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Corrosion issues in nuclear waste disposal

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ABSTRACT

This paper summarized some corrosion issues specific to nuclear waste disposal and illustrates them by the French geological clay concept for the reliable prediction of container degradation rate and engineering barrier integrity over extended periods, up to several thousands years. Among the items, the following are included:

- The importance of the underground repository conditions.
- The necessity of developing comprehensive semi-empirical models and also predictive models that must be based on the mechanisms of corrosion phenomena.
- The use of archaeological artefacts to demonstrate the feasibility of long term storage and to provide a database for testing and validating the models.

1. Introduction

The reliable prediction of container degradation rate over extended periods, up to several thousands or more years for geological disposal, represents a great scientific and technical challenge to face the technical community. The generally accepted strategy for dealing with long-lived high level nuclear waste (HLNW) is deep underground burial in stable geological formations. The purpose of the geological repository is to protect man and environment from the possible impact of radioactive waste by interposing various barriers capable of confining the radioactivity for several hundreds of thousands of years (packages containing the waste, repository installations, and geological medium). The multi-barrier concept, which involves the use of several natural and/or engineered barriers to retard and/or to prevent the transport of radio-nuclides into the biosphere, is applied in all geological repositories over the world.

The main corrosion issues have been already discussed, compared, and explored with the corrosion community which has to face new challenges for corrosion prediction over millenniums on a scientific and technical basis. The scientific and experimental approaches have been compared between various organisations worldwide for predicting long term corrosion phenomena, including corrosion strategies for geological disposal, not only during workshops [1,2] and congresses, but also some specific projects have been devoted to these exchanges, like the COBECOMA in Europe [3] which proceeded to an extensive reviewing of the literature on the corrosion behaviour of a range of potential materials for radioactive waste disposal container. Among the comparison items, the following should be emphasized: very different underground host rock formations (together with buffer materials) are being considered as potential disposal environments within nuclear countries. The compositions of the various potential host rock formations (including unsaturated systems) vary greatly and the composition significantly influences the selection of the candidate container materials. In short, different environments and different disposal strategies lead to the choice of different materials with two main strategies or concepts [3]: the *corrosion-allowance alloys* and the *corrosion-resistant alloys*. The *corrosion-allowance* materials corrode at a significant, but low and predictable general corrosion rate. The risk of localised corrosion of these materials is low under aerobic conditions and no localised corrosion is expected under anaerobic conditions. The *corrosion-resistant* alloys exhibit a very high corrosion resistance in the disposal environment. These materials are passive and their uniform corrosion rate is very low. Therefore, they can be used with a relatively small thickness. However, for these materials, the risk of localised corrosion, such as pitting and crevice corrosion has to be taken into account because the passive film may break down locally.

The French national radioactive waste management agency, Andra, was conferred the mission of assessing the feasibility of deep geological disposal of high level long-lived radioactive waste by the 30 December 1991 Act. The 'Dossier 2005' is a synthesis of work performed for the study of a geological repository in deep granite and clay formations. This paper will focus on some

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corrosion issues of the French concept for disposal in clay which has been published in the 'Andra – Dossier 2005 Argile' [4–8]. It is important to underline that the purpose of the 'Dossier 2005' is to demonstrate the existence of technical solutions which are not definitively frozen. The concepts may evolve along the stages to the opening of a repository. So, the proposed technological solutions do not pretend to be optimised. High level nuclear waste (HLNW) results from spent fuel reprocessing and is confined in a glass matrix and poured into stainless steel containers. The studies have encompassed the possibility of non-reprocessed spent fuel, although spent fuel is not considered as waste (in France, Japan, China, Russia, UK, etc.) and is planned for reprocessing to extract uranium and plutonium which are reused in new fuels elements. The overpack (or sur-container) is not only part of the high integrity barriers but is also a major component of the reversibility which is required for the French geological repository. Reversibility means the possibility to retrieve emplaced packages as well as to intervene and modify the disposal process and design.

Long-term safety and reversibility are the guiding principles which lead to the basic layout of geological repository in an argillaceous formation as shown in Fig. 1. The repository is located on a single level in the middle of the Callovo-Oxfordian and organised into distinct zones according to the package types and subdivided into modulus which is composed of several cells, an example of which is given for vitrified nuclear waste elements (Fig. 2). Vitrified waste cells are dead-end horizontal tunnels, 0.7 m in diameter and 40 m long. They have a metal sleeve as ground support which enables packages to be emplaced in and, if necessary, retrieved out. They contain a single row of 6–20 disposal packages, depending on their thermal output. Packages with a moderate thermal output are lined up without spacer; otherwise, they are separated by spacing buffers (dummy package without waste, but providing spacing in between packages to decrease heat output). When it is decided to close the cell, it is sealed by a swelling clay plug.

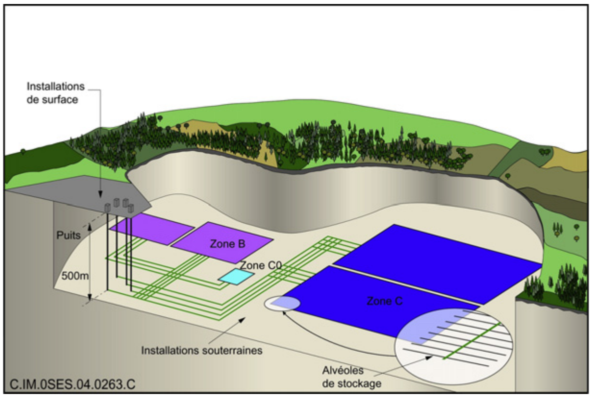

Fig. 1. Illustration of a clay geological concept [5].

Fig. 3 illustrates the non-alloyed steel overpacks designed for vitrified nuclear waste. The main aim is to prevent any water from coming into contact with the glass during the reversibility phase. Carbon steel has been adopted as the first choice material for the overpack. It presents two advantages that limit the risk of failure damaging the container tightness and durability. (i) This type of material presents a robust behaviour, known since several millenniums and its corrosion processes are quite well understood. It is less prone to localised corrosion than passive materials which also are quite new materials (e.g., stainless steels, nickel based alloys). (ii) Its use (metallurgy, weldability, control) is based on industrially proven technologies. In conclusion, non-alloy steel was preferred at this stage, because of the controlled, predictable nature of its corrosion process and because it is easy to weld. The solution selected for its simplicity and robustness in the light of current knowledge and techniques, is that of an individual overpack made of 55 mm thick non-alloy steel. The overpack consists of a body and a lid made of the same material. After inserting the primary packing into the body, the lid is welded onto it using the electron beam method. Its lifetime is estimated at several thousand years which is much longer than the thermal phase (around one thousand years maximum).

Nevertheless, the knowledge on the corrosion of steels over periods of several thousand years has to be and has been developed. As pointed out in the Introduction to the first Workshop on 'Prediction of long term corrosion behaviour in nuclear waste systems' [9], the life-times of industrial materials are mainly in the range of a few seconds or minutes (rocket engines, for instance) to several tens of years for nuclear power plants, and up to one hundred years for civil engineering infrastructural systems (e.g., bridges and roads). The robust and reliable prediction of corrosion damage is an absolute necessity in any repository concept evaluation. This paper illustrates the French approach followed to demonstrate the feasibility of predicting corrosion over long periods of time. This approach may be divided into three main parts:

- Data acquisition and development of semi-empirical models are first needed in order to perform estimations of service life-times and to demonstrate the feasibility.
- Predictive models should be based on the mechanisms of corrosion phenomena in order to be robust and reliable.

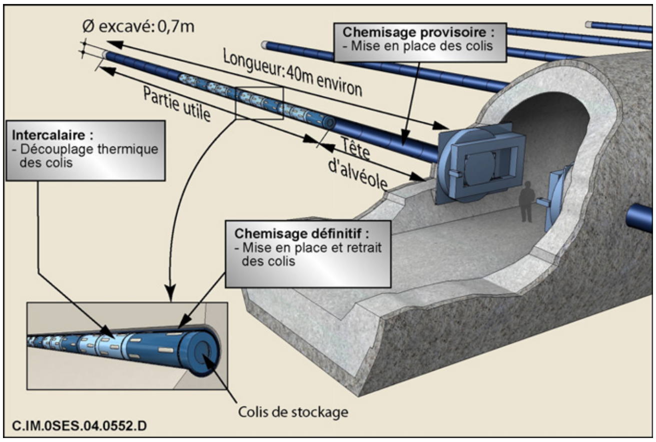

Fig. 2. Schematic view of a vitrified cell [5].

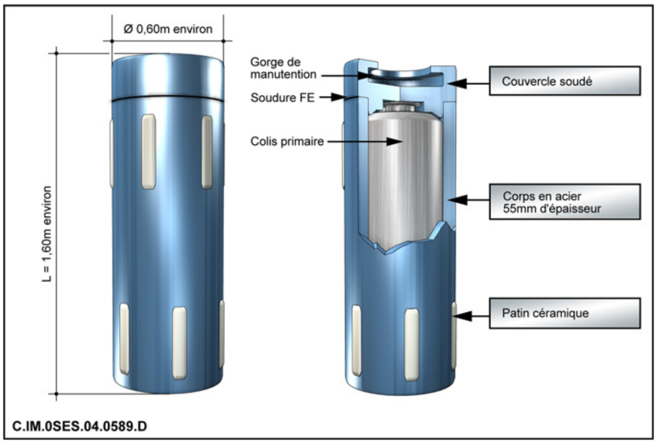

Fig. 3. Design view of carbon steel overpacks for vitrified nuclear waste [4].

- Archaeological artefacts are used to demonstrate also the feasibility of long term storage and to provide a database for testing and validating the models.

Of course, this approach is iterative and allows progressively orienting the choices toward solutions offering the greatest robustness with respect to the evolution of the knowledge. For the development of mechanistically based models and the validation of these models, laboratory tests are no longer sufficient, because the prediction regime extends well beyond the available laboratory times. Archaeological analogues provide useful information, and hence a strong need exists for detailed examination of objects that have been exposed to corrosive environments for very long times. However, the differences between ancient and modern materials, and also the usually poor knowledge of the initial conditions and the evolution of the environment have to be taken into account.

Basic diagram of a repository layout during operation: disposal cells are excavated underground in the host formation and are grouped in modules. These modules are integrated in a drift network linked to surface by access shafts. Waste package management such as reception and conditioning is performed in surface installations.

2. Semi-empirical modelling

The Callovo-Oxfordian geological formation has very low permeability, which greatly reduces water flow. When the repository returns to the saturated state and hydrostatic equilibrium with its surroundings, the water flows are determined by the hydraulic loads imposed by the aquifers surrounding the host layer of the repository. It is possible to calculate, for example, that a flow of 10^{-2} L m^{-2} year^{-1} limits the corrosion rate of iron, assumed to be uniform, to 3 μm year^{-1}, i.e. 3 mm of metal corroded in 1000 years, as shown on Fig. 4. For flows below 10^{-3}–10^{-2} L m^{-2} year^{-1}, the corrosion rate of iron appears to be limited by the water flow. Beyond 0.1–1 L m^{-2} year^{-1}, the water flow no longer limits the corrosion rate: this is controlled by the kinetics of the interface reactions, regardless of the water flow. The permeability values could be important not only for the diffusion of radio-nuclides, but also for the uniform corrosion assessments. It could be emphasis also that during the resaturation period, the water flow will be probably the limiting parameter of the overpack corrosion rate.

Alternatively, mass transfers at the oxide/solution interface are quite slow for the dissolved iron to transform into oxide on the surface of the metal. The thickness of the oxide layer increases and the corrosion slows down over time: the progression of the corrosion tends to become almost zero and this state can last indefinitely if the environment is stable. Several types of corrosion kinetics have been suggested to account for the experimental results, for example parabolic-type kinetics. In principle, this scheme describes the conditions expected in a repository (confined medium, pronounced relationship between the surface of metal and the volume of solution). Average, constant rates overestimate the true rate of long-term corrosion if the material tends towards a protective oxide layer and if the duration of the test is not long enough. A more realistic and less conservative approach consists of measuring a stabilised corrosion rate obtained for long-term exposure. As shown on Fig. 5, the kinetics determined by the UK AEA, JNC, SCK-CEN, NAGRA and CEA in different clays and with various water chemistries but in fairly reducing conditions at 80 or 85 °C, are below 5 μm year^{-1} after 2 or 4 years of exposure. This type of results underline also that the corrosion rates of non-alloyed steels are very slightly sensitive to water chemistry and require less precision concerning the chemical environmental conditions (in particular, they are compatible with uncertainties concerning the composition of the Callovo-Oxfordian interstitial water).

Compilation of the results obtained during these types of experiments lead to semi-empirical models that are useful for design purposes and initial estimates of life time. Using published data and data generated by CEA and EDF in representative repository conditions, Arrhenius diagram (Fig. 6) has been drawn where corrosion rates of buried iron archaeological objects are also included (Section 4). Based on these data, the following laws have been proposed to represent the rates of generalised corrosion of low or non-alloy steels as function of the temperature in a repository with or without oxygen:

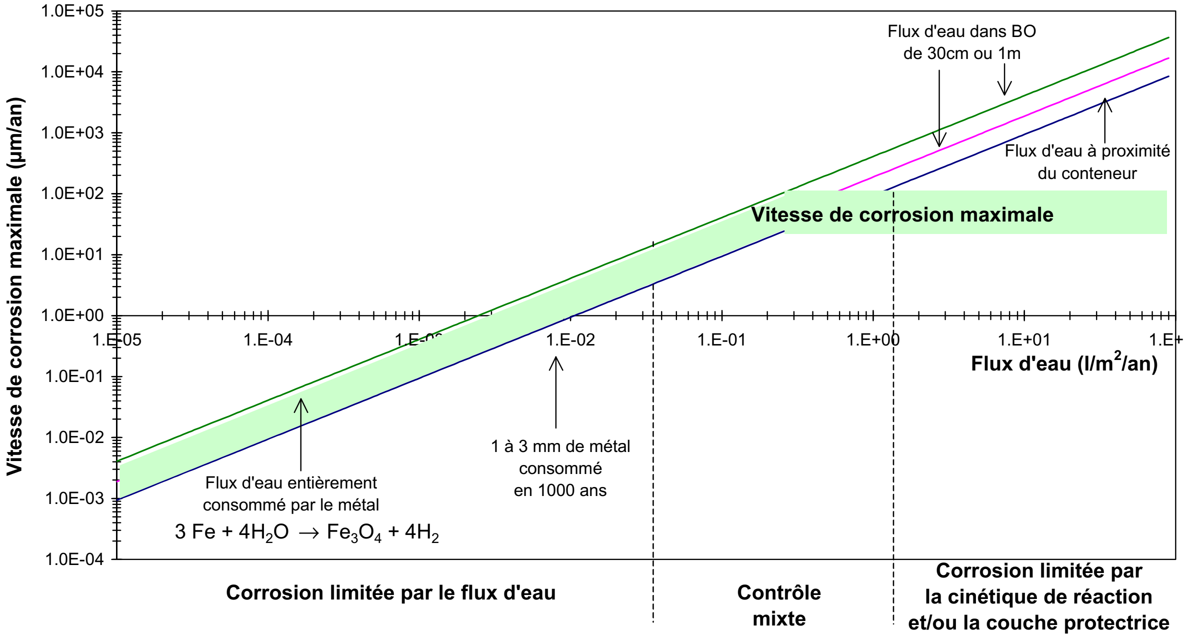

Fig. 4. Influence of the water flow on the corrosion rates with the expected kinetic control domains [10].

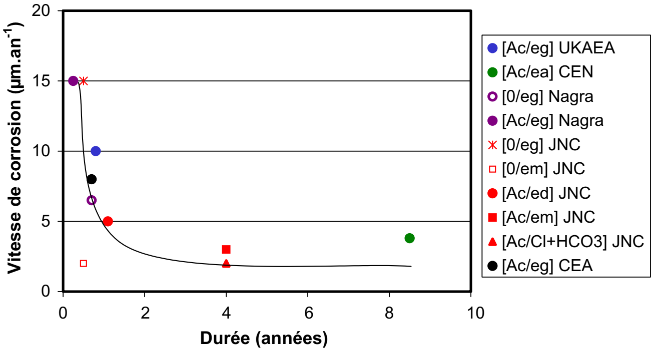

Fig. 5. Evolution of average generalised corrosion rate of carbon steels as a function of time in fairly reducing conditions at 80 or 85 °C [11].

- during the aerated phase:
  $V_{\mathrm{corr}}\ (\mathrm{mm\ year}^{-1}) = 1.042 \exp(-1340/T)$,
- during the de-aerated phase:
  - for short periods:
    $V_{\mathrm{corr}}\ (\mathrm{mm\ year}^{-1}) = 0.364 \exp(-1300/T)$,
  - for long periods (several years):
    $V_{\mathrm{corr}}\ (\mathrm{mm\ year}^{-1}) = 0.162 \exp(-1300/T)$.

These relationships correspond to apparent activation energy of around 11 kJ mol^{-1}.

This approach has been taken not only for general corrosion but also for pitting corrosion. Localised corrosion of non-alloy steels is hardly likely to be initiated in a reducing medium. The same does not apply to oxidising conditions where pitting is possible. It seems likely, therefore, that conditions could be met during which pitting initiation is possible at some moments in the life of a repository, mainly at the beginning if the overpack is exposed both to oxidising conditions (oxygen) and liquid water, so just after the resaturation period if some oxygen is still available for instance.

It is what has been observed on non-alloy steel coupons, exposed for eight months at 80 °C in compacted and saturated clay, which underwent localised degradation similar to that presented in Fig. 7. The maximum pitting depth is in the order of 50 µm, whereas the generalised corrosion is estimated at approximately 5 µm. Several interpretations have been suggested to explain this pitting, including inclusions in the material, heterogeneity in the compaction of the clay, preferential water flow, the role of oxidising species, bacterial activity, etc.

So low alloy steels are not completely immune to pitting under oxidising conditions mainly. For this reason, detailed analyses have been performed in Europe and Japan on a large number of carbon steel or cast iron objects that have been in contact with soils and/or water for extended periods of time. These analyses include laboratory investigations and observations on historical specimens. It was shown that the evolution of both pit depth and mean corrosion depth with time could be fitted by decreasing power functions and that the pit depth decreased more rapidly than the mean corrosion depth. Accordingly, localised corrosion becomes, with time, less and less significant, compared with uniform corrosion. An empirical envelope law was derived, linking the pitting factor P (ratio of the maximal pit depth to the mean corrosion depth) to the mean corrosion depth, X, by a decreasing power law: as shown in Fig. 8, where all of the available results lie systematically below the envelope curve. Such behaviour yields a means for predicting the risk of pitting corrosion semi-empirically.

3. Mechanistically based modelling

Different approaches have been used to predict and model the corrosion of a steel container in a repository and serve to fix its sizing criteria. As they complement each other they must be incorporated into a global approach to make the demonstration credible and reliable. As partly described already, there are three distinct types of approach:

- an approach taking into account the inventory and availability of the different oxidising species in the near-field of the repository: the corrosion is controlled by a material balance (Fig. 4);

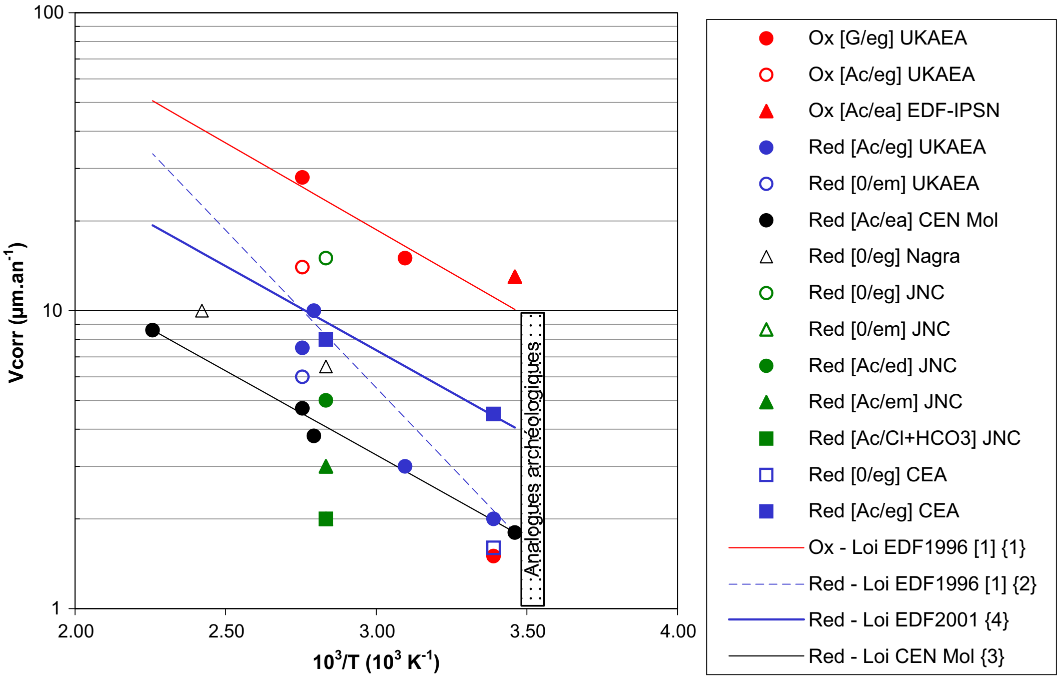

Fig. 6. Influence of temperature on the generalised corrosion rate of carbon steels in a repository situation [11].

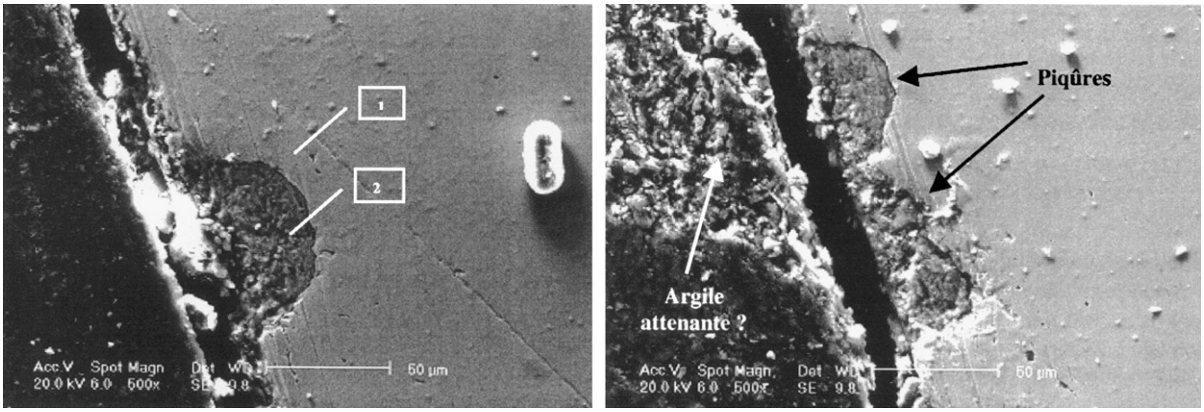

Fig. 7. Pitting observed in a non-alloy steel exposed for eight months at 80 °C in compacted and saturated clay (section view).

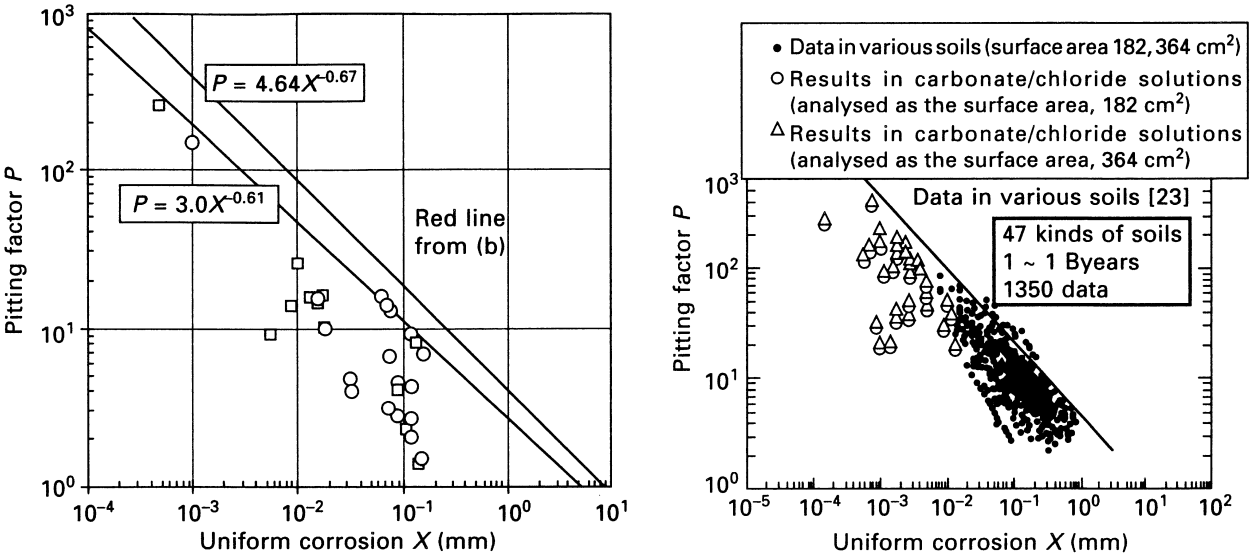

Fig. 8. Evolution of the pitting factor as a function of the average corrosion depth. Results obtained for different carbon steels and cast iron in contact with various soils or waters [12].

- an 'overall' approach relying on feedback and based on semi-empirical laws (Figs. 6–8);
- a more theoretical, mechanistically based approach based on a phenomenological description of corrosion and bringing into play different interface reactions, the transport of species in protecting layers, etc.

The semi-empirical laws based on experimental data can be used to assess material lifetime. Nevertheless, we cannot be sure that the mechanisms of corrosion will remain the same as conditions within storage or the repository evolve. To increase the robustness and the reliability of the corrosion behaviour in repository conditions, the evidence clearly stipulates that mechanistically based modelling of corrosion process is needed.

On the other hand, determinism does not mean that the behaviour of every particle in the system has to be predicted, since systems may be described in terms of average properties (density, temperature, etc.). One of the greatest challenges in devising a deterministic model is to decide what phenomena or processes should be included in describing the global system.

As noted above, a deterministic model is simply the model author's current perception of reality and there is no such thing as 'the correct model', notwithstanding the occasional claims to the contrary. Several modelling developments have been exposed based on the point defect model (PDM), which considers a solid oxide between the metal and the environment, through which chemical species and vacancies must diffuse to react at the internal and external interfaces. The PDM has been applied or describing both the evolution of oxide films on carbon steels [10] in clay environments, as shown in Fig. 9, and for the growth and breakdown of passive films on high alloyed nickel alloy in saturated brine [7,11]. In the PDM, in order to simplify the resolution, several hypotheses are made like the hypothesis that the difference in potential at the external interface varies linearly with the difference in total potential through the oxide.

In order to go deeper in the modelling of the species movements through the solid oxide, as represented in the Fig. 10, developments are made to use the Poisson equations for modelling the transport of species and of electrons in an oxide layer. In the framework of these and other hypotheses, it is possible to calculate impedance diagrams, in other words the response in metallic electrode current subjected to sinusoidal stress in potential. The calculated diagrams provide an interesting method of comparing the model with experience, as the experimental diagrams can be produced by electrochemical impedance spectroscopy. The validation of this type of model necessitates the acquisition of overall data: this consists of comparing the modelling predictions with the test results to assess the influence exerted by the major categories of

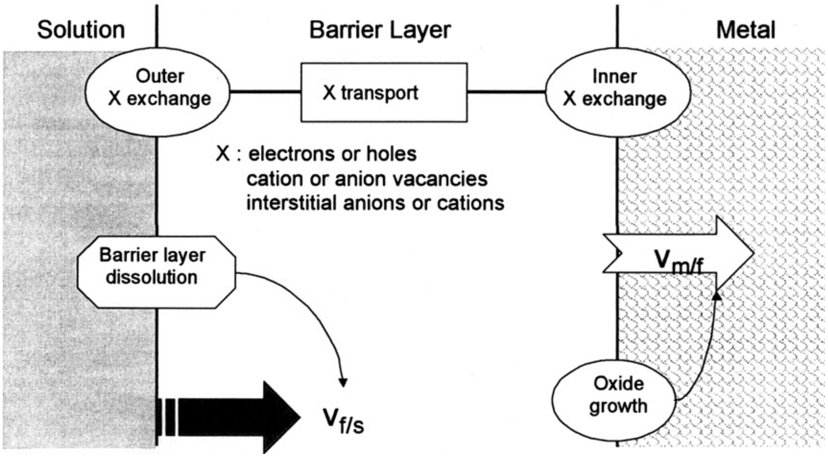

Fig. 9. General description of the point defect metal for carbon steel in clay environment [13].

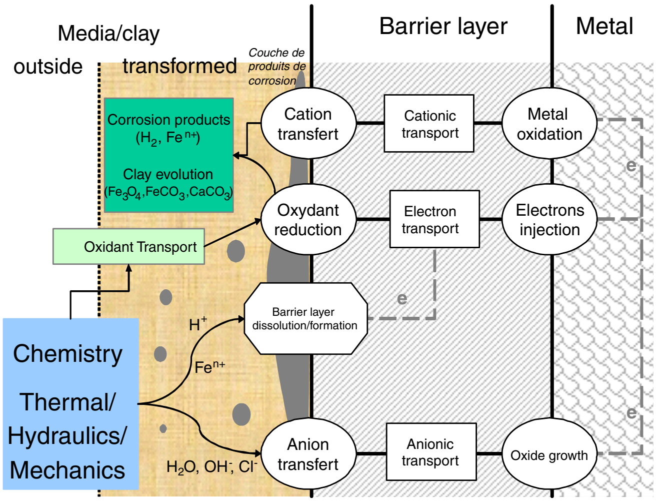

Fig. 10. General description of the corrosion phenomena of carbon steel in clay environment [14].

physico-chemical parameters (temperature, pH, redox potential, etc.). It also necessitates the acquisition of specific data: quantitative kinetic and/or thermodynamic data for numerical calculations and therefore for comparing modelling predictions with the results of experience.

All deterministic models should be continually validated. However, it is necessary to insure that the experiments that are designed to test a model are compatible with regards to the underlying assumptions and postulates. A classical example is that electrochemical polarisation data, which are commonly obtained potentiodynamically, are not always measured at sufficiently low scan rate that the system can be considered to be in quasi-steady state. These data are then used to evaluate models that assume steady state conditions.

The development of models to predict, in a robust and convincing way, the life-times of the engineering barriers and the evolution of corrosion products (iron species and hydrogen) is far from having been achieved. A better understanding of the corrosion mechanisms and processes is necessary and has to be included in deterministic models. Rather than fostering competition between models and modelling approaches (e.g., determinism versus empiricism), it would be highly advantageous to the field as a whole if a complementary approach was taken in which empirical and deterministic methods were co-jointly employed, but that the limitations of each with regard to the ultimate prediction of damage were recognized.

4. Archaeological analogues

Laboratory corrosion tests can only take place over very short periods in the time scale of a repository (a few years at most). The study of analogous archaeological items gives access to far longer periods and may serve to validate average corrosion rates and the understanding of the corrosion mechanisms. Apart from feedback on the conservation of buried industrial objects, which is quite accurate but only covers a few decades, the scientific community is becoming more and more interested in archaeological items (particularly from the Roman period) and ferrous meteorites. Although most of these objects have been conserved in conditions which are hardly representative of a deep disposal (i.e. in fairly aerated media with very variable chemistry over time), their behaviour over a long period can form a basis for predicting the durability of a repository container. Archaeological analogues show that definitively, iron or copper materials may last over several thousands years when environmental conditions are favourable.

An overall estimation of the corrosion rate of archaeological objects was made some years ago in US where listed 44 iron-based samples buried in varied and frequently ill-known conditions, and updated more recently. Despite the diversity in origin and environment, the majority of the objects corroded at a rate of between 0.1 and 10 mm per thousand years ($0.1–10\ \mu m\ year^{-1}$), Fig. 11. It is important to precise that these values are mean corrosion rates over large periods of time while it is probable that the main degradation occurred at the beginning of the exposure [16]. The huge number of objects confirms the statistical value of this estimation which to a certain extent compensates for the uncertainties surrounding their initial state. The highest corrosion rates correspond to oxidising environments (presence of air or oxygen in the water or the soil) whose aggressivity has sometimes been increased by the presence of chlorides (cannonballs lying in sea water for example). Dry media and reducing media (non-aerated water or soil) and the presence of corrosion products form a protective gangue corresponding to the lowest rates of generalised corrosion.

However, some prudence is called for:

- many old metallic materials either buried or exposed to air have corroded away and this may therefore introduce a non-conservative bias in the estimated corrosion rate;

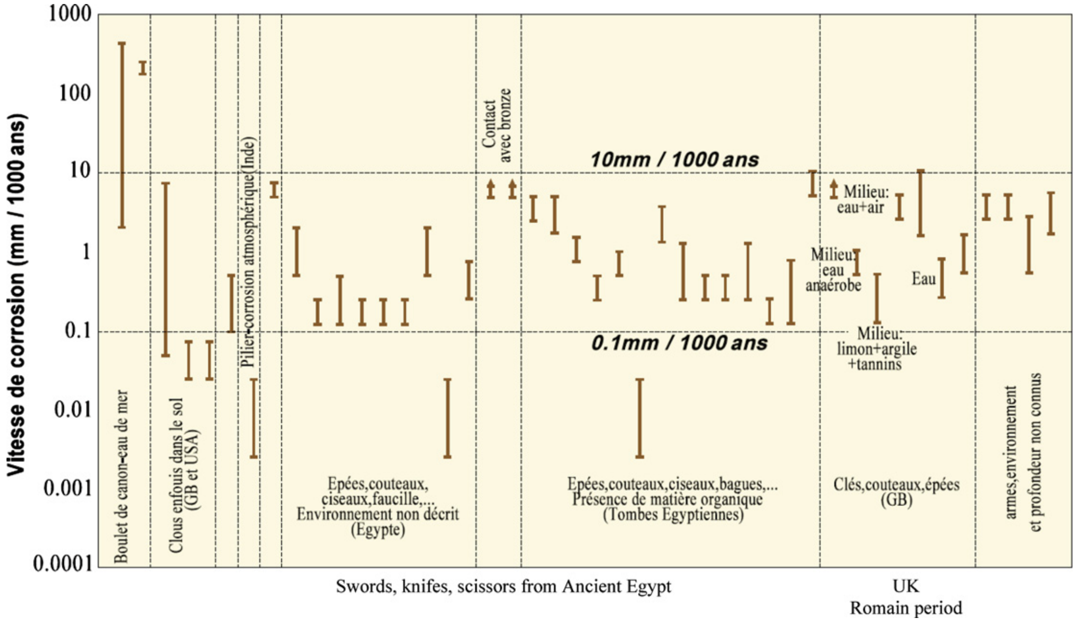

Fig. 11. Corrosion rates of buried archaeological iron objects [15,16].

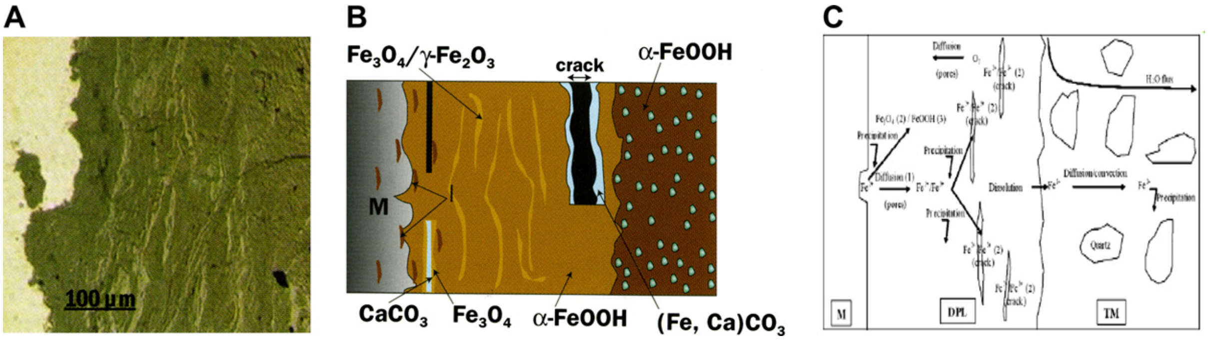

Fig. 12. Marble-like patterns observed on an iron historical object (Montbaron, 12th–13th century AC) [17]. (A) Overview of the corrosion layer. (B) Synthetic sketch of the morphology and composition of corrosion products (M = metal). (C) Corrosion mechanisms of iron archaeological objects in aerated soils at pH 8 (DPL = dense corrosion product layer–TM = transformed media).

- candidate HLNW canister materials are quite different from ancient materials; this is obvious for stainless steels and nickel and titanium alloys that have been produced only in recent times and have no counterparts in archaeology.

As stated previously, often environmental conditions, in which the artefacts were exposed, differ substantially from underground disposal or interim storage environments.

Detailed investigations are needed on artefacts with the purpose of estimating not only the corrosion rate, but also the composition and shape of the corrosion product layers, structure and composition of the ancient substrates, and environmental factors, when possible. This type of information should provide useful documentation for the mechanistic modelling of the long term corrosion behaviour, as shown in Fig. 12 for aerated soils. However, because the archaeological and repository environments are generally dissimilar, the results must be used with great caution and only general ‘fingerprints’ are liable to be relevant. The main difficulty is to screen efficiently the numerous interconnected clues, in order to detect what is liable to be sufficiently general to be applicable. Combinations of this approach with theoretical, especially thermodynamic, calculations, and also with the results of laboratory experiments, will probably help in this delicate, but essential, task.

5. Conclusions

This paper illustrates the approach followed and developed in the ‘Andra Dossier 2005’ to predicting corrosion over long periods of time. The long term corrosion behaviour in clay nuclear waste disposal is based on:

- National experimental studies, data of which are compared to those obtained by other international laboratories, and the developments of comprehensive semi-empirical models in order to perform estimations of service life-times and to demonstrate the feasibility.
- Predictive models should be based on the mechanisms of corrosion phenomena in order to be robust and reliable and are under development. Mechanistically based models lead also to an improved understanding of damage evolution and of corrosion product evolution (iron species and hydrogen evolutions).

- Archaeological artefacts are used to demonstrate the feasibility of long term storage and to provide a database for testing and validating the models. Investigation of artefacts appears to be a promising approach for validating deterministic models, provided that the limitations of archaeological data are understood and recognized.

Of course, this paper presents only few corrosion aspects which are developed in the 'Andra Dossier 2005'. Moreover, this approach is iterative and allows progressively orienting the choices toward solutions offering the greatest robustness with respect to the evolution of the knowledge. During these iterations, some processes which has been considered as minor risks, has to be confirmed as not important during the repository lifetime:

- *Corrosion phenomena*: Microbial corrosion, stress corrosion cracking and hydrogen embrittlement.
- *Corrosion prediction strategies*: Evolution of the near-field environment (for instance hydrogen evolution coming from corrosion), corrosion evolutionary path, coupling between the near-field and far-field environments, and long term materials ageing.

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