



Review

A review of the archaeological analogue approaches to predict the long-term corrosion behaviour of carbon steel overpack and reinforced concrete structures in the French disposal systems

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ARTICLE INFO

Article history:

Received 11 February 2010

Accepted 6 May 2010

ABSTRACT

This paper gives a review of several years of research on archaeological analogues in order to predict the long term behaviour of the steel canisters or the reinforced concrete structures involved in disposal or interim storage of nuclear wastes in France. This article aims at showing the specific methodology, the complementarity with different other approaches and the complete integration of the research on analogues in the frame of research programs on long term prediction. Archaeological sites on which field measurement can be performed were referenced and described. A significant number of artefacts collected from these sites was selected for study. Detailed chemical and microstructural characterisation of the artefacts were undertaken by a combination of microbeam analytical techniques (μ Raman, μ XRD, μ Raman spectroscopy, ...). Hypotheses on the corrosion mechanisms were then tested using specific isotopic markers during re-corroding experiments on analogues. Specific parameters were measured, allowing crucial steps in modelling long-term corrosion of steel.

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1. Introduction

Natural and archaeological analogues [1,2] have been studied many times in order to help the prediction of the behaviour of

the different parts of the multi-barrier systems that are envisaged for disposal and interim storage of nuclear wastes (glass [3,4], metals as copper [5] and iron [6], cementitious materials [7], clay [8], ceramics and glass ceramics [9], etc.). Nevertheless, except some recent examples dealing with glass corrosion [10–12], their use has been relatively limited for the material's design itself [13]. They were actually more considered for benchmarking, for giving

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general tendencies or empirical models. This is particularly the case for ferrous materials [14–19].

For nuclear waste disposal and interim storage in France, it is envisaged that the waste will be encapsulated in a glassy matrix encased within an inner stainless steel canister surrounded by an outer container made of low alloy steel. It is asked to this overcontainer to resist to degradation during about 1000 years [17,20–25]. The advantage of low alloy steel is that this material is only submitted to general corrosion processes, easier to predict than pitting mechanism which occur on stainless steels. It is thus necessary to evaluate the corrosion rates of low alloyed steel in such desaturated environments. Moreover corrosion of low alloy steel in desaturated water leads to H_2 production. The effects of this production on the entire storage system must also be evaluated. Furthermore, interim storage facilities will be planned for periods of several hundred centuries. In that case, after a period of relatively high temperature and a progressive decrease of this parameter, wet/dry cycles will occur on the low alloy steel overcontainer. This phenomenon will render possible the alternating condensation and evaporation of a water film, causing degradation due to atmospheric corrosion. This degradation must be predicted in a reliable way. Another use of ferrous alloys in the context of nuclear waste disposal and interim storage is in reinforced concrete [26,27]. Numerous structures of the disposal facilities will be built using that material and it is necessary to predict the effect of rebar's corrosion on the mechanical behaviour of the concrete. Lastly, in some particular cases, reinforced concrete could be used as an overcontainer and it is also necessary to predict its behaviour.

To that purpose, it is envisaged to set up a phenomenological modelling of the corrosion processes, based on understanding of the mechanisms which control the behaviour of the corrosion system. The aim of the present paper is to enlighten the specific role of archaeological analogues in that wide frame. The approach of corrosion research on archaeological analogue is inspired by the philosophy proposed by Miller et al. [1,2] and different complementary aspects: benchmark, gathering of specific parameters impossible to reach in laboratories and crucial for the model, etc. The specificity here is that the research on analogues is completely integrated in the corrosion research programs dealing with the design of the disposal and interim storage facilities.

2. Phenomenological modelling and archaeological analogues

Concerning very long-term corrosion, during the last decades in Europe, archaeological analogues were only used to approximate

the average corrosion rates. In several cases [28], the corroding environment was not even taken into consideration. Finer studies focused on particular corrosion conditions in good agreement with those linked to nuclear waste disposal but did not perform any studies on the involved mechanisms. Some other were axed on the electrochemical studies of several archaeological samples [19], but, unfortunately, the corroding environment did not fit with the one of the disposal or interim storage. More complete studies including archaeological analogues in a wide corpus of artefact tried to produce a general envelope curve of the corrosion rates on the one hand and on local pitting penetration on the other hand [14,15,17]. More recently, in France, the research programs on analogues were totally integrated in studies dedicated to corrosion on very long term, bringing original and new data to build models.

The phenomenological approach needs to understand the long-term corrosion mechanisms at different scales [29,30]. These experiments allow to perform precise measurements of the important parameter evolution (pH, pCO_2 , pO_2 , alkalinity, etc.). They also allow to realise electrochemical tests of the system, and to deduce corrosion rates and mechanisms hypotheses. However, crucial aspect of corrosion, increased by the long term effect, is the role of the thick corrosion product layer developed on the metal. This layer could control many aspects of the mechanisms (transport, reactivity of the system, anodic and cathodic reaction decoupling, etc.). Consequently, the challenge of laboratory simulation is to recreate, by imposing forced electrochemical conditions, the growing of thick layers that must be representative of the reality. In that frame, the archaeological analogues, presenting such thick layer naturally formed during several 100 years are ideal to benchmark the laboratory simulation on the one hand and for measuring particular parameter on the other hand. Nevertheless it must be verified that the corrosion environment is as close as possible than the one of nuclear waste interim storage and disposal. Thus, in addition to the laboratory measurement validation, measuring the thick layer's specific parameters is the second axe of research linked to the archaeological analogues. It has been demonstrated that, for example, the transport of species in the pore of the thick layer (more or less saturated in water depending on the system) can totally control the mechanisms. Moreover, some of the phases constituting the corrosion layer can be more or less conductive, allowing or not the transport of electron from the metal to the surrounding environment. This can drastically change the behaviour and the mechanisms that control the corrosion rates. Thus, measuring these parameters on archaeological thick layers becomes now an important aspect of the research linked to the long-term corrosion prediction.

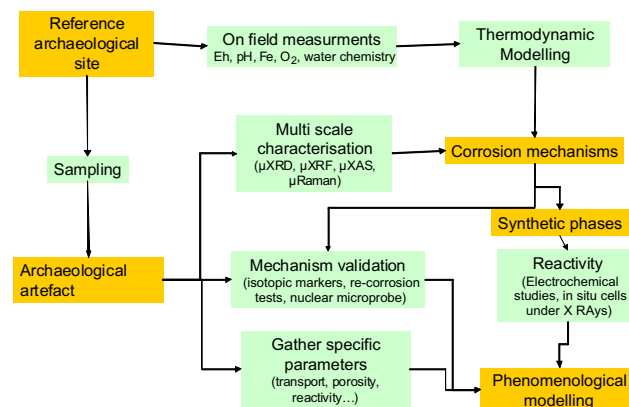
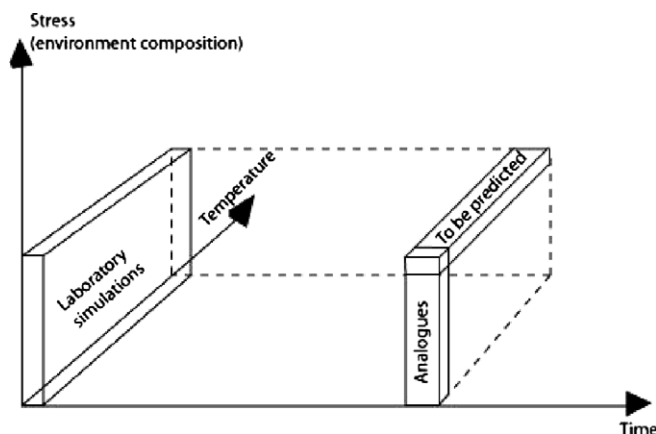


Fig. 1. (Left) Place of the archaeological analogues in the long-term corrosion behaviour prediction phenomenological modelling approach, (right) specific methodology adopted in France for archaeological analogues studies.

Lastly, if all the crucial parameters can be measured on a corroded archaeological system (constituted of the archaeological artefact and the corroding environment) and if a corrosion mechanism can be proposed, a modelling of the system behaviour can be attempted. The results of this modelling can then be compared to the reality observed on the corrosion system. Consequently the model can be validated but also the global methodology and philosophy of the phenomenological modelling. This approach, based on an integrated and independent research on the archaeological analogues is for instance followed in France in the frame of the ANR Arcor project, involving multidisciplinary research on the corrosion mechanisms of complex archaeological system. Fig. 1 sums up the specific methodology developed in France on archaeological analogues in the frame of the general long-term corrosion prediction studies.

3. The reference sites: measuring accurate environmental data

Environmental parameters have strong influence on corrosion processes at short and very long terms. Depending on their nature, mechanisms change drastically. Thus, for this reason, a new approach has been decided, based on choice of reference sites, representative of the specific conditions of nuclear industry. The choice is based on different condition as:

- close environmental characteristics to a corrosion system linked to nuclear waste interim storage and disposal;
- alteration periods of several 10 to several 100 years;
- the precise and reliable dating of the artefact of the site, linked to a dedicated and adapted archaeological study;
- the possibility of sampling a wide range of artefact and to process to destructive studies allowing to assess the different scale of the corrosion system (transverse sections) or to re-corrode the artefact (see below);
- the possibility to perform on field measurement of crucial environmental parameters as RH, pH, pO_2 , pCO_2 , water composition, at least on durations of about several years.

Table 1 sums up the various sites studied and the nature of the measurements performed during the last 10 years in the frame of the French research.

Concerning reference sites, a crucial step, is to model, taking into account the parameters measured on field, the thermodynamic domains of predominance of the different species and phases that can form. For example, Fig. 2 shows the potential versus pH diagram with the water composition of the Glinet site (see Table 1) [31]. The circle indicated the potential and pH values measured on the site. The calcium bicarbonate-type water and the high Fe amount in the water induce an equilibrium between iron carbonates and oxides. The presence of these phases was confirmed by fine physico-chemical characterisation on the artefacts sampled on the site (see next paragraph).

This approach is systematically performed on each archaeological reference site and needs sometimes to establish or precise some thermodynamic data that are not available in the literature (or are available with too low precision). Specific studies dedicated to that point are then necessary.

4. Fine physico-chemical description of the system: a contribution to modelling

The second important step in the general methodology for studying archaeological analogues is to characterise the different

Table 1
Examples of reference sites used for the archaeological analogue studies.

Name	Type	Location	Dating	Corrosion	Artefacts/samples	Measurements	Waste disposal problematic	References
Nydam Mose	Sacrifice site	Denmark	500 AD	Anoxic soil	Lances	Electrochemistry on coupon, T° , pH, oxygen, pCO_2 , water composition	Deep disposal in clay	[31,36,48]
Amiens cathedral Glinet	Building	France (Picardy)	1496 AD	Atmospheric	Rods positioned in the triforium	T° , RH cycles	Interim storage	[38,45,49]
	Ironmaking site	France (Normandy)	15–16 c. AD	Anoxic soil	Iron and steel artefacts, cast iron, iron in contact with glass (slag)	T° , pH, oxygen, pCO_2 , water composition	Deep disposal in clay particular case of iron/glass/clay system	[36,39,40,48]
Onera blowing machine	Building	France (Ile de France)	1950 AD	Concrete	Reinforcements embedded in concrete	T° , carbonation, concrete composition, RH	Unsaturated concrete structures	[50]
Avignon Popes Palace	Building	France (Provence)	14th. C. AD	Hydraulic binder	Ferrous alloys embedded in hydraulic binders	T° , RH	Unsaturated concrete structures	[37]

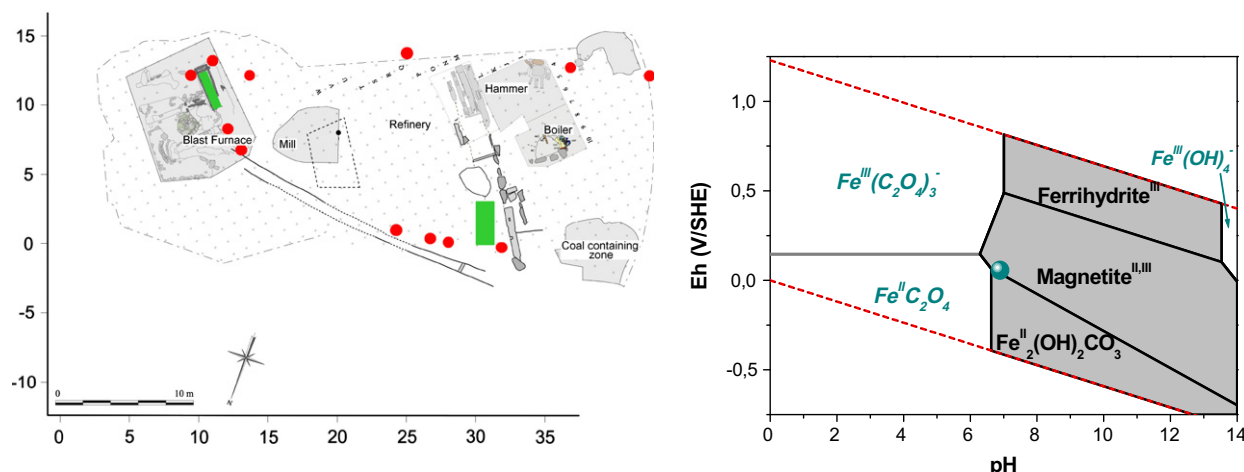


Fig. 2. (Left) On field measurements on the archaeological site of Glinet. Map of the archaeological site. Red dots: dipwell location. (Right) Example of potential (SHE = Standard Hydrogen Electrode) versus pH diagram made using water composition of the Glinet archaeological site. $[\text{Fe}]_{\text{tot}}: 1.73 \times 10^{-4} \text{ (mol/L)}$, $C_{\text{tot}}: 1.83 \times 10^{-2} \pm 2 \times 10^{-4} \text{ (mol C/L)}$ [31]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

parts of the corrosion system. Indeed, whatever the corrosion medium is, this system can always be described as follows:

- the metallic substrate that remains uncorroded;
- the Dense Product Layer (DPL): this part of the system is characterised by the iron corrosion product that formed a continuous layer around the artefact;
- the Transformed Medium (TM): it is constituted of a mix of the corrosion products and compounds coming from the surrounding environment (soil, binder, ...);
- the environment (E): constituted by the “unaltered” environment. Indeed, some iron species could have migrated in the pores of this medium, more or less far from the corrosion system. Moreover, in the case of concrete, it can be more or less carbonated.

To propose a corrosion mechanism, for a given system, each part must be characterised at different scales: from the macroscopic to the nanometric one (Fig. 3) [32]. First it must be verified that the metallic core has a composition and a structure that are comparable to those of the steel that will be used for the overcon-

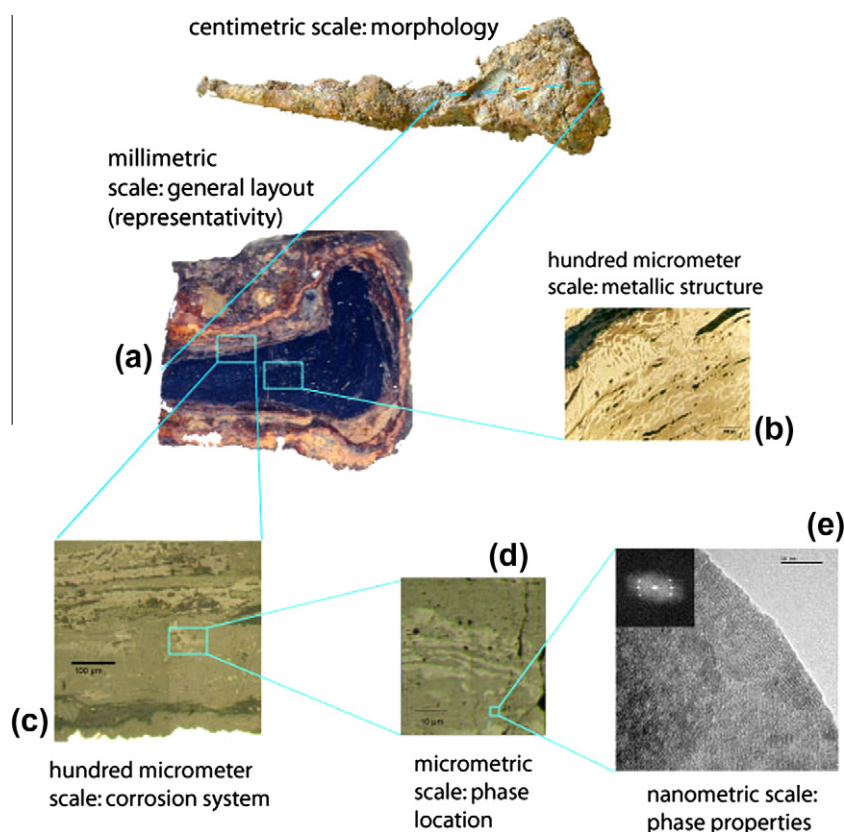


Fig. 3. General layout of corrosion system on archaeological analogues and different characterisation scales: (a) binocular picture; (b–d) optical microscope microphotograph; (e) TEM microphotograph and associated diffraction pattern obtained on the entire field [32].

tainer. The ancient ferrous alloys never present Cr or Ni as alloying elements. Consequently the only iron based analogues found in archaeological contexts are those of low alloy steels. However, some studies on meteorite could provide useful information about the corrosion of stainless steels, in spite of the unknown corrosion conditions in most cases. All the range of carbon contents can be found in iron based archaeological artefacts, from relatively pure ferritic iron ($\%C < 0.02$) up to hypereutectoid steels ($>0.8\%$) and even cast iron for samples younger than the 14th c. in Europe. It has to be noted that artefacts often present very heterogeneous structures that allow to find in the same sample, various amounts of carbon. That characteristic allows to study the behaviour of different steel kinds in the same sample. Nevertheless, because former ironmaking processes were performed at relatively lower temperatures than contemporary processes [33], ancient ferrous alloys could contain much more and larger slag inclusions than contemporary steels. Nevertheless, because every artefact is very heterogeneous, it is possible to find on every sample, zones without any inclusion. So, as well as for the carbon, for the same sample it is possible in a given environment, to study the potential effect of the presence of slag inclusions incorporated into the metallic matrix on the local mechanisms of corrosion. Furthermore, some minor elements as phosphorus [34] can be present in the metallic substrate of ancient iron based artefacts. This element is avoided in contemporary metal industry and it must be verified that it is not present in objects considered as analogues.

The DPL is formed on the metallic substrate by the iron oxidation. Its thickness can reach in certain cases several millimeters (according to the nature of the environment and the age of the sample). According to the nature of the phases which constitute this layer and their electrochemical properties, its role in the mechanisms of corrosion can be very different and the layer can

be more or less protective. That is why the detailed characterization of these phases is an important step in the methodology. To that purpose, different methods are coupled in order to precisely locate and identify the constitutive phases on transverse sections of the system. They are summarised in Table 2. The coupling of these methods is needed by the fact that some phases, despite of the same stoichiometry can have very different electrochemical reactivity. This is for example the case of goethite (α FeOOH) and lepidocrocite (γ FeOOH) – see next paragraph. These two phases can not be distinguished by using chemical analyses. Structural investigations, as μ XRD and μ Raman spectroscopy are needed. Moreover, some phases that also could play an important role in some cases are very difficult to identify by the two latter methods because they have a poor crystallinity and/or close crystallographic parameters. This is the case for example of ferrihydrite, ferroxhyte or of magnetite and maghemite. To distinguish them, it is necessary to perform relatively fine characterisation techniques based on the use of synchrotron radiation as μ XAS (XANES and EXAFS techniques) that allow to study the local environment of a given atom at the micrometric scale [35]. Fig. 4 shows the example of μ EXAFS data that allow distinguishing maghemite from ferroxhyte and ferrihydrite by comparison with reference spectra obtained on synthesised powders.

Depending on the environment, the nature of the phases in the DPL can be very different. For example in anoxic soils, the DPL is formed mainly of carbonates and iron oxides [36] (Fig. 5a). At the contrary, in concrete [37] or in the case of atmospheric corrosion [38], the DPL is mainly constituted by iron oxihydroxides containing marblings of oxides or poorly crystallised phases (Fig. 5b and c).

The TM is formed by corrosion products which migrated in the pores of the surrounding environment (soil or concrete). Depending on the local chemical conditions (pH, aeration), this migration

Table 2
Characterisation methods used for the study of archaeological analogues.

Method name	Scale of analyse	Information	References
Optical microscopy	mm to μ m	General layout of the system	[37,38–40]
Scanning electron microscope coupled to energy dispersive spectrometry	mm to μ m	Layout of the system, local chemical composition	[37,38–40]
Electron probe micro analyses	μ m	Local composition	[37]
Micro-X ray diffraction	μ m	Local structure, nature of the phases	[35,38–40,51,53]
Micro-Raman spectroscopy	μ m	Local structure, nature of the phases	[35,37–40,52,53]
Micro X ray absorption spectrometry under synchrotron radiation	μ m	Local environment of the studied atom, local structure, identification of low crystallised phases	[35,38–40,53]
Transmission electron microscope	nm	Local structure and composition	[38]

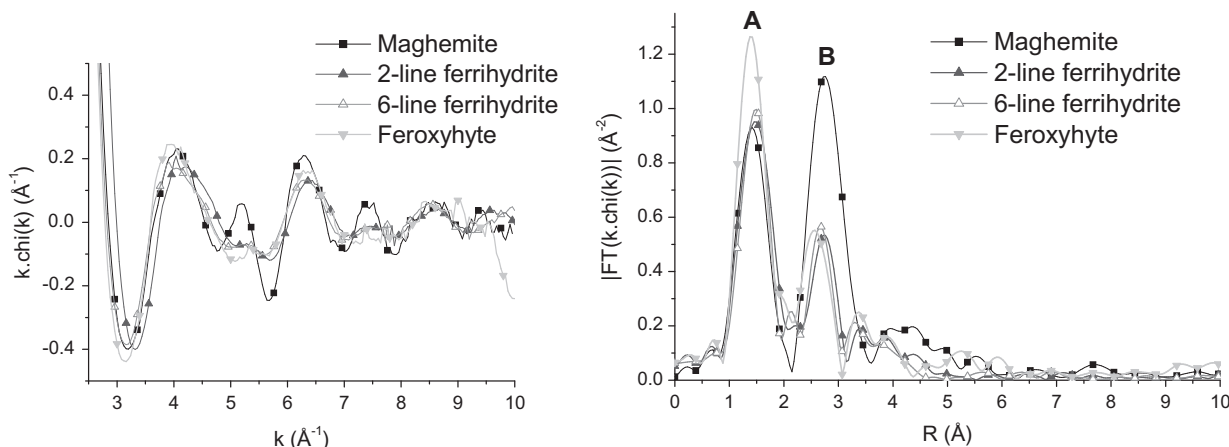


Fig. 4. EXAFS data obtained on iron containing phases present on archaeological samples; (left) $k\text{-}\chi(k)$ EXAFS signal and (right) $\text{FT}(k\text{-}\chi(k))$ Fourier Transform [35].

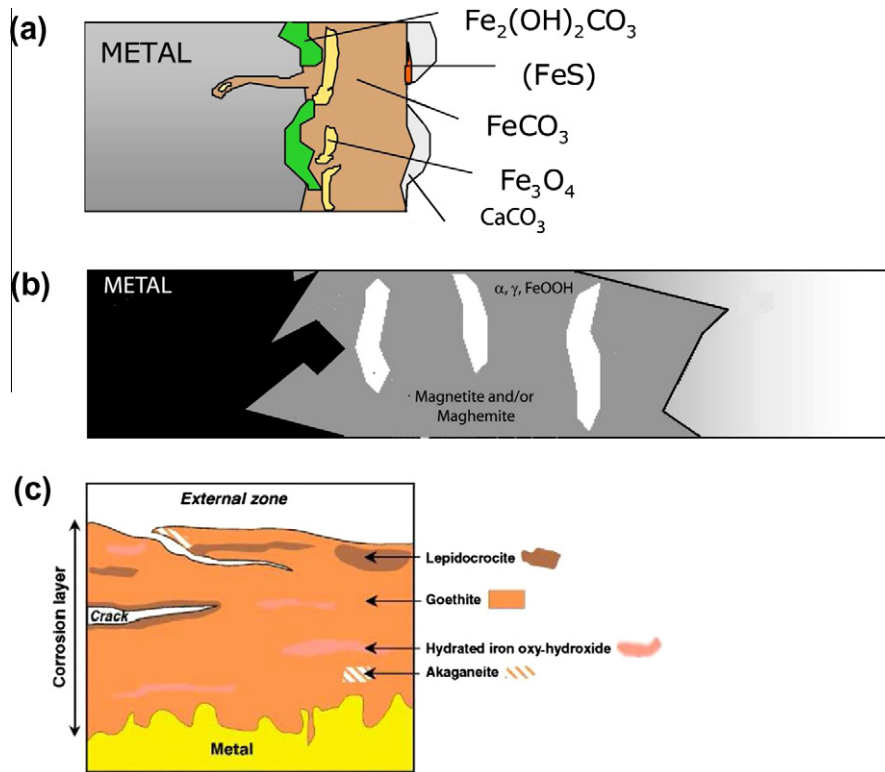


Fig. 5. Corrosion layouts observed in different environments: (a) anoxic soils [49]; (b) concrete [37]; (c) atmospheric corrosion [38,50].

can be more or less significant. Thus, its effect on the porosity characteristics has to be studied.

It has to be underlined that, for reliable and representative results, because of the relative variability linked to the ancient systems, a significant number of samples (artefact) must be analysed by coupling different techniques. Only this way of working allows to determine the most representative corrosion layout.

5. Validating mechanism

As said before, depending on the local porosity and the electrochemical properties of the DPL, the corrosion behaviour of the sys-

tem can be very different. For example, if the DPL is non conducting (for example when it is constituted of iron oxyhydroxide as goethite or carbonates), the oxidant specie (oxygen in the case of atmospheric corrosion or corrosion in concrete) must be transported through the pores of the DPL before provoking the oxidation of the metal (M) at the M/DPL interface. In that case, the transport properties of the DPL, strongly linked to the nature of the porosity, are crucial. On the contrary, if conductive phases are present in the DPL and connected to the metal, they can transport electrons and provoke the decoupling of the anodic reaction (iron corrosion) and of the cathodic reaction (oxidant reduction). The first reaction occurs at the metal/DPL interface, the second one inside the DPL or even at its outer surface if the conductive

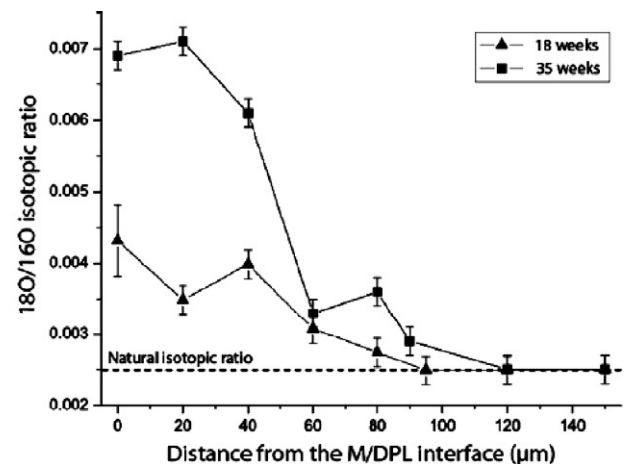
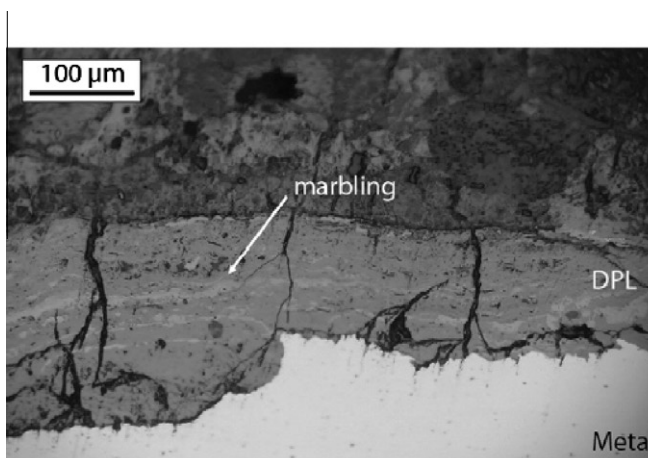


Fig. 6. (Left) Transverse section of the DPL of a sample corroded in hydraulic binder during 350 years, Saint Gervais Church, Paris, Optical microscope microphotograph. (Right) $^{18}\text{O}/^{16}\text{O}$ profile on that sample re-corroded during 18 and 35 weeks in water containing dissolved ^{18}O [37].

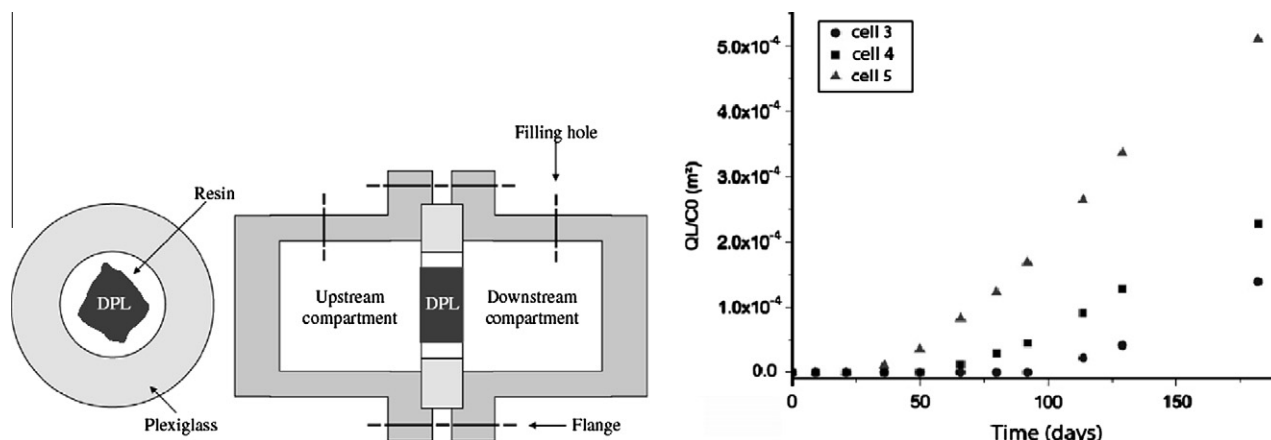


Fig. 7. (Left) Permeation cell used to test the transport properties of thick archaeological layers. The membrane is constituted by the corrosion layer sampled on the analogue [37]. (Right) Effective diffusivity tritiated water measurements made on an archaeological analogue: tritiated water diffusion flux (QL/C_0 , where L is the DPL thickness, C_0 the initial concentration in the upstream compartment, Q the quantity of tritiated water that diffused through the membrane) in the downstream compartment of the diffusion cell.

phases connect this zone to metal. In that case, the transport properties of the DPL are much less crucial for the phenomenological model. To discriminate these two cases, a step of the methodology consists in corroding the archaeological artefacts with their former corrosion layers. This is performed in the conditions determined by measurements on the archaeological site (water composition, RH cycles, etc.) and by replacing the oxidant specie (oxygen, water) by isotopic markers. Thus, in aerated environments (atmosphere and reinforced concrete), ^{16}O , the most abundant oxygen isotope in natural atmosphere is replaced by ^{18}O . In anoxic environments, H_2O is replaced by D_2O . After several months of treatment, samples are transversely cut and the phases recently precipitated containing isotopes are detected and localised on the transverse section using a nuclear microprobe. Fig. 6 shows the example of the $^{18}\text{O}/^{16}\text{O}$ profile obtained on the transverse section of a sample already corroded 350 years in hydraulic binder and re-corroded in water containing dissolved ^{18}O . The sharp increase of this ratio at the M/DPL interface clearly shows that the oxygen migrated through the DPL to oxydise the metal at the M/DPL interface. As a consequence, in that environment, the transport properties of the layer have to be taken into account for the modelling. Up to now this isotopic labelling of the cathodic site has been carried out for corrosion in soils [39,40], in reinforced concrete [37] and for atmospheric corrosion.

6. Gathering of crucial parameters

As it was demonstrated in the precedent paragraph, the evaluation of some physico-chemical properties of the different parts of the corrosion system is crucial for modelling. For example, the transport properties in the pore of the constitutive layers of the corrosion system, that can be more or less saturated in water, is a necessary step. In fact, the thin layers formed in the short term during the simulations in laboratory are not representative enough to estimate in a reliable way these parameters on the long term. That is why it is necessary to collect these parameters on archaeological layers of corrosion.

Fig. 7 shows an example of the effective diffusivity of tritiated water measured on thick archaeological corrosion layer separated from the metallic substrate and put in a permeation cell. Using this approach on a significant number of archaeological layers, effective diffusivity coefficient have been determined for different species and layer nature in saturated water [37]. This value is now integrated in the numerical modelling. Work is pursued in the case

of unsaturated pores. A complementary approach to the effective diffusivity is to determine the porosities of the different constituent of the corrosion system (DPL, TM and E). This has been done using different methods as mercury porosimetry and BET experiments [41].

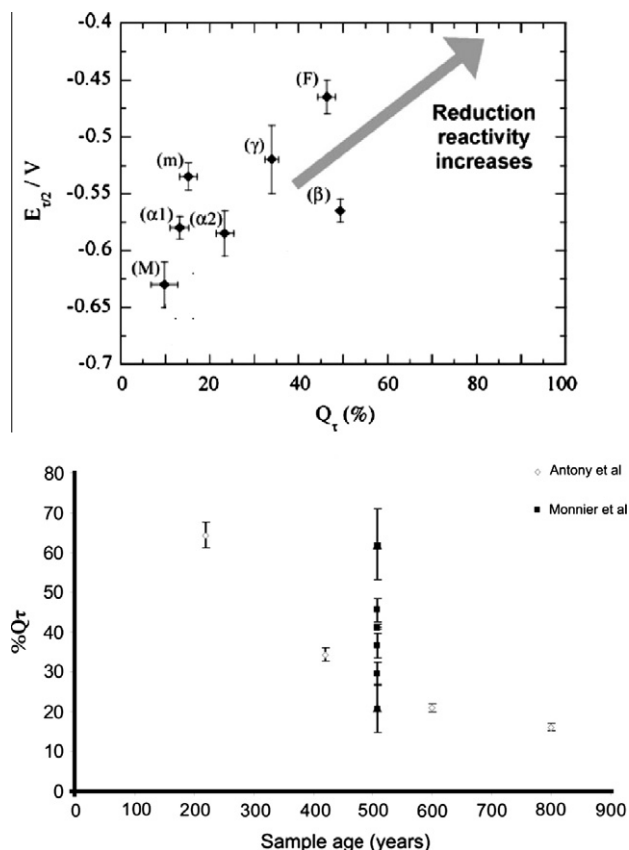


Fig. 8. (Left) Reduction reactivity of the different phases identified in the corrosion layers, $\%Q_{\tau}$: electron quantity of the iron from the initial phase that can be involved in a reduction process when a current is imposed to that phase, $E_{\tau/2}$: potential measured when half of Q_{τ} is reached during imposed current experiment. The more these values are high, the more the tested phase can be considered as reactive, m: maghémite, M: magnetite, $\alpha 1$, $\alpha 2$: goethite, γ : lépidocrocite, β : akaganeite, F: ferrihydrite [42–44]. (Right) Reactivity measurements made on different archaeological rust samples taken on the Amiens cathedral [45].

As indicated previously, besides measuring the properties of transport of the DPL, it is crucial to estimate the electrochemical properties of each of the phases of the system. Especially two parameters must be evaluated: conductivity and electrochemical reactivity. Indeed it has been proven that certain Fe^{3+} phases constituting the rust layer could be reduced in specific conditions (linked to RH cycle for example) and thus, provoke the oxidation of the metallic substrate. To evaluate electrochemical reactivity a combination of measurements performed on the ancient rust layers and on reference powders synthesised in laboratories can be undergone. Fig. 8a shows the compared reactivity of different iron oxides and oxihydroxides reference powders. This reactivity is evaluated by galvanostatic measurements, comparing the reduction potential (E/V) and the current quantity necessary to totally

reduce the studied sample ($\%Q_T$) [42–44]. The same test was performed on different samples submitted during several centuries to indoor atmospheric corrosion (Fig. 8b) [45]. In a comparable way, other parameters as local conductivity, effect of grain sizes, presence of nanolayers can be studied by combining experiments on reference phases and archaeological analogues. This is performed in different French laboratories in the frame of the Arcor project.

7. Modelling and benchmarking

Two complementary philosophies are followed for modelling. The first way of doing is to model the behaviour of the system

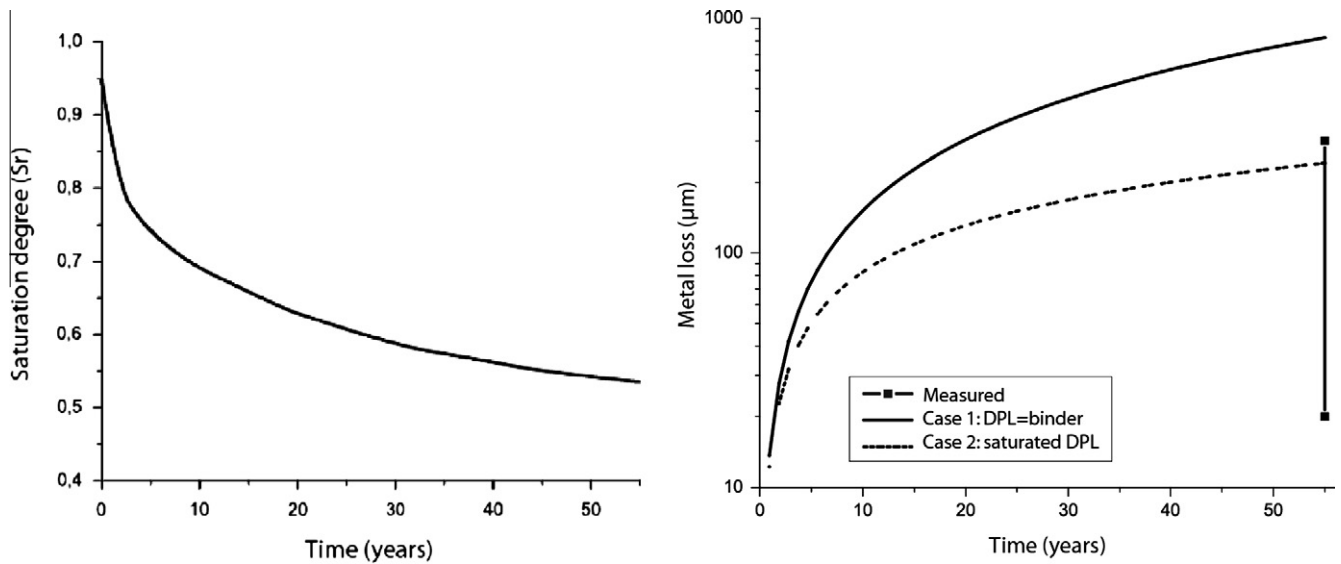


Fig. 9. (Left) Drying kinetic of the binder used in the Perret's water tower (France) at the cover depth corresponding to the rebar location ($L = 4$ cm), (right) long-term corrosion modelling of samples taken from the Perret's water tower, Saclay (France) [46].

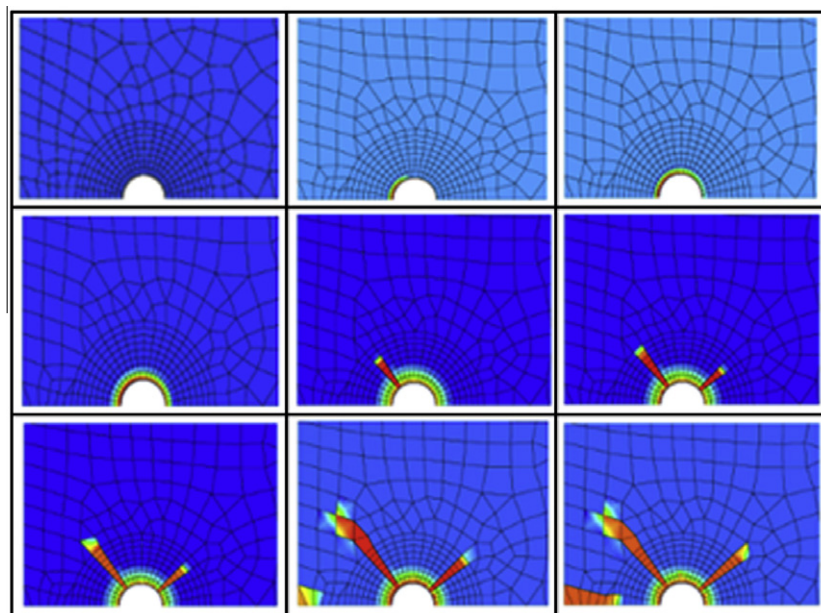


Fig. 10. 2D modelling of the concrete (3 cm concrete cover) cracking caused by the corrosion of rebars. View of the transverse section of the rebar. Evolution of the crack pattern at different times. Blue zones: damage equal to 0, red zones correspond to a damage equal to 1 [47] (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

formed by the archaeological analogues in order to evidence the most influent parameters on the corrosion rate, that must be determined as precisely as possible for the phenomenological and numerical modelling in the frame of nuclear waste interim storage and disposal. For example, Fig. 9 shows the results of the modelling of the corrosion of a reinforcement embedded in 10 cm concrete in the water tower of the CEA Saclay. Taking into account the porosities measured in the concrete and in the DPL and the effective diffusivity of oxygen measured on corrosion layers formed on archaeological artefacts, considering that oxygen must migrate through the porous DPL to provoke the corrosion of the substrate, the metal loss was modelled with or without DPL. RH cycles in the system were modelled using the meteorological data. The protective role of the DPL layer is clearly evidenced [46].

The second possibility that offer archaeological analogues is to help to gather specific parameters, linked to the long-term corrosion systems that are impossible to assess by another way. These parameters (as the DPL porosities, the diffusivity of some species in the pores, the reactivity of constitutive phases,...) can directly be put in the complex phenomenological models developed by other laboratories. For example, Fig. 10 shows the results obtained by the finite element model of concrete cracking under the effect of the rebar corrosion [47]. To model the growing of the corrosion layer, mechanisms and parameters (oxygen diffusivity, etc.) established on archaeological analogues have been used.

8. Conclusions and perspectives

This short review aimed to present the methodology and the philosophy of studies carried out in France on archaeological analogues to predict very long-term corrosion of different elements of the multi barrier envisaged for waste interim storage and disposal in this country. It has been showed that the studies are based on archaeological reference sites, on which environmental parameters can be measured. Moreover the fine analyses of transverse section of artefacts gathered on these reference sites allow to propose mechanisms. These mechanisms can then be validated by specific experiments on archaeological artefacts using isotopic tracers or electrochemical methods.

Next years, research will focus on the role of specific phases or protective layers at nanometric scale and on the studies of their properties. Moreover, new corrosion systems are going to be tested as the complex interaction between glass, ferrous alloys and clay. This will be achieved by looking on specific glassy slag produced by former ironmaking processes that can be found on production sites. For this new system, the same methodology will be followed, combining thermodynamically modelling and fine characterisation studies of the corrosion system.

Acknowledgements

In addition to the support of hosting institutions of the authors, studies on archaeological analogues are founded by the French National Research Agency ANR in the frame of the ARCOR project. Moreover all archaeologists who allow us to make on field measurement on their sites and to take artefacts for analogues studies are gratefully thanked, especially Danielle ARRIBET, Christophe COLLIOU, Florian TEREYGEOL, Maxime L'HERITIER. People that participates to the studies in different laboratories must also be acknowledged especially François MIRAMBET, Ludovic BELLOT-GURLET, Emmanuel ROCCA, Ivan GUILLLOT.

References

[1] W. Miller, *Geological Disposal of Radioactive Wastes and Natural Analogues: Lessons from Nature and Archaeology*, Pergamon, 2000.

[2] W. Miller, R. Alexander, N. Chapman, I. McKinley, J. Smellie, *Natural Analogue Studies in the Geological Disposal of Radioactive Wastes*, Studies in Environmental Science, Vol. 57, Elsevier, 1994.

[3] J. Sterpenich, G. Libourel, J. NonCryst. Solids 352 (2006) 5446–5451.

[4] J. Sterpenich, G. Libourel, *Chem. Geol.* 174 (2001) 181–193.

[5] B. Rosborg, L. Werme, *J. Nucl. Mater.* 379 (2008) 142–153.

[6] N.R. Smart, R. Adams, *Natural analogues for expansion due to the anaerobic corrosion of ferrous materials*, Swedish Nuclear Fuel and Waste Management Technical Report TR-06-44, Stockholm, 2006.

[7] I.G. McKinley, *Waste Manage.* 12 (1992) 253–259.

[8] E.C. Gaucher, P. Blanc, *Waste Manage.* 26 (2006) 776–788.

[9] W.E. Lee, M.I. Ojovan, M.C. Stennett, N.C. Hyatt, *Advances in Applied Ceramics* 105 (2006) 3–12.

[10] A. Verney-Carron, S. Gin, P. Frugier, G. Libourel, *Geochim. Cosmochim. Acta* 73 (2009) A1379.

[11] A. Verney-Carron, S. Gin, G. Libourel, *Geochim. Cosmochim. Acta* 72 (2008) 5372–5385.

[12] A. Verney-Carron, S. Gin, G. Libourel, *Geochim. Cosmochim. Acta* 74 (2010) 2291–2315.

[13] J.-C. Petit, *J. Geochem. Explor.* 46 (1992) 1–33.

[14] H. Yoshikawa, E. Gunji, M. Tokuda, *J. Nucl. Mater.* 379 (2008) 112–117.

[15] H. Yoshikawa, *Corrosion (March)* (2008) 16–20.

[16] H. Yoshikawa, K. Ueno, T. Honda, S. Yamagushi, M. Yui, *Analyses of the excavated archaeological iron using X-ray-CT*, in: *The 9th International Conference on Radioactive Waste Management and Environmental Remediation*, ASME, Oxford, 2003 (CD-ROM).

[17] F. Focet, J.-M. Gras, *Semi-empirical model for carbon steel corrosion in long term geological nuclear waste disposal*, in: D. Féron, D.D. Macdonald (Eds.), *Prediction of Long Term Corrosion Behaviour in Nuclear Wastes System*, European Federation of Corrosion, Cadarache, France, 2003, pp. 91–102.

[18] E.B. Munoz, J.C. Fernandez, J.G. Arasanz, R.A. Peces, A.J. Criado, C. Dietz, J.A. Martinez, A.J.C. Portal, *J. Nucl. Mater.* 349 (2006) 1–5.

[19] E. Pons, L. Uran, S. Joiret, A.H.-L. Goff, C. Lemaître, D. David, *Long term behaviour of iron in clay soil: a study of archaeological analogues*, in: *Prediction of Long Term Corrosion Behaviour in Nuclear Wastes System*, European Federation of Corrosion, Maney, 2003, pp. 334–345.

[20] F. Cattant, D. Crusset, D. Féron, *Mater. Today* 11 (2008) 32–37.

[21] S. Ben Lagha, D. Crusset, I. Mabilie, M. Tran, M.C. Bernard, E. Sutter, *J. Nucl. Mater.* 362 (2007) 485–492.

[22] D. Féron, D. Crusset, J.M. Gras, *J. Nucl. Mater.* 379 (2008) 16–23.

[23] D. Féron, D. Crusset, J.M. Gras, *Corrosion* 65 (2009) 213–223.

[24] D. Féron, D. Crusset, J.-M. Gras, D.D. Macdonald, *Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems*, Science and Technology Series, ANDRA, 2004.

[25] D. Féron, D.D. Macdonald, *Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems*, European Federation of Corrosion, Maney, 2003.

[26] V. L'Hostis, F. Focet, D. Féron, *NUCPERF 2006 Corrosion and Long Term Performance of Concrete in Npp and Waste Facilities*, EDP Science, Paris, 2006.

[27] V. L'Hostis, R. Gens, C. Gallé, *Long-term performance of cementitious barriers and reinforced concrete in nuclear power plants and waste management*, in: *EFC, RILEM Proceedings PRO64*, 2009, pp. 342–351.

[28] A. Accary, B. Haijink, *La paléométallurgie – Outil de prévision*, in: P. Fluzin (Ed.), *Journées de paléométallurgie*, Université de Technologie de Compiègne, Compiègne, 1983, pp. 9–32.

[29] C. Bataillon, F. Bouchon, C. Chainais-Hillairet, C. Desgranges, E. Hoarau, F. Martin, S. Perrin, M. Tupin, J. Talandier, *Electrochim. Acta* 55 (2010) 4451–4467.

[30] C. Bataillon, C. Musy, M. Roy, *J. Phys. IV France* (2001) 267–274.

[31] M. Saheb, D. Neff, M. Descostes, P. Dillmann, *Geochim. Cosmochim. Acta* 72 (2008) A818.

[32] P. Boulanger, B. Nowack, A.C. Scheinost, A. Wahner, M. Ammann, L. Charlet, P. Dillmann, S. Gin, T. Lieven, M. Morrisson, I. Nenner, *Environment*, in: H. Dosch, M.V.d. Voorde (Eds.), *GENNESYS White Paper: A New European Partnership Between Nanomaterials Science and Nanotechnology and Synchrotron Radiation and Neutron Facilities*, Max Planck Gesellschaft, Stuttgart, 2009, pp. 219–239.

[33] P. Dillmann, M. L'Héritier, *J. Archaeol. Sci.* 34 (2007) 1810–1823.

[34] R. Balasubramaniam, A.V.R. Kumar, P. Dillmann, *Curr. Sci.* 85 (2003) 101–110.

[35] J. Monnier, S. Reguer, D. Vantelon, P. Dillmann, D. Neff, I. Guillot, *X-rays absorption study on medieval corrosion layers for the understanding of very long term indoor atmospheric iron corrosion*, *J. Appl. Phys.* A 99 (2010) 399–405.

[36] M. Saheb, D. Neff, P. Dillmann, H. Matthiesen, E. Foy, *J. Nucl. Mater.* 379 (2008) 118–123.

[37] W.-J. Chitty, P. Berger, P. Dillmann, V. L'Hostis, *Corros. Sci.* 50 (2008) 2117–2123.

[38] J. Monnier, D. Neff, S. Réguer, P. Dillmann, L. Bellot-Gurlet, E. Leroy, E. Foy, L. Legrand, I. Guillot, *Corros. Sci.* 52 (2010) 695–710.

[39] E. Vega, P. Berger, P. Dillmann, *Nucl. Instrum. Methods B* 240 (2005) 554–558.

[40] E. Vega, P. Dillmann, P. Berger, P. Fluzin, *Species transport in the corrosion products of ferrous archaeological analogues: contribution to the modelling of long-term iron corrosion mechanisms*, in: P. Dillmann, G. Béranger, P. Piccardo, H. Matthiesen (Eds.), *Corrosion of Metallic Heritage Artefacts: Investigation Conservation and Prediction for Long Term Behaviour*, Woodhead Publishing, Cambridge, 2007, pp. 92–108.

[41] P. Dillmann, F. Mazaudier, S. Hoerle, *Corros. Sci.* 46 (2004) 1401–1429.

- [42] H. Antony, Etude électrochimique des composés du fer – Apport à la compréhension des processus environnementaux, PhD, Université d'Evry, 2005.
- [43] H. Antony, L. Legrand, L. Maréchal, S. Perrin, P. Dillmann, A. Chaussé, *Electrochim. Acta* 51 (2005) 745–753.
- [44] H. Antony, S. Perrin, P. Dillmann, L. Legrand, A. Chaussé, *Electrochim. Acta* 52 (2007) 7754–7759.
- [45] J. Monnier, L. Legrand, L. Bellot-Gurlet, E. Foy, S. Reguer, E. Rocca, P. Dillmann, D. Neff, F. Mirambet, S. Perrin, I. Guillot, *J. Nucl. Mater.* 379 (2008) 105–111.
- [46] W.-J. Chitty, P. Dillmann, V. L'Hostis, A. Millard, *Corros. Sci.* 50 (2008) 3047–3065.
- [47] A. Millard, V. Leyre, V. L'Hostis, Application of an atmospheric corrosion model to the prediction of induced damage in reinforced concrete structures, in: V. L'Hostis, R. Gens, C. Gallé (Eds.) *Long-term Performance of Cementitious Barriers and Reinforced Concrete in Nuclear Power Plants and Waste Management*, RILEM Proceedings PRO64, 2009, pp. 175–184.
- [48] M. Saheb, D. Neff, P. Dillmann, H. Matthiesen, E. Foy, L. Bellot-Gurlet, *Mater. Corros.* 60 (2009) 99–105.
- [49] J. Monnier, L. Bellot-Gurlet, L. Legrand, P. Dillmann, S. Reguer, D. Neff, I. Guillot, The long term indoor atmospheric corrosion of iron: rust layer characterisation and electrochemical study, in: C. Degryny, R.V. Langh, I. Joosten, B. Ankersmit (Eds.) *Metal07*, Amsterdam, 2007, pp. 47–54.
- [50] V. L'Hostis, D. Neff, L. Bellot-Gurlet, P. Dillmann, *Mater. Corros.* 60 (2009) 93–98.
- [51] P. Dillmann, D. Neff, F. Mazaudier, S. Hoerle, P. Chevallier, G. Beranger, *J. Phys. IV France* (2002) 393–408.
- [52] D. Neff, S. Reguer, L. Bellot-Gurlet, P. Dillmann, R. Bertholon, *J. Raman Spectrosc.* 35 (2004) 739–745.
- [53] S. Reguer, P. Dillmann, F. Mirambet, J. Susini, P. Lagarde, *Appl. Phys. A* 83 (2006) 189–193.