

Characterization of Corrosion Products Formed on Steels in the First Months of Atmospheric Exposure

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The corrosion products of carbon steel and weathering steel exposed to three different types of atmospheres, at times ranging from one to three months, have been identified. The steels were exposed in an industrial site, an urban site (São Paulo City, Brazil), and a humid site. The effect of the steel type on the corrosion products formed in the early stages of atmospheric corrosion has been evaluated. The corrosion products formed at the various exposure locations were characterized by Raman microscopy, X-Ray diffraction (XRD) and their morphology was observed by Scanning Electron Microscopy (SEM). Three regions of different colours (yellow, black and red) have been identified over the steel coupons by Raman microscopy. Analysis carried out on each of these areas led to the characterization of the correspondent oxide/hydroxide phases. The main phases present were lepidocrocite (γ -FeOOH) and goethite (α -FeOOH). Small amounts of magnetite (Fe_3O_4) were also eventually encountered.

Keywords: *corrosion products, Raman microscopy, X-ray diffraction*

1. Introduction

The chemical characterization of the oxide layer formed on metals and the understanding of its formation mechanisms are important factors for the development and improvement of materials corrosion resistance.

Weathering steels contain alloying elements such as copper, chromium and silicon that improve their corrosion resistance comparatively to carbon steels¹.

Many authors²⁻⁹ have studied the corrosion products formed on carbon and weathering steels exposed to various atmospheres by X-ray diffraction and Raman microscopy. The main phases reported are lepidocrocite (γ -FeOOH), goethite (α -FeOOH) and magnetite (Fe_3O_4). Lepidocrocite is usually formed in the early stages of atmospheric corrosion³ but as the exposure time increases it is transformed into goethite.

The morphology of the oxide layer formed on carbon and weathering steels has been observed by several authors¹⁰⁻¹⁴. The phases more frequently found (lepidocrocite, goethite and magnetite) present typical structures. For instance, the lepidocrocite appears like small crystalline glob-

ules (sandy crystals) or like fine plates (flowery structures). The goethite looks like globular structures, called cotton balls (semicrystalline goethite), interconnected by formations as nests or even like acicular structures (crystalline goethite). The magnetite comes out as dark flat regions, with circular disks.

However, despite the several works in this area there is still little information about the steel oxide phases formed in Brazilian tropical sites. The aim of this investigation was to identify the components of the oxide layer formed on coupons of carbon and weathering steels, exposed to atmospheric corrosion for periods from one to three months, in three different atmospheres (a humid site located in a tropical forest area, an industrial site and a densely populated urban site) in São Paulo, Brazil. The techniques used for corrosion products characterization were X-ray diffraction and Raman microscopy.

2. Experimental

Two types of steels were used in this study: a carbon steel and a weathering steel. Their chemical composition is

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Table 1. Chemical composition of steels used.

Type of steel	Composition (weight %)							
	C	S	Al	Cu	Mn	P	Si	Cr
C steel	0.037	0.009	0.062	<0.005	0.27	0.020	0.011	<0.005
Weathering	0.056	0.007	0.017	0.26	0.59	0.023	0.23	0.52

presented in Table 1. The chemical analysis was carried out according to standard NGP 360006, using an equipment ICP Optima 3000DV/ Leco Cs444.

Coupons of 150 × 100 mm were used for atmospheric exposure. They were degreased with carbon tetrachloride and blasted until a finishing Sa 2 1/2, according to SIS SS 055900¹⁵.

Three atmospheres were used in the corrosion tests, specifically: *Cubatão* - SP, (industrial atmosphere), *Alto da Serra*, also in *Cubatão* - SP (an humid site located in a tropical forest area), and at *Paula Souza* Street, in Sao Paulo city (densely populated urban area).

The coupons exposure was carried out according to ASTM G50-76¹⁶. At increasing times, one specimen of each steel was taken from each atmospheric site and their corrosion products were characterized by X-ray diffraction and Raman microscopy. In this paper only results corresponding to one, two and three months of test are presented.

X-ray diffraction analysis was carried out with a Rigaku, model DMAX-2000 equipment, using Cu-K α radiation. X-ray diffraction spectra were obtained directly on the specimen surface. For X-ray diffraction analysis specimens of 10 × 20 mm were cut from the coupons whereas for Raman microscopy and Scanning Electron Microscopy they were 15 × 15 mm in size. Raman spectroscopy was undertaken using a Renishaw Raman microscope (System 3000), coupled to an Olympus metalographic microscope and fitted with a CCD detector (Wright, 600 × 400 pixels). The specimens were excited with the 632.8 nm line from an air cooled He-Ne laser (Spectra Physics, mod. 127). A 80× lens was used to focus the laser (ca. 0.4 mW) on the samples and to collect the scattered light.

SEM was carried out with a XL20 Phillips equipment. The samples were covered with a gold film prior to the observations.

3. Results and Discussions

3.1 Raman Microscopy

All specimens analysed by Raman microscopy showed regions of three different colors, yellow, red and black. Three spectra were obtained for each of these regions, in three different areas: at the center and closer to the borders. A total of nine spectra were obtained for each specimen: three

of the yellow areas, three of the red and three of the black areas. The results shown are characteristic of each region, for each specimen.

The products identified in the oxide layer of carbon or weathering steel exposed to the three sites (*Alto da Serra*, *Cubatão* and *Paula Souza*) were lepidocrocite (γ -FeOOH), goethite (α -FeOOH) and magnetite (Fe_3O_4). This was observed for all the three exposure times reported in this paper (one, two and three months). Since the corrosion products characterization by Raman microscopy was performed in a small area (laser spot of ca. 4 μm^2), a quantitative contribution of each phase found is not possible even probing different regions. However, it was possible to associate the color of the oxide to a particular phase. It was found that the red oxide showed Raman spectra typical of lepidocrocite (γ -FeOOH), as reported in a previous work¹⁷, with the most intense bands at 245 and 375 cm^{-1} ¹⁸⁻²². Figure 1 shows a representative lepidocrocite spectrum, for a specimen of carbon steel exposed at *Alto da Serra* site for three months. The Raman spectra of yellow oxides indicated that they correspond to a mixture of lepidocrocite and goethite (most representative bands at 245, 299, 385, 479 and 550 cm^{-1} ¹⁸⁻²²). In spite of some band overlapping (particularly the 245 cm^{-1} mode) the spectra allow an unequivocal differentiation between goethite and lepidocrocite. Figure 2 shows a spectrum typical of yellow regions, obtained from a weathering steel specimen exposed to *Paula Souza* site for one month.

The black oxides showed Raman spectra with bands of magnetite at 662 and 535 cm^{-1} together with lepidocrocite and goethite bands (Fig. 3). Magnetite is a black oxide¹⁷ and therefore its detection on black areas is not surprising. The spectrum shown in Fig. 3 was obtained from black areas on carbon steel exposed for two months at *Cubatão*.

Similar spectra were obtained at black areas for all the three exposure times (one, two and three months), both on carbon or weathering steels, independently of the atmospheric sites (*Alto da Serra*, *Cubatão* and *Paula Souza*).

3.2 X-Ray Diffraction

For oxide identification the JCPDS²³ system was used, after estimating the distance between the planes and the intensity relative to each phase. A common feature in all X-ray diffractograms obtained, either for carbon steel or weathering steel, is the predominance of lepidocrocite, goethite

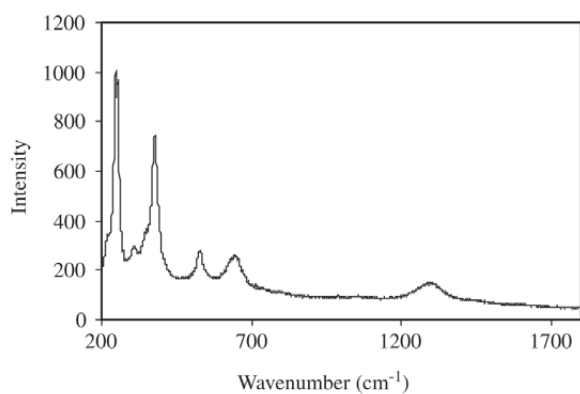


Figure 1. Raman spectrum of a carbon steel specimen exposed at *Alto da Serra* site, for three months, showing characteristic peaks of lepidocrocite from red oxide region.

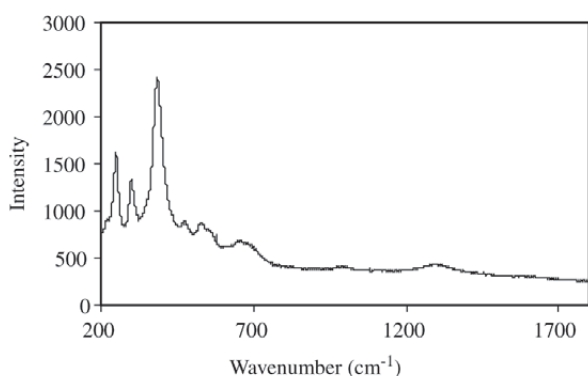


Figure 2. Raman spectrum of a carbon steel specimen exposed for one month at *Paula Souza* site, showing characteristic peaks of goethite and lepidocrocite from yellow oxide region.

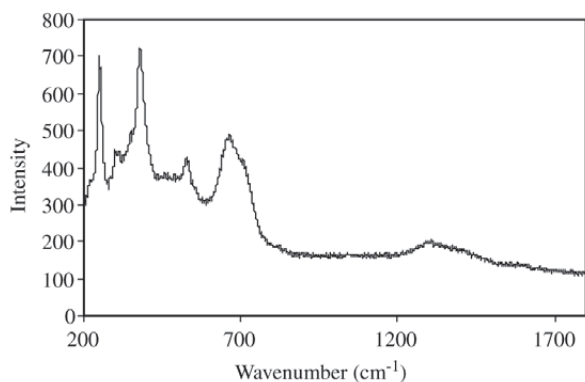


Figure 3. Raman spectrum of a carbon steel specimen, exposed for two months at *Cubatão* site, showing characteristic peaks of magnetite, goethite and lepidocrocite from black oxide region.

(α -FeOOH) and hydrated maghemite (γ -Fe₂O₃·H₂O). Reflection lines corresponding to hematite (Fe₂O₃) have also been observed in many specimens. Akaganeite (β -FeOOH) was found on some specimens of weathering steel exposed at *Cubatão* site.

In many specimens magnetite (Fe₃O₄) or maghemite (γ -Fe₂O₃) were detected. The diffraction pattern for these two oxides are very close and based only on X-ray diffraction results it is difficult to determine whether a mixture or just one compound is present. Peaks relative to maghemite were not detected by Raman microscopy, but magnetite was found in many specimens. Therefore it is more likely that the peaks (reflection lines) observed in the X-ray diffraction spectra are due to magnetite rather than to maghemite. It cannot be ruled out, however, that maghemite also occurs in small amounts, even not being detected by Raman microscopy. For practical purposes, in this work it is assumed only the presence of magnetite. Table 2 shows the X-ray diffraction data for carbon steel and weathering steel exposed for three months at *Cubatão*. Only the more intense peak of each phase is shown.

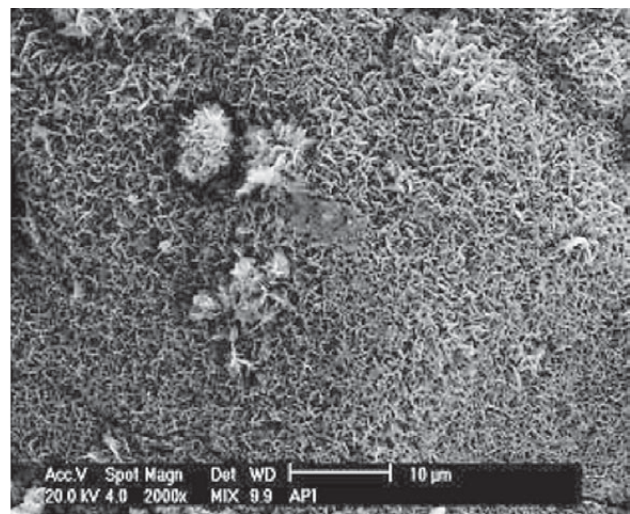
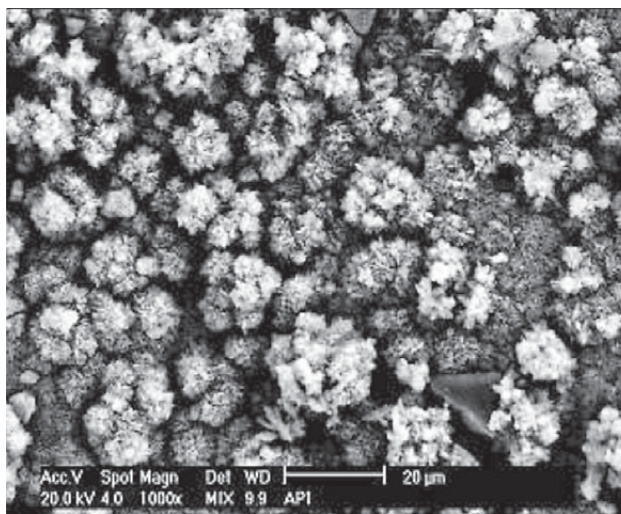
The data presented in Table 2 show that the main phase in the oxide layer formed on carbon steel exposed at *Cubatão*, is lepidocrocite, with a strong reflection line at 2.47 Å, followed by hydrated maghemite (reflection line at 2.36 Å), goethite (4.18 Å), and finally magnetite (2.97 Å) and hematite (1.37 Å). The main phase in the oxide layer formed on weathering steel is also lepidocrocite (2.47 Å) followed by akaganeite (3.32 Å), goethite (2.69 Å), hydrated maghemite (2.35 Å) magnetite (1.60 Å) and hematite (1.37 Å). As it can be seen, the phases detected for weathering steel are the same as for the carbon steel, except for akaganeite, which was only found on weathering steel exposed at *Cubatão*. This phase was detected on all specimens of weathering steel tested at *Cubatão* site, at all exposure times considered (one, two or three months), but not on any of the specimens exposed either at *Alto da Serra* or *Paula Souza*. This oxide phase is usually found on specimens submitted to atmospheres with high chloride concentrations². According to the literature¹⁷ at the *Cubatão* site the chloride concentration is higher than at the other two sites and, therefore, the presence of akaganeite on specimens exposed at *Cubatão* site and its absence on specimens tested at *Alto da Serra* or *Paula Souza* can be explained based on the different chloride concentrations in the atmosphere.

3.3 Scanning Electron Microscopy (SEM)

All specimens observed by SEM showed morphological structures typical of lepidocrocite and goethite. Figure 4 shows a micrograph of a weathering steel specimen exposed at *Alto da Serra* for one month. Cotton ball structures,

Table 2. X-ray diffraction data for carbon steel and weathering steel specimens exposed for three months at *Cubatão* site.

Exposure site	Carbon Steel			Weathering Steel		
	d (Å)	Phase	I/I ₀	d (Å)	Phase	I/I ₀
<i>Cubatão</i>	2.47	γ -FeOOH	100	2.47	γ -FeOOH	100
	2.36	γ -Fe ₂ O ₃ ·H ₂ O	32	3.32	β -FeOOH	72
	4.18	α -FeOOH	16	2.69	α -FeOOH	46
	2.97	Fe ₃ O ₄	14	2.35	γ -Fe ₂ O ₃ ·H ₂ O	46
	1.37	Fe ₂ O ₃	14	1.60	Fe ₃ O ₄	20
				1.37	Fe ₂ O ₃	14

**Figure 4.** Micrographs of weathering steel specimen exposed at *Alto da Serra*, for one month, showing “cotton ball” structures, on the right, and nest formations, on the left, interconnecting the cotton balls.

typical of semicrystalline goethite¹¹, interconnected by formations as nests were often found on all specimens analysed.

The micrograph of a carbon steel specimen exposed for three months at *Cubatão* is presented in Fig. 5. Sandy crystals (Fig. 5a), typical of lepidocrocite¹⁴, are frequently found, in agreement with the X-ray diffraction data discussed above which showed that lepidocrocite is the main phase of the oxide layer on this specimen. .

In Fig. 5b, the micrograph of a carbon steel specimen that was exposed at *Cubatão* site for two months is displayed. It can be seen that this oxide layer has an irregular and open structure, permitting the easy access of corrosive species to the metallic substrate.

A comparison of the oxide layer formed on the steels exposed at *Cubatão* with those formed on exposure at *Alto*

da Serra and *Paula Souza*, shows that the oxide layer related to exposure at *Cubatão* was usually more irregular and opened, supporting the hypothesis that this site has the most corrosive atmosphere. For instance, Fig. 5c shows a micrograph of a carbon steel specimen exposed for two months at *Paula Souza* showing that the corrosion products formed are more compact when compared to the corrosion layer formed at *Cubatão*, Fig. 5b thus favouring the protection of the metallic substrate.

Figure 5d, shows an example of flowery structures (center of photo, appearing as thin plates) another morphology typical of lepidocrocite¹⁰, formed on weathering steel, exposed for one month, at *Paula Souza* site. The magnetite pattern (flatten and dark areas, with circular disks) was not found in any of the specimens analysed.

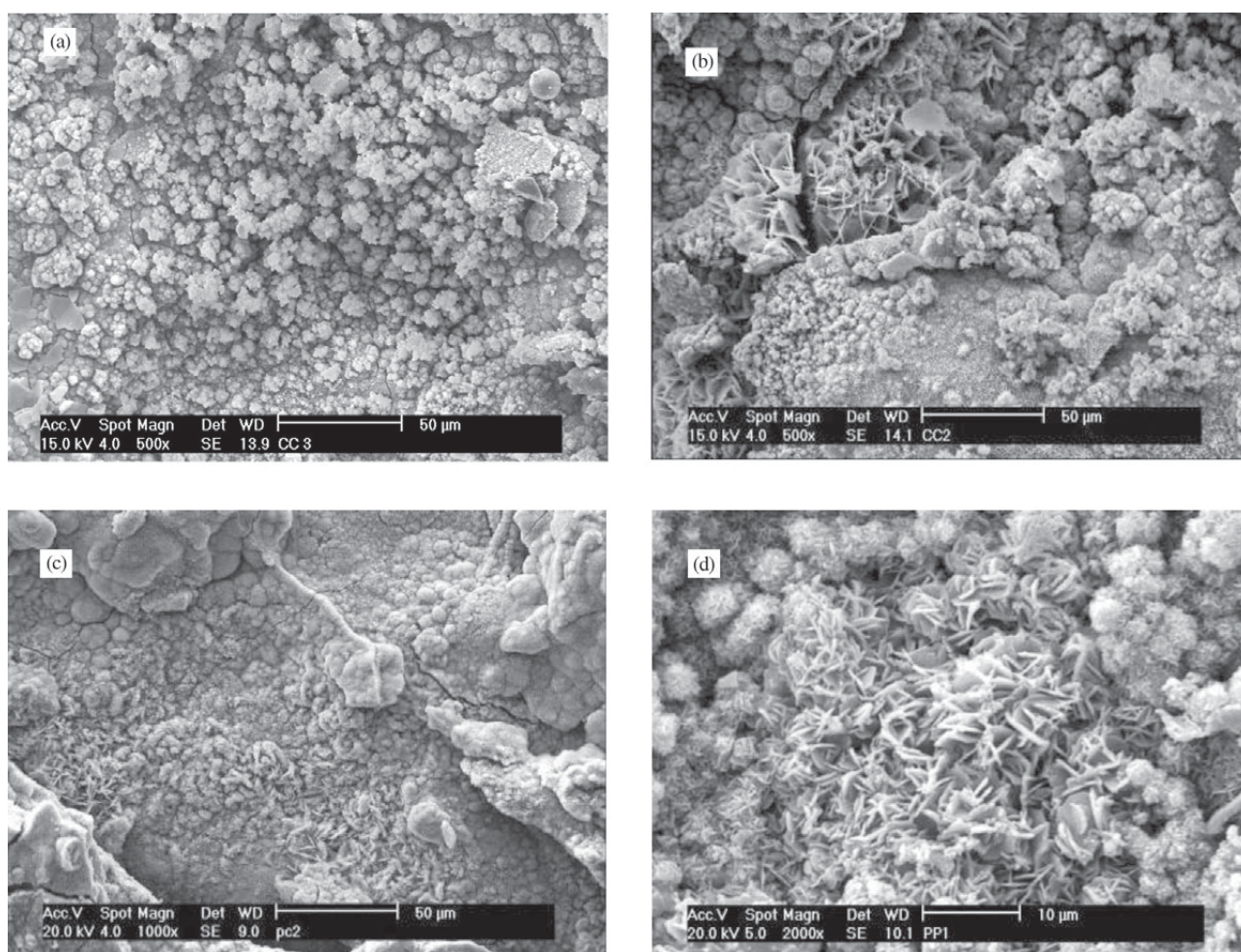


Figure 5. Micrographs showing: a) sandy crystals (lepidocrocite); b) irregular and not protective oxide layer formed on carbon steel specimen exposed at *Cubatão*; c) compact oxide layer on carbon steel specimen exposed at *Paula Souza* and d) flowery structures (centre of photo), typical of lepidocrocite on weathering steel specimen.

4. Conclusions

The main components found in the oxide layer of the specimens analysed were lepidocrocite, goethite and magnetite. For all the three exposure times (one, two and three months) the main phase, either on carbon steel or on weathering steel, was lepidocrocite, followed by goethite and magnetite. In the periods evaluated the composition of the various oxide phases did not present differences, either qualitative or quantitative, suggesting that at the first stages of atmospheric corrosion no significant transformations in the external oxide layer occur.

The oxide layer was more irregular and cracked in the specimens exposed at *Cubatão* (industrial atmosphere) than for the other exposure sites, suggesting higher aggressiveness of *Cubatão* site. The presence of akaganeite, confirmed

by XRD data, which is characteristic of sites with elevated chloride concentration, only in specimens exposed in *Cubatão* supports this fact.

The morphological structures found are typical of lepidocrocite (sandy crystals and flowery structures) and goethite (cotton balls) for all the exposure sites. Structures typical of magnetite were not observed in any of the specimens.

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