

# Nuclear Corrosion: Achievements and Challenges

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Corrosion science faces new challenges in various nuclear environments. Three main areas may be identified where increases of knowledge and understanding have been done and are still needed to face the technical needs: (i) the extension of the service time of nuclear power plants from 40 years, as initially planned, to 60 years and probably more as expected now, (ii) the prediction of long term behaviour of metallic materials in nuclear waste disposal where the corrosion processes have to be predicted over large periods of time, some thousands years and more, (iii) the choice of materials for use at very high temperatures as expected in Generation IV power plants in environments like gas (helium), supercritical water, liquid metals or salts. Service time extension, deep geological waste repositories and high temperature reactors sustain researches and developments to model corrosion phenomena at various scales, from atoms to components.

*Keywords* : corrosion, generation 4, nuclear energy, nuclear power plant, nuclear waste disposal

## 1. Introduction

Nuclear energy is a carbon-free source of power and so a meaningful option in the context of global warming. At the end of 2013, 434 commercial nuclear reactors were in operation, including the 4 reactors connected to the grid during 2013, and 72 nuclear power plants were under construction<sup>1)</sup>. The nuclear electricity accounts for about 15 % of electric power generation in the world. Several countries have decided to make large investments in developing nuclear energy (e.g. China, South Korea, Russia, India, USA...) including new comers like UAE. The incident in Three Mile Island (1979), the accidents of Chernobyl (1986) and of Fukushima (2011) deeply impacted the development of nuclear energy and the acceptance of this energy in many countries. The future of nuclear energy in many countries will depend largely on its social acceptance and its economical evaluation for which safety and security together with nuclear waste management are key issues.

Corrosion of nuclear materials, i.e. the interaction between these materials and their environments, is a major issue for the plant safety, but also for the nuclear economic competitiveness. Current stakes are particularly high for today operators who want to extend the service or operation time of their reactors. Third and fourth generations

of nuclear power plants (NPPs) are requested now to last sixty years which is nearly twice the time initially scheduled for the previous reactor generation. This is possible thanks to the research efforts which are aimed at predicting and mitigation corrosion and has been initiated long ago. Since the 1950's, time and money have been spent to select the right materials with the right environment, to develop prediction and mitigation of corrosion phenomena in nuclear systems in order to prevent failures and to increase safety and operation time of these systems. Over time, substantial progresses have been made towards understanding, preventing, monitoring and modeling the interactions between materials and their environments. Effective waste management stays a challenge for sustainable nuclear energy; more precisely it includes predicting the behaviour of materials over very long term (thousands and even millions of years) for assessing the feasibility of a deep geological waste repository.

This paper reflects the development of the corrosion knowledge in the nuclear field. Large progresses are still expected and new material challenges are faced with high temperatures (generation IV reactors, fusion facilities) and with very long term times (geological disposals).

## 2. Nuclear Power Plants

From the pioneering period, nuclear corrosion community faced many challenges<sup>2)</sup>. In the former days, the se-

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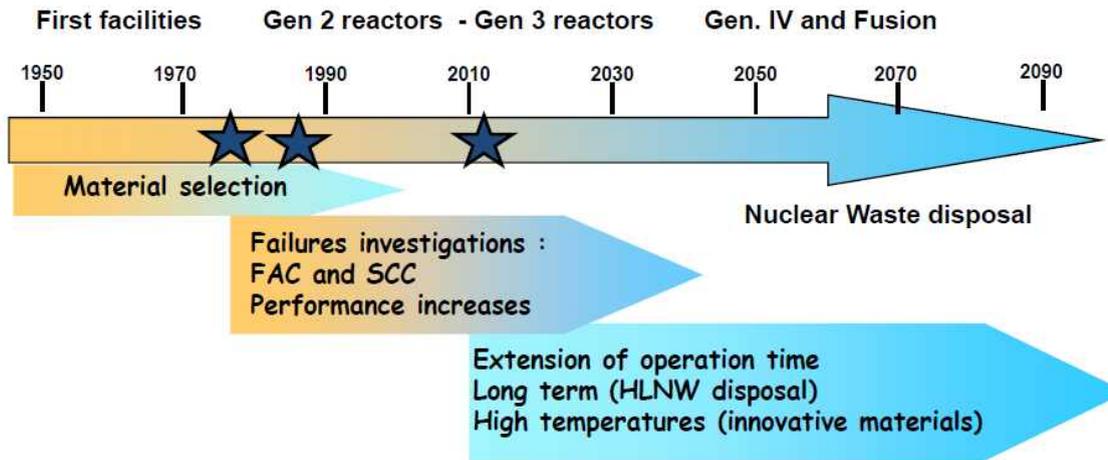


Fig. 1. Evolution of the main corrosion issues and corrosion challenges for nuclear reactors and facilities.

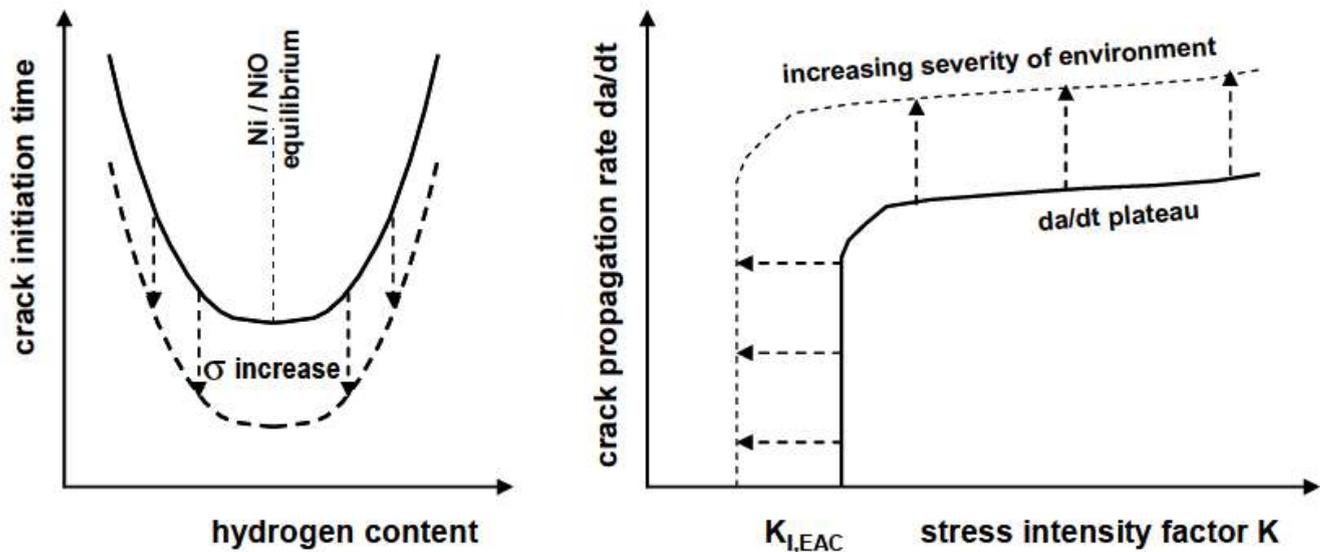
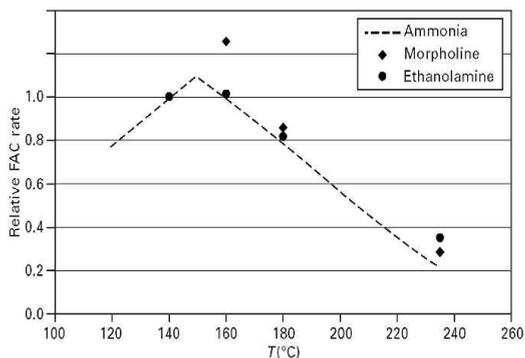


Fig. 2. Schematic representation of : a. crack initiation time in alloy 600 as a function of environmental conditions, here hydrogen content in primary water of PWR, for a given initial stress state and b. crack propagation rate as a function of stress intensity factor for given electrochemical conditions with stress intensity factor threshold ( $K_{I,EAC}$ ) and its evolution with the severity of the environment<sup>3)</sup> – reproduced with the permission of Woodhead Publishing.

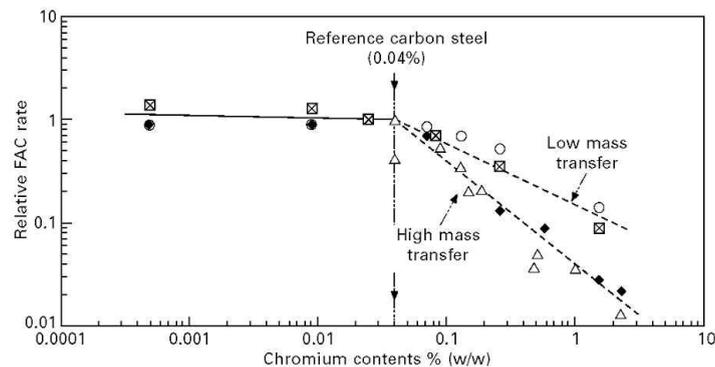
lection of materials was the major activity. At that time, water reactors were not believed to have aggressive environments. Expected highly corrosion resistance alloys such as stainless steels, nickel base alloys or zirconium alloys have been selected. However, nuclear power plants have suffered numerous failures of these alloys since the 1970's and corrosion in water reactors became rapidly one of the major concerns. As illustrated in Fig. 1, flow accelerated corrosion (FAC) and stress corrosion cracking (SCC) have been major issues for boiling water reactors (BWRs) and pressurized water reactors (PWRs).

SCC has been one of the main challenges since the

beginning of commercial operation of BWRs with the first cracks on stainless steels welds, during the 70's. For PWRs, alloy 600, a nickel base alloy with 15 % of chromium, cracks in the 80's at steam generator tubes and at vessel head penetrations in the 90's. Even though the materials and the chemistries are quite different in BWRs and PWRs, through extensive research and collaborations, corrosion engineers and scientists have succeeded in mitigating these phenomena. To occur, SCC needs a combination of 3 factors: a susceptible material, an aggressive environment and high stresses. Regarding BWRs, stainless steels welds have been improved by using less sensitive



**Fig. 3.** Evolution of the FAC rate of a carbon steel with the temperature and the chemical conditioning of a secondary circuit of PWR<sup>5)</sup> – reproduced with the permission of Woodhead Publishing.



**Fig. 4.** Influence of the chromium content of the steel on the FAC rate for two hydrodynamic regimes<sup>5)</sup> – reproduced with the permission of Woodhead Publishing.

materials (lower carbon content); residual stresses have been decreased by thermal treatments and water chemistry has been improved with hydrogen additions. In PWRs, 15 % Cr-Ni alloys have proven to be very sensitive to primary water SCC (“the Coriou effect”). SCC initiation and propagation have been and are still intensively investigated (Fig. 2). The most common cracks and leaks concern alloy 600 and welding alloys 82 and 182 (tubes, plates and welds), and lead to repairs (pressurizer nozzles) or replacements (steam generators, reactor pressure vessel upper head). The alternative alloys (alloy 800 or alloy 690 for tubes and plates, alloys 152 and 52 for welds) which are now in use, are much more resistant to SCC, probably due to their lower nickel content and higher chromium concentration<sup>4)</sup>.

All NPPs had to face flow accelerated corrosion phenomena (FAC). Catastrophic failures due to FAC occurred in PWRs and brought attention: (i) on December 9<sup>th</sup>, 1986, an elbow in the condensate system of the Surry plant, Unit 2 (USA) ruptured killing four workers; (ii) on August 9<sup>th</sup>, 2004, a piping rupture took place downstream of a condensate line orifice of the secondary circuit of the Mihama-3 plant (Japan) resulted in five workers being killed and six others injured. For BWRs, all carbon steel materials (main feedwater lines, purification and condensate systems) are susceptible. CANDU plants experienced FAC in both secondary and primary systems. Boiler tube failures due to FAC occurred also in Magnox type reactors. FAC is a corrosion phenomenon assisted by mass transfer. It affects single-phase (liquid) and two-phase (wet steam) systems but there is no FAC if the piping is exposed to dry or superheated steam. This phenomenon is well known and well described today. The influence of many parameters have been determined and simulated such as temperature and water chemistry (Fig. 3), steel

composition (Fig. 4), flow rate.... The use of software to evaluate susceptible components and FAC rates are now integrated into guidelines and coupled to periodic on-site examinations leading to a better distribution of the non-destructive tests<sup>5)</sup>.

The objective of extending the service life of many NPPs goes through a good material selection and technology choices made by the nuclear corrosion community during the pioneering period and a the good work performed after for improving the material performances. The extension of the service life beyond the initial design life, ensuring the cost competitiveness and matching enhanced safety requirements is one of the main challenges that the corrosion community faces nowadays. In 2013, 44 commercial NPPs were 40 years old or more in the world<sup>1)</sup>. During the last years, the various forms of SCC (including irradiation assisted stress corrosion cracking- IASCC) affected plant lifetime management and availability, mainly depending of the fluence effects (Fig. 5).

Great knowledge and expertise has been built up by facing the ageing issues, using a wealth of experience (not far from 1500 reactor-years of operation in France for instance) coupled with close links between fundamental knowledge and engineering practices. The “persistent” radiation effects with the increase of irradiation time are responsible of the importance of the irradiated assisted corrosion of in-core reactor components. Irradiation causes significant changes in local composition near grain boundaries and other defect sinks. The susceptibility to irradiated assisted stress corrosion cracking (IASCC) of stainless steels is affected by the enrichment of nickel and silicon and by the depletion of chromium for instance. Large R&D programmes, like PERFORM 60 at the European scale<sup>7)</sup>, are needed to identify IASCC mechanisms and to develop simulation tools towards a compre-

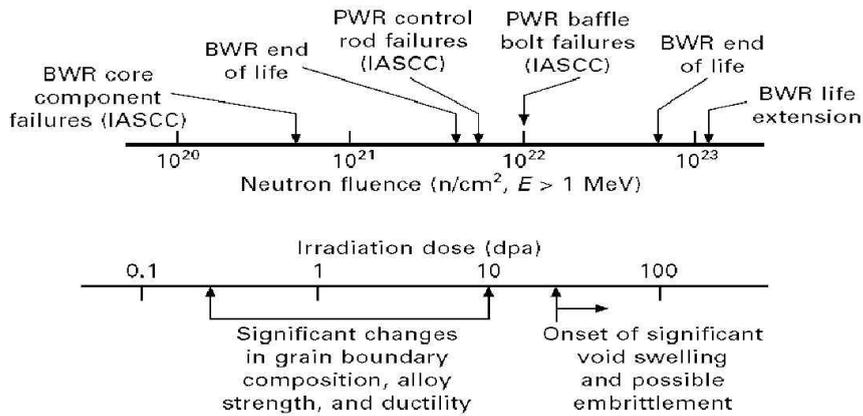


Fig. 5. Neutron fluence effects on irradiation-assisted stress corrosion cracking susceptibility of type 304SS in BWR and PWR environments<sup>6)</sup> – reproduced with the permission of Woodhead Publishing.

hensive prediction methodology. Emphasizes on qualitative and quantitative descriptions of chemical and mechanical elements are made at atomistic, meso-, micro- and macroscopic levels in environments of water-cooled reactors.

### 3. Nuclear waste disposal

The safe disposal of long-living radioactive waste during geological timescale is one of the most important issues in the acceptance of nuclear energy. It involves the scientific understanding of the behaviour of the various engineered and natural barriers in the geological repository. Predicting the corrosion performance of containers of high level radioactive waste over such timescales (millenniums to millions of years) presents a worldwide challenge for scientists and engineers. It is rather obvious that semi-empirical modeling and experience feedbacks, on which often

the evaluation of the lifetime of the materials is based, are not sufficient any more. Over such long durations, a new approach is necessary. It was refined since more than ten years at an international level. 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:

- An experimental investigation in laboratory which allows apprehending the phenomena, studying the parameters of them, obtaining initial kinetics with their evolution and determining the main parameters and their physicochemical mechanisms.
- A mechanistic modeling (based on physicochemical mechanisms of the phenomena of corrosion) which allows some simulation and the use of this simulation

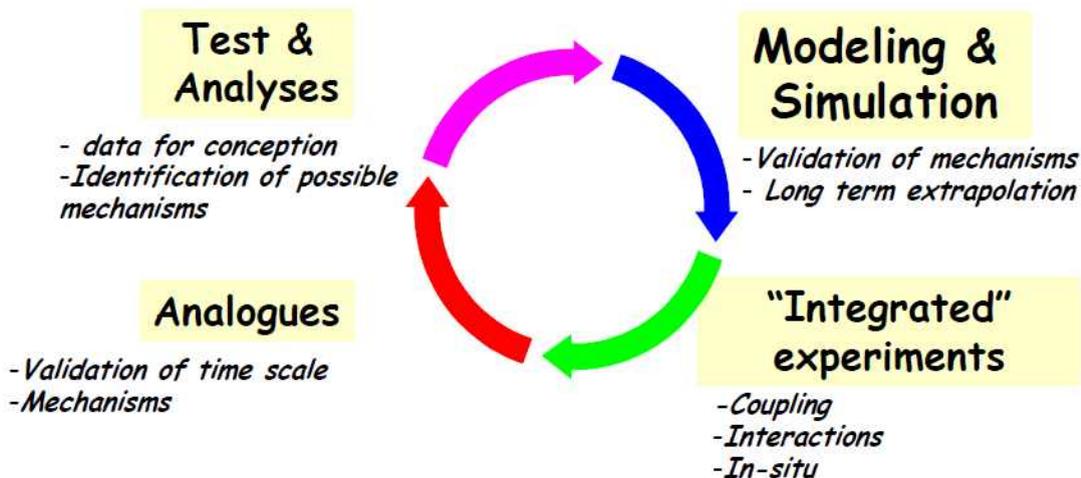


Fig. 6. Iterative approach for the evaluation of the corrosion behavior of metals and alloys over long terms.

for an extrapolation on the long term.

- The use of the archaeological analogues for with the time to check the kinetics and the validity of the given mechanisms previously on experiments “short term”.
- An integrated approach which consists in realizing experiments in conditions as representative as possible, therefore with complete coupling of the effects of the medium, material and other environmental parameters such as stress, flow, bacteria, ...

The iteration consists in checking for example that the corrosion kinetics or the modeled mechanisms are coherent with what is observed on short terms experiments and on the analogues. This global approach is schematized Fig. 6 which highlights the iterations as well as the exchanges needed between the various international communities which work on nuclear waste management. It is also important to point out that the environment evolves and moves on such scales of time. For example, in the case of the geological storage of the nuclear waste as envisaged in the argillaceous or granitic sites in Europe, the environment will be successively oxidizing (exploitation phase of storage), then it will become anoxic and reducing after the closing phase of the storage cells. The transition period between these two phases (exploitation and closing) during which the metallic materials can be in conditions oxidizing at certain places and reducing with others, is certainly more to fear for localized corrosion which can be initiated either by well-known phenomena like differential aeration, or by the simultaneous presence of aerobic and anaerobic bacteria. To face these less foreseeable evolutions of the natural environments, an analysis of sensitivity can prove to be necessary; however the contribution of the archaeological analogues is often important too. Many developments were carried out these last years on the corrosion of the archaeological analogues. It appears that studying metals of the past allows predicting their behavior in the future.

In the French concept, the overpack is not only part

of the high integrity barriers but is also a major component of the reversibility which is required for the French geological repository. Reversibility means the possibility to retrieve emplaced packages as well as to intervene and modify the disposal process and design. Long-term safety and reversibility are the guiding principles which lead to the basic layout of geological repository. This concept integrates safety right from the farthest upstream phases of the design and allows progressively orienting the choices toward solutions offering the greatest robustness with respect to knowledge uncertainties, and introducing prevention and protection measures against the identified risks. The overall approach is of course iterative.

#### 4. Generation iv reactors

Six nuclear systems have been selected by the Generation IV Forum: GFR (a gas-cooled fast neutron reactor with fuel recycling), SFR (a sodium-cooled fast neutron reactor with fuel recycling), LFR (a lead or lead-bismuth-cooled fast neutron reactor with fuel recycling), VHTR (a helium cooled, thermal neutron reactor with a very high core outlet temperature -1000 °C- dedicated to hydrogen generation, without fuel recycling), SCWR (a supercritical water-cooled reactor with a thermal or fast neutron spectrum and fuel recycling), MSR (a molten salt thermal neutron reactor with fuel recycling). These systems are mostly aimed at generating electric power, but some of them are also able to supply high-temperature heat for industrial processes. These reactors have designed temperatures higher than those of today commercial NPPs. The success of these international initiatives depends mainly on the choice and/or the development of suitable materials able to sustain high temperatures and environments which become aggressive at high temperatures (supercritical water, helium at 800 - 1000 °C, molten salts, liquid metals).

In molten salt reactors, fertile and/or fissile elements such as UF<sub>4</sub>, PuF<sub>3</sub> and/or ThF<sub>4</sub> are mixed with carrier salts to form fluids which flows at temperatures between

**Table 1. Corrosion rates observed on alloys exposed in a fluoride molten salt (FLiNaK) at 677 °C<sup>10</sup>**

Alloy	Chromium content	Corrosion rate
Hastelloy N	6.3 %	0.045 mm/y
Hastelloy X	21.3 %	0.28 mm/y
Incoloy 800H	20.4 %	0.63 mm/y
Inconel 617	22.1 %	0.62 mm/y
Haynes 230	22.5 %	1.0 mm/y

550 °C (core inlet) and 700 °C (core outlet), as estimated in the Generation IV forum. In 1954, a 2,5MWth MSR, called Aircraft Reactor Experiment (ARE), was built and fuelled with UF<sub>4</sub> dissolved in a mixture of zirconium and sodium fluorides, moderated with beryllium oxide. It operated successfully during 9 days with an outlet temperature near 900 °C. ARE structural material (nickel base alloy) corroded too rapidly. Research and development activities on corrosion behaviour in molten salts lead to development of a new alloy called Hastelloy-N which is a nickel base alloy with mainly 15 - 18 % molybdenum, 6 - 8 % chromium and 5 % iron. During test performed between 1965 and 1969 under reactor operating conditions, Hastelloy-N piping and components showed intergranular cracks attributed to interactions with the fission products like tellurium. Corrosion is the “Achilles heel” of MSR. Consequently, recent activities of R&D developing this type of reactors focus on (i) the control of the chemical purity and the electrochemical redox of the molten salts, and on (ii) the development of new materials, the whole being based upon a thorough understanding of corrosion mechanisms<sup>10</sup>.

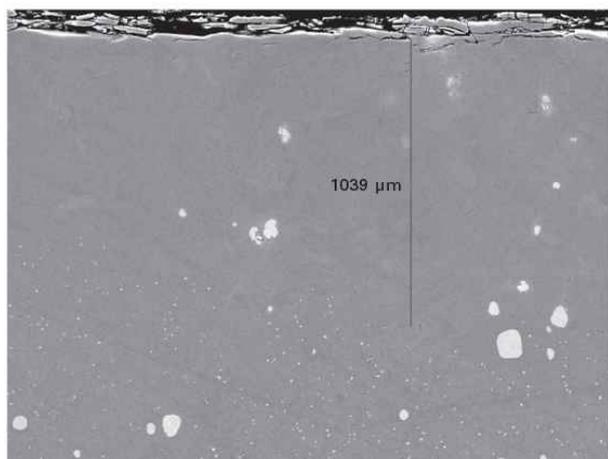
As shown by the experiences gained in the seventies and eighties with helium-cooled experimental reactor, traces of pollutants such as H<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>O contaminate the coolant. Although only very low concentrations are involved (few vppm), these gaseous impurities interact with metallic materials at high temperatures. Competition takes place between the growth of a protective superficial oxide, i.e. a “passive” oxidation regime ensuring alloy integrity in the long term, and carburization or decarburization reactions (Fig. 7), which irreversibly alter microstructure and properties of the alloys. Experience issued from gas cooled reactor (GCR) related studies provides a rich corpus of both theoretical and practical data dealing with corrosion phenomena in impure helium. Nevertheless, essential knowledge is lacking for selecting and qualifying materials for VHTR. In these innovating systems, structures will be exposed to temperatures considerably higher (>750°C) than formerly (600 °C max.). Moreover, materials themselves might be particularly different from those of early GCRs, i.e. mainly Alloy 800 and chromium-rich nickel alloys reinforced with Co and/or Mo (IN617, Hastelloy X...). Nowadays, other grades are assumed to be more performing at high temperature, particularly owing to their optimized creep resistance: Cr-rich nickel alloys reinforced with tungsten (typically, Alloy 230), coated materials featuring a three-layer system (with typically an yttrium stabilized zirconia thermal barrier), oxide-dispersion-strengthened (ODS) steels or nickel alloys, molybdenum alloys... Therefore, corrosion studies under representative atmospheres and at upper-bound tem-

peratures are required to know new materials behavior, select materials compatible with the environment to be encountered in gas-cooled fast reactors, prescribe optimal operating conditions with associated margins (temperature, pollutants in helium), and, further in time, propose parameterized laws for in-service prediction of lifetime<sup>11</sup>.

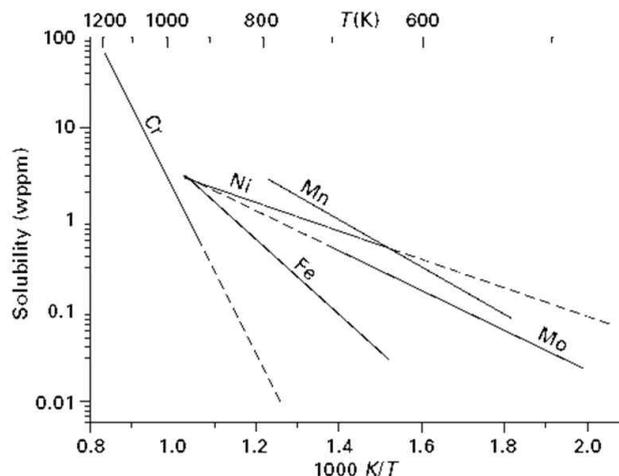
High power density requires using a coolant endowed with very good thermal properties (thermal conductivity, specific heat): this is the reason why liquid metals are very attractive. Nowadays two paths are being investigated around the world<sup>12</sup>. Sodium-cooled fast neutron reactors have been developed in the early fifties. Some reactors of this type are in operation in Russia since many years. Others are under construction (CEFR in China, BN800 in Russia, PFBR in India). Generally, it is considered that ferritic and austenitic steels or alloys that do not contain more than 32 % of nickel (as nickel solubility is high in liquid sodium) can be used in sodium cooled reactors. Corrosion by liquid sodium appears as controllable: the corrosion rate can be kept at very low values by only maintaining oxygen content as low as possible in the liquid sodium. Dissolution or embrittlement phenomena by liquid metal penetration are also negligible providing a temperature lower than 550 °C is maintained. The major difficulty is the risk of cracking corrosion induced by aqueous soda, which may be generated in the case of wet air ingress during maintenance or repair operations. This risk can be controlled through implementing suitable intervention procedures. Lead-cooled fast reactors are an alternative to the sodium-cooled fast neutron reactor. Lead or lead-bismuth eutectics are contemplated for hybrid reactors (Accelerator Driven Systems) designed for waste transmutation, both as coolants and for neutron generation in the spallation target. Lead-bismuth eutectics are also considered for the intermediate coolant circuit of sodium-cooled fast reactors, and the lead-lithium eutectic for tritium-generating blankets of fusion reactors. In contrast with liquid sodium, corrosion by liquid lead alloys appears as a true problem, which will probably impose using coated materials, as well as maintaining highly controlled oxygen content in the liquid metal. Despite significant advances, controlling corrosion phenomena in lead environment has not yet been fully acquired, and here lies one of the major handicaps of the “lead reactors”.

## 5. Summary

Since the pioneering periods, nuclear engineers and scientists have accumulated large experience regarding the corrosion of materials in NPPs. Ongoing developments include to understand, to simulate and to predict degrada-



**Fig. 7.** Decarburation zone (1039  $\mu\text{m}$ ) in a nickel base alloy (Haynes 230) after 60h in nitrogen-argon-hydrogen gas at 1000  $^{\circ}\text{C}^{(1)}$  – reproduced with the permission of Woodhead Publishing.



**Fig. 8.** Solubility of metallic elements in liquid sodium as function of the temperature<sup>(2)</sup> – reproduced with the permission of Woodhead Publishing.

tions mechanisms in order to assume the reliability and the integrity of these components beyond their initial design exploitation time, increasing safety margins. The feasibility of deep geological repositories for nuclear wastes requires an increase in fundamental knowledge of corrosion to predict corrosion behaviour over geological scales. The success of Generation IV Forum depends mainly on the development of suitable materials able to sustain high temperatures and environments which become aggressive at these high temperatures (supercritical water, helium at 800 - 100  $^{\circ}\text{C}$ , molten salts... ). Corrosion and compatibility of a wide range of new materials are under extensive investigations in laboratories for high temperature reactor technology.

Since the beginning of nuclear industry, time and money have been spent to select the right materials with the right environment, to develop prediction and mitigation of corrosion phenomena in nuclear systems in order to prevent failures and to increase safety and service time of these systems. Over time, substantial progresses have been made towards understanding, preventing, monitoring and modeling the interactions between materials and their environments leading to the development of the corrosion knowledge in the nuclear field. Large progresses are still expected and new material challenges are faced with high temperatures (generation IV reactors, fusion facilities) and with very long term prediction (geological disposals).

## References

1. Nuclear Power Reactors in the World, reference data series N°2, 2014 edition, IAEA, Vienne, May (2014).
2. D. Féron, P. Berge, Fifty years of nuclear corrosion in

- Europe: from the pioneering period to a safe and mature industry, (In) Progress in Corrosion – the first 50 years of the EFC, EFC publications N°52 (Ed.) P. McIntyre, J. Vogelsang, p. 87, Maney publishing, Leeds (2009).
3. K. Wolski, Environmental assisted cracking (EAC) in nuclear reactor systems and components, (In) Nuclear Corrosion Science and Engineering, p. 104, Woodhead Publishing, Cambridge (GB) (2012).
4. M. Le Calvar, I. De Currieres, Corrosion issues in pressurised water reactors (PWR) systems, (In) Nuclear Corrosion Science and Engineering, p. 473, Woodhead Publishing, Cambridge (GB) (2012).
5. S. Trevin, Flow accelerated corrosion (FAC) in nuclear power plant components, (In) Nuclear Corrosion Science and Engineering, p. 186, Woodhead Publishing, Cambridge (GB) (2012).
6. G. S. Was, P. L. Andresen, Irradiation assisted corrosion and stress corrosion cracking (IAC/IASCC) in nuclear reactor systems and components, (In) Nuclear Corrosion Science and Engineering, p. 131, Woodhead Publishing, Cambridge (GB) (2012).
7. S. Leclercq, D. Lidbury, S. Van Dyck, D. Moinereau, A. Alamo, A. Al Mazouzi, *J. Nucl. Mater.*, **406**, 193 (2010).
8. F. King, C. Padovani, *Corros. Eng. Sci. Techn.*, **46**, 82 (2011).
9. F. Cattant, D. Crusset, D. Féron, *Mater. Today*, **11**, 32 (2008).
10. P. Calderoni, C. Cabet, Corrosion issues in molten salt reactor (MSR) systems, (In) Nuclear Corrosion Science and Engineering, p. 842, Woodhead Publishing, Cambridge (GB) (2012).
11. M. Grosse, High temperature oxidation in nuclear reactor systems, (In) Nuclear Corrosion Science and Engineering, p. 265, Woodhead Publishing, Cambridge (GB) (2012).
12. T. Gnanasekaran, R. K. Dayal, Baldev Raj, Liquid metal corrosion in nuclear reactor and accelerator driven systems, (In) Nuclear Corrosion Science and Engineering, p. 301, Woodhead Publishing, Cambridge (GB) (2012).