Crystallization pressure and volume variation during rust development in marine and urban-continental environments: Critical factors influencing exfoliation

David M. Bastidas^{a,*}, Jacob Ress^a, Ulises Martin^a, Juan Bosch^a, Angel La Iglesia^b, José M. Bastidas^c

^a National Center for Education and Research on Corrosion and Materials Performance, NCERCAMP-UA, Dept. Chemical, Biomolecular, and Corrosion Engineering. The University of Akron, 302 E Buchtel Ave, Akron, OH 44325-3906, United States ^b Institute of Geosciences (IGEO), CSIC, UCM, José Antonio Novais 2, 28040 Madrid, Spain ^c National Centre for Metallurgical Research (CENIM, CSIC), Av. Gregorio del Amo 8, 28040 Madrid, Spain

(*Corresponding Author: dbastidas@uakron.edu)

Submitted: 08 February 2020; Accepted: 26 February 2020; Available On-line: 20 July 2020

ABSTRACT: The rust layer formed on carbon steel exposed to natural marine and urban-continental environments for up to 50 years was studied. Mineralogical phase composition of the rust layer was evaluated by X-ray diffraction (XRD), akaganeite, goethite, lepidocrocite, magnetite, and amorphous phases were identified. Morphological characterization of the specimens was performed using scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) microanalysis. Mechanical stress generated during the formation of the oxide causes exfoliation-induced breakout of the rust layer. Volume variation generated by structural transformations and crystallization pressure (Δp) of the crystalline phases were analyzed to assess the mechanical stress on the rust and a linear relationship was found between the molar volume expansion ratio coefficient (α) and the Δp parameter. The highest Δp was vielded by goethite (374.99 MPa), while akaganeite presented the highest α value (3.29).

KEYWORDS: Carbon steel; Corrosion; Crystallization pressure; Rust exfoliation; Volume variation; XRD

Citation/Citar como: Bastidas, D.M.; Ress, J.; Martin, U.; Bosch, J.; La Iglesia, A.; Bastidas, J.M. (2020). "Crystallization pressure and volume variation during rust development in marine and urban-continental environments: Critical factors influencing exfoliation". Rev. Metal. 56(1): e164. https://doi.org/10.3989/revmetalm.164

RESUMEN: Influencia de la presión de cristalización y variación de volumen durante la formación de herrumbre en ambientes marino y continental-urbano: Factores críticos en la exfoliación. Este artículo estudia la capa de óxido formada en acero al carbono expuesto a ambientes marinos naturales y urbano-continentales durante 50 años. La composición de la fase mineralógica de la capa de óxido se evaluó mediante difracción de rayos-X (DRX), se identificaron las fases akaganeita, goetita, lepidocrocita, magnetita y amorfa. La caracterización morfológica de las muestras se realizó mediante microscopía electrónica de barrido (MEB) y microanálisis por dispersión de energía de rayos-X (EDX). La tensión mecánica generada durante la formación del óxido provoca la ruptura mediante exfoliación de la capa de herrumbre. La variación de volumen causada por las transformaciones estructurales y la presión de cristalización (Δp) de las fases cristalinas se analizaron para evaluar la tensión mecánica sobre la herrumbre y se encontró una relación lineal entre el coeficiente de expansión de volumen molar (α) y el parámetro Δp . La Δp más elevada fue producida por la goethita (374.99 MPa), mientras que la akaganeita presentó el valor α más alto (3.29).

PALABRAS CLAVE: Acero carbono; Corrosión; DRX; Exfoliación herrumbre; Presión cristalización; Volumen molar

ORCID ID: David M. Bastidas (https://orcid.org/0000-0002-8720-7500); Jacob Ress (https://orcid.org/0000-0002-5702-931X); Ulises Martin (https://orcid.org/0000-0002-0657-5484); Juan Bosch (https://orcid.org/0000-0001-5225-721X); Angel La Iglesia (https://orcid.org/0000-0002-2026-4279); José M. Bastidas (https://orcid.org/0000-0001-9616-0778)

Copyright: © 2020 CSIC. This is an open-access article distributed under the terms of the Creative Commons Attribution 4.0 International (CC BY 4.0) License.

1. INTRODUCTION

Three stages have been reported in the formation of rust on steel exposed to natural environments (Hoerlé *et al.*, 2004). In the first stage, a thin oxyhydroxide layer is formed, in the second stage, this layer is transformed in near-neutral aqueous environments into transitory green rust compounds, and in the third stage, these green rusts evolve into a fragile brownish layer (Misawa *et al.*, 1974; Graedel and Frankenthal, 1990).

The mechanical stress is a source of alterations of the rust, such as swelling, cracking, spalling, and exfoliation. For instance, exfoliation corrosion is a stratified form of surface stress corrosion that results in layer-by-layer detachment of a corroding metal (Morcillo *et al.*, 2017). The mechanical breaking process due to rust development of the steel rebar in concrete exposed to the action of marine environments is a common phenomenon (Chatterji, 2005). The volume expansion caused by the rust layer on concrete surrounding to a steel rebar causes spalling and cracking (Sánchez-Deza *et al.*, 2017).

Depending on the atmospheric conditions, particularly the environmental humidity and chloride salinity levels in a marine environment, rust eventually becomes detached from the steel surface due to exfoliation processes. It has been reported that the rust layers generated in chloride-rich environments present a heterogeneous and porous structure, containing five crystalline phases, lepidocrocite (γ -FeOOH), and goethite (α -FeOOH) at the outermost surface (lepidocrocite upper and goethite lower), and akaganeite (β-FeOOH), magnetite (Fe₃O₄), and maghemite (γ -Fe₂O₃) in the inner part of the rust adhering to the steel substrate (Morcillo et al., 2017). Lepidocrocite and akaganeite are formed in dry periods of atmospheric corrosion and both are reduced to magnetite during wet periods (Schwarz, 1972; Lair et al., 2006; Tanaka et al., 2014). Akaganeite is formed in marine environments with a high chloride deposition rate and high relative humidity (RH) and is the least dense of the five compounds due to its open structure containing chloride ions (Mackay, 1960; Remazeilles and Refait, 2008).

The aim of this paper is to study the influence of volume variation which may produce mechanical stress on the rust and thus give rise to rust breaking. The pressure generated during the crystallization of mineral phases of the rust, lepidocrocite (γ -FeOOH), goethite (α -FeOOH), akaganeite (β -FeOOH), magnetite (Fe₃O₄), and maghemite (γ -Fe₂O₃) is also analyzed as another parameter influencing the mechanical stress.

2. MATERIALS AND METHODS

Rusted carbon steel specimens exposed to different natural environments were studied, 13 from marine environments, and 4 from urban-continental

environments. At least, three to four specimens were tested from each place localization. MADRID 1, and MADRID 2 specimens were withdrawn, after 25 years of exposure in an atmospheric corrosion test station located at the terrace roof of CENIM, the urban-continental environment of the City of Madrid, Spain. GRA 1 specimen was collected from a warehouse of construction materials in the city of Granada, Spain, the steel rebars have never been used and were stored outdoor for at least 10 years. The climate of Granada is an urban-continental environment, and it is located ~60 km far from the Mediterranean Sea coast, so the influence of marine aerosols is not expected. The morphology of the specimens presented a thick porous rust layer. GRA specimen was also collected from the city of Granada, Spain, and belonging to a collapsed reinforced concrete building 50 years old.

Deteriorated steel gratings were collected from a marine environment, LAGUARDIA specimens, belonging to the infrastructure of the seaport of A Guarda, Spain, at the Atlantic Ocean coast, receiving directly the marine aerosols spray. The steel grating was 30 years old, abundant corrosion products were observed. TUERCA, NORAY, and ESCOTILLA specimens were collected from a scrapped merchant ship from the port of Alicante, Spain, at the Mediterranean Sea coast. The specimens were at least 25 years old. These specimens showed a morphology with a conglomerate of particles containing cavities showing swift stratification. CORUNA 3 and CORUÑA $\tilde{2}$ specimens were taken from a dock of the port of A Coruña, Spain, at the Atlantic Ocean coast, the specimens were 25 years old. The BARNA specimen was collected from a dock of the port of Barcelona, Spain, at the Mediterranean Sea coast, the specimens were 30 years old. ALM PO, and ALM CA specimens were collected from the posts that support a thick chain located at the seashore of Almuñecar, Spain, at the Mediterranean Sea coast. This promenade was built in 1997 and the specimens were 22 years old. ALM 4, and ALM 3 specimens were collected from the fish market reinforced concrete building also from Almuñecar, Spain, at the Mediterranean Sea coast, 32 years old. At 200 m from the seacoast, the waters were loaded with chlorides which accelerated corrosion on the reinforcements, large cracks and detachment of corroded rebars were observed. Finally, 153C and 253C specimens were withdrawn after two years exposure at Cabo Vilano, Spain, a marine environment at the Atlantic Ocean coast located at 150 and 730 m from the shoreline, respectively, with high RH, mild temperature, high precipitation, and strong marine winds. The rust layer showed a laminar morphology with abundant exfoliation of thin sheets.

Table 1 includes the chemical composition of the 17 carbon steel specimens utilized. In general, the elemental composition is very similar for all the

	Element, wt.% ^(a)					
Specimen	С	Si	Mn	Р	S	Cr
MADRID 1	0.35	0.22	0.72	0.001	0.02	0.13
MADRID 2	0.34	0.26	0.51	0.002	0.01	0.15
GRA 1	0.37	0.34	0.47	0.001	0.03	0.12
GRA	0.40	0.38	0.56	0.001	0.02	0.10
LAGUARDIA	0.40	0.18	0.62	0.002	0.01	0.14
TUERCA	0.35	0.25	0.55	0.003	0.03	0.13
NORAY	0.38	0.30	0.65	0.001	0.02	0.12
ESCOTILLA	0.40	0.20	0.45	0.002	0.03	0.14
CORUÑA 3	0.25	0.37	0.50	0.001	0.02	0.15
CORUÑA 2	0.28	0.29	0.57	0.001	0.02	0.14
BARNA	0.27	0.20	0.65	0.002	0.02	0.11
ALM PO	0.25	0.29	0.68	0.001	0.01	0.12
ALM CA	0.29	0.25	0.62	0.001	0.02	0.13
ALM 4	0.20	0.26	0.51	0.002	0.01	0.13
ALM 3	0.19	0.32	0.59	0.002	0.02	0.14
153C	0.13	0.09	0.55	0.02	0.02	0.12
253C	0.13	0.09	0.55	0.02	0.02	0.12

TABLE 1. Chemical composition of specimens (wt.%) determined by X-ray fluorescence (XRF) analysis.

^(a) Fe balance

specimens studied, with a carbon content ranging from 0.13-0.40 wt.%.

The morphology of the rusted specimens was analyzed using a JEOL JSM-6400 scanning electron microscope (SEM), equipped with a LINK System energy-dispersive X-ray (EDX) micro-analyzer, operating in secondary electron (SE) and backscattered electron (BSE) imaging modes.

The X-ray diffraction (XRD) study of powdered specimens was performed using a Phillips PW 1730 diffractometer provided with a graphite monochromator and using Cu K_{α} radiation. The XRD patterns were registered from 2 to 65 degrees (2 θ). The quantitative analysis was carried out using the matrix-flushing method (Chung, 1974), which can calculate the amorphous phase content by addition of silicon powder as standard reference material (SRM), which does not interfere with the lines of the other crystalline phases (Degen et al., 2014). The program used for phase identification was Highscore Plus Suite from PANalytical with the ICDD database (ICDD, 2018). The Rietveld refinement method was also applied for quantitative phase analysis (Rietveld, 1969).

3. RESULTS

Figure 1 shows XRD patterns of the 17 carbon steel specimens studied. These patterns highlight the small height and the scarcity of diffraction peaks and the low peak intensity/background intensity ratio. Both factors are typical of specimens with very low crystallinity. The crystalline phases identified were: akaganeite, goethite, lepidocrocite, and magnetite. Amorphous phases were also identified.

Table 2 includes the results of XRD analysis using the matrix-flushing method Chung (1974), and Rietveld (1969) method. Analysis by matrixflushing method found that the amorphous phases are the main components in all specimens, with a composition ranging from 27 to 62 wt.%, with an average content value of 41 wt.%. The secondmost abundant phase is magnetite with a range between 8–58 wt.% in composition, and an average value of 25 wt.%. The amount of goethite is in the range between 7-39 wt.%, with an average content value of 21 wt.%. Akaganeite and lepidocrocite are the minor components with average content values of 9.3 and 4 wt.%, respectively. It should be noted that akaganeite phase is not present on the specimens collected from urban-continental environment (MADRID 1, MADRID 2 and GRA 1), except for the specimen labelled GRA which presented an akaganeite content of 12 wt.%. In the same way, ESCOTILLA and CORUÑA 3 specimens collected from marine environments do not contain akaganeite.

Figure 2 shows XRD patterns and Rietveld analysis for the rust layer formed on carbon steel specimen 153C after exposure to marine environment (150 m from the shoreline) for 2 years. The sharp Si peaks used as standard reference can be observed on a complex diagram corresponding to the mixture of akaganeite (ak), goethite (go), lepidocrocite (le), and magnetite (ma). Figure 3 shows XRD patterns and Rietveld analysis for the rust layer formed on carbon steel specimen 253C, after exposure to marine environment for (730 m from the shoreline) 2 years. Quantitative analysis of crystalline and amorphous phases measured by XRD using the Rietveld refinement method (Rietveld, 1969) is shown in Table 2. The phase contents determined by Rietveld refinement method were 32.6 and 46.2 wt.% amorphous, 21.0 and 23.1 wt.% magnetite, 20.5 and 27.2 wt.% goethite, 8.1 and 14.1 wt.% akaganeite, and finally 3.0 and 4.2 wt.% lepidocrocite. Similar results were obtained by both Rietveld and matrix-flushing quantitative analysis methods. Weighted profile values (R_{wp}) of 6.17% and 6.5% were obtained for 153C and 253C specimens, respectively. The silicon peak comes from the SRM material used. Table 2 indicates that, (i) in all the specimens the content of amorphous phases is high (27 to 62 wt.%), which is independent of the type of environment, marine or urban-continental; (ii) there is not a relationship between the percentage of amorphous phases and the crystalline phases; and (iii) the akaganeite phase appears on carbon steel specimens exposed to marine environments, except for the GRA specimen (urban-continental environment).



FIGURE 1. XRD patterns of the 17 carbon steel specimens exposed to atmospheric corrosion in different natural environments (marine and urban-continental).

Figure 4 shows a SEM micrograph of carbon steel (153C specimen) of exfoliated flakes of \sim 1200 µm thickness and an intense fracture producing cleavage facets of \sim 300 µm thickness. A typical dissolution process can be observed (see the arrows). In general, the texture of the rust is typical of an

amorphous phase. EDX microanalysis of the spots showed an atomic O/Fe ratio between 1.05 and 2.23 and an atomic Cl/Fe ratio between 0.03 and 0.17.

Figure 5 shows a SEM micrograph of carbon steel (153C specimen), a rust with great porosity can be observed. The rust layer shows the growth

			Phase Content, w	t.%	
Specimen	Akageneite	Goethite	Lepidocrocite	Magnetite	Amorphous
MADRID 1	0	39	4	19	38
MADRID 2	0	17	10	17	56
GRA 1	0	34	7	32	27
GRA	12	19	3	23	43
LAGUARDIA	10	25	2	25	38
TUERCA	16	11	2	32	39
NORAY	6	7	2	34	51
ESCOTILLA	0	15	2	41	42
CORUÑA 3	0	11	3	58	28
CORUÑA 2	4	8	3	23	62
BARNA	24	11	2	17	46
ALM PO	11	26	4	22	37
ALM CA	12	31	7	19	31
ALM 4	20	21	4	9	46
ALM 3	17	30	3	8	42
153C ^a	13	21	5	22	39
253C ^a	13	29	3	24	31
153C ^b	8.1	20.5	4.2	21.0	46.2
253C ^b	14.1	27.2	3.0	23.1	32.6

TABLE 2.	Crystalline and	l amorphous	phases content	(wt.%)) in all 17	specimens	determined	by X-ray	diffraction X	RD.
----------	-----------------	-------------	----------------	--------	-------------	-----------	------------	----------	---------------	-----

^a Determined by XRD using the matrix-flushing method (Chung, 1974). ^b Determined by XRD applying Rietveld method (Rietveld, 1969). Weighted profile values (R_{wp}) of 6.17% and 6.5% for 153C and 253C specimens, respectively.



XRD pattern and Rietveld refinement quantitative analysis results of carbon steel specimens exposed to marine environment, Cabo Vilano (Spain), specimen 153C (150 m from shoreline) after 2 years of exposure. FIGURE 2.



FIGURE 3. XRD pattern and Rietveld refinement quantitative analysis results of carbon steel specimens exposed to marine environment, Cabo Vilano (Spain), specimen 253C (730 m from shoreline) after 2 years of exposure.



FIGURE 4. SEM cross-section micrograph of carbon steel exposed to marine environment, Cabo Vilano (Spain), specimen 153C (150 m from the shoreline) after 2 years of exposure. Typical dissolution process, see the arrows.

of lepidocrocite and/or goethite mineral phases of \sim 3 µm particle size (right), and amorphous phases (left) separated by a crack, along with new growing of lepidocrocite and/or goethite phases (see the arrow). The atomic O/Fe ratio measured using EDX

microanalysis varied from 1.92 to 2.15, and the atomic Cl/Fe ratio varied from 0.00 to 0.07.

Figure 6 shows a SEM micrograph of carbon steel (253C specimen) of the inner surface of exfoliated flakes. Different arrays of lepidocrocite and/



FIGURE 5. SEM surface micrograph of carbon steel exposed to marine environment, Cabo Vilano (Spain), specimen 153C (150 m from the shoreline) after 2 years of exposure.



FIGURE 6. SEM surface micrograph of carbon steel exposed to marine environment, Cabo Vilano (Spain), specimen 253C (730 m from the shoreline) after 2 years of exposure.

or goethite mineral phases of $\sim 4 \ \mu m$ in size can be observed. Many cracks, pores and particles containing a chloride atomic percentage of $\sim 5\%$ can be seen, which may be attributed to the formation of akaganeite (see the arrows).

Figure 7 shows a SEM micrograph of carbon steel (253C specimen) presenting a laminar array of edge-edge joined lepidocrocite and/or goethite mineral phases with a size of up to ~20 μ m, giving rise to high porosity. EDX microanalysis showed an atomic O/Fe ratio from 2.20 to 2.25, and the atomic Cl/Fe ratio varied from 0.02 to 0.07.

Figure 8 shows a SEM micrograph of carbon steel (CORUÑA 3 specimen), the formation of goethite-lepidocrocite crystals on a matrix of amorphous phases can be observed, as indicated by its brotoidal morphology. Large cracks can be observed, possibly due to the volume variation of the amorphous phases. EDX microanalysis showed an atomic Cl/Fe ratio between 0 and 0.08.

Figure 9 shows a SEM micrograph of carbon steel (GRA specimen) in which the presence of a rust layer between the steel bar (lower left area) and the concrete layer (upper right area) can be observed. The rust layer has a thickness of 285 μ m, and it is very heterogeneous. EDX microanalysis showed a variation of O/Fe ratio from 2.00 to 2.80,

and Cl/Fe ratio from 0 to 0.12, depending on the area where the measurement was made. An extensive network of cracks can be observed.

Figure 10 shows a SEM micrograph of carbon steel (ALM 3 specimen). A rounded particle of 18 µm in diameter can be observed, gelatinous in appearance, deposited on a base of the same material. A large number of shrinkage cracks appear. Rounded surfaces and their gelatinous appearance indicate a newly formed material. Small crystals appear on the gelatinous masses, some with cubic morphology, their chemical analysis proves to be sodium chloride. EDX microanalysis showed that O/Fe ratio measured in different areas varied between 2.10 and 2.40.

3.1. Mechanical stress generated during rust development

The rust formed on steel in an atmospheric corrosion process generates stress, both on the rust and on the steel substrate (Chatterji, 2005). As the density of the rust is lower than the steel, the stress generated is compressive on the rust and tensile (σ) on the steel. Assuming that the growth in volume of goethite, as an example, with respect to the steel substrate is isotropic, the steel and goethite



FIGURE 7. SEM surface micrograph of an exfoliated rust layer of carbon steel exposed to marine environment, Cabo Vilano (Spain), specimen 253C (730 m from the shoreline) after 2 years of exposure.



FIGURE 8. SEM surface micrograph for carbon steel exposed to marine environment, dock of the port of A Coruña, Spain, (specimen CORUÑA 3) after 25 years of exposure. Goethite-lepidocrocite crystals on a matrix of amorphous phases.



FIGURE 9. SEM surface micrograph for carbon steel embedded in concrete (specimen GRA) exposed to urban-continental environment, Granada (Spain), after 50 years in service, with a rust layer of ~285 μm.



FIGURE 10. SEM surface micrograph for carbon steel embedded in concrete (ALM 3 specimen) exposed to marine environment, Almuñecar (Spain), after 32 years in service. Gelatinous rounded particle, containing sodium chloride crystals.

molar volume (V_m) (cm³ mol⁻¹) can be calculated: $V_{m(steel)}=x^3$, and $V_{m(goethite)}=y^3$, where x=1.990 cm, and y=2.751 cm are the conventional lattice parameters. Thus, $V_{m(steel)}=7.88$ cm³ mol⁻¹, and $V_{m(goethite)}=20.82$ cm³ mol⁻¹, see Table 3. The V_m of a crystalline phase is defined as the ratio between the molar mass and its density.

In order to calculate the mechanical stress (σ), the strain (ε) is first calculated, taking into account the plasticity criterion of Treska: $\sigma_1 - \sigma_3 = \sigma_y/2$, where $\sigma_{\rm v}$ is the yield strength of steel (Chen, 1975). The ε value for carbon steel can be calculated in any direction using its conventional parameters: $\varepsilon = [(2.75 - 1.99)/1.99] \times 100 = 38\%$. This ε value of 38% overcomes the breakage strain of a lowalloyed construction steel, such as the low carbon steel C15 (BS EN 10277-2, 2008), or the carbon steel C25 (BS EN 10250-2, 2000). The conventional ϵ value until breakage of C25 carbon steel is approximately of 24%, and the yield strength is of 400 MPa. This means that if the adhesion between goethite and the steel substrate is supposed to be perfect, the stresses to which they are subjected, both steel and goethite would be quite large and would also affect the steel producing small cracks. However, given that the resistance of the goethite is much lower than steel, since it is a highly oxidized crystalline compound, goethite would break as is formed.

3.2. Volume variation caused by structural transformations

Structural transformations between different rust phases have been reported in the literature (Schwertmann and Taylor, 1972; Tanaka *et al.*, 2014), they induce variations in the $V_{\rm m}$ of a crystalline phase in terms of expansion or contraction. For instance, the transformation of magnetite into maghemite produces expansion, while the transformations of lepidocrocite into goethite, and akaganeite into magnetite or maghemite generate a contraction. In all cases, these transformations lead to the generation of stresses in the rust layer (Chatterji, 2005).

Table 3 summarizes the $V_{\rm m}$ of the five crystalline phases, iron and steel analyzed in the present work, calculated using data from Navrotsky *et al.* (2008), and Robie *et al.* (1979). Considering Table 3 results, it is simple to estimate the variation in volume ($\Delta V_{\rm m}$) caused by the transformation of a given crystalline phase, for instance in the transformation of magnetite into lepidocrocite (Fe₃O₄+3/2H₂O+1/ 4O₂ \rightarrow 3(γ -FeOOH)). $\Delta V_m = 3V_{m(\gamma-FeOOH)} - V_{m(Fe3O4)}$; $\Delta V_{\rm m}$ =(3×22.42)-44.52=22.74 cm³ mol⁻¹, $\Delta V_{\rm m}$ is positive, i.e. expansion. Only solid phases should be considered to calculate the $\Delta V_{\rm m}$.

sidered to calculate the $\Delta V_{\rm m}$. The percentage in $\Delta V_{\rm m}$ (%) is calculated using the expression: $\Delta V_{\rm m}$ (%) = [$(V_{\rm mi}/V_{\rm mf})$ -1]×100, where $V_{\rm mf}$

Crystalline Phase	$V_{\rm m}, {\rm cm}^3 {\rm mol}^{-1}$	a	ΔG_{c}^{θ} k.J mol ⁻¹
Iron	7.09	-	-
Carbon Steel	7.88	-	-
Akaganeite (β-FeOOH)	23.32	3.29	-481.70
Goethite (α-FeOOH)	20.82	2.94	-490.60
Lepidocrocite (y-FeOOH)	22.42	3.16	-482.70
Maghemite (γ -Fe ₂ O ₃)	32.89	2.32	-731.40
Magnetite (Fe ₃ O ₄)	44.52	2.09	-1012.57

TABLE 3. Molar volume $(V_{\rm m})$ (cm³ mol⁻¹), molar volume expansion ratio coefficient (α) ($\alpha = V_{\rm m(oxide)}/V_{\rm m(Fe)}$), and standard free energy of formation (ΔG_f^0) (kJ mol⁻¹), for the studied crystalline phases (Robie *et al.*, 1979; Navrotsky *et al.*, 2008).

TABLE 4. Phase transformation, variation in molar volume ($\Delta V_{\rm m}$, cm³ mol⁻¹), and percentage variation in molar volume ($\Delta V_{\rm m}$, %).

Phase Transformation	$\Delta V_{\rm m}$, cm ³ mol ⁻¹	$\Delta V_{\rm m}$, % ^(a)
Magnetite (Fe ₃ O ₄) \rightarrow Lepidocrocite (γ -FeOOH)	22.74	51.08
Magnetite (Fe ₃ O ₄) \rightarrow Akaganeite (β -FeOOH)	25.44	57.14
Magnetite (Fe ₃ O ₄) \rightarrow Goethite (α -FeOOH)	17.94	40.30
Magnetite (Fe ₃ O ₄) \rightarrow Maghemite (γ -Fe ₂ O ₃)	4.82	10.82
Maghemite $(\gamma$ -Fe ₂ O ₃) \rightarrow Lepidocrocite $(\gamma$ -FeOOH)	11.95	36.33
Maghemite (γ -Fe ₂ O ₃) \rightarrow Akaganeite (β -FeOOH)	13.75	41.82
Maghemite $(\gamma$ -Fe ₂ O ₃) \rightarrow Goethite (α -FeOOH)	8.75	26.60
Lepidocrocite (γ -FeOOH) \rightarrow Akaganeite (β -FeOOH)	0.90	4.01
Goethite (α -FeOOH) \rightarrow Akaganeite (β -FeOOH)	2.50	12.01
Goethite (α -FeOOH) \rightarrow Lepidocrocite (γ -FeOOH)	1.60	7.68

^a $\Delta V_{\rm m}$ (%) = [$(V_{\rm mi}/V_{\rm mi})$ -1]×100, where $V_{\rm mf}$ and $V_{\rm mi}$ are the molar volumes of the final and initial phases, respectively.

and $V_{\rm mi}$ are the molar volumes of the final and initial phases, respectively.

Table 4 sets out the possible phase transformations between the five crystalline phases present in the rust, the $\Delta V_{\rm m}$ caused by the transformation, and the $\Delta V_{\rm m}$ (%). Table 4 indicates that the highest $\Delta V_{\rm m}$ (%) was yielded by the transformation of magnetite into any of the three oxyhydroxide phases considered (lepidocrocite, akaganeite, and goethite), with a $\Delta V_{\rm m}$ (%) (expansion) of between 40.30% and 57.14%. Obviously, if the transformation is reversed (i.e. the three oxyhydroxide phases into magnetite), a similar $\Delta V_{\rm m}$ (%) is produced, but in this case as a contraction. The transformation of magnetite into maghemite causes a $\Delta V_{\rm m}$ (%) of 10.82% (expansion). With regard to the other crystalline phases, the transformation of maghemite into lepidocrocite, akaganeite or goethite causes a $\Delta V_{\rm m}$ (%) (expansion) of 26.60% to 41.82%. The transformation of goethite into akaganeite or lepidocrocite produces a $\Delta V_{\rm m}$ of 12.01% or 7.68% (expansion), respectively. Finally, the transformation of lepidocrocite into akaganeite causes a small $\Delta V_{\rm m}$ of 4.01% (expansion). These changes in the $V_{\rm m}$ account for the mechanical stresses produced when weathering conditions vary (Suda et al., 1993).

The $V_{\rm m}$ parameter can also be used to calculate the molar volume expansion ratio coefficient (α) of an oxide to iron metal dissolved in the corrosion process defined as: $\alpha = V_{\rm m(oxide)}/V_{\rm m(Fe)}$.

Table 3 shows the calculated α parameter. It is found that akaganeite presents the highest value of α (3.29), followed by lepidocrocite (3.16), goethite (2.94), maghemite (2.32), and magnetite (2.09). These results may be interpreted in terms of the capacity to generate stresses within the rust layers producing an irreversible damage of the rust layer in the following order from high lo low α value: akaganeite > lepidocrocite > goethite > maghemite > magnetite.

3.3. Crystallization pressure generated during rust development

It is known that the crystallization process of a solid phase from a solution in a confined space generates a pressure known as crystallization pressure, which can originate stress in the confined space (Steiger, 2005; Espinosa *et al.*, 2008; Sánchez-Deza *et al.*, 2017). Crystallization pressure is generated during the growth of a crystalline phase, and not in the formation of an amorphous phase (Sánchez-Deza *et al.*, 2017).

According to Correns (1949), the pressure caused by the crystallization of a solid compound can be expressed by the super-saturation of a solution using the equation: $\Delta p = p_c - p_e = (RT/V_m) \ln S$, where Δp is the variation of crystallization pressure (Pa), $p_{\rm c}$ is the pressure on the growing crystal, $p_{\rm e}$ is the environmental pressure, R is the molar gas constant (8.3145 MPa cm³ K⁻¹ mol⁻¹), T is the temperature (K), $V_{\rm m}$ was defined above as the molar volume of the crystalline phase, and S is the super-saturation, which is defined as the ratio of the solute concentration (c) to the saturated solution concentration (c_0) $(S=c/c_0)$. In accordance with Neugebauer (1973), in the current study the activity of the solutions was used instead of their concentrations. In this way, $S=a/a_0$ where a is the activity of the solute for the saturated solution, and a_0 is the activity of the solute for the super-saturated solution.

The amorphous phases are probably the most soluble phases in a rust and can lead to a super-saturated solution with respect to the crystalline phases (higher density, higher melting point and largest crystalline lattice energy). The solubility of the rust compounds is unknown and cannot be calculated because of the lack of thermodynamic data in literature. The only thermodynamic data available for similar compounds are for ferric hydroxide (Fe(OH)_{3(pp)}) and ferrous hydroxide precipitates (Fe(OH)_{2(pp)}) (Wagman et al., 1982). If the activity value for the dissolution of ferric oxide is similar to the amorphous phase, it makes possible to calculate the chemical equilibrium constants (K_{eq}) of the goethite, lepidocrocite, akaganeite, magnetite, maghemite crystalline phases, Eqs. (1-5), and ferric hydroxide precipitates, Eq. 6. The log K_{eq} values included in Table 5 (Sanchez-Deza et al., 2017), were obtained by calculation of the standard free energy of reaction (ΔG_r^0) , using the standard free energy of formation (ΔG_f^0) from the literature, see Table 3 (Wagman *et al.*, 1982; Chatterji, 2005; BS EN 10277-2, 2008).

If the $a_{Fe^{3+}}$ values from Eq. (1) to Eq. (5) (see Table 5) are considered as the saturated solution, $a_{Fe^{3+}}$ value from Eq. (6) (see Table 5) as the supersaturated solution, and the V_m values (see Table 3), it is possible to estimate the Δp caused by the crystallization process using the Correns' equation. Table 5 includes the calculated values of Δp for the five crystalline phases studied. The Δp of goethite presents the highest value (374.99 MPa), followed by lepidocrocite (260.14 MPa), akaganeite (239.38 MPa), maghemite (189.22 MPa), and magnetite (26.45 MPa), ordered from high to low: goethite > lepidocrocite > akaganeite > maghemite > magnetite.

4. DISCUSSION

The model based on the α parameter is useful to explain the mechanical stress generated on the rust layer (Morcillo *et al.*, 2017). However, the exclusive use of α for the particular case of akaganeite as the main parameter may be risky, because it is only 3.29 times higher than iron (see Table 3), and it is closed to the lepidocrocite (3.16), and goethite (2.94) values. Thus, even though being the α parameter very important, it is necessary to discuss the influence of other parameters that generate mechanical stress, such as the Δp produced during the growth of a crystalline phase, and the mechanical stress generated during the formation of a rust layer.

As described above, if the adhesion between goethite and the steel substrate is perfect, the steel substrate and goethite are subjected to high mechanical stress. The ε values for conventional carbon steel and C25 steel are 38% and 24%, respectively. From a mechanical point of view, the disruptive effect of crystalline phases on the rust layers is due to the generation of a mechanical stress that is greater than the cohesive forces of the rust (Tomlison, 1927; Chatterji, 2005).

In all the carbon steel specimens studied in this work, important quantities of amorphous phases

TABLE 5. Chemical equilibrium equations from Eqs. (1–6), and equilibrium constants from $\log(K_1)$ to $\log(K_6)$, ferric ions activity as $\log a_{Fe^{3+}}$, and Δp (MPa) for the crystalline phases studied.

Chemical Equilibrium Equation	Equilibrium Constant	$\log a_{Fe^{3+}}$	$\Delta p^{(a)}$, MPa
α -FeOOH _(goethite) + H ₂ O \leftrightarrows Fe ³⁺ + 3OH ⁻ , Eq. (1)	$\log(K_1) = -43.67$	-11.27	374.99
γ -FeOOH _(lepidocricite) + H ₂ O \leftrightarrows Fe ³⁺ + 3OH ⁻ , Eq. (2)	$\log(K_2) = -43.27$	-11.18	260.14
β -FeOOH _(akaganeite) + H ₂ O \leftrightarrows Fe ³⁺ + 3OH ⁻ , Eq. (3)	$\log(K_3) = -42.47$	-10.97	239.38
$Fe_3O_{4(magnetite)} + 4H_2O \leftrightarrows 2Fe^{3+} + Fe^{2+} + 8OH^-, Eq. (4)$	$\log(K_4) = -108.21$	-10.25	26.45
γ -Fe ₂ O _{3(maghemite)} + 3H ₂ O \leftrightarrows 2Fe ³⁺ + 6OH ⁻ , Eq. (5)	$\log(K_5) = -85.83$	-11.09	189.22
$Fe(OH)_{3(pp)} \leftrightarrows Fe^{3+} + 3OH^{-}, Eq. (6)$	$\log(K_6) = -38.56$	-10.00	-

^a Estimated using Correns' equation, $\Delta p = p_c - p_e = (RT/V_m) \ln S$ (Correns, 1949).



FIGURE 11. Variation in crystallization pressure (Δp) as a function of the molar volume expansion ratio coefficient (α) for carbon steel specimens exposed to marine environment at three different locations Alicante, Barcelona, and Cabo Vilano, Spain.

have been identified along with smaller quantities of crystalline phases. In this way, rust specimens should be considered as a heterogeneous system formed by different phases whose mechanical and chemical properties depend on the content of each of the constituents, with the amorphous phases having a predominant role. The use of XRD technique aided by the matrix-flushing method (Chung, 1974), and the Rietveld refinement quantitative analysis method (Rietveld, 1969), allowed to highlight these high amorphous contents.

The current study also considered α and Δp parameters to assess the breaking of the rust. The crystalline phase transformations are favored by the atmospheric conditions found in marine environments, 80% RH or higher, a high level of chloride ions, and alternating wet/dry cycles. Especially in wet periods, the amorphous iron oxyhydroxides may be solubilized to start a dissolution-crystallization process which leads to the transformation of the amorphous phases into crystalline materials. In dry periods these processes cannot be taken place.

The hypothesis is that akaganeite, goethite, and lepidocrocite polymorphs show a correlation between the calculated Δp and their α parameter, in the sense that a high Δp value for a crystalline phase is accompanied by a high α value. Figure 11 shows the relationship between the calculated Dp value and the α parameter due to structural transformations for the Alicante, Barcelona, and Cabo Vilano specimens. It can be observed that Dp and α parameters are linearly related: $\Delta p=189\alpha-291$, with a correlation coefficient of $R^2=0.7029$. This linear relationship would support the hypothesis that α parameter may control the stress generated on the rust.

The extraordinarily high value of Δp calculated using the Correns' equation, between 374.99 and 26.45 MPa (see Table 5), indicates that the crystallization process can easily crack the rust layer. For comparative purposes, it is interesting to note that Δp values obtained in Table 5 greatly exceed the uniaxial tensile strength (σ) of concrete, which is of the order of 0.2–10 MPa, leading to failure of the concrete cover surrounding a rust layer generated on a steel reinforcement (Noiriel *et al.*, 2010; Castorena-González *et al.*, 2019).

The presence of akaganeite at different depths of the rust layer, exerting a high crystallization pressure (239.38 MPa), and with a high α value (3.29), may produce a mechanical fracture along the inner rust layer at different depths (see Fig. 4). Thus, cracks appearing on the stratified rust bulk can be associated with changes in the compactness of the rust, caused by the presence of loose rust interlayers (Sánchez-Deza *et al.*, 2018). The low compactness of the rust hinders the SEM analysis of chloride profile and the correlation with the formation of akaganeite to explain the exfoliation process on 153C and 253C specimens.

5. CONCLUSIONS

 The similar chemical composition of the 17 carbon steels specimens tested did not show significant differences of the crystalline and

amorphous phases identified, and neither on the morphological characteristics including the qualitative EDX microanalysis. A high content level of amorphous and magnetite phases was found.

- Atmospheric corrosion of carbon steel causes volume variations, crystallization pressure, and mechanical stress that trigger the rust breaking process. The crystallization pressure values obtained using the Correns model, are in the range between 374.99 to 26.45 MPa, those Δp value for all cases are higher than the cohesion forces of the rust. The *a* parameter of the crystalline phases can be ordered from high to low: akaganeite (3.29) > lepidocrocite > goethite > maghemite > magnetite (2.09). The mechanical stress generated during the formation of a rust layer is greater than the cohesive forces of the rust, for the particular case of a perfect adhesion between goethite and the steel substrate.
- A linear relationship between Δp and α was found ($\Delta p = 189\alpha - 291$) allowing to relate the tendency to generate mechanical stress with volume expansion of a crystalline phase. The linear relationship would support the hypothesis that α may be used to analyze the stress generated on the rust.

ACKNOWLEDGEMENTS

D.M. Bastidas, J. Ress, U. Martin and J. Bosch acknowledge funding from The University of Akron, Fellowship Program FRC-207367.

REFERENCES

- BS EN 10250-2 (2000). Open steel die forgings for general engineering purposes. Non-alloy quality and special steels. European Committee for Standardization, Brussels.
- BS EN 10277-2 (2008). Bright steel products. Technical delivery conditions. Steels for general engineering purposes. European Committee for Standardization, Brussels
- Castorena-González, J.H., Gaona-Tiburcio, C., Bastidas, D.M., Núñez-Jáquez, R.E., Bastidas, J.M., Almeraya-Calderón, F.M. (2019). Finite element modelling to predict reinforced concrete corrosion-induced cracking. *Rev. Metal.* 55 (3), e150. https://doi.org/10.3989/revmetalm.150.
- Chatterji, S. (2005). Aspects of generation of destructive crys-tal growth pressure. J. Cryst. Growth 277 (1-4), 566–577. https://doi.org/10.1016/j.jcrysgro.2004.12.036. Chen, W.-F. (1975). Limit Analysis and Solid Plasticity, Elsevier,
- NY, US.
- Chung, F.H. (1974). Quantitative interpretation of X-ray dif-Chung, F.H. (1974). Quantitative interpretation of X-ray diffraction patterns of mixtures. I. Matrix-flushing method for quantitative multicomponent analysis. J. Appl. Cryst. 7, 519–5251. https://doi.org/10.1107/S0021889874010375.
 Correns, C.W. (1949). Growth and dissolution of crystals under linear pressure. Discuss. Faraday Soc. 5, 267–271. https:// doi.org/10.1039/DF9490500267.
- Degen, T., Šadki, M., Bron, E., König, U., Nénert, G. (2014). The highscore suite. *Powder Diffr.* 29, 13–18. https://doi. org/10.1017/S0885715614000840.
- Espinosa, R.M., Franke, L., Deckelmann, G. (2008). Model for the mechanical stress due to the salt crystallization in porous materials. *Constr. Build. Mater.* 22 (7), 1350–1367. https://doi.org/10.1016/j.conbuildmat.2007.04.013.

- Graedel, T.E., Frankenthal, R.P. (1990). Corrosion mechanisms for iron and low alloy steels exposed to the atmosphere. J. Electrochem. Soc. 137 (8), 2385–2394. https://doi. org/10.1149/1.2086948.
- Hoerlé, S., Mazaudier, F., Dillmann, P., Santarini, G. (2004). Advances in understanding atmospheric corrosion of iron. II. Mechanistic modelling of wet-dry cycles. *Corros. Sci.* 46 (6), 1431–1465. https://doi.org/10.1016/j. corsci.2003.09.028.
- ICDD (2018). International Centre for Diffraction Data (ICDD). PDF-4+2018 (Powder Diffraction File- Database), S. Kabekkodu (Ed.), Newtown Square, PA, USA.
- Lair, V., Antony, H., Legrand, L., Chaussé, A. (2006). Electrochemical reduction of ferric corrosion products and evaluation of galvanic coupling with iron. Corros. Sci. 48 (8),
- 2050–2063. https://doi.org/10.1016/j.corsci.2005.06.013. Mackay, A.L. (1960). β-Ferric oxyhydroxide. *Mineral. Mag.* 32 (250), 545–557. https://doi.org/10.1180/ Makay, Mal. (250), 545–557. https://doi.org/10.1180/ minmag.1960.032.250.04.
 Misawa, T., Hashimoto, K., Shimodaira, S. (1974). The mechanism of formation of iron oxide and oxyhydroxides in
- aqueous solutions at room temperature. Corros. Sci. 14 (2), 131-149. https://doi.org/10.1016/S0010-938X(74)80051-X
- Morcillo, M., Chico, B., de la Fuente, D., Alcántara, J., Odnevall Wallinder, I., Leygraf, C. (2017). On the mechanism of rust exfoliation in marine environments. J. Electrochem. Soc.
- Navrotsky, A., Mazeina, L., Majzlan, J. (2008). Size-driven structural and thermodynamic complexity in iron oxides. *Science* 319 (6870), 1635–1638. https://doi.org/10.1126/ science.1148614.
- Neugebauer, J. (1973). The diagenetic problem of chalk -the role of pressure solution and pore fluid. Neues Jahrb. Geol. Pal-aeontol Abh. 143, 223–245.
- Noiriel, C., Renard, F., Doan, M.L., Gratier, J.P. (2010). Intense fracturing and fracture sealing induced by mineral growth in porous rocks. *Chem. Geol.* 269 (3-4), 197–209. https:// doi.org/10.1016/j.chemgeo.2009.09.018.
- Rémazeilles, C., Refait, Ph. (2008). Formation, fast oxidation and thermodynamic data of Fe(II) hydroxychlorides. *Corros. Sci.* 50 (3), 856–864. https://doi.org/10.1016/j. corsci.2007.08.017.
- Rietveld, H.M. (1969). A profile refinement method for nuclear and magnetic structures. J. Appl. Crystallogr. 2, 65-71. https://doi.org/10.1107/S0021889869006558.
- Robie, R.A., Hemingway, B.S., Fisher, J.R. (1979). Thermody-namic properties of minerals and related substances at 298.15 K and 1 bar (10⁵ Pascal) pressure and at higher tem-peratures. U.S. Geol. Surv. Bull. 1452, 18–22. https://doi. 100.0107/01.1475. org/10.3133/b1452
- Sánchez-Deza, A., Bastidas, D.M., La Iglesia, A., Bastidas, J.M. (2017). A simple thermodynamic model on the cracking of concrete due to rust formed after casting. Anti-Corros. Method. Mater. 64 (3), 335–339. https://doi.org/10.1108/ ACMM-11-2015-1602.
- Sánchez-Deza, A., Bastidas, D.M., La Iglesia, A., Mora, E.M., Bastidas, J.M. (2018). Service life prediction for 50-yearold buildings in marine environments. Rev. Metal. 54 (1), e111. https://doi.org/10.3989/revmetalm.111.
- Schwarz, H. (1972). Über die wirkung des magnetits beim atmosphärischen rosten und beim unterrostten von anstrichen, Werkst Korros 23 (8), 648-663. https://doi.org/10.1002/ maco.19720230805.
- maco.19/20230805.
 Schwertmann, V., Taylor, R.M. (1972). The transformation of lepidocrocite to goethite. *Clays Clay Miner.* 20, 151–153. https://doi.org/10.1346/CCMN.1972.0200306.
 Steiger, M. (2005). Crystal growth in porous materials–I: The crystallization pressure of large crystals. *J. Cryst. Growth* 282 (3-4), 455–469. https://doi.org/10.1016/j. jcrysgro.2005.05.007.
 Suda, K. Misra, S. Motohashi, K. (1993). Correction of the context of the crystal statement of the context of the contex
- Suda, K., Misra, S., Motohashi, K. (1993). Corrosion products of reinforcing bars embedded in con-crete. *Corros. Sci.* 35 (5-8), 1543–1549. https://doi. org/10.1016/0010-938X(93)90382-Q.
- Tanaka, H., Mishima, R., Hatanaka, N., Ishikawa, T., Nakayama, T. (2014). Formation of magnetite rust

- particles by reacting powder with artificial α-, β- and g-FeOOH in aqueous media. *Corros. Sci.* 78, 384–387. https://doi.org/10.1016/j.corsci.2013.08.023.
 Tomlison, G.A. (1927). The rusting of steel surfaces in contact. *Proc. Roy. Soc.* A 115 (771), 472–483. https://doi.org/10.1098/rspa.1927.0104.
- Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., Nuttall, R.L. (1982). The NBS tables of chemical thermodynamic prop-erties. Selected values for inorganic and C₁ and C₂ organic substances in SI units. *J. Phys. Chem. Ref. Data.* 11, 1–392. https://srd.nist.gov/JPCRD/jpcrdS2Vol11.pdf.