

Indoor atmospheric corrosion of conventional weathering steels in the tropical atmosphere of Panama

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Abstract One year indoor atmospheric corrosion examinations have been carried out on two conventional weathering steels for a year, at two test sites, Tocumen and Sherman Breakwater in Panama. They are environmentally classified by ISO 9223 as $S_1P_0\tau_4$ and $S_3P_0\tau_5$, respectively. In this humid-tropical marine climate corrosion rates are rather high, especially at Sherman Breakwater test site, mainly due to the high deposition of chloride, among other environmental conditions. Our results indicate that indoor corrosion is highly determined by the time of wetness and chloride ions. A-588 weathering steel corroded at a generally lower rate than COR-420 weathering steel. Rust characterization was performed by XRD, FTIR, and Mössbauer spectroscopy. Lepidocrocite, goethite, maghemite and akaganeite were found as corrosion products. Akaganeite is only detected when high chlorides deposition rates are obtained, and no washing effect occurs. This phase, together with maghemite, is obtained when there is greater aggressiveness in the environment.

Keywords Weathering steel · Mössbauer spectroscopy · X-ray diffraction · IR spectroscopy · Indoor corrosion

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1 Introduction

Weathering steels belong to the group of steels of high strength low alloy (HSLA), in which certain alloying elements contribute to the formation of a stable, adherent and protective rust layer called patina. They are materials with very good resistance to certain corrosive atmosphere without being painted or protected by another type of coating.

The atmospheric corrosion of weathering steels initially occurs in a manner similar to the corrosion of carbon steel, but decreases significantly with increasing exposure time because of the patina. The protective properties of the patina, depends on the chemical composition of metal, the humid–dry cycles, pH and composition of rainwater and atmospheric pollutants [1]. The salinity of aerosols may play an adverse role in the formation of protective patina accelerating the process of atmospheric corrosion, even in indoor conditions [2, 3]. Such was the case of the Luling Bridge, which crosses the Mississippi River in New Orleans, Louisiana [4, 5]. The protective characteristics of patinas also depend on the porosity and adherence of the different phases of rust formed on the steel surface. The knowledge of the morphology and growth characteristics provides information on the composition and protective potential of the patina [6].

Centennial Bridge, the new cable-stayed bridge over the Panama Canal, was built with steel delta frames made out of high performance steel (HPS) ASTM A709, Grade HPS-70W. This sparked a renewed interest in studying the performance of weathering steels in the humid-tropical marine climate of Panama. This paper presents the results of exposing conventional weathering steels in indoor /interior/ conditions for a period of one year, compared with outdoor exposure. The steels were exposed in a urban test site near the Pacific Ocean, and at the entrance of the Panama Canal in the Caribbean coast of Panama.

2 Materials and methods

Weathering steels (A-588 and CSN COR 420) used in this study have been described elsewhere [7, 8]. Coupons of 150 mm × 100 mm were used after blasting, cleaning and degreasing with acetone. In outdoor conditions, the samples were exposed for a year at 45° to the horizontal in the Tocumen site (T) (9° 4′ 2″ N 79° 24′ 16″ W) and at 30° in Fort Sherman Breakwater site (SB) (9° 22′ 25″ N 79° 56′ 50″ W). On the other hand, for indoor conditions metallic samples in vertical position and pollutant collectors were located inside booths made of “Fiber-Cement”, avoiding heat trap effect. Cabinets had windows that allowed natural ventilation. Because of practical reasons, exposure of the A-588 samples started during dry season (January), whereas exposure of steel COR 420 started during the rainy season (July). During the dry season (from the middle of December through the end of April) there is little or no precipitation; however in the wet season (from May to the beginning December) there is frequent and heavy precipitations.

Environment is characterized at each site for meteorological and atmospheric pollution data [9], both outside and inside cabins, but in this paper we set out indoor results. The chloride deposition rate and SO₂ deposition rate were determined monthly. Data for temperature and relative humidity (RH) were processed in order

to determine time of wetness (TOW). After exposure, corrosion rates (corrosion penetration p) were calculated by weight loss according to standard methods [10].

The corrosion products were characterized by XRD using Cu ($K\alpha$) radiation with a Bruker D8 Advance diffractometer, equipped with a detector angle Vantek 2000 at the Materials Institute of Universidad Autónoma de México (UNAM). IR spectra were recorded using a Nicolet Avatar 360 FTIR spectrometer. The resolution of the spectra was 4 cm^{-1} . Mössbauer spectra (MS) were recorded using a conventional spectrometer of constant acceleration with a $^{57}\text{Co}(\text{Rh})$ source of nominal activity of 10 mCi (370 MBq). A closed-cycle cryostat (CCS 850 Janis) was employed for low temperature measurements. Calibrations were done with a standard α -iron foil absorber at room temperature. The Mössbauer data was evaluated with the Recoil software (University of Ottawa, Canada) using Voigt base fitting.

3 Results and discussion

Panama is a tropical country, very humid and warm, with temperatures averaging $27\text{ }^\circ\text{C}$ all year long. The two test sites, Tocumen and Sherman Breakwater, are environmentally classified by ISO 9223 [9] as $S_1P_0\tau_4$ and $S_3P_0\tau_5$, respectively. In Sherman Breakwater test site, being a splash zone, conditions are particularly harsh due to the high deposition of chloride, among other environmental conditions. As shown in Fig. 1, deposition of chlorides inside the booths is very high in Sherman Breakwater station, though significantly diminishes compared to outside [8]. During indoor exposures the temperatures and relative humidity were practically the same as outside the booths, and SO_2 deposition rate is negligible. TOW is also higher in indoor conditions (given in Fig. 2) than outdoors in both sites [8], though always higher in Sherman Breakwater. This is an important factor influencing indoor corrosion aggressivity, since adsorbed water is present longer times, affecting the wet-dry cycles.

We have found [8] that the outdoor corrosivity in Tocumen and Sherman Breakwater test sites, according to ISO 9223, is C3 and $>C5$, respectively. Nonetheless, metals exposed to indoor conditions presented lower corrosion rates compared to outdoors, as shown in Fig. 3. Vera et al. [11] demonstrated that the exposure angle has some influences in outdoor corrosion rate. It is estimated that the difference in outdoor corrosion rates between 45° and 90° is ca. 1.3. The fact that in outdoor conditions, chloride and other pollutants deposit on the surface, but rain and other precipitations periodically clean the surface and that in indoor conditions there is no washing of the contaminants, so they accumulate on the metal surface compel us to look for different explanation for the significance of the observed corrosion rates. Even though the temperatures and relative humidity were practically the same as outside the booths, surface drying is slower than in outdoors due to the influence of air and sun radiation and rainfall (thicker water layers). This explains why indoor vertical corrosion rates are significantly lower than outdoors. In indoor conditions, the chloride deposition rate is significantly lower than outdoors contributing to lower corrosion rates. Both steels exposed to indoor conditions had not tendency of corrosion rates to decrease with the time, in contrast to the usual parabolic diminishing behavior observed in outdoor conditions. This can be interpreted as a

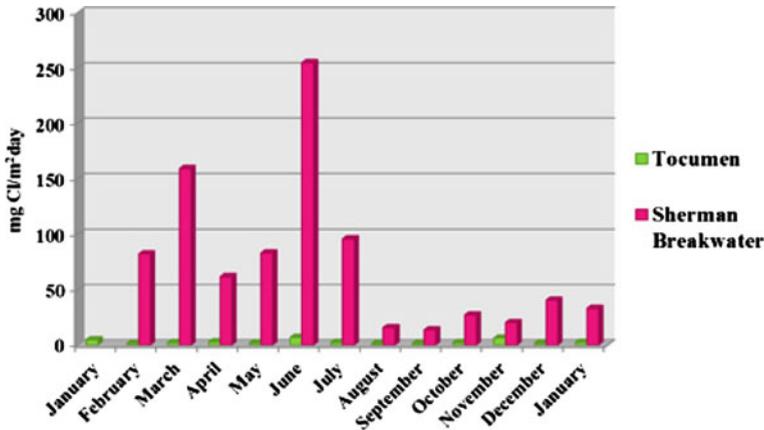


Fig. 1 Monthly average of deposition rate of chlorides inside booths for Tocumen and Sherman Breakwater sites

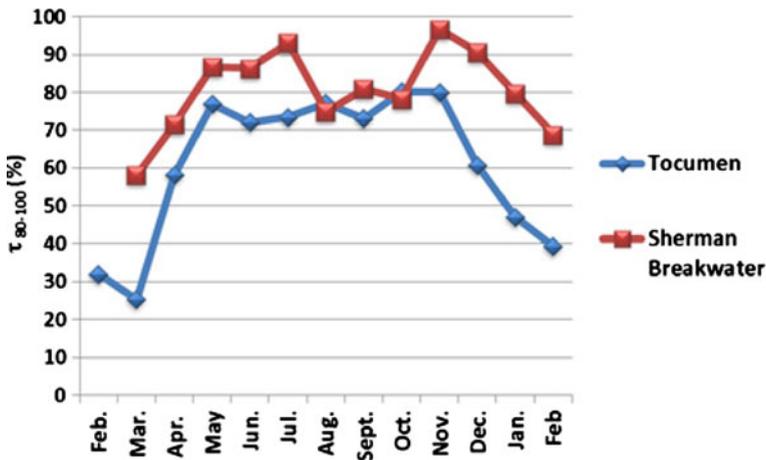


Fig. 2 Time of wetness (RH 80–100 %) under indoor conditions obtained at the Tocumen and Sherman Breakwater areas

lack of protective effect of the corrosion products. In Table 1 the indoor corrosion aggressivity results is summarized.

X-ray powder diffraction pattern for all samples were recorded to obtain a basic identification of the oxides present due to corrosion. As in the case of outdoor corrosion for these steels [8], the main phases constituting the rust layers formed after a year of indoor exposure are lepidocrocite γ -FeOOH, goethite α -FeOOH, and the iron oxide maghemite γ -Fe₂O₃. Interestingly, no akaganeite β -FeOOH is observed in Tocumen site (due to low chloride), whereas in Sherman-Breakwater site the formation of akaganeite is observed for both steels (see Fig. 4). In indoor conditions there is no washing effect on the metallic surface by precipitations, and

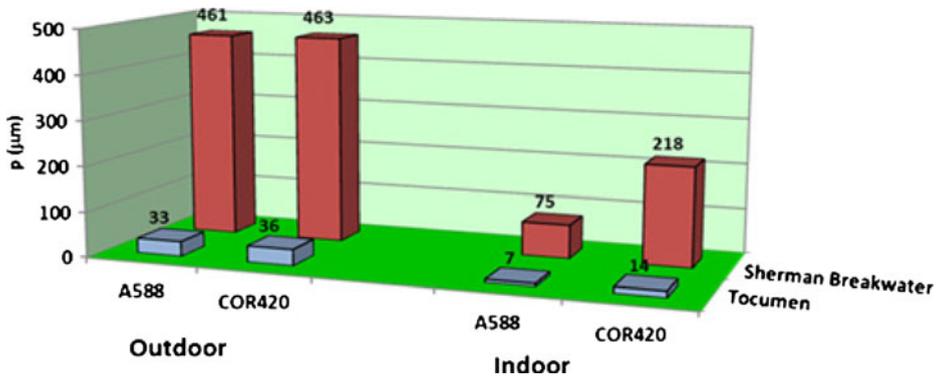


Fig. 3 Average corrosion rate (µm) depending on exposure condition and location of test site

Table 1 Classification of corrosivity for indoor samples

| Classification norm | Test site | Type of steel | |
|---------------------|--------------------|----------------|-------------------|
| | | A-588 | COR 420 |
| ISO 9223 [9] | Tocumen | C2 low | C2 low |
| | Sherman-Breakwater | C4 high | >C5 very high |
| ISO/CD 11844 [12] | Tocumen | IC2 low indoor | IC2 low indoor |
| | Sherman-Breakwater | IC2 low indoor | IC3 medium indoor |

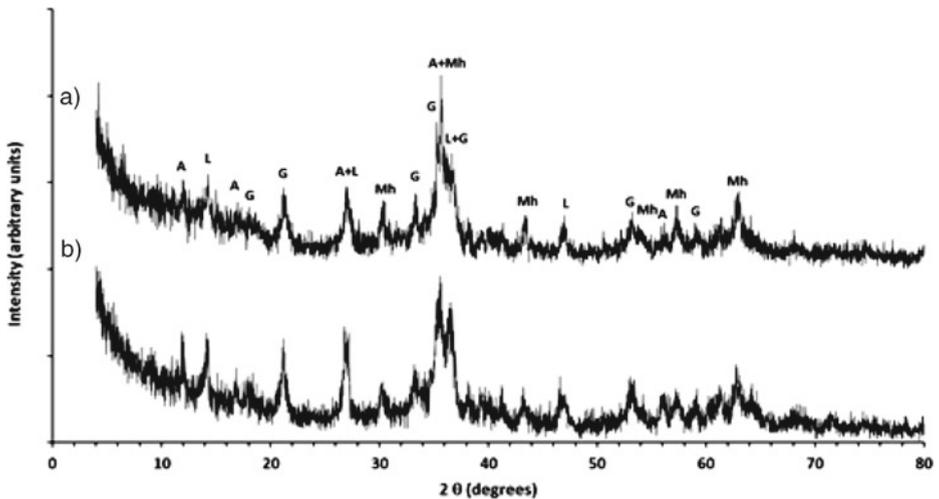
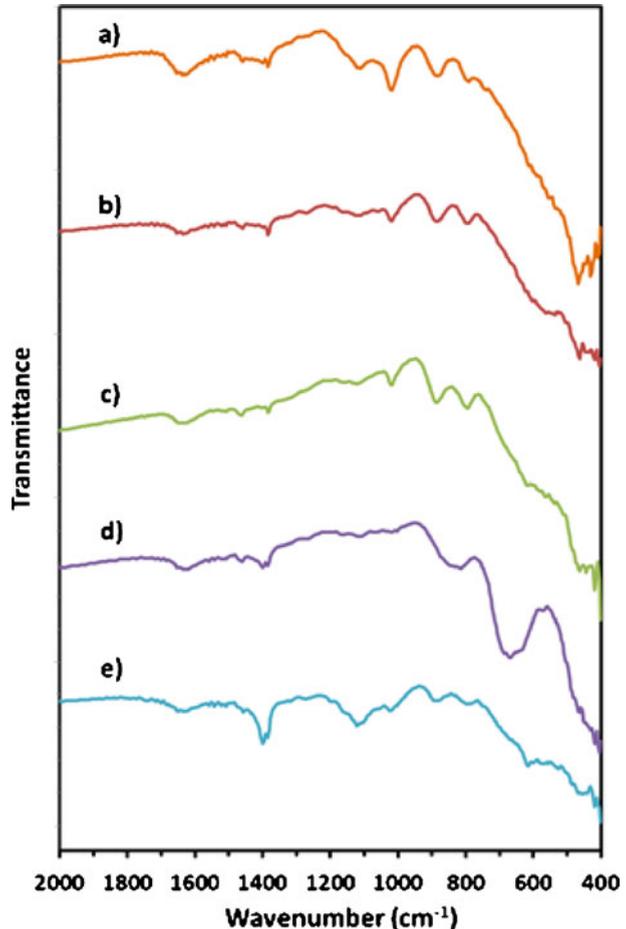


Fig. 4 XRD patterns of some characteristic samples of indoor corrosion products from Sherman-Breakwater site **a** A-588 and **b** COR 420 for 1 year. A, G, L, and Mh stand for akaganeite, goethite, lepidocrocite, and maghemite, respectively

Fig. 5 Fourier transformed infrared spectra of indoor rusts formed at **a** Tocumen site A-588, **b** Tocumen site COR 420, **c** Sherman-Breakwater rust A-588, **d** Sherman-Breakwater internal rust A-588, **e** Sherman-Breakwater rust COR 420

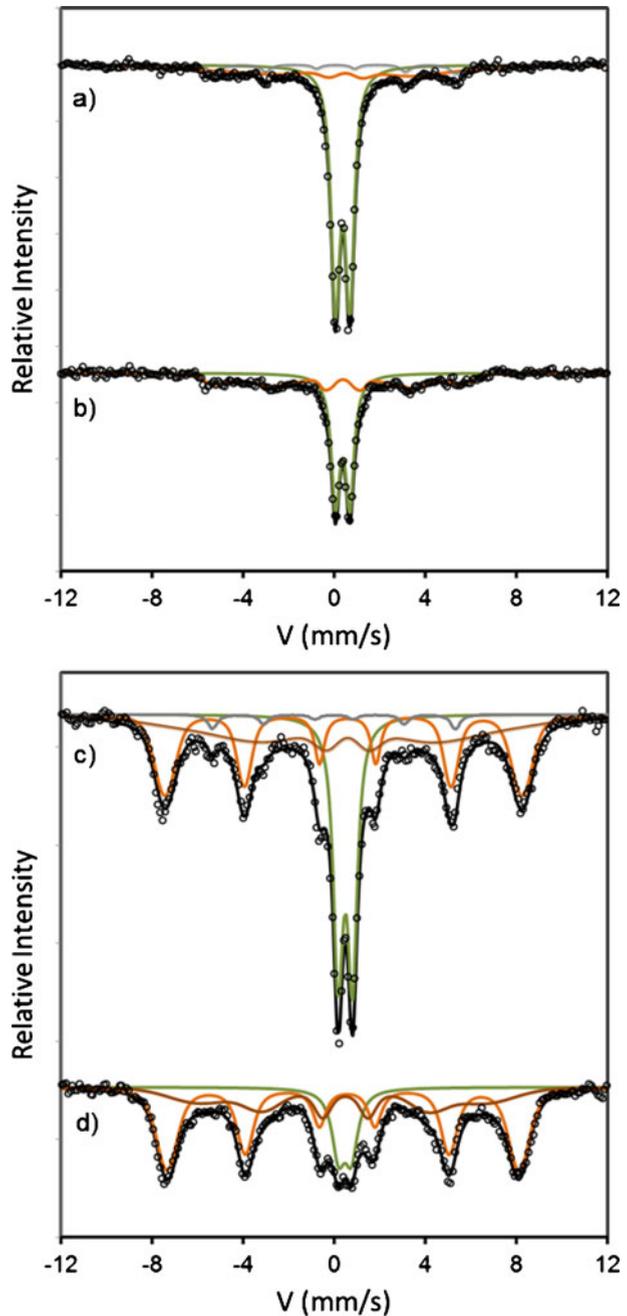


chloride ions are retained in the metal-rust interface. In outdoor conditions, this phase is only observed in regions in which chloride ions are occluded.

The FTIR spectra of indoor corrosion products of the weathering steels is given in Fig. 5. It can be noted from this figure that the presence lepidocrocite γ -FeOOH, goethite α -FeOOH, is confirmed by the appearance of OH bending peaks at 1021 cm^{-1} , at 887 cm^{-1} and 795 cm^{-1} . The absorptions in the wavenumber range $550\text{--}670\text{ cm}^{-1}$ (Fe-O range) are attributed to maghemite. The FTIR spectrum of the corrosion product scrapped from the internal parts of delaminated sheets show peaks at 887 cm^{-1} y 795 cm^{-1} hinting at akaganeite β -FeOOH as a main constituent under this conditions, as shown in Fig. 5d for internal weathering steel A-588 after exposure in Sherman-Breakwater. The presence of akaganeite in other samples from Sherman-Breakwater is evident after examining the profile of FTIR spectra of Fig. 5.

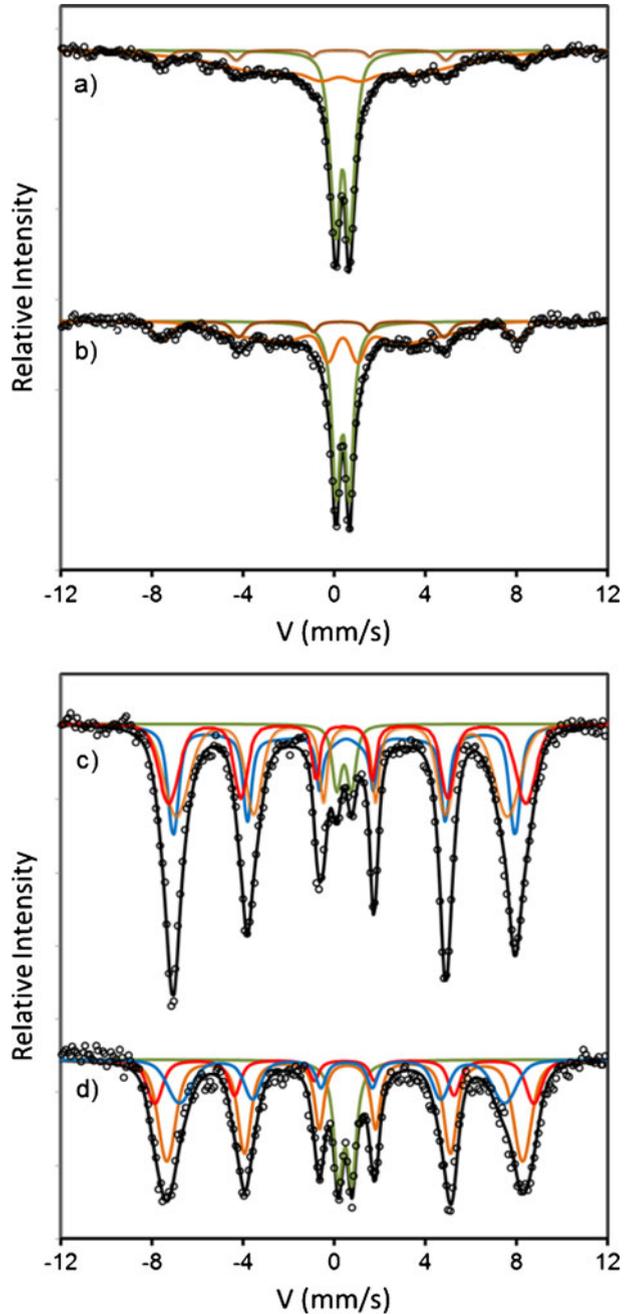
Mössbauer analysis of samples from weathering steel A-588 and COR 420 confirmed the compositions of the indoor corrosion products identified with XRD and FTIR. Transmission Mössbauer measurement performed at room temperature and liquid nitrogen are presented in Figs. 6 and 7.

Fig. 6 Transmission Mössbauer spectra of rust of weathering steels formed after one year indoor exposure at Tocumen site at 295 K: **a** A-588, **b** COR 420 **c**, and at 80 K: **c** A-588, **d** COR 420



The RT (295 K) spectra of corrosion products of weathering steels formed after one year indoor exposure at Tocumen (Fig. 6) consist of broadened magnetic component and a dominant paramagnetic doublet. A small contribution of an extra

Fig. 7 Transmission Mössbauer spectra of rust of weathering steels formed after one year indoor exposure at Sherman Breakwater site at 295 K: **a** A-588, **b** COR 420 **c**, and at 80 K: **c** A-588, **d** COR 420



sextet of α -Fe from the scraping contamination of steel plates is observed. The Mössbauer parameters of the doublet ($\delta = 0.37$ mm/s and $\Delta = 0.62$ mm/s) are in good agreement with those published for lepidocrocite and superparamagnetic component

Table 2 Area percentages of corrosion products calculated from 78 K Mössbauer spectra

| Type of steel | Test site | α -FeOOH | γ -FeOOH | γ -Fe ₂ O ₃ | β -FeOOH |
|---------------|--------------------|-----------------|-----------------|--|----------------|
| A-588 | Tocumen | 70 | 30 | – | – |
| | Sherman Breakwater | 37 | 5 | 25 | 33 |
| COR 420 | Tocumen | 85 | 15 | – | – |
| | Sherman Breakwater | 46 | 14 | 17 | 23 |

of goethite and maghemite at RT [13]. The magnetic component of each spectrum were fitted to a distribution with magnetic field in the range of 22–28 Tesla and are assigned to goethite with particle size >15 nm. At 80 K there is remarkable change compared to the RT spectra with an important increase in the relative intensity of the magnetic component (see Fig. 6), fitted using two distributions with magnetic fields around 48 Tesla and 37 Tesla. These subspectra are assigned to goethite of particle size ca. 17 nm and 9 nm, respectively. The remaining doublet is attributed to lepidocrocite, phase detected using XRD and FTIR.

Rather similar spectra of corrosion products of weathering steels formed after one year indoor exposure at Sherman Breakwater, but with two clear differences. In first place, the magnetic field of the goethite component is now in the range of 25–32 Tesla. Second and more important, another magnetic component is produced, having a magnetic field of 48–49 Tesla. This phase is ascribed to maghemite γ -Fe₂O₃. The magnetic hyperfine field of the well crystallized maghemite is in the range of 48–51 Tesla [13]. For both weathering steels, the goethite component has magnetic fields approx. 48 Tesla, thus the particle size should be ca. 17 nm.

Area percentages of all coupons exposed in indoor conditions calculated from 78 K Mössbauer spectra are collected in Table 2. The ratio (β -FeOOH + γ -Fe₂O₃) to (β -FeOOH + γ -FeOOH + γ -Fe₂O₃) suggest that the rust obtained after one year exposure under indoor conditions is non-protective, in agreement with the observations in the corrosion rate measurements.

4 Conclusion

It is concluded that corrosion rates of weathering steels significantly decrease in the tropical atmosphere of Panama atmosphere when exposed in indoor environments. A-588 weathering steel corrodes at a generally lower rate than COR-420 weathering steel.

The interaction between the chloride depositions rates with the time of wetness are the most significant variables influencing the indoor corrosion of weathering steels. Because of that, corrosivity is higher Sherman Breakwater site as compared to Tocumen.

The nature of corrosion products is correlated with the observed corrosion rates. The major compounds are lepidocrocite, goethite, followed by maghemite. Akaganeite is only detected under high chlorides deposition rates, and no washing effect occurs. Maghemite and akaganeite were identified as prominent components obtained in the most aggressive conditions of Sherman Breakwater.

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