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Micromechanical and microstructural investigation of steel corrosion layers of variable age developed under impressed current method, atmospheric or saline conditions

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Abstract

In this paper, we have gathered the conclusions of an experimental campaign dedicated to the microstructural characterization and the determination of the local elastic properties of various natural and artificial corrosion product layers. The results of micro-indentation testing and Raman spectroscopy coupled with a semi-quantitative analysis have been presented for the whole set of investigated materials, from early-age (2 weeks) corrosion products to 660 years-old massive corroded samples. An interpretation of the local Young's modulus and hardness values has been proposed by relying on a Gaussian mixture model. The relation between the observed morphologies of the corrosion products layers, their composition and the distribution of elastic modulus and indentation hardness has finally been discussed.

Keywords: A. Steel reinforced concrete
B. Raman spectroscopy
C. Atmospheric corrosion
C. Rust

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1. Introduction

The long-term isolation of radioactive waste in deep repositories relies on a multi-barrier concept in order to guarantee that no significant environmental releases occur over a long period after disposal. The immobilized or compacted waste packages are sealed inside reinforced concrete canisters and surrounded with bentonite clay before being located deep underground in a stable rock structure. In this multi-barrier concept, the reinforced concrete canisters are aimed to contribute to the mechanical stability of the storage, as well as to limit the mass transfer between the waste and the biosphere [1]. Consequently, it seems essential to understand the hydro-mechanical behaviour of all the materials involved and the possibly evolving interfaces between the various materials appear as a key aspect in the assessment of their long term performance.

Owing to the lack of available data concerning the mechanical properties of iron oxides at the mesoscopic scale of corrosion layers, the presence of evolving corrosion product layers at the interface between the concrete and the rebar cannot be explicitly taken into account in multiphase or multiscale models. For such a reason, our project has been dedicated to the mechanical characterization of corrosion layers formed within carbonated reinforced concrete [2, 3]. As our work is mainly concerned with natural corrosion layers developed over the long term, such corrosion products have been sampled from old constructions, whose steel is completely corroded [4, 5, 6, 7]. However, in order to compare our findings with the data available in the

published literature, which deal generally with artificially created corrosion, our study also encompasses corrosion samples developed in the laboratory under an imposed electric current (accelerated corrosion) [8, 9] or under a saline environment [10, 11, 12, 13].

The Dense Product Layer (DPL) of iron oxides that develop at the interface between the remaining reinforcement and the concrete presents a complex, highly heterogeneous structure. At the micrometer scale, different phases are encountered in varying proportions. A small porosity (around 10 %) is also present, consisting mostly of cracks of finite extension approximately oriented along the initial rebar [2, 14, 15, 16, 17]. Depending on the kind of corrosion - natural or synthetized, the environmental conditions of corrosion and the age of the samples, the estimated modulus of the DPL at the mesoscopic scale is comprised between 0.1 GPa and 200 GPa [2, 9, 13, 18]. Apart from the heterogeneous microstructure, the great dispersion of the published data is also due to the identification procedure. The lowest values of Young's modulus, of the order of 0.1 GPa, are found in [8, 13, 9, 19, 20], and may not be viewed as intrinsic values of the elasticity modulus. In those references, macroscopic experiments on composite samples comprising the concrete and the rebar corroded under impressed current, are numerically simulated in order to reproduce the time for cover-crack initiation. The latter approach requires the back-calculation of the elastic properties of corrosion layers using Finite Element computations based on an analogy with thermo-elasticity, the thermal expansion coefficient representing the expan-

47 sion ratio of the corrosion products. Such an analogy has proved convenient
48 to express some effects of the corrosion development on the damage of the
49 cover concrete, and requires very low values of Young modulus for corrosion
50 products as an input data in order to obtain realistic predictions. In other
51 studies [21, 22, 23], the mechanical properties have been measured on macro-
52 scopic samples of rust particles reduced to powder, using oedometer tests.
53 The resulting moduli are comprised between 0.3 and 5 GPa, this may be
54 explained by the fact that the initial structure of the corrosion products has
55 been completely destroyed, the investigated samples behave consequently as
56 granular materials instead of the initial layered structure with strong cohesion
57 between the different corrosion layers. In [21], the exploitation of oedome-
58 ter test results using Hertz theory of contacting spheres leads in contrast
59 to very high values of elasticity modulus, comprised between 307 and 477
60 GPa. The latter values are close to Young's moduli measured by [24, 25] on
61 mono or poly-crystals of magnetite. In recent studies, depth sensing nano-
62 indentation [18, 26] or micro-indentation [3] have been employed in order to
63 identify the local elasticity modulus and Vickers hardness of corrosion layers
64 at the micrometer scale of the heterogeneous corrosion layers. The resulting
65 values measured on natural [18, 3] or artificial [26] corrosion products are
66 comprised between 51 and 158 GPa.

67 Owing to the great dispersion of the mechanical properties identified for
68 iron oxides, and to their complex microstructure, it appears therefore neces-
69 sary to study the porous DPL at the level of its components, with an aim

70 to characterize the mechanical behaviour of corrosion layers at the meso-
 71 scopic scale in relation with typical microstructural features. In the con-
 72 tinuity of a preceding work [3], Raman micro-spectrometry coupled with
 73 semi-quantitative interpretation using CorATmos software [4, 27], and depth
 74 sensing micro-indentation have been employed on a variety of corrosion sam-
 75 ples. For all the investigated materials, the results of more than 440 micro-
 76 indentation points and 1500 Raman spectra are summarized and discussed in
 77 the present paper. Whenever possible, the indentation test results have been
 78 interpreted using a Gaussian mixture model [28] which allows differentiat-
 79 ing between groups characterized by statistically distinguishable mechanical
 80 properties (hardness and local elasticity modulus). The interpretation of mi-
 81 crostructural and micromechanical data has enabled us then to identify a
 82 number of representative constituents and microstructural arrangements for
 83 each sample depending on the kind of corrosion (natural or artificial) and its
 84 age, as well as average mechanical properties for each representative groups
 85 of constituents.

86 **2. Experimental**

87 *2.1. Materials*

88 The study has been conducted on different types of corrosion products,
 89 from early-age corrosion synthesized in the laboratory to on-site, massive
 90 corrosion layers sampled on ancient buildings.

91 *Corrosion products of reinforcing bars embedded in a concrete building*

92 A specimen of reinforced concrete building, aged approximately 50 years, has
 93 been taken in the urban area of Paris (France), Figure 1(a). This specimen
 94 is composed of ordinary concrete and the remaining part of a corroded rebar,
 95 and presents the advantage of maturation under the atmospheric cycles of
 96 the Parisian region. This sample allows to investigate atmospheric corrosion
 97 in a contemporary concrete under known carbonation conditions. From the
 98 test with phenolphthalein displayed in Figure 1(a), we can notice that the
 99 upper surface of the mortar as well as a few localized areas around the cor-
 100 rosion layers are carbonated. However, the amount of corrosion products is
 101 limited (the maximum width of the corrosion layer is about 2 mm) and is
 102 not sufficient to conduct a complete experimental investigation.

103 *Atmospheric corrosion of ferrous archeological artefacts*

104 For this reason, and also because we are investigating long-term corro-
 105 sion, we have chosen to focus our study on ancient ferrous artefacts embedded
 106 in aerial and hydraulic unsaturated binders exposed to atmospheric condi-
 107 tions. Such corroded samples originate from the Palais des Papes in Avi-
 108 gnon, France, and are aged about 660 years [3, 14, 16], Figure 1. Although
 109 the composition of the mortar surrounding the reinforcement and the steel
 110 employed differ from the materials employed in modern constructions, a thor-
 111 ough experimental study at several scales on such multisecular samples has
 112 enabled us to estimate the long-term elastic properties of steel corrosion [2].
 113 These samples are completely corroded, and appear as a highly heteroge-
 114 neous porous material, essentially composed of iron, oxygen, with crack-like

115 pores. As illustrated in Figure 2 displaying X-ray tomography results ob-
116 tained using a resolution of $7\ \mu\text{m}$, we observe a dark matrix crossed with
117 clear marblings characterized by a higher proportion of steel. In the (x,y)-
118 and (z,x)- planes, we observe nearly parallel and very elongated pores in
119 black, while in the (y,z)-plane no noticeable porosity can be detected. The
120 porosity is essentially plane and of variable length (along z) but finite lateral
121 extent (along y).

122

123 *Corrosion synthesized in the laboratory under impressed current method*
124 Most of the mechanical studies encountered in the available literature con-
125 cern corrosion layers synthesized under an imposed electrical current. Con-
126 sequently, the micromechanical characterization procedure has also been ex-
127 tended to such artificial corrosion products, in view of comparison with ex-
128 isting data.

129 The parallelepiped samples, of dimensions $2 \times 3 \times 5\ \text{cm}^3$, consist in a steel
130 plate surrounded by mortar, Figure 1. The plates employed, of width 0.2
131 mm, are composed of non-alloy steel F12. The mortar is a cement CEM I
132 52.5. In order to maximize the pore volume and to facilitate the mass trans-
133 fers responsible for carbonation, we have chosen a cement-to-water ratio of
134 $C/E=0.6$, and a sand-to-cement ratio $S/C=3$. The normalized sand used
135 (CEN, 0.08/2 mm) is a natural siliceous sand [2]. The development of corro-
136 sion products is accelerated under an imposed electrical current, following a
137 procedure similar to [9, 19]. Sodium chloride (NaCl), amounting to 3.5 wt. %

138 of the mixing water, is added. The samples are then partially immersed in a
139 basic solution ($\text{pH} = 13$), composed of KOH (4.65 g l^{-1}) and NaCl (30 g l^{-1}),
140 and afterwards the acceleration of corrosion takes place under an imposed
141 current of $100 \mu\text{A cm}^2$.

142 *Corrosion in laboratory samples of reinforced concrete under saline envi-*
143 *ronment*

144 For comparison purposes, we have also tried to characterize the corrosion
145 products developed in the laboratory within several macroscopic structures
146 of ordinary reinforced concrete, of variable age, Figure 1. Samples corroded
147 in the laboratory under a controlled saline environment [11], of age comprised
148 between 3 and 25 years, have thus been characterized at the scale of the mi-
149 crostructure. The testing sample aged of 3 years has been extracted from a
150 wall of 1100 mm width. After a curing period of 28 days in water at 293 K,
151 the sample has been dried at 323 K until reaching a constant mass, before
152 being immersed in brine (35 g l^{-1} of NaCl). Afterwards, cycles of 7 days in
153 brine have been alternated with 15 days of drying, we refer to [29] for a de-
154 tailed description of the procedure. We did not observe any visible cracks on
155 the surface of the sample. The 14 years old cylindrical sample aged 14 years
156 has been stored in a conservation room under brine before being subjected to
157 wetting/drying cycles The sample aged 25 years has been taken from a beam
158 submitted to a three-point flexion test conducted until rupture [10, 12]. The
159 corroded beams have been exposed to a saline environment during 6 years,
160 followed by cycles of wetting/drying during seven years [11].

161 Regarding the preparation procedure in view of micromechanical testing,
162 all the samples were completely cast in epoxy resin at room temperature,
163 cross-sectioned and polished to 3 μm with ethanol, before being cleaned in
164 an ultrasonic bath, rinsed with ethanol and dried.

165

166 *2.2. Physico-chemical and mechanical characterization at the micrometer* 167 *scale*

168 *2.2.1. Raman microspectroscopy*

169 The identification of the elementary constituents has been conducted for
170 all the samples using Raman and SEM EDS analysis (with a Stereoscan 120,
171 Cambridge Instruments). Raman imaging has been performed with a micro-
172 Raman spectrometer Renishaw Invia reflex with the WIRE software. The
173 laser has a wavelength of 532 nm and the applied power is less than 100 μW
174 in order to prevent any possible sample degradation. The selected samples
175 were observed with a 50 $\times$ objective, the analyzed section covers a surface
176 area of 3 $\mu\text{m} \times 3 \mu\text{m}$, while the depth of investigation is 2 μm . Reference
177 spectra have been obtained in [30] for each individual phase of the corrosion
178 products, on samples synthesized in the laboratory or on commercial pow-
179 ders.

180 The analyzed samples generally display areas with a superposition of differ-
181 ent phases, each phase being characterized by different response intensities
182 and overlapped peaks. The CorATmos software [4, 27] employed during our

183 experiments overcomes this difficulty by using a semi-quantitative analysis,
184 which involves adjusting each spectrum with a combination of reference spec-
185 tra. In this way, semi-quantitative localization mappings can be drawn for
186 each phase.

187

188 2.2.2. *Vickers Micro-indentation*

189 The micro-indentation tests on corrosion product layers have been de-
190 scribed in [3], we recall briefly the principle of those tests. A depth sensing
191 microindentation apparatus (V-G 60 Micro Hardness Tester from CSM In-
192 struments) has been employed for the characterization of local mechanical
193 properties. Quasi-static loadings comprised between 0.03 and 30 N can be ap-
194 plied at the tip of the Vickers diamond indenter/probe, with a load resolution
195 of 0.3 mN and a resolution in displacement of 1 nm, the microscope magni-
196 fication ratio being equal to 5 or 50 [31]. From Oliver and Pharr's method
197 [32] commonly employed in the exploitation of the load/depth curves, we
198 identify at the level of each impression a local elasticity modulus and a local
199 hardness. In addition, the impression produced by the Vickers probe hav-
200 ing a side length approximately equal to 10 μm , the effect of nanoporosity
201 (of pore access diameter comprised between 3 and 30 nm, [14]) is indirectly
202 taken into account in the measurement of the local mechanical properties of
203 corrosion products [2]. For each sample investigated, between 50 and 150
204 impressions have been recorded.

205

206

207

208 *2.2.3. Statistical analysis*

209 The local mechanical phase properties (elasticity modulus and hardness)
210 have been interpreted using the statistical indentation method. This exper-
211 imental analysis of phase properties, originally developed for cement based
212 materials and extended to structural ceramics [28, 33], is carried out with
213 the aid of Gaussian Mixture Modeling. allow to test whether the apparent
214 groupings are Mixture models assume that data originate from a source con-
215 taining several populations. Each population group (cluster) is modeled in a
216 separate way (with its proper average, its covariance ...). Among the existing
217 mixture models, the Gaussian Mixture Model employed consists in a density
218 probability of a parameter function modelled by a weighted sum of N Gaus-
219 sians. According to [33], the Gaussian law is well adapted to represent the
220 dispersions of indentation testing on a material with strong microstructural
221 heterogeneities. The statistical analysis consists in determining the average,
222 the variance and the range of each Gaussian by estimating the Maximum
223 Likelihood through the algorithm of Expectation-Maximization [28, 34]. The
224 number of components is identified by relying on the Bayesian Information
225 Criterion proposed by [35] and employed by [28] in the exploitation of nanoin-
226 dentation tests on fired clay brick.

227 The input experimental data are the set of values taken by the elasticity
 228 modulus and the hardness at each indentation point, represented by the
 229 vectors $\mathbf{x}_i$, $\mathbf{x}$ designating the set of vectors $\mathbf{x}_i$.

$$\mathbf{x}_i = [E_i, H_i]. \quad (1)$$

230 The density function can be written as the sum of the density functions
 231 of each phase, weighted by their respective proportions, g representing the
 232 total number of components:

$$f(\mathbf{x}; \phi) = \sum_{j=1}^g \pi_j f_j(\mathbf{x}; \varphi_j), \quad (2)$$

$$\sum_{j=1}^g \pi_j = 1, \pi_j \geq 0, \quad (3)$$

$$0 \leq \pi_j \leq 1. \quad (4)$$

235 π_j is the proportion of component j . The vector ϕ contains all the unknown
 236 parameters: $\phi = [\pi_1, \dots, \pi_g, \varphi_1, \dots, \varphi_g]$ and $\varphi_j = [\mu_j, \Sigma_j]$ (μ_j is the average
 237 vector of phase j and Σ_j the covariance matrix), the parameters of the law
 238 f_i .

239 The function of density of components takes the form of a bivariate Gaus-
 240 sian distribution:

$$f_i(\mathbf{x}_j; \varphi_i) = \frac{1}{\sqrt{2\pi}} (|\Sigma|)^{-1/2} \exp\left\{-\frac{1}{2}(\mathbf{x} - \mu)^T \Sigma^{-1}(\mathbf{x} - \mu)\right\}. \quad (5)$$

241 The problem is to determine the vector of unknown parameters ϕ .

242 The likelihood function of the unknown parameter to maximize is defined
243 in the following way, in a logarithmic form:

$$-\frac{1}{2} \log L(\mathbf{x}; \phi) = \sum_{j=1}^N \log f(\mathbf{x}; \phi), \quad (6)$$

244 for N indentation test points in $\mathbb{R}^2$.

245

246 The estimation of vector ϕ by the Maximum Likelihood approach requires
247 the resolution of the following problem:

$$\frac{\partial \log L(\phi)}{\partial \phi} = 0. \quad (7)$$

248 The resolution takes place iteratively. The Expectation-Maximization al-
249 gorithm is employed to solve this problem with the following criteria (by
250 default in *gmdistribution.fit* Matlab[®]):

- 251 1. Maximum number of iterations : 100 ;
- 252 2. Convergence criterion : 10^{-6} .

253

254 We start with a model ϕ picked at random in $\mathbf{x}_i$ and a number of com-
255 ponents g , and we estimate a new model $\bar{\phi}$ such that $L(\mathbf{x}; \bar{\phi}) \geq L(\mathbf{x}; \phi)$. The
256 new model becomes the initial model for the next iteration. The iterations
257 are continued until convergence is reached according to the chosen criterion,

258 giving the averages, covariances and the proportions of the model as well as
 259 the value of the likelihood function and the Bayesian Information Criterion.

260 In order to determine the number of components which is the most appro-
 261 priate to the experimental data, *gmdistribution.fit* is evaluated several times
 262 by using the same input data $\mathbf{x}_i$, while the number of components g is varied.
 263 The Bayesian Information Criterion is recorded at each computation. The
 264 most appropriate number of components g is the number corresponding to
 265 the highest probability of minimization of the following criterion:

$$-2\log L_g(\hat{\phi}) + k_g \log N, \quad (8)$$

266 where $\log L_g(\hat{\phi})$ is the likelihood function of model g , k_g is the number of
 267 parameters of the model and N the sampling size.

268 **3. Experimental results**

269 *3.1. Characterization of the composition*

270 *3.1.1. Natural corrosion layers*

271 The analysis of the crystalline phases present in the samples of the archeo-
 272 logical artefacts has been partly presented in [3]. Experimental investigations
 273 of [14, 16, 30, 36] have shown that after a corrosion period of about 50 years,
 274 the same corrosion products may be encountered during atmospheric corro-
 275 sion, independently from the hydraulic binder composition : the ferric oxy-
 276 hydroxides are mainly goethite α -FeOOH and lepidocrocite γ -FeOOH, crossed

277 by oxide marblings composed of magnetite Fe_3O_4 and possibly maghemite
 278 $\gamma\text{-Fe}_2\text{O}_3$. Raman microspectrometry in Figure 4, comprising more than 600
 279 points, displays well-defined spectra of goethite and lepidocrocite which com-
 280 pare well with the reference spectra displayed in Figure 3)(a and b). Mag-
 281 netite has also clearly been identified in several regions, Figure 3(c). However,
 282 it is more difficult to distinguish magnetite from maghemite or ferrihydrite
 283 owing to the occurrence of mixtures of several phases, Figure 4(e,f) and Fig-
 284 ure 3(c). Certain Rama spectra are characterized by an enlarged peak at 700
 285 cm^{-1} , which may be representative of the occurrence of different oxides, such
 286 as magnetite, maghemite or ferrihydrite, and have been exploited with the
 287 semi-quantitative CorATmos procedure, Figure 3(d). SEM-EDS mappings
 288 show that the overall composition consists mainly of iron and oxygen, with a
 289 mass percentage of iron comprised between 60 % and 72 %. The latter results
 290 are in agreement with the stoichiometric formulas of the phases determined
 291 by coupling Raman spectroscopy with CorATmos semi-quantitative analysis,
 292 Table 1. Based on the Raman spectra and the SEM EDS compositions, we
 293 have identified two main classes of phases in the ancient ferrous artefacts:
 294 the oxyhydroxides (goethite and lepidocrocite) and the oxides (magnetite,
 295 maghemite, ferrihydrite), Figure 4.

296 Concerning the distribution of crystalline phases, the semi-quantitative
 297 analysis with CorATmos indicates that the dark matrix is essentially com-
 298 posed of goethite, which may be mixed with other phases. We also encounter
 299 lepidocrocite in a very localized way. The regions of clear marblings, char-

acterized by a higher proportion of iron, correspond to a mixture of oxides such a magnetite or maghemite.

A Raman cartography of 360 spectra has been performed on the sample originating from the 50 years-old concrete building. The spectra of the main phases are illustrated in Figure 5. The main products encountered are goethite, and a phase which is likely a mixture of ferrihydrite and maghemite [2].

3.1.2. Corrosion under impressed current method

A Raman microcartography of 120 points has been realized for the sample of corrosion synthetized under imposed current. The investigated zone is mainly composed of ferrihydrite with localized inclusions of akaganeite, Figure 6.

3.1.3. Corrosion under controlled saline environment

Raman cartographies have been made for the 14 years-old (LMDC14) and 25 years-old (LMDC25) samples of concrete beams corroded under salt fog, comprising 376 and 390 spectra respectively. The distribution of the various phases resulting from the CorATmos interpretation of Raman mappings is illustrated in Figure 7. The main phases of the 14 years-old sample are goethite corresponding to the dark matrix, a mixture of maghemite and ferrihydrite in the clear marblings, with local inclusions of akaganeite.

The 25 years-old sample is composed mainly of goethite (dark matrix) and marblings of magnetite/maghemite, with a clearer distribution than the

14 years-old sample, as illustrated in Figure 8 on the Raman cartography results interpreted with CorATmos.

3.2. Characterization of the local mechanical properties

3.2.1. Vickers depth sensing micro-indentation

Figure 9 synthetizes the micro-indentation results, the values of local hardness H and elasticity modulus E identified from each impression are reported for the whole set of investigated corrosion layers. The Young's modulus and hardness values reported cover a wide range, varying from 1 to 12 GPa for H , and from 30 to 159 GPa for E . As expected, H increases with E . We also observe that the obtained values are gathered along a narrow range, with an average ratio $\frac{H}{E} \approx 0.0628$. Such a ratio describes the relative resistance of plastic and elastic strains. A similar $\frac{H}{E}$ ratio for the various corrosion products suggests that the deformation mechanisms and the chemical bonds may be similar for the different corrosion layers.

Nevertheless the various corrosion products investigated present distinct ranges of Young's modulus values.

The corrosion layers developed under carbonatation in the long term (50 years for the concrete building and 660 years for the ancient artefacts) present the highest values of elasticity modulus, comprised between 64 and 159 GPa. We notice the strong similitude of the results obtained with these two types of samples, however for the sample corroded during 50 years we observe a higher proportion of local elasticity moduli close to 90 GPa. The average

344 Young's modulus deduced from 115 indentation points is equal to 99 GPa
345 for the corrosion taken on the reinforced concrete building. For the ferrous
346 artefact, the average Young's modulus reaches the value of 116 GPa, based
347 on 91 indentation points. In [18], nano-indentation on a corroded steel rebar
348 in a reinforced concrete port in service for decades has resulted in a variable
349 Young's modulus depending on the sample orientation : 61 GPa and 86 GPa
350 for the samples parallel and orthogonal to the steel bar respectively. The
351 latter results, identified at the depth range of 0.6 to 1.6 μm , are very similar
352 to the local elasticity moduli identified in the present study for the corroded
353 rebar at the depth range of 2 μm .

354 The corrosion products synthetized under imposed current are charac-
355 terized by lower values of Young's modulus and hardness, as compared to
356 corrosion products formed under natural conditions. The average of elastic-
357 ity moduli obtained from 49 points of indentation is equal to 56 GPa, with
358 a standard deviation of 9 GPa. In [18], nano-indentation has also been per-
359 formed on corrosion products generated by impressed current, resulting in
360 fluctuations of the measured elasticity modulus owing to the thinness of the
361 rust layer. The average Young's modulus is estimated to be 47 GPa, and is
362 of the same order of magnitude as the value identified in our study.

363 The number of indentation grid points made on the three samples cor-
364 roded in a saline environment (LMDC3, LMDC14 and LMDC25) varies be-
365 tween 46 and 77 points. The results obtained for the elasticity modulus and
366 the hardness present an important dispersion, with elasticity moduli that

may be very low. The hardness is comprised between 1 and 11 GPa, while Young's modulus is comprised between 30 and 150 GPa. Consequently, the statistical analysis could not be performed under such conditions, and additional indentation grids would be necessary. We observe that H and E seem to increase with the age of the sample. LMDC3 and LMDC14 present an important number of impressions leading to values lower than ($H = 4$ GPa; $E = 70$ GPa), which may be due to the occurrence of ferrihydrite.

The results obtained from the combined micro-indentation and Raman analysis are gathered in Table 3.

3.2.2. Statistical interpretation of micro-indentation results

For the natural corrosion products, the indentation grids have been performed on the regions mapped with Raman spectroscopy beforehand. We have observed in [3] that if we retain the indentation results corresponding to a percentage of the main phase higher than 85 %, we may distinguish between two groups. If goethite is the dominant phase, the elasticity modulus is comprised between 92 and 111 GPa, whereas if magnetite/maghemite is the main component, the elasticity modulus takes higher values, comprised between 107 and 158 GPa. However, the comparison between the phase proportions and the corresponding elasticity moduli do not allow us to associate an average value of Young's modulus to a given phase. Indeed, the proportions of the various phases vary for each impression, while the part played by nanoporosity is difficult to assess. For this reason, the average val-

ues of elasticity moduli per phase have been determined using a statistical analysis based on a Gaussian mixture model, by considering for each impression the couple (H, E) . Figure 10 details the statistical analysis performed on a grid of 91 indentation points from the archeological analogues. We distinguish two indentation groups displaying different Young's moduli and hardness values. Each of these groups corresponds to specific compositions of corrosion products.

Table 2 summarizes the results of the statistical study concerning the number of representative phases, their relative proportions and corresponding Young's moduli. This study has been conducted on the corroded rebar from the reinforced concrete building, the ferrous artefact and the artificial corrosion developped under impressed current. We find two groups with statistically distinguishable properties for the corroded rebar and the ferrous artifacts, as well as for the artificial corrosion.

For the corrosion synthetized under impressed current, we observe that phase 1 with the lower elasticity modulus (ferrihydrite) is largely dominant with respect to the second phase. The second phase presents an elasticity modulus lower than the modulus associated with goethite, which may indicate a mixture of phases including goethite and ferrihydrite. For the corrosion developed under atmospheric conditions, the analysis highlights similar average values of Young's modulus for the dark matrix regions mainly composed of goethite (phase 1). According to Raman analysis, phase 2 corresponds to the marblings of maghemite/ferrihydrite, the statistical analysis gives an average

412 elasticity modulus of 113 GPa for the concrete building, and a higher value of
 413 139 GPa for the archeological artefact. The discrepancy between those values
 414 could be due to a higher crystallization level in the older sample. The sta-
 415 tistical analysis also provides the various proportions of both samples, which
 416 are close to the proportions inferred from the Raman spectroscopy coupled
 417 with CorATmos [2]. For instance, we obtain the following proportions for
 418 the main components of the concrete building sample with CorATmos: 69 %
 419 for phase 1 and 31 % for phase 2. Our study tends to show that the goethite
 420 phase is predominant for the two samples of natural corrosion. Furthermore,
 421 the older sample (aged 660 years) presents a smaller proportion of goethite
 422 as compared to the concrete building (aged 50 years).

423

424 4. Discussion

425 4.1. *Typical layouts of corrosion products and associated elasticity moduli*

426 We can conclude that the various samples present distinct compositions.
 427 The early-age corrosion products developed in the laboratory under imposed
 428 current are mainly composed of ferrihydrite which average Young's modulus
 429 is rather low, around 56 GPa. The study of the local elasticity modulus of
 430 the different corrosion layers has evidenced the fact that the dark matrix of
 431 goethite presents a nearly constant value of Young's modulus, between 90 and
 432 95 GPa. The clear marblings are characterized by a composition which differs
 433 for each sample, and imply an evolution of the local mechanical properties.

434 The sample originating from a 50 years-old concrete building is composed of
 435 a dark matrix consisting mainly of goethite, and clear marblings correspond-
 436 ing to a mixture of ferrihydrite and maghemite with an average Young's
 437 modulus of 113 GPa. The sample taken from the historical monument and
 438 aged over 660 years displays a dark matrix composed of goethite and clear
 439 marblings of magnetite/maghemite, with an elasticity modulus around 140
 440 GPa. The samples corroded under a controlled saline environment offer the
 441 same kind of phase distribution, characterized by a main phase of goethite
 442 and marblings of variable composition : mainly ferrihydrite and local traces
 443 of akaganeite owing to chloride ions for the 3 years old sample, a mixture of
 444 maghemite and ferrihydrite and traces of akaganeite for the 14 years-old sam-
 445 ple, and a mixture of magnetite and maghemite for the 25 years-old sample.
 446 For the sample aged 3 years, the confrontation between micro-indentation
 447 data and Raman analysis leads to the following estimates for the elasticity
 448 moduli of the phases : 94 GPa for the goethite matrix, and 51 GPa for the
 449 matrix of ferrihydrite. By using the same approach with the 14 years-old
 450 sample, we obtain an average value of 91 GPa for the goethite matrix, and
 451 an average value of 59 GPa for the marblings. For the sample of 25 years,
 452 we identify three different elasticity moduli : the value of 90 GPa may be
 453 attributed to the goethite matrix, the average value of 63 GPa is more dif-
 454 ficult to interpret but may be associated with ferrihydrite (not detected in
 455 our Raman mappings), while the higher value of 124 GPa corresponds to
 456 a mixture of magnetite and maghemite and possibly ferrihydrite. The con-

457 clusions of our study are in agreement with the findings of other authors.
 458 [37, 38, 39] have assumed that the clear marblings are initially composed
 459 of ferrihydrite/feroxyhyte, which would evolve towards better crystallized
 460 phases such as magnetite/maghemite due to the progressive disappearance
 461 of less stable phases after successive reduction/oxidation cycles.

462

463 4.2. *Relation between elastic modulus and hardness*

464 Table 4 summarizes the average Vickers hardness measured H for each
 465 phase or group of phases identified on the investigated corrosion samples.
 466 Hardness is related to the elastic and plastic properties of a material [40].
 467 As already illustrated in Figure 9, the hardness values are rather low, which
 468 indicates a ductile behaviour with important plastic deformations [41, 40].
 469 Similar to Young's moduli values listed in Table 3, we observe an overall
 470 increase of H with the age of the specimen. As expected, we obtain from
 471 Tables 3 and 4 and Figure 9 that the Young's modulus E or more precisely
 472 the shear modulus G (since in our case $G = \frac{E}{2(1+0.3)}$) and H are strongly
 473 correlated, for the whole set of samples and also for the identified phases.
 474 Although no general and quantitative relationship has been established, nu-
 475 merous studies have been dedicated to correlate hardness with bulk modulus
 476 or shear modulus [42, 41, 40]. [41] investigate linear empirical fittings between
 477 elastic properties and hardness, and obtain that the shear modulus G shows
 478 the best linear dependence on the Vickers hardness, while the bulk modulus

cannot be linearly correlated with H . This fact is explained by dislocation theory : hardness depends mainly on the plastic deformation associated with the nucleation and motion of dislocations [41, 40], which may be more easily caused by shear deformation than by volume change. We also observe that the relative incertitude concerning both E and H has a tendency to decrease with the age of the sample. The standard deviation measured on the different samples is not negligible and is more important than for Young's modulus, this may be explained by the fact that Vickers hardness is not an intrinsic property, and is strongly affected by extrinsic factors such as surface defects, local stress field, and morphology [41, 40]. In our case the effect of these factors are amplified by the strongly heterogeneous and evolving microstructure. However, the relative decrease of the data scatter is consistent with the fact that hardness is also strongly related to intrinsic properties such as bond strength and cohesive energy [42, 41, 40], which may increase with the age of the sample as we evolve towards better crystallized phases. Vickers hardness is also related to crystal structure, which is more stable for the older samples. Finally, $\frac{H}{E}$ ratio or resilience describes the relative resistance to elastic and plastic deformation, and is potentially predictive of the limit yield strain to failure, fracture toughness, and wear resistance [43]. From Tables 3 and 4, we obtain similar $\frac{H}{E}$ ratios for all the identified phases, from which we may deduce that the goethite matrix and the marblings (of varying composition with age) have to sustain similar mechanical wear stress, and there is no privileged zone for crack initiation at the mesoscopic scale.

502 4.3. Time evolution of the phase composition and mechanical properties

503 From the identification of the local elasticity properties presented in this
504 paper, we can also formulate the assumption of a progressive increase of
505 the mechanical properties of the corrosion samples concurrently with the
506 evolution of the phases constituting the marblings: starting from ferrihydrite
507 ($E = 56$ GPa) in the early-age samples, we go through goethite ($E \simeq 92$ -95
508 GPa) and a mixture of maghemite/ferrihydrite ($E \simeq 113$ GPa) in the 50
509 years-old sample, before reaching the phase of magnetite/maghemite ($E \simeq$
510 139 GPa) in the older samples. Consequently, the average Young's modulus
511 would increase with the age of the corrosion product layers, from about 50
512 GPa for early-age samples to 140 GPa for samples aged several hundred
513 years. As the conditions of corrosion differ from one sample to the other,
514 we cannot directly compare the whole set of results of physico-chemical and
515 micromechanical analysis conducted on the various samples. However, the
516 study of samples corroded under saline environment tends to corroborate
517 the assumption of an increase of the elasticity modulus with the age of the
518 corrosion product layers. The average value of Young's modulus is plotted
519 in Figure 11 with respect to the age of the sample. Based on the limited
520 data available, it may be interesting to notice that there are two regions: the
521 elasticity modulus increases abruptly during the first 25 years of ageing, and
522 tends to stabilize afterwards with a very moderate increase.

523 5. Conclusion

524 Using micro-indentation testing coupled with Raman microspectrometry (and CorATmos semi-quantitative analysis) and statistical analysis on
525 the same impressed zones, we have been able to relate the local mechanical
526 properties (elasticity modulus and hardness) of steel corrosion products to
527 typical phase distribution layouts. The main conclusions are the following
528 ones:
529

- 530 1. The microstructure of the investigated corrosion samples is composed
531 of different phases which may present themselves as mixtures at the
532 mesoscopic scale. A dark matrix composed essentially of goethite is
533 crossed by marblings of varying composition.
- 534 2. The local Vickers hardness varies between 1 and 12.1 GPa, while the lo-
535 cal elasticity modulus varies between 30 and 160 GPa on the whole set
536 of indented samples (448 impressions). To our knowledge, the hard-
537 ness and Young's modulus distributions identified at the level of the
538 elementary corrosion products constitute a unique set of data with no
539 equivalent in the published literature.
- 540 3. We have identified typical elasticity and hardness values per phases.
541 The lowest values of Young's modulus and hardness are associated with
542 ferrihydrite, and the highest E and H values have been measured on
543 marblings of magnetite/maghemite.
- 544 4. The $\frac{H}{E}$ ratio is quite similar for all the encountered phases, which may

545 indicate that the matrix and the marblings can sustain similar me-
546 chanical fatigue stress, and that there is no preferred zone for crack
547 initiation.

548 5. The corrosion products may evolve with time: the corrosion under
549 impressed current contains mainly ferrihydrite; apart from goethite,
550 chloride corrosion is composed of ferrihydrite, maghemite/ferrihydrite,
551 and magnetite/maghemite/ferrihydrite for the samples aged 3, 14 and
552 25 years respectively; the corroded rebar aged 50 years presents a ma-
553 trix of goethite with marblings of maghemite and ferrihydrite; and for
554 the ferrous artefacts aged 660 years, the goethite matrix is crossed by
555 marblings of magnetite and maghemite. The time evolution towards
556 better crystallized phases is associated with an increase of E and H .

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750 Indentation tests results and resulting Gaussian distribution for the ancient

751 artefacts.

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753 Figure 11. Variation of the average Young's modulus with the age of the

754 corroded samples.

755

Table 1: Components of corrosion product layers and their percentages by mass of iron.

Component	Chemical formula	Mass percent of iron (%)
Magnetite	Fe_3O_4	72.4
Maghemite	$\gamma - \text{Fe}_2\text{O}_3$	70.0
Goethite	$\alpha\text{-FeOOH}$	62.9
Lepidocrocite	$\gamma\text{-FeOOH}$	62.9

Table 2: Exploitation of the indentation grids using a Gaussian mixture model.

Sample	Phases	E (GPa)	Proportion (%)
Concrete building (115 points)	1	92 ± 10	66
	2	120 ± 13	34
Archeological artefact (91 points)	1	95 ± 8	58
	2	139 ± 10	42
Artificial corrosion (49 points)	1	51 ± 4.7	82
	2	81 ± 9	18

Table 3: Average Young's moduli per phase for all the investigated samples. F : Ferrihydrite; G : Goethite; Magn. : Magnetite; Magh. : Maghemite;

Sample	Phase	E (GPa)
Artificial corrosion (49 points)	F	56 ± 9
Chloride corrosion 3 years (46 points)	G	94 ± 10
	F	51 ± 14
Chloride corrosion 14 years (70 points)	G	90 ± 10
	Magh./F	59 ± 11
Chloride corrosion 25 years (77 points)	G	90 ± 9
	F	63 ± 8
	Magn./Magh./F	124 ± 12
Corroded rebar 50 years (115 points)	G	92 ± 10
	Magh./F	120 ± 13
Ferrous artefact 660 years (91 points)	G	95 ± 8
	Magn./Magh.	139 ± 10

Table 4: Average Hardness values per phase for all the investigated samples. F : Ferrihydrite; G : Goethite; Magn. : Magnetite; Magh. : Maghemite;

Sample	Phase	H (GPa)
Artificial corrosion (49 points)	F	3.11 ± 1.02
Chloride corrosion 3 years (46 points)	G	4.76 ± 0.80
	F	2.43 ± 0.96
Chloride corrosion 14 years (70 points)	G	6.26 ± 1.33
	Magh./F	3.21 ± 0.90
Chloride corrosion 25 years (77 points)	G	6.08 ± 1.49
	F	4.10 ± 1.24
	Magn./Magh./F	9.68 ± 1.39
Corroded rebar 50 years (115 points)	G	5.51 ± 0.87
	Magh./F	8.68 ± 1.23
Ferrous artefact 660 years (91 points)	G	5.35 ± 0.86
	Magn./Magh.	9.53 ± 1.29

Figure 1: Investigated samples. (a) Sample of reinforced concrete building aged 50 years; (b) ancient ferrous artefact aged 660 years; (c) corrosion synthesized under imposed current. Corrosion developed in the laboratory under controlled saline conditions : (d) 3 years-old sample; (e) 14 years-old sample; (f) 25 years-old sample.

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