



Archaeological analogues and corrosion prediction: from past to future. A review

P. Dillmann, D. Neff & D. Féron

To cite this article: P. Dillmann, D. Neff & D. Féron (2014) Archaeological analogues and corrosion prediction: from past to future. A review, Corrosion Engineering, Science and Technology, 49:6, 567-576, DOI: [10.1179/1743278214Y.0000000214](https://doi.org/10.1179/1743278214Y.0000000214)

To link to this article: <http://dx.doi.org/10.1179/1743278214Y.0000000214>



Published online: 09 Jul 2014.



Submit your article to this journal [↗](#)



Article views: 242



View related articles [↗](#)



View Crossmark data [↗](#)

Archaeological analogues and corrosion prediction: from past to future. A review

P. Dillmann^{*1}, D. Neff¹ and D. Féron²

A new approach including the use of archaeological analogues is needed to predict corrosion phenomena over extended time periods lasting centuries to several millennia. The corrosion rates observed on analogues generally range from 0.1 to 10 $\mu\text{m}/\text{year}$, depending on the medium. Isotopic markers (deuterium or oxygen-18) can be used on archaeological objects to determine and localise the anodic and/or cathodic mechanisms. Modelling and simulation take into account statistical aspects (modelling by cellular automata) and kinetics, including localised corrosion phenomena (pitting factor).

Keywords: Analogues, Corrosion, Long term, Steel, Modelling, Mechanism, Methods, Conservation

This paper is part of a special issue on 'Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems'

Introduction

The lifetimes of structures and the metallic materials used for their construction are continually increasing: the service life of industrial facilities is frequently extended; civil engineering structures are built today for at least a century, and in the case of repositories for long lived intermediate and high level nuclear waste, the time scales extend over several hundred or several thousand years. Predicting corrosion phenomena and their kinetics over such long durations is not a routine task. It is obvious that semiempirical modelling and experience feedback are no longer sufficient as a basis for estimating the lifetime of the materials. Over durations of centuries to several millennia, a new approach is necessary.¹ It has been refined in the last decade and consists in a four-step iterative process:

- experimental investigation in the laboratory to understand the phenomena, investigate their parameters, measure the initial kinetics and their evolution and determine their physicochemical mechanisms
- mechanistic modelling (based on the physicochemical mechanisms of corrosion phenomena) to allow simulation, and the use of this simulation for long term extrapolation
- the use of archaeological analogues to confirm the long term kinetics and the validity of the mechanisms previously identified by short term experiments
- an integrated approach involving experiments under conditions as representative as possible, with full coupling of the effects of the medium, the materials and other environmental parameters such as stress, flow, bacteria, etc.

Iteration consists in checking, for example, that the corrosion kinetics or the modelled mechanisms are coherent with what is observed in short term experiments and on the analogues. This overall approach is schematised in Fig. 1, which highlights the iterations as well as the exchanges necessary between the various international communities working on long term predictions. It is important to remember that on these time scales the environment is subject to predictable or random evolution. For example, in the case of the geological disposal of nuclear waste as envisaged in clay or granitic sites in Europe, the environment will initially be oxidising during the operation of the repository, but it will then become anoxic and reducing after closure. The transition between these two phases, when metallic materials can be in oxidising conditions in some zones and reducing conditions in others, certainly increases the risk of localised corrosion which can be initiated either by well known phenomena such as differential aeration, or by the simultaneous presence of aerobic and anaerobic bacteria, as in thick seawater biofilms. A sensitivity analysis may be necessary to address these less foreseeable changes in the natural environment; however, the contribution of archaeological analogues is often decisive. Inspired by reflections and proposals of some predecessors on natural²⁻⁴ and archaeological⁵⁻⁷ analogues for metals⁸ and other materials such as glass,⁹⁻¹¹ work has progressed in recent years on the corrosion of archaeological analogues and the lessons that can be learned from them. This paper is a brief review of the contribution of analogues to assessing the corrosion of ferrous metals.

Although with regard to the degradation process, archaeological objects can be considered as analogues of materials intended for future use, the study of their corrosion mechanisms is also of interest for the protection of cultural heritage materials for which it is often necessary to determine the degree of deterioration before deciding on a suitable restoration treatment.¹² For example, many old or ancient monuments are

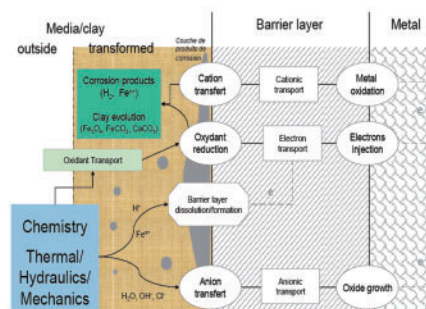
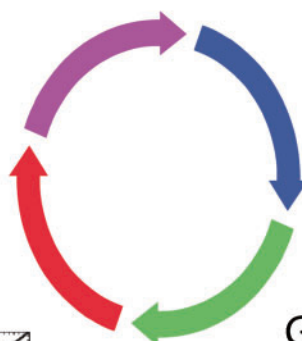
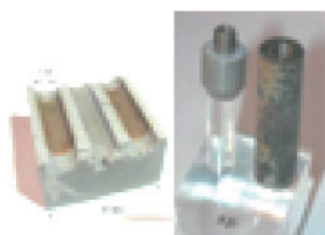
¹LAPA: NIMBE, SIS2M, UMR3299 CEA/CNRS and IRAMAT UMR5060 CNRS, CEA Saclay, 91191 Gif sur Yvette, France

²Commissariat à l'Energie Atomique et aux Énergies Alternatives, DEN/DANS/DPC/SCCME, CEA Saclay, Bât. 458, PC50, 91191 Gif-sur-Yvette, France

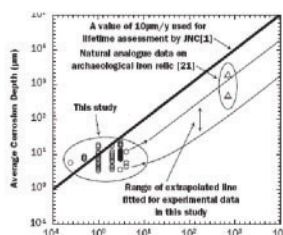
^{*}Corresponding author, email philippe.dillmann@cea.fr

Simulation and modelling

Laboratory experiments



Global and in-situ experiment



Archaeological analogues

1 Steps for predicting corrosion phenomena and kinetics over extended time periods (from few centuries to several millennia)

reinforced by metal components, which therefore have an intrinsic patrimonial value.^{13,14} It is thus important to diagnose the degree of deterioration before any decision can be made regarding a possible restoration or removal and/or conservation strategy. The key is to understand the mechanisms of deterioration and if possible model this behaviour. The same approach is adopted in Northern Europe with *in situ* conservation: archaeological objects remain buried on the site while controlling the processes of deterioration,^{15,16} in particular by measuring environmental parameters such as the pH or redox potential, by determining the mechanisms involved and by implementing a predictive methodology.¹⁷ In many cases, it appears that studying metals of the past can help to predict their behaviour in the future, especially corrosion, but also to more effectively preserve historical materials.^{18,19}

Among various metals concerned in civil engineering, in nuclear waste disposal and in the protection of our cultural heritage, iron is the most studied. It has constituted a very large fraction of historical metals since the Iron Age, and is a component of a large number of engineering structures that are intended to last for a long time. This article therefore focuses on iron in reviewing the various approaches and issues in materials and corrosion science related to archaeological metals.

Long term corrosion systems

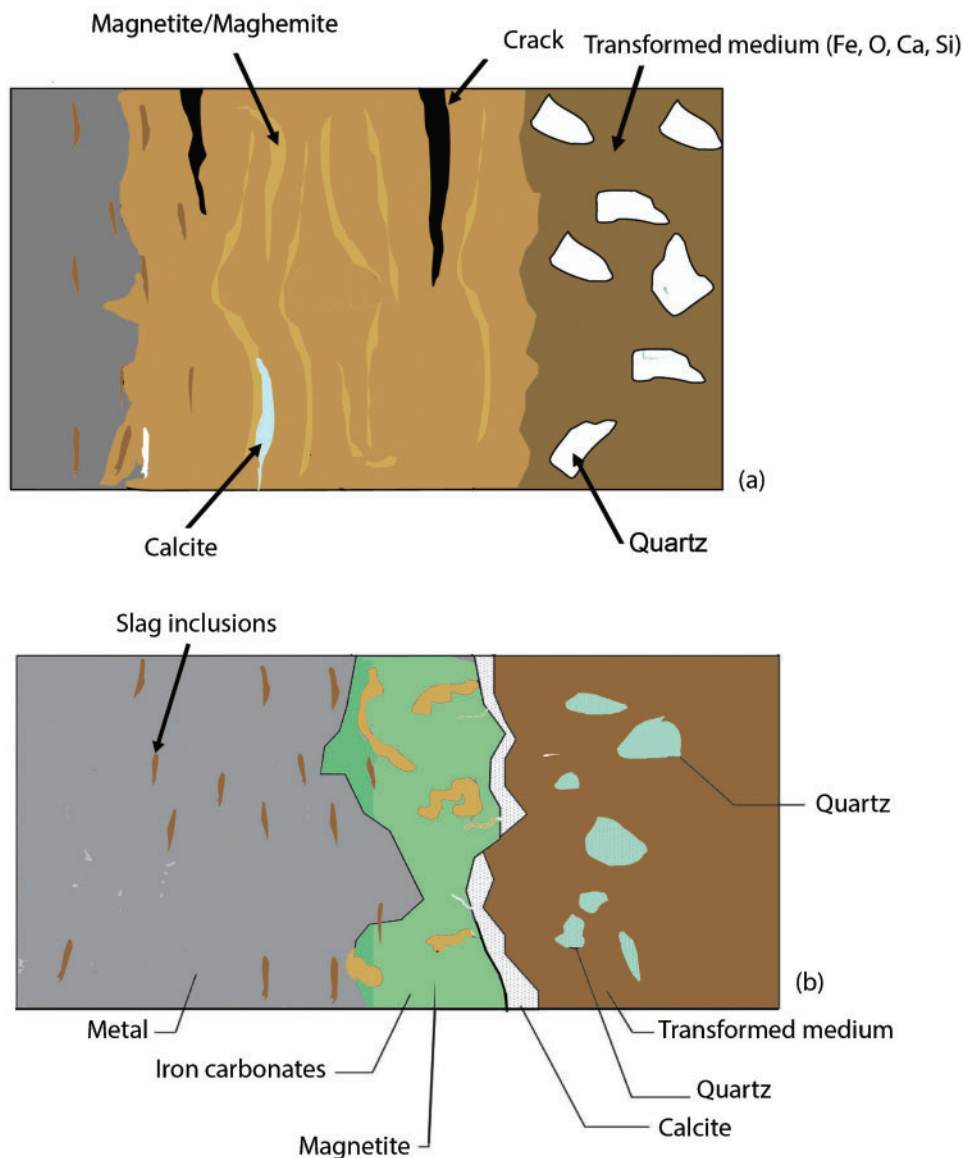
Whatever the medium in which ferrous archaeological objects deteriorate, over the long term they form corrosion thick layers that on some specimens may reach a few hundred micrometres or even a few millimetres. From the metal core, whether or not it is

still preserved, the following layers can be distinguished (Fig. 2):

- the metal core itself, sometimes heterogeneous from the standpoint of its minor element composition (carbon, phosphorus, etc.) or the quantity of secondary phases (inclusions);
- a layer of corrosion products (CPs) consisting of various oxides, oxyhydroxides, carbonates, and possibly sulphides, sulphates and phosphates, and of variable porosity, depending on the medium
- a transformed medium containing a large proportion of the surrounding medium (clay, quartz, calcite) together with precipitated corrosion products when the object is embedded in a solid medium (soil, concretion, cementitious binder, etc.)
- finally, the solid medium itself.

Corrosion rates

The observation of archaeological corrosion systems makes it possible to define a bounding curve of corrosion rates for ferrous metals over durations of several centuries. The mean corrosion rates can be deduced from the total quantity of corroded metal (estimated by measuring the thicknesses of corrosion products and/or by the chemical fraction of iron released into the environment). Extending the seminal work of Johnson,^{20,21} Fig. 3 reviews the corrosion rates measured in various media for corroded objects over periods exceeding 100 years. The error bars are due for certain objects to the measurement inaccuracy, and for others to the considerable irregularity of the penetration of corrosion. It can be seen that although the corrosion rates can be very high, especially in a marine aerated environment, most of the rates lie between 0.1 and



2 Schematic representation of cross-sections of typical corrosion patterns on archaeological artefacts *a* in aerated soil or cementitious binder and *b* in deaerated soil with corrosion product (CP) layer: each system is constituted by metallic core, CP and outer transformed medium, consisting of mix of corrosion products and medium in which metal was embedded

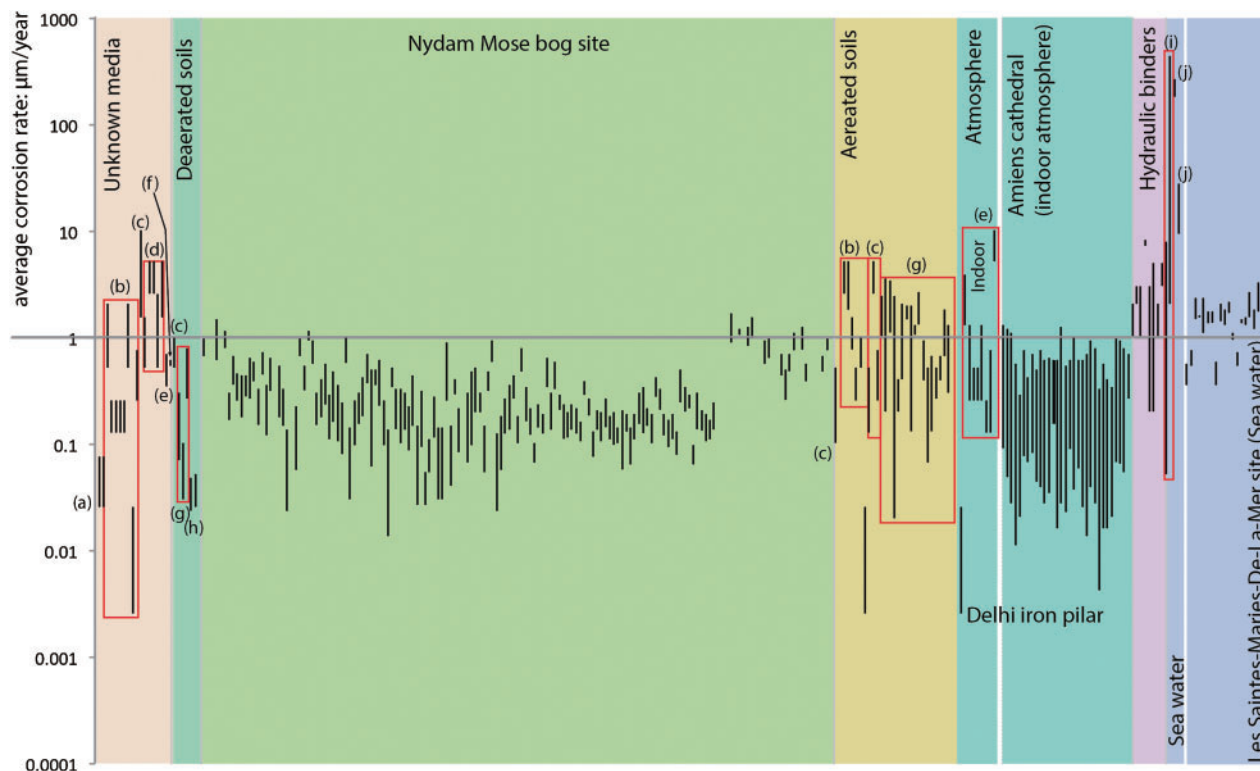
10 $\mu\text{m}/\text{year}$. These rather low rates compared with shorter term measurements on the same types of materials reveal control of the kinetics by the corrosion product layer. Outlying values beyond the mean corrosion rates are due to specific conditions of the medium or the material which will be discussed below.

It is also possible to measure instantaneous corrosion rates: the archaeological object is placed in an environment reproducing the initial one and the corrosion rates are followed for example by using electrochemical measurements^{37,38} or isotopes (see the section on 'Mechanisms and models').

Influence of environment

Variations of the environmental conditions were followed on the archaeological site of Glinet,³⁹ regarded as a reference by some research teams working on analogues. This ferrous metal production site is dated from the late mediaeval period. Moreover, because hydraulic power was used to move the blowers of the furnaces, a dam

was constructed above the site to provide water. Consequently, from its abandonment, the site remained under water and in anoxic conditions as proved by extensive water measurements studies made at Glinet.³⁹ The site offers a large number of ferrous alloys that have been corroded in various media under anoxic and aerated conditions, depending on the burial depth. A change in the nature of the corrosion systems can be identified according to the oxygen content. The corrosion rates associated with these two conditions are significantly different. Measurements on the objects corroded in oxidising media give values between 2.3 and 3.5 $\mu\text{m}/\text{year}$, while those measured in deaerated media lie between 0.15 and 0.3 $\mu\text{m}/\text{year}$ ^{37,40} (see also Fig. 3). The same trends were observed at the Danish site of Nydam Mose^{30,40} on lances and swords thrown into a sacrificial lake between the second and fifth centuries, where levels of dissolved oxygen are considered to be anoxic, based on measurements with micro sensors; only the upper few centimetres of the bog

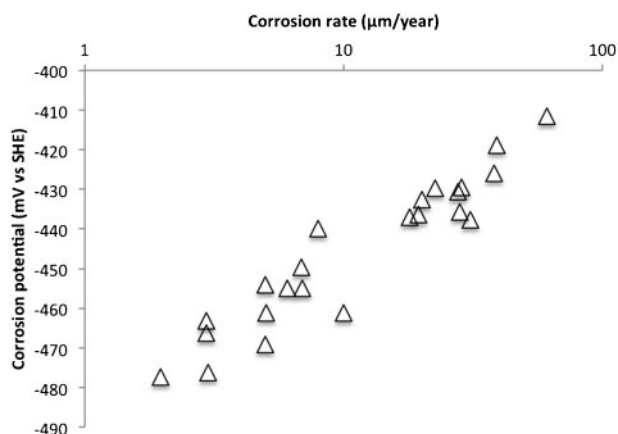


3 Mean corrosion rates measured on archeological objects corroded in various media for durations of more than century: (a) England;^{21,22} (b) Egypt;²³ (c) England;²³ (d) no indication;²³ (e) Egypt;²⁴ (f) Heeten, The Netherlands;²⁵ (g) Glinet, France;^{26–28} (h) Fiskerston, England;²⁹ Nydam Mose site, Denmark;³⁰ Delhi, India;²⁰ Amiens cathedral, France;³¹ cementitious binders of French monuments;³² (i) diverse marine environments;³³ (j) Australian coast;^{34,35} Les-Saintes-Maries-de-la-Mer, France³⁶

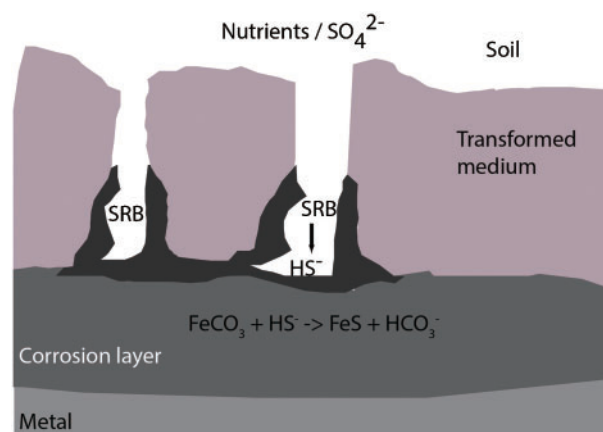
contain oxygen.⁴¹ The highest corrosion rates were recorded for the objects closest to surface, while for the most buried objects, the corrosion rates were significantly lower. Very low corrosion rates were also observed on modern steel samples buried on this site, for which the free redox potential was monitored.^{30,42,43} The corrosion rates are the lowest when the free corrosion potential of the samples is low (Fig. 4), therefore, in the absence of oxidising agents (oxygen) and in the presence of reducing agents (probably sulphides). It should, however, be noted that on this site few analogues were completely corroded and that some high corrosion rates are also observed on modern steels (50–130 μm/year depending on the techniques

used). This variability is due in part to the environment (oxygen content and sulphide concentration, which differ according to the sites, and the presence of bacteria) and in part to the stochastic nature of corrosion.

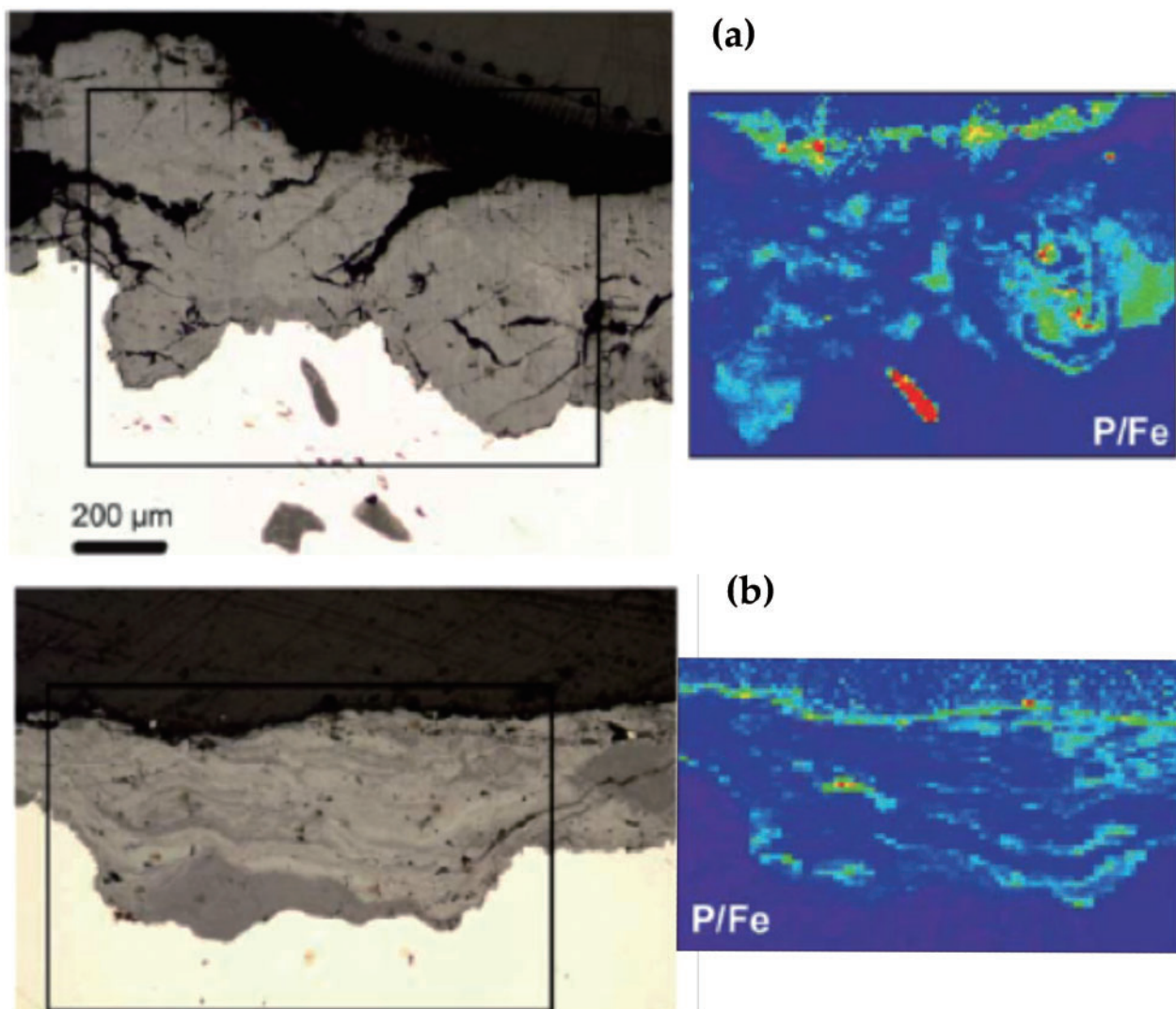
Corrosion rates can thus be significantly higher in the presence of oxygen. This is the case, for example, of aerated seawater in which corrosion rates higher than 100 μm/year were observed on cannonballs.³⁴ Conversely, anoxic media usually result in low or even very low generalised corrosion rates, most often between 0.1 and 10 μm/year even in sea water: for example, a Roman ingot immersed for 2000 years at a depth of 12 m (see Fig. 3: 'Les-Saintes-Maries-de-la-Mer') in anoxic



4 Corrosion potential versus corrosion rates measured on coupons corroded for 2 years at Nydam Mose site

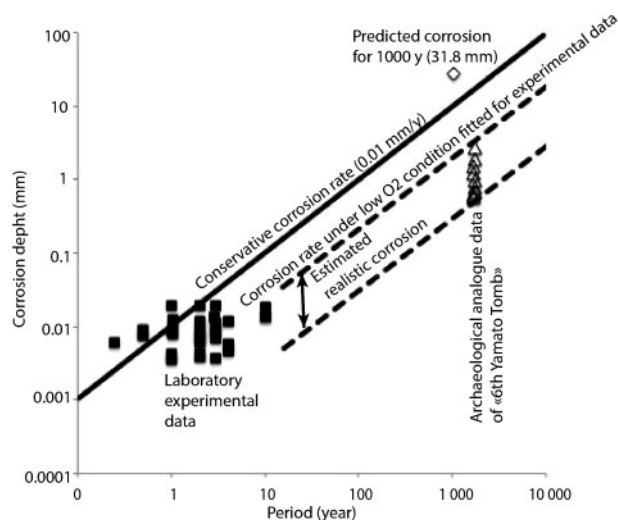


5 Schematic representation of influence of sulphate reducing bacteria on archaeological corrosion systems⁴⁵

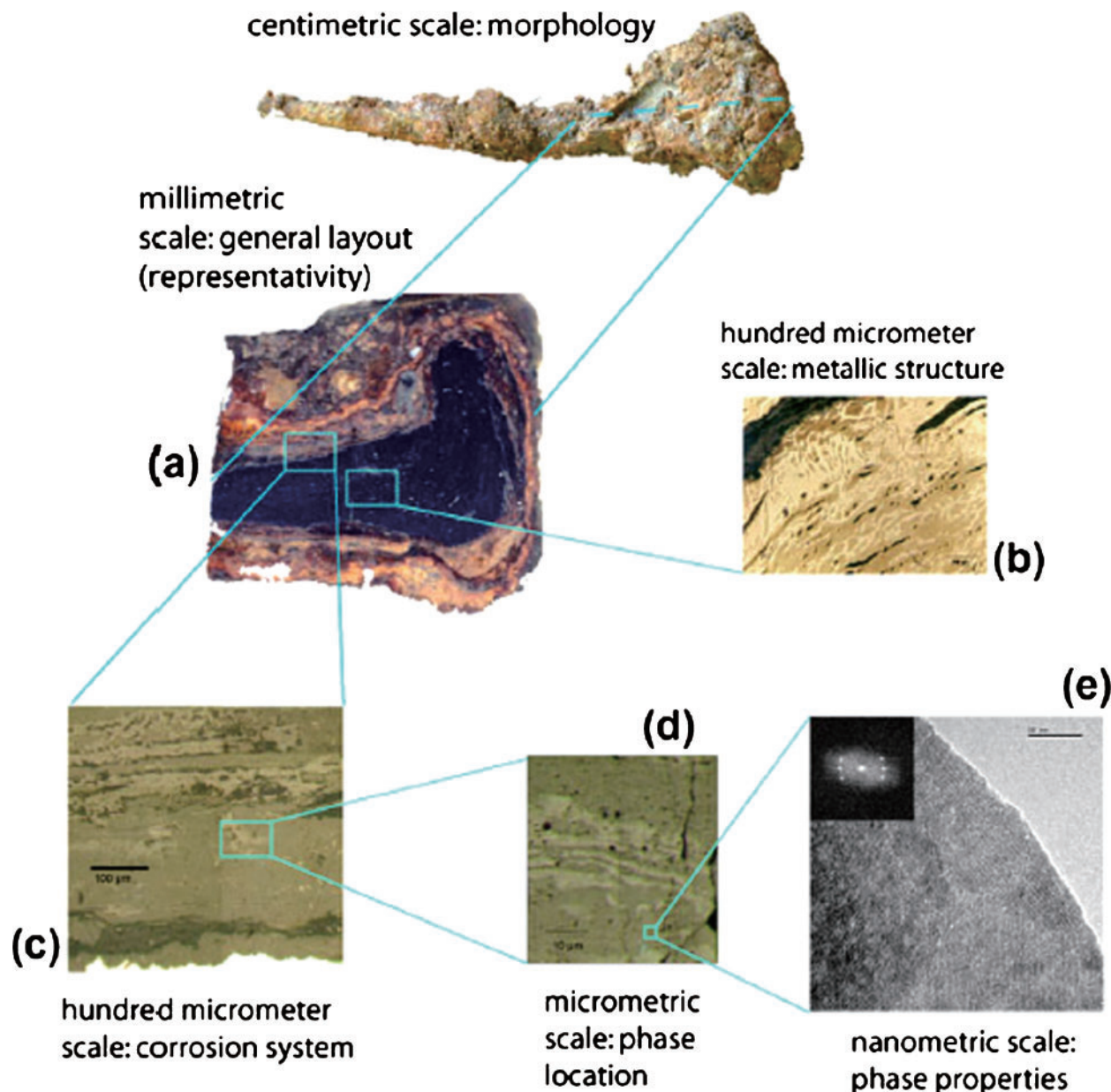


6 Distribution of phosphorus on cross-section of sample from *a* Amiens cathedral (France) and from *b* Deogarh temple (India), contemporaneous with Delhi iron pillar: light marbling on optical micrograph (upper) corresponds mainly to reactive phases; distribution of P in corrosion products roughly follows initial distribution in former metallic substrate; high P concentration zones in substrate correspond to non-metallic slag inclusions⁵⁹

conditions created by concretions and a biofilm that covered them entirely appears very well preserved, even though mackinawite (FeS) is observed among the corrosion products. FeS is due to the presence of sulphate reducing bacteria, most often presented as very detrimental to metallic materials.⁴⁴ Although sulphur pollution and the presence of sulphate-reducing bacteria are regarded by industry as harmful for steels, the archaeological analogues do not appear to confirm this behaviour. At the Nydam Mose site, for example, generalised corrosion rates as low as 0.03 $\mu\text{m}/\text{year}$ were observed on the most deeply buried objects. Chemical and biochemical analyses of this site, now marshland, reveal the presence of sulphides (up to 2.2 mg L^{-1})⁴¹ probably related to sulphate reducing bacteria. The presence of sulphate reducing bacteria has also been observed at a number of archaeological sites, for example, Glinet,⁴⁵ where their presence in the external layer of corrosion products could be related to that of FeS (Mackinawite) and Fe_3S_4 (Greigite), as illustrated in Fig. 5.



7 Comparison of depths of corrosion observed on archaeological analogues with laboratory experimental data⁶¹



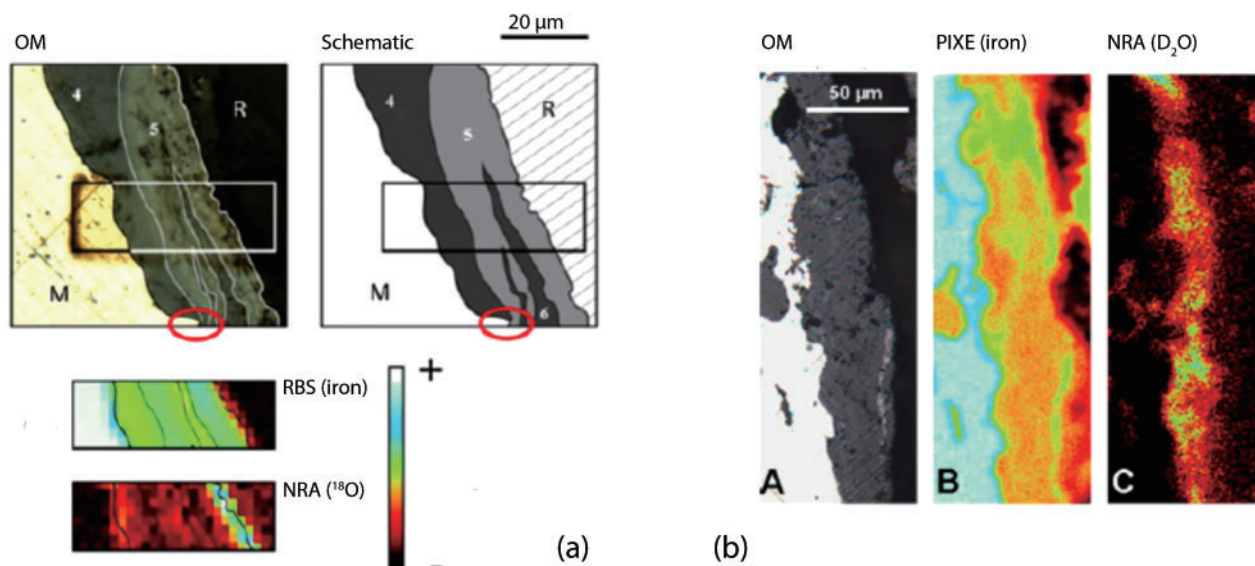
8 Various scales of observation of corrosion system several centuries old. From macroscopic to nanometre scale, texture, structure and chemistry must be observed to understand corrosion properties of system;^{62,63} General layout of corrosion system on archaeological analogues and different characterisation scales: a binocular image; b–d optical micrograph; e TEM image and associated diffraction pattern obtained over entire field

Influence of materials

The techniques for producing ancient ferrous alloys differ from modern practice by the fact that smelting of the iron ore was carried out at temperatures below the melting point of iron. Archaeological ferrous materials are thus by nature heterogeneous and the same object may contain variable quantities of carbon and non-metallic inclusions.^{46,47} These parameters were in certain cases controlled by the blacksmiths (in particular through case hardening and workhardening by hammering) to obtain materials comparable to those currently employed, but this control was far from systematic, especially for routine objects of little value. Archaeological objects can thus have a structure favoring localised corrosion (intergranular or along particles of secondary phases). Very often^{24,47,48} an object buried in a given environment contains several types of materials

(with variable amounts of carbon or inclusions) that can be corroded.

Even if the archaeological metal of the objects never contains additives such as Cr or Ni, minor elements such as P can be present, as attested in ancient iron worldwide. It can be distributed heterogeneously in the metallic substrate due to the thermodynamic conditions during the ancient processes.^{49,50} Its influence is significant in the corrosion process, in particular for atmospheric corrosion, and has already been highlighted by short term studies.⁵¹ This has been confirmed on historical alloys, such as the Delhi pillar (India) dating from the Gupta period and presenting exceptionally low corrosion damage despite its age (more than 1500 years).^{52–57} It appears that the presence of this element in ancient corrosion layers of P containing ferrous alloys follows the initial heterogeneous distribution of the former metallic



9 *a* optical micrograph (OM) and schematic view of cross-section of layer containing conductive phases formed after several centuries of corrosion in cementitious binder. Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) map showing ^{18}O distribution after 6 months of exposure in a labelled environment.⁶⁴ M: metal, R: resin, 4: iron oxyhydroxides, 5, 6: magnetite. Accumulation of ^{18}O near conductive magnetite phase (5) indicates that O_2 reduced at location. *b* A: OM, B: RBS and C: NRA maps showing deuterium distribution after 6 months of corrosion in deuterated water of nail initially corroded for 400 years in anoxic water³⁷

core as illustrated on Fig. 6 for a sample from another Indian site from the Gupta period, the Deogarh temple⁵⁷ and on mediaeval samples from the Amiens Cathedral (France).⁵⁸ The presence of phosphorus in the corrosion products is assumed to lower the reactivity of certain phases of the corrosion products, which would otherwise contribute significantly to oxidation of iron during humidification/drying cycles.^{59,60}

Mechanisms and models

Short term versus long term

The corrosion rates obtained on archaeological objects can be compared with data from laboratory experiments of shorter duration under representative conditions. Their objective is to give a certain robustness to predictions of the lifespan of steel containers planned for nuclear waste storage in a clay formation. The corroded depths observed on iron objects aged more than 1500 years buried in an argillaceous sediment⁶¹ (Yamato sixth century tumulus) were compared with the degradations observed during laboratory tests lasting a few months to a few years, after ensuring that the corrosion products observed in both cases were similar (presence of magnetite and goethite, lepidocrocite and akageneite, consistent with a slightly oxidising medium). This is summarised in Fig. 7 which puts in perspective the data obtained during short term laboratory tests (in which damage evolves little during the first years) with the data obtained on the archaeological objects (corrosion depths substantially lower than expected). The total damage varies from 0.5 mm (which corresponds to a mean rate of uniform corrosion of approximately 0.3 $\mu\text{m}/\text{year}$, characteristic of a reducing environment) to 2 mm (or a mean corrosion rate of 1.3 $\mu\text{m}/\text{year}$, characteristic of an environment with low oxygen content, not oxidising in general). The total damage includes the few pits initially observed on the analogues

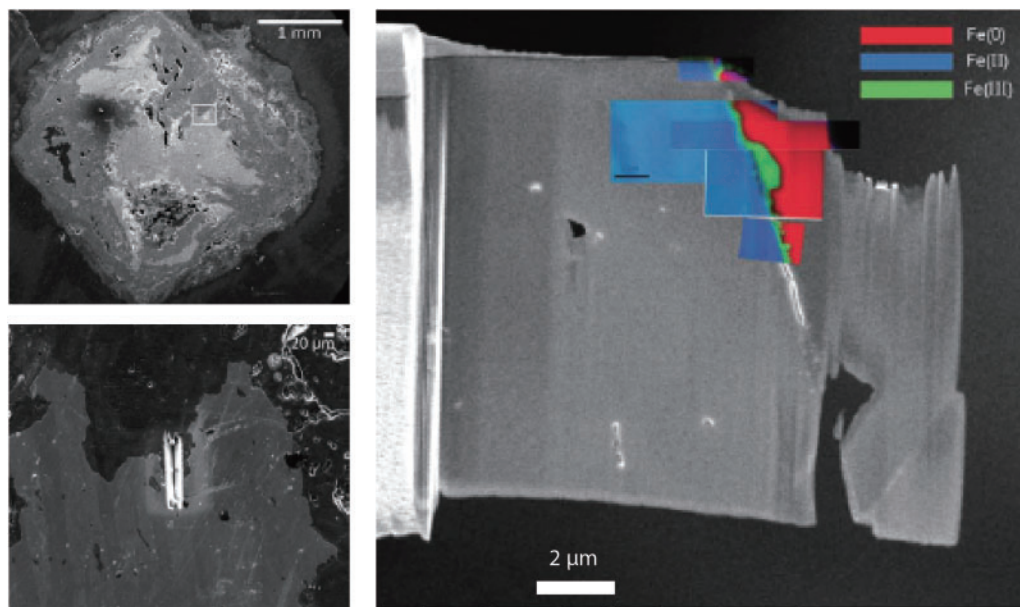
and attributed to an oxidising environment (presence of oxygen, quickly consumed either by corrosion or by bacteria). These results highlight the fact that the 31.8 mm of corrosion predicted for the containers in argillaceous conditions are very conservative.

Phenomenology

Analogues are also used to elucidate the mechanisms of corrosion implied by their alteration with the objective of predicting the deterioration based on phenomenological modelling, which needs to understand the mechanisms and the parameters that control the kinetics. This approach involves a fine description of the corrosion systems from millimetre to nanometre scale, requiring the use of complementary physicochemical characterisation methods (electron microscopy, Raman microspectrometry, X-ray microdiffraction, X-ray microabsorption spectrometry, etc.) as illustrated in Fig. 8.

This multiscale approach is often supplemented by localising the physicochemical processes involved, i.e. transport phenomena in the solids or in porous environments, local reactivity (anodic and cathodic reactions),⁶⁴ conductivity of the phases constituting the corrosion products. It is possible to test assumptions about the mechanisms by testing archaeological systems in the laboratory (electrochemistry, use of isotopic or chemical tracers). Figure 9 gives two illustrations of this type of approach:

- the layers formed on rebars corroded for several hundred years in cementitious binders and then placed for several months in a wet/dry environment doped with ^{18}O exhibit decoupling of the anodic and cathodic reactions due to the presence of conducting phases in the corrosion products (Fig. 9a)⁶⁴
- in a different way, the corrosion products of a nail initially altered for 400 years in anoxic conditions and then immersed in deuterated water (D_2O) reveal the presence of deuterium throughout the thickness and



10 **a** cross-section of nail corroded for 400 years in an anoxic medium and localisation of thin film sample and **b** localisation by scanning transmission X-ray microscopy (STXM) on transmission electronic microscope (TEM) of thin nanometric film (green) situated between metal (red) and thick layer of corrosion products (blue)⁶⁵

an increase in precipitated D containing phases within the first microns near the metal/oxide interface (Fig. 9b), which localises the cathodic reaction in these zones.³⁷

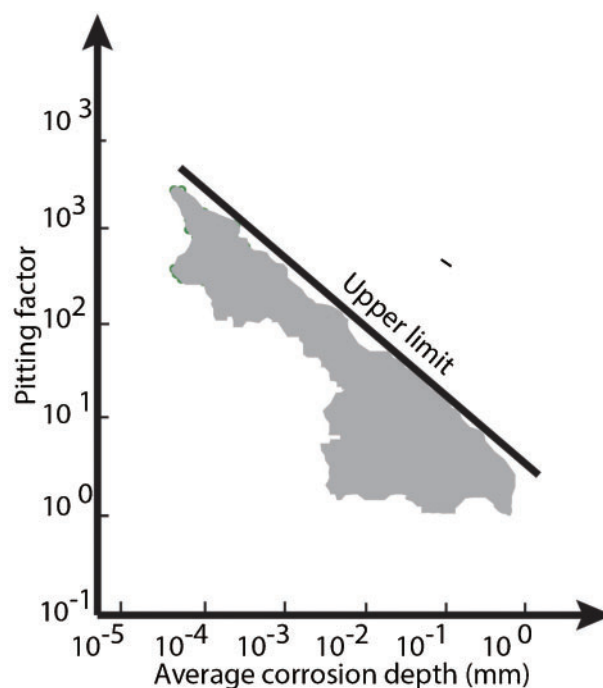
Another important outcome of the multiscale approach was to link macroscopic behaviours and corrosion rates to specific mechanisms at nanometre scale. In particular, despite the presence of corrosion layers several hundred micrometres thick on alloys corroded for several centuries, it has been shown that in anoxic environments a specific layer less than 1 μm thick controlled the kinetics of corrosion by limiting the access of the electrolyte to the metal substrate (Fig. 10).⁶⁵ This layer had also been identified by electrochemical studies during laboratory simulations^{66,67} under similar conditions on archaeological artefacts.

Moreover, observing the systems developed over the long term makes it possible to supply the models with a number of inaccessible parameters. Thus, with regard to the transport of species,^{27,68} the porosity of layers several centuries old can be measured and added to the corrosion models. Similarly, it has been shown that the reactivity of archaeological phases could be extremely different from that of phases synthesised in the laboratory.^{69–72}

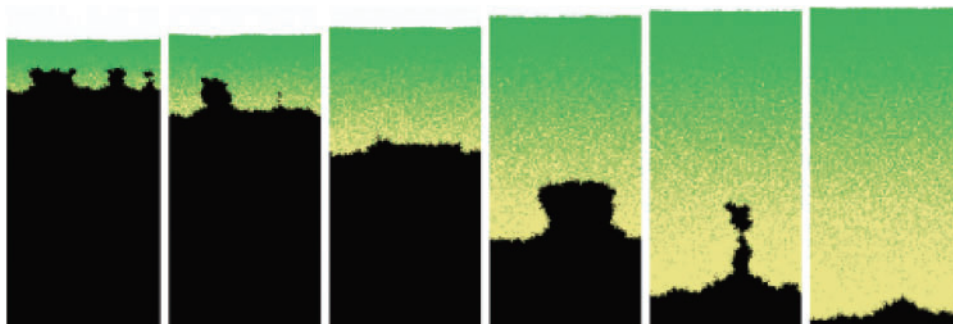
Semiempirical model

Corrosion rates are expressed in terms of metal loss per annum (μm/year), assuming more or less implicitly that the corrosion is uniform. However, while steel corrosion is well generalised, it is seldom uniform, and it is advisable to estimate the depth of localised corrosions (pits) which can develop. The concept of the pitting factor F was introduced for this purpose.⁷³ It is defined as the ratio of the maximum pit depth to the average depth of generalised corrosion: $F(T) = P/X$, where P is the maximum depth of localised corrosion at time T and X is the average loss of metal thickness due to generalised corrosion at time T .

Establishing curves such as the one in Fig. 11 requires samples with relatively large corrosion depths. The points corresponding to the natural environment and the greatest corroded depths are generally found on archaeological analogues. Analogues are therefore essential to this semiempirical model of pitting corrosion. The localised corrosion observed on these archaeological objects does not differ, in term of the pitting factor, from the values obtained with modern steels under more controlled conditions in laboratory tests. This is certainly attributable to the continuity of the same basic mechanisms: anodic and cathodic reactions.



11 Pitting factor versus depth of corrosion (data compiled by Taniguchi *et al.*⁷³)



12 Morphological evolution of interface obtained by cellular automaton modelling: metal (black)/oxide (yellow) medium⁷⁴

Stochastic model

Archaeological analogues clearly show non-linear weathered interfaces (Figs. 7 and 8), sometimes with small metal inclusions in the middle of a layer of corrosion products. This aspect is related to the stochastic character of the anodic and cathodic reactions, which can be distributed heterogeneously in space and time, although both reactions must be equal in terms of electron transfer. Models based on cellular automata, which allow a probability to be assigned to defined transformation rules, are particularly powerful for representing the more or less random distribution of anodic and cathodic reactions at metal/corrosion products/solution interfaces leading to the heterogeneity in the morphological evolution of the corrosion interfaces. For instance, with a simple cellular automata model accounting for two probabilities (corrosion kinetics) following the relative spatial localisation of the corrosion site, the different forms of corrosion morphologies is reproduced, from uniform to localised corrosion (pitting and cracking).⁷⁴ A morphological example of evolution of a metal (black)/oxide (yellow) interface is given in Fig. 12. It illustrates the possibility of finding small islands of uncorroded metal in oxide corrosion products. This is obtained by assigning a probability of anodic reaction that is dependent on the roughness of the metal/oxide interface.

Conclusion

The study of the corrosion of archaeological objects has advanced in recent years. Considerable progress has been made on iron archaeological objects, notably in the following areas:

- The observed corrosion rates generally range from 0.1 to 10 $\mu\text{m}/\text{year}$ depending on the medium, and particularly on the oxygen content and the redox potential.
- The description of the phenomenology of the metal itself, the corrosion products, the transformed medium, and the initial medium.
- The use of isotopic markers (deuterium or oxygen-18) on archaeological objects restored to corrosive conditions, to identify and localise the anodic and/or cathodic mechanisms.
- Modelling and simulation to account for the statistical aspects (modelling by cellular automata) and the kinetics, including localised corrosion phenomena (pitting factor).

This significant progress is only the first step: we can expect a generalisation of the use of analogues to predict

the degradation of other metals (such as the iron–chromium–nickel alloys present in meteorites) and non-metals (such as glass). Modelling and simulation are carried out primarily at mesoscopic scale today, but will be increasingly based on physicochemical and multiscale phenomena, from atomic simulation to the degradation of the object itself.

Acknowledgements

The authors are grateful to H. Mathiesen for providing raw data on the corrosion rates of Nydam Mose artefacts.

References

1. D. Feron, D. Crusset, J.-M. Gras and D. D. Macdonald: 'Prediction of long term corrosion behaviour in nuclear waste systems', 201; 2004, Chatenay-Malabry, ANDRA.
2. W. M. Miller, N. Chapman, I. McKinley, R. Alexander and J. A. T. Smellie: 'Natural analogue studies in the geological disposal of radioactive wastes'; 1994, Amsterdam, Elsevier.
3. W. Miller, R. Alexander, N. Chapman, J. C. McKinley and J. A. T. Smellie: 'Geological disposal of radioactive wastes and natural analogues'; 2000, Oxford, Elsevier.
4. N. R. Smart and R. Adams: 'Natural analogues for expansion due to the anaerobic corrosion of ferrous metals', Technical Report TR-06-44, Svensk Kärnbränslehantering AB, Stockholm, Sweden, 2006.
5. R. C. Ewing and M. J. Jercinovic: *Mater. Res. Soc. Symp. Proc.*, 1987, **84**, 67–83.
6. B. Miller and N. Chapman: *Radwaste Mag.*, Jan. 1995, 32–42.
7. M. Goodway: 'Ancient metallurgy and nuclear waste containment', *Materials Research Society Proceedings*, 1992, **294**. DOI: <http://dx.doi.org/10.1557/PROC-294-605>.
8. B. Rosborg and L. Werme: *J. Nucl. Mater.*, 2008, **379**, (1–3), 142–153.
9. R. C. Ewing: *Nucl. Waste Manage.*, 1979, **1**, 57–68.
10. G. Libourel, A. Verney-Carron, AndreasMorlok, S. Gin, J. Sterpenich, A. Michelin, D. Neff and P. Dillmann: *CR Geosci.*, 2011, **343**, (2–3), 237–245.
11. J. Sterpenich and G. Libourel: *J. Non-Cryst. Solids*, 2006, **352**, 5446–5451.
12. P. Dillmann, D. Watkinson, E. Angelini and A. Adriens: 'Corrosion and conservation of cultural heritage metallic artefacts', 599; 2013, Oxford, Woodhead Publishing.
13. M. L'Héritier, P. Dillmann, A. Timbert and P. Bernardi: 'The role of iron armatures in gothic constructions: reinforcement, consolidation or commissioner's choice', in 'Nuts and bolt of construction history. Culture, technology and society', Vol. 2, (ed. R. Carvais *et al.*); 2012, Paris, Picard, 557–564.
14. R. Bork (ed.): 'De re metallica: the uses of metal in the Middle Ages', Vol. 4; 2005, Burlington, Ashgate.
15. H. Matthiesen, L. R. Hilbert and D. J. Gregory: *Stud. Conserv.*, 2003, **48**, (3), 183–194.
16. B. Soerensen and D. Gregory: 'In situ preservation of artifacts in Nydam Mose', Proc. Int. Conf. on 'Metals conservation', Draguignan-Figanières, France, May 1998, Maney, 94–99.
17. H. Matthiesen, D. Gregory, B. Sørensen, T. Alström and P. Jensen: 'Monitoring methods in mires and meadows: five years of studies at

- Nydam mose, Denmark', Proc. 2nd 'Preserving Archaeological Sites *In Situ* (PARIS2)' Conf., London, UK, September 2001, Museum of London Archaeology Service, 91–97.
18. E. Jorgensen and P. V. Petersen: 'Nydam Bog – new finds and observations', in 'The spoils of victory. The north in the shadow of the Roamn Empire', (ed. L. Jorgensen *et al.*), 258–285; 2003, Copenhagen, National Museum of Denmark.
 19. D. A. Scott and G. Eggert: 'Iron and steel in art: corrosion, colorants, conservation', 232; 2009, Plymouth, Archetype Publications Ltd
 20. A. B. Johnson and B. Francis: 'Durability of metals from Archaeological objects, metal meteorites and native metals', PN 3198, Pacific Northwest Laboratory, Washington, DC, USA, 1980.
 21. A. B. Johnson: 'Lessons in metal durability from the ancient metals', Proc. CEC Natural Analogue Working Group 3rd Meet., Snowbird, UT, USA, June, 1988, Commission of the European Community, 228–231.
 22. H. Coghlan: *Sibrium*, 1956, 3, 129–136.
 23. A. B. Johnson and B. Francis: 'Durability of metals from archaeological objects, metal meteorites, and native metals', Pacific Northwest Laboratory, Washington, DC, USA, 1980.
 24. B. Abdu and R. Gordon: *J. Archaeol. Sci.*, 2004, 31, 979–998.
 25. E. Cogfrey and M. van Nie: *J. Archaeol. Sci.*, 2004, 31, (8), 1117–1125.
 26. M. Saheb, D. Neff, P. Dillmann, H. Matthiesen, E. Foy and L. Bellot-Gurlet: *Mater. Corros.*, 2009, 60, (2), 99–105.
 27. E. Vega: 'Altération des objets ferreux archéologiques sur le site de Glinet (Seine-maritime, France, XVIe siècle). Caractérisation des produits de corrosion et étude des mécanismes', PhD thesis, Université de Technologie de Belfort Montbéliard, Belfort, France, 2004.
 28. D. Neff, P. Dillmann, L. Bellot-Gurlet and G. Beranger: *Corros. Sci.*, 2005, 47, (2), 515–535.
 29. V. Fell and J. Williams: 'Monitoring of archaeological and experimental iron at Fiskerton', in Proc. Conf. Metal 04, (ed. J. Ashton, *et al.*), 17–27; 2004, Canberra, ACT, National Museum of Australia.
 30. H. Matthiesen, E. Salomonsen and B. Sørensen: *J. Archaeol. Sci.*, 2004, 31, 1451–1461.
 31. J. Monnier, D. Neff, S. Réguer, P. Dillmann, L. Bellot-Gurlet, E. Leroy, E. Foy, L. Legrand and I. Guillot: *Corros. Sci.*, 2010, 52, (3), 695–710.
 32. W.-J. Chitty: 'Etude d'analogues archéologiques pour la prévision de la corrosion pluri-séculaire des armatures du béton armé: caractérisation, mécanismes et modélisation', PhD thesis, Université de Technologie de Compiègne, Compiègne, France, 2006.
 33. N. A. Nielsen: 'Corrosion and metal artifacts: a dialogue between conservators and archaeologists', 17–37; 1977, Washington, DC, National Bureau of Standards.
 34. C. Pearson: *Stud. Conserv.*, 1972, 17, 91–110.
 35. N. A. North: *Stud. Conserve.*, 1982, 27, 75–83.
 36. F. Kergourlay: 'Etude des mécanismes de déchloration d'objets archéologiques ferreux corrodés en milieu marin – Cas des traitements en solutions alcalines aérée et désaérée', PhD thesis, Créteil Paris Est, Paris, France, 2012.
 37. M. Saheb: 'Etude des mécanismes de corrosion à très long terme des objets ferreux en milieu anoxique: Apport des analogues archéologiques', PhD thesis, Université Paris Est, Paris, France, 2009.
 38. E. Pons, C. Lemaitre, D. David and D. Crusser: 'Electrochemical study of steel artefacts from WWI: contribution of A. C. impedance spectroscopy and chronoamperometry to describe the behaviour of the corrosion layers', in 'Corrosion of metallic heritage artefacts, investigation, conservation and prediction for long term behaviour', (eds. P. Dillmann *et al.*), 77–91; 2007, London, Woodhead Publishing.
 39. M. Saheb, M. Descostes, D. Neff, H. Matthiesen, A. Michelin and P. Dillmann: *Appl. Geochem.*, 2010, 25, (12), 1937–1948.
 40. D. Gregory and H. Matthiesen: *Conserv. Manage. Archaeol. Sites*, 2012, 14, (1–4), 479–486.
 41. H. Matthiesen, D. Gregory, P. Jensen and B. Sørensen: *J. Wetland Archaeol.*, 2004, 4, 55–74.
 42. H. Matthiesen, L. R. Hilbert, D. Gregory and B. Soerensen: 'Long term corrosion of iron at the waterlogged site Nydam in Denmark: studies of environment, archaeological artefacts, and modern analogues', Proc. 2nd Int. Workshop On 'Prediction of long term corrosion behaviour in nuclear waste systems', Nice, France, September, 2004. European Federation of Corrosion, 114–127.
 43. E. Vega, P. Dillmann, P. Berger and P. Fluzin: 'Species transport in the corrosion products of ferrous archaeological analogues: contribution to the modelling of long-term iron corrosion mechanisms', in 'Corrosion of metallic heritage artefacts: investigation, conservation and prediction for long term behaviour', (ed. P. Dillmann *et al.*), 92–108; 2007, Cambridge, Woodhead Publishing.
 44. C. Remazeilles, A. Dheilly, S. Sable, I. Lanneluc, D. Neff and P. Refait: *Corros. Eng. Sci. Technol.*, 2010, 45, (5), 388–394.
 45. C. Remazeilles, M. Saheb, D. Neff, E. Guilminot, K. Tran, J.-A. Bourdoiseau, R. Sabot, M. Jeannin, H. Matthiesen, P. Dillmann and P. Refait: *J. Raman Spectrosc.*, 2010, 41, (11), 1425–1433.
 46. M. Berranger and P. Fluzin: *Archaeometry*, 2012, 54, (4), 664–684.
 47. G. Pagès, P. Dillmann, P. Fluzin and L. Long: *J. Archaeol. Sci.*, 2011, 38, 1234–1252.
 48. M. Fulford, D. Sim, A. Doig and J. Painter: *J. Archaeol. Sci.*, 2005, 32, (2), 241–250.
 49. J. W. Stewart, J. A. Charles, and E. R. Wallach: *Mater. Sci. Technol.*, 2001, 16, 291–303.
 50. T. Misawa, T. Kyuno, W. Suetaka and S. Shimodai: *Corros. Sci.*, 1971, 11, (1), 35.
 51. R. Balasubramaniam and P. Dillmann: 'Corrosion resistance of the Delhi Iron Pillar – scale characterisation and passive film growth models', Proc. Int. Workshop On 'Prediction of long term corrosion behaviour in Nuclear Wastes System', Cadarache, France, 2002, London, IOM, 261–279.
 52. R. Balasubramaniam: *Curr. Sci.*, 2002, 82, (11), 1357–1365.
 53. R. Balasubramaniam: 'Delhi Iron Pillar – new insights', 168; 2002, New Delhi, Aryan Book International.
 54. R. Balasubramaniam and A. V. R. Kumar: *Corros. Sci.*, 2000, 42, 2085–2101.
 55. R. Balasubramaniam: *Corros. Sci.*, 2000, 42, 2103–2129.
 56. J. C. Hudson: *Nature*, 1953, 172, 499–500.
 57. P. M. S. Vats and M. A. Hony: 'The Gupta temple at Deogarh', 48; 1999, New Delhi, Archaeological Survey of India.
 58. E. Lefebvre: 'Les tirants de fer de la cathédrale Notre-Dame d'Amiens', in 'L'emploi du fer et du plomb dans l'architecture gothique', (ed. A. Timbert), 141–147; 2009, Paris, Picard.
 59. J. Monnier, D. Vantelon, S. Reguer and P. Dillmann: *J. Anal. Atom. Spectrom.*, 2011, 26, 885–891.
 60. M. Yamashita, H. Miyuki, Y. Matsuda, H. Nagano and T. Misawa: *Corros. Sci.*, 1994, 36, (2), 283–299.
 61. H. Yoshikawa, E. Gunji and M. Tokuda: *J. Nucl. Mater.*, 2008, 379, 112–117.
 62. L. Bertrand, P. Dillmann, M. G. Dowsett and A. Adriens: 'Ancient and historical systems', in 'GENNESYS White Paper: a new European partnership between nanomaterials science and nanotechnology and synchrotron radiation and neutron facilities', (ed. H. Dosch *et al.*), 241–246; 2009, Stuttgart, Max Planck Gesellschaft.
 63. D. Neff, M. Saheb, J. Monnier, S. Perrin, M. Descostes, V. L'Hostis, D. Crusset, A. Millard and P. Dillmann: *J. Nucl. Mater.*, 2010, 402, (2–3), 196–205.
 64. E. Burger, J. Monnier, P. Berger, D. Neff, V. L'Hostis, S. Perrin and P. Dillmann: *J. Mater. Res.*, 2011, 26, (24), 3107–3115.
 65. A. Michelin, E. Drouet, E. Foy, J. J. Dynes, D. Neff and P. Dillmann: *J. Anal. Atom. Spectrom.*, 2013, 28, (1), 59–66.
 66. C. Bataillon, F. Bouchon, C. Chainais-Hillairet, C. Desgranges, E. Hoarau, F. Martin, S. Perrin, M. Tupin and J. Talandier: *Electrochim. Acta*, 2010, 55, (15), 4451–4467.
 67. C. Bataillon, C. Musy and M. Roy, *J. Phys IV France*, 2001, 11, 267–274.
 68. W.-J. Chitty, P. Dillmann, V. L'Hostis and A. Millard: *Corros. Sci.*, 2008, 50, (11), 3047–3065.
 69. H. Antony, S. Peulon, L. Legrand and A. Chaussé: *Electrochim. Acta*, 2004, 50, 1015–1021.
 70. H. Antony, S. Perrin, P. Dillmann, L. Legrand and A. Chaussé: *Electrochim. Acta*, 2007, 52, (27), 7754–7759.
 71. V. Lair, H. Antony, L. Legrand and A. Chausse: *Corros. Sci.*, 2006, 48, 2050–2063.
 72. J. Monnier, P. Dillmann, L. Legrand and I. Guillot: *Corros. Eng. Sci. Technol.*, 2010, 45, (5), 375–380.
 73. N. Taniguchi, M. Kawasaki, S. Kawakami and M. Kubota: 'Corrosion behaviour of carbon steel in contact with bentonite under anaerobic condition', Proc. 2nd Int. Workshop On 'Prediction of long term corrosion behaviour in nuclear waste systems', Nice, France, September, 2004. European Federation of Corrosion and ANDRA: Nice.
 74. D. di Caprio, C. Vautrin-UI, J. Stafiej, J. Saunier, A. Chausse, D. Feron and J. P. Badiali: *Corros. Sci.*, 2011, 53, (1), 418–425.