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Corrosion of Copper in a Tropical Marine Atmosphere Rich in H_2S Resulting from the Decomposition of *Sargassum* Algae

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Abstract: The atmospheric corrosion of copper exposed in Martinique (Caribbean Sea) for 1 year was reported. This island suffered the stranding of *sargassum* algae, which decompose and release toxic gases such as hydrogen sulfide (H_2S) or ammonia (NH_3). Four sites in Martinique (France) more or less impacted by *sargassum* algae strandings were selected. The corrosion rate was studied via mass loss determination. The morphology and properties of the corrosion products were determined using Scanning Electron Microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The samples were exposed for up to 12 months. The mass loss results after 1-year exposure were from 4.8 µm for the least impacted site to 325 µm for the site most affected by *sargassum* algae. This very high value proves that the presence of *sargassum* algae caused a significant degradation of copper. The morphological structures and properties of the corrosion products obtained at the impacted and non-impacted sites differed significantly. In the absence of *sargassum* algae, classical corrosion products of copper were reported such as Cu_2O and $Cu_2Cl(OH)_3$. In the sites near the stranding of the *sargassum* algae, the CuS product is the main corrosion product obtained, but copper hydroxylsulfate is created.

Keywords: atmospheric corrosion; *sargassum* algae; corrosion of copper; H_2S; SEM/EDS; XRD

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1. Introduction

Copper is a noble metal effectively utilized for its high electrical and thermal conductivities in many applications (communication, electronic/electrical components, construction, etc.) [1]. The atmospheric corrosion of copper is an electrochemical process that mainly depends on the relative humidity in the atmosphere and the presence of pollutants. Indeed, the water in the atmosphere may condense and form a liquid film on the surface, facilitating interactions between the metal and corrosive pollutant [2,3]. The atmospheric corrosion of copper has been the subject of numerous studies in several regions of the world [4–13]. These works have shown that whatever the type of atmosphere (rural, urban or marine), the copper corrosion layer is initially composed of Cu_2O cuprite or a Cu_2O/CuO duplex (CuO tenorite) [14,15]. In a purely marine atmosphere rich in chlorides, copper chloride CuCl (nantokite) is initially formed on the Cu_2O, and then, $Cu_2Cl(OH)_3$ appears, which exists in several crystalline forms [12,16,17]. The corrosion rate of copper is usually estimated at a few µm the first year. However, the presence of pollutants in the atmosphere can change the behavior of the corrosion layer and accelerate the corrosion process [18].

Martinique, located in the center of the Caribbean Sea, has a harsh tropical marine climate. The relative humidity is very high with an average of 75%. Temperatures are constant all year round with an average of 30 °C. These climatic conditions have always been favorable to corrosion [19]. However, in recent years, the tons of *sargassum* algae washing up and decomposing on its shores have mainly resulted in the release of toxic gases such as hydrogen sulfide (H_2S) or ammonia (NH_3). The strong impact of this pollution on human heath was recently reported [20]. Moreover, since the intensification of this phenomenon, the abnormally premature degradation of electronic devices has been reported. Several studies have already been carried out on the atmospheric corrosion of copper in the presence of H_2S alone under indoor conditions with controlled parameters (concentration, temperature, humidity, etc.) and the corrosive aggressiveness of these gases towards copper has already been demonstrated [21–26]. Moreover, to date, no study has been carried out on the corrosion of copper by H_2S in a marine atmosphere, and even less so in the presence of decomposing *sargassum* algae.

In this work, we were interested in the corrosion process of pure copper in a marine atmosphere polluted by gases emanating from the decomposition of *sargassum* algae to specifically determine the role of H_2S/chloride ion coupling. Copper was exposed to different environmental conditions on the island of Martinique under outdoor conditions. To realize this study, four sites more or less impacted by *sargassum* algae strandings were selected. The samples were exposed for up to 12 months. The corrosion process was examined using the gravimetric method. The corrosion products were characterized via X-ray diffraction and via Scanning Electron Microscopy coupled with energy-dispersive X-ray spectroscopy.

2. Materials and Methods

2.1. Selection of Sites, H_2S and Chlorides Ion Measurement Techniques

Selection sites: Four sites were selected for this study: Vert pré, Diamant, Vauclin and Frégate est. Figure 1a presents the positions of the sites on the map of Martinique. The atmosphere at these sites is considered as marine (high chloride ion concentrations) with different distances from the seashore. The temperature and relative humidity at these sites were homogeneous and very high (evaluated between 25 °C and 35 °C and 75%, Table S1) due to the geographical position of Martinique. So, the time of wetting (TOW) that governs copper corrosion was essentially the same at the different sites. We can also note that the dominant winds in Martinique are northeast, east and southeast. *Sargassum* algae stranding is effective in the southeast coast near Fregate est site. Given their distance to the coast and the quantity of *sargassum* seaweed washed ashore, the sites can be ranked from the most to the least impacted by the H_2S resulting from the decomposition of *sargassum* algae: Vert pré, Diamant, Vauclin and Frégate est.

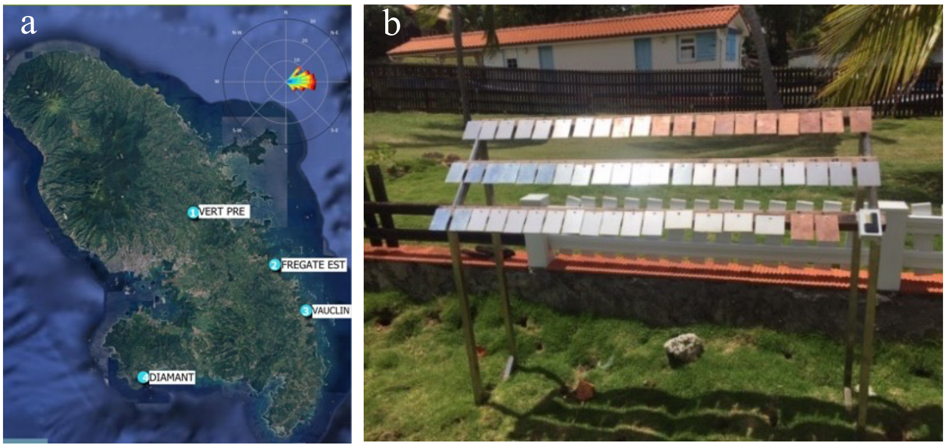

Figure 1. Positions of the different sites studied on the map of Martinique (**a**), exposition desks (**b**).

H_2S measurements: The measurement of hydrogen sulfide (H_2S) was carried out using the Cairpol microsensor system (Envea company, Poissy, France), as presented in the Supplementary Information (Figure S1). This consisted of a GPRS module, Cairnet, coupled to a pair of sensors, Cairsens (located inside the Cairnet). It allowed for the continuous real-time measurement of pollutant concentrations such as hydrogen sulfide. As each device was autonomous, the minute data were transmitted remotely every ten minutes to a database that centralized all the measurements made by the network. These devices constituted the fixed *sargassum* algae network and permanently monitored the concentrations of gases emitted by the putrefaction of algae in real time.

Chloride ion measurement: Sampling was carried out in accordance with the NF X 43-014 standard. The samples were taken using a cylindrical Owen-type plastic collector of sufficient height to avoid sample loss. It was equipped with a funnel with a diameter that was known precisely in order to evaluate the atmospheric deposition in mg/L. Samples were collected every 30 days for analysis.

2.2. Sample Preparation

The copper samples used in this study were 99.9% pure (100 mm × 70 mm × 1 mm). Prior to exposure, all copper samples were mechanically polished with 1200-grade SiC, rinsed with distilled water, dehydrated with ethanol, air dried and then weighed to the nearest 10^{-4} g in an Adam Nimbus 210-001 microbalance and stored in a desiccator. The copper samples were exposed to outdoor atmospheric conditions on inclined desks at 45 °C according to EN13523-19 [27]. Figure 1b shows the samples installed in the selected sites. Samples were collected after 3, 6, 9 and 12 months of exposure.

2.3. Gravimetric Measurements

The mass loss technique was used to assess the corrosion rates of the metal. The mass loss was the difference between the initial mass of the sample before exposure and its mass after exposure and the removal of corrosion products. Copper corrosion products were removed according to ISO 8407 [28]. Before any chemical treatment, the surfaces of the copper samples were mechanically brushed to remove loose corrosion products. The samples were then immersed in a sulfuric acid solution (100 mL in 900 mL of distilled water) for 1–3 min at 20–25 °C. The treatment was carried out in an ultrasonic bath to optimize the process. The samples were then rinsed with distilled water and ethanol and air-dried before being weighed to determine the lost mass. This process was repeated several times for each sample until a mass plateau was reached. The mass loss was calculated for each period and each exposure site from a triplicate of samples. The thickness loss was deduced from these measurements.

2.4. Characterization and Identification of the Corrosion Products

The morphological and chemical analyses of the corrosion products were carried out, respectively, via scanning electron microscopy (SEM, S800, Hitachi, Tokyo, Japan) and via energy-dispersive X-ray spectroscopy (EDS). Crystallographic studies of the Cu corrosion products were conducted by means of X-ray diffraction (XRD) using PANalytical Empyrean apparatus with CuKα radiation (1.5408 Å) [29].

3. Results

3.1. H_2S and Chloride Ions Measurements

The concentrations of H_2S and chlorides in the atmosphere at the different sites were measured continuously during the copper exposure period. Figure 2 shows the variation in the monthly average H_2S and chloride ions concentrations in the different sites. The H_2S concentration in Diamant and Vert pré sites was weak near 10 ppb due to the remoteness of the *sargassum* algae stranding areas. On the other hand, in Frégate est, where *sargassum* stranding was observed, the H_2S concentration was very high, at about 2–3 ppm. During the period, no strong seasonal evolution was reported, indicating the presence of algae during the year, except maybe in month 5. In Vauclin, the impact of algae decomposition was less important, with an annual average of 0.2 ppm.

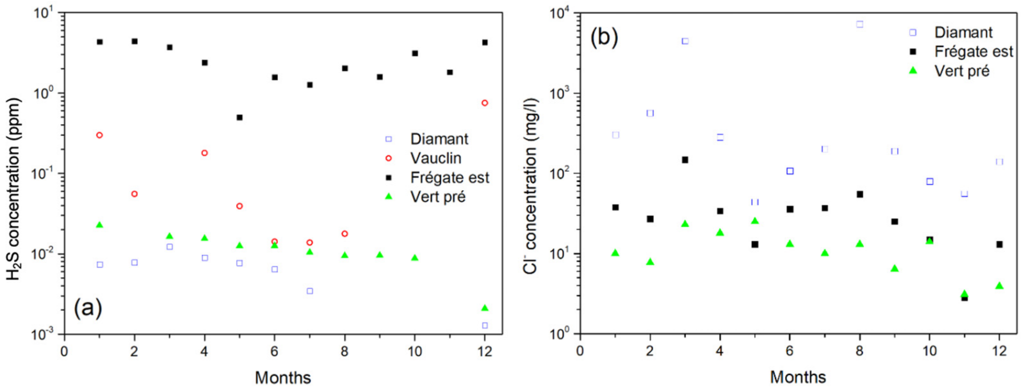

Figure 2. Monthly average concentration of H_2S (**a**) and chloride (**b**) in different sites during 1 year.

Concerning the chloride concentration, the Diamant site (25 m from seashore) presented a very high value due to the rough seas, leading to the suspension of spray rich in sodium chloride. The low concentrations in Fregate est and Vert pré can be explained by the wind direction and the distance to the sea, respectively. So, the corrosion process has to be governed by H_2S emissions in Fregate est and by classical marine atmosphere in Diamant/Vert pré. Due to technical problems, no data on chloride were extracted from the Vauclin site. However, we may suppose that the values would have been similar to those measured in Frégate est.

3.2. Determination of the Corrosion Rate after 1-Year Exposure

The corrosion rate was determined after 1-year exposure by measuring the copper thickness loss for each site. Firstly, the mass loss was obtained by calculating the difference between the initial mass of the sample and the mass of the exposed sample after the removal of corrosion in the products. The thickness loss corresponded to the mass loss divided by the sample surface and the copper density.

The values obtained for Vert pré, Diamant, Vauclin and Frégate est were 4.8, 20, 60 and 325 µm, respectively. These values are high compared to the literature [11,13]. The MICAT project measured the 1st-year corrosion rate in many sites in South America, Spain and Portugal including different atmospheres: rural, marine, urban/industrial and mixed; the copper corrosion rate values were between 0.09 and 7.1 µm [11]. Our high values can be explained by the tropical climate of Martinique but also by the short distance from the sea (few meters to few km) and so by the high concentration of pollutants. Since the corrosion rates exceeded the upper limits of the CX class, these atmospheric environments are considered extreme.

The corrosion rate reported in Vert pré corresponded to a classical value in a marine tropical atmosphere (5 km from the sea). The higher measured rate in Diamant could be correlated to the very short distance to the seashore. The corrosive aggressiveness of the atmosphere at this site was high due to an intense aerosol of chlorides from the sea winds [12,30], as shown in Figure 1b.

The values measured in Vauclin and Fregate est were very high even for a marine tropical environment. To our knowledge, there is no equivalent values in the real atmosphere in the literature. However, these values are consistent with the severe corrosion of electronic cards observed by people living near these sites. These values can be correlated to the concentration of H_2S (see Figure 1a), the aggressive behavior of which is well known [22,24].

3.3. Evaluation of Copper Thickness Loss Dynamics

To understand the corrosion process, copper thickness loss was measured every 3 months of exposure in all sites. Figure 3 shows the copper thickness loss from 3 to 12 months of exposure. The values measured in the Diamant and Vert pré sites are presented in Figure 3a, whereas those of Frégate est and Vauclin are in Figure 3b. Their thickness loss evolution was not linear: the corrosion rate decreased with the exposure, indicating the protective nature of the corrosion products on the surface.

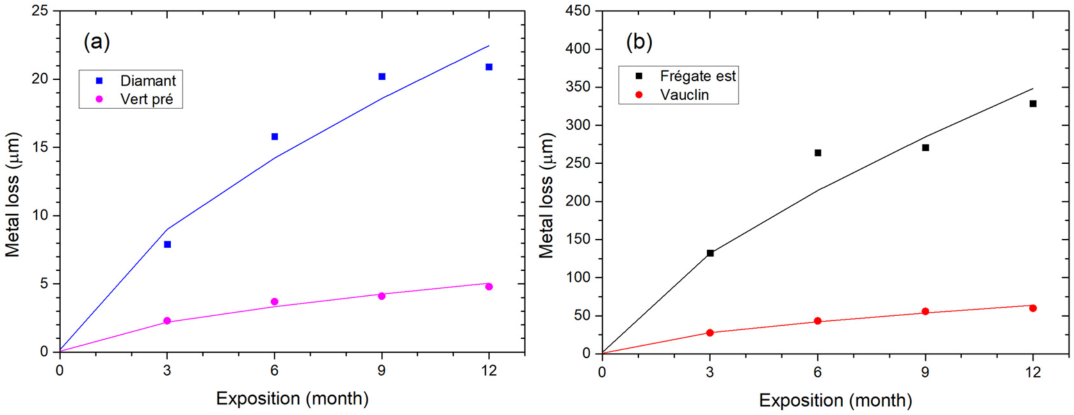

Figure 3. Thickness loss of copper exposed in 4 sites: Diamant/Vert pré (**a**) and Vauclin/Frégate est (**b**) for 12 months.

The experimental data were fitted by the well-known power model [18]. Classically, the constant is the amount of the corrosion after 1 year. Our fits were obtained with an exponent n of 0.66 for all the sites in agreement with previous studies on copper [18,30]. This result shows that the corrosion dynamic only depends on the material, no matter the environment. These values, in agreement with the literature [18], confirm the protective nature of the corrosion products of copper. Note that no impact of the season is reported given the climate of Martinique.

3.4. SEM/EDS Analysis

To understand the corrosion process, the corroded surfaces were analyzed via SEM/EDS techniques in complement to the gravimetric measurements. Surface photographs (SEM) at 3, 6, 9 and 12 months of exposure in the different sites are presented in Figure 4. In Vert pré, the morphology of the surface changed slowly during the exposure: the corrosion products weakly affected the morphology. This observation is in agreement with the reported low metal loss value. In Diamant, the same behavior was observed with an increase in the corrosion rate.

The SEM pictures of Vauclin and Fregate est show severe modifications of the surfaces: the surfaces present non-homogeneous granular aspects. Some cracks appeared through the pictures. The irregularity seemed to increase with exposure time. The result was non-compact, rough structures with elevations and depressions, which prevented, to some degree, the formation of protective films in agreement with previous results in Rapa Nui [31]. The existence of different corrosion products could explain the differences observed in the different sites in mass loss and morphology.

To determine the composition of the corrosion products, EDS analysis was performed to obtain a quantitative analysis after 12 months of exposure, and it is summarized in Table 1. The main presence of copper, oxygen, chloride, carbon and sulfur was reported in the corroded surfaces. The data extracted from the Vert pré and Diamant sites were almost similar: they presented a clear domination of oxygen content. This corresponded to the presence of oxide, hydroxide or carbonate species. Carbon species were also reported. The presence of chloride in the corrosion products was clearly due to the marine atmosphere.

The presence of sulfur could be explained by H_2S emissions after *sargassum* stranding. All the observations (gravimetry, SEM and EDS) were consistent with the tropical marine atmosphere with low pollutant contamination in both sites.

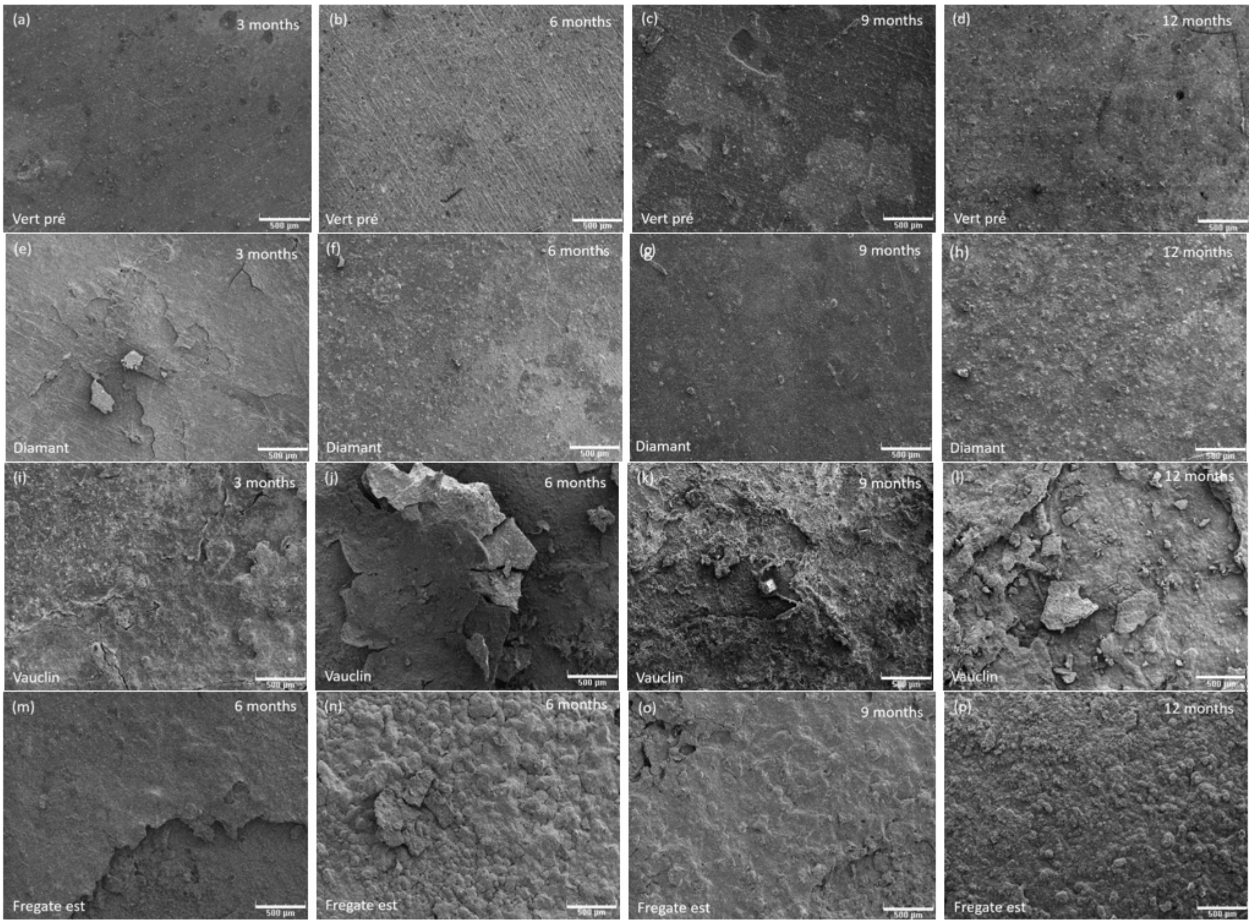

Figure 4. SEM images after 3, 6, 9 and 12 months of exposure in Vert pré (**a**–**d**), Diamant (**e**–**h**), Vauclin (**i**–**l**) and Fregate est (**m**–**p**). The scale bar corresponds to 500 µm.

Table 1. EDS elemental composition in Vert pré, Diamant, Vauclin and Fregate est after 1 year of exposure (atomic percentage).

	Cu	O	Cl	S	C	Si	Mg	Al	Ca	Fe
Vert pré	34.4	48.9	6.6	0.8	7.0	0.8	0.6	0.7	0.1	0.1
Diamant	22.6	57.6	6.0	0.7	7.6	0.3	3.5	0.5	1.0	0.2
Vauclin	28.5	33.7	1.9	15.1	17.7	1.5	0.3	0.8	0.1	0.4
Frégate est	28.1	36.4	1.6	22.4	7.6	2.5	0.2	1.0	0.0	0.2

The EDS data measured in Vauclin and Fregate presented similar values. The chloride and oxygen contents were clearly lower than the previous values. On the other hand, the values of sulfur atoms were very high, showing its presence in the corrosion products. This is consistent with the high corrosion rates of the copper induced by H_2S gas emitted by *sargassum* stranding. The corrosion process seems to be governed by sulfur rather than chloride. In the Fregate est site, the sulfur value was higher: this can be explained by the very high concentration of H_2S measured in this site (shown Figure 1a) and so the extreme corrosion rate reported via gravimetry.

3.5. XRD Analysis

The characterization of corrosion products formed on the surface was performed via XRD. Figure 5 presents the XRD results of all sites after 1-year exposure. As shown previously, two cases could be distinguished according to the atmosphere containing or not containing sulfur. In Vert pré and Diamant, the XRD diffractograms were dominated by Cu_2O cuprite. This result is in agreement with previous works in atmospheric conditions, which showed that cuprite is the initial component of the corrosion products [11]. Indeed, the corrosion of copper in the atmosphere takes place once an aqueous layer has formed on the surface as a result of rainfall and condensed humidity. The possible anodic and cathodic reactions would, in principle, be as follows [31]:

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{+} + \mathrm{e}^{-} \tag{1}$$

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+} + 2\mathrm{e}^{-} \tag{2}$$

$$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^{-} \rightarrow 4\mathrm{OH}^{-} \tag{3}$$

The formation of cuprite takes place according to the overall reaction:

$$2\mathrm{Cu}^{+} + 2\mathrm{OH}^{-} \rightarrow \mathrm{Cu}_2\mathrm{O} + \mathrm{H}_2\mathrm{O} \tag{4}$$

The second corrosion product reported in the XRD data was atacamite ($Cu_2Cl(OH)_3$), which is observed in chloride atmospheres [11,12,32]. Its formation can be obtained following the reactions with chloride [32,33]:

$$2\mathrm{Cu} + 2\mathrm{Cl}^{-} + 3\mathrm{OH}^{-} \rightarrow \mathrm{Cu}_2\mathrm{Cl}(\mathrm{OH})_3 + 4\mathrm{e}^{-} \tag{5}$$

$$2\mathrm{CuCl}^{-} + \frac{1}{2}\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{Cu}_2\mathrm{Cl}(\mathrm{OH})_3 + \mathrm{H}^{+} + 3\mathrm{Cl}^{-} \tag{6}$$

Structures attributed to metal copper were also reported. This indicated that at some points, the corrosion layer was thinner than the depth of analysis, which was approximately 1 μm. This could be explained by a partial leaching of corrosion products with the rain. Note that copper peaks were less intense in Diamant; this can be explained by the higher corrosion rate due to the proximity of the sea. This was consistent with the EDS data presented Table 1. Note that the high oxygen values associated with the carbon could be explained by amorphous carbonates. No tenorite (CuO) was observed because of its instability. However, the observed corrosion products were rather usual in marine atmospheric corrosion [33]. The corrosion products observed via XRD were consistent with the EDS data. So, to summarize, it can be concluded that the corrosion process was of the same nature for both sites: tropical marine corrosion. The corrosion rates differed due to the distance from the seashore.

Figure 5d shows an XRD diffractogram corresponding to a sample exposed in Fregate est; it was clearly dominated by structures attributed to covellite (CuS). This observation was consistent with the high level of H_2S concentration measured at this location. Based on the literature [34,35], a two-step dissociation of H_2S into S^{2-} ions could lead to the formation of CuS by reacting with Cu^{2+} ions, and the following pathway was proposed with equations:

$$\mathrm{Cu} \rightarrow \mathrm{Cu}^{+} + \mathrm{e}^{-} \tag{7}$$

$$\mathrm{H}_2\mathrm{S} \rightarrow \mathrm{H}^{+} + \mathrm{HS}^{-} \tag{8}$$

$$2\mathrm{HS}^{-} \rightarrow 2\mathrm{S}^{-} + \mathrm{H}_2 \tag{9}$$

$$\mathrm{Cu} + \mathrm{H}_2\mathrm{S} \rightarrow \mathrm{CuS} + \mathrm{H}_2 \tag{10}$$

The existence of copper sulfide in corrosion products in an H_2S atmosphere has already been observed [23,30]. In a recent study in a controlled H_2S atmosphere [24], it has been shown that Cu_2S and/or CuS can exist at different H_2S concentrations. It seems complicated to predict whether Cu_2S or CuS may be formed by atmospheric corrosion since they are both considered as sulfide copper. However, this finding can be explained by the transformation of the corrosion product Cu_2S to CuS following Equation (11), as suggested by Zaafarany et al. [36]:

$$Cu_2S + S^{2-} \rightarrow 2CuS + 2e^- \quad (11)$$

This reaction could indeed be possible regarding the very high concentration of H_2S in atmosphere found at Frégate est, inducing the high probability of S^{2-} ions being present in solution. This would then suggest that the nature of the formed corrosion product is directly impacted by the concentration of H_2S in the atmosphere. However, another corrosion product was reported: copper sulfate pentahydrate $Cu(SO_4).5H_2O$. This results from the oxidation of $CuSO_3$ in a sulfate atmosphere [2]. These observations are in agreement with the EDS data. One should note that chloride and carbonate species can exist in amorphous phases.

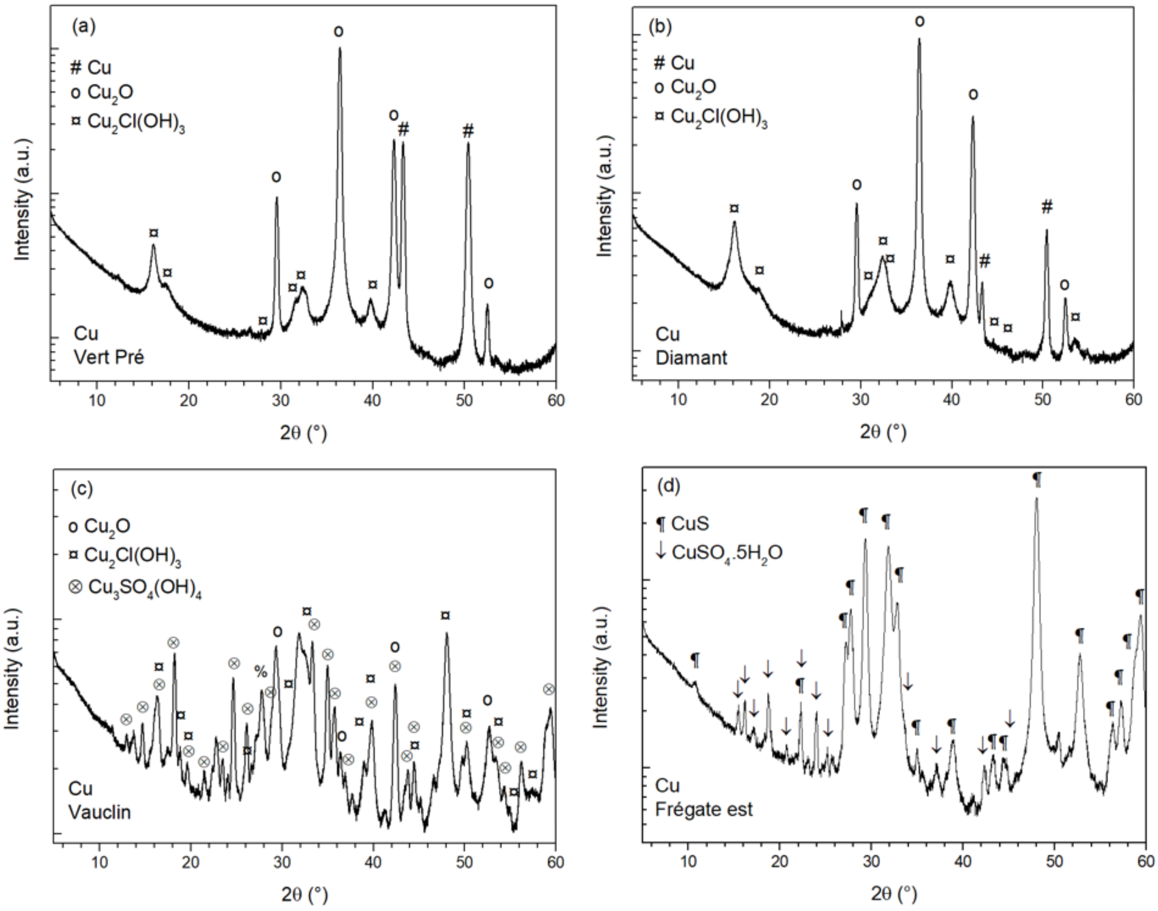

Figure 5. XRD diffractograms of copper samples exposed for 12 months in Vert pré (**a**), Diamant (**b**), Vauclin (**c**) and Frégate est (**d**).

Note that Cu_2O and $Cu_3(OH)_4SO_4$ were present in minor proportions after 3 months of exposure (Figure S2). According to Zittlau et al. [37], the formation of $Cu_3(OH)_4SO_4$ is made possible by the interaction between Cu^{2+} ions and sulfate/hydroxide in the aqueous ad-layer to form antlerite, as described in Equation (12). The presence of sulfates ions in this aqueous ad-layer can be the result of H_2S oxidation via dissolved O_2, forming H_2SO_4 [38].

$$3.Cu^{2+} + SO_4^{2-} + 4OH^- \leftrightarrows Cu_3(OH)_4SO_4 \tag{12}$$

All of these observations confirm the strong impact of *sargassum* stranding in Martinique, which increases the corrosion rate and drastically modifies the corrosion products. The modification of the corrosion products may be also due to the washing via the precipitations.

The XRD diffractogram corresponding to sample exposed for 12 months in Vauclin presented in Figure 5c shows many peaks with similar intensities. The cuprite and atacamite were reported as in the Diamant and Vert pré sites. This can be explained by the classical marine atmosphere. However, antlerite ($Cu_3SO_4(OH)_4$) species were reported. Following the results of Krätschmer [33], its formation is possible after exposure lasting several months. In a high sulfur/sulfate atmosphere, copper is initially transformed to cuprite; then, after days or weeks of exposure, amorphous copper sulfate is formed, followed by the formation of hydroxysulfate species such $Cu_{2.5}SO_4(OH)_3$ and $Cu_4SO_4(OH)_6$. Finally, in a high-sulfur-concentration atmosphere, antlerite can be formed, as observed in Vauclin. This is in agreement with the high content of sulfur measured via EDS.

Moreover, XRD diffractograms corresponding to other exposures presented additional corrosion products, as seen in the Supplementary Information. CuS was clearly present at 3 and 6 months of exposure, as observed in Fregate est, and was attributed to H_2S pollution. In the corrosion products reported during 3, 6 and 9 months, another peak observed at 11.8° could be attributed to $CuClN(CH_3)_4$. It could have been formed by the interaction with chloride and ammonia coming from *sargassum* degradation. It is worth noting that despite the relatively similar atmospheres in Vauclin and Frégate est at first sight (marine environments impacted by sargassum stranding), the resulting corrosion products were different. This could be explained by a combined effect of both corrosions in Vauclin: marine corrosion for one part, and corrosion under H_2S for the other part. This would explain the variety of corrosion products and the strong corrosion rate found. However, this was due to the fluctuation of the H_2S concentration during the year, due to the periodic strandings of *sargassum* algae.

4. Conclusions

This study reveals that *sargassum* seaweed strandings have a considerable impact on the kinetics and morphology of copper corrosion through the release of H_2S. Indeed, samples placed in an atmosphere without significant *sargassum* algae stranding showed the formation of classical corrosion products (Cu_2O and $Cu_2Cl(OH)_3$) and a corrosion rate close to that observed in a tropical marine atmosphere. However, samples placed in a marine atmosphere strongly impacted by *sargassum* seaweed stranding (presence of H_2S) presented very high corrosion rates. The corrosion layer formed was essentially composed of CuS, but the existence of hydroxylsulfate was reported.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/met13050982/s1, Figure S1: Photograph of Cairpol sensor system; Figure S2: XRD patterns obtained for samples exposed in Diamant, Vert pré, Vauclin and Frégate est from 3 to 9 months; Table S1: Monthly average Humidity Rate (%) during the experiment.

Author Contributions: Conceptualization, M.L. and C.R.; methodology, M.S.A., M.L., C.R., B.L. and S.R.; software, M.S.A.; validation, M.L.; formal analysis, M.S.A., M.L.,B.L., S.R. and J.P.; investigation, M.S.A., M.L.,B.L., S.R., O.A. and C.B.; resources, C.R.; data curation, M.S.A.; writing—original draft preparation, M.S.A., M.L., B.L. and S.R.; writing—review and editing, M.S.A., M.L., B.L. and S.R.; visualization, M.S.A. and M.L.; supervision, M.L. and C.R.; project administration, C.R.; funding acquisition, C.R. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are openly available in a public repository.

Conflicts of Interest: The authors declare no conflict of interest.

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