Advances in understanding atmospheric corrosion of iron.

I. Rust characterisation of ancient ferrous artefacts exposed to indoor atmospheric corrosion

Ph. Dillmann a,b,*, F. Mazaudier c, S. Hœrlé c

Abstract

Metallic substrates and rust layers of several hundred year old (y.o.) ferrous artefacts were characterised. Composition, structure and porosity of the rust were analysed by different methods: OM, SEM, EDS, EPMA, XRD, μXRD, SAXS, BET and mercury porosimetry. Several important parameters to describe an old rust layer were determined and measured. These parameters will be used for the modelling of long-term indoor atmospheric corrosion. © 2003 Elsevier Ltd. All rights reserved.

Keywords: A. Low alloy steel; B. SEM, EPMA, μXRD; C. Atmospheric corrosion

1. Introduction

The present study takes place in the specific context of the long-term interim storage of nuclear wastes. In France, these wastes could be packaged in metallic (e.g. Low alloy steel).
low alloy steels) containers and disposed in very long-term interim dry storage for about 300 years [1,2]. For the low level radioactive wastes or after the radioactive decay of the high level waste, the temperature of the container walls will be nearly the same as the temperature of the cooling air. The thermal inertia of the containers, the fluctuations of air temperature and humidity will probably cause the periodic condensation of water on the containers (wet and dry cycles) and then lead to the indoor atmospheric corrosion (AC) of the containers.

Numerous data are available on outdoor AC of iron or low alloy steels, including quite long-term testing periods (i.e. over 10 years). Results from a number of AC testing show that the behaviour of low alloy steels or iron can be characterised by two parameters $K$ and $n$ as far as a linear bilogarithmic law between penetration $P$ and time $t$ (i.e. $P = K \cdot t^n$) is valid for outdoor conditions. Although these laws are helpful in extrapolating results of corrosion tests over 20–30 years, they are not reliable enough for the long-term predictions (a few hundred years) required for interim storage of nuclear wastes.

To predict the corrosion behaviour of the containers for longer periods, very few data are available. Thus a physico-chemical description of the corrosion phenomena with the effects of wet–dry cycles is needed for a more reliable modelling.

This paper presents the analytical part of a general study dealing with the modelling of the long-term AC behaviour of iron or low alloy steels. The modelling part is presented in another paper in this volume [3]. The data obtained by the analyses of ancient rusts (several hundred y.o.) are discussed here and then used for the modelling.

The main phases constituting the rust layers formed on low alloy steels exposed to AC are either amorphous or crystallised iron oxyhydroxides (lepidocrocite $\gamma$-FeOOH, goethite $\alpha$-FeOOH, akaganeite $\beta$-FeOOH (this phase is linked with the presence of chlorides in the environment) and ferrihydrite $\delta$-FeOOH) and iron oxides (magnetite $\text{Fe}_3\text{O}_4$). Moreover, specific phases in the rust could be detected with some alloying elements in the metallic substrate, like copper, phosphorus or chromium. These particular phases have the ability to change, generally improve, the AC resistance of the steel substrate (see below). Up to day, an unresolved question deals with the presence of amorphous phase in the rust layer and the evolution of its quantity with the exposure time.

The initial stage of the AC on iron and steel will not be considered here, because it is up to day not very well understood and is not very important as far as interim storage is concerned. In the brief following description, we assume that a rust layer already exists on the material. As proposed by Evans [4] and experimentally confirmed by Stratmann [5,6,9] and Cox [7], AC of iron can be described using the electrochemical processes connected with the wet–dry cycles as their number and their frequency are correlated to the corrosion rate and the rust layer transformation. The model proposed in the second part of the study, entirely dedicated to the modelling of AC [3], is mainly based on these wet–dry cycle phenomena.

Earlier investigations [4–6,9] have shown that during a wet–dry cycle, the AC of iron or low alloy steel can be divided into three stages. During the first stage (wetting), the anodic dissolution of iron is balanced by the reduction of the oxy-
hydroxide $\gamma$-FeOOH within the rust layer, as, on the opposite, goethite $\alpha$-FeOOH is assumed to be a non-reactive phase with a more important protective ability [11]. In our modelling, we assume that the metal damage is proportional to the rust layer specific area as far as the reduction of lepidocrocite occurs at the surfaces of the pores.

After the reducible $\gamma$-FeOOH is used up, the second stage (wet surface) begins: the oxygen reduction starts and takes place at the pore surfaces. It is assumed, in our work, that this step is a diffusion limited process.

During the end of the drying, the third stage of the cycle, the reduced layer of $\gamma$-FeOOH and the other ferrous species are reoxidized by the oxygen leading to the formation of goethite $\alpha$-FeOOH and regenerating lepidocrocite. The electrolyte film is used up, stopping the corrosion process completely. It is during this final stage that the rust layer composition changes leading to a different intensity in the corrosion process for the next wet–dry cycle.

Yamashita et al. [11,12] defined and studied the goethite-content to lepidocrocite-content ratio $\alpha/\gamma$ in the rust layers, the so-called protective ability index. Other parameters, very important in this stage, are thickness, porosity and specific area of the pores. These parameters influence directly the amount of lepidocrocite that will be in contact with the electrolyte and that will be reduced. In a first approach, the thermal inertia of the containers, as well as the climatic data, having a great importance in the AC damaging [8], are not considered in our modelling.

Thus, the characteristics of the rust layer directly influence the AC mechanisms. That is the reason why, in the development of the modelling, it is necessary to identify, understand, and measure some critical parameters related with the structure, morphology (porosity,...) and the composition ($\alpha/\gamma$ ratio) of the old rusts.

In the first part of this paper, a concise literature review will expose some analytical studies concerning these points. Especially, studies on old irons will be highlighted. This short review will show that, if numerous data can be found about the rust formed on mild and weathering steels exposed to AC, no consistent information seems to exist for exposure times over 50 years. Moreover, if a lot of data are available about the rust composition, very few were found about the porosity of this rust. As explained before, in the specific context of long-term interim storage it is necessary to model AC for secular exposure times and to assume the evolution of the rust layer on such a duration. To complete this lack of information, secure the prediction and give experimental data to the modelling, we investigate in this paper the useful characteristics (regarding the modelling) of the rust layers of 11 iron and steels samples exposed to indoor AC during 100–1600 years. To complete this study, some rusts formed on steels exposed several decades to more classical aqueous corrosion were also examined. Moreover, some experimental wet–dry cycles have been performed on contemporary low alloy steel to better understand the first stages of the AC.

After presenting the analysed corpus and the different analytical methods, we will sum up the properties of the metallic substrate of the selected samples. In a second part, we will present the rust properties. First, the thickness, morphology, composition and structure of the rust will be investigated and then the rust layer porosity, with more specific experiments. Lastly, all these results will be discussed and the
parameters useful for modelling the wet–dry cycle will be highlighted and commented. A first simplified model for rust layers is proposed.

2. Literature data on the rust layer

2.1. Structure of the constitutive phases

In order to determine the proportion of the different constitutive phases and the amorphous part of the rust, numerous authors tried to study the structure of the corrosion products formed on steel exposed to atmosphere, by quantitative powder X-ray diffraction (XRD). Yamashita and Misawa [19] studied the rust composition formed on mild and weathering steels. α-, β-, γ-FeOOH, and Fe₃O₄ were found as crystallised phases. An $\alpha/\gamma$ ratio was determined where $\gamma$ is defined as the sum of β-FeOOH, γ-FeOOH and Fe₃O₄. This ratio is about 1 for weathering steels exposed during 5–10 years and higher than 2 for steels exposed more than 10 years. A link between this ratio and the potential in a 0.1 M NaCl solution measured in open air conditions using a SCE reference electrode and monitored during the exposure is evidenced [10]. Lastly, the part of amorphous phases is evaluated to be about 53 mass% in the rust of a 32 years exposed weathering steel. Katayama et al. [13] determined the composition of rust sampled on two weathering steels exposed to AC during 35 years. α- and γ-FeOOH were identified as crystallised phases. The $\alpha/\gamma$ ratio was about 1–1.3. The part of amorphous phase reached 28 mass%. Takemura et al. [14] analysed rust formed on a weathering steel exposed during 41 years to rural atmosphere. α- and γ-FeOOH were found as main crystallised phases. Less than 1 mass% of Fe₃O₄ was detected. The $\alpha/\gamma$ ratio was 2.2. The part of amorphous phase was 70 mass%. Keller [15] analysed several 20 rust samples without any precision about the steel substrate composition and the exposure time. The amount of amorphous phase varies from 20 to 70 mass%. Misawa [16] made some rust characterisation by quantitative powder XRD and infrared spectrometry (IR) on a mild steel and on a low alloy steel exposed 2.5 years to atmosphere, he found α- and γ-FeOOH and an amorphous ferric oxyhydroxide. In both samples, the amorphous part was about 85 mass%. Yamashita et al. [11] analysed the rust on a mild steel and on a weathering steel containing copper exposed to rural atmosphere during 0.5–26 years. Moreover, they analysed the rust formed on a 400 y.o. Chinese cast iron. α- and γ-FeOOH and a little quantity of Fe₃O₄ were detected on the contemporary steels. The authors observed that the $\alpha/\gamma$ ratio increases proportionally with the exposure time. The fraction of amorphous substance that is between 20 and 60 mass% in the initial stages of exposure increased in the first decade and can reach 70 mass%. Then, it seems that this amorphous phase amount decreases causing an increase of the α-FeOOH part. In the cast iron rust, only crystallised phases were observed. It is important to underline that all these quantitative data were obtained by the same method, i.e. the part of amorphous phase is the difference between the sum of all the proportions of crystallised phase and 100%. Because powder XRD quantitative measurements are not very precise (about 10–20 relative percent error),
the measurements of the amorphous part of the rust with this method have to be considered very carefully. As seen before, in some case, IR spectroscopy was used to complete the XRD observation. For example, the quantitative results given by Misawa [16] are relatively consistent with those obtained by XRD. By this method, Raman [17] identified $\gamma$-FeOOH, amorphous oxyhydroxides and quartz grains in an old iron axe rust.

Some authors tried to investigate the nanostructure of the rust by transmission electron microscope (TEM) observations. Shiotsu et al. [23] showed that the goethite grains on the inner layer of a weathering steel have a size of about few nanometres. Yamashita et al. [25] showed that there is a difference in the goethite crystals size in mild steel and in weathering steel rust. In the weathering steels, these grains are smaller than 10 nm whereas, in the mild steels the mean diameter is about several 100 $\mu$m.

All these structural results are summarised in Table 1.

2.2. Influence of the minor elements present in the substrate—weathering steels

In the particular case of weathering steel, some authors [19] report that the presence of minor elements like chromium, copper and phosphorus could favour the appearance of amorphous phases in the first decades of the exposure. In fact, the presence of chromium in $\alpha$-FeOOH could decrease the grain size of this phase under 10 nm resulting in a broadening of the diffraction peaks that can conduct to assimilate it to an amorphous phase [19]. Old iron can contain high quantities of phosphorus [20,21]. That is the reason why the influence of this element on AC behaviour was studied on old samples. XRD experiments made on the rust of the Delhi Iron Pillar, a 1500 years old monument that is well known for its corrosion resistance [22], reveal, in addition to the presence of crystallised $\alpha$- and $\gamma$-FeOOH and amorphous phases, a specific crystallised iron phosphate: $\text{FeH}_3\text{P}_2\text{O}_8\cdot4\text{H}_2\text{O}$ as well as amorphous ones.

Table 1
Summary of the structural data reported in literature

<table>
<thead>
<tr>
<th>Reference</th>
<th>Steel</th>
<th>Age (years)</th>
<th>Conditions</th>
<th>% Amorphous phase</th>
<th>$\alpha/\gamma$ ratio</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>[11]</td>
<td>W</td>
<td>5–10</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>$\alpha/\gamma$ ratio ($\gamma^* = \beta + \gamma + \text{Fe}_3\text{O}_4$)</td>
</tr>
<tr>
<td>[14]</td>
<td>W</td>
<td>41</td>
<td>Rural</td>
<td>70</td>
<td>2.2</td>
<td>–</td>
</tr>
<tr>
<td>[15]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>20–70</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[16]</td>
<td>M/W</td>
<td>2.5</td>
<td>–</td>
<td>85</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>[11]</td>
<td>M</td>
<td>0.5–26</td>
<td>Rural</td>
<td>20–60 (initial 70 (first decades) stages)</td>
<td>Increases with exposure time</td>
<td></td>
</tr>
<tr>
<td>[11]</td>
<td>Cast iron</td>
<td>400</td>
<td>–</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

M: mild steel; W: weathering steel.
The localisation of the different phases in the rust layer thickness was also studied. Especially for the weathering steels, different authors found that the rust is made of two distinct layers. Shiotani et al. [23] observed by polarised optical microscopy two different zones in the rust layer formed on a weathering steel exposed to marine atmosphere during 27 years. The inner zone is mainly light annihilating, the outer zone is light polarising. Micro-Raman spectroscopy and transmission electron microscope observations reveal that the inner layer seems mainly to be constituted of magnetite, goethite and an amorphous substance. On the opposite, lepidocrocite and sometimes akaganeite are present in the outer layer. Chromium and nickel analysed by electron probe microanalyses (EPMA) were detected in the inner layer. Takemura et al. [14] and Fujiwara et al. [18] observed by polarised optical microscopy that the inner zone of the weathering steel rust was light annihilating and the outer zone light polarising. They do not give information about the structure of these zones. Nevertheless, Fujiwara et al. located chromium and copper in the inner layer and chloride in the outer layer. Yamashita et al. [24] by combining XRD analyses, Mössbauer spectroscopy and micro-Raman spectroscopy, showed that the inner layer of the rust formed on a weathering steel containing chromium and copper exposed 16 years to a rural atmosphere is mainly made of Cr substituted goethite that cannot be detected by XRD (because of the small grain size) and the outer layer of lepidocrocite. Yamashita and Misawa [19] showed the same results on the weathering steel they analysed (see above). In addition, nanostructure of the protective rust layer was examined using synchrotron radiation and it was pointed out that Cr\(^{3+}\) in the rust is coordinated with O\(^2-\), which increased the protective ability of the rust layer [25]. Moreover, these authors found Cr, Cu and P in the inner layer and Si in the outer layer. No double layer structure has been reported on mild steels exposed to AC. Dillmann et al. [26] found that the phosphorus concentration variation, in the rust formed on a 1500 years old Indian phosphoric iron follows the mesoscopic variation (several hundred micrometers) observed in the metallic substrate. The oxide high phosphorus zones can contain amorphous phases detected by \(\mu\)XRD but can also contain crystallised phosphate Fe\(_2\)(PO\(_4\))\(_3\)(OH). In the phosphorus-free zones, magnetite seems to be present in higher quantities near the metal/oxide interface. Table 2 sums up these different results.

2.3. Exogenous elements and permeability of the rust layer

Exogenous elements e.g. coming from environment can be entrapped in the rust layer. For example, Yamashita et al. [25] showed some Si in the outer layer of a weathering steel. Chloride can be detected in some cases at the metal/oxide interface but also in the outer layer [23].

As seen before, another important property of the rust, that can influence the corrosion behaviour, is the permeability of corrosion products, i.e. their porosity \(\varepsilon\), to aqueous species like ions. To clarify the chloride ion permeation mechanisms, Takemura et al. [14] made some wet–dry cyclic exposure tests under conditions simulating a coastal atmosphere on a Cu–P weathering steel already exposed 41 years to a rural atmosphere. After 5 h, Cl\(^-\) ions could be detected by EPMA at the
metal/oxide (M/O) interface on a transverse section of the tested sample at a place where the rust layer thickness was about 100 µm. After 24 h the Cl⁻ concentration at the M/O interface further increased. Except these observations, no evidence of the rust layer modification was found. The amount of Fe²⁺ formed during this cyclic test was evaluated by atomic absorption spectrometry of collected pure water washing the specimen surface. It seems that this amount rose together with the NaCl deposition in the rust and that the rust formed on weathering steel can be destabilised when enough NaCl is deposited.

3. Analysed samples

To complete these literature data and obtain some specific parameters that will be used for modelling, several objects coming from French old architectural monuments were chosen to be analysed. Different criteria were taken into account: the indoor atmospheric exposure and the relatively good dating of the artefact considering the building history (see Table 3). All the artefacts were exposed to rural atmosphere until the 19th century. No sample was exposed to marine atmosphere. Then, some of them may have been exposed to semi-industrial atmosphere (NO01 for example). Fig. 1 shows the localisation of the different samples on the French territory. Because of their very old age (1600 years), two samples coming from India were analysed, with the support of Prof. R. Balasubramaniam. These samples were also exposed to rural indoor atmospheres.

When possible, the iron object itself was sampled, but, in most case, it was only possible to get little volumes (some cm³ of metal and rust).

In a complementary way, some cyclic tests in a climatic chamber were performed on contemporary mild steels (EN 10083-1:1996) in order to study the evolution of the α/γ ratio in the first stages of the corrosion process. Before carrying on the wet–dry cycle tests in the climatic chamber, a pre-rusting immersion (24 h) treatment of the samples was performed in an aqueous solution of H₂SO₄ (5×10⁻⁵ M) and Na₂SO₄.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Age</th>
<th>Inner layer</th>
<th>Outer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>[23]</td>
<td>27</td>
<td>LA</td>
<td>LP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr, Ni</td>
<td>β-FeOOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe₂O₄</td>
<td>γ-FeOOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>α-FeOOH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>amorphous</td>
<td></td>
</tr>
<tr>
<td>[14]</td>
<td>LA</td>
<td>LP</td>
<td></td>
</tr>
<tr>
<td>[18]</td>
<td>LA</td>
<td>LP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr, Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[24]</td>
<td>16</td>
<td>Cr</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr substituted α-FeOOH</td>
<td></td>
</tr>
</tbody>
</table>

LA: light annihilating, LP: light polarising.
(5 × 10^{-5} \text{ M}) \text{ at room temperature. The wet–dry cycles consist in alternating dry periods (4 h, 25\% RH) and wet periods (8 h at 100\% RH). Five samples were observed. The first one is a reference sample, which was only pre-rusted. The four other ones, after the pre-rusting treatment were submitted respectively to 20, 50, 70 and 100 cycles. For each of these samples, the $\alpha/\gamma$ ratio was evaluated by powder XRD.}

In order to perform several complementary analyses on morphology and porosity (small angle X-ray scattering (SAXS), Brunauer, Emmett and Teller (BET) measurements, Hg intrusion porosimetry), some rusts were taken from steels exposed several decades to AC. Finally, to understand species transfer in the rust layer and its permeability to ions, a rusted archaeological specimen (PP01), was put in a NaCl saturated aqueous solution during 24 h. Assuming a global porosity volume of the rust of 10\% and an average pore diameter of 10 nm, diffusion calculation shows that after 24 h all porosity of this rust is saturated by the two ions. So that, the concentration profiles of Na$^+$ and Cl$^-$ will give an idea of the pore distribution in the rust layer. These concentration profiles were made on transverse section by electron probe microanalyses (EPMA).

Finally, in order to perform several complementary analyses on morphology and porosity, some rusts were taken on steels exposed several decades to AC. The first rust sample is not precisely dated; the second is about hundred y.o.

### 4. Experimental procedure

Classical methods of materials and corrosion science were used to investigate the metallic substrates and the rust layers. Moreover, to understand the local structure of the rust, a more original one was performed: micro-X-ray Diffraction under

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Table 3

<table>
<thead>
<tr>
<th>Samples name</th>
<th>Literature reference</th>
<th>Age (years)</th>
<th>Location</th>
<th>Sample type and size</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR01</td>
<td>?</td>
<td>Saclay—France</td>
<td>Only rust</td>
<td></td>
</tr>
<tr>
<td>CR02</td>
<td>100</td>
<td>Orsay—France</td>
<td>Only rust</td>
<td></td>
</tr>
<tr>
<td>NO01</td>
<td>[32]</td>
<td>120</td>
<td>Noisiel mill—France</td>
<td>Sheet fragment—1 cm$^3$</td>
</tr>
<tr>
<td>CC01</td>
<td>[32]</td>
<td>150</td>
<td>Conques church—France</td>
<td>Big nail</td>
</tr>
<tr>
<td>MAR01</td>
<td>[32]</td>
<td>220</td>
<td>Marly aqueduct—France</td>
<td>Circular rod length: 80 cm; diameter: 1 cm</td>
</tr>
<tr>
<td>MO01</td>
<td>[32]</td>
<td>250</td>
<td>Montbard castle—France</td>
<td>Rod—length: 20 cm; section: 1 cm$^2$</td>
</tr>
<tr>
<td>CV01</td>
<td>[32]</td>
<td>420</td>
<td>Larrazet castle—France</td>
<td>“Iron” piece coming from a keystone</td>
</tr>
<tr>
<td>ME01</td>
<td></td>
<td>700</td>
<td>Meaux cathedral—France</td>
<td>Rod fragment—1 cm$^3$</td>
</tr>
<tr>
<td>CBB01</td>
<td>[32]</td>
<td>750</td>
<td>Breuil Benoit church</td>
<td>Clamp fragment—1 cm$^3$</td>
</tr>
<tr>
<td>PP01</td>
<td>[32]</td>
<td>800</td>
<td>“Palais des Papes” in Avignon—France</td>
<td>Clamp fragment—5 cm$^3$</td>
</tr>
<tr>
<td>CP02</td>
<td></td>
<td>800</td>
<td>Popes castle in Chateauneuf du Pape—France</td>
<td>Clamp fragment—5 cm$^3$</td>
</tr>
<tr>
<td>GU01</td>
<td>[34]</td>
<td>1600</td>
<td>Temple of Eran—India</td>
<td>Clamp fragment—1 cm$^3$</td>
</tr>
<tr>
<td>DE01</td>
<td></td>
<td>1600</td>
<td>Temple of Deogar—India</td>
<td>Clamp fragment—1 cm$^3$</td>
</tr>
</tbody>
</table>
synchrotron radiation (μXRD). This method will be rapidly described here. Further precision can be found in literature [26,28]. To measure the sample porosity, SAXS, mercury intrusion porosimetry and BET measurements were performed. In the next paragraph, the different sample preparation ways, adapted to each analytical method, will be described. Then, will follow a description of the operating modes corresponding to each method.

4.1. Sample preparation and treatment

Before any preparation, some rust was carefully sampled on ancient iron artefacts having sufficient sizes and on the contemporary mild steel samples tested in climatic chamber. This rust was then grinded to perform XRD, SAXS and BET experiments.

Then, all ancient artefacts were mounted in epoxy resin and two cross sections per artefact were made. The first one of these sections was mechanically dressed (SiC
papers, grade 180–2400) and polished with diamond paste (3 and 1 μm). The second cross section was prepared to a 50 μm thin film by mechanical polishing in order to proceed to μXRD experiments. All samples were polished under ethanol.

After rust observations and composition analyses, the different cross sections were etched with Nital 4% to determine the carbon content. Then, after repolishing, samples were etched with Oberhoffer reagent [20] in order to reveal a possible phosphorus presence and study its distribution.

4.2. Experimental methods

All metallographic structures and corrosion product observations were made with a LEICA DMRXA optical microscope (OM) and a Stereoscan 200 Scanning Electron Microscope (SEM).

Rust layer compositions were investigated by Energy Dispersive Spectrometry (EDS) coupled to SEM. Minor elements in metallic substrates and rusts were analysed by EPMA with a 2×2 μm² beam (accelerating voltage 15 kV, current 40 nA).

Powder XRD analyses were made in grazing incidence with a Philips diffractometer. A Co anticathode was used (40 kV, 40 mA). Spectra were collected for a 2θ value between 5° and 130°.

To study the phase distribution in the scales, μXRD experiments were performed at different points of the oxide on thin film cross sections. The μXRD experiments were conducted on the D15 beamline at LURE (Laboratoire pour l’Utilisation du Rayonnement Electromagnétique—Orsay, France). The detailed beamline setup can be found elsewhere [28]. The white X-ray synchrotron beam was focused and monochromatised by a carbon/tungsten Bragg Fresnel Multilayer Lens (BFML) down to a 20×20 μm² beam. Photons around 14 keV (λ = 0.08857 nm) were selected. Diffraction patterns were collected with an image plate, downstream from the sample. The FIT2D software, developed at the European Synchrotron Radiation Facility (ESRF) [29] gives $I = f(\theta)$ spectra that were compared with the JCPDS database using the Diffrac+ program.

In order to obtain some semiquantitative informations on the relative proportion of the different crystallised phases and to evaluate the $\alpha/\gamma$ ratio on XRD and μXRD spectra, intensity corrections were performed using Nishimura et al. [30] data. These authors gave for several phases mixed with a given amount of CaF₂, the measured intensity of some diffraction peaks corresponding to the 2θ angles (Cu anticathode) at 30.09°, 21.22°, 11.84° and 14.14° for respectively magnetite Fe₃O₄, goethite α-FeOOH, akaganeite β-FeOOH and lepidocrocite γ-FeOOH. These measurements were obtained in same conditions for each separate phase mixed with the same weight of the internal CaF₂ reference. The ratio of respectively magnetite, goethite, akaganeite and lepidocrocite to CaF₂ peak heights are respectively 0.29, 0.64, 0.14 and 0.4. We used these peaks intensity ratios to correct the measured intensity of each correspondent diffraction peak on the experimental diffraction spectra. This calculation was made only when these phases were identified and no typical amorphous shape was detected. Moreover, it was only per-
formed if the number of diffracted grains was sufficient and randomly distributed i.e. when the powder is sufficiently homogenised and when perfect rings can be observed on the μXRD patterns. At last, comparisons were made between different phases but only on the same spectrum, so that the matrix absorption effect is the same and have not to be taken in account. Corrected intensities could then be compared and relative phase concentrations were obtained for each spectrum. Thus, a relative percentage of the identified, i.e. crystallised phases and the $\alpha/\gamma$ ratio was evaluated.

BET experiments with $N_2$ adsorption were performed at the Laboratoire de Diffusion des Rayons X (DSM/DRECAM/SCM) in the CEA Saclay, France. Before experiments, rust powders were maintained 1 h at 150 °C under vacuum for outgassing. Under 150 °C and for short times, the increasing of the specific surface due to temperature can be considered as negligible [31]. Moreover, to be sure that no phase transformation had appeared during the heating of the rust powder, XRD analyses were performed before and after the BET experiments.

Mercury intrusion porosimetry experiments were performed at the Laboratoire d’Etude du Comportement des Bétons et Argiles (DPC/SCCME), CEA Saclay, France. Before measurements, rust powder samples were dried 2 h at 200 °C.

SAXS experiments were performed on rust powder samples at the Laboratoire de Diffusion des Rayons X (DSM/DRECAM/SCM) in the CEA Saclay, France. Sample was deposited on a kapton foil. A Cu anode was used. To attenuate the Fe K$_\alpha$ X-ray fluorescence of the sample, lead foils were used except in the small angles. To simplify calculations, in this first experiment, the rust was assumed to be a mixture of 50/50 Fe$_2$O$_3$ and Fe$_3$O$_4$.

5. Results

5.1. Metallic substrate of ancient iron specimens

The metallographic observations reveal only hypoeutectoid steel structures. The most carburised sample (PP01) contains 0.4 mass% carbon and most of the samples contains about 0.1 mass% carbon.

The grain sizes (a few tens of micrometers) are higher than in contemporary iron and steels and can reach several hundred micrometers for some samples containing phosphorus (see Table 4). All observed microstructures show equiaxe grains.

Ancient iron can contain high amounts of non-metallic slag inclusions coming from the iron ore reduction stage [27,32,33]. Fig. 2(a) shows a microphotograph taken on a zone of the MO01 sample containing numerous slag inclusions. These inclusions are elongated perpendicularly to the hammering plane. The constitutive phases of this kind of inclusion were recently studied by XRD and μXRD [32,34] and are mostly wüstite (FeO) dendrites entrapped in a glassy and fayalitic (Fe$_2$SiO$_4$) matrix. Some other elements could be present in solid solution in the inclusions e.g. aluminium, calcium, phosphorus. Fig. 2(b) shows an OM microphotograph of the dendritic structure of slag inclusions. Ancient iron are very heterogeneous, thus, even
Table 4
Metallographic observations and minor alloying elements

<table>
<thead>
<tr>
<th>Sample</th>
<th>C(^a) w%</th>
<th>Mass% P(^b)</th>
<th>Metallographic structure</th>
<th>Grain size (µm)</th>
<th>Inclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO01</td>
<td>0.1</td>
<td>–</td>
<td>Ferrite and pearlite</td>
<td>10–20</td>
<td>Small sulphurs</td>
</tr>
<tr>
<td>CC01</td>
<td>0.02</td>
<td>–</td>
<td>Equiaxe ferrite and some tertiary cementite</td>
<td>10</td>
<td>Multiphased slag inclusions</td>
</tr>
<tr>
<td>MAR01</td>
<td>&lt;0.02</td>
<td>0.05–0.25</td>
<td>Equiaxe ferrite</td>
<td>50</td>
<td>Numerous multiphased slag inclusions Presence of S</td>
</tr>
<tr>
<td>ME01</td>
<td>&lt;0.02</td>
<td>–</td>
<td>Equiaxe ferrite</td>
<td>30–40</td>
<td>Numerous multiphased slag inclusions</td>
</tr>
<tr>
<td>MO01</td>
<td>&lt;0.02</td>
<td>&lt;0.02–0.10</td>
<td>Equiaxe ferrite</td>
<td>100–200</td>
<td>Some rare multiphased slag inclusions</td>
</tr>
<tr>
<td>CV01</td>
<td>0.1</td>
<td>–</td>
<td>Ferrito-pearlitic structure</td>
<td>30–40</td>
<td>Multiphased slag inclusions</td>
</tr>
<tr>
<td>CBB01</td>
<td>0.1</td>
<td>&lt;0.02–0.15</td>
<td>Ferrito-pearlitic structure</td>
<td>20</td>
<td>Rare multiphased slag inclusions</td>
</tr>
<tr>
<td>PP01</td>
<td>0.3–0.4</td>
<td>–</td>
<td>Acicular ferrite and pearlite</td>
<td>40</td>
<td>Numerous multiphased slag inclusions</td>
</tr>
<tr>
<td>CP02</td>
<td>0.02</td>
<td>–</td>
<td>Equiaxe ferrite</td>
<td>50</td>
<td>Multiphased slag inclusions</td>
</tr>
<tr>
<td>GU01</td>
<td>0.02–0.3</td>
<td>0.06–0.23</td>
<td>Ferrito-pearlitic structure</td>
<td>30</td>
<td>A lot of multiphased slag inclusions</td>
</tr>
<tr>
<td>DE01</td>
<td>0.1</td>
<td>0.12–0.25</td>
<td>Ferrito-pearlitic structure Presence of phosphorus ghost structures</td>
<td>70–100</td>
<td>A lot of slag inclusions</td>
</tr>
</tbody>
</table>

\(^a\) Determined by quantitative metallography. 
\(^b\) Determined by EPMA and Oberhoffer etching.

Fig. 2. (a) Slag inclusions in a ferritic matrix (MO01 sample), (b) dendritic structure of a slag inclusion.
when sample contains a lot of slag inclusions, clean zones can be located and used to study corrosion.

In addition to carbon, the only other minor element detected in high amounts is phosphorus. It is present over 0.1 mass% in five samples (see Table 4). This element is often detected in ancient ferrous artefacts [21,35] and is distributed in a heterogeneous manner. Mesoscopic (several hundred micrometers) variations combined to microscopic ones were observed. They can be revealed by Nital etching like on the microphotograph presented in Fig. 3(a). Because of their metallographical aspect these concentration heterogeneities are called ghost structures [20]. The Oberhoffer reagent also clearly reveals all phosphorus heterogeneities. Fig. 3(b) shows mesoscopic variations of the phosphorus content observed on the GU01 sample. Dark and clear zones correspond respectively to low and high P contents.

Even if sulphur was sometimes present in slag inclusions, this element could not be detected by EPMA in the metallic matrix i.e. the S amount is below 200 ppm. The same remark can be made for manganese.

5.2. Rust layer thickness

Average thickness of rust layers were determined by OM and SEM observations. Fig. 4 shows the minimal and maximal values that were observed on each sample, versus the age. Points presented in open squares are values found in literature [11–14,19]. The overall tendency is an increase of the thickness with the age of the sample. Nevertheless, a high dispersion of the results can be observed for samples of about the same age, e.g. CBB01, ME01, PP01 and CP02. Several explanations are proposed: different exposure atmospheres, different substrate compositions and material history. None of these four samples contain significant amounts of phosphorus that could explain a better corrosion resistance. Another interesting point is...
that PP01 and CP02, which were sampled in the same area of the French territory and have the same age, present a very similar thickness. Thus, different exposure conditions seem to be the most probable hypothesis to explain the thickness variation of samples with the same age.

5.3. Ancient samples rust morphology

OM and SEM observations revealed three kinds of morphology. The first type is relatively homogeneous. The second type is made up of two different layers (see Fig. 5). This double layer was observed on six samples. Nevertheless, no correlation was made between the presence of this double layer and a particular substrate composition. On some samples, an “overlayer”, containing some impurities like quartz grains was observed on the outer zone of the rust. This third layer may be contaminated by the dust coming from the stone and the cement of the building walls. Fig. 6 shows an “overlayer” observed by SEM on the CV01 sample. Quartz grains are clearly identified on the high magnification view.

The aspects of the M/O interface are various. On some samples, this interface is relatively regular (see Fig. 7). On other ones, some local penetrations were observed (Fig. 8(a)), that are always larger than the grain size. It is important to note, that on the contemporary samples, tested in climatic chamber, the same local penetrations were observed on transversal sections (see Fig. 8(b)). On samples containing inclusion rich zones, some of these inclusions are entrapped in the oxide scale near the interface (see Fig. 9). No inclusion was detected by OM and SEM observations in the outer layer of the rust.
Fig. 5. Inner and outer layers observed on a cross section of the CC01 sample.

Fig. 6. SEM microphotograph of a rust layer with an “overlayer” containing quartz grains (CV01 sample).

Fig. 7. (a) Regular M/O interface observed on sample CC01. (b) Irregular metal/oxide interface observed on sample PP01.
In all the samples, some cracks, sometimes of several hundreds micrometers, were observed in the rust. These cracks can be perpendicular or parallel to the layers. Rust layer morphologies observed on ancient iron samples are summarised in Table 5.

### 5.4. Composition of the rust layers

After this general overview of rust morphology, composition and structure of these layers were considered. Fe, O, P, Cl, Si, S and Ca quantitative concentration profiles were made on the cross sections by EPMA. No other element could be detected in the layer with this technique. These results are confirmed for major elements by EDS analyses.

Phosphorus distribution profiles were made in the rust layers of the samples (MAR01, MO01, CBB01, DE01 and GU01) that contain more than 1000 ppm of...
this element in the metal. For all these samples, the P-distribution was very heterogeneous across the rust layers thickness (see Fig. 10). In fact, the phosphorus content in the oxide follows the mesoscopic variation of phosphorus in the metallic matrix. This is corroborated by analyses already published [26]. Oxides situated near a high P substrate contain a higher quantity of P than oxides formed near low P zones.

Sulphur content measured in rust layers vary from 100 to several thousand ppm (see Fig. 11 and Table 6). These values are relatively high compared to the data available in literature for rural AC of contemporary steels. For the CV01 sample, the enrichment of the external part of the rust layer (overlayer) is very sharp. This external enrichment can be explained by an exogenous pollution from the dust coming from the building wall or the cement used to hold the iron clamp in the wall. It is known that this cement is partly made of gypsum (CaSO4). For some samples like NO01, the high sulphur enrichment could be due to an exogenous pollution of the oxide scale by the SO2 present in atmosphere since the middle of the 19th century.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cracks and porosity</th>
<th>Metal/oxide interface</th>
<th>Layers: inner (I), outer (O) “overlayer” (OV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC01</td>
<td>10 µm Po in outer layer</td>
<td>Regular</td>
<td>I (50 µm)/O (50 µm)/OV</td>
</tr>
<tr>
<td>NO01</td>
<td></td>
<td></td>
<td>and ⊥ cracks</td>
</tr>
<tr>
<td>MO01</td>
<td>Numerous</td>
<td></td>
<td>and ⊥ cracks</td>
</tr>
<tr>
<td>MAR01</td>
<td></td>
<td>Very irregular</td>
<td>I (50 µm)/O (60–70 µm)</td>
</tr>
<tr>
<td>CV01</td>
<td></td>
<td></td>
<td>and ⊥ cracks</td>
</tr>
<tr>
<td>CBB01</td>
<td></td>
<td></td>
<td>and ⊥ cracks</td>
</tr>
<tr>
<td>PP01</td>
<td></td>
<td></td>
<td>and ⊥ cracks</td>
</tr>
<tr>
<td>CP02</td>
<td>Numerous</td>
<td></td>
<td>and ⊥ cracks</td>
</tr>
<tr>
<td>ME01</td>
<td>Po in several zones</td>
<td>Very irregular</td>
<td>No visible scales</td>
</tr>
<tr>
<td>GU01</td>
<td>Po in several zones</td>
<td>LP</td>
<td>I/O</td>
</tr>
<tr>
<td>DE01</td>
<td>Presence of Po</td>
<td>Very irregular</td>
<td>No visible layers</td>
</tr>
</tbody>
</table>

Po: porosity; || parallel to the M/O interface; ⊥ perpendicular to the M/O interface; LP: local penetration.
The presence of sulphur in the internal zone of the rust layers is detected. As the mobility of sulphur was already pointed out by Ross [36], who observed a seasonal distribution variation of ferrous sulphates (transfer of $\text{SO}_2^-$) in the rust layers of

![Fig. 10. Phosphorus distribution in the rust layers (EPMA) of different samples (MAR01, NO01, GU01 and CBB01), $d$: distance from the metal/oxide interface.](image1)

![Fig. 11. Sulphur distribution in the rust layers (EPMA) of different samples (MAR01, NO01, GU01 and CBB01), $d$: distance from the metal/oxide interface.](image2)
some steels and as the sulphur dioxide can reach the M/O interface as a gaseous species, one can understand the presence of sulphur at the M/O interface but cannot conclude on the contribution of the two types of transfer (gaseous or aqueous way).

Chlorine was only found in the outer layer of the CV01 sample. Because no sample was exposed to marine atmospheres, the presence of this element could be attributed to the water dripping from the building walls contaminated by the cement that could contain chlorine.

Other elements like Ca and Si were detected in relatively high quantities (several thousand ppm) in the ancient rust layers. The presence of these elements is attributed mainly to an exogenous pollution from the dust of the building walls. A minor contribution of an endogenous pollution coming from the slag inclusion, very rich in these elements, is also to be considered.

The presence of relatively high quantities of exogenous minor elements in all the rust layer thickness seems to show that some dissolved species can easily move in the rust layer through well connected porosity.

### Table 6
Sulphur concentration in the rust layers (EPMA)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average mass% S, inner layer</th>
<th>Max. mass% S, outer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBB01</td>
<td>0.058</td>
<td>0.15</td>
</tr>
<tr>
<td>CV01</td>
<td>&lt;0.01</td>
<td>0.45</td>
</tr>
<tr>
<td>MO01</td>
<td>0.038</td>
<td>0.52</td>
</tr>
<tr>
<td>NO01</td>
<td>0.2</td>
<td>0.25</td>
</tr>
<tr>
<td>CC01</td>
<td>0.08</td>
<td>0.35</td>
</tr>
<tr>
<td>MAR01</td>
<td>0.35</td>
<td>0.85</td>
</tr>
<tr>
<td>PP01</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>DE01</td>
<td>0.02</td>
<td>0.15</td>
</tr>
</tbody>
</table>

5.5. Rust layer structure

On the contemporary steels tested in climatic chamber, SEM observations made on the sample surfaces reveal the presence of crystallites with typical shapes (see Fig. 12). Some little spheroids could correspond to $\alpha$-FeOOH phases as reported in literature [37]. Other crystallites look more like rods and could correspond to $\gamma$-FeOOH.

For some ancient iron samples (CV01, PP01 and MA01) and for contemporary steels treated in climatic chamber, rust powder was mechanically withdrawn in order to conduct XRD analyses. Some phases, identified on all samples were $\text{Fe}_3\text{O}_4$, $\alpha$-FeOOH and $\gamma$-FeOOH. On CV01, whose rust contains high amounts of chlorine, $\beta$-FeOOH, a Cl containing iron oxyhydroxide, was also observed. The characteristic diffraction pattern shape linked to the presence of amorphous phases was not detected in the diffraction data.

In order to study the distribution of these different phases in the rust layer, $\mu$XRD profiles were made on thin films of cross sections of four samples (CV01, DE01,
Contemporary steel after climatic chamber test

Accicular aggregates of α-FeOOH spheroids

γ-FeOOH
α-FeOOH

Fig. 12. SEM microphotographs made on the contemporary steel sample surface after climatic chamber tests.

Fig. 13. 2D microdiffraction pattern and corresponding integrated $I = f(\theta)$ spectrum. PP01 sample. Vertical lines correspond to the JCPDF 81-462 reference file of goethite. Beam size: $20 \times 20$ µm$^2$. Energy: 14 keV.
NO01 and PP01). At different points of the rust layer μXRD spectra were collected. Fig. 13 shows the 2D diffraction pattern obtained at a particular point of the rust layer of the CV01 sample and the corresponding $I = f(\theta)$ integrated spectrum. The complete diffraction rings observed on the 2D diffraction pattern showed that the constitutive phases of the rust layer are not textured. This was observed for all the analysed samples. After intensity corrections (see above), the relative proportion of the different identified phases was obtained (see Fig. 14).

Several general tendencies concerning the four samples can be observed. Goethite is present in more important proportions in the inner layers and lepidocrocite in the outer layers. On three samples, (NO01 CV01 and PP01), the main phases are these two oxyhydroxides ($\alpha$- and $\gamma$-FeOOH) and the magnetite part is about 10%. For the Indian iron sample (DE01), magnetite is the main phase. As said before, EPMA analyses and OM observations reveal the presence of an overlayer containing high amounts of chlorine on the CV01 sample. This is confirmed by the μXRD profile that shows the presence of $\beta$-FeOOH in this overlayer. μXRD were also performed on the GU01 Indian sample and are published elsewhere in details [26]. It is the only sample where an amorphous phase could be detected at certain points of the rust layer. Moreover, due to the high P content in the metallic matrix, some phosphate phases were also identified at some places.

This phase distribution (goethite more present in the inner layer and lepidocrocite in the outer layer) was also observed by two authors on weathering steels exposed to atmosphere during 16 and 26 years [11,24]. Nevertheless, these authors found also

![Graphs showing phase distribution](attachment:image.png)
amorphous phases in the inner layer. It is not the case here, even if μXRD is not the most suitable method to detect such phases.

From these μXRD profiles, average compositions of the entire rust layer were deduced by integration of the concentration profile curve of each phase on all the layer thickness. It was then possible to obtain, for each sample, the protective ability index $\alpha/\gamma$. When it was feasible, this ratio was also calculated from the powder XRD data using the same correction method as for the μXRD spectra. These ratios were in good agreement with those calculated from the μXRD data. In a complementary way, to obtain data for short exposure times, the protective ability index was de-
determined from the XRD spectra obtained on the contemporary steels after 20, 50, 70 and 100 wet–dry cycles in climatic chamber. These results are given in Fig. 15 for the “short exposure times” i.e. contemporary steels treated in climatic chamber. Fig. 16 gives the evolution of the protective ability index for all the analysed samples. On this last figure, the first points concern the contemporary steels.

For short exposure times as for very long times, the \( \alpha/\gamma \) ratio increases with the age of the sample. This can be explained by the progressive transformation of lepidocrocite in goethite with the succession of wet–dry cycles during the AC process. Because magnetite and akaganeite were also identified in the rust layers, we propose to introduce an other ratio that is: \( \alpha'/\gamma' = (\text{mass}\% \ \alpha-\text{FeOOH} + \text{mass}\% \ \text{Fe}_3\text{O}_4)/(\text{mass}\% \ \gamma-\text{FeOOH} + \text{mass}\% \ \beta-\text{FeOOH}) \). Despite of the fact that magnetite is a conducting phase, it can be considered as protective because of its relatively good stability. Thus, this new protective ability index \( \alpha'/\gamma' \) seems to be more able to characterise the stability of the old rust layer. The general tendency is the same that for \( \alpha/\gamma \) ratio. Nevertheless, the \( \alpha'/\gamma' \) ratio is much higher for the DE01 sample because the rust layer is mainly constituted of magnetite.

The protective ability index \( \alpha/\gamma \) values are globally lower than those reported in literature for much shorter times (see Section 1). As far as very long exposure times (i.e. a few centuries) are concerned, the only reference we have found in literature deals with a 400 years atmospheric exposure old pig iron [11]. The protective ability index of the rust layer of this old pig iron is about 4 and is in good agreement with our data.

5.6. Rust layer porosity

Global porosity (\( \varepsilon \)), pore diameter (\( D \)) and specific surfaces (\( S_a \)) were characterised by different complementary methods (mercury intrusion porosimetry, BET, SAXS) on two ancient iron rust (PP01 and CV01) and two contemporary rust samples (CR01 and CR02) (Table 7).

Despite of the fact that these methods do not give exactly the same kind of data (for example mercury intrusion porosimetry is able to detect only open porosity with a diameter higher than 3 nm, SAXS gives open and closed porosity...), these different experimental results can be compared in first approximation. Several observations can be made. All obtained values are roughly in the same decade of magnitude and in good agreement with literature data [14]. Porosity (\( \varepsilon \)) is about 10\% for all samples. The specific area of the rust layers is about 10 m\(^2\)/g. An important part (about 50\%) of the porous volume is constituted by nanometric porosity (pore access diameter: \( D < 50 \text{ nm} \)). It can be assumed that the micrometer scale porosity corresponds to those observed by OM merely in the outer zones of the rust layers. Unfortunately, up to day, no quantitative data were obtained by these methods about the pore three-dimensional distribution in the rust layer, their tortuosity and their connectivity. That is the reason why we attempted to evaluate this data by another way. Fig. 17 shows Na and Cl concentrations profiles obtained on a PP01 rust cross section after 24 h immersion in a NaCl saturated aqueous solution. As said before, after this immersion time, one can assume that the rust layer is saturated in Na and Cl. Thus, the
concentration profiles of these elements should give an idea of the porosity distri-

bution in the rust layer. The two elements were detected in relatively high quantities in all the thickness of the rust. This fact is in good agreement with the presence of endogenous elements detected in all the ancient iron rusts. As expected, the profile shapes are not in concordance with a diffusion profile. These shapes are roughly the same for Na\(^+\) and Cl\(^-\) and seem to correspond to a pore distribution profile that can be seen after rust saturation. Considering these profiles, it seems that porosity is roughly higher in the external zone and at the metal/oxide interface.

**Table 7**

<table>
<thead>
<tr>
<th>Samples</th>
<th>Age (years)</th>
<th>Corrosion phenomena</th>
<th>Method</th>
<th>Results</th>
<th>Specific area, (S_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP01</td>
<td>800</td>
<td>Indoor AC</td>
<td>SAXS</td>
<td>2% &lt;few 10 nm</td>
<td>(S_a = 6 \text{ m}^2/\text{g})</td>
</tr>
<tr>
<td>CV01</td>
<td>420</td>
<td>Hg poro.</td>
<td></td>
<td>≈qq% % (V\text{porux}) D</td>
<td>(D =&lt;5 \text{ nm})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 &lt;5 nm</td>
<td>(50 &lt;10 \text{ nm})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≈30 5–60 nm</td>
<td>(\approx 10 \text{ nm})</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≈30 &gt;10 \text{ μm}</td>
<td>(&gt;10 \text{ μm})</td>
</tr>
<tr>
<td>216G</td>
<td>1895</td>
<td>Indoor AC</td>
<td>Hg porosity</td>
<td>Few% 1–10 nm ?</td>
<td>(S_a = 15.4 \text{ m}^2/\text{g})</td>
</tr>
<tr>
<td>216D (rust)</td>
<td>10–15%</td>
<td>Indoor AC</td>
<td>Hg porosity</td>
<td>Few% 1–10 nm ?</td>
<td>(S_a = 15.4 \text{ m}^2/\text{g})</td>
</tr>
<tr>
<td>SAT (rust)</td>
<td>70s</td>
<td>Concrete corrosion</td>
<td></td>
<td>10–15% 50 &lt;30 nm</td>
<td>(S_a = 15.4 \text{ m}^2/\text{g})</td>
</tr>
<tr>
<td>FAC (corroded sample)</td>
<td>?</td>
<td>AC</td>
<td>BET</td>
<td>Few% 1–10 nm ?</td>
<td>(S_a = 15.4 \text{ m}^2/\text{g})</td>
</tr>
</tbody>
</table>

Fig. 17. Na (a) and Cl (b) concentration profiles in PP01 rust after 24 h immersion in a NaCl saturated solution. EPMA.
6. Discussion

In the first part of this paragraph, results obtained in this study are summarised and commented. Then, in a second part, the important data, that will be used to describe the rust layer for indoor AC modelling will be highlighted and discussed.

6.1. Characteristics of old rust layers

The iron archaeological analogues examined here are all hypoeutectoid steels containing ferritic or ferrito-pearlitic structures. Grain sizes are higher than in contemporary low alloy steels. In some samples, high phosphorus contents were evidenced. The particularity of old iron is to contain sometimes numerous slag inclusions coming from the reduction process used to obtain the metal, but it is always possible to find clean zones in the sample to proceed to corrosion studies.

Rust layers on ancient irons are relatively dense and adhering, despite of the presence of some cracks parallel or perpendicular to the M/O interface. The average thickness of the rust layer increases with the age of the sample. Some double layer stratifications, as reported in literature for weathering steels, were observed on some samples. Nevertheless, no clear relation with the substrate composition could be made. Moreover, an “overlayer” containing elements and compounds coming from the external environment (building walls and water) can be sometimes evidenced.

The M/O interface is relatively irregular and some local penetrations over 150 µm in the metal and not linked to the presence of slag inclusions can be detected. This kind of local penetrations was also evidenced on contemporary samples rusted in climatic chamber.

As mentioned in literature, the present study shows that the main crystallised phases constituting the AC products are: magnetite (Fe₃O₄), goethite (α-FeOOH) and lepidocrocite (γ-FeOOH). µXRD experiments show that these phases are localised in a particular way in the rust layer: goethite was found in the inner layer and lepidocrocite more in the outer layer of the rust. This is also confirmed by other authors. This phase distribution evolution appears not to be very sharp. Moreover, in agreement with the electrochemical processes connected with the wet–dry cycle, the older is the rust, the more magnetite and/or goethite are formed to the detriment of lepidocrocite, which is an active phase in the AC process. This is verified by the evolution of the protective ability indexes \( \alpha/\gamma \) and \( \alpha'/\gamma' \). No amorphous phase was detected with the analysis techniques that were used here. This point seems to be in contradiction with some authors that found very often amorphous phases in the inner layer of the rust. Nevertheless, the analysed samples found in literature are far younger that those studied here. The old age of the rusts could be an explanation of the apparent absence of amorphous phases. This hypothesis is also proposed by Yamashita [11] who explains that during a long period of exposure, the amorphous inner layer can transform to a densely packed aggregate of nanoparticles of goethite.

It is important to note that some authors [22] mention that phosphates, that could be present in the rust layers of high phosphorus irons, are mainly amorphous in very
old layers—like in the Delhi Iron Pillar rust—despite of the fact that some crystal-

lised phosphates could locally be identified.

Rust layers porosity measured on ancient iron samples, but also on contemporary

steels is about 10% and mainly nanometric (10 nm < \( D < 50 \) nm), where \( D \) is the pore

access diameter. The specific area is about 10 m\(^2\)/g. Considering the Na\(^+\) and Cl\(^-\) concentration profiles after saturation of the rust layer with these two ions, porosity

seems not to be homogeneously distributed in the rust layer but more important in

the external zone as well as near the M/O interface. The internal porosity could be

linked to a cationic migration of Fe\(^{2+}\). This hypothesis is in good agreement with the

presence of lepidocrocite (the youngest phase) preferentially in the external zone. The

porosity is also confirmed by the presence in the rust of exogenous elements (Si, Ca,

S, . . . ) in relatively high quantities.

6.2. Important parameters to describe the rust layer

The precedent considerations show that, despite of the relative dispersion of the

different measured data that is linked to the nature of the sample, some parameters,

relatively reproducible for all samples and that play an important role in AC (see

Section 1), can be considered to describe the rust layer. These parameters, given in

the following, will be used in the other part of this study [3], for the modelling of the

wet–dry cycle and AC.

In a first approximation, the rust layer thickness will be assumed to be of about

100 \( \mu \)m for several 10 y.o. samples.

For simplification reasons, even if Fe\(_3\)O\(_4\), \( \alpha \)- and \( \gamma \)-FeOOH were identified in the

old rust samples, only two phases will be considered for modelling. \( \alpha \)-FeOOH is an

isolating phase and inert in the AC conditions whereas \( \gamma \)-FeOOH is an active phase.

Fe\(_3\)O\(_4\), despite of the fact that it is an electric conductor, is mainly characterised by

its high compacity and stability. But, only \( \alpha \)-FeOOH will be used in the model. \( \gamma \)-FeOOH

is electrochemically active and a semiconductor, and will also be used in the

model. In a first approach, the distribution of these phases in the rust layer will not

be considered. The rust layer will be assumed as homogeneous. But, the \( \alpha / \gamma \) ratio (or

\( \beta \), the fraction of lepidocrocite, in the rust layer, defined as \( \beta = \frac{\gamma}{\alpha + \gamma} = \frac{1}{1+\frac{\alpha}{\gamma}} \) ) will be

used to traduce the global composition and structure. Moreover, minor elements

will not be considered in the model.

Very important parameters are those linked to porosity. Porosity and tortuosity

will directly influence the species transfer in the rust layer (evacuation of corrosion

products, the penetration of dissolved oxygen, . . . ). Indeed, it seems clear that, with

pore access diameter of several 10 nm and cathodic reaction on the pore walls,

oxygen will not penetrate deeply in the rust layer. Moreover, a precipitation of solid

corrosion products in the pores could conduct to an obstruction and an inhibition of

the corrosion mechanisms. The specific area of porosity will influence the lepidoc-

crocite quantity in contact with the solution containing Fe\(^{2+}\) i.e. the possibility of

this phase to be reduced in the first stage of the wet–dry cycle (see Section 1 of this

paper). For this reason, the specific surface can be assumed as a “reactive surface” in

the model. Porosity and specific surface were quantified in this study but the pore
tortuosity and connectivity have to be more precisely determined in the future. Nevertheless, the presence of exogenous elements in relatively high quantities deep in the rust layer gives a rough idea of these two parameters.

As a summary, for modelling, following parameters will be used:

- $\beta$: average $\gamma$-FeOOH fraction in the rust layer
- $L$: thickness of the rust layer
- $\varepsilon$: average porosity of the rust layer
- $\tau$: tortuosity of the rust layer
- $S_a$: specific area of the rust layer, assumed to be the active surface

Fig. 18 gives the first simplification step used for modelling after considering the results given in this study.

### 7. Conclusion

This first part of a more general study concerning indoor AC of low alloy steels, concerns the analytical study of ancient rust formed on archaeological irons (several hundred y.o.) and artificially rusted samples in climatic chambers.

The ancient sample metallic substrates were characterised. Then, the morphology, the composition and the structure of the ancient rust were analysed.

Despite of the fact that ancient rust layers could be very complex and that the artefact history could influence its formation, general tendencies have been observed. The major phases of the rust layers are magnetite ($\text{Fe}_3\text{O}_4$), goethite ($\alpha$-FeOOH) and lepidocrocite ($\gamma$-FeOOH). Lepidocrocite seems to be more present in the outer layer. Goethite seems to be the major constituent of the inner layer. No amorphous phases have been clearly identified. The older the rust layers, the higher the protective ability.
indexes ($\pi/\gamma$ and $\pi'/\gamma'$ ratios). Lastly, high quantities of minor elements (P, Si, S and Ca) have been detected in the rust layers. Moreover, the porosity of the rust layer was evidenced and quantified.

All these parameters will be used in the second part of the study, concerning the modelling itself. Thus, a first simplification is proposed to describe the ancient rust layer formed after several hundred years and to be used in further modelling.

Acknowledgements

O. Spalla for SAXS and BET analyses. R. Balasubramaniam for providing the Indian iron samples. D. Vingtain and P. Bernardi for providing the samples coming from the Popes Palace in Avignon. A. Texier for providing all the other old iron samples. C. Blanc, V. Vigneau, D. Besnard and A.G. Chénierè for the help during SEM and XRD analyses and sample preparation. P. Chevallier for the help on D15 beamline.

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