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## Contribution to the micro-mechanical analysis of corrosion products formed during long-term carbonation induced corrosion of steel

Marijana Serdar, Valerie L'Hostis, Stéphane Poyet, Damien Feron

#### Abstract

- Use micro-indentation to distinguish different phases of corrosion products, confirmed with Raman and SEM
- Obtain spatial distribution of different phases, in relation to the surface of the steel
- Compare mechanical properties of same phases at different age

#### Keywords

#### 1. INTRODUCTION

At the micro-scale level a typical corrosion pattern is composed of four successive layers: the uncorroded metal, the corrosion layer or dense product layer DPL (or inner corrosion product layer), the transformed medium containing phases originating from both the DPL and the binder (or the outer corrosion product layer) and the binder [1]–[3]. During corrosion different types of corrosion products form, composed of different ratios of ferrous ions and oxide, hydroxides. Different products have different physical and mechanical properties, mainly density, resistivity, volume and modulus of elasticity compared to iron. Knowing properties of each of these levels is indispensable for service life modelling and durability management of structures. One of the methods that can be employed for evaluating micro-mechanical properties of corrosion products is micro or nano-indentation. Micro-indentation has been a widely-used method to interpret the local elastic properties and hardness of different materials at the micro-scale. It was previously used to study micromechanical properties of products found on thicker layers of products found on

archaeological analogues [2], [5], [6]. More recently nano-indentation is used to study mechanical properties of cement hydration products [7]–[9]. Micro-indentation and nano-indentation tests performed on corrosion layers reveal that local elastic modulus values are in the range of 50 and 200 GPa [2]. Other results indicate several magnitudes lower values, obtaining modulus of elasticity as low as 0.1 GPa [10], [11]. In the present literature there is still a lack of distinction between the mechanical properties of different layers of corrosion products, and there is still a high discrepancy between the values obtained, depending on the methods used (nano, micro-indentation) and sample preparation (pure corrosion products, cross section). Taking into account the importance of this parameter in time to cracking of concrete predictions, it is evident that further efforts should be focused at evaluating this parameter with higher precision.

It is not only the type of products that influence the stresses formed in the concrete during corrosion, it is their position compared to the surface of the steel. The spatial distribution of products formed during long-term corrosion can reveal history of their consecutive formation, dissolution of one and formation of the other phase. Since the mechanical properties are different, hypothesis is that the information on their mechanical properties can be used for differentiating them and analysing their spatial distribution.

The aim of the present research is to perform micro-indentation analysis to distinguish different phases of corrosion products formed during long-term corrosion. Since samples from building of different age were taken, obtain values were also compared in a sense of changes in the corrosion products.

#### 2. MATERIALS AND METHODS

In order to perform analysis of corrosion products it is necessary to have thicker products available. Products can be formed artificially, using electrochemical or environmental acceleration [10], [17]. Other strategy is to use samples of archaeological analogues [6] or

samples from old concrete structures [2], which went through the natural long-term process of corrosion of steel. In the present research corrosion samples were taken from three different old buildings. One sample is cored from Maison du Bresil, Cite Universitaire (1957 - 1959) and is approximately 50 years old corrosion sample. Second is a sample from ONERA wind tunnel, Meudon (1950), which is approximately 60 years corrosion sample. The last sample is from Bourse du travail in Bordeaux (1938), approximately 70 years old corrosion sample. Samples were previously mounted in epoxy resin and cut to obtain thinner cross sections. They were grinded with SiC papers and then polished with a 3  $\mu$ m diamond paste under ethanol. On all of the samples used in this research there are available information that can be found elsewhere [1], [15], [18].

Micro-mechanical properties of corrosion products were obtained using a depth sensing Micro Indenter (MHT) of CSM Instruments. Indentation tests were carried out under constant room temperature of 20 °C. Quasi-static loadings comprised between 0.03 and 30 N was applied by means of a Vickers diamond indenter/probe, with a load resolution of 0.3 mN and a resolution in displacement of 1 nm, and a microscope magnification of 5x or 50x. The load and depth (or relative displacement of the indenter), were continuously monitored during a programmed micro-indentation load cycling through differential capacitive sensors, resulting in a typical load-indenter displacement curve [19]. Under increasing loading, the impression produced consists of permanent or plastic deformations, and elastic deformations recoverable under unloading. Determination of the elastic recovery by analysing the unloading data according to a model for the elastic contact problem leads to a solution for calculation of elastic or Young's modulus and also micro-hardness of the test area, according to Oliver and Pharr's method [2], [19].

Raman microspectroscopy has been carried out locally in order to determine and locate precisely the constitutive phases of the corrosion system and to correlate them to the results of micro-indentation. Raman microspectroscopy is often used for determination of different iron phases formed as corrosion products [20]–[23]. Raman spectra were obtained using spectrometer Jobin Yvon Horiba with a Laser at 532 nm. The laser power is filtered under 100 mW in order not to transform under laser heat the corrosion phase during measurements. The diameter of analysed area under the 100x objective is of about 3  $\mu$ m. Acquisition and analysis of data was performed using software Labspec 5. The acquisition time ranged from 10 to 40 s. Most of the phases are easily distinguishable, but some have similar spectra, such as magnetite (Fe<sub>3</sub>O<sub>4</sub>) and wüstite (FeO) [20]. The most usual corrosion products, together with their wavenumbers obtained from Raman microspectroscopy and their density are listed in the table below.

Oxides		Density, g <sup>cm-3</sup>	Wavenumbers, cm <sup>-1</sup>	Elastic modulus, GPa
Fe(OH) <sub>2</sub>	Iron hydroxide		460, 550	
Fe(OH) <sub>3</sub>	Iron trihydroxide		395, 696, 1335, 692	
α-FeOOH	Goethite	4,3 - 3,3	205, 247, 300, 386, 418, 481, 549	
$\beta$ - FeOOH	Akaganeite	3,8 - 3,6	314, 380, 549, 722	
γ - FeOOH	Lepidocrocite	~ 4	219, 252, 311, 349, 379, 528, 648	
$\delta$ - FeOOH	Feroxyhite	4,2	297, 392, 666	
α-Fe <sub>2</sub> O <sub>3</sub>	Hematite	5,23	226, 245, 292, 411, 497, 612	
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	Maghemite	4,87	381, 486, 670, 718	
Fe <sub>3</sub> O <sub>4</sub>	Magnetite	5,18	300, 532, 667	
FeO	Wüstite	~ 6	655	

 Table 1 List of the most often corrosion products with their Raman spectra

 wavenumbers [20], [21], [24]

#### 3. **RESULTS**

#### **3.1.** Corroded steel in concrete

The first analysed sample was the sample from Maison du Brésil (Paris, France), which is a sample of 50 years old corroded reinforcing steel in concrete, Fig 1. Corrosion products in the case of 50 year old sample are formed on one side of the sample. All around the steel a 40  $\mu$ m thin layer of corrosion products was evident, probably original mill scale. On part of the rim there is a thicker layer of corrosion products forming between the steel and the mill scale, forming inner layer of corrosion products. On some other part, there are both inner and outer corrosion products evident, formed beyond the mill scale, Fig 5 b.



# Figure 1 Cross section of sample with reinforcing steel, concrete and layer of corrosion products

On the layer of mill scale micro indentation measurements were performed and values around 110 GPa were obtained. On the same locations Raman micro-spectroscopy was performed to evaluate which phases form the mill scale.



Figure 2 Raman spectra collected on mill scale

Raman spectra obtained on locations 1, 2 and 3 on mill scale indicate that the mill scale is constituted of wüstite and/or magnetite. These phases are usually hard to distinguish, since the strongest peak around 655 cm<sup>-1</sup> for wüstite lays closely to 667 cm<sup>-1</sup> for magnetite [20]. It is possible to distinguish the two by additional peaks at around 300 and 532 cm<sup>-1</sup> observed for magnetite but absent in the case of wüstite [20]. In the same study it was also observed that peak of wüstite at 655 cm<sup>-1</sup> is broader than the closely positioned peak of magnetite. Looking at the obtained spectra, it is possible that both phases are present, since spectra 3 lacks peaks at 300 and 532 cm<sup>-1</sup> and has a broader peak at around 655 cm<sup>-1</sup>, compared to spectra 1 and 2. Wüstite was also found to be the densest phase between the corrosion products because of its high Fe/O ratio [21].

Raman spectra were next collected on the phase between the steel surface and the mill scale, or inner corrosion products. The collected spectra showed that this phase is mostly composed of goethite.

Fig 3 shows optical image and obtained micro-indentation results on the corresponding locations. Next to the surface of the steel there is a layer of corrosion products with lower value of modulus of elasticity (between 20 to 40 GPa), followed by a layer of dense products

with higher value of modulus of elasticity (around 100 GPa), Fig 3 b). After the dense layer approximately 100  $\mu$ m thick, there is a layer of mixed corrosion products and cement matrix, so called transformed medium, with modulus of elasticity around 20 - 40 GPa. Raman microspectroscopy indicated that the dense layer is composed of a mix of magnetite, goethite and potentially hematite, Fig 3 c). Goethite has lower density (3,8 g/cm<sup>3</sup>) compared to wüstite, but higher coefficient of expansion, 3,3 for goethite compared to 1,7 for wüstite.



Figure 3 Optical image a), micro-indentation b) and Raman spectra c) results on corresponding locations

Therefore, in the case of this sample, after the steel (185 GPa), there is a layer of dense corrosion products, probably mill scale, composed of wüstite and magnetite and with modulus

of elasticity of 120 GPa. On locations where mill scale was cracked there is an inner layer of corrosion products formed mostly of goethite, with elastic modulus of 40 to 60 GPa. After the dense layer, there is a layer of transformed media with modulus of elasticity around 40 GPa, composed mostly of goethite. Concrete has values of modulus of elasticity around 20 GPa.



Figure 4 Frequency analysis of elastic modulus values

The second sample was from ONERA building, a sample of 60 years old corroded reinforcing steel in concrete. In the case of this sample there is no mill scale evident as a continuous layer around the steel. However, on some points around the surface of the steel there is leftover mill scale visible, mixed with inner and outer corrosion products.



Figure 5 Layers of corrosion products: inner layer, leftover mill scale, outer layer and transformed media

Location with all visible layers was chosen and both micro-indentation and Raman microspectroscopy were performed. Following three highlighted lines of micro-indentation measurements it can be observed that steel has modulus of elasticity around 200 GPa. Next, there is an instant decrease in the values of elastic modulus to 80 GPa, since lines are passing through the first layer of corrosion products. On line 9 it is visible an increase in values once the line passes through the leftover mill scale, with values of elastic modulus around 120 GPa. Lastly, lines go through outer layer of products and values of elastic modulus decrease to 60 and 40 GPa.



Raman microspectroscopy performed on the same location revealed that the inner layer of products, products that are formed between mill scale and steel (points 1, 6 and 11), and outer layer, products that are formed after the mill scale (point 10), are mostly composed of goethite. Marblings of leftover mill scale are mostly composed of maghemite and magnetite.





Map on Figure was obtained by performing automatic micro-indentation on a matrix with 25 points in x direction, with 50  $\mu$ m distance, and 25 points in y direction, with 50  $\mu$ m distance, comprising a total area of 1200  $\mu$ m x 1200  $\mu$ m. Map shows layer of steel, inner corrosion products, part of the leftover mill scale and outer corrosion products. On the upper right of the grid there is an aggregate visible. Layers can also be distinguished on the map of micro-indentation. Steel has a modulus of elasticity of around 220 GPa. Inner corrosion layer, which are mostly formed of goethite have modulus between 60 and 80 GPa, mill scale composed of maghemite and magnetite between 90 and 120 GPa, and outer corrosion layer between 40 and 60 GPa.





The last analysed sample was the sample from Bourse du Travail de Bordeaux (France), which is a sample of 80 years old corroded reinforcing steel in concrete. In the case of this sample, all around the steel a 30  $\mu$ m thin layer of corrosion products was evident, original mill scale, Fig 8 a. The same as in the case of 50 year old sample, at a certain point there is a layer of corrosion products forming between the steel and the mill scale and evident penetration of corrosion products further outside the mill scale, Fig 8 b.



Figure 6 Mill scale layer around the steel a); Inner and outer corrosion products b)

Several locations where all layers were evident (steel, corrosion products, mill scale, outer corrosion products, concrete matrix) were chosen and analysed using micro-indentation and Raman microspectroscopy.



Figure 7 a) Optical microscope image, b) Modulus of elasticity of different phases (numbers on both the optical image and the micro-indentation diagram indicate points for Raman microspectroscopy)



Figure 8 Line 6 Raman spectra obtained on inner layer a); mill scale b)

Goethite is the main phase forming between the mill scale and the steel (points 1, 2, 3 on Figure 23 a), while magnetite is the main phase of the mill scale (points 5-1, 5-2 on Figure 23 b). Goethite closer to the surface of the steel has modulus of elasticity of around 50 GPa, while magnetite in the mill scale has modulus of 80 GPa. Outer layer (away from the mill scale) is composed from goethite and has modulus of around 50 GPa, which is decreasing with the increase of distance from the steel, due to the mixing of corrosion products layer with cement matrix. Beside the goethite, hematite is observed.

Map on Figure 12 was obtained by performing automatic micro-indentation on a matrix with 15 points in x direction, with 50  $\mu$ m distance, and 15 points in y direction, with 50  $\mu$ m distance. Map shows layer of steel, inner corrosion products, mill scale and outer corrosion products.



Figure 9 Optical microscope image of location 2 after micro-indentation and map of values of modulus of elasticity

For this sample it can be concluded that the modulus of elasticity od steel is between 150 - 200 GPa, that the inner layer is mostly composed of goethite with modulus of elasticity between 40 and 60 GPa, mill scale composed of magnetite with modulus of elasticity between

70 and 90 GPa and outer layer of corrosion products composed mostly of goethite with modulus of elasticity between 20 and 40 GPa.



Figure 10 Frequency analysis of elastic modulus values

#### 4. **DISCUSSION**

#### 4.1. Layers of corrosion products in reinforced concrete

In the present study it was confirmed on three different that transition zone between the steel and concrete during corrosion is composed of several consecutive layers: i) inner layer of corrosion products that form between the surface of the steel and the original mill scale, ii) original mill scale, iii) outer corrosion products, iv) transformed medium. The inner corrosion layer is mostly composed of goethite and had modulus of elasticity between 50 to 70 GPa for 80 years old sample and 40 GPa for 50 years old sample. The layer of original mill scale is evident in the case of all tested samples, around the whole surface of the steel, in a thick layer of 55  $\mu$ m for 50 years old sample and of 20  $\mu$ m for 80 years old concrete. For both tested samples it was observed that the layer is mostly composed of magnetite and wüstite and has modulus of elasticity around 115 GPa for younger concrete sample and around 70 - 90 GPa for older one. The presence of remains of former mill scales made of wüstite, magnetite and hematite formed during the manufacturing process is usually found on old samples [15], [16]. This layer can be visible next to the surface of the steel, or away of the surface, depending how far corrosion has propagated. It usually has higher values of modulus of elasticity compared to other corrosion products, between 90 and 130 GPa [16], and is denser (light in colour, higher iron amount). It is reported in the literature that this layer has lower values of modulus of elasticity in the case of older samples, since it had time to additionally oxidize [16].

It was previously reported that the layer of mill scale has higher values of modulus of elasticity compared to corrosion products [17]. It was also observed, as is the case of tested samples, that mill scale tends to have lower values of modulus of elasticity for older samples, due to the long-term oxidation of the mill scale [16]. Both samples showed that the inner layer of products is composed of goethite. In the case of younger sample hematite is also observed, while in the case of older maghemite. Outer corrosion products are also formed of goethite, being less dense and more mixed with concrete matrix, further from the surface. The modulus of elasticity of this layer was found to be around 30 - 40 GPa for younger concrete and around 50 GPa for older concrete. It is spread into around 800 µm and 1150 µm layer for younger and older concrete sample, respectively.

The influence of mill scale on the corrosion of steel in concrete has been investigated in different studies. Mahallati *et al.* [29] showed using cyclic potentiodynamic polarization that in chloride-free environment mill scale diminishes protective properties of passive film formed on rebars. At the same time their study showed that in chloride rich environment all of the tested rebars will corrode from the beginning no matter if they have mill scale or not. In the study of corrosion products and mill scale in chloride environment and under loading, performed by Jaffer and Hansson [30], it was indicated that porous mill scale on the surface of the steel allows ingress of chloride ions, but could potentially delay the onset of corrosion.

Studies performed on iron carbonate (FeCO<sub>3</sub>) corrosion scale, forming in the presence of oxygen-free carbon dioxide and a water phase, showed that this scale provides some protection of the steel from further corrosion [31]. However, if defects exist inside the scale, such as a crack, any mechanical load will lead to the crack propagating inside the scale, resulting in the scale spalling. Additionally, if the interface between the scale and steel includes voids or cracks, the expansion of these defects will cause the delamination of the scale from steel [32]. Similar was shown on the mill scale, in research performed by Ghods et al. [33]. Both the cracks and delamination voids connected by pore solution by micro-cracks serve as pathways for concrete pore solution to reach the steel surface, hence allowing ion movement between the pore solution and the crevices [33]. As is usual for crevice corrosion, the chemical composition of the pore solution within the crevices begins to differ from that of the bulk solution and favourable conditions for corrosion occur. Therefore, through the porous, cracked or delaminated mill scale oxygen dissolved in pore water reaches the metal/oxide interface and formation of inner corrosion products starts. These inner layer of goethite is evident both in the case of 50 years old concrete, Figs. 6 b), 11 a), and in the case of 80 years old concrete, Figs. 19, 21, 22. Also, because of the difference between steel and mill scale, galvanic corrosion can occur, which is potentially observed on Fig 16. It is evident that there are layers of different corrosion products, which have different density and different electrical resistivity. It is possible then that due to the favourable conditions for the corrosion, corrosion products transform from one phase to the other due to the galvanic corrosion.

Outer layer, found between the mill scale and transformed medium is formed during an aqueous corrosion process, since it is mostly formed from an oxyhydroxide phase goethite. In study by Demoulin *et al.* [15] it is hypothesised that this layer is formed from iron ions liberated on the metal/oxide interface, which migrate through the mill scale forming oxyhydroxides on the outer part of the mill scale.

- Mill scale is not loving during time
- Inner products form, since mill scale is porous and oxide reaches the surface of the steel
- Also possible that due to the galvanic corrosion phases switch from one to another
- At a certain point products start to form also outside the mill scale
- Question remains whether this products are diffusing from the inner to the outer side through the mill scale
- Mill scale has a higher modulus of elasticity, it is not easily deformable and it stays untouched
- The hypothesis would be that only once the product start to diffuse outside the mill scale, corrosion products form stresses in concrete and create cracks

#### Literature

- [1] W. Chitty, P. Dillmann, V. L'Hostis, and C. Lombard, "Long-term corrosion resistance of metallic reinforcements in concrete a study of corrosion mechanisms based on archaeological artefacts," *Corr Sci*, vol. 47, no. 6, pp. 1555–1581, Jun. 2005.
- [2] a. Dehoux, F. Bouchelaghem, Y. Berthaud, D. Neff, and V. L'Hostis, "Micromechanical study of corrosion products layers. Part I: Experimental characterization," *Corros. Sci.*, vol. 54, pp. 52–59, Jan. 2012.
- [3] A. Millard and V. L'Hostis, "Modelling the effects of steel corrosion in concrete, induced by carbon dioxide penetration," *Eur. J. Environ. Civ. Eng.*, vol. 16, no. 3–4, pp. 375–391, Apr. 2012.
- [4] Y. Zhao, Y. Wu, and W. Jin, "Distribution of millscale on corroded steel bars and penetration of steel corrosion products in concrete," *Corros. Sci.*, Sep. 2012.
- [5] S. Reguer, P. Dillmann, and F. Mirambet, "Buried iron archaeological artefacts: Corrosion mechanisms related to the presence of Cl-containing phases," *Corros. Sci.*, vol. 49, no. 6, pp. 2726–2744, Jun. 2007.
- [6] J. Monnier, D. Neff, S. Réguer, P. Dillmann, L. Bellot-Gurlet, E. Leroy, E. Foy, L. Legrand, and I. Guillot, "A corrosion study of the ferrous medieval reinforcement of the Amiens cathedral. Phase characterisation and localisation by various microprobes techniques," *Corros. Sci.*, vol. 52, no. 3, pp. 695–710, Mar. 2010.
- [7] C. Hu and Z. Li, "Micromechanical investigation of Portland cement paste," *Constr. Build. Mater.*, vol. 71, pp. 44–52, Nov. 2014.
- [8] D. Davydov, M. Jirásek, and L. Kopecký, "Critical aspects of nano-indentation technique in application to hardened cement paste," *Cem. Concr. Res.*, vol. 41, no. 1, pp. 20–29, Jan. 2011.
- [9] K. Velez, S. Maximilien, D. Damidot, G. Fantozzi, and F. Sorrentino, "Determination by nanoindentation of elastic modulus and hardness of pure constituents of Portland cement clinker," *Cem. Concr. Res.*, vol. 31, no. 4, pp. 555–561, Apr. 2001.
- [10] S. Care, Q. Nguyen, V. L'Hostis, and Y. Berthaud, "Mechanical properties of the rust layer induced by impressed current method in reinforced mortar," *Cem Concr Res*, vol. 38, no. 8–9, pp. 1079–1091, Aug. 2008.
- [11] Y. Zhao, H. Dai, H. Ren, and W. Jin, "Experimental study of the modulus of steel corrosion in a concrete port," *Corros. Sci.*, vol. 56, pp. 17–25, Mar. 2012.
- [12] F.-J. Ulm, M. Vandamme, C. Bobko, J. Alberto Ortega, K. Tai, and C. Ortiz, "Statistical Indentation Techniques for Hydrated Nanocomposites: Concrete, Bone, and Shale," J. Am. Ceram. Soc., vol. 90, no. 9, pp. 2677–2692, Sep. 2007.

- [13] L. Sorelli, G. Constantinides, F.-J. Ulm, and F. Toutlemonde, "The nano-mechanical signature of Ultra High Performance Concrete by statistical nanoindentation techniques," *Cem. Concr. Res.*, vol. 38, no. 12, pp. 1447–1456, Dec. 2008.
- [14] G. Constantinides, F. Ulm, and K. Van Vliet, "On the use of nanoindentation for cementitious materials," vol. 36, no. April, pp. 191–196, 2003.
- [15] A. Demoulin, C. Trigance, D. Neff, E. Foy, P. Dillmann, and V. L'Hostis, "The evolution of the corrosion of iron in hydraulic binders analysed from 46- and 260-year-old buildings," *Corros. Sci.*, vol. 52, no. 10, pp. 3168–3179, Oct. 2010.
- [16] Y. Zhao, H. Dai, and W. Jin, "A study of the elastic moduli of corrosion products using nano-indentation techniques," *Corros. Sci.*, vol. 65, pp. 163–168, Dec. 2012.
- [17] Y. Zhao, H. Dai, and W. Jin, "A study of the elastic moduli of corrosion products using nano-indentation techniques," *Corros. Sci.*, vol. 65, pp. 163–168, Dec. 2012.
- [18] V. L'Hostis, D. Neff, L. Bellot-Gurlet, and P. Dillmann, "Characterization of long-term corrosion of rebars embedded in concretes sampled on French historical buildings aged from 50 to 80 years," *Mater. Corros.*, vol. 60, no. 2, pp. 93–98, Feb. 2009.
- [19] W. Oliver and G. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments," J. Mater. Res., 1992.
- [20] D. de Faria, S. Venancio Silva, and M. Oliveira, "Raman microspectroscopy of some iron oxides and oxyhydroxides," *J. Raman ...*, vol. 28, no. February, pp. 873–878, 1997.
- [21] P. Colomban, "Potential and Drawbacks of Raman (Micro) Spectrometry for the Understanding of Iron and Steel Corrosion," *New Trends Dev. Automot.* ..., 2011.
- [22] R. A. Antunes, I. Costa, and D. L. A. De Faria, "Characterization of corrosion products formed on steels in the first months of atmospheric exposure," *Mater. Res.*, vol. 6, no. 3, pp. 403–408, Jun. 2003.
- [23] S. Joiret, M. Keddam, X. R. Nóvoa, M. C. Pérez, C. Rangel, and H. Takenouti, "Use of EIS, ring-disk electrode, EQCM and Raman spectroscopy to study the film of oxides formed on iron in 1 M NaOH," *Cem Concr Comp*, vol. 24, no. 1, pp. 7–15, Feb. 2002.
- [24] S. Oh, D. Cook, and H. Townsend, "Characterization of iron oxides commonly formed as corrosion products on steel," *Hyperfine Interact.*, 1998.
- [25] D. Koleva, J. Hu, A. L. A. Fraaij, P. Stroeven, N. Boshkov, and J. H. W. de Dewit, "Quantitative characterisation of steel/cement paste interface microstructure and corrosion phenomena in mortars suffering from chloride attack," *Corr Sci*, vol. 48, no. 12, pp. 4001–4019, Dec. 2006.

- [26] W. Chitty, P. Dillmann, V. L. Hostis, and A. Millard, "Long-term corrosion of rebars embedded in aerial and hydraulic binders – Parametric study and first step of modelling," *Corros. Sci.*, vol. 50, no. 11, pp. 3047–3055, 2008.
- [27] D. Neff, P. Dillmann, L. Bellot-Gurlet, and G. Beranger, "Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system," *Corros. Sci.*, vol. 47, no. 2, pp. 515–535, Feb. 2005.
- [28] G. Duffo, W. Morris, I. Raspini, and C. Saragovi, "A study of steel rebars embedded in concrete during 65 years," *Corr Sci*, vol. 46, no. 9, pp. 2143–2157, Sep. 2004.
- [29] E. Mahallati and M. Saremi, "An assessment on the mill scale effects on the electrochemical characteristics of steel bars in concrete under DC-polarization," *Cem. Concr. Res.*, vol. 36, no. 7, pp. 1324–1329, Jul. 2006.
- [30] S. J. Jaffer and C. M. Hansson, "Chloride-induced corrosion products of steel in cracked-concrete subjected to different loading conditions," *Cem. Concr. Res.*, vol. 39, no. 2, pp. 116–125, Feb. 2009.
- [31] C. Palacios and J. Shadley, "Characteristics of corrosion scales on steels in a CO2-saturated NaCl brine," *Corrosion*, no. February, pp. 122–127, 1991.
- [32] K. Gao, F. Yu, X. Pang, G. Zhang, L. Qiao, W. Chu, and M. Lu, "Mechanical properties of CO2 corrosion product scales and their relationship to corrosion rates," *Corros. Sci.*, vol. 50, no. 10, pp. 2796–2803, Oct. 2008.
- [33] P. Ghods, O. B. Isgor, G. a. McRae, J. Li, and G. P. Gu, "Microscopic investigation of mill scale and its proposed effect on the variability of chloride-induced depassivation of carbon steel rebar," *Corros. Sci.*, vol. 53, no. 3, pp. 946–954, Mar. 2011.
- [34] M. Sancy, Y. Gourbeyre, E. M. M. Sutter, and B. Tribollet, "Mechanism of corrosion of cast iron covered by aged corrosion products: Application of electrochemical impedance spectrometry," *Corros. Sci.*, vol. 52, no. 4, pp. 1222–1227, Apr. 2010.
- http://visites.aquitaine.fr/bourse-du-travail-de-bordeaux, http://structurae.info/ouvrages/maison-du-bresil