APPLICATION OF DIFFRACTION PEAK PROFILE ANALYSIS TO STUDY THE FORMATION OF ZINC PRODUCTS IN THE INITIAL CORROSION STAGES.

P. Quintana, L. Veleva and L. Baños*


ABSTRACT

Zinc flat sheet specimens were exposed at two different corrosion atmospheres: marine and rural-urban, in a humid tropical climate of the Peninsula of Yucatan, Southeast Mexico. The test plates were exposed on racks with an inclination of 45° with the horizontal, facing to the sea. The corrosion product characterization was made by X-ray diffraction after 1, 3, 6, 9 and 12 months. The semi-quantitative evaluation was applied on the highest diffraction maxima of the formed phases using a fitting profile program.

The identified phases were, namely: zincite (ZnO), zinc hydroxychloride (also known as simonkolleite, Zn$_5$(OH)$_8$Cl$_2$·H$_2$O); zinc chlorohydroxysulfates (NaZn$_4$Cl(OH)$_6$SO$_4$·6H$_2$O; Zn$_4$Cl$_2$(OH)$_4$SO$_4$·5H$_2$O) and various types of zinc hydroxysulfates (as: ZnSO$_4$·3Zn(OH)$_2$·xH$_2$O where x = 1 to 5).

The variations in the relative proportions of the formed phases had a strong dependence on the changes of the content of the main pollutant such as SO$_2$ and chlorides, as well as on the rainy and dry seasons during the annual exposure time.

We present the formation and transformation of corrosion products with time of exposure and a schematic description of the phase sequences formed in this type of environments. The development of the phases showed good agreement with the corrosion rates of zinc in the studied atmospheres.

INTRODUCTION

The excellent resistance of zinc to atmospheric corrosion under natural conditions is largely responsible for the many and varied applications of the metal. In many tropical environments zinc is used in the form of galvanized sheet, as in flashings on roof, as die castings and as a coating on steel, either hot dipped or electroplated. In fact, nearly half the world consumption of zinc is in the form of coatings for the prevention of corrosion of steel exposed to the atmosphere and to water.

The high degree of zinc resistance to atmospheric corrosion, is due to the formation of a protective corrosion layer of zinc oxide and hydroxides of various basic salts. When this layer has formed and completely covers the metallic surface, corrosion proceeds at a greatly reduced rate. Environmental conditions that interfere with formation of such films may attack zinc quite rapidly. The most important factors that control the corrosion rate of zinc exposed to the atmosphere are: humidity, temperature (especially between daily variation that promotes condensation or evaporation of moisture and dryness), the frequency of rainfall and dew, the acidity of the atmosphere and the amount of air-borne salinity.

In dry air, zinc is slowly attacked by atmospheric oxygen. A thin, dense layer of oxide is formed on the zinc surface, and a porous outer layer forms on top of it. Although the outer layer
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breaks away occasionally, the thin underlayer remains and protects the metal by restricting its interaction with oxygen. Under these conditions, which occur in some inland tropical climates, zinc oxidizes very slowly. The rate of drying is also an important factor because a thin moisture film with a high oxygen concentration promotes corrosion [1-3].

In coastal areas the rate of corrosion may increase somewhat by the air contaminated with water containing considerable amounts of dissolved salts, mainly NaCl but also MgCl₂ and CaCl₂, which are present in marine atmospheres. Nonetheless, the corrosion rates are much lower than those prevailing in the heavily polluted industrial areas [1,4].

In the tropics, a great condensation occurs at high temperatures (25-30°C) therefore the corrosion of zinc is rapid, particularly in the absence of the washing effect of heavy rains. A white rough layer of corrosion products forms on the surface and when it is contaminated by chlorides tends to be hygroscopic and to retain a very reactive moisture film. During the anodic oxidation, metallic zinc transforms into zinc oxide. In some cases, this film appears to be slightly alkaline due to the cathodic partial corrosion reaction (between water, oxygen and zinc) which forms zinc hydroxide. At other times, it appears slightly acidic with atmospheric carbon dioxide (CO₂) which leads to the formation of basic zinc carbonate, with a soluble bicarbonate ion. Its presence on the surface depends on duration of the wet-dry cycles. In the absence of acidic deposition and marine influences, the atmospheric corrosion of zinc involves the formation of zinc oxide or zinc hydroxide [4-6].

In non-polluted environments, in the absence of acidic deposition, zinc hydroxide or zinc carbonate, can dissolve in precipitation and they are washed away from the surface. When acidic species are present in wet or dry deposition basic zinc corrosion occurs. A soluble salt, such as zinc sulfate, which can be washed from the metal surface is the product of this reaction [6]. It has been reported [7,8] that in the rural atmosphere, characterized by low levels of sulfur containing species (mainly SO₂ and (NH₄)₂SO₄) and insignificant chloride deposition, the corrosion sequence can be divided in two steps. The first step involves the formation of zinc hydroxy carbonate (hydrozincite) and in the second step, zinc hydroxysulfate appears, which is the final corrosion product in this specific atmosphere. In the marine atmosphere the principal pollutants are species containing chloride (mainly NaCl) but the sulfur containing species such as Na₂SO₄ and SO₂ also influence the corrosion behaviour. The corrosion sequence at the marine region can be divided into three steps. Within minutes and hours a zinc hydroxy carbonate forms on the surface by the formation of zinc hydroxychloride (simonkolleite) which appears within days. The last step is the formation of sodium chlorohydroxysulfate (NaZn₄Cl(OH)₆SO₄·6H₂O) within weeks of exposure [9,10].

The atmospheric corrosion of zinc has been widely studied in laboratory and field exposures [2]. However, research based on semi-quantitative X-ray diffraction data of the corrosion products of zinc formed in a tropical humid climate correlated with the atmospheric corrosion rate, has not been published.

EXPERIMENTAL PART

Field exposure corrosion tests were conducted at several sites, which are located in the Peninsula of Yucatan, characterized by a tropical humid climate. Several of them were located in the coastal Caribbean region and the rest were inland at different distances from the seashore. We will present the results obtained in two regions with different type of atmosphere: a marine one, Puerto Morelos (specimens were placed at 30 m from the seashore) and a rural-urban, Merida (located 30 km from the coast).
Zinc electrolyte flat specimens (150x100x1 mm) were exposed to the open-air atmospheric corrosion test according to ISO 8565 [11], during 1, 3, 6, 9 and 12 months on racks facing to the sea (North- North East) with an angle of inclination of 45° with the horizon. The corrosion rates of the specimens were determined by the gravimetric method according to ISO 9226 [12], as an average of three specimens in each exposure period.

A register atmospheric and aerochemical parameters (daily and monthly, respectively) in the rural-urban and marine environments were monitored during the exposure period. The annual average temperature in these areas is 26°C and the average relative humidity (RH) is 80%. The annual time of wetness is about 8500 (for Puerto Morelos) and 4800 h/year (for Merida) with a rainfall precipitation of 550 and 1284 mm/year, respectively. The dominant annual wind directions are NE and sometimes E in the rainy season. The presence of high hygroscopic pollutants such as chlorides (288.22 and 10.21 mg/m²d) and SO₂ (3.78 and 4.20 mg/m²d) for the marine and rural-urban atmospheres respectively, accelerates the development of the corrosion process.

Small samples of 20x20x1 mm were cut from the central part of the corroded plates to analyze the phases formed in the corrosion products. The characterization was made directly on the skyward surface of the specimens with a Siemens D5000 diffractometer with Bragg-Brentano geometry (monochromatic radiation, Cu Kα₁, λ=1.5405 Å). The tube voltage was 35 kV and the current, 30 mA. The qualitative analysis of the diffractograms was made with the software Diffrac AT and the identification of the phases with the data base PDF-1 and PDF-2 [13,14].

Due to the large amount of samples to be evaluated, it was initially considered to carry out a high register rate (step time of 0.3 sec and step size of 0.01°, i.e. 2°/min), Fig.1, and the main phases detected were simonkolleite (S = Zn₅(OH)₈Cl₂·H₂O) and zinc sodium chlorohydroxysulfates (N= NaZn₄Cl(OH)₆SO₄·6H₂O). However, in the register diffractograms, it was not possible to distinguish the main diffraction maximum between metallic zinc and zinc oxide (Z = ZnO, zincite) formed from the initial corrosion stages on both test sites (Fig. 1).

![Fig. 1. X-ray diffraction pattern of corroded zinc plate, in a marine test site after three months of exposure. Zn = zinc; Z = zincite; N = sodium zinc chlorohydroxysulfate and S = simonkolleite.](image)

At the same time, electrochemical studies were carried out as potenciostatic cathodic reduction and the analysis of the polarization curves showed the presence of small amounts of other phases that were not initially detected by X-ray diffraction [15]. Therefore, it was necessary to change to a much slower register speed conditions (i.e. 8 sec and 0.01°) and to use the peak
profile fitting program (FIT SOCABIM) to obtain semi-quantitative data to analyze phase formation and transformation of the corrosion products with time of exposure and correlate them with the corrosion rate.

The main profile shape function utilized was Pseudo-Voigt1 and the Gaussian function was used when the phases were poorly crystallized. The profile fitting was applied only on the strongest reflections in each of the zinc phases.

RESULTS

The corrosion products formed on the metallic surface of zinc with time of exposure in a rural-urban atmosphere, are shown in Fig. 2. It can be observed that the majority phases appear at 6.78 and 8.05(20) which corresponds to zinc sodium chlorohydroxysulfate and zinc hydroxysulfate \((N= \text{NaZn}_4\text{Cl(OH)}_6\text{SO}_4\cdot 5\text{H}_2\text{O})\) and \(A= \text{ZnSO}_4\cdot 3\text{Zn(OH)}_2\cdot 5\text{H}_2\text{O}\), respectively, and their diffraction maxima increases with the development of corrosion. Another phase at 11.24(20), zinc hydroxychloride \((S= \text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot 2\text{H}_2\text{O})\), was maintained relatively constant in a low proportion during the studied period, and near the noise level at 11.90(20) zinc hydroxysulfate, similar to phase \(A\) with less water content \((B= \text{ZnSO}_4\cdot 3\text{Zn(OH)}_2\cdot \text{H}_2\text{O})\) was also detected.

![Fig. 2 Diffractograms showing the corrosion products development with time of exposure (1, 3, 6, 9 and 12 months) in a rural-urban atmosphere. A, B and F are zinc hydroxysulfates phases; S= simonkolleite; N= sodium zinc chlorohydroxysulfate and C is a calcium silicate hydroxide hydrate phase.](image)

However, at 12 months of exposure phase \(N\) and \(A\) were not observed, only simonkolleite \((S)\) and two other phases were detected with a very low proportion and poor crystallinity, at 9.70 and 8.46(20), which corresponds to a less hydrated zinc hydroxysulfate \((F= \text{ZnSO}_4\cdot 3\text{Zn(OH)}_2\cdot 3\text{H}_2\text{O})\) and probably a zinc chlorohydroxysulfate \((D= \text{Zn}_{12(\text{OH})_{15}}\text{SO}_4\cdot 3\text{Cl}_3\cdot x\text{H}_2\text{O})\).

When the profile fitting computer program was applied, the values obtained for the reliability factor varied between 1.2 and 2.6 % in such a way that when the sum of deconvolution of the diffraction maxima was performed, a good approximation was obtained for the experimentally determined diffractogram (Fig. 3 and 4).
Incorporated in the corrosion products a calcium silicate hydroxide hydrate \((Ca_{4.5}Si_6O_{15}(OH)_3 \cdot 2H_2O, \text{phase C})\) at 7.63(20) was also found. The elemental composition of this phase was confirmed by SEM/EDXA, in a stochastic distribution of inclusions of grains which come from the calcareous soil of the region. This phase was also identified in the marine environment and does not play an important role in the corrosion process, so it will not be considered as a corrosion product [16].

In the marine test site the main phases observed with time of exposure were N and S and at 8.24(20) another zinc chlorohydroxysulfate \((M=Zn_4Cl_2(OH)_4SO_4 \cdot 5H_2O)\) was also detected [10]. The S and M maxima diffraction increased until the third month of exposure and then diminished gradually at the end of the experiment. On the other hand, phase N presented a continuous decrease up to six months and then started to increase until twelve months (Fig. 5).
Fig. 5 Corrosion products formed with time of exposure in the marine atmosphere. M = zinc chlorohydroxysulfate phase.

With the profile fitting applied it was possible to distinguish zincite from pure zinc and simonkolleite at higher d-spacings, i.e. 2.478, 2.474 and 2.468 Å, respectively. The reliability factor show a relatively small variation, from 0.94 to 2.51% (Fig. 6).

Fig. 6 The calculated profile fitting for the metallic zinc and zincite, at three months, exposed in the marine test site. Zn = pure zinc, Z = zincite and S = simonkolleite.

When comparing the values of the integrated intensities (in mm$^2$) of the diffraction maxima with the values of the corrosion rates expressed as depth of penetration (μ/year) of the corrosion products (Table 1), formation of zincite and the basic salts which contain chloride and sulfate (phases N, M, D and S) can be observed. The majority phases ZnO, N and S increase with time of exposure but between six and nine months (i.e. January and March) they decrease due to the cold fronts coming across the Gulf of Mexico from the North American continent, called "Nortes" which increase the air-borne salinity. In this period the corrosion products and probably zincite and phase M transform to the chlorides and sulfates phases (N and S). After that, when the rainy season starts, the wash off effects have an influence on the soluble corrosion products and in the layer corrosion development [2].
Table 1. Integrated intensities (mm$^2$) of the diffraction maxima and depth of penetration ($\mu$y) of the observed corrosion products with time of exposure.

<table>
<thead>
<tr>
<th>Months*</th>
<th>$\mu$y</th>
<th>N</th>
<th>A</th>
<th>M</th>
<th>D</th>
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</table>

*Time of exposure

On the other hand, in the rural-urban test site, zincite, basic salts with chloride and sulfate (N, S, and D) and a mixture of basic salts containing only sulfates with different proportions of water molecules (phases A and B) were detected. These type of compounds are observed in sulfur dioxide containing environments. The most frequently observed zinc hydroxysulfate is the phase with four water molecules, but corrosion products with different water molecules also exist [7].

The relative intensities of zincite and the zinc basic salts with chloride and sulfate (N, A and B) increased with time of exposure. However, with the rainy season similar effects as in the marine environment were observed, a sharp reduction occurs in the phase content after nine months, showing the initial formation of zinc hydroxysulfate (D) and probably a zinc chlorohydroxysulfate (phase F, not shown in Table 1).

The integrated intensity data obtained by X-ray diffraction for the detected phases, show good agreement with the experimental corrosion rate values (depth of penetration). In general, the semi-quantitative intensities of the corrosion products are lower for the rural-urban atmosphere than for the marine one.

When a pure zinc surface is exposed in a moist atmosphere, i.e., rain, dew, zincite will be the first phase to appear. Afterwards, the formation of carbonates and basic chloride and sulfates will occur depending on the concentration of the main pollutants.

Zincite in contact with carbon dioxide (CO$_2$) reacts and forms zinc hydroxycarbonate (hydrozincite, Zn$_5$(CO$_3$)(OH)$_6$). This is a common observation described by several authors [6, 9, 17, 18]. The formation of the layer is a rapid process, in which a thin layer is formed within minutes or hours. Continuous growth can be observed between five minutes and six days in a benign environment, which points to a more or less instantaneous formation of a carbonate during and after sample preparation.

From the above, it can be established the following corrosion mechanism of zinc in the two different studied atmospheres (marine and rural-urban) in a humid tropical climate of the Peninsula of Yucatan (Fig. 7). Zincite and hydrozincite are followed by a parallel growth of
simonkolleite (S) and zinc sodium chlorohydroxysulfate (N). Later on, in the marine atmosphere, where the level of chloride concentration is high, a condition favoring zinc chlorohydroxysulfate (M) formation is attained. In the rural-urban atmosphere, with low chloride and sulfate deposition, favours the formation of several zinc hydroxysulfates with different content of water molecules (A and B phases).

\[
\begin{align*}
\text{Zn} & \quad \text{H}_2\text{O} \quad \downarrow \text{O}_2 \\
\text{ZnO} & \quad \downarrow \text{CO}_2 \\
\text{Zn}_5(\text{CO}_3)(\text{OH})_6 & + \\
\text{Cl}^- & \quad \text{SO}_2
\end{align*}
\]

\[\text{Zn}_5(\text{OH})_8\text{Cl}_2\text{H}_2\text{O} \quad \iff \quad \text{NaZn}_4\text{Cl}(\text{OH})_6\text{SO}_4 \quad 6\text{H}_2\text{O} \quad \text{MARINE} \downarrow \]

\[\text{Zn}_4\text{Cl}_2(\text{OH})_4\text{SO}_4 \quad 5\text{H}_2\text{O} \quad \iff \quad \text{ZnSO}_4 \quad 3\text{Zn}(\text{OH})_6 \quad n\text{H}_2\text{O} \quad \text{RURAL-URBAN} \downarrow \]

Fig. 7 Schematic representation of atmospheric corrosion products formed in the marine and rural-urban environments.

These phases can exist simultaneously with other [7-10]. The structural resemblance between the end products (zinc hydroxycarbonate, zinc hydroxychloride, and sodium zinc chlorohydroxysulfate) have layered structures with sheets of zinc (II) in octahedral and tetrahedral coordination. The main difference is the content and bonding between the sheets. This structural resemblance may facilitate the transformation from one phase to another, giving the proper environmental conditions. Layered structures are common in basic salts of divalent cations containing hydroxide groups and other anions, such as carbonates, and sulfates. The species between these layers are not strongly bonded, that's why ions, through an ion exchange mechanism, can enter between the sheets, forming other corrosion products. This happens when zinc hydroxysulfate and zinc hydroxychloride are formed from hydroxycarbonate. Carbonate ions are replaced by incorporated sulfate and chloride ions, respectively, since the exact structure of zinc chlorohydroxysulfate has not been determined, one can only speculate on the structural chemistry of the formation of zinc chlorohydroxysulfate (phase M).

**CONCLUSIONS**

The application of diffraction peak profile analysis is a useful technique to study zinc corrosion products formed in a humid tropical climate. This technique allows one to obtain a
good diffraction maxima deconvolution and to make a semi-quantitative analysis on the changes of the phases. The obtained data are in a good agreement with corrosion rates.

The majority phases detected were zincite, sodium zinc chlorohydroxysulfate and simonkolleite on the two different studied atmospheres. Since chloride is the main contaminant in the marine environment, zinc chlorohydroxysulfate phases, M and D, were also observed. On the other hand, in the rural-urban test site, where SO₂ is the main pollutant, zinc hydroxysulfate phases A and B were detected.

A general schematic sequence of the changes of the products formed during the atmospheric corrosion process is proposed.

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