

## Workshop

# SACNUC Sulphur-Assisted Corrosion in Nuclear Waste Disposal Systems

Brussels, Belgium  
21-23 October 2008



EUROPÄISCHE FÖDERATION KORROSION  
EUROPEAN FEDERATION OF CORROSION  
FEDERATION EUROPEENNE DE LA CORROSION

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**SCK•CEN**  
Boeretang 200  
BE-2400 Mol  
Belgium  
<http://www.sckcen.be>

## Workshop

# **SACNUC** **Sulphur-Assisted Corrosion in Nuclear** **Waste Disposal Systems**

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**SCK•CEN, Boeretang 200, BE-2400 MOL, Belgium**

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## Introduction

In the different disposal concepts for high-level nuclear waste, corrosion of the metallic barriers and in particular the overpack/container is a major issue. It is imperative for performance assessment to predict the lifetime of these containers. One particular issue hampering the lifetime prediction is the presence of sulphur species that may cause localised corrosion. The aim of the SACNUC workshop is to provide an exchange of information on the influence of sulphur species on the corrosion of metallic barriers. The workshop consists in a series of lectures focusing on diverse aspects of sulphur-assisted corrosion.

In an introductory session, an overview is given of European concepts for the disposal of high-level nuclear waste, with a particular focus on the Belgian Supercontainer concept. During these opening lectures, the role of corrosion knowledge in the preparation of safety cases, and the possible impact of sulphur-related corrosion are discussed. Evidence of sulphur-related corrosion phenomenae are presented, both from within and outside the nuclear disposal field. This is complemented with a lecture on the fundamental aspects of sulphur-induced corrosion. To conclude the introductory session, the role of sulphur-assisted corrosion in lifetime prediction is discussed.

A central session in the workshop is devoted to the role of microbial processes in sulphur-assisted corrosion. An introductory lecture gives an overview of microbial processes that may occur in deep repository environments and how they may affect corrosion. This lecture is followed by presentations of investigations of microbially influenced corrosion of both container materials and concrete.

Two lectures discuss the modelling of corrosion in disposal conditions and the influence of sulphur species in particular.

A series of presentations discusses the influence of sulphur species on the corrosion of several materials that may be present in disposal concepts, i.e. carbon steel, copper, and components of rust.

To conclude the workshop, a discussion panel takes place in order to identify open issues in the investigation of sulphur-assisted corrosion phenomenae and how to incorporate these in robust lifetime prediction of metallic barriers.

The International Workshop on Sulphur-Assisted Corrosion in Nuclear Waste Disposal Systems is a co-organization of SCK•CEN and ONDRAF/NIRAS under the auspices of the European Federation of Corrosion.

## Programme

### Tuesday, 21 October 2008

- 08:15 Reception and welcome coffee  
 08:45 Opening words by Geert Volckaert (SCK•CEN) and Maarten Van Geet (NIRAS/ONDRAF)

Chair: Maarten Van Geet (NIRAS/ONDRAF)

- 09:00 An overview of European concepts for the disposal of high-level nuclear waste  
*R. Gens (NIRAS/ONDRAF)*
- 10:00 The Belgian Supercontainer concept  
*B. Kursten, F. Druyts, R. Gens (SCK-CEN, NIRAS/ONDRAF)*
- 11:00 Coffee Break
- 11:30 The geochemistry of sulphur species in disposal concepts related to corrosion phenomenae  
*P. De Cannière, L. Wang, S. Aerts, M. De Craen (SCK•CEN)*

12:30 Lunch

Chair: Fraser King (Integrity Consulting)

- 14:00 Fundamental aspects of sulphur-induced localized corrosion  
*D. D. Macdonald, O. Azizi (Pennsylvania State University)*
- 15:00 Sulphur-assisted corrosion outside nuclear disposal  
*L. Smith (Intetech Ltd.), B. Craig (MetCorr)*
- 16:00 Coffee break
- 16:30 Lifetime prediction of metallic barriers in nuclear waste disposal systems: overview and open issues related to sulphur-assisted corrosion  
*D. Féron (CEA)*
- 17:30 End of Day 1
- 18:30 Welcome cocktail

### Wednesday, 22 October 2008

Chair: Damien Féron (CEA Saclay)

- 09:00 Microbial processes in deep repository environments and their influence on corrosion  
*K. Pedersen (Göteborg University)*
- 10:00 Experimental investigation on microbial corrosion for repository conditions  
*V. Madina, I. Azkarate, L. Sanchez (INASMET)), M. A. Cuñado (ENRESA)*
- 10:45 Coffee break
- 11:15 Sulphurous bacteria and concrete deterioration  
*S. Roux, F. Feugeas (INSA de Strasbourg)*

12:00 Role of microbial activity on corrosion of materials used for radioactive waste disposal  
*H. El Hajj, A. Abdelouas, B. Grambow (SUBATECH)*

12:45 Lunch

Chair: Bruno Kursten (SCK•CEN)

14:15 Reactive-transport modelling of the sulphide-assisted corrosion of copper nuclear waste containers  
*F. King (Integrity Consulting), M. Kolar (LS Computing Ltd.), M. Vähänen (Posiva Oy)*

15:00 Could one transfer corrosion modelling expertise from reactor to disposal systems?  
*M. Vankeerberghen (SCK•CEN)*

16:00 Coffee break

16:30 Anaerobic corrosion of carbon steel and the potential influence of sulphur species  
*N. R. Smart (Serco)*

17:30 End of day 2

19:30 Workshop dinner

## Thursday, 23 October 2008

Chair: Robert Gens (NIRAS/ONDRAF)

09:00 The influence of chloride on the corrosion of copper waste containers in aqueous sulphide solutions  
*J.M. Smith, Z. Qin, D.W. Shoesmith (University of Western Ontario), F. King (Integrity Consulting)*

09:45 Interactions between sulphide species and components of rust  
*J.A. Bourdoiseau, M. Jeannin, R. Sabot, Ph. Refait (Université de La Rochelle)*

10:30 Coffee break

11:00 General discussion on open issues: what is further required in the study of sulphur-assisted corrosion phenomenae for robust lifetime prediction?  
*Discussion panel*

12:30 Lunch

14:00 End of the workshop

## **An overview of European concepts for the disposal of high-level nuclear waste**

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### **Abstract**

This paper provides an overview of current repository and engineered barrier system (EBS) designs in selected high-level waste (HLW) and spent fuel (SF) disposal concepts from European countries. The rationale underlying the choice of the overpack material in the different concepts is presented. Up to now, three types of materials are mainly considered: corrosion-allowance materials (e.g. carbon steel, low-alloy steels, cast irons and copper in oxidising environments) which corrode actively under the conditions expected during geological disposal at significant but relatively easily predictable general corrosion rates; corrosion-resistant materials (e.g. austenitic stainless steels, Ni-Cr-Mo alloys, titanium alloys) passivate in aqueous environments due to the formation of a protective oxide film, which considerably reduces the rate of general corrosion. Copper is thermodynamically stable in reducing environment free of complexing agents.

Most of the HLW and/or SF disposal programmes in European countries are pursuing disposal options in which the primary waste container (e.g. the KBS-3 copper canister, the Belgian carbon steel overpack, the French or Swiss steel overpack) is designed, in conjunction with the surrounding EBS materials, to provide complete containment of the waste for at least the period when temperatures in the disposal system are significantly raised by radioactive decay.

The assessment of waste container corrosion is central to the safety cases being developed, but it is important that the assessments consider the complementary roles of the surrounding engineered barriers (e.g., the bentonite or concrete buffer) in protecting the canister and providing chemical conditions that will limit corrosion, and it is also important for the assessments to consider couplings between processes such as the feedback between hydrogen gas production, corrosion and waste dissolution. Available understanding of corrosion processes has allowed the development of a high degree of confidence in several alternative proposed solutions to the waste containment and disposal problem, which have been tailored to the particular wastes and host rocks in question. This level of confidence also derives from the results of considerable programmes of work that have been conducted to assess the feasibility, performance and safety of waste disposal.

## The Belgian Supercontainer Concept

**Bruno Kursten**<sup>(1)</sup>, **Frank Druyts**<sup>(1)</sup> and **Robert Gens**<sup>(2)</sup>

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### Abstract

The Supercontainer (SC) Design is the preferred Belgian option for the final disposal of vitrified high-level waste (VHLW) and spent fuel (SF) in deep underground clay layers. The SC comprises a carbon steel overpack, containing two VHLW canisters or four SF assemblies, surrounded by a Portland cement (PC)-based buffer, which in turn, is entirely encased in a stainless steel envelope. The SC Design was developed based on the Contained Environment Concept (CEC), which intention is to fix and preserve a favourable chemical environment in the immediate vicinity of the overpack, so that it will be exposed to essentially unchanged conditions for a long time, at least for the duration of the thermal phase. Under the predicted conditions within the SC (highly alkaline concrete buffer), the carbon steel overpack is expected to undergo uniform corrosion (passive dissolution).

An integrated R&D strategy is developed to demonstrate and defend that the integrity of the carbon steel overpack can be ensured at least during the thermal phase. This integrated approach, proposed to estimate the lifetime of the carbon steel overpack, consists of three steps: lifetime prediction, validation, and confidence building.

The main advances in the development of the SC Design are presented. Gas generation calculations indicate that hydrogen production due to gamma radiolysis of water is not expected to pose a threat to the integrity of a sealed stainless steel envelope (no pressure build up). Scoping calculations based on a local equilibrium-diffusion transport model indicate that the near-field will likely remain alkaline ( $\text{pH} > 12.5$ ) for a geological time span ( $10^5$  years). Modelling of the thermo-hydro behaviour of the concrete buffer indicate that heating should not adversely affect its properties. An overview of the R&D program related to the corrosion of the overpack is given. The approach to be followed for dealing with localised corrosion processes ('exclusion principle') is addressed. For the geochemical boundary conditions expected to prevail after closure of the repository, uniform corrosion should proceed at a very low rate. The main remaining uncertainties and future key issues are identified. One of the remaining questions is the role of sulphur species.

## Geochemistry of Sulphur Species Harmful for Metallic Barriers in clay Environment in the Frame of Geological Disposal of Radioactive Waste

**Pierre De Cannière, Lian Wang, Sven Aerts and Mieke De Craen**  
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### Abstract

Reduced-sulphur species are potent aggressive agents for the corrosion of metals. Thiosulphate ( $S_2O_3^{2-}$ ) may induce pitting corrosion while dissolved sulphide ( $H_2S$  and  $HS^-$ ) and elemental sulphur ( $S^0$ ) can give rise to crevice corrosion and stress corrosion cracking. Two of the most ubiquitous sulphur-containing minerals found in clay environments are pyrite ( $FeS_2$ ) and gypsum ( $CaSO_4 \cdot 2 H_2O$ ). In the sulphur cycle, pyrite can easily undergo oxidation by air oxygen while sulphate reduction may be mediated by bacteria.

Abiotic and microbial processes are important in the redox reactions taking place in the sulphur cycle. In deep geological environments under reducing conditions pyrite is stable. However, during mining works and after construction of the underground installations, pyrite oxidation very easily occurs when oxygen from the air of open galleries enters the clay formation in the excavation disturbed zone (EDZ). Sulphate profiles along boreholes perpendicular to galleries reveal pyrite oxidation in the first 1 – 2 meters of clay. Efflorescences of sulphate and chloride also crystallise on the walls of ventilated galleries. Pyrite oxidation and salt accumulation near open galleries are important processes to define the initial and boundary chemical conditions for the metallic overpack corrosion.

Thiosulphate (up to  $1\ 100\ mg\ dm^{-3}$ ;  $10^{-2}\ mol\ dm^{-3}$ ) has been observed in water squeezed out of oxidised Boom Clay cores or collected from air-drilled piezometers, and in large-scale heating experiments. Microbially-induced reducing perturbations have also been evidenced by the presence of hydrogen sulphide in water sampled from boreholes drilled with nitrogen, and from  $H_2S$  emanations produced by the putrid decomposition of wood pieces installed during excavation works behind the concrete lining of galleries.  $H_2S$  was freshly formed by sulphate-reducing bacteria (SRB) growing in water without space restriction. Up to  $5 \times 10^{-4}\ mol\ dm^{-3}\ HS^-$  was also measured in a large-scale mock-up filled with bentonite and heated during 5 years.

As a conclusion, pyrite oxidation and microbially-mediated sulphate reduction can both produce dissolved reduced-sulphur species potentially aggressive for the corrosion of metallic barriers in direct contact with altered porewater. This, with the chloride accumulation near open galleries, should be considered for the geochemical boundary conditions required by the corrosion studies. In the case of the Belgian Supercontainer concept, the transport of aggressive species through the cementitious buffer should be studied in a quantitative way, in order to determine what is their concentrations at the surface of the metallic overpack and if it represents a risk of corrosion.

## Fundamental aspects of sulphur-induced localized corrosion

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### Abstract

Certain labile sulphur compounds are well-known, deleterious species in the localized corrosion of metals, including iron, nickel and copper-based alloys, particularly in the absence of chromium. Much of the aggressiveness of the labile sulphur species can be attributed to the multitude of oxidation states displayed by this element ranging from -2 to +8, with many species having fractional oxidation states. For example the species  $S_3^{2-}$  has an average oxidation state for sulphur of -2/3. The second aspect of many sulphur-containing species is their ability to donate atomic sulphur to a metal surface (e.g.,  $S_3^{2-} \rightarrow S + S_2^{2-}$ ). Atomic sulphur is a powerful depassivator, particularly for Fe, Ni, and Cu-based alloys, through the formation of the respective sulphides in preference to the passivating oxides. If the atomic sulphur is donated at a crack tip, for example, labile sulphur species are powerful promoters of stress corrosion cracking (SCC) and hydrogen induced cracking (HIC). Indeed, adsorbed sulphur is a strong inhibitor of the hydrogen atom recombination reaction on a metal surface, with the result that labile sulphur species promote the entry of hydrogen into the base metal, with the hydrogen being produced by corrosion. In this talk, the chemistry of sulphur species in aqueous environments will be reviewed by examining classical Pourbaix diagrams and the more explicit Volt Equivalent Diagrams for sulphur. The thermodynamics of various metal-sulphur-water systems will also be examined, including the Pourbaix diagrams for Fe-S-H<sub>2</sub>O, Ni-S-H<sub>2</sub>O, and Cu-S-H<sub>2</sub>O. Finally, the kinetics of the interaction of sulphur species with various metals will be reviewed and mechanistic aspects of depassivation by labile sulphur species will be discussed. The final objective of the talk will be to identify the fundamental reasons for the aggressiveness of certain sulphur species when in contact with metal in aqueous environments.

## Corrosion mechanisms and material performance in environments containing hydrogen sulphide and elemental sulphur

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### Abstract

This paper provides an overview of corrosion mechanisms and materials' performance in environments containing H<sub>2</sub>S and elemental sulphur (S), particularly in the presence of chloride ions. Based on this information the factors affecting the service life of materials in highly sour environments are discussed. The source of the data summarised is drawn from the experience of the oil and gas industry in handling sour environments.

Although there are considerable data in the literature concerning corrosion from H<sub>2</sub>S and S (and the same is true for field experience), there is essentially no accepted set of guidelines for the selection of materials in these environments. To date most oil companies have based materials selection in these environments solely on their own field experience around the world or that of other operators. Many factors determine the corrosion rate of steels and corrosion resistant alloys (CRAs) in H<sub>2</sub>S and S bearing environments. In fact so many factors that simply basing materials selection decisions on experience can easily lead to the wrong choices and in some cases, premature failure.

Generally speaking the issue of material choice and corrosion control approach is strongly influenced by the consideration of the factors that will enhance the stability of the sulfide film, or will tend to destabilise it and encourage pit initiation. The evaluation of all of the influencing factors, based on the review of the literature and best practice from many operators, gives a good basis for evaluation of new producing conditions with aggressive environments.

It is considered that it is possible to handle aggressive, high H<sub>2</sub>S and S –containing environments safely and with expectation of long service life if care is given to the materials selection at the beginning of a project.

## **Lifetime prediction of metallic barriers in nuclear waste disposal systems: overview and open issues related to sulphur-assisted corrosion**

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### **Abstract**

For high level nuclear waste disposals, the lifetime prediction of metallic barriers is more often over millenniums. The objective of this paper is to give a short overview of the influences of sulphur (in the metal or in the environment) on the corrosion behaviour of metals and alloys in conditions encountered in geological storages.

The presence of sulphur inclusions is well known to initiate localised corrosion phenomena on passive alloys and non alloyed steels: this phenomenon occurs rather at the beginning of exposure. For long term exposure, it has been also demonstrated that even low levels of sulphur in the metallic materials (nickel or stainless steels) may accumulate in the passive layer and lead to the destruction of the passivity.

Emphasis will be placed on the role played by dissolved sulphur species on the corrosion behaviour with and without bacteria. Examples will include the influence of sulphides on stress corrosion cracking and hydrogen embrittlement. In presence of pyrites, the role played by sulphide oxidising bacteria in oxidising conditions will be discussed in one end. In the other end, the role played by sulphate reducing bacteria under anaerobic conditions will be also addressed. On stainless steels and in chlorinated environments, mineral sulphides or sulphides produced by sulphate reducing bacteria have the same effects on the passive layer which is much less resistant with than without sulphides, the worse conditions for metallic passive alloys being the coupling of areas exposed to sulphide (anaerobic) and to oxidising conditions in other parts.

Some data coming from iron archaeological artefacts exposed to sulphide conditions will be also presented and analysed.

## Microbial processes in deep repository environments and their influence on corrosion

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### Abstract

There are several microbial processes with corrosive end products. The microbial oxidation of sulphide with oxygen generates sulphuric acid. Reduction of sulphur in sulphate during the oxidation of organic compounds, methane or hydrogen produces sulphide. The reduction of carbon dioxide with hydrogen generates acetate that can be utilised by microorganisms reducing sulphate to sulphide. These processes take place inside the living cells where they are separated from the external environment by a semi-permeable cell membrane. The biochemical reaction pathways that microorganisms utilize are complicated and they often include cascades of biochemical enzyme-catalysed reactions that are strictly controlled by the genetic code (i.e., DNA) of the individual cells. In addition, feedback and substrate-level control mechanisms may also be active. It is important to understand that the biochemistry behind microbial processes take place in the cytoplasm of cells at conditions very different from what are found at the outside of the cell membrane, through which the end products such as acid, acetate and sulphide are expelled. Microorganisms are generally more active at the boundaries between systems, where gradients of electron donors, carbon sources, and electron acceptors meet, than in homogenous, mixed systems. Such gradients can be found, for example, between the engineered part of a repository and the surrounding geological environment. Many microorganisms are opportunistic as well: they wait for favourable conditions when they can prosper and multiply. While waiting, they may enter various dormancy states, e.g. spores, desiccation or starvation. Opportunistic microbes in stagnant systems such as dry commercial bentonite and compacted clay buffers can wait for many years for conditions to change. When conditions change to a favourable situation, it is very likely that dormant opportunists will respond with rapid growth and microbial processes will speed up significantly for as long as the new, favourable conditions last. The prediction and modelling of microbial processes in repository environments should preferably rely on experimental data from *in situ* models and simulations of the repository system of interest. There are very good methods in microbiology that can be employed. Cultivation in the laboratory is a pre-requisite for all microbiology. In the field, the use of radioactive isotopes will reveal *in situ* process rates. Recent qualitative and quantitative advances in the analysis of genetic material in cells (DNA and RNA) can be used to analyse types of microorganisms present in any system and the rate of the processes they are performing.

## Experimental investigation on microbial corrosion for repository conditions

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### Abstract

Under disposal conditions high level waste (HLW) metallic containers can suffer from microbiologically influenced corrosion (MIC). Microbial activity from bacteria arising from the bentonite surrounding the canister and groundwater can initiate localized corrosion phenomena or even accelerate corrosion modes already existed. In order to evaluate the susceptibility to MIC of several candidate metal containers, electrochemical testing has been performed for periods up to 60 days.

For this study, *Desulfotomaculum alkaliphilum* a species of sulphate reducing bacteria (SRB) and *Thiobacillus versutus* for the sulphur oxidizing bacteria (SOB) type has been selected. These two groups of bacteria have been previously identified in the Spanish reference bentonite. Moreover, both types of bacteria are responsible for some of the most severe cases of MIC. The anaerobic SRB play a major role in metal corrosion due to the conversion of sulphate into sulphide. Aerobic SOB is an acid producing bacteria and is also involved in the sulphur cycle.

The steels coupons were immersed in an inoculated granitic simulated groundwater. A sterile electrochemical corrosion cell was also used as control system. General corrosion rates were measured with the polarization resistance methodology. Tested specimens were analyzed by optical and scanning electron microscopy (SEM). Energy dispersive X-ray (EDS) analysis of the biofilm and corrosion products generated were also performed.

Results with SRB inoculated media indicate higher corrosion rates for the carbon steel, with respect to the values obtained in sterile conditions. A biofilm growth was observed for this steel. In contrast, in SOB inoculated media the biofilm generated on the surface of the carbon steel seemed to produce a barrier effect, resulting in a substantial decrease in the corrosion rate of the metal.

## Sulphurous bacteria and concrete deterioration

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### Abstract

As all the materials, concrete and cementitious materials are sensitive to ageing phenomena. Among the weathering factor the biological one is often neglected although microorganisms can lead to the formation of colored stains on concrete facing up to the failure of concrete structure. The chemical biodeterioration of cementitious materials induces the formation of expensive products or soluble products. The sulfo-oxidizing bacteria (SOB) such as the Thiobacilli are known as acting in concrete structure deterioration by metabolization of sulphuric acid. This acid then reacts with the cement matrix to form gypsum and ettringite.

The influence of environmental sulphurous bacteria on the concrete deterioration on different cement paste samples is studied. The cements are a CEM I, a CEM III and a CEM V (NF EN 196-1). Cement paste samples have been immersed in selective culture media using SOB, sulphato-reducing (SRB) and thiosulphate-reducing bacteria (TRB) extracted from the Rhenish ground water. These bacteria colonize the samples *in situ*; they have been identified in the biofilms on the surface of three cement samples after one year immersion.

Energy dispersive spectrometry (EDX) and X-rays diffraction have been used to analyze and to compare the surface chemical composition of:

- sound samples,
- sample after 3 months immersion in the three culture media,
- sample after 3 months immersion in the three sterilized culture media.

Whatever the cement base and the medium considered, the immersion of the samples leads to the formation of calcium carbonate. The SOB metabolic activity acidifies the medium up to pH 4.5 and induces the formation of calcium hydrogen phosphate. The SRB metabolic activity leads to the formation of calcite linked to the metabolization of carbonic acid. The TRB metabolic activity causes the formation of calcium carbonate and of dolomite on the CEM I samples. These tests show that the chemical surface evolution of the different cement paste samples, resulting from the microorganisms' metabolic activity, is not only influenced by the cement paste composition but also by the microorganisms' species and the culture media.

## **Role of microbial activity on corrosion of materials used for radioactive waste disposal**

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### **Abstract**

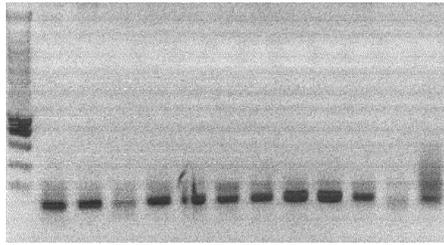
The role of microbial activity on the alteration of materials such as oxides (glass,  $\text{UO}_2$ ) and metals (metal containers) is increasingly discussed in recent literature. In surface (aerobic) or deep (anaerobic) geological conditions growth of microorganisms can cause corrosion of materials through various processes such as acidification of the environment, modification of redox conditions, and production of organic acids and products of metabolism such as hydrogen sulphide ( $\text{H}_2\text{S}$ ).

We propose to study the corrosion of iron containers in the presence of indigenous microorganisms in Callovo-Oxfordien argillite, which is considered as a potential host rock for high-level radioactive waste disposal in France. Indeed, the hydrogen produced in the disposal site could be a tremendous source of energy for the growth of anaerobic bacteria, in particular the sulphate-reducing (e.g. Lovley and Phillips, 1992). The sulphate reducing bacteria can combine the oxidation of organics or hydrogen to the reduction of radionuclides such as uranium and technetium (Abdelouas et al. 2000, 2005).

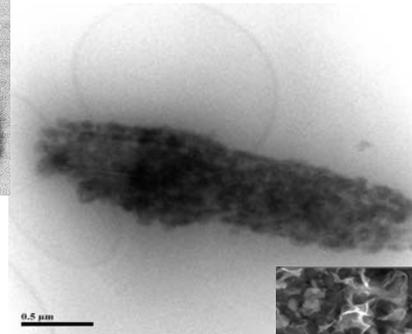
Water/argillite batch experiments showed the presence of sufficient nutrients and trace elements for bacterial growth. Hence, sulphate-, nitrate- and metal-reducing bacteria were isolated from argillite under anaerobic conditions. The bacteria isolated were characterized and identified by 16sARN sequencing (Figure 1) and observed by transmission electron microscopy (TEM) (Figure 2).

Batch experiments with iron samples in contact with argillite were conducted under anaerobic conditions. The corrosion of the iron was studied by weighing the sample after an acid dissolution of the corroded surface and the samples were observed by scanning electron microscopy (SEM) (Figure 3). The corrosion rate of the iron sample in presence of microbial activity is higher than the iron sample corroded under sterile conditions.

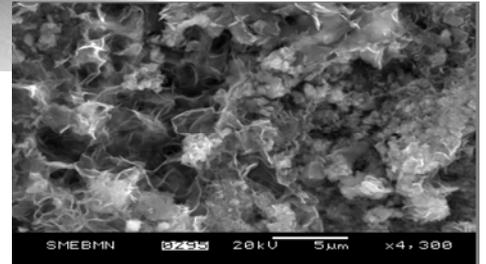
Future work will be conducted in diffusion cells with argillite cores to better simulate to disposal site conditions. In addition to the methods described above electrochemical studies will be conducted to study the corrosion process of the iron.



**Figure 1 :** amplification- 16sARN bacteria.



**Figure 2:** Photo TEM showing a sulphate reducing bacteria



**Figure 3:** Photography SEM showing corroded steel products ( $\text{FeS}_2$ ).

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## Reactive-transport modelling of the sulphide-assisted corrosion of copper nuclear waste containers

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### Abstract

A mechanistically based mixed-potential model has been developed to predict the corrosion behaviour of copper canisters in the presence of sulphide ions. The model is based on a mechanistic description of the interfacial reactions involved in the corrosion process coupled to various mass-transport and homogeneous reactions expected to occur in the near- and far-fields of the repository. The model is capable of predicting the time dependence of the corrosion potential ( $E_{\text{CORR}}$ ) as the repository redox conditions evolve from initially aerobic to eventually anoxic and dominated by the presence of sulphide.

The mechanistic basis for the model has been developed from the results of experimental work performed at the University of Western Ontario, described in another presentation at this Workshop. The anodic reaction involves the formation of a  $\text{Cu}_2\text{S}$  film (with trace amounts of digenite  $\text{Cu}_{1.8}\text{S}$ ). This film is only partially protective and dissolution continues via a two-step process involving an adsorbed intermediate Cu(I)-sulphide species. Under freely corroding conditions similar to those expected in the repository, the anodic reaction is second order with respect to the  $[\text{HS}^-]$  and exhibits a Tafel slope of  $\sim 40$  mV. At more positive potentials, the reaction becomes transport limited due to the supply of  $\text{HS}^-$ . The cathodic reaction involves the reduction of  $\text{HS}^-$  with the evolution of  $\text{H}_2$ . Under repository conditions in the presence of compacted bentonite, the overall corrosion rate is limited by the supply of  $\text{HS}^-$  to the canister surface. The film is less protective in the presence of high  $\text{Cl}^-$  concentrations, as dissolution as  $\text{CuCl}_2^-$  ions competes with  $\text{Cu}_2\text{S}$  film formation.

A series of steady-state mixed-potential models have been developed to explain the experimental observations. These models are based on various combinations of anodic and cathodic rate-determining steps. The experimental  $E_{\text{CORR}}$  data in bulk solution are best described by a combination of a kinetically controlled anodic reaction and a constant cathodic current at  $E_{\text{CORR}}$  in fully deaerated solution.

The basis for a fully-coupled transient mixed-potential model has been developed. This model, referred to as the Copper Sulphide Model (CSM) couples the interfacial reactions (including film formation) to mass-transport, adsorption/desorption, redox, and precipitation/dissolution processes in the clay-based sealing materials surrounding the canister. The reaction mechanism has been defined and the mathematical basis for the model described in some detail.

The basis for the model and the results of preliminary simulations will be presented.

## Could one transfer corrosion modeling expertise from reactor to disposal systems?

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### Abstract

During the course of the last decade the corrosion group at SCK•CEN walked an evolutionary path in respect of stress corrosion crack (SCC) modelling for *nuclear reactor systems*. The main threat throughout the development has been our pursuit to calculate environmental conditions in arbitrary geometries. This separation of the scientific basis from the geometry will eventually allow comparison between laboratory and component results. A similar approach would be relevant to nuclear waste disposal systems where the link between short-term and long-term results is to be guaranteed by the scientific basis of the models.

Our roadmap for the development of modelling activities relevant to corrosion issues in nuclear reactor systems contained mixed potential, crevice corrosion, crack growth rate and oxide film topics.

*Mixed potential modelling* - Electrode kinetics in flowing media are often represented by generalized Butler-Volmer equations. These have been modified to base them on local rather than bulk concentrations. Local concentration-based Butler-Volmer equations have been derived for two systems: 304 stainless steel in dilute sulphuric acid solutions (BWR-relevant) and 316 stainless steel in boric acid – lithium hydroxide solutions (PWR-relevant).

*Crevice corrosion modelling* – Crevices are invariably present in engineering structures. Hence, it is of interest to develop the ability to predict which geometries will, or will not, lead to crevice corrosion. Many crevice corrosion theories are floating around in the literature and their applicability depends on the material-environment combination. Two systems have been studied: mild steel under anodic polarization in a sodium acetate – acetic acid buffer solution and aluminium in a sodium chloride solution. The onset of crevice corrosion is respectively believed to be determined by a critical potential drop and a critical species' concentration. In both cases, these critical values can be translated, by computation, into a critical characteristic crevice dimension determining the onset of crevice corrosion. Furthermore we co-developed ECHEM316PWR to predict the electrochemistry in 316 stainless steel crevices exposed to PWR-relevant conditions, including reduced reaction set radiolysis.

*Crack growth rate modelling* – In our approach to SCC propagation modelling we consider two driving forces, an electrochemical and a mechanical. In terms of a film rupture model these are, respectively, the electrode potential and the strain rate at the crack tip. In CGR304H<sub>2</sub>SO<sub>4</sub> (crack growth rate for 304 stainless steel in dilute sulphuric acid solutions) and CGR316Bli (crack growth rate for cold-worked 316 stainless steel in boric acid – lithium hydroxide solutions) the electrochemical conditions are calculated by computational electrochemistry and the crack tip strain rate using an analytical

expression. CGR304H<sub>2</sub>SO<sub>4</sub> contains pre-calculated case, whereas CGR316Bli calculates crack growth rates on the fly.

*Oxide film modelling* – Stainless steel and nickel-based alloys rely on an oxide layer for their resistance to uniform corrosion, making them susceptible to crevice corrosion and SCC. Hence, the performance of the oxide layer is of utmost importance. A point defect model with mixed electron conduction is being considered for modelling the behaviour of the oxide film. Up to the present we have modelled a artificial bi-carrier mono-layer oxide film, including film growth and/or potential transient.

In respect of *nuclear waste disposal systems* it are especially the mixed potential and oxide film topics that need to be addressed first. They set the scene for the general corrosion loss. Later, if needed, the crevice corrosion, crack initiation and crack growth topics can be dealt with. At SCK•CEN we strive for a generalized, kinetic oxide film model that could be applied to low alloy steels, stainless steels and nickel-based alloys. Hitherto, oxide film modelling has to be progressed beyond the state-of-the-art to multiple-layer, passive oxide films for alloys.

## The anaerobic corrosion of carbon steel and the potential influence of sulphur species

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### **Abstract**

The conditions in geological radioactive waste repositories are expected to become anoxic within a relatively short period after closure, due to consumption of residual oxygen by microbial and geological processes. Under these conditions any iron or carbon steel in the repository is expected to corrode anaerobically, resulting in the generation of hydrogen and a solid iron corrosion product, such as magnetite or ferrous hydroxide. In some repository concepts a wide range of sulphur species may be present, depending on the oxidation state of the sulphur. Most laboratory studies carried out to date to investigate the anaerobic corrosion process and to measure the anaerobic corrosion rate in the absence of microbial activity have been carried out in the absence of sulphur species. This paper will (i) provide an overview of the anaerobic corrosion processes affecting carbon steel in the repository environment, (ii) summarise the properties of the sulphur-based species that may be present in the aqueous phase in contact with iron-based waste containers, (iii) review the limited amount of literature data available on the effect of sulphur on the anaerobic corrosion process, (iv) consider how the sulphur-based species present may affect the anaerobic corrosion of carbon steel, based on a discussion of the fundamental electrochemical and thermodynamic principles determining corrosion behaviour, (v) identify areas requiring further research.

## The influence of chloride on the corrosion of copper waste containers in aqueous sulphide solutions

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### Abstract

The remote production of sulphide, either from mineral redox processes or by the action of sulphate reducing bacteria on groundwater sulphate, and its transport to the container surface could lead to corrosion of copper nuclear waste containers. In the presence of sulphide, copper becomes unstable in water, and corrosion would lead to the accumulation of copper sulphide films on the container surface. The formation and properties of these films have been studied using a range of electrochemical, corrosion, and surface analytical techniques. In this paper, the influence of chloride, varied over the concentration range 0.1 mol/L to 5.0 mol/L, will be described.

Scanning electron microscopy shows that a bilayer of  $\text{Cu}_2\text{S}$  is formed under natural corrosion conditions; a thin base layer, which partially passivates the copper, and an outer deposited layer, which is less protective. Electrochemical impedance spectroscopy was used to follow the development, and monitor the properties, of the sulphide film. The ability of the base layer to protect the copper decreases as the chloride concentration increases. Increasing chloride concentration leads to the opening of pores in the base layer, allowing enhanced corrosion, possibly due to the high chloride to sulphide ratio in the pores. This would enhance the dissolution and transport of Cu, as  $\text{CuCl}_2^-$ , out of the pores. SEM observations also indicate that the outer layer deposit is less protective. Whether or not this indicates the soluble copper (as  $\text{CuCl}_2^-$ ) is not as readily redeposited (as  $\text{Cu}_2\text{S}$ ) at high chloride concentration is under investigation.

## Interactions between sulphide species and components of rust

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### Abstract

The kinetics of corrosion expected for the overpack in the disposal concept for high-level nuclear waste are low and will stay low if the somehow protective rust layer that will develop initially on the steel surface keeps undamaged. Local changes of the physico-chemical conditions may however degrade this layer, inducing localised corrosion processes that could, provided that they are autocatalytic, lead to catastrophic kinetics of corrosion, similar to those encountered on steel structures in marine environments, often associated with sulphate reducing bacteria.

In order to estimate the probability of a localised corrosion phenomenon induced by sulphide species on the steel surface of the overpack, the interactions between sulphide and various components of rust are to be studied. Two kinds of effects could be involved, depending on the oxidation number of Fe: (1) the reductive effect of S(-II) could lead to a dissolution, at least partial, of the Fe(III) compounds (e.g.  $\alpha$ -FeOOH or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and (2) the low solubility of iron sulphides could lead to a dissolution of Fe(II) compounds (e.g. FeCO<sub>3</sub>) and reprecipitation of FeS. In a preliminary study, goethite  $\alpha$ -FeOOH and lepidocrocite  $\gamma$ -FeOOH were prepared. The powder obtained was then placed in Na<sub>2</sub>S solutions at various pH values and left in anoxic conditions. The products resulting of the interactions of S(-II) with Fe(III) oxyhydroxides were analysed by micro-Raman spectroscopy. Similarly, suspensions of FeCO<sub>3</sub> were synthesized from FeSO<sub>4</sub> and NaHCO<sub>3</sub> solutions. The products obtained after addition of Na<sub>2</sub>S were analysed by micro-Raman spectroscopy and X-ray diffraction.

Micro-Raman spectroscopy was chosen as the main analytic tool for this study since it is the most suitable method for the characterisation of the corrosion products generated by localised corrosion processes. As the Raman data of iron sulphides are scarce, it proved necessary to synthesise and characterise iron sulphides in order to interpret our results. This study allowed us to describe the evolution of the Raman spectrum of FeS with dehydration, crystallisation and oxidation.

## Biographies

### Robert Gens

Robert Gens obtained his PhD in Radiochemistry, regarding the study of thermodynamic and structural properties of complex perovskite oxides of actinides, from the University of Liège in 1985. From 1986 till 1988, he was the reactor radioisotope production manager at the National Institute for Radioisotopes in Fleurus (IRE, Belgium), where he was in charge of the production and conditioning of fission products (reprocessing of highly enriched irradiated uranium targets) and activation products (radioactive sources, labelling of compounds) for medical and industrial applications. He joined the Belgian Agency for Radioactive Waste and Enriched Fissile Materials (ONDRAF/NIRAS) in 1989. First, he was active in the field of treatment and conditioning of radioactive waste at the Study and Project Department (1989-1991). Then, he moved to The Technical Operations Department (1992-1995) where he was mainly involved with activities focused on the characterisation and compatibility studies with host rock of conditioned radioactive waste and the establishment of waste acceptance criteria. From 1996 up to now, he is working at the Final Disposal HLW Department (main field of activity: near field phenomenology).

### Bruno Kursten

Bruno Kursten has almost 15 years of experience in the field of materials science, metal corrosion, electrochemistry and surface analysis techniques. He obtained an engineering degree with a major in chemistry (KHO, Belgium) in 1988 and a university degree in metallurgy from the Free University of Brussels (VUB, Belgium) in 1992. He joined the Belgian Nuclear Research Centre (SCK•CEN) in 1993 where he has been in charge of the corrosion studies of candidate metallic container materials (mainly carbon steel and stainless steels) in argillaceous and cementitious environments in the framework of the geological disposal of long-lived highly radioactive waste. He has been involved in the set-up and/or analysis of the corrosion aspects of several other national and European projects such as CERBERUS (investigation of the influence of  $\gamma$ -radiation), CORALUS (integrated *in-situ* experiment), OPHELIE (on-surface demonstration test) and PRACLAY (*in-situ* simulation of a disposal gallery). He has authored or co-authored over 30 scientific publications.

### Pierre De Cannière

Pierre De Cannière is a nuclear chemist with a PhD in Sciences from the Louvain University (Belgium) in 1989. He has 18 years of experience in the geoscientific aspects of radioactive waste management. He joined the Belgian Nuclear Research Centre (SCK•CEN) in 1990 to conduct R&D projects on clay characterisation and radionuclide and gas transport. He is working on a variety of scientific and industrial projects including diffusion and sorption of radionuclides in clay, the geochemical characterisation of clay, and various perturbations comprising pyrite oxidation and the effect of reductive disturbance induced by sulphate-reducing bacteria on clay. He has contributed to various multidisciplinary studies dealing with the mineralogical and geochemical characterisation of *in situ* and on-surface experiments studying the effects of heat and radiation on clay (Cerberus test and large-scale Ophelie mock-up). In the frame of these experiments he contributed to evidence reduced-sulphur species (thiosulphate and free sulphide) in Boom Clay and bentonite and to the study of the chemical boundary conditions prevailing in Boom Clay for metal corrosion. He is also involved in the geochemical and diffusion

studies at the Mont Terri rock laboratory in Switzerland and at the Andra underground laboratory of Meuse and Haute Marne at Bure in France.

### **Digby D. Macdonald**

Dr. Digby D. Macdonald has been a professor at PSU since 1991 and has held the title of Distinguished Professor of Materials Science and Engineering for the past five years. From 1991 until 1999 he served as Director of the Center for Advanced Materials at PSU and is currently Director of the Center for Electrochemical Science and Technology at Penn State. Prior to that, he served as Director of the Chemistry Laboratories and as Director of the Materials Research Laboratory at SRI International (1984–1991), Vice President of the Physical Sciences Division at SRI (1998/1999, while on leave from PSU), and Director of the Fontana Corrosion Center at Ohio State University (1979–1984). He is a native of New Zealand, coming to the US in 1977. He has been a US citizen since 1984. While discharging these administrative responsibilities, he has maintained very active personal research program of not less than \$1 million per year, resulting in the publication of more than 700 peer reviewed papers and contributions to conference proceedings, presentation of more than 500 seminars, and the publication of one book. He has been honored for his work by winning many awards, including the Whitney Award from NACE International; the W. B. Lewis Memorial Lecture from Atomic Energy of Canada, Ltd., for his contributions to the development of nuclear power in the service of mankind; the Wagner and Uhlig Awards from the Electrochemical Society; and the 2002 UR Evans Award from the British Corrosion Institute. In 2006 he was the recipient of the 20<sup>th</sup>. Khwarazimi International Award in fundamental science. He is also Fellow of NACE International, Fellow of the Electrochemical Society, Fellow of the International Society of Electrochemistry, Fellow of the Royal Society of Canada, Fellow of the Royal Society of New Zealand, Fellow of ASM International (of which he is also a Trustee), Fellow of The Corrosion Institute (UK), and Fellow of the World Innovation Foundation. From 1993 to 1997, he served as a member of the USAF Scientific Advisory Board (SAB), where he participated in studies of aging aircraft, logistics, and hypersonic flight. During this term he held the protocol rank of Lieutenant General in the US Air Force. He also chaired the Materials Panel in the SAB New World Vistas study. He was awarded the US Air Force Medal for Meritorious Civilian Service in 1997. Over the past five years he has been recognized as a ISI "Highly Cited Researcher".

### **Liane Smith**

Liane Smith has 27 years experience as a materials and corrosion expert in the Oil and Gas industry. After 10 years with the Shell Group of Companies she set up Intetech Ltd in 1991 to provide consultancy internationally. Her work has taken her to many of the major oil and gas producing regions of the world, including some of the most aggressive environmental conditions, both internally and externally. She has been involved in the selection of materials for "sour" fields, producing hydrogen sulphide and elemental sulphur. She formed the European Federation of Corrosion Working Party for the Oil and Gas Industry and chaired it for 5 years, during which it published key guideline documents on materials for sour service. Those guidelines were incorporated within the ISO standards now used internationally.

## **Damien Féron**

Damien Féron is working at the French Atomic Energy Commission (CEA), in the field of nuclear corrosion since 30 years. He has a PhD on chemical engineering from the "Institut National Polytechnique de Toulouse – INPT". He has been the Head of the "Laboratory of Physico-Chemistry and Corrosion – LPCC" and then the Head of the "Laboratory of Aqueous Corrosion – LECA". He is presently Director of Research at CEA, chairman of the "Science and Technology Advisory Committee – STAC" and of the "Working Party on nuclear corrosion" of the European Federation of Corrosion (EFC). He is one of the two French representatives at the International Corrosion Council (ICC). He owns four patents and is the author or the co-author of more than 100 papers and has been involved in the edition of several books, mainly on biocorrosion, seawater corrosion and nuclear corrosion. He received the "Grande Medaille" of the CEFRACOR, the French corrosion association.

## **Virginia Madina**

Virginia Madina is BS/MS in Chemistry. Since 1991 she has been working as research scientist at INASMET. INASMET is a non-profit Technological Center created in 1962 in San Sebastián (Spain), focusing on material technologies and their processes. INASMET is a member of the TECNALIA technological corporation employing 1300 people.

Currently, her work interests lie in the Materials and Reliability Department within the Energy Unit. Her activity is mainly focused in the following fields:

- Corrosion, high temperature and metallic characterization of materials,
- Materials and components for solar renewable energy applications, and
- Management of High Level Radioactive Wastes (HLW), particularly in the selection of metallic materials for the fabrication of containers for deep geological disposal of HLW, in collaboration with the Spanish Nuclear Waste Management Agency (ENRESA).

## **Sébastien Roux, Françoise Feugeas**

Françoise Feugeas is associate professor at the Strasbourg Graduate School of Science and Technology (INSAS). She is graduated from the Strasbourg National School of Arts and Industry (ENSAIS now called INSAS) as civil engineering engineer and graduate from the Strasbourg Louis Pasteur University as material science Doctor. Her PhD was about carbon and stainless steel biodeterioration.

Sébastien Roux is graduated from the Strasbourg Graduate School of Science and Technology (INSAS) as mechanical engineer graduate from the Strasbourg Louis Pasteur University as engineering science Doctor. His PhD at the LGECO-LISS concerned concrete biodegradation and was directed by Françoise Feugeas and Alain Cornet (professor). Françoise Feugeas and Sébastien Roux work about concrete biodeterioration and the efficiency of different techniques to increase the resistance of environmental friendly concrete to natural media.

## **Hicham EL HAJJ**

Hicham EL HAJJ is a graduate of a master public health and environmental, option evaluation and management of environmental and professionals risks at the University Henri Poincare-Nancy-France. He is working on a thesis in subatomic physics laboratory and associated technologies (SUBATECH, Nantes, France), department of radiochemistry. Within the group of laboratories "Glass-Iron-Clay" ANDRA, this thesis explores the process of corrosion storage materials in the presence of indigenous microorganisms of argillite.

## **Fraser King**

Dr. Fraser King has B.Sc. and Ph.D. degrees in chemistry and electrochemistry from Imperial College of Science and Technology, University of London, U.K. He is a Fellow of the National Association of Corrosion Engineers (NACE International), a member of the American Nuclear Society, the Electrochemical Society, and the Canadian Institute of Chemistry, and was elected to serve on the NACE International Research Committee in 2004.

Fraser has 25 years experience in corrosion, materials science, and applied electrochemistry in the nuclear and oil and gas industries. His research interests include: corrosion, applied electrochemistry, lifetime prediction, safety and risk assessments, reactive-transport modelling, environmental impact analysis, the design, fabrication, and performance of nuclear waste containers, the performance of used nuclear fuel under disposal conditions, corrosion of reactor and steam generator components, and the chemical cleaning of nuclear steam generators.

Dr. King is a consultant for nuclear waste management programs in Canada, Sweden, Switzerland, Finland, Japan, the United States, and the IAEA in the areas of waste container performance and used fuel alteration. More recently, Fraser has also become involved in the assessment of the performance of L&ILW containers during both storage and disposal in a deep underground repository.

## **Marc Vankeerberghen**

Marc Vankeerberghen obtained his university degree in engineering from the Katholieke Universiteit Leuven (Belgium) in 1983. After some post-graduate research at the University of the Witwatersrand (South Africa), he worked in the research department of large South-African corporations (Boart International, Atlas Aircraft, and De Beers). In the meantime he obtained a post-graduate degree in control engineering and was trained in middle management. Upon his return to Belgium in 1993 he joined the Belgian Nuclear Research Centre (SCK•CEN). First, he was involved in nuclear plant decommissioning. Then, from January 1995 he was seconded to the Halden Reactor Project in Norway, where he mainly performed data-analysis of nuclear fuel experiments. Upon his return to SCK•CEN in 1996 he joined the corrosion group, where he has been driving the modelling activities. In this context he was a visiting scientist at Penn State University in 2000. The main thread throughout his career has been the modelling of equipment and processes. Presently that entails stress corrosion cracking and oxide film modelling.

## **Nick R. Smart**

Nick Smart obtained a B.Sc. in Chemistry from Bristol University before joining the United Kingdom Atomic Energy Authority at Harwell laboratory in 1979. After two years working with surface analysis techniques he joined the corrosion team, where he obtained an

M.Sc. from UMIST in 1986 by research into the electrochemical mechanisms of stress corrosion. Since the early 1990s, he has worked on a wide range of corrosion projects related to radioactive waste disposal in the U.K., Sweden, Switzerland and Belgium. He became the leader of the corrosion team at Culham, U.K. in 2000. Since 2001 he has worked for Serco Technical and Assurance Services.

### **Philippe Refait**

Philippe Refait is a materials science engineer (ESSTIN – Univ. Nancy 1, France) with a PhD in materials science (Univ. Nancy 1, France). He is a professor at the University of La Rochelle (France) and a researcher at the Laboratoire d'Etude des Matériaux en Milieux Agressifs (LEMMA), where he is in charge of the research axis 'Corrosion in aqueous media and marine environments'. His main fields of expertise include corrosion of iron and steel, rust (iron oxides, oxyhydroxides and hydroxysalts, sulfides, etc.), electrochemistry and materials characterisation by Raman and IRTF Spectroscopy and X-ray diffraction.