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Insight

Corrosion issues in nuclear industry today

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In the context of global warming, nuclear energy is a carbon-free source of power and so is a meaningful option for energy production without CO₂ emissions. Currently, there are more than 440 commercial nuclear reactors, accounting for about 15% of electric power generation in the world, and there has not been a major accident in over 20 years. The world's fleet of nuclear power plants is, on average, more than 20 years old. Even though the design life of a nuclear power plant is typically 30 or 40 years, it is quite feasible that many nuclear power plants will be able to operate for longer than this.



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The re-emergence of nuclear power today is founded on the present generation of nuclear reactors meeting the demands of extended service life, ensuring the cost competitiveness of nuclear power and matching enhanced safety requirements. Nuclear power plant engineers should be able to demonstrate such integrity and reliability of their system materials and components as to enable nuclear power plants to operate beyond their initial design life.

Effective waste management is another challenge for sustainable nuclear energy today; more precisely, a solution is needed for the management of high-level and long-lived intermediate-level radioactive waste over the very long term. Most nuclear countries are cur

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Nuclear power plants

At the forefront of the energy challenge is the necessity of operating plants for as long as possible in a safe and cost-effective manner. In order to fulfill such a task, the ageing of materials, components and structures must be kept under control.

Nuclear power plants have suffered various failures through corrosion since the 1970s, costing the industry billions of euros. By design, supposedly highly corrosion resistant alloys have been used, such as Ni-based alloys, stainless steels and Zr alloys. However, the field is rich with examples of corrosion failures of these alloys. A comprehensive review of these failures would require too many pages, so this article focuses on just some of the major forms of corrosion.

Materials in nuclear power plants

Although there are several types of nuclear power plants (NPPs), pressurized water reactors (PWRs) and boiling water reactors are the most common. [Fig. 1](#) presents the schematic layout of a PWR.

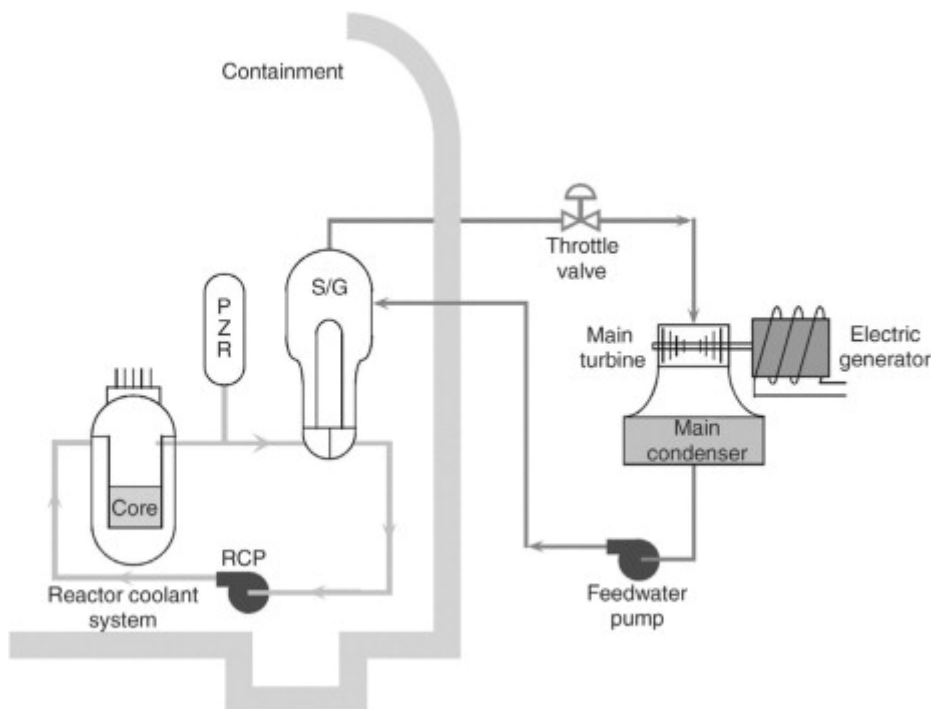
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Fig. 1. PWR general layout. (Reproduced from the NRC website.)

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connected to the electric generator; it is then condensed and the cold water returns to the SGs through feedwater pumps. A throttle valve sets the reactor power.

In a BWR, the steam generated by the core in the reactor pressure vessel (RPV) goes straight to the main turbine as there are no SGs in this type of NPP.

The main metallic materials used in PWRs and BWRs are:

- Ni alloys, also known as Inconels®, which contain 15% Cr (alloys 600 and 182), 20% Cr (alloy 82) or 30% Cr (alloys 690, 52 or 152). These alloys are mainly used for SG tubes (alloys 600 and 690), some RCS penetrations (RPV top and bottom heads) and RCS welds (alloys 182, 82, 52 and 152). Alloy 800 (Incoloy® 800), which is not a Ni-based alloy but contains 33% Ni and 22% Cr with 45% Fe, is also used mainly for SG tubes. The alloys used for SG tubes (mainly alloys 690 and 800) are selected for their good general or stress corrosion resistance, along with high mechanical properties.
- Stainless steels (SSs). The most typical are the 300 ASTM series (304, 308, 309, 316, 321, 347), which contain around 10 wt% Ni and 20 wt% Cr, some containing other elements such as Mo and Ti. The vast majority of the components holding radioactive water or gas are made of SSs: RCS pipes and welds, RPV cladding, RPV internals, RCPs, piping, welds, pumps, valves, heat exchangers of the various nuclear systems (e.g. chemical and volume control system, safety injection systems, reactor residual heat removal system) and some condenser tubes. ASTM 400 series (403, 405) steels are also used, but to a lesser extent. SSs are selected for their good corrosion resistance.
- Zr alloys. Zr alloyed with elements such as Nb, Sn or Fe is used as cladding for fuel rods. Zr is selected because of its low tendency to capture neutrons. Zr alloys also exhibit good corrosion resistance, along with high mechanical properties.
- Low alloyed steels. In terms of mass, low alloyed steels (and carbon steels) are prevalent in NPPs. They are used for the RPV, SG shells and tubes support plate, most PWRs balance of plant pipes, turbine casing, etc. Cost and mechanical properties are the main drivers for the selection of low alloyed steels.
- Copper alloys. These alloys are mainly found in condenser tubes and balance of plant heat exchangers. Copper alloys have good corrosion resistance, together with a very high heat transfer coefficient.
- Ti is used in the condenser tubes of seashore plants. Ti is very seawater corrosion resistant and has very high mechanical properties.

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microbiologically influenced corrosion (MIC). Examples of some of these forms of corrosion are presented below.

Stress corrosion cracking can be trans- or intergranular. However, in primary water, SCC is mostly intergranular. To occur, SCC needs a combination of three factors: a susceptible material, an aggressive environment and high stresses. 15% Cr—Ni alloys have proven to be very susceptible to primary water SCC (PWSCC). The most common problems concern alloy 600 and 182 failures, such as in steam generator tubes (Fig. 2), RPV head penetrations and pressurizer nozzles. These cracks and leaks lead to repairs (pressurizer nozzles) or replacements (SGs, RPV upper head). The replacement alloys (690, 52, 152) are much more resistant to SCC, probably because of their higher Cr content. SCC is probably the major corrosion issue in PWRs and BWRs with IASCC.

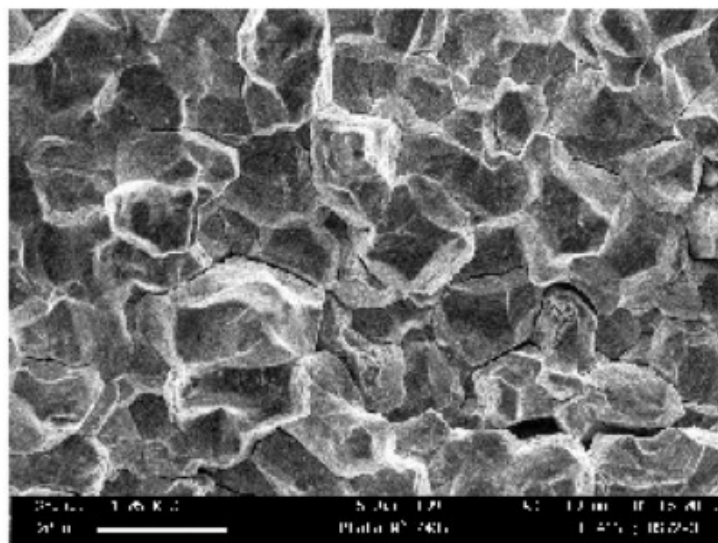
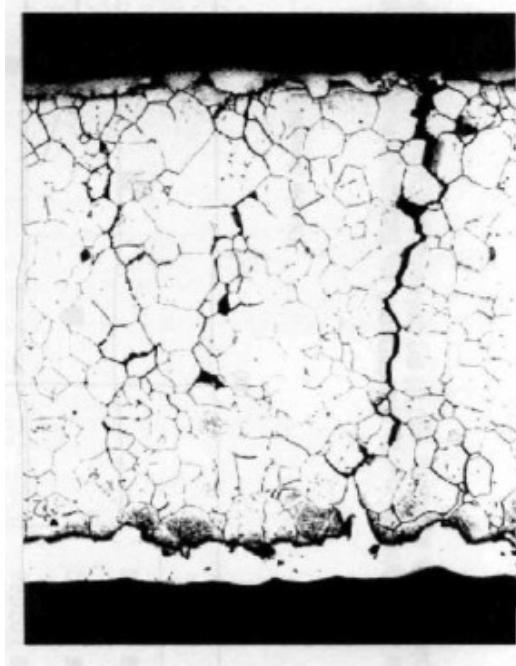
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Fig. 2. Stress corrosion cracking observed on a steam generator tube made of alloy 600.

Irradiation-assisted stress corrosion cracking, like PWSCC, requires a susceptible material, an aggressive environment and high applied stresses. However, whereas in PWSCC the material is susceptible when the exposure to the environment begins, in IASCC the material becomes

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air. Some 403 turbine blades have failed under EAC.

In theory, **intergranular attack**, which is a uniform attack of all grain boundaries, can occur without any stress. However, low stresses can increase the IGA rate. When the electrochemical potential shifts and stresses are high enough, IGA can develop into SCC. One typical example of IGA is the corrosion that occurs in flow-restricted areas of SGs equipped with mill-annealed alloy 600 tubes. The integrity of the SG tubes can be challenged with very significant IGA. This problem can be solved by replacing alloy 600 with alloy 690.

Flow-assisted corrosion is generally attributed to the presence of two-phase flow with high velocities and water droplet impingement, and sometimes to the presence of abrasive magnetite particles. The consequence of FAC is wall thinning, which can lead to pipe leak or burst if not properly monitored or managed. FAC can be mitigated by adjusting the pH of the water, increasing the Cr content of the carbon steel pipes or using SSs.

General corrosion is widespread in NPPs, affecting almost all kinds of materials. However, the three most worrisome GC types are:

- the GC of fuel cladding. By picking up oxygen from the reactor water, Zr alloys can oxidize to form zircon. Too thick a layer of zircon can lead to an increased oxidation rate, clad thinning (when the zircon peels off) and eventually clad rupture. Over the years, better GC-resistant Zr alloys have been developed to minimize these risks;
- the GC of steam generator tubes made of Ni alloys. These tubes release Ni, which can be activated into radioactive Co in the core and generate doses rates. The reactor water can be chemically conditioned to minimize this GC;
- the GC of feedwater carbon steel piping can foul the SGs, inducing their loss of performance or power output. The chemical conditioning of the water can be optimized to minimize this GC.

Ammonia or similar amines are used for the conditioning of water—steam systems. Ammonia can concentrate, along with residual air, in the coolest area of condensers. Some Cu alloys, such as brass, can suffer from corrosion in these areas. **Ammonia corrosion** can be mitigated by replacing Cu alloys with SS.

Microbiologically influenced corrosion may occur in all systems where natural waters are used and particularly in those systems, such as fire protection systems, that are composed of stagnant lines at room temperature. These lines are often conditioned with phosphate-based chemicals. These conditions are favorable for anaerobic bacteria to develop. Pits have been

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However, over the years, the nuclear industry has developed techniques to mitigate or minimize the consequences of all the various types of corrosion. During the last decade, the most relevant phenomena affecting the plant availability and the plant lifetime management include various forms of SCC (PWSCC, IASCCS and IGSCC) on the one hand and FAC on the other. Great expertise has been built up by facing the ageing issues of existing NPPs, based on the analysis of a wealth of experience (more than 1000 reactor-years in France, for instance, for PWRs), and the very close link between fundamental knowledge and operational decisions. Much progress still needs to be made to understand, simulate and predict the degradation mechanisms that could affect existing NPPs: corrosion and stress corrosion cracking of austenitic alloys, thermal fatigue, corrosion fatigue, irradiation-assisted corrosion, behaviour of oxide layers, polymers and concrete ageing are all major issues today, with the emphasis on replacement materials like alloy 690.

Nuclear waste disposal

The generally accepted strategy for dealing with high-level nuclear waste (HLNW) is deep underground burial in stable geological formations. The purpose of the geological repository is to protect both man and the environment from the possible impact of radioactive waste by interposing various barriers capable of confining the radioactivity for several hundreds of thousands of years. These barriers include packages containing the waste, repository installations and the 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 radionuclides into the biosphere, is applied in all the geological repositories across the world. These issues have been already discussed, compared and explored with the corrosion community, which faces the challenge of predicting corrosion over millennia on a scientific and technical basis. The scientific and experimental approaches of various organizations worldwide have been compared to predict long-term corrosion phenomena, including corrosion strategies for interim storage and geological disposal, not only during workshops^{1, 2} and congresses, but also in specific programmes devoted to these exchanges, like the COBECOMA in Europe³. Among the factors being compared, the following should be emphasized: very different underground host rock formations (together with buffer materials, if any) are being considered as potential disposal environments within nuclear countries (Table 1). The compositions of the various potential host rock formations (including unsaturated systems) vary greatly. The composition significantly influences the selection of the candidate container and overpack materials. A wide variety of metallic materials have been investigated as candidates by a number of national corrosion programmes, which have all developed separately and not with the same agenda.

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Country	Waste Type	Overpack	Buffer Material	Host Rock	Temperature max. at overpack surface
Belgium	HLRW	carbon steel	Portland cement	Boom Clay	~95°C
	SF				
Finland	SF	Copper	Bentonite	Granite	~70-90°C
France	HLRW	Non-alloy steel	None	Callo-Oxfordian	~90°C
	SF	(alternative: passive alloys)	Bentonite	Clay	
Sweden	SF	Copper	Bentonite	Granite	
Switzerland	HLRW	Non-alloy steel	Bentonite	Opalinus Clay	~90°C
	SF	–	Bentonite		~140-160°C
USA	SF	Ni-Alloy (C-22)	None	Tuff	250°C
		(Ti grade 7 for drip shield)	non-saturated environment		

HLRW = High Level Radioactive waste/SF = Spent Fuel

16-, K.B.S. Rao, MRS bulletin, Vol. 33, pp 327-337, April 2007

Materials for nuclear waste disposals

Over the years, two basic approaches have been considered to potentially satisfy the lifetime requirement imposed on the waste overpack: the corrosion-resistant and the corrosion-allowance concepts⁴.

- In the corrosion-allowance concept, materials (e.g. carbon steel, Cu in oxidising environments) corrode at a significant but low and relatively predictable rate. These materials can be used if sufficient thickness is allowed for the depth of corrosion expected during the desired lifetime.
- In the corrosion-resistant concept, relatively thin and highly corrosion-resistant materials are relied upon to provide the required container lifetime. Corrosion-resis

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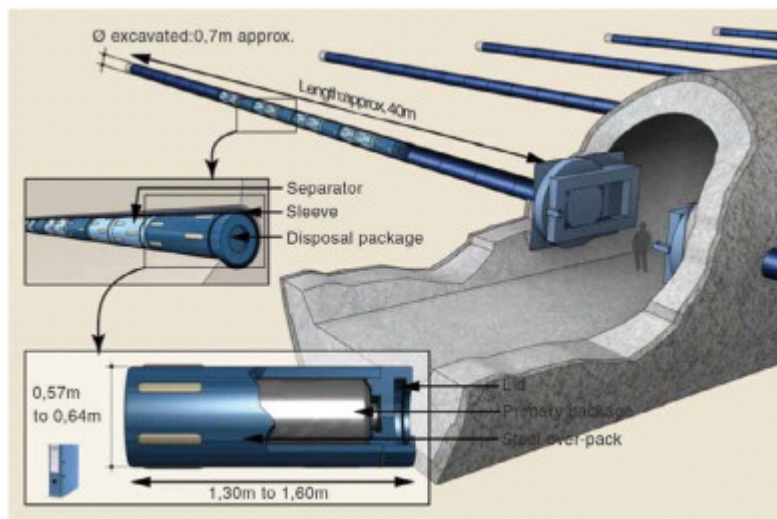
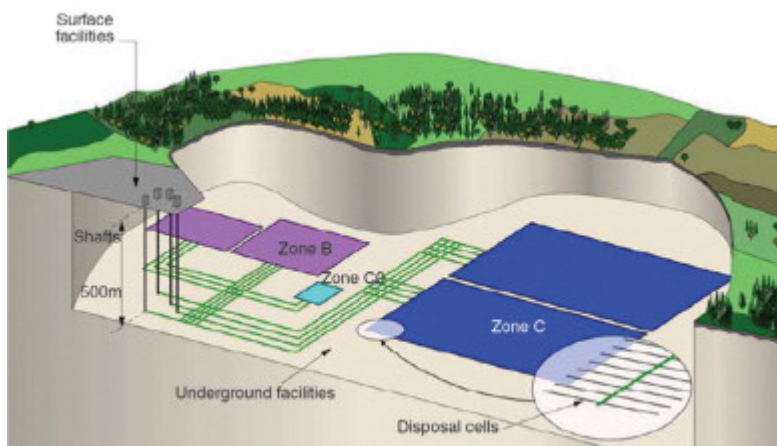


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into account, because this can cause sudden large and unpredictable increases in the rate of corrosion.

Evaluating the suitability of candidate container materials for the disposal of HLW/SF in deep geological formations (rock salt, clay, granite, tuff) and predicting the corrosion performance of waste containers over long periods of time have presented a worldwide challenge from the materials, engineering and corrosion points of view for several decades. In the French concept, the overpack (or sur-container) not only forms part of the high-integrity barriers but is also a major component of the reversibility that is required for the French geological repository. Reversibility means the possibility of retrieving emplaced packages as well as of intervening and modifying the disposal process and design. Long-term safety and reversibility are the guiding principles that have led to the basic layout of the geological repository in an argillaceous formation shown in Fig. 3. This concept integrates safety from the very first phases of the design and allows the progressive orientation of choices toward solutions offering the greatest robustness with respect to knowledge uncertainties, and introducing prevention and protection measures against identified risks. The overall approach is iterative.



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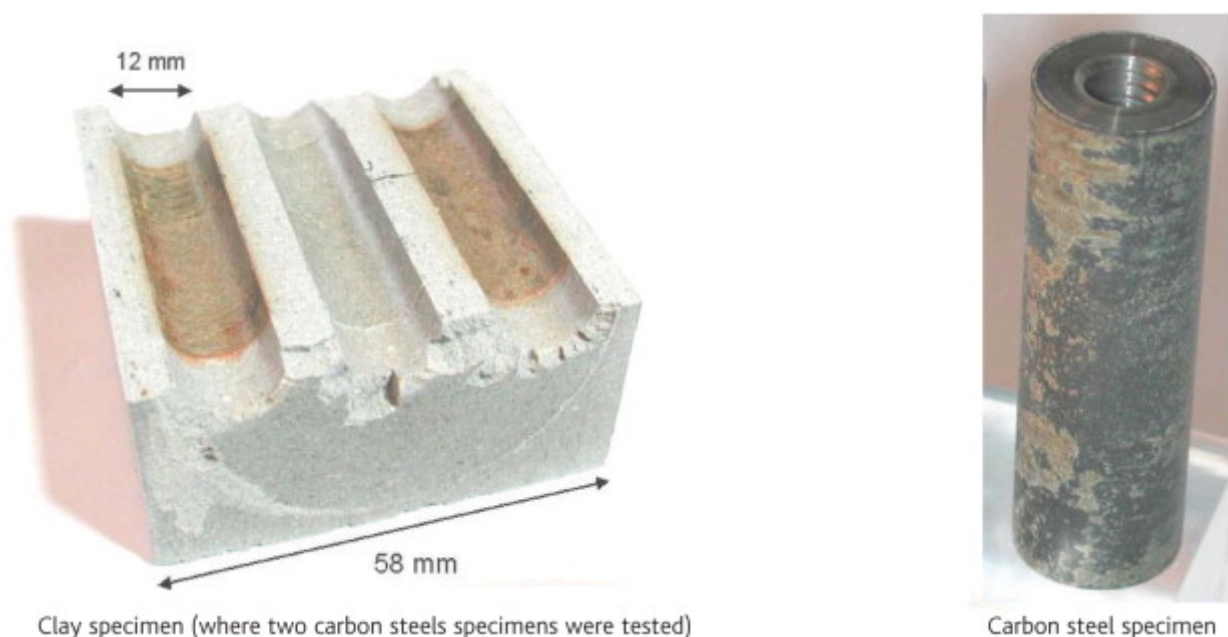
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access shafts. Waste package management such as reception and conditioning is performed in surface installations.

Corrosion behaviour

Much knowledge has been gained about the corrosion behaviour of metallic materials over periods of several thousands of years, but this base needs to be developed further. As pointed out in the introduction to the first Workshop on 'Prediction of Long Term Corrosion Behaviour in Nuclear Waste Systems'⁶, the lifetimes of most industrial materials range from a few seconds or minutes (e.g. rocket engines) to several tens of years for nuclear power plants, and up to a hundred years or more 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. The international approaches to demonstrate the feasibility of predicting corrosion of non-alloy steels over long periods of time are based on the following:

- Data from experimental studies are compared to those obtained by other international laboratories, and semi-empirical models are developed in order to perform initial estimations of service lifetimes and demonstrate their feasibility. These include corrosion rate evaluations, parametric investigation and observations of the corrosion products (Fig. 4).

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- Predictive models should be based on the mechanisms of corrosion phenomena in order to be robust and reliable, and are currently under development. Mechanistically based models also lead to an improved understanding of damage evolution.
- Archaeological artifacts are used to demonstrate the feasibility of long-term storage and to provide a database for testing and validating the models. Investigation of artifacts appears to be a promising approach for validating deterministic models, provided that the limitations of the archaeological data are understood and recognized.

Of course, these steps are iterative and allow the progressive orientation of choices toward solutions offering the greatest robustness with respect to the evolution of the knowledge. During these iterations, some corrosion phenomena will be confirmed as being unimportant during the repository lifetime, such as microbial corrosion, stress corrosion cracking and hydrogen embrittlement, evolution of the near-field environment (e.g. the evolution of hydrogen from corrosion), corrosion evolutionary path, coupling between the near-field and far-field environments, and long-term materials ageing.

Conclusion

In the past few decades, nuclear materials scientists and engineers have accumulated a wealth of experience in the behaviour of materials used in the present generation of nuclear power plants. To understand, simulate and predict the degradation mechanisms that could affect existing NPPs, are the ongoing developments which assume the integrity and the reliability of materials to operate NPPs beyond their initial design life. The feasibility of deep geological waste repositories is the subject of sustained research, and requires an increase in our fundamental knowledge of corrosion processes and the accurate prediction of corrosion behaviour over millennia.

Furthermore, the increase in the global energy demand, coupled with an increasing awareness of environmental issues, has prompted the development of next-generation nuclear energy systems. High temperature reactors of Generation IV are for tomorrow (the first prototypes are planned by 2020), while fusion-type reactors are expected by the end of the century. The success of these international initiatives depends mainly on the development of suitable materials that are able to withstand high temperatures and the environments which become aggressive at these high temperatures (supercritical water, helium at 800-100°C, molten salts, liquid metals, etc.). The corrosion and compatibility of a wide range of new materials

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