13, and 18, the dissolution of zinc oxysulfates and zinc hydroxysulfates may occur. In this context, sodium (Na^+) and sulphate (SO_4^{2-}) ions may be added to simonkolleite leading to the formation of zinc chlorohydroxysulfate. The presence of Na^+ ions in this compound relates to the exposure to a marine environment [16,40]. Conversely, the small ToW values occurring in test sites 2, 9, and 12, originate longer drying cycles instead. Increased compactness and thickening of the surface layers of corrosion products result, and zinc ions (Zn^{2+}) are coordinated to Na^+ and SO_4^{2-} ions to form zinc chlorohydroxysulfate.

Sulphate-free corrosion product layers were obtained in test sites 6, 21, and 24, despite the rather high SO_2 contents and ToW values operating in these locations. Instead, a nitrate-containing compound, zinc diamminenhydroxynitrate ($Zn_5(OH)_8(NO_3)_2 \cdot 2NH_3$) [41], was found. It must be noticed that this compound was also observed in stations 3 and 7, both of them clearly located in a mixed marine and industrial environment. Though this result may seem rather surprising at first, it must be realized that both sulphur- and nitrogen-based compounds are emitted into the atmosphere as result of industrial activities. The aggressive role of NO_2 on the atmospheric corrosion of zinc is still rather controversial. For instance, some studies have reported that the effect of NO_2 becomes relevant only in the case of atmospheres poor in SO_2 [41], because nitrate ions scarcely enter zinc corrosion products under natural exposures [7,16]. Conversely, other works reported considerable amounts of nitrites and nitrates in zinc corrosion products when zinc was exposed to a combination of SO_2 and NO_2 [42-46]. From our own results, it is observed that the reduction of NO_2 by zinc metal may occur under weathering conditions rich in chloride contents and with long times of wetness, without the onset of a synergic effect with SO_2 as suggested by Svensson and Johansson [44]. Likewise, an ionic exchange mechanism may occur on simonkolleite, a porous corrosion product presenting a great number of potential sites for ionic exchange involving ions with the same charge. That is, the nitrate (NO_3^-) ions present in the electrolyte may be exchanged with the chloride ions constituting the porous precipitates, with the formation of zinc diamminenhydroxynitrate [41]. Furthermore, zinc has been shown to fix ammonia from industrial atmospheres [41].

Figure 3. Photographs of the zinc samples retrieved after 2 years from the test sites labelled on the images. For each metal plate, the side directly exposed to the atmosphere (above) as well as the rear surface (below) are shown. Extensive corrosive attack is observed to occur on both sides of the samples.

The remaining corrosion product identified in this work was a mixed salt containing chloride (Cl^-) and sulphate anions (SO_4^{2-}), which was described by Odnevall et al. [17] to be zinc(I) chlorohydroxysulfate ($Zn_{12}(SO_4)_3Cl_3(OH)_{15}\cdot 5H_2O$), a corrosion product exclusively found in urban and industrial environments as result of human activity. This mixed compound was found from samples retrieved at test sites 3, 4, and 7; high chloride depositions and ToW values occurred there, and originated the most aggressive environments for the atmospheric corrosion of zinc encountered in this work. Figure 3 shows the morphology of the samples retrieved from these stations. Severe corrosive attack on zinc is observed on both sides of the samples, which greatly contrast with the less corroded sample retrieved from test site 2. Odnevall et al. [17] reported that the first stage in the process leading to the formation of zinc(I) chlorohydroxysulfate consists in the formation of a zinc hydroxycarbonate, which is followed by the production of a zinc hydroxychloride. Indeed, zinc(I) chlorohydroxysulfate was detected from test sites 3 and 7 in combination with simonkolleite, whereas at test site 4 both simonkolleite and zinc hydroxysulfate were detected. In summary, the characterization of the corrosion products retrieved from test sites distributed over the islands of Gran Canaria, Fuerteventura, and Lanzarote, shows that their composition and their corrosion protection characteristics greatly depend on the amount of pollutants (namely chloride ions and SO_2), and the time of wetness (ToW), existing at the specific locations. From a qualitative standpoint, the widest variety of corrosion products in the surface layers formed on zinc was found from test sites 2, 4, 13, and 23. This situation results from the accumulation of dissolution-precipitation processes triggered at the metal surface by the weathering factors. Conversely, locations 1, 5, 6, 15, 16, 17, 18, 20, 22, and 25, exhibit the smallest variation of corrosion products. High ToW values are found, resulting in uncompensated drying and wetting cycles. Zinc dissolution prevails over product precipitation during these long wet periods. On the other hand, during the drying cycles, corrosion products become dehydrated and cracks are formed on their surface, which allow both atmospheric pollutants to penetrate in the surface layers, and the uptake of water from the humid air in the case of hygroscopic species as the chlorides. The corrosive attack can thus progress in the metal samples.

4. CONCLUSIONS

Simonkolleite ($Zn_5(OH)_8Cl_2$), and hydrozincite ($Zn_4CO_3(OH)_6\cdot H_2O$), are the main corrosion products occurring in the atmospheric corrosion of zinc exposed to archipelagic subtropical environments. These two compounds are usually found in marine atmospheres.

Zinc oxysulfate ($Zn_3O(SO_4)_2$), and zinc hydroxysulfate ($Zn_4SO_4(OH)_6$), were also found. These compounds result from the combined effect of a rather low rainfall and a high solubility of SO_2, which favours the nucleation of corrosion products containing sulphate ions. The formation of a mixed ionic compound containing sulphate and chloride ions, namely gordaite ($NaZn_4Cl(OH)_6SO_4\cdot 6H_2O$), is also reported.

Finally, zinc diamminehydroxynitrate ($Zn_5(OH)_8(NO_3)_2\cdot 2NH_3$) was found in test sites placed in the proximity of both electric power stations and airports. This corrosion product may have resulted from the migration of nitrate ions and ionic exchange in simonkolleite.

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