Characterization of the corrosion products of one of the pedestrian paths of the bridge “Punto Cero” in the city of Medellin, Colombia

A. A. Velásquez1,2 and D. Jaramillo Raquejo1

1Grupo de Electromagnetismo Aplicado, Universidad EAFIT, A.A. 3300, Medellín, Colombia.
2Author to whom any correspondence should be addressed.

Abstract. In this work, we present the structural and magnetic characterization of the rust products formed on one of the pedestrian paths of the bridge “Punto Cero” of the city of Medellin, Colombia. The rust products were obtained by scraping three zones of the surface of the pedestrian path, namely: a surface that faces the sky, a surface that faces the floor of the path and a surface with a crack, where a high corrosion state was observed. The rusts were characterized by X-ray Diffraction, Fourier Transform Infrared Spectroscopy, room temperature Mössbauer Spectroscopy and Vibrating Sample Magnetometry. The analyses made by these techniques show that the rust products formed on the surfaces facing the sky and floor are composed mainly by goethite, lepidocrocite and maghemite, in percentages of 74%, 24% and 2% respectively, while the rust taken from the more corroded substrate presented 55% of goethite, 28% of lepidocrocite and 17% maghemite. Mössbauer and X-ray measurements were highly consistent with the percentages of each phase found in all rusts. The results suggest that in addition to the type of steel and the atmospheric conditions which the structure is exposed, the specific location of some surfaces plays an important role in the type and percentage of phase formed on them, being higher the presence of spinel phase in the zones more prone to moisture accumulation. On the other hand, the formation of maghemite could be an indication of an important state of corrosion of some surfaces, which could serve as a guide to start preventive maintenance actions on the structure.

1. Introduction
In Colombia, industries lose around 8.5 million dollars per year due to corrosion of materials, while in industrialized countries these losses represent around 3-5% of gross domestic product [1]. The main structures affected by this phenomenon are those based on carbon steels, such as bridges, pipelines, electric turbines, electric towers, industrial machinery, among others. The bridge Punto Cero is an emblematic structure of the city of Medellin, built in 1997, with an installation time of 18 months. Its name is due to the fact that this structure is considered the start point of the road development of the city, where a big pendulum, which hangs from the top of the structure is a representation of this concept. The bridge, constructed with weathering steel A588, is located in a place considered the midpoint of the city, where a high traffic of buses, trucks, cars and motorcycles takes place daily. In the particular case of Colombia, there are only a few studies developed on corrosion of structures...
exposed to different atmospheres, we highlight the work developed by Castaño and coworkers [2], who studied the evolution of substrates of carbon steel exposed to six different atmospheres during 14 months. Other remarkable work, although not developed in Colombia, was developed by Jaen and coworkers [3], who analyzed the corrosion products formed on substrates exposed to different zones of the Caribbean coast of Panamá, where the effect of coast and urban atmospheres on the type of rust formed was compared. Cook and coworkers [4], [5] also analyzed the corrosion products formed on carbon and weathering steels exposed to rural and industrial atmospheres during 16 years. All works mentioned before, point at least five kind of iron oxides formed on carbon steels exposed to different atmospheric conditions, namely, lepidocrocite (γ-FeOOH), goethite (α-FeOOH), akaganeite (β-FeOOH), magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃). Akaganeite has been observed as corrosion product in carbon steels exposed to atmospheres with important chloride content, such as coast zones, while lepidocrocite and goethite are the most common phases formed on carbon steels and weathering steels exposed to rural and urban zones. Spinel phases as magnetite and its highly oxidized state of maghemite have been observed in carbon steels with high corrosion state, where the rust present a poor adherence to the substrate. Although the corrosion processes of carbon steels and weathering steels have been a subject very explored in the world, we do not have notice of a particular study of the rust layer formed on the bridge “Punto Cero” of Medellín, where the analysis by Mössbauer spectroscopy could be an important tool to identify and correlate the kind of rust with the atmospheric conditions of the bridge, especially nowadays, where the city has critical months where the air quality is highly degraded by pollutants coming especially from fossil fuel combustion.

2. Experimental

2.1. Obtaining the rusts
The rusts were obtained by scraping three zones of one of the pedestrian paths of the bridge “Punto Cero” of the city of Medellín, Colombia, namely: 1. A zone of the railing that faces the sky, 2. A zone of the railing that faces the floor and 3. A zone highly corroded, close to the bottom of the railing, where a crack was observed. The rusts detached from the zones 1 and 2 were very adherent to the substrate, while the rust taken from the zone 3 was weakly adhered to the substrate, detaching easily to the first contact with the glass spatula used to scrape all surfaces. Figure 1 shows the three zones described before, as well as a panoramic view of the bridge and the pedestrian path where we took the rusts. Table 1 shows the chemical composition of the rust forms A588 of the bridge and its pedestrian paths.

2.2. Experimental techniques
The acquisition of X-ray diffractograms of the rusts was performed with a diffractometer X Pert PANalytical Empyrean Series II Alpha1, with Co-Kα radiation (λ= 1.7890100 Å), operating at 40 kV, 40 mA, in the angular range of 2θ = 10-80° and step of 0.02°. FTIR measurements were developed in a Perkin-Elmer UATR Two spectrometer, with wavenumbers between 400 and 4000 cm⁻¹ and step of 1 cm⁻¹. Iron oxide phases and hyperfine interactions in the particles were studied by Transmission Mössbauer Spectroscopy at room temperature, by using a Mössbauer spectrometer developed in our laboratory [6], which works in the mode of constant acceleration, with a radioactive source of ⁵⁷Co(Rh), with initial activity of 25 mCi and velocities between -12 and 12 mm s⁻¹. For Mössbauer measurements we prepared thin disk-shaped absorbers with effective thickness of 6 mg-Fe cm⁻², being the iron concentration controlled by dilution of the sample in sugar and the sample covered with an

Table 1. Chemical composition of the steel A588 of the bridge and its pedestrian paths.

| Element | C  | Mn  | P   | S   | Si  | Cr  | Ni  | Nb  |
|---------|----|-----|-----|-----|-----|-----|-----|-----|
| Percentage (wt. %) | 0.15 | 0.76 | 0.013 | 0.012 | 0.19 | 0.206 | 0.031 | 0.018 |
aluminum foil. Hysteresis loops at room temperature were obtained with a vibrating sample magnetometer developed in our laboratory, which has a resolution of $3 \times 10^{-4}$ emu in magnetic moment and a range of 5 kOe in magnetic field.

3. Results and discussion

3.1. X-ray diffraction measurements

The X-ray diffractograms of the samples are presented in Figure 2. We applied the Rietveld method to the diffractograms to refine some structural and phase parameters, among them: lattice parameters, mean crystallite diameters and percentage of each phase; for this purpose, we used the software MAUD [7]. Table 2 presents the phases identified in the three rusts, as well as the main parameters refined in each of them.

In the diffractogram of the rust with skyward view, we identified only peaks of goethite and lepidocrocite, with percentages around 79% and 21% respectively. The best fitting that we could obtain by applying the Rietveld refinement gave us the lattice parameters $a$, $b$, and $c$ specified in Table 2.

![Figure 1](image)

**Figure 1.** a. Panoramic view of the bridge “Punto Cero” of Medellin, b. pedestrian path, c. Zone of the railing with skyward view, d. Zone of the railing with floorward view, e. Zone neighboring the floor, highly corroded.

| Rust             | Phase     | Percentage (%) | $a$ (Å)  | $b$ (Å)  | $c$ (Å)  | $D$ (Å)  |
|------------------|-----------|----------------|----------|----------|----------|----------|
| Skyward view     | Goethite  | 79(2)          | 4.629(3) | 9.996(4) | 3.035(1) | 135(2)   |
|                  | Lepidocrocite | 21(2)       | 3.899(2) | 12.515(1) | 3.071(4) | 233(12)  |
| Floorward view   | Goethite  | 73(2)          | 4.619(2) | 9.979(3) | 3.029(1) | 121(2)   |
|                  | Lepidocrocite | 24.6(1)      | 3.880(1) | 12.502(8) | 3.062(2) | 237(6)   |
|                  | Maghemite | 2.4(3)         | 8.380(2) | --       | --       | 433(6)   |
| Highly corroded zone | Goethite  | 55(1)          | 4.6267(9) | 9.967(2) | 3.0269(5) | 233(3)   |
|                  | Lepidocrocite | 29.1(5)      | 3.8753(3) | 12.535(2) | 3.0732(2) | 704(10)  |
|                  | Maghemite | 15.9(5)        | 8.3691(5) | --       | --       | 450(2)   |

Conventions for the parameters is: $a$, $b$, $c$ lattice parameters, $D$ mean crystallite diameter.
Table 1, which are consistent with those reported by Lee and coworkers [8] for polycrystalline powder goethite and lepidocrocite. The diffractogram of the rust with floorward view presented, in addition to Figure 2. X-ray diffractograms of the rusts. a. Rust with skyward view, b. Rust with floorward view, c. Rust of the highly corroded zone.
goethite and lepidocrocite, a small percentage of maghemite, which, as we will see later, was corroborated by Mössbauer spectroscopy. The diffractogram of the rust taken from the highly corroded zone. Letters G, L and W accounts for goethite, lepidocrocite and water, respectively.

Figure 3. FTIR spectra of the rusts. a. Rust with skyward view, b. Rust with floorward view, c. Rust of the highly corroded zone. Letters G, L and W accounts for goethite, lepidocrocite and water, respectively.
corroded zone presented a considerable content of maghemite and a reduction of 31% in the content of goethite with respect to the rust with skyward view. The peaks of lepidocrocite and maghemite found in this rust are noticeably more acute and intense than those found in the other rusts, indicating that the corrosion process in this zone leads to more crystalline products than the ones formed in less corroded zones. The high mean crystallite size D observed in lepidocrocite and maghemite of the rust of the highly corroded zone can be an indication of the formation of particles with sub-micrometric sizes, which are less protective than smaller particles formed in less corroded zones. The formation of nanostructured goethite and lepidocrocite covering the substrate has been pointed for several researchers [4] as a mechanism to obtain protective rusts in weathering steels, being this effect consistent with our observation.

3.2. FTIR measurements
The FTIR spectra of the rusts are presented in Figure 3. In all spectra we identified bands characteristic of bending modes OH of goethite, placed around 800 and 900 cm⁻¹, and lepidocrocite, placed around 1020 cm⁻¹. The bands associated with vibrational modes FeO of maghemite are very weak in all cases, being not distinguishable in the sample with skyward view. The band located around 1600 cm⁻¹ in all spectra is associated with molecular vibrations of water present in the rust, while the band located around 3200 cm⁻¹ is associated with stretching vibration of OH bonds in goethite and lepidocrocite. It is important to note that the spectrum of the rust taken from the more corroded zone presents a band of lepidocrocite, around 750 cm⁻¹, which is not evident in the other rusts. On the other hand, the bands associated with iron oxides in this rust are narrower than those of the other rusts. A possible explanation for this effect is the good crystallinity of the iron phases found in the rust taken from the highly corroded zone, which can make more selective the energy where the infrared radiation is absorbed by OH bonds in lepidocrocite and goethite, leading to narrower bands than those observed in less crystalline phases.

3.3. Mössbauer spectroscopy measurements
Room temperature Mössbauer spectra of the samples are presented in Figure 4 and the hyperfine parameters obtained by fitting of the spectra with the least square fitting software MOSF [9] are presented in Table 3. We assumed Lorentzian profile lines in all spectra and all spectral parameters remained free during fittings.

The spectrum of the rust taken from the substrate with skyward view was well fitted with two doublets. We attribute the first doublet, with spectral area of 75%, to superparamagnetic goethite (SP α-FeOOH), whose average quadrupole splitting at room temperature has been reported around 0.55

| Table 3. Chemical composition of the steel A588 of the bridge and its pedestrian paths. |
|----------------------------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Rust                            | Sub-spectrum     | B (T)           | δ (mm/s)        | Δε 2ε (mm/s)    | Γ (mm/s)        | A (%)           |
| Skyward view                    | SP-Goethite      | --              | 0.36 ± 0.02     | 0.71 ± 0.02     | 0.54 ± 0.02     | 75 ± 2          |
|                                 | Lepidocrocite    | --              | 0.36 ± 0.02     | 0.51 ± 0.02     | 0.38 ± 0.02     | 25 ± 2          |
| Floorward view                  | SP-Goethite      | --              | 0.36 ± 0.02     | 0.72 ± 0.02     | 0.47 ± 0.02     | 68 ± 2          |
|                                 | Lepidocrocite    | --              | 0.37 ± 0.02     | 0.42 ± 0.02     | 0.40 ± 0.02     | 23 ± 2          |
|                                 | Maghemite        | 30.0 ± 0.2      | 0.36 ± 0.02     | 0.00 ± 0.02     | 0.80 ± 0.02     | 9 ± 2           |
| Highly corroded zone            | Goethite         | 26.0 ± 0.2      | 0.39 ± 0.02     | -0.19 ± 0.02    | 0.55 ± 0.02     | 36 ± 2          |
|                                 | SP-Goethite      | --              | 0.35 ± 0.02     | 0.65 ± 0.02     | 0.46 ± 0.02     | 31 ± 2          |
|                                 | Lepidocrocite    | --              | 0.35 ± 0.02     | 0.33 ± 0.02     | 0.25 ± 0.02     | 10 ± 2          |
|                                 | Maghemite        | 44.4 ± 0.2      | 0.31 ± 0.02     | 0.08 ± 0.02     | 0.68 ± 0.02     | 23 ± 2          |

Convention for spectral parameters is: B hyperfine magnetic field, δ isomer shift relative to α-Fe, Δε quadrupole splitting for doublets and sextets, respectively, Γ linewidth of the inner lines, A spectral area.
mm/s [10]. The second doublet is attributed to lepidocrocite (\( \gamma \)-FeOOH), which typically exhibits a broaden doublet at room temperature, with a quadrupole splitting between 0.55-0.70 mm/s [10]. Although the similarity of the hyperfine parameters of both phases at room temperature makes very

Figure 4. Room temperature Mössbauer spectra of the samples. a. Rust with skyward view, b. Rust with floorward view, c. Rust of the highly corroded zone.
difficult to assign them univocally by Mössbauer spectroscopy, X-ray measurements support our assignment, because the percentages of both phases are in good agreement within the error bars of the spectral areas measured by both techniques.

Figure 5. Hysteresis loops of the rusts. a. Rust with skyward view, b. Rust with floorward view, c. Rust of the highly corroded zone.
The Mössbauer spectrum of the rust with floorward view was better fitted with one doublet of superparamagnetic goethite, one doublet of lepidocrocite and one sextet attributed to maghemite, whose spectral area is around 9%. The sub spectrum of maghemite presents broaden lines and a hyperfine magnetic field of 30.0 T, value which is lower than that of a crystalline maghemite, around 50 T [10], which is an indication of the presence of nanoscale particles of maghemite, distributed in size, which are magnetically ordered at room temperature. The spectral area of the sub spectrum of goethite diminishes around 7% with respect to the area found in the Mössbauer spectrum of the rust with skyward view and the content of lepidocrocite is approximately the same, within the error bar of the area. These contents are similar to the ones found by Rielved refinement. The Mössbauer spectrum of the rust taken from the highly corroded zone was fitted with one doublet of superparamagnetic goethite, one doublet of lepidocrocite and one sextet attributed to maghemite, whose spectral area is around 23%. In this case, the sub spectrum of lepidocrocite presented lines narrower than those of the other rusts, indicating a better crystallinity of this phase with respect to the same phase in the other rusts. This observation is coherent with the X-ray measurements, where the peaks of lepidocrocite were more acute than those of the other diffractograms. The content of maghemite identified by Mössbauer spectroscopy in the rust of the highly corroded zone was more than twice the one found in the floorward view zone, being also its peaks narrower in this case, which is consistent with the X-ray measurements, where the peaks of magnetite are more acute than those observed in the other diffractograms.

3.4. Magnetization measurements
Room temperature hysteresis loops of the rusts are presented in Figure 5, on the other hand, the Table 4 presents the main parameters extracted from these loops, such as specific saturation magnetization $M_s$, coercive magnetic field $H_c$ and remanent magnetization $M_r$. The rust taken from the substrate with skyward view presented the lower saturation magnetization, typical of antiferromagnetic phases as goethite and lepidocrocite, while this parameter was higher in the rusts taken from the substrates with floorward view and highly corroded zone, which is consistent with the presence of maghemite, which, in its crystalline and stoichiometric state has a specific magnetization of 60 emu g$^{-1}$ [11], value higher than that of a crystalline and stoichiometric goethite or lepidocrocite, around 2 emu g$^{-1}$ [8].

Percentages of 23 % of maghemite and 77 % of antiferromagnetic phases, as predicted by Mössbauer spectroscopy in the rust taken from the highly corroded zone, are consistent with a saturation magnetization around 15 emu g$^{-1}$, value very close to 18.7 emu g$^{-1}$ obtained in our measurements with natural rusts, which shows consistency in the contents given by Mössbauer and X-ray techniques.

| Rust            | $M_s$ (emu g$^{-1}$) | $M_r$ (emu g$^{-1}$) | $H_c$ (Oe)   |
|-----------------|----------------------|----------------------|--------------|
| Skyward view    | 1.1 ± 0.1            | 0.2 ± 0.1            | 164 ± 2      |
| Floorward view  | 3.4 ± 0.1            | 0.7 ± 0.1            | 219 ± 2      |
| Highly corroded zone | 18.7 ± 0.2        | 3.8 ± 0.2            | 250 ± 2      |

4. Conclusions
We have analyzed the corrosion products formed on one of the pedestrian paths of the bridge “Punto Cero” in the city of Medellin, Colombia. The structural and magnetic techniques employed to analyze the products showed that the main adherent rust formed on the surface of the path is composed by goethite, lepidocrocite and maghemite, being goethite the more abundant phase in all rusts analyzed. The highest content of goethite, around 80 %, was observed in the rust of the surface with skyward view, where more exposure to the sun takes place. The rust taken from the surface facing to the floor presented less content of goethite, more content of lepidocrocite and a small fraction of maghemite, less than 10 %. Finally, the more corroded surface presented a significant content of maghemite.
around 20%. Although more measurements have to be made to corroborate any hypothesis about the type of phases formed in different places of the structure, our preliminary analysis suggests that the type of rust formed has relation with the specific position of the substrate in the structure, being the zones more prone to moisture accumulation those where the formation of maghemite is promoted. On the other hand, further experiments would be pertinent to correlate the presence of spinel phase with high corrosion states on the surface of the bridge, which could serve to activate maintenance plans of the bridge.

References
[1] Cortés M T and Ortiz P 2004 Corrosión Hipótesis: Apuntes Científicos Uniandinos 4 14–18
[2] Castaño J G, Botero C A, Restrepo A H, Agudelo E A, Correa E and Echeverría F 2010 Atmospheric corrosion of carbon steel in Colombia Corros. Sci. 52 216–223
[3] Jaén J A and de Araque L 2006 Caracterización de los productos de corrosión de aceros al carbono en el clima tropical marino de Sherman (provincia de Colón, Panamá) Tecnociencia 8 49–63
[4] Cook D C, Oh S J, Balasubramanian R and Yamashita M 1999 The role of goethite in the formation of the protective corrosion layer on steels Hyp. Interact. 122 59–70
[5] Cook D C 2004 Application of Mössbauer spectroscopy to the study of corrosion Hyp. Interact. 153 61–82
[6] Velásquez A A, Trujillo J M, Morales A L, Tobón J E, Reyes L and Gancedo J R 2005 Design and construction of an autonomous control system for Mössbauer spectrometry Hyp. Interact. 161 139–145
[7] Lutterotti L, Matthies S and H. R. Wenk 1999 MAUD: a friendly Java program for Material Analysis Using Diffraction Int. Union Crystallogr. Newsl. 21 14–15
[8] Lee G H, Kim S H, Choi B J and Huh S H 2004 Magnetic properties of needle-like α-FeOOH and γ-FeOOH nanoparticles J. Korean Phys. Soc. 45 1019–1024
[9] Vandenberghe R E, De Grave E and De Bakker P M A 1994 On the methodology of the analysis of Mössbauer spectra Hyperfine Interact. 83 29–49
[10] Vandenberghe R E 1990 Mössbauer spectroscopy and applications in geology (Gent: International Training Centre for Post-Graduate Soil Scientists State University Gent)
[11] Cornell R M and Schwertmann U 2003 The iron oxides: structure, properties, reactions, occurrences and uses (Hoboken: Wiley VCH)