# Preservation of historical buildings: understanding of corrosion mechanisms of metallic rebars in concrete

*Delphine Neff[a]*, Elisabeth Marie-Victoire[c,d], Valérie L'Hostis[b], Emmanuel Cailleux[c], Laurent Vincent[b], Annick Texier[c,d], Ludovic Bellot-Gurlet[e] and Philippe Dillmann[f]*

[a] Laboratoire Pierre Süe, CEA/CNRS UMR 9956, CEA Saclay, 91191 Gif/Yvette cedex, France
[b] LECBA, CEA Saclay, 91191 Gif/Yvette cedex, France
[c] Laboratoire de recherche des monuments historiques (LRMH), 29 rue de Paris, 77420 Champs-sur-Marne, France
[d] Cercle des Partenaires du Patrimoine, 29 rue de Paris, 77420 Champs-sur-Marne, France
[e] LADIR, 2, rue H. Dunant, 94320 Thiais, France
[f] IRAMAT LMC CNRS UMR5060 and Laboratoire Pierre Süe CEA/CNRS UMR9956, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

* Corresponding author: Delphine.neff@cea.fr

## Abstract

*Numerous monuments of the 20th century made of reinforced concrete are decaying due to the corrosion of their metallic reinforcements, the growth of the corrosion products generally inducing spalling. In order to prevent these degradations before the concrete cracks, it would be interesting to determine by non destructive methods the state of corrosion of the embedded rebars. Three types of corrosion forms have been evidenced on samples collected on three monuments: first is original and contains wüstite, the second is a mixture of the first and thicker layers containing oxy-hydroxides, characteristic of the third type.*

**Keywords**: iron, corrosion, concrete, Raman microspectroscopy

### Introduction

In France, carbonation induced corrosion is a major source of decay in the field of historical buildings made of concrete. The consequential cracking and spalling phenomena generate loss of material incompatible with conservation ethics. Therefore it is crucial to understand the corrosion process of embedded steel and to be able to evaluate precisely the corrosion activity on site, in order to predict and possibly prevent such decays.

Beyond the theory, recent studies have evidenced that long term corrosion patterns of iron embedded in several types of mortar are quite complex. Therefore it was interesting to study both passive and early stages of corrosion activity to understand the long term corrosion layout observed.

On another hand, on site non destructive tools such as potential mapping or corrosion rate measurements are commonly used for diagnosis of corrosion progress. But in areas heavily affected by spalling phenomena, low corrosion activity is often evidenced, so that the interpretation of the results can be problematic. Such electrochemical techniques are clearly season influenced, and corrosion rates induced by carbonation are

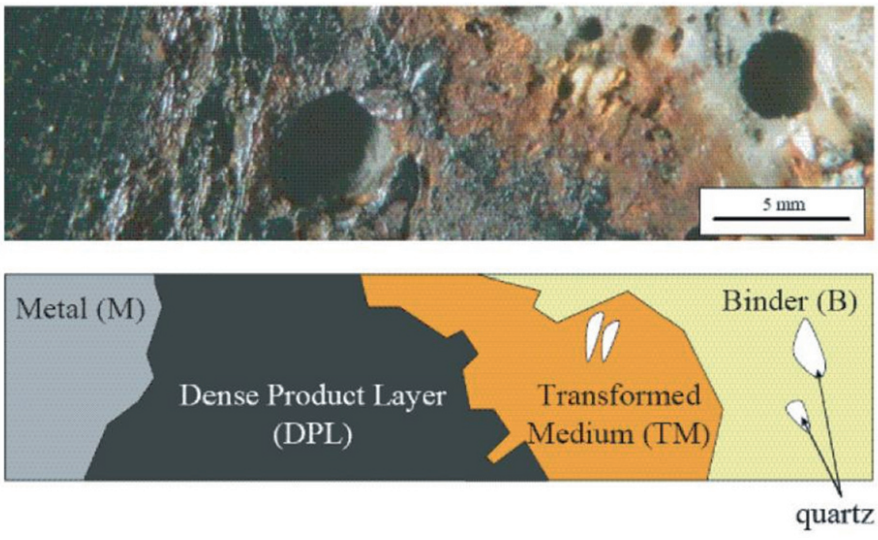



*Figure 1: Microphotography and schematic representation of a transverse section of an iron rebar corroded in a hydraulic binder after Chitty (Chitty et al. 2006)*

often very low and therefore can be difficult to measure. But another hypothesis could be that the oxide layer formed is so resistive that the conductivity necessary for the measurement is lost. As a consequence, in the aim of improving the reliability of those diagnosis tools, it seems interesting to correlate on site measurements with the identification of corrosion patterns.
The methodology adopted in this study is based on two parallel sets of characterization. One part deals with electrochemical and chemical tests realized on site and the other concerns the characterization of the corrosion products observed on reinforced concrete cores. Three reference sites, respectively 47, 56 and 68 years old were considered for sampling: Paris "House of Brazil", Meudon "Air Purifier" and Bordeaux "Union Trade Center". The correlation between on site electrochemical tests and corrosion layout identification being still in progress, only this last point will be developed in this paper.

**Corrosion mechanisms of iron rebars in concrete – previous studies**

Concrete, due to its high alkalinity, represents a protective medium for embedded steel. But carbonation or chloride ingress can induce physicochemical conditions favourable to corrosion (Huet 2005). When an active corrosion of the rebars develops, the expansion linked to the corrosion product formation is supposed to provoke mechanical damages of the concrete matrix (Molina et al. 1993; Petre-Lazar 2000). The process can be divided into two steps (Tuutti 1982):

- at its early ages, concrete pH varies between 12 and 14 so that the steel rebars are maintained in a passive state.
- later on and during a "dormant period" depending on the environmental conditions and the concrete properties, $CO_2$ contained in the atmosphere penetrates through the concrete, generating in the presence of both water and alkaline salts a carbonation of the cement paste (Marie-Victoire 2006). The consequent transformation of essentially calcium hydroxide (Portlandite) into calcium carbonate (Calcite) induces a decrease of pH under 9. So that if enough water and oxygen are available, active corrosion of the rebars can develop when the carbonation front reaches the steel/concrete interface. Steel then depassivates and an active corrosion state is initiated. High corrosion rates can then be recorded.

Nevertheless corrosion mechanisms of steel rebars embedded in concrete have been mostly studied through laboratory experiments in controlled media (Pourbaix et al. 2006) and oxide layers formed on steel in either passive or active states were not much examined. Yet, recent studies have shown (Chitty et al. 2006) that after several ten years, the corrosion system is constituted of a complex non-conductive oxide layer (iron oxy-hydroxides as goethite and lepidocrocite in which strips of magnetite appear).
Indeed, iron or steel bars embedded in several types of mortars and concrete for ten up to a hundred years were examined, revealing the presence of a several hundreds micrometers-thick oxides layer surrounding the remaining metallic core (Chitty et al. 2005a; Chitty et al. 2005b; Chitty et al 2007). Two distinct zones were identified on the corrosion pattern (see figure 1):

- the Dense Product Layer (DPL) on contact with the metal, mainly formed of iron oxy-hydroxides (goethite, α-FeOOH), streaked with maghemite ($\gamma$-$Fe_2O_3$) /magnetite ($Fe_3O_4$) strips;
- the Transformed Medium (TM), composed of iron oxy-hydroxides and several minerals characteristic of the mortar. This layer can extend several millimetres around the metallic core and contains high iron quantities coming from the metal. The formation of this layer is supposed to be due to a dissolution-precipitation process of the corrosion products.

But in order to understand the corrosion mechanism of steel rebars embedded in concrete, the corrosion patterns must be studied from the passive state to the early stage of corrosion, up to multi-decade one.



*Figure 2: Concrete spalling observed on ONERA site*

**Reference sites and samples corpus**

Three reference sites dating back to the 1930s up to the end of the 1950s were selected:

- Bordeaux "Union Trade Center" (south-west of France),
- Meudon "Air Purifier" of the French Aerospatiale Research Agency (ONERA, Paris suburb),
- Paris "House of Brazil".

For the Bordeaux "Union Trade Center", built between 1934 and 1938, the tests were performed on pieces of wall, collected during a recent rehabilitation operation. Due to heavy corrosion phenomenon linked to a carbonation process, the walls of the last floor were sawed and replaced. This CPA-HTS-based concrete (silicate rich cement paste), with a relatively high cement content (445 kg/m$^3$), and a medium compactness (15.4% average open porosity) presented carbonation depths up to 9.7 cm depth on 10 cm-thick walls. Therefore active state of corrosion of the rebars was expected.
In the Meudon ONERA "air purifier", built in 1950, a generalized spalling phenomenon was observed, visibly linked to the corrosion of the rebars. In some spalled areas, thick corrosion layers were observed (see figure 2). But surprisingly, this con-

crete presented low depths of carbonation (up to 1 cm, on 60 cm-thick pillars). The observed decays were clearly linked to local defects (honeycombing…). Consequently in this second site, both passive and active states of corrosion were expected.
The last reference site, the House of Brazil of the Parisian "Cité Universitaire" was built between 1957 and 1959. During a recent restoration operation a majority of the pre-cast panels fixed on the surface were removed. The decision of removal was based on an unexpected important carbonation phenomenon that happened from the internal face of the panel. Indeed the back-side of the panels was filled with a concrete containing only 290 kg/m$^3$ of cement, and presenting a quite low compactness (open porosity of 17%). Thus up to 4 cm carbonation depths (higher than the concrete cover) were measured. Therefore, like the Union trade center, diagnostic on the House of Brazil was performed on pieces of pre-cast panels, removed in 1999.
Reinforced concrete samples were cored on each reference site (see table 1), so that 15 cores containing steel rebar were examined.

*table 1 : studied corpus*

| Site | Age (years) | Number of studied samples |
|---|---|---|
| Union Trade Center (Bordeaux, France) | 68 | 5 |
| ONERA Air Purifier (Meudon, France) | 56 | 4 |
| House of Brazil (Paris, France) | 47 | 6 |

**Testing protocol**

In order to characterize either the concrete carbonation, the corrosion activity and the corrosion layouts, 3 types of tests were performed:

- carbonation depths were evaluated by spraying phenolphtalein on the cored sampled, newly fractured. Phenolphtalein is a colour indicator uncoloured when pH ranges between 8.3 and 10, and turning pink for upper pH values. As carbonation

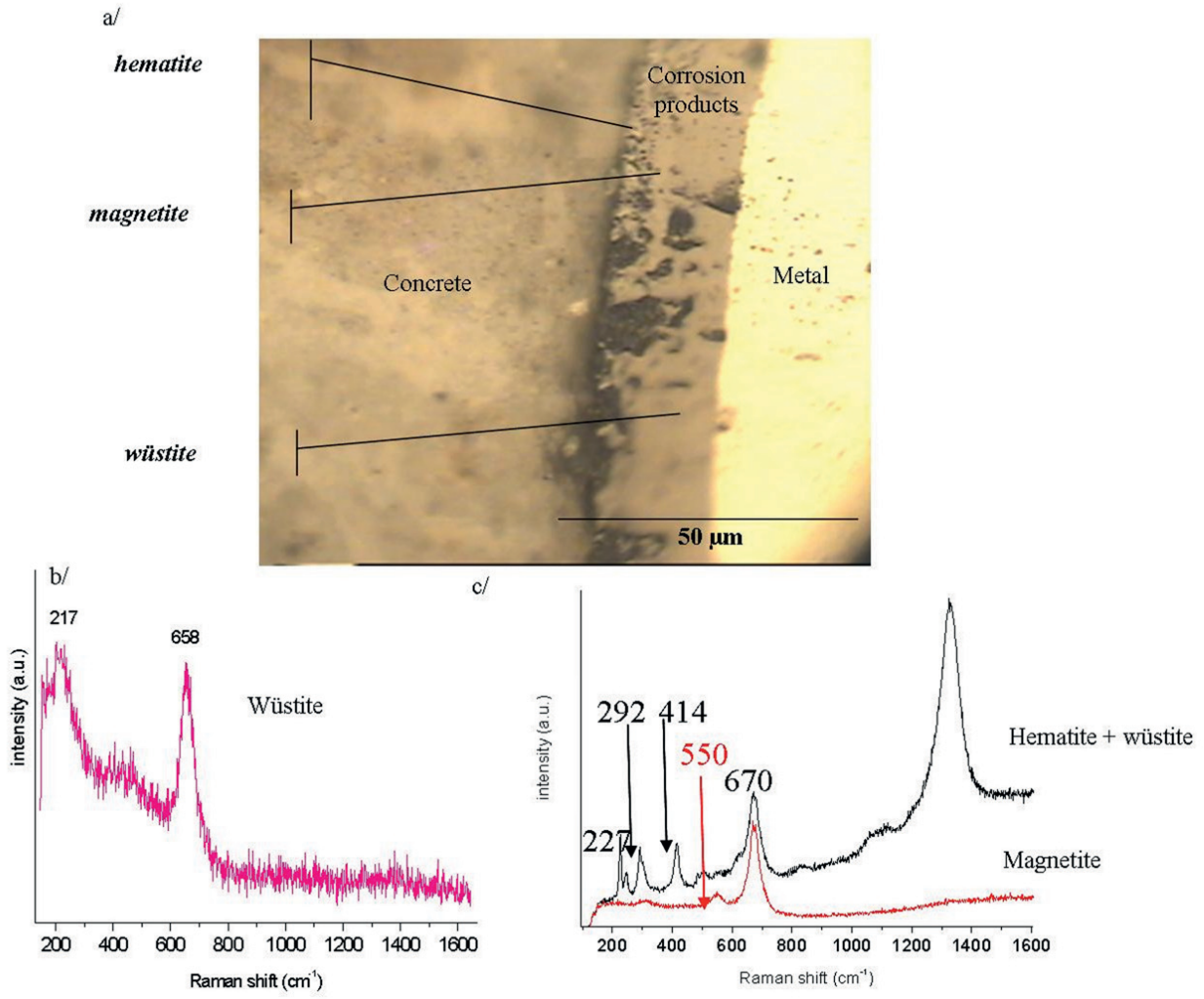



*Figure 3: Microphotography (a) and Raman spectra (b and c) of a corrosion layer of the first type, 532 nm, 80 µW, 300s acquisition, "Bourse du Travail" sample*

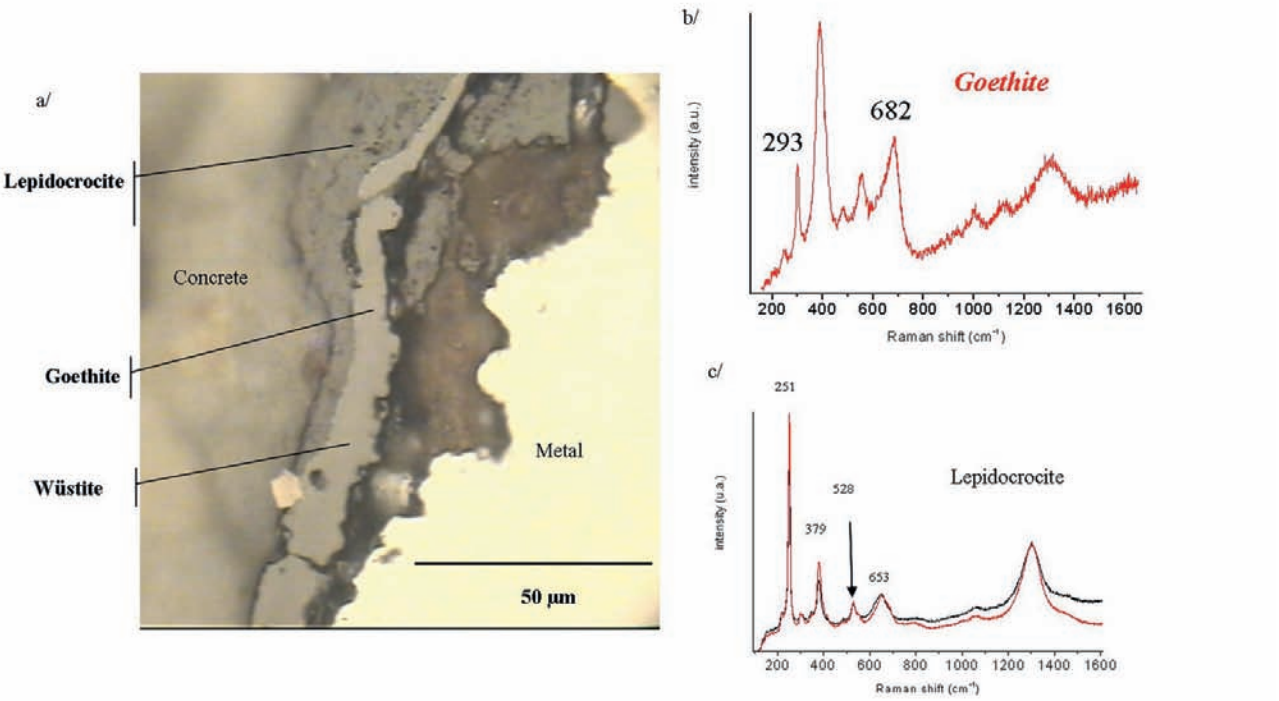



*Figure 4: Microphotography (a) and Raman spectra (b and c) of a corrosion layer of the second type, 532 nm, 80 µW, 300 s acquisition, ONERA sample*

induces a decrease of the concrete pH to values lower than 9, phenolphtalein is a good carbonation indicator. Nevertheless, it is known that the carbonation process affects not only Portlandite, but also Calcium Silicates, Aluminates…, and that the pH only decreases down to 8.4 when all the cement hydrates are carbonated. Therefore, phenolphtalein tends to underestimate the carbonation (Marie-Victoire 2006);

- the corrosion activity was evaluated through on site electrochemical measurements (potential mapping, resistivity and corrosion rate measurements), which are not developed in this paper;
- reinforced concrete cores samples are mounted in epoxy resin and cut in order to work on cross sections. They are grinded with SiC papers and then polished with a 3 µm diamond paste under ethanol. Complementary techniques of analyses have been involved to determine the characteristic of the corrosion layers at the metal/concrete interface. First optical and scanning electron microscopes (SEM) are used. Elementary compositions are collected with energy dispersive spectroscopy (EDS) coupled to SEM (Jeol Stereoscan 120, acceleration voltage of 15 kV). Detection is assumed by a Si(Li) detector equipped with a beryllium window allowing to quantify oxygen with an error of 2% and other elements under 0.5wt% with 1% of error. Lastly Raman microspectroscopy has been carried out locally in the corrosion scales in order to determine and locate precisely, thanks to comparison with reference powders (Neff et al. 2005; Chitty et al. 2006), the constitutive phases of the corrosion system. Two apparatus have been used: a Labram Infinity at 532 nm and a Labram HR at 514 nm (both Jobinyvon Horiba). On both the laser power is filtered under 100 µW in order not to transform the corrosion phase under laser heat. The beam size under the x50 objective is of 3 micrometers.

**Corrosion products identification**

Three types of corrosion forms (that could be observed on the same sample) were evidenced on the 3 monuments:

- the first one corresponds to thin corrosion layers (less than 50 micrometers-thick).
- the second one presents characteristics of both the first and the third types.
- the third one is composed of a mixed form where thin zones alternate with thicker corrosion scales that can reach several hundred micrometers,

Locally calcium was detected in the corrosion layers and was encountered at levels up to 10wt% in the corrosion layers certainly coming from the concrete.

On the first type of layout, corrosion scales were analyzed by Raman micro-spectroscopy (see figures 3 and 6). They are mainly composed of magnetite ($Fe_3O_4$) surrounding the metallic core, but some wüstite (FeO) could be observed as a dense layer in contact with the metal. This last phase was mainly identified on the Air purifier and the Union Trade Center samples. Locally, on the external part of the corrosion layer, haematite ($\alpha$-$Fe_2O_3$) was detected. The succession of these three phases from the metallic core to the external zone is characteristic of a high temperature corrosion layout (over 570°C). In fact wüstite can not form below this temperature. Its presence could be due to hot working of the rebars before the casting. Therefore the rebars would have been directly embedded in the concrete

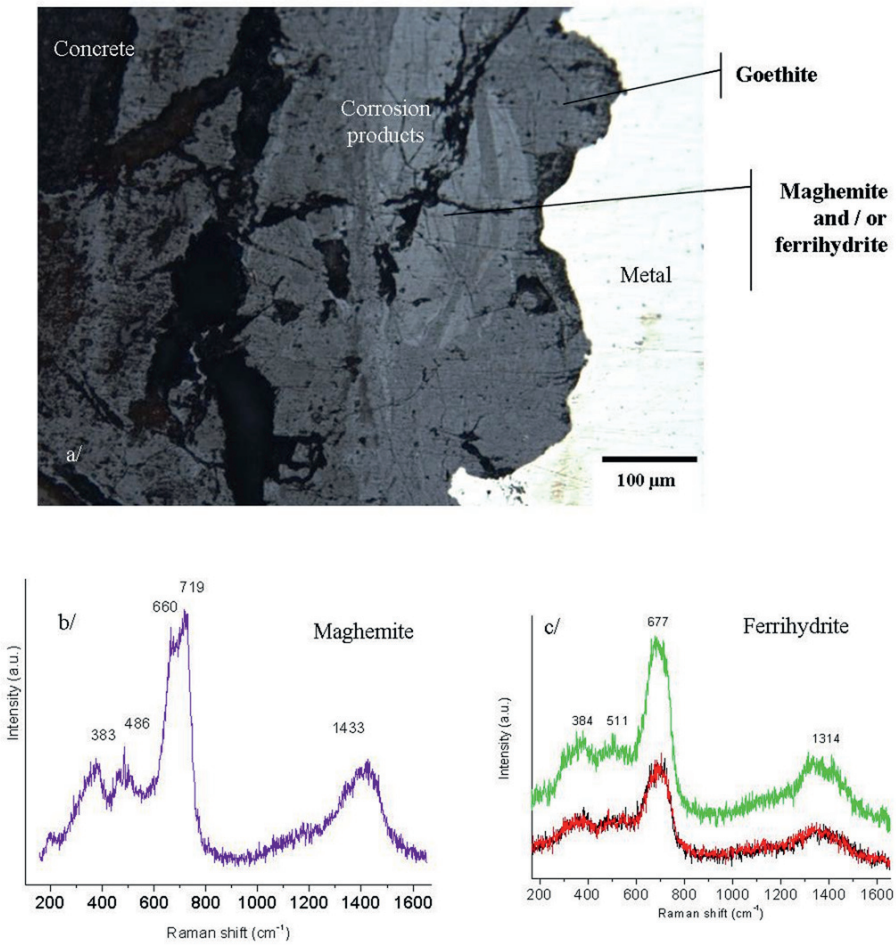



*Figure 5: Microphotography (a) and Raman spectra (b and c) of a corrosion layer of the third type, 532 nm, 80 µW, 300s acquisition*

without any removal of this oxidation layer.

In the second type of corrosion form, in addition to the thin corrosion layers of the first type, thicker ones were also observed. They contain wüstite or magnetite strata surrounded by goethite (see figures 4 and 6) and sometimes lepidocrocite on the external part of the corrosion products.

The third type of corrosion layer is only formed of oxy-hydroxides (figure 5 and 6). The main one is goethite, but some akaganeite (β-FeOOH, containing chloride) can also be locally present in confined areas, located on the external part of the corrosion layers. Lepidocrocite (γ-FeOOH) is more present in the external part of the layer. Moreover, at some locations, the corrosion layers present lighter marbling containing less crystallized phases more difficult to identify with Raman spectroscopy and interpreted as ferrihydrite (of chemical formula still not determined) or of feroxyhite (δ-FeOOH).

**Discussion**

The probable succession of the different observed corrosion layouts is exposed on figure 6. First a thin corrosion layer is formed on the rebars during their handling by hot working. This layer is made of wüstite or magnetite and could passivate the metal. After a certain period, corrosion products characteristic of aerated confined medium and mainly composed of goethite are observed surrounding the wüstite/magnetite layer. This indicates on one hand that the corrosion front progresses inside the material (i.e. from the hot temperature layer to the metal) and on the other hand that corrosion products probably grow in the external zones by dissolution and precipitation, but this hypothesis has to be confirmed. An important point is that the hot temperature phases (i.e. magnetite and wüstite) react during the aerated corrosion processes and that they can completely disappear from the corrosion layout: in some cases, neither wüstite nor magnetite was detected in the thick iron oxy-hydroxide layer. It is also interesting to observe that these different corrosion forms can be observed on the same rebar so that the corrosion rate is not heterogeneous around the metal.

Thick corrosion layers have been correlated to two kinds of defaults in the concrete:

- First one is cracks that can be connected with air through entire walls. These important cracks do not seem to have been formed during sampling because thick corrosion layers are directly formed at the intersection between the cracks and the rebar, indicating a correlation between the presence of cracks and the high corrosion level.
- The second type of default is linked to the presence of vacuole near the rebar, so that an air reservoir is locally available just after the casting operation. It seems that this could be responsible for a more active corrosion process on the metal linked to the presence of important quantities of oxygen in the sys-

tem. Indeed, from these observations it is still not evident to determine if the corrosion products lead to the formation of macro-cracks or if the cracks lead to an activation of the corrosion processes. In all likelihood, both phenomena could occur in the system.

Lastly, correlation between macroscopic on site measurements and microscopic variation of the corrosion layout is not clearly established and is still under study. All the rebars presenting only the first type of wüstite/magnetite thin layout are always embedded in a high pH medium. Nevertheless, some rebars presenting type 1 and type 2 or even type 3 corrosion forms can also be situated in high pH areas. This confirms the discrepancy existing between the macroscopic pH evaluation (using the phenolphtalein test) and the microscopic transition.

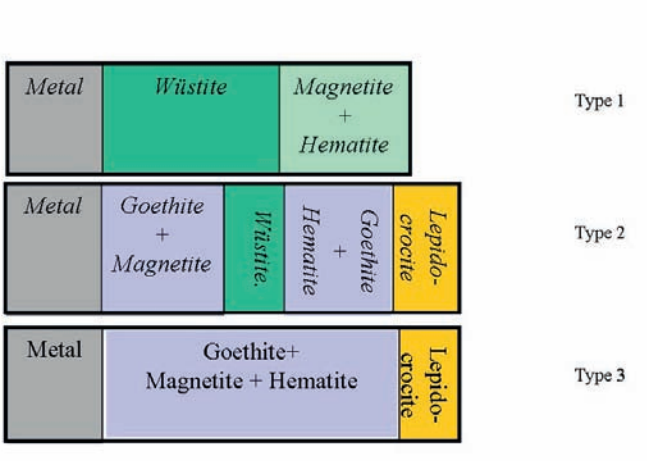



*Figure 6: Hypothesis of evolution of the corrosion form from type 1 to type 3*

## Conclusion

This paper presents the first results of a study initiated to understand the corrosion mechanisms of rebars in concrete with the first physico-chemical characterization of embedded rebars observed on transverse sections.

The corrosion forms are heterogeneous and can be divided into three categories. The first one corresponds to the original layer that has been formed on the rebar before the casting and is constituted of wüstite and/or magnetite. The second one is thicker and still contains wüstite/magnetite but presents also goethite on the inner and the outer part of the corrosion layer. The third one is characteristic of corrosion forms observed in previous studies on ancient rebars and contains mainly goethite and lepidocrocite in the outer part of the scale. These corrosion forms can be identified on a same rebar. As the work is in progress, these data have not been fully exploited so that a correlation between electrochemical techniques and the corrosion forms observed is still not clearly evidenced.

From this study realized on 3 buildings built in reinforced concrete it can be seen that the notion of passive/active state is complex to understand for monuments at least of 50 years old. Moreover it is difficult to consider homogeneously this state for one rebar as it has been observed on several samples that various corrosion forms, thin and thick, can be present on the same sample.

## References


- Chitty W-J., P. Dillmann, V. L'Hostis and C. Lombard, 2005a. Long term corrosion resistance of metallic reinforcements in concrete - A study of corrosion mechanisms based on archaeological artefacts, Corrosion Science, 47, 1555-1581
- Chitty W-J., P. Dillmann, V. Lhostis and G. Béranger. 2005b. Use of ferrous archaeological artefacts in binders to improve the knowledge on long term corrosion mechanisms of reinforced concrete. Eurocorr2005, Lisbon
- Chitty W-J., P. Berger, P. Dillmann, V. L'Hostis and G. Béranger. 2006. Contribution of archaeological analogues to the comprehension of long term corrosion of concrete reinforcement, Journal de Physique, IV 136, 295-304
- Chitty W-J., B. Huet, P. Dillmann, V. L'Hostis, G. Béranger and H. Idrissi. 2007. Long term behaviour of iron embedded in concrete: from the characterisation of archaeological analogues to the verification of the oxygen reduction as the limiting step for corrosion rate, in Corrosion of metallic heritage artefacts - Investigation, conservation and prediction for long-term behaviour, EFCP n°48, P. Dillmann, G. Béranger, P. Piccardo and H. Matthiessen (eds.), Woodhead Publishing, 109-130
- Huet B. 2005, Comportement à la corrosion des armatures dans un béton carbonaté. Influence de la chimie de la solution interstitielle et d'une barrière de transport, PhD Thesis, INSA Lyon1 University, France
- Marie-Victoire E., E. Cailleux and A. Texier. 2006. Carbonation and historical buildings made of concrete, Journal de Physique, IV 136, 305-318
- Molina F.J., C. Alonso and C. Andrade. 1993. Cover cracking as a function of bar corrosion: Part I-Numerical model, Mat. and Struc., 26, 453-464
- Neff D., P. Dillmann, L. Bellot-Gurlet and G. Béranger. 2005. Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system, Corrosion Science, 47, 515-535
- Petre-Lazar I. 2000. Evaluation du comportement en service des ouvrages en béton armé soumis à la corrosion des aciers - Outil d'aide à la décision, PhD Thesis, Laval University, France
- Pourbaix A. and V. L'Hostis. 2006. Passivation, localised corrosion and general corrosion of steel in concrete and bentonite. Theory and experimentals. Proceedings of the NUCPERF 2006 Workshop, 27-30 Mars 2006, Cadarache, France, Journal de Physique, IV 136, 71-78
- Tuutti K. 1982. Corrosion of Steel in Concrete, Swedish Cement and Concrete Research Institute