

DU COMBUSTIBLE NUCLÉAIRE AUX DÉCHETS :
RECHERCHES ACTUELLES

FROM NUCLEAR FUELS TO WASTE: CURRENT RESEARCH

**Life prediction for HLW containers – issues related to
long-term extrapolation of corrosion resistance**

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Abstract

Traditionally, the corrosion behaviour of container materials can be predicted by extrapolation from relatively short-term experiments. Approaches to life prediction are described for two kinds of materials: carbon steel (corrosion allowance material) which must resist general corrosion, and passive materials (corrosion-resistant materials) which may suffer localized corrosion phenomena (pitting and crevice corrosion). The current theoretical and empirical basis for extrapolating the behavior of these materials to long periods emphasizes the significant gaps in understanding. To improve the credibility of life prediction, and to prove the robustness of geological disposal systems, predictive models based on mechanistic understanding are needed. This work is probably more difficult for the corrosion-resistant materials than for corrosion-allowance materials. *To cite this article: J.-M. Gras, C. R. Physique 3 (2002) 891–902.*

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high-level waste / container / carbon steel / passive materials / general corrosion / pitting / crevice corrosion

**La corrosion des matériaux de conteneurs pour déchets HAVL –
crédibilité scientifique de la prévision à long terme**

Résumé

La résistance à la corrosion des matériaux de conteneur en situation de stockage est généralement prédite à partir de résultats d'expériences de durée limitée, courte à l'échelle des temps d'un stockage. La situation est illustrée pour deux classes de matériaux aux comportements bien typés et assez différents : les aciers non ou faiblement alliés, qui subiront une corrosion généralisée, et les matériaux passivables (aciers inoxydables ou alliages Ni–Cr–Mo), qui sont susceptibles de subir une corrosion par piqûres ou une corrosion cavernueuse. Pour améliorer la crédibilité scientifique de la prévision à long terme et accroître la robustesse de la démonstration, il est nécessaire d'approfondir notre compréhension des mécanismes de la corrosion du conteneur couplée avec son champ proche. La tâche est vraisemblablement plus difficile pour les matériaux passivables que pour les matériaux dits consommables. *Pour citer cet article : J.-M. Gras, C. R. Physique 3 (2002) 891–902.*

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conteneur / acier au carbone / matériaux passivables / corrosion généralisée / corrosion par piqûres / corrosion en crevasse

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1. Introduction

Within the concept for geological disposal of high-level radioactive waste (HLW), the container has an important role to fulfil. As part of the multibarrier system the container is a high integrity barrier: it needs to have a sufficiently long lifetime: at least 500 years in the Andra's concept for vitrified HLW and thousands of years for spent nuclear fuel. So the corrosion resistance of container materials in underground repositories is an important issue for the safe disposal of HLW.

The container lifetime, i.e. its durability as a tight barrier, is controlled by its corrosion resistance in repository, insofar as other modes of container failure can a priori be avoided by engineering design, appropriate fabrication and careful inspection. The corrosion modes of metallic materials are well identified and the corrosion mechanisms rather well understood. However the industrial stakes and needs concerning HLW disposal present new questions in the field of materials science. It especially points out its capability to predict the long term integrity of the container material, and the proof of the robustness and tolerance of the system.

These stakes will be illustrated by considering two types of metallic materials with specific and different behaviors, which correspond to the solutions actually investigated by Andra: carbon steel or low alloy steel, passivable materials (stainless steels, nickel-based alloys).

2. Candidate materials for nuclear waste containers

With regard to their corrosion resistance, container materials generally belong to one of two main categories:

- corrosion-allowance (or *consumable*) materials, for which the lifetime is attained by providing appropriate wall thickness [1–7]: carbon steels, low alloy steels, cast irons, and copper (in oxidizing environments);
- corrosion-resistant (or *non-consumable*) materials, among which it is possible to distinguish:
 - the thermodynamically stable materials: copper, in reducing environments and free of complexing agents (argument justifying the long life expectancy of copper containers) [8,9];
 - the passive materials (thermodynamically unstable but kinetically stable): austenitic stainless steels, Ni–Cr–Mo alloys [10–13] and titanium alloys [14,15]. In water, these materials form a protective or passive film which makes their general corrosion rate extremely low over a long period. In return, they may be susceptible to localized corrosion processes.

Table 1. Main life limiting factors of container materials

Materials	Countries	Possible modes of attack
Carbon steels, Low alloy steels, Cast irons	France Germany Japan, Spain Switzerland, UK	General corrosion Pitting and/or crevice corrosion Stress corrosion cracking Microbial induced corrosion
Copper	Canada Finland Sweden	General corrosion Pitting and/or crevice corrosion Stress corrosion cracking
Titanium and its alloys	Canada Japan	Crevice corrosion Hydrogen embrittlement
Stainless alloys (austenitic stainless steels, nickel-based alloys)	Belgium France USA	Pitting and/or crevice corrosion Stress corrosion cracking Microbial induced corrosion

Life expectancies vary between 10^5 – 10^6 years for copper, and 500–10 000 years for the other materials. Table 1 gives a summary of the solutions considered in different countries and the main types of corrosion which may limit the life expectancy of container materials. In France, two main categories of metallic materials are taken into account for HLW and spent fuel packaging: carbon steel or low alloy steel as the reference option, corrosion-resistant alloys (austenitic stainless steels, Ni–Cr–Mo alloys) as the alternative option.

3. Post-closure chemistry of the environment in the near field of disposal

Several factors may influence the corrosion resistance of the container: temperature and radiation dose rate of the waste, the properties of geological materials surrounding the container, engineering pack design, the chemistry and flow rate of groundwaters, etc. The most important parameters for corrosion are the pH, the redox conditions and the concentrations of some species in water (Cl^- , sulfur species). The expected pH values are close to neutrality or weakly alkaline; redox conditions may vary in a large range.

For a waste disposal in crystalline rock or in clay formations, a current understanding retains a standard and conservative scenario showing firstly an oxidizing period then a reducing one:

- after closure, the low permeability geological material surrounding the container progressively becomes saturated with groundwater. The expected environment is then oxidizing, because of the presence of dissolved oxygen in water and air trapped in the near field. With time, oxygen will be depleted by the container corrosion and other oxidation processes (e.g. oxidation of minerals in the buffer and available organic matter). This period could last less than about a hundred years;
- beyond, i.e. without oxygen, the container corrosion will result from the reduction of another available oxidizing agent: mainly water itself and perhaps some bacteria. In these anaerobic conditions, the deep groundwaters are reducing.

The influence of temperature depends on materials considered and corrosion modes. Concerning the influence of γ -irradiation, a modification of redox conditions may be expected due to the radiolysis of water. The potential effect of this phenomenon decreases as a function of the container thickness and time. Its influence is rather important for thin containers.

4. Life prediction for carbon steel and low alloy steel

The state of knowledge is important on the corrosion mechanisms and kinetics of carbon steels in the environmental conditions expected during the different phases of geological disposal (dry hot oxidation, humid-air atmospheric corrosion, aqueous corrosion in aerobic or anaerobic conditions, corrosion in porous argillaceous or cementitious environments).

Basically, general corrosion and localized corrosion (pitting or crevice corrosion) can be described by semi-empirical laws using the longest available data of corrosion in soils or clay materials. Semi-empirical laws were proposed for general and pitting corrosion of carbon steels and cast irons in geological disposal conditions (Figs. 1 and 2). Old analogues, when they still exist (case of iron archaeological artefacts), may be relevant to assess the long-term behaviour of carbon steels.

General corrosion is considered as the prevailing corrosion mechanism in the mean and the long-term. Actually, pitting or crevice corrosion, which occurs on the short-term, especially during the periods when oxygen is still present, tends to fade away because of the progress of general corrosion (Fig. 2).

Iron-based consumable materials show several attractive characteristics for the robustness of the performance prediction at long term:

- they are tolerant to large variations of chemistry in the environments close to neutrality. For example, no threshold corrosion effect is related to chloride concentration of water, as opposed to stainless steels;
- chemical composition and heat treatment of steels are not the most influential parameters of general corrosion resistance;

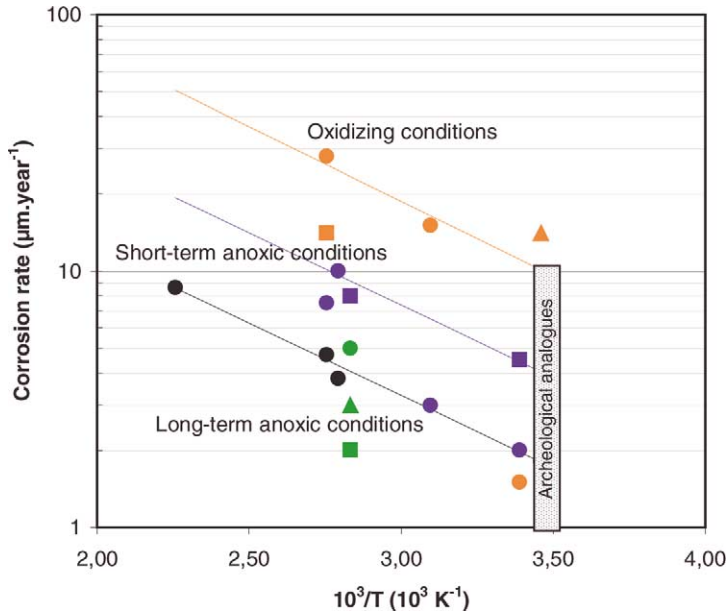


Figure 1. Influence of temperature on the general corrosion rate of carbon steels in argillaceous environments; compilation of data issued from [7].

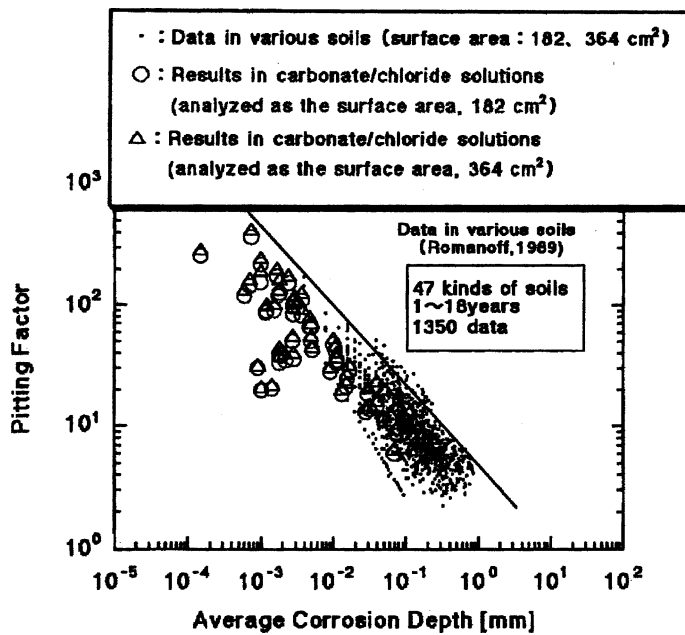


Figure 2. Evolution of the pitting factor of carbon steels or cast irons as function of the average general corrosion depth in various geomaterials or waters [16]. The pitting factor is defined as the ratio between the maximum pit depth and the average general corrosion depth.

- general corrosion is weakly activated by temperature ($\sim 11 \text{ kJ}\cdot\text{mol}^{-1}$);
- other corrosion modes, e.g. stress corrosion cracking and hydrogen-induced cracking are assumed to be possible to avoid by appropriate dispositions.

The use of semi-empiric laws based on experimental data, taking into account the mass-balances and overestimating corrosion parameters allow a realistic assessment of corrosion lifetime, which could be attained by providing an appropriate wall thickness. Containers or overpacks of ‘reasonable’ thickness can be sized with these overestimating approaches.

However, the time scales involved can raise questions about this approach, and a better understanding of the base mechanisms is needed in order to prove the life prediction of containers in a more convincing and robust way.

Some authors [1,5] have developed mechanistic models for the corrosion of carbon steel to be able to make long-term predictions of container lifetimes. The corrosion processes are modeled as a combination of electrochemical reactions at the carbon steel surface and mass transport of oxidants and corrosion products. These models do not take into account the effect of the corrosion products on lowering the corrosion rate. As can be seen in Fig. 3, the average corrosion depth after 1 year of exposure estimated with such a model is five times larger than the experimental result and the difference between experimental results and estimated results increase with the exposure time. This lack of agreement is attributed to the fact that the inhibition of corrosion by the buildup of corrosion products is neglected in the model.

A new model is actually developed by Andra and partners, which is supposed to take into account the possibility of having a layer above the steel surface susceptible to be responsible for the pseudo-passivity of the steel. This model considers a solid oxide, which adheres to the metal and through which the chemical species must diffuse to be able to react at the internal and external interfaces (Fig. 4).

The goal of future studies is to integrate the comprehension of general corrosion mechanisms by using a mechanistic approach, coupling corrosion with clay environments to provide quantitative data concerning the phenomenology of the corrosion and to determine the corrosion kinetics.

5. Life time prediction for passive materials (stainless steels, Ni–Cr–Mo alloys)

Passive materials such as stainless steels, nickel-based alloys, etc., spontaneously passivate in aqueous environments due to the formation of a protective oxide film, which considerably lowers the rates of general corrosion. The uniform corrosion rate is negligibly small as long as this passive layer, which is known to be stable over a relatively wide range of environments, is intact.

The occurrence of localized corrosion (pitting and/or crevice corrosion) is the most credible failure mode in geological disposal for corrosion-resistant materials, if the passive film is locally damaged and the metal unable to restore this layer. Among the different forms of localized corrosion, crevice corrosion is considered as the most dangerous, because it is the easiest to initiate, even on highly alloyed materials.

The initiation of localized corrosion is highly dependent on redox conditions. In reducing environments, no localized corrosion is expected but oxidizing conditions make pitting or crevice corrosion likely; the chloride concentration contained in water is a very influential factor (Fig. 5). Temperature is a factor, which

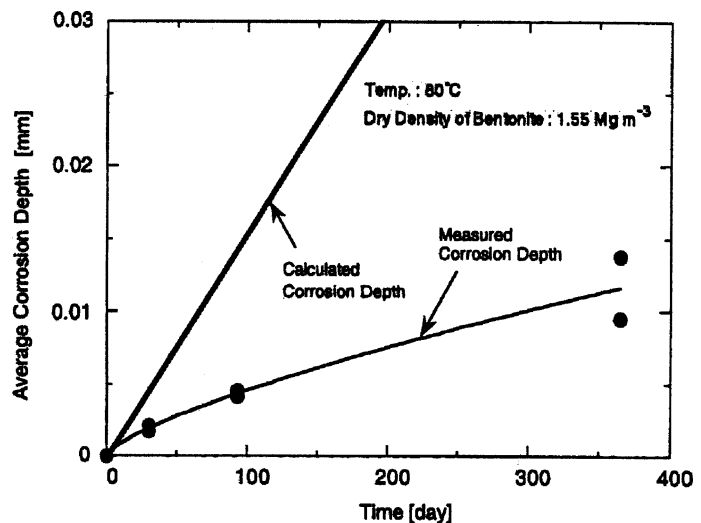


Figure 3. Predicted corrosion penetration depth as a function of time at 80 °C compared with experimental results [5,16].

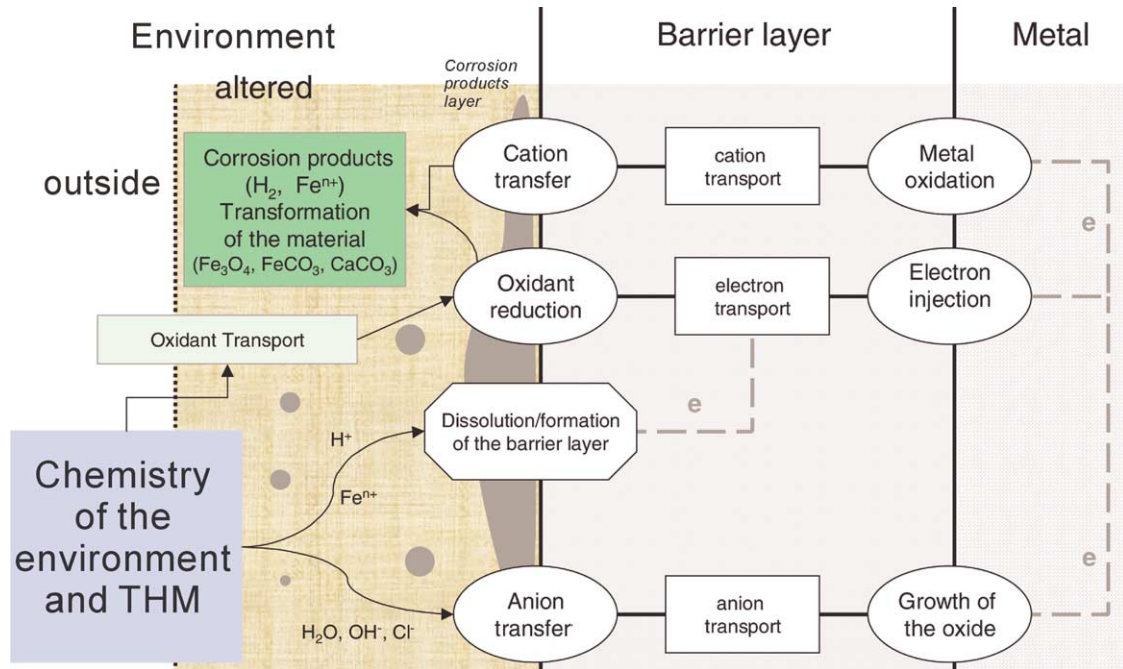


Figure 4. Mechanistic modeling of corrosion processes, after Bataillon from CEA [17].

aggravates and accelerates pitting and crevice corrosion. In other respects, the manufacturing and handling processes are very important factors towards initiation of localized corrosion insofar as they can generate modifications of surface composition and structural state during heat treatments, welding or grinding. Industrial experience shows that the initiation phase of corrosion (drop in pH) may last several months or years, but, on the contrary, the propagation phase may be rapid.

The state of knowledge and the theoretical basis for making long-term extrapolations of corrosion resistance of passivable materials are still limited. Moreover, there is no natural or archaeological analogue of these alloys to gain confidence in the models used for long-term performance prediction. As remarked by the Nuclear Waste Technical Review Board which is charged with performing an independent evaluation of the potential disposal at Yucca Mountain in Nevada, there is no experience with ‘metals protected by passivity for periods longer than 100 years’ [18].

Practically, because of this limited understanding of the fundamental mechanisms underlying long-term corrosion and passive film behaviour, empirically derived parameters are used to assess localized corrosion and to determine the circumstances of initiation and propagation of corrosion as well as the conditions of repassivation (Fig. 5). For a given bulk environment, pitting or crevice corrosion appears to be dependent on the corrosion potential of the free surfaces: initiation occurs when this potential exceeds a critical value. Propagation may occur at significantly lower potentials than the potential of initiation. Propagation stops below a critical potential for the pit or crevice repassivation (E_{pp} and E_{pc} on Fig. 5). No-propagation of corrosion is required, because propagation is rather rapid when localized corrosion happens. The critical potential for crevice repassivation may be used as criterion to avoid localized corrosion.

Increasing the aggressiveness of the environment (e.g. increasing the chloride content or temperature) causes a decrease of the critical potentials of initiation and repassivation. A typical effect of the chloride concentration appears in Fig. 6, dealing with the crevice corrosion resistance of Alloy 825 (42Ni–22Cr–30Fe–3Mo), the container material previously selected for the Yucca Mountain project. At low levels of chloride concentration, the repassivation potential is relatively high which allows the use of the alloy in

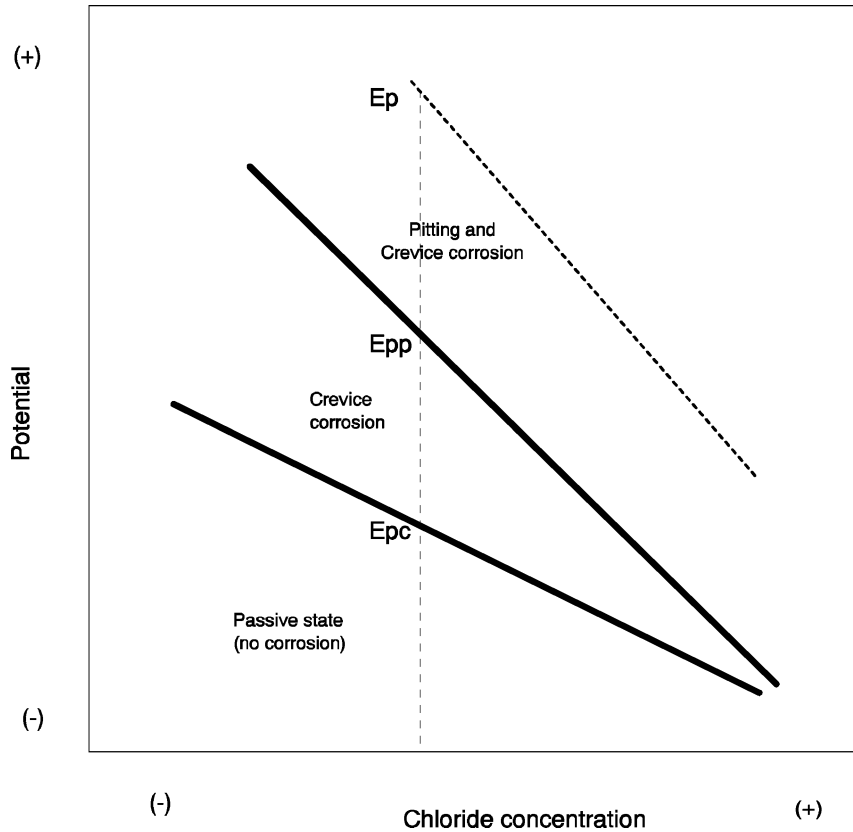


Figure 5. Schematic behaviour of a passive material regarding localized corrosion in chlorided waters.

aerated environments. Increasing the chloride concentration ($> 10^{-2}$ M) causes a sharp decrease of the repassivation potential towards low values. The alloy may then suffer crevice corrosion if water radiolysis occurs (with the formation of H_2O_2) at the surface of the container.

So, it is in principle possible to predict the corrosion resistance of a passive material in a given bulk environment by knowing its repassivation potential and its free corrosion potential (E_{corr}). The electrochemical criterion considers that a passive alloy can be safely used if its corrosion potential never exceeds its repassivation potential during the life of the container. This approach was developed by Cragnolino et al. [10,19–21] in the framework of the Yucca Mountain project evaluation, and is also being used in Japan, France and Belgium as a criterion of resistance of candidate passive alloys for HLW containers [22,23].

To take into account the influence of the environment, susceptibility diagrams have been introduced, which summarize the effects of temperature and chloride content (Fig. 7(a)). On these diagrams, two domains are separated by a single line: on the lower left corner which corresponds to low temperature and chloride content, the material is resistant to crevice corrosion. On the upper right corner, crevice corrosion is possible although not systematic.

Three different and schematic conditions of redox potential must be considered during the life of the containers in contact with groundwater [24]:

- anoxic conditions with a corrosion potential < -250 mV/SHE;
- natural aeration which leads to moderately oxidizing conditions and a corrosion potential around 200 mV/SHE;

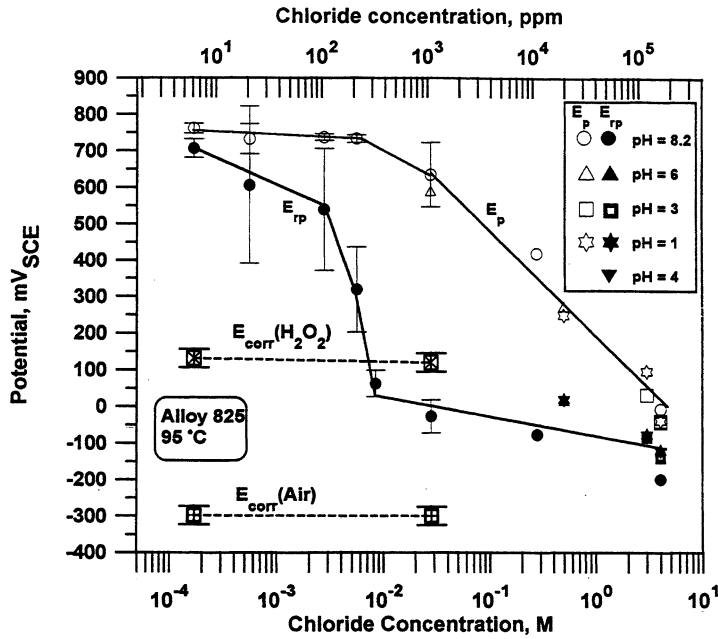


Figure 6. Effect of chloride content on the crevice and repassivation potentials of Alloy 825 at 95 °C [19].

- highly oxidizing conditions due to water radiolysis leading to a corrosion potential estimated at 400 mV/SHE.

The susceptibility diagrams of AISI 304 and 316 L stainless steels, and Ni-based alloys 625 (61Ni–22Cr–9Mo–4Fe–3.5Nb) and C22 (56Ni–22Cr–13Mo–3Fe–3W) are reported in Figs. 7(a) to 7(c), respectively, for the three relevant environment conditions for temperature up to 100 °C. They can be summarized as follows:

- in anoxic conditions, 316 L stainless steel may be used even if some chloride concentration occurs;
- in moderately oxidizing (aerated) conditions, no stainless steel can be used safely, or only at low temperature and in weakly chlorided waters. Alloy 625 is safe up to 100 °C in water containing 1200 mg/L of chloride. Alloy C22 selected for the Yucca Mountain project must be used up to 100 °C if the solute concentration can lead to higher values of chloride concentration at the contact of the container [21];
- in highly oxidizing conditions, the only possible material is alloy C22, but the occurrence of crevice corrosion cannot be entirely excluded if solute concentration occurs when the temperature exceeds 80 to 90 °C. So crevice corrosion of alloy C22 was observed in 5.5 M NaCl, pH 1, 90 °C, ~ 1 V/SHE [23].

6. Conclusions

For the HLW packages as a whole, the corrosion of metallic materials stands for the central aspect in the long-term lifetime prediction. The development of models to predict the lifetimes of nuclear waste containers is still incomplete. To be able to extrapolate corrosion phenomena up to thousands of years, a thorough understanding of the mechanisms and processes induced is necessary.

Corrosion-allowance materials (e.g. carbon steel and low alloy steels) are *tolerant* to large chemistry variations and show several attractive characteristics for reversibility and safety requirements. Different pragmatic approaches were developed for long-term performance predictions. Complementary, they take into account balance and availability of the different oxidizing species in the near field of disposal, and are based on semi-empirical laws drawn from a wide experience. To render the demonstration credible and sure,

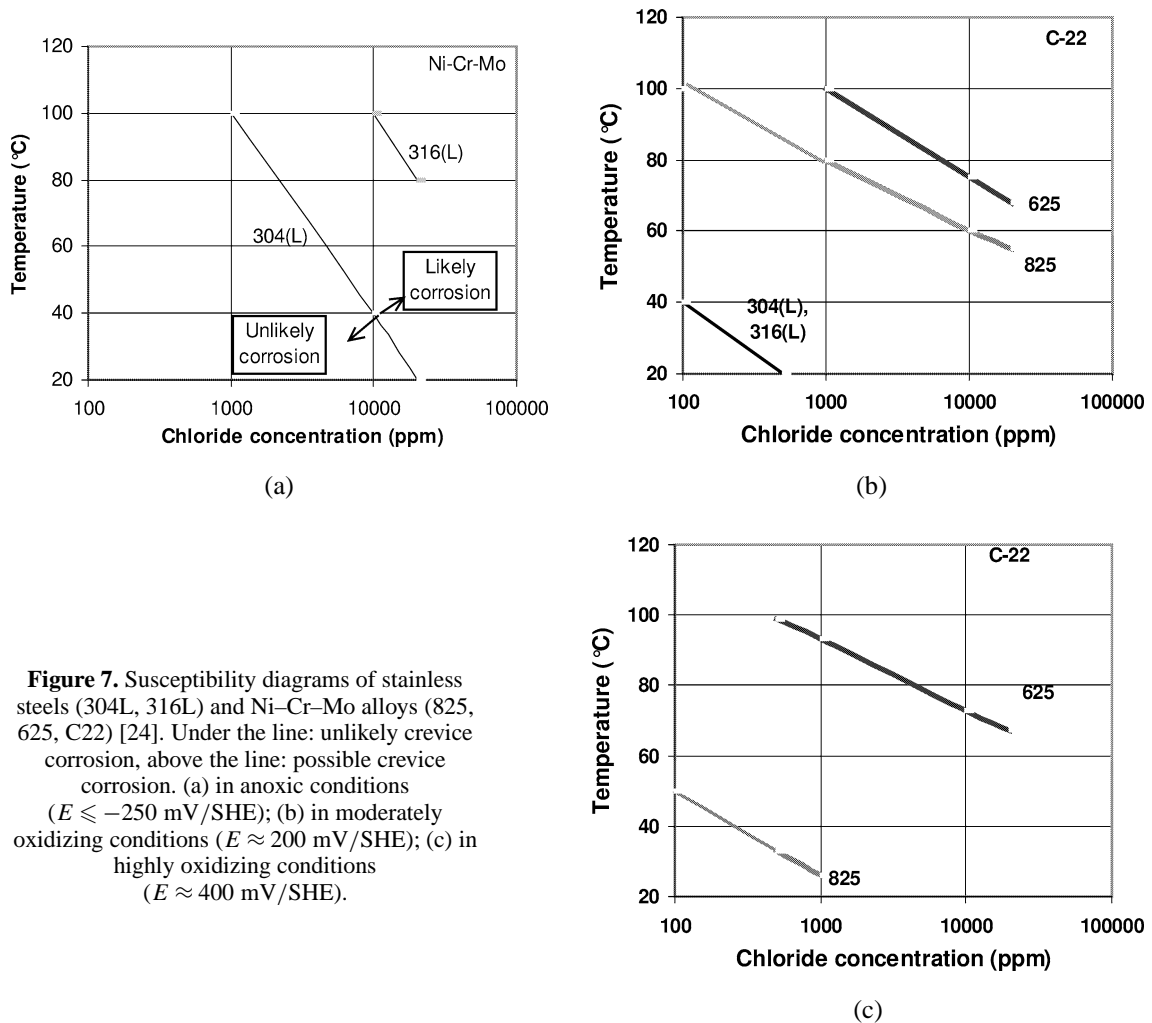


Figure 7. Susceptibility diagrams of stainless steels (304L, 316L) and Ni–Cr–Mo alloys (825, 625, C22) [24]. Under the line: unlikely crevice corrosion, above the line: possible crevice corrosion. (a) in anoxic conditions ($E \leq -250$ mV/SHE); (b) in moderately oxidizing conditions ($E \approx 200$ mV/SHE); (c) in highly oxidizing conditions ($E \approx 400$ mV/SHE).

it is necessary to develop a more theoretical model, surer concerning the prediction on the long-term, based on a phenomenological description of the corrosion taking into account the different interface reactions, the species transport in the protective layers. . .

The use of passivable materials (stainless steels, nickel-based alloys, titanium alloys) for HLW containers may guarantee a low level of general corrosion consistent with the very long expected lifetime. However, they are weakly *tolerant* towards crevice corrosion in highly-chlorided water, which makes difficult the selection of the good alloy. The aim of the research is to demonstrate, in a robust and convincing way, the absence of propagation of the crevice corrosion. This is the only way such alloys could conceivably be used in geological waste disposal.

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Discussion

Question de R. Dautray

Les dernières livraisons de Science et Nature parlent de matériaux « gradués » ; nous sommes dans le long terme ; où en êtes-vous ? cela vous semble-t-il être une voie d'étude ?

Réponse de J.-M. Gras

Dans l'élaboration des concepts de stockage, les études sur le conteneur ont privilégié, dans un premier temps, le principe d'un objet constitué d'un seul matériau en s'intéressant principalement à la tenue à long terme de l'enveloppe des colis. Au demeurant, ce sont bien à des objets multi-matériaux qu'aboutissent les études de concepts industriels, attribuant à chaque matériau des propriétés fonctionnelles différentes ou graduées :

- dans le conteneur suédois de combustibles usés, le cuivre constitue en quelque sorte un « revêtement externe » garantissant la résistance à la corrosion alors que le conteneur interne en fonte assure la tenue mécanique du colis (voir exposé de C. Thegerström) ;
- un des concepts envisagé pour le projet Yucca Mountain faisait appel à un conteneur en alliage passivable utilisé en sous-couche d'une enveloppe externe en acier faiblement allié. Cette configuration permet de « graduer » la résistance à la corrosion du système en établissant un couplage galvanique entre l'acier non encore corrodé et l'alliage passivable. Le « démonstrateur » de conteneur de combustibles usés étudié actuellement par le CEA, EDF et l'Andra est constitué d'une enveloppe en acier faiblement allié recouvrant un étui étanche en acier inoxydable à l'intérieur duquel sont placés les assemblages combustibles ;
- des traitements de surface ont aussi été considérés, sans beaucoup de crédibilité jusqu'à présent.

Question de É. Brézin

Quel est l'effet de l'élévation de température sur la cinétique de corrosion ?

Réponse de J.-M. Gras

Cet effet dépend de la nature des matériaux considérés.

Pour les matériaux consommables (e.g. les aciers non ou faiblement alliés), la corrosion généralisée est le mécanisme de corrosion dominant à moyen et long terme dans le stockage. Sur cette forme de corrosion, l'effet de la température est peu marqué et continu (énergie d'activation apparente d'environ $11 \text{ kJ}\cdot\text{mol}^{-1}$ d'après Fig. 1 de l'article). En conditions anoxiques, la vitesse de corrosion a même tendance à diminuer à température élevée (vitesse de corrosion 7 fois plus faible à $250 \text{ }^\circ\text{C}$ qu'à $100 \text{ }^\circ\text{C}$ par exemple, d'après [1]). Cette variation est attribuée à une stabilité accrue de la couche passive (magnétite adhérente) au-dessus de $100 \text{ }^\circ\text{C}$.

Pour les alliages passivables (e.g. les aciers inoxydables et les alliages de nickel), la forme de corrosion dimensionnante dans les conditions de stockage est la corrosion localisée (par piqûres ou caverneuse). Pour cette forme de corrosion, il existe une température critique au-dessus de laquelle la résistance de l'alliage à la corrosion localisée diminue brutalement. Ainsi, un alliage aussi résistant à la corrosion que l'actuel matériau des conteneurs du projet Yucca Mountain (un alliage contenant 22% Cr, 56% Ni, 13% Mo) voit sa résistance diminuer considérablement lorsque la température dépasse $100\text{--}120 \text{ }^\circ\text{C}$ [2]. Cet effet de la température conduit d'ailleurs souvent à caractériser la résistance des matériaux passivables, dans un milieu donné et pour un potentiel donné, par une température critique qui est la température au-dessus de laquelle s'amorce la corrosion localisée dans les conditions considérées.

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Question de H. Métivier

Prenez-vous en compte dans vos recherches la corrosion bactérienne ?

Réponse de J.-M. Gras

La possibilité d'interactions entre les micro-organismes présents dans un site de stockage et les matériaux de conteneur est prise en compte dans les études, et le risque de corrosion bactérienne effectivement envisagé. Ces interactions sont souvent considérées, à tort, comme des phénomènes singuliers et mystérieux. En fait, elles interviennent en modifiant les réactions anodiques ou cathodiques de formes de corrosion qui sont étudiées par ailleurs (corrosion généralisée, corrosion sous dépôt (le biofilm)).

Vis-à-vis de la corrosion généralisée des matériaux consommables, la corrosion bactérienne peut être prise en compte au travers de bilans matières. Dans le cas des bactéries sulfatoréductrices par exemple, on considère que tous les ions sulfate présents dans le champ proche du stockage sont réduits en sulfure par les bactéries et que les ions sulfure sont intégralement disponibles pour corroder le conteneur.

Sur les alliages passivables, l'influence des micro-organismes se traduit par une augmentation du risque de corrosion localisée, notamment des nuances les moins alliées.

En résumé, la corrosion bactérienne est donc examinée, et on n'a pas considéré qu'elle était suffisamment critique pour risquer a priori de remettre en cause les concepts.