

Kari Mäkelä

Development of techniques for electrochemical studies in power plant environments



VTT PUBLICATIONS 415

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VTT Manufacturing Technology



TECHNICAL RESEARCH CENTRE OF FINLAND
ESPOO 2000

ISBN 951-38-5571-6 (soft back ed.)

ISSN 1235-0621 (soft back ed.)

ISBN 951-38-5572-4 (URL: <http://www.inf.vtt.fi/pdf/>)

ISSN 1455-0849 (URL: <http://www.inf.vtt.fi/pdf/>)

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JULKAISIJA – UTGIVARE – PUBLISHER

Valtion teknillinen tutkimuskeskus (VTT), Vuorimiehentie 5, PL 2000, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 456 4374

Statens tekniska forskningscentral (VTT), Bergsmansvägen 5, PB 2000, 02044 VTT
tel. växel (09) 4561, fax (09) 456 4374

Technical Research Centre of Finland (VTT), Vuorimiehentie 5, P.O.Box 2000, FIN-02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 4374

VTT Valmistustekniikka, Voimalaitosten materiaalitekniikka, Kemistintie 3, PL 1704, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 456 7002, (09) 456 5875

VTT Tillverknings teknik, Material och strukturell integritet, Kemistvägen 3, PB 1704, 02044 VTT
tel. växel (09) 4561, fax (09) 456 7002, (09) 456 5875

VTT Manufacturing Technology, Materials and Structural Integrity,
Kemistintie 3, P.O.Box 1704, FIN-02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 7002, + 358 9 456 5875

Technical editing Maini Manninen

Otamedia Oy, Espoo 2000

Mäkelä, Kari. Development of techniques for electrochemical studies in power plant environments. Espoo 2000. Technical Research Centre of Finland, VTT Publications 415. 46 p. + app. 128 p.

Keywords power plants, corrosion, nuclear reactors, water chemistry, high temperature, oxide films, electrodes, electrochemistry

Abstract

The properties of the oxide films on the engineering alloys used as construction materials in power plants change as a result of exposure to aqueous environments. The susceptibility of the materials to different forms of corrosion is influenced by the properties of these oxide films. Their structure and electrochemical properties are in turn dependent on the applied water chemistry. Therefore, water chemistry control has been used in minimising the impact of different corrosion phenomena in operating power plants. Since there is not only one ideal operational specification for all light water reactors, individually designed water chemistry programs are needed to take into account plant-specific design features and particular problem areas. The applicability of alternative water chemistry practices require fast and reliable in-line electrochemical techniques to monitor possible changes in the oxidation behaviour of nuclear power plant materials.

This thesis summarises the work done at the Technical Research Centre of Finland over the past 10 years to increase the knowledge of factors affecting the oxidation behaviour of construction materials in aqueous coolants at high temperatures. The work started with the development of electrodes for measurement of high temperature water chemistry parameters such as pH and the corrosion potential of construction materials. After laboratory testing these electrodes were used both in test reactors and in operating nuclear power plants. These measurements showed that high temperature water chemistry monitoring may be more accurate than corresponding room temperature measurements, particularly during transient situations. However, it was also found that understanding the processes taking place within and on oxide films requires a combination of electrochemical techniques enabling characterisation of the electronic properties of these films. This conclusion resulted in development of a controlled-distance electrochemistry arrangement. The arrangement was used to obtain data on different transport processes in the oxide films exposed to aqueous solutions. This information was then used to model the oxidation behaviour of construction materials in these solutions.

Preface

Without extensive financial and technical support from VTT Manufacturing Technology the development work described in this thesis would not have been possible. Similarly the role of The Finnish Ministry of Trade and Industry, the Radiation and Nuclear Safety Authority, Finland, and the OECD Halden Reactor Project, Norway, in the financial support of this work as part of the Nuclear Power Plant Structural Safety Research Programme 1990–1994, the Finnish Research Programme on the Structural Integrity of Nuclear Power Plants 1995–1998 and the Research Programme on Operational Safety and Structural Integrity 1999–2002, is gratefully acknowledged.

The constructive criticism and valuable support of Professor Hannu Hänninen and Dr. Björn Beverskog in preparing this thesis is gratefully recognised. However, this work would not have been completed without valuable contribution from Professor Markku Leskelä, Dr. Martin Bojinov, Dr. Timo Laitinen and Dr. Timo Saario. Their patience and guidance proved to be invaluable.

I am also very grateful to Mr. Pertti Aaltonen, Mrs. Marketta Mattila, Mr. Matti Mäkelä, Mr. Lauri Selin, and Mr. Pekka Sirkiä for their support and innovative ideas during the development work of these techniques and for not giving up during the times it seemed that nothing was working.

My beloved wife Taina Hirvonen has given me the most devoted and valuable support during the years needed to finish this thesis. Also my parents Seppo and Paula Mäkelä and my sister Kati Virkkala have always encouraged me to push myself a little bit further. For all this I am eternally grateful.

List of publications

This thesis consists of a summary of the work performed and eight appended publications (Appendices I–VIII)

- I MacDonald, D.D., Hettiarachchi, S., Song, H., Mäkelä, K., Emerson, R. and Ben-Haim, M. 1992. Measurement of pH in subcritical and supercritical aqueous systems. *J. Solution Chem.* Vol. 21, No. 8, pp. 849–881.
- II Mäkelä, K. and Aaltonen, P. 1993. On-line monitoring for further corrosion reduction and better understanding of the activity build-up in LWR primary coolant systems. *Int. J. Pres. Ves. Piping*, Vol. 55, No. 1, pp. 163–177.
- III Mäkelä, K., Aaltonen, P. and Buddas, T. 1995. The effect of hydrazine dosing on high temperature pH_T and redox potentials under PWR environments. *Corrosion 95*, The NACE international annual conference and corrosion show, Orlando, USA, March 1995, Paper 100. USA: NACE International. Pp. 1–9.
- IV MacDonald, D.D., Song, H., Mäkelä, K. and Yoshida, K. 1993. Corrosion potential measurements on type 304 SS and alloy 182 in simulated BWR environments. *Corrosion*, Vol. 49, No. 1, pp.8–16.
- V Aaltonen, P., Mäkelä, K. and Buddas, T. 1995. Characterisation of oxide scales from Loviisa Units 1 and 2. *Proceedings of the seventh international symposium on environmental degradation of materials in nuclear power systems-water reactors*, August 1995, Breckenridge Colorado, Vol. 1. USA: NACE International. Pp. 151–162.
- VI Bojinov, M., Hinttala, J., Laitinen, T., Muttilainen, E., Mäkelä, K., Reinvall, A., Saario, T. and Suksi, S. 1998. Development of electrochemical techniques to study oxide films on construction materials in high temperature water. *Proceedings of JAIF International Conference*

on Water Chemistry in Nuclear Power Plants, Kashiwazaki, October 1998. Japan: Japan Atomic Industry Forum, Inc. Pp. 111–115.

- VII Bojinov, M., Laitinen, T., Mäkelä, K. and Saario, T. A conduction mechanism of the passive film on iron based on contact electric impedance and resistance measurements. Submitted to J. Electrochem. Soc., 17.1.2000.
- VIII Bojinov, M., Kinnunen, P., Laitinen, T., Mäkelä, K., Mäkelä, M., Saario, T. and Sirkiä, P. Detection of soluble species released during metal corrosion in high temperature aqueous solutions. Submitted to Corrosion, 14.3.2000.

The author of this thesis is scientifically and technically responsible for the work done in publications II, III and VIII. He has taken active part in the experimental work and in reporting publications I, IV, V and VI. He also assisted in writing publication VII.

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***Appendices of this publication are not included in the PDF version.
Please order the printed version to get the complete publication
(<http://otatrip.hut.fi/vtt/jure/index.html>)***

List of abbreviations and used terminology

BWR	boiling water reactor
CEI	contact electric impedance
CER	contact electric resistance
CDE	controlled-distance electrode
Cold leg	part of the primary circuit downstream of the steam generator
C_p	steady state ion charge carrier concentration in the film (mol cm^{-3})
D_e	diffusion coefficient of electrons (cm^2s^{-1})
D_i	diffusion coefficient of interstitial cations (cm^2s^{-1})
DEHA	diethylenediamine
$E (V_{\text{SHE}})$	potential in standard hydrogen scale (V)
ECP	electrochemical corrosion potential (V_{SHE})
EPBRE	external pressure balanced reference electrode
ESSRE	external solid state reference electrode
Hydrogen line	thermodynamic equilibrium line of the H^+/H_2 couple in a potential-pH diagram
HWC	hydrogen water chemistry (used in BWR)
IGA	intergranular attack
IRE	internal reference electrode
LWR	light water reactor; either PWR or BWR
NMCA	noble metal chemical addition
NWC	normal water chemistry (used in BWR)
pH_T	thermodynamic pH at measured temperature
PWR	pressurised water reactor; boric acid ($\text{B}(\text{OH})_3$), lithium hydroxide (LiOH) or potassium hydroxide (KOH) is used in the primary water together with hydrogen (H_2)
SCC	stress corrosion cracking
Shut-down	cool down period for a reactor
Start-up	period during which a reactor is heated up for steady state operation
TLEC	thin-layer electrode
VVER	PWRs designed in former Soviet Union
Type 304 SS	construction material (Cr: 18–20%, Ni: 8–12%, C: 0.03%, Mn: 2%, Fe: bal.)

Type 316L SS construction material (Cr: 16–18%, Ni: 10–14%, C: 0.03%,
Mn: 2%, Mo: 2.5–3%, Fe: bal.)

Alloy 182 weld metal (Cr: 14–17%, C: 0.04%, Mn: 7.75%,
Fe: 7.5–9.0%, Nb: 1.75%, Ni: bal.)

Type 321 SS construction material (Cr: 17–19%, Ni: 9–12%, C: 0.08%,
Mn: 2.00%, Ti min 5*C%, Fe: bal.)

1. Introduction

Operating light water reactors (LWR) have been built according to the best technological knowledge available at the time of their design and construction. In spite of that some primary circuit components in plants have been replaced during outages with new designs and materials known to be more corrosion resistant than the original ones. Even though considerable success has been achieved in minimising the impact of corrosion on nuclear power plant availability, there are indications of increased degradation in boiling water reactor (BWR) vessel internals, in pressurised water reactor (PWR) steam generators and reactor pressure vessel penetrations in ageing power plants. The trends towards higher fuel burn-up and longer fuel cycles impose a demand also for better corrosion and hydrating resistance of fuel cladding materials.

The properties of the oxide films on the construction materials in nuclear power plants change as a result of exposure to aqueous environments. The susceptibility of the materials to different forms of corrosion is greatly influenced by the physical and chemical properties of these oxides. These properties are in turn dependent on the applied water chemistry. Therefore, water chemistry control has been used in minimising the impact of different corrosion phenomena [1, 2]. There are some fundamental differences in the used water chemistries in light water reactors. In PWRs the primary side coolant contains boric acid. To control the pH_T , either lithium or potassium hydroxide is injected into the coolant. In addition, PWR primary coolants contain 35–45 mlkg^{-1} dissolved hydrogen. Thus the concentrations of oxygen and other oxidising species which form due to the radiolytic decomposition of water are low in the reactor water. In the secondary side of PWRs different types of chemistries have been used during the past decades. The main goals have been to minimise the transport of corrosion products and other impurities to the steam generators and to obtain reducing conditions in the steam generator feed water. In BWRs high purity water circulates in the primary loops. The oxygen concentrations vary typically between 100 and 300 μgkg^{-1} under normal BWR water chemistry operation (NWC). Injection of hydrogen gas into the water has been used to suppress concentrations of oxygen and other oxidising species in the boiling water reactors (hydrogen water chemistry, HWC). Since there is not only one ideal operational specification for all PWRs and BWRs, individually designed water chemistry programs are needed to take into account plant-specific design

features and particular problem areas. As alternative water chemistry practices become available, there is a need not only for improved water chemistry control but also for fast and reliable in-line techniques to monitor possible changes in oxidation behaviour of nuclear power plant materials.

Extensive instrumentation and laboratory analysis programs are applied to provide rapid and reliable diagnosis of water chemistry in power plants. Conventionally water chemistry monitoring is carried out at low pressures and temperatures. This has some shortcomings, because most of the parameters affecting corrosion reactions, such as thermodynamic pH at measured temperature (pH_T) and the corrosion potential of construction materials (ECP) change as a function of temperature. In addition to this, long sampling lines may affect the measurement results. Therefore, in-line monitoring should be carried out on-site in real operating conditions at high temperatures and pressures. A variety of high temperature electrochemical techniques and sensors have been routinely used in laboratories for determination of different corrosion phenomena as well as corrosion rates of different materials. Thus, techniques like voltammetry, electrochemical impedance spectroscopy and contact electric resistance measurements as well as electrochemical noise could provide important information about the corrosion processes occurring in and on the oxide films on construction materials. Concerning different types of corrosion, it can with good reason be assumed that these reactions involve steps in which charged species are transported through the oxide layers on material surfaces. At the moment a sufficient characterisation and a satisfactory model is not available for the electrochemical behaviour and electric properties of the oxide films formed in nuclear power plants. This lack of sufficient understanding of different processes in oxide films has complicated the assessment of the applicability and possible side-effects of novel water chemistries prior to their application at operating plants.

This thesis summarises the work done at the Technical Research Centre of Finland (VTT) during the past 10 years to understand factors affecting the oxidation behaviour of construction materials in contact with the coolant in typical nuclear power plant conditions. The work started with the development of electrodes to measure high temperature water chemistry parameters such as pH_T and the electrochemical corrosion potential of the components. To get a more comprehensive picture of the effects of water chemistry parameters on the

processes taking place in and on oxide films, samples were removed from the primary circuit and analysed using different *ex-situ* surface-sensitive techniques. However, not enough information was obtained to understand and model the different processes. Thus, development work was focused on techniques which can provide information about ion transport and the nature of mobile species or defects in the oxides. This work resulted in a controlled-distance electrochemistry (CDE)-arrangement which allows performing electrochemical measurements such as contact electric resistance, contact electric impedance and other electrochemical techniques even in poorly conductive solutions. Since the high temperature water chemistry sensors are already field-proven, this thesis gives a general discussion of the electrode development work, but also more detailed information on the novel electrochemical techniques as their optimisation is still in progress.

2. Development of sensors for water chemistry control

2.1 Development of pH and reference electrodes for high temperature use

The interest in the corrosion behaviour of structural materials in high temperature aqueous systems has resulted in the need for reliable high temperature reference electrodes and pH_T sensors. In developing electrodes for measuring the electrochemical corrosion potential (ECP) of different materials and pH_T of aqueous solutions, it is necessary to recognise two fundamental problems: the thermodynamic stability of sensor materials, and electrode design integrity as the temperature and pressure are cycled between the expected operational extremes (e.g. 25–400 °C, 0.1–25 MPa). Furthermore, experimental difficulties are typically associated with problems in bringing electrochemical information across different pressure boundaries.

Over the past decade Niedrach [3], Macdonald *et al.* [4–7] and Danielson *et al.* [8] have developed a variety of oxygen-ion-conducting ceramic membrane pH_T sensors based on yttrium stabilised zirconium oxide, $\text{ZrO}_2(\text{Y}_2\text{O}_3)$.

The performance of these ceramic sensors can be characterised as follows [9]:

- For a given water activity and pH_T , the equilibrium potential depends only on the standard potential of the internal metal oxide/metal reference couple. The best internal reference is the one having a stoichiometric composition, a single oxidation state and accurately known thermodynamic properties. Of all metal oxide/metal couples available, HgO/Hg appears to fulfil these requirements most completely. However, because of the toxicity of mercury, other couples such as NiO/Ni can be used at the expense of accuracy.
- Yttrium stabilised zirconia is a insulator material and therefore electric conductivity of the material itself is negligible. Thus the sensor does not respond to possible redox species in the measurement system.

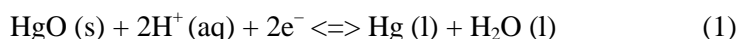
A suitable reference electrode is needed to determine the pH_T of a solution and to measure ECP. Reference electrodes used in high temperature aqueous studies to date fall into two classes: external, pressure balanced reference electrodes (EPBRE) and internal reference electrodes (IRE). EPBRE is less accurate than IRE due to uncertainty in the thermal liquid junction potential. On the other hand, this electrode offers considerable advantages in terms of long term stability and serviceability. The accuracy of the EPBRE has been improved quite recently by Lvov *et al.* [10], who introduced a flow-through EPBRE which allows accurate potentiometric measurements to within a few mV. However, the design feature of having the reference solution flowing through the electrode restricts the use of the sensor to laboratory applications.

The following main characteristics are desired for reliable reference electrodes (both EPBRE and IRE):

- The electroactive element of the reference electrode must be thermodynamically and chemically stable at the operating temperatures.
- The isothermal liquid junction potential between the solutions is reduced to as low as possible. Furthermore, the thermal liquid junction potential existing along the teflon tube inside the EPBRE should be as low as possible or accurately known, enabling conversion of the potentials to the conventionally used standard hydrogen electrode scale (SHE).

The work related to this thesis concentrated on verifying the operation of the pH_T sensor and calibration of the sensor developed at VTT. In addition, experiments were performed to develop a reference electrode with chloride immobilised in an inorganic matrix, capable of operating at temperatures above 300°C. Experimental details and results are shown in Appendix I. Some additional results are discussed in the following chapters.

It has been shown that the ceramic sensor with HgO/Hg internal reference couple follows the changes in hydrogen ion activity in high temperature aqueous solutions [11, 12]. The electrode reaction can be written as follows:



This type of pH_T sensor can be used to measure the pH_T of high temperature aqueous solutions at temperatures up to 300°C within ± 0.10 pH units. The inaccuracy of pH_T measurements has been due to difficulties in calibrating precisely enough the high temperature reference electrodes [13–17]. However, for power plant applications the obtained accuracy is high enough.

The most effective way of establishing thermodynamic viability of the pH_T sensor at temperatures above 300°C is to compare its potential directly against the hydrogen electrode [18]. This way possible inaccuracies in the reference electrode operation can be eliminated and, in addition, the measured potential difference is independent of the solution pH_T . The measured potential differences are shown for a series of test solutions at temperatures up to 374°C in Appendix I. Additional measurements were carried out in a temperature range of $200\text{--}398^\circ\text{C}$ [19] and a set of these results is shown in Fig. 1.

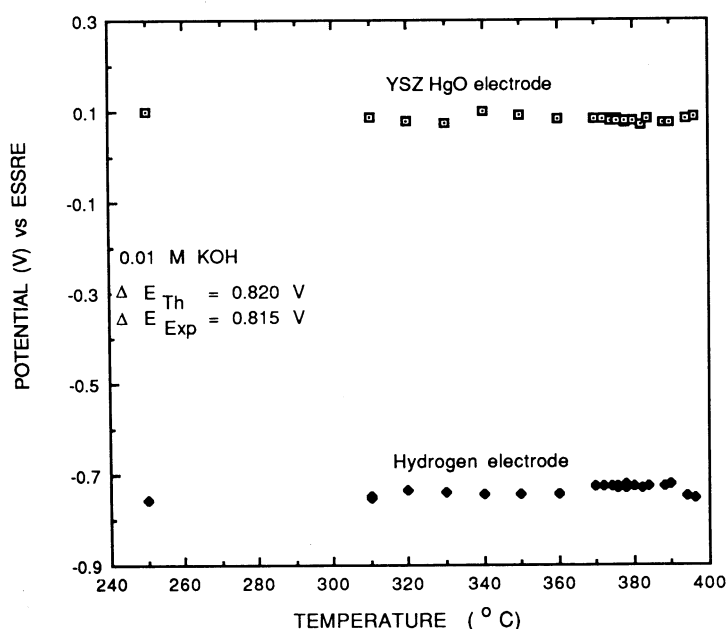


Figure 1. Variation of ZrO_2 (Y_2O_3) sensor and hydrogen electrode potential measured against the same solid state reference electrode (ESSRE) [19].

The measured potential difference (ΔE_{EXP}) between the ZrO_2 (Y_2O_3) pH_T sensor and the hydrogen electrode in 0.01 M KOH solution is in good agreement with the theoretically calculated value (ΔE_{Th}). This indicates that the ZrO_2 (Y_2O_3) pH_T sensor behaves as a true pH electrode also in supercritical water temperatures.

To measure the pH_T of a supercritical water, a solid state reference electrode was used. The idea in immobilising the chloride ions into a solid matrix was to achieve a constant chloride concentration in the sensor for long measurement periods. As discussed in Appendix I, a solid state AgCl/Ag reference electrode with soda glass (KCl) electrolyte was developed and tested. Unfortunately, this electrode exhibited an extraordinarily high impedance at low temperatures, and therefore a new idea to immobilise Cl^- ions was tried. Solid AgCl was melted into the reference electrode tube (made of Al_2O_3) which was half full with Al_2O_3 powder [20]. Al_2O_3 was used as a hydrophilic filler in the AgCl melt. The potentials of this reference electrode were measured against a ceramic pH_T sensor in two different solutions up to 374°C (0.01 m $\text{B}(\text{OH})_3$ + 0.001 m KOH and 0.001 M HCl). The agreement (i.e. 0.27 pH units at 374°C) is reasonable considering the inaccuracies associated with calculated values of pH_T in two different solutions.

3. Measurement of high temperature water chemistry conditions

High temperature electrodes (conventional EPBRE and pH_T) have been used at operating PWR plants in Finland and the USA to follow in-line the changes in high temperature water chemistry parameters. Monitoring campaigns have consisted of water chemistry measurements both in primary and in secondary sides of PWRs. Additional measurements have been performed in in-core locations of a PWR test reactor and during laboratory tests in typical BWR conditions. A set of results obtained during these measurements is discussed in the following chapters.

3.1 ECP and pH_T measurements in PWR environments

The high temperature pH_T and corrosion potential of titanium stabilised stainless steel (similar to Type 321SS) was measured before and during the shutdown for refuelling outage at Loviisa 1 PWR in summer 1989 (Appendix II). The goal of the work was to establish a link between high temperature water chemistry parameters and the behaviour of corrosion products during different operational environments. In addition, the pH_T and redox potential of the primary coolant in a PWR loop at the Rez research reactor in the Czech Republic were monitored during accurately controlled water chemistry conditions (Appendix III). These studies were performed to determine whether the electrochemical corrosion potentials of construction materials are lower during hydrazine dosing than during normal ammonia dosing in both out-of-core and in-core locations. The measurement locations and other test parameters are shown in more detail in Appendices II, III and in ref. 21.

3.1.1 ECP and pH_T measurements in primary circuit conditions in PWRs

During steady-state operation the ECP of construction materials at Loviisa unit 1 (Finnish nuclear power plant) was close to $-0.740V_{\text{SHE}}$ as expected due to the hydrogen concentration of the coolant ($35\text{--}45 \text{ mlkg}^{-1}$) and pH_T of 7.4. As

hydrogen was degassed from the primary system, the ECP of the stainless steel started to move in the positive direction. After hydrogen removal the primary coolant was borated, which rapidly decreased the pH_T from 7.4 to about 6.4 and further increased the ECP. However, soon after boration the measured pH_T values started to fluctuate (Appendix II). The rapid decrease in pH_T after boration increased the concentrations of all cations analysed from the water, but the dissolution reactions were stopped by subsequent pH_T fluctuations together with a simultaneous decrease in temperature. This type of pH_T and temperature effect is in good agreement with the corrosion product dissolution studies performed by Berry *et al.* [22].

After boration of the primary coolant the ECP of stainless steel increased continuously with decreasing temperature. A dissolution burst of nickel to the coolant occurred as the temperature decreased and the solution became increasingly oxidising. The measured concentrations of cobalt and iron decreased, which is in good agreement with the results reported by Sandler *et al.* [23] for the behaviour of nickel ferrites during a shutdown period. This type of corrosion product behaviour has also been observed in Spanish plants during shutdowns [24]. The additional follow-up measurements, which were carried out in 1992 at Loviisa, confirmed the earlier results [25].

The high temperature water chemistry measurements at the Loviisa 1 unit showed that the corrosion potential of stainless steels is close to the hydrogen line during steady-state boric acid/potassium hydroxide/ammonia operation. Some published data in the literature suggest that even lower ECPs are achieved if hydrazine is used instead of ammonia [26–28]. Therefore ECP measurements were performed in the Rez test reactor in in-core and out-of-core locations under different ammonia and hydrazine dosing periods (Appendix III). The measured corrosion potentials in out-of-core location were fairly similar during the different periods, even though rather high hydrazine concentrations ($\sim 30 \mu\text{gkg}^{-1}$) were used. This indicates that once the potentials are already near or on the hydrogen line, it is difficult to decrease them even though high concentrations of reducing agents are used.

The in-core redox potential measurements at the Rez test reactor showed that hydrazine dosing did not change the in-core potentials significantly when compared to normal ammonia water chemistry conditions. This test reactor data

are consistent with laboratory measurements reported by Brunning *et al.* [29], but disagree with plant observations in some eastern VVERs [30] where lower ECP values are obtained during hydrazine dosing than during normal ammonia operation. The major difference between the test reactor experiments, as well as the work done by Brunning *et al.*, and the real VVERs is the exposure history of oxide films to high temperature water. The importance of hydrazine in some eastern VVER reactors could also be due to the fact that it effectively scavenges trace levels of oxygen during start-ups and from make-up water, thus affecting the corrosion behaviour of oxides on the primary circuit surfaces.

3.1.2 ECP measurements in secondary side environments in PWRs

One of the major corrosion concerns in the secondary side of PWRs has been the localised corrosion of steam generator (SG) components in regions where water flow is restricted. Therefore, the transport of corrosion products and other impurities to the steam generator should be minimised, because they can result in the formation of local, aggressive environments and thus increase the corrosion rates of the component in question. In addition, reducing conditions in the SG circulating water are considered essential, because an oxidising environment increases the ECP of the steam generator construction materials and thereby increases the possibility of occurrence of intergranular attack (IGA) or stress corrosion cracking (SCC). Of all the available high temperature monitoring techniques, the measurement of ECP has been of prime interest. In-line ECP measurements are already successfully performed in many operating power plants [31–35]. In the Comanche Peak PWR unit ECP measurements have been used to obtain information about the efficiency of different oxygen scavengers to remove oxygen from the steam generator feed water. One set of results is shown in Fig. 2.

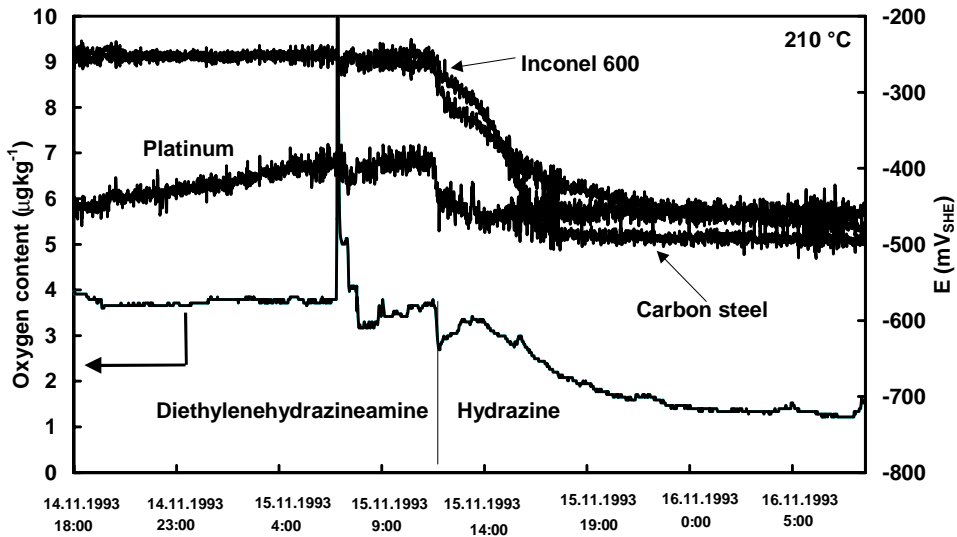


Figure 2. Changes in corrosion potential of different materials as dissolved oxygen is removed from the coolant using different scavengers [32].

The results clearly show that $30 \mu\text{gkg}^{-1}$ hydrazine is more efficient in decreasing the oxygen concentration in the feed water than $50 \mu\text{gkg}^{-1}$ of diethylenehydrazineamine (DEHA). Therefore, lower corrosion potentials of different construction materials can be achieved with lower oxygen scavenger concentrations resulting, for example, in a reduced need to change the ion exchange resins [32]. The ECP measurements of typical construction materials in the secondary side of Loviisa Unit 2 showed that a reducing environment existed on top of the tube bundle in both studied horizontal SGs. This means that the concentrations of oxidising species like oxygen and copper ions were low in the feed water [33].

ECP measurements have provided information about the prevailing conditions that affect corrosion behaviour of used materials both in bulk water and crevices. The key question is whether the monitoring should be performed in the feed water inside the steam generators, in the blow-down water or in some other location. Furthermore, the lack of a common reference value complicates the decision making process for required water chemistry optimisation. The incorporation of the ECP in-line measurements in some kind of computerised

expert system is most likely needed for plant operators to be able to start using and interpreting the data.

3.2 ECP measurements in simulated BWR conditions

Despite the strict water chemistry guidelines, the sensitised microstructure of stainless steel used in the primary circuit components, coupled with residual stresses and the presence of oxidising species, produces susceptibility of construction materials to stress corrosion cracking (SCC) in BWR coolants [36, 37]. The sensitised microstructures and stresses cannot be eliminated in existing plants. Therefore, the obvious remedy to mitigate SCC is to optimise the operational environment. Laboratory tests and actual power plant measurements indicate that to prevent crack formation and propagation in the stainless steel parts in BWRs, the corrosion potential of components has to be kept below $-0.230 V_{SHE}$ in high purity water (conductivity less than $0.3 \mu S cm^{-1}$). To decrease corrosion potentials, hydrogen is injected into the feed water in many BWRs. The ECP measurements in operating power plants have shown that out-of-core locations can be protected using the hydrogen injection (HWC). However, due to the water radiolysis in the in-core locations, the corrosion potential of some in-core components still remains too high, and these components remain susceptible to SCC [38].

It is not practical to install electrodes, even if they last long enough, to all important locations in BWR cores and primary loop locations. Thus, model calculations are needed to predict the ECP in the whole reactor. As a first step in addressing the problem to describe the in-core environments, particularly ECP, and hence in assessing the risk of in-core components failing by SCC, more reliable data are needed for corrosion potentials of BWR structural materials under various simulated conditions. Appendix IV describes the work undertaken to determine the ECP of type 304 stainless steel and Inconel weld metal 182 during normal water chemistry and hydrogen water chemistry conditions. Additionally, the effect of water flow rate on ECP under various water chemistry conditions was studied to detect and illustrate the importance of hydrodynamic factors in determining the ECP of BWR components. Experimental details are shown in Appendix IV, but the main results are discussed below.

Characterisation of the transition from high to low ECP is important, because this transition is the basis of HWC. It relies on reducing the content of oxidising species to an extent that the ECP is displaced below the critical potential for SCC ($-0.230 V_{SHE}$). The results in Appendix IV show that oxygen concentrations lower than $200 \mu\text{gkg}^{-1}$ should be sufficient enough to shift potentials below the threshold value, whereas the results of Indig *et al.* [39] show that the required oxygen concentration is 5 to 10 times lower. The origin of the discrepancy between these two results may be due to different flow rates in the experiments. Macdonald has shown in laboratory measurements the importance of hydrodynamic factors in determining the ECP of stainless steel in simulated BWR environments [40]. While the ECP is predicted and found experimentally to be insensitive to hydrodynamic effects at high oxygen concentrations, very high sensitivity is both predicted and found experimentally at intermediate oxygen levels ($20 \mu\text{gkg}^{-1} < O_2 \text{ content} < 100 \mu\text{gkg}^{-1}$).

Hydrogen peroxide, a by-product of water radiolysis, is a powerful oxidising agent in high temperature water with the consequence that relatively small concentrations are able to increase significantly the ECP of stainless steel. Both of the studied materials in Appendix IV behaved in a similar way during the hydrogen peroxide injections, but again, a fair agreement exists with our results and data reported by Lin *et al.* [41] and reviewed by Nelson *et al.* [42]. In our experiments the measured ECP values were significantly lower during high hydrogen peroxide concentrations than the values reviewed by Nelson *et al.* [42]. On the other hand, during low hydrogen peroxide conditions our measured corrosion potential values were significantly higher than those reported by Lin and co-workers [41]. Part of the difference may be attributed to different hydrodynamic conditions, but a substantial part is most likely due to different decomposition of H_2O_2 in the experimental apparatus. Because the H_2O_2 reaction occurs on the metal surfaces, the differences in volume/surface ratio of the test loop leads to different final hydrogen peroxide concentration in the test apparatus.

Since the HWC has been used to minimise the effects of oxidising species in BWR water, the effects of six different $O_2/H_2O_2/H_2$ combinations on electrochemical corrosion potentials were studied in Appendix IV. When significant amounts of oxygen ($200, 400 \mu\text{gkg}^{-1}$) and hydrogen peroxide ($100, 150 \mu\text{gkg}^{-1}$) were present in the solution, the potentials remained quite high even

though the hydrogen content was increased to $100 \mu\text{gkg}^{-1}$. This indicates that once the oxides are formed under very oxidising conditions the required reducing agent concentrations have to be fairly high in order to decrease the ECP to acceptable levels. In operating BWRs this would mean that fairly high hydrogen concentrations are needed to suppress potentials below the critical value for SCC.

In plant applications the amount of hydrogen needed to reduce potentials enough has shown to be plant-specific and is always in excess of the stoichiometric amount required for the recombination with oxygen to form water. Furthermore, plants have experienced an increase in the ^{16}N concentration in the main steam during HWC operation, causing elevated dose rates in the turbine building [43]. To reduce the amount of hydrogen needed to bring down the ECP, noble metal chemical addition (NMCA) technology was introduced to BWRs. The idea in NMCA is to catalyse the reaction between hydrogen and oxidising species in the coolant [44, 45]. Plant measurements show that a fairly low hydrogen concentration results in low corrosion potential of core components during the fuel cycle after the application of NMCA. However, there are several unknown parameters in the core of BWRs such as water flow rates, radiation flux, dissolved hydrogen and oxygen concentrations, etc. It is possible that neither HWC nor NMCA can provide a sufficient decrease in the ECP of construction materials simply because of very high oxidant concentrations, the difficulty in achieving excess of hydrogen, or because these technologies may be unattractive to plant operators [46]. Another possibility to reduce the susceptibility of stainless steel components to stress corrosion cracking is to apply dielectric coatings onto the metal surface. By using dielectric coatings, the reactor components can be protected against stress corrosion cracking even without HWC. However, it is not yet clear if different coating techniques can be developed to the stage where real plant experiments will be performed [46, 47].

4. Oxide films and mechanism of radioactivity incorporation

In addition to the susceptibility of the materials to different forms of corrosion, the incorporation of radioactive species on the surfaces of the primary circuit in nuclear power plants is greatly influenced by the physical and chemical properties of the oxide films. Oxide films formed at high temperatures in various kinds of environments generally consist of a compact inner layer and of a more porous outer layer. The overall corrosion rate of stainless steels is likely to be controlled totally by ion transport through this compact, inner oxide layer. However, ion transport through the whole oxide film affects the extent of corrosion product deposition from the water layer next to the oxide surface and thus has an influence on the total thickness of the oxide films [48, 49].

During the deposition of corrosion products, activated species are incorporated into the oxide films. The incorporation of activated corrosion products into oxide films can basically proceed via at least three different mechanisms: surface adsorption/complexation, ion exchange or direct reaction/crystallisation [53]. In addition, diffusion along the pores and cracks in the outer part of the duplex oxide film, as well as diffusion along the grain boundaries in the dense part of the oxide, enables the activity to be spread throughout the thickness of the oxide film. A schematic picture of a typical oxide film growing on a stainless steel surface in typical PWR water is shown in Fig. 3.

A correlation between oxide film structures and activity incorporation was observed on cold leg surfaces at Loviisa Unit 2, where activity levels started to increase significantly in the late 1980s (Appendix V). At the same time activity levels at Unit 1 remained low. The room temperature and high temperature water chemistry history was analysed by comparing available documents of the water chemistry practices from both units during full power operations. However, it was not possible to indicate any fundamental difference between the two units. The only recorded anomaly was the higher dissolved iron and nickel concentrations in the primary coolant of Unit 1. Since the water chemistry parameters did not explain the higher activity levels, material samples were cut from the surfaces exposed to the primary coolant. These samples were analysed using different surface analysis techniques and the detailed results are shown in Appendix V.

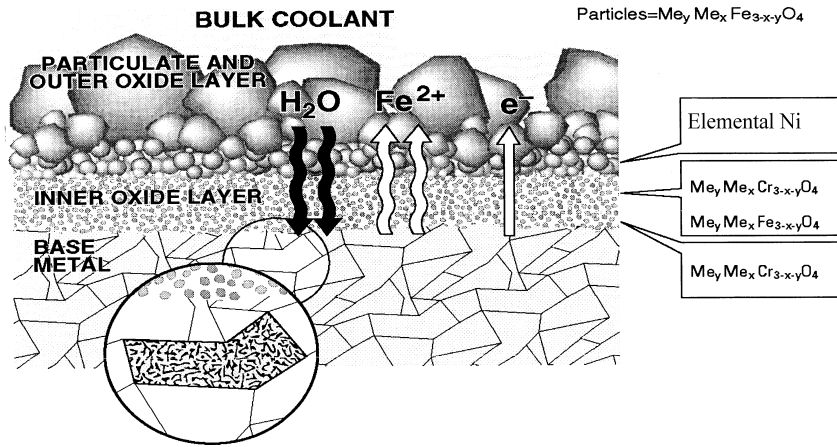


Figure 3. Schematic picture of an oxide film formed on type 316 stainless steel in PWR water.

The pronounced activity build-up was found to be clearly connected to the deviating oxide structure in the cold leg of Unit 2. The sample from Unit 2 did not contain a real deposited iron/nickel rich film which was observed on the samples from Unit 1. For some reason a typical non-stoichiometric nickel ferrite ($Ni_{1-x}Fe_{2+x}O_4$) layer for PWR conditions [23, 50–52] did not exist on the sample from the cold leg of Unit 2. The dominating oxide film on this sample was chromium-rich film of type $Ni_{1-x}Fe_{2+x-y}Cr_yO_4$ spinel [23, 50–52]. This was similar to the thinner, inner grown-on oxide layer on the sample from the cold leg of Unit 1. According to Lister [51], the chromium-rich oxide film incorporates ^{60}Co strongly, but since it is typically rather thin, a relatively small amount of activity is incorporated. However, at Loviisa Unit 2, the cold leg oxide films had a thick chromium-rich layer and were therefore able to incorporate more ^{60}Co than the oxide films at Loviisa Unit 1. Probably due to the outer nickel ferrite film, the activity levels in Unit 1 have remained low even today. It is still unknown what caused the differences in the oxide film structures between the units.

The models for high-temperature aqueous oxidation of metals lack confirming experimental evidence. One reason for this is the fact that the properties of the

surface films accommodate to the temperature of the environment and to the composition of the coolant, i.e. applied water chemistry. A reliable characterisation of the properties and behaviour of oxide films should be performed in relevant conditions and cannot be carried out without appropriate *in-situ* techniques. The next chapters discuss in some detail the development of different *in-situ* high temperature electrochemical techniques for this purpose.

5. The CDE-arrangement for electrochemical studies of construction materials

5.1 Description of the CDE-arrangement

The contact electric resistance (CER) technique was developed at VTT during the 1990s as a first step in characterising the electronic properties of oxide films in aqueous high-temperature high-pressure environments [54]. Due to the possibility to control accurately the distance between two electrodes, the CER system has been modified to a controlled distance electrochemistry (CDE)-arrangement. This enables electrochemical measurements to be performed in poorly-conductive media such as simulated BWR coolant. Application of the CDE-arrangement to various electrochemical measurements has already been described in several communications [55–57, Appendix VI]. This experimental set-up is shown schematically in Fig. 4.

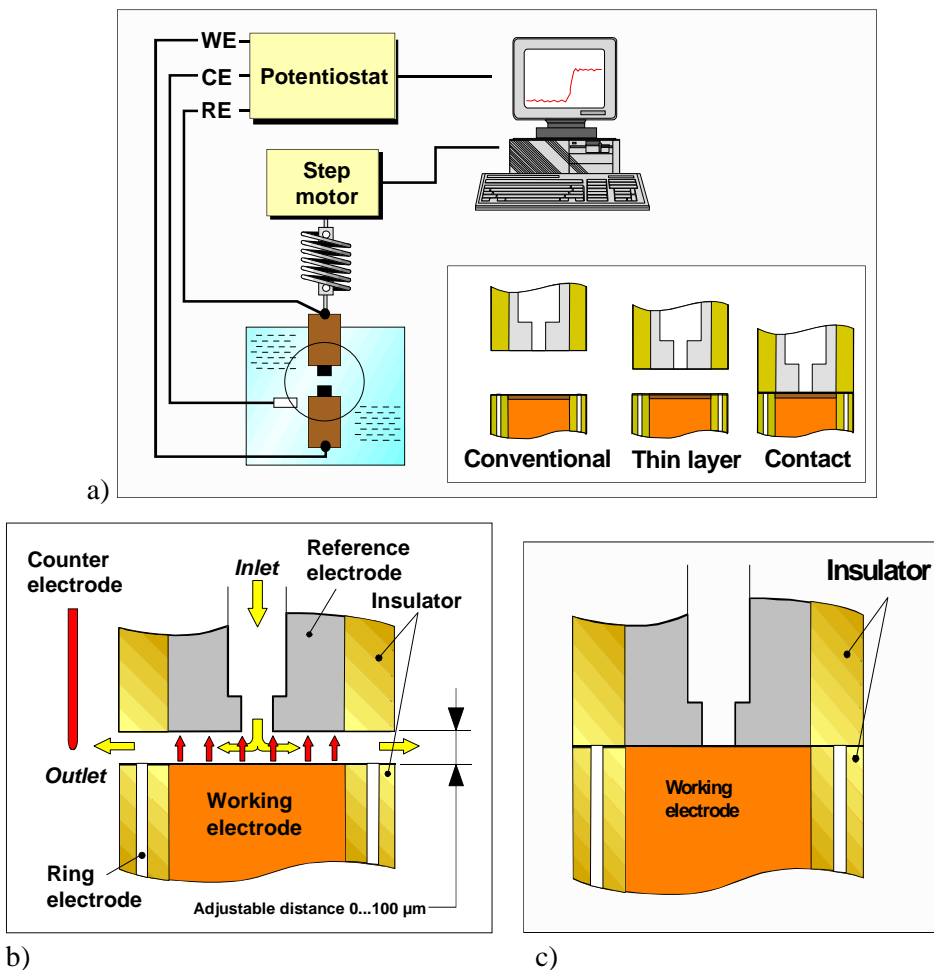


Figure 4. Schematic representation of the controlled-distance electrochemistry (CDE) -arrangement (a) and its different applications; (b) position of electrodes in thin-layer electrochemistry measurements, (c) position of electrodes in solid contact measurements.

The CDE-arrangement can be employed for conventional electrochemical measurements, in which the gap between the working and reference electrodes may be large but more importantly for the following measurements:

Thin-layer electrochemistry (TLEC) measurements

- Thin-layer electrochemical impedance measurements to characterise the oxidation and reduction kinetics and mechanisms of metals as well as the properties of metal oxide films even in low-conductivity aqueous environments [Appendix VI].
- Other controlled-potential and controlled-current measurements in low-conductivity aqueous environments [Appendix VI].

Solid contact measurements

- Contact electric resistance (CER) measurements [54] to investigate and/or to monitor the electronic properties of surface films.
- Contact electric impedance (CEI) measurements [Appendix VI, VII] to measure the solid contact impedance spectra of oxide films.

Wall-jet measurements

- Detection of soluble species released from the working electrode [Appendix VI, VIII].
- Influence of electrolyte flow rate on electrode reactions.

An extensive test matrix was used to optimise the electrode configuration in the CDE- arrangement during TLEC measurements. The main conclusions of the work can be summarised as follows:

- The standard TLEC configuration, in which the Ir tip is used as a reference electrode and the counter electrode is situated outside the gap, can be used for electrochemical measurements both in pure water (BWR coolant) and in more conductive solutions such as PWR coolant.
- The location of the counter electrode does not have a significant influence on the impedance response when using the standard TLEC configuration.

- The alternative TLEC configuration, in which the Ir tip is used as a counter electrode and the reference electrode is situated outside the gap, is suitable for electrochemical measurements with both small and large polarisation currents in typical BWR water. In solutions with a slightly higher conductivity ($\kappa \cong 100 \mu\text{Scm}^{-1}$), the use of the Ir tip as a reference is recommended.

5.2 Application of the CDE-arrangement to characterise the oxide film on type 316L stainless steel

In the CDE-arrangement the combination of impedance, dc resistance (CER) and other electrochemical measurements allow characterisation of the electronic properties of the oxide films formed on construction materials, ionic transport through these films, and provides information about corrosion reactions at the interface between film and environment. Appendix VI shows the results obtained in the test during which the oxide film forming on type 316 L stainless steel was characterised using the CDE-arrangement in high temperature fairly low conductivity water.

A combination of electrochemical measurements was performed at the potential where the electronic resistance of the film on type 316 L stainless steel was highest and remained constant. The dc electronic resistance of such a film was about $2.5 \Omega\text{cm}^2$ determined with the CER technique. A similar result was also obtained from the CEI spectrum. In addition, the CEI results suggested that at least two stages of electron transfer take place through the film or that two different types of charge carriers exist in the oxide film. In Appendix VII the CEI technique was used to identify the conduction mechanisms in the anodic oxide film on iron at ambient temperature in borate solution. The main observations from the measurements are summarised in the following chapter.

5.3 Application of the CDE-arrangement to characterise the oxide film on iron

A considerable amount of work has already been carried out on iron to clarify the electronic properties of the oxide film [58–62] and the mechanism of ionic

transport through it [63–67]. Because of the need to combine the understanding of passive film structure and transport processes in oxide films, a model has been presented for the coupling between ionic defect structure and electronic conduction in steady-state passive films [68, 69]. However, the model was not able to predict quantitatively the transport properties of anodic films, because reliable data on the mobility of electronic charge carriers were not available. Thus, the objective of Appendix VII was to predict quantitatively the electronic and ionic transport properties of oxide films on iron.

The electrochemical impedance measurements showed that electronic contribution dominates the impedance response of an anodic film on Fe in a nearly-neutral electrolyte [69]. The electronic resistance of the oxide film was roughly $3 \Omega\text{cm}^2$ measured using ac CEI and dc CER techniques. In addition, the CEI results indicated that at least two different relaxation processes take place in the system. The high-frequency one strongly suggested an electronic relaxation process, which may be either interfacial charge transfer or charging of the space charge layer. The lower characteristic frequency may be due to a transport process. It is reasonable to connect this process with the diffusion-migration transport of electronic and ionic charge carriers within the film. These experimental observations may suggest that both an electronic charging process and defect transport contribute to the contact electric impedance response. In order to model quantitatively the electronic conductivity and ion transport processes involved in corrosion, it is necessary to have values for diffusion coefficients of ions and electrons (D_i and D_e). To determine these values, estimates for the film thickness L and the steady state ionic charge carrier concentration c_p were needed. A detailed description of how these terms were obtained is given in Appendix VII. Knowing the oxide film thickness and the ionic charge carrier concentration it was possible to calculate the diffusion coefficients for the ionic charge carriers ($D_i = 10^{-16} \text{cm}^2 \text{s}^{-1}$) and for the electronic charge carriers ($D_e = 10^{-11} \text{cm}^2 \text{s}^{-1}$). The calculated values in Appendix VII indicate that the values of both diffusion coefficients are practically independent of potential in the investigated range. The difference of roughly five orders of magnitude between the values of D_e and D_i , ($D_e \gg D_i$) supports the assumption of the predominance of electronic conductivity over ionic conductivity in the passive film on iron.

5.4 Application of the CDE-arrangement to study the transpassive dissolution of Fe-Cr-Mo alloys

As a fresh metal surface oxidises, ions may be released into the aqueous environment. These soluble species can be detected in high temperature and high pressure environments by using the wall-jet application of the CDE-arrangement shown in Fig. 4. Electrochemical detection of soluble species in a flowing system can be performed by controlling the potential of the detecting electrode at a fixed value and monitoring the current. In the CDE-arrangement, the test solution can be pumped through the inert electrode perpendicularly onto the working electrode surface. When the corrosion reaction takes place on the working electrode surface, the soluble reaction products are hydrodynamically transported to the ring where they are oxidised or reduced, depending on the ring potential, and the resulting current is measured. As the potential of the ring electrode is changed, different soluble species in the solution can be detected. By changing the pumping rate of the solution through the inert electrode or the distance between working and inert electrodes, it is possible to change significantly the flow rate ($0\text{--}5\text{ ms}^{-1}$) on the working electrode surface. By pumping the solution on to the working electrode surface, the relevant composition of the solution is maintained, which is of utmost importance when e.g. the effects of novel water chemistries are studied or when new materials are tested for their corrosion resistance.

The aim of the preliminary measurements described in the Appendix VIII was to study the influence of molybdenum on the transpassive dissolution of Cr from Fe-Cr-Mo alloys at high temperatures. It has been demonstrated earlier in ambient conditions that the addition of Cr and Mo results in increased general corrosion in highly oxidising environments due to enhanced transpassive dissolution of chromium [70, 71].

Voltammograms for the Fe-Cr-Mo alloys were first measured using stationary samples exposed freely to $0.1\text{ M Na}_2\text{B}_4\text{O}_7$ at 200°C in a static autoclave. One set of these results is shown in Fig. 5. The results show that transpassive dissolution starts at the same potential which was earlier measured for pure Cr due to oxidation of Cr(III) to Cr(VI). Unlike in the case of pure chromium, a clear secondary passivation is observed for all the alloys. This may be due to the fact that as the film gets depleted in Cr due to transpassive dissolution, an iron-rich

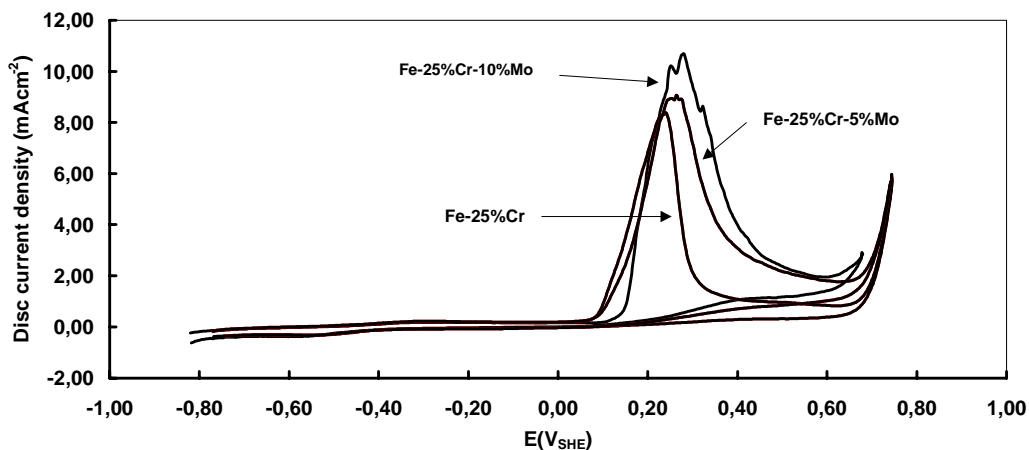


Figure 5. Linear sweep voltammograms for stationary samples of Fe-25%Cr, Fe-25%Cr-5%Mo and Fe-25%Cr-10%Mo at 200 °C in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ in a static autoclave. Sweep rate 2 mVs^{-1} .

secondary oxide film is formed on the alloy [71]. Furthermore, the transpassive dissolution currents are higher the higher the molybdenum content in the alloy.

The transpassive dissolution of Cr starts at 200 °C in the same potential range ($E > 0 \text{ V}_{\text{SHE}}$) for the samples in the wall-jet arrangement (see Appendix VIII) as for the stationary samples shown in Fig. 5. However, the results obtained with the wall-jet arrangement show two significant differences compared to the stationary samples: Firstly, the higher the Mo content of the alloy, the lower were the transpassive oxidation currents measured with the wall-jet arrangement, while the opposite behaviour was found with the stationary samples. Secondly, the secondary passivation was much less pronounced for all the studied alloys when using the wall-jet arrangement.

The measured ring currents demonstrated that the production of soluble species during transpassive oxidation of the studied alloys is higher the higher the Mo content of the alloy, although the anodic disc currents in the CDE-arrangement showed the opposite trend. These two observations indicate that in these experimental conditions the addition of Mo results in a smaller overall oxidation

rate, but simultaneously in a considerably higher production rate of soluble species from Fe-Cr-Mo alloys.

In order to perform quantitative measurements, further development is required. Hydrodynamic analysis indicated that an exact quantification of the results requires uniform conditions over the working electrode surface. Another approach offered by the present wall-jet configuration is to study the influence of flow rates on corrosion phenomena at room temperature and at high temperatures. The results of this work already indicated that e.g. the secondary passivation of Fe-Cr-Mo alloys may depend strongly on hydrodynamic conditions. It is likely that similar phenomena exist for other materials in other potential regions.

6. Summary of the main results

This thesis summarises the work done at the Technical Research Centre of Finland to understand factors affecting the oxidation behaviour of construction materials in typical nuclear power plant conditions. The main results obtained in this work are summarised below:

- The work started by manufacturing the external pressure-balanced reference electrode (Finnish Patent No. 94988, issued 27.11.1995; inventors: L. Selin, K. Mäkelä, P. Aaltonen). In addition to calibration of the sensor in question, the first pH_T measurements were performed at 380°C using solid state reference electrodes.
- Measurements in operating nuclear power plants indicated that during transient situations fluctuations in some water chemistry parameters may be significant even though not observed during room temperature monitoring. These fluctuations may have a significant impact on corrosion product behaviour in primary coolants.
- The first published in-core water chemistry measurement in a typical PWR in-core location indicated that reducing conditions existed at least in those locations where the sensors were located.
- The corrosion potential of type 304 stainless steel and nickel based alloy 182 is sensitive to flow conditions at low and intermediate concentrations of oxygen. The results indicate that determination of kinetic parameters for reduction of oxygen and hydrogen peroxide is needed for more accurate corrosion potential modelling work to be successful.
- High radioactivity incorporation into the oxide films on construction materials in one of the units at the Loviisa nuclear power plant was related to significant changes in the oxide film structure.
- Combination of different electrochemical measurement techniques into a CDE-arrangement gives comprehensive information about the electronic and ionic transport properties of oxide films in relevant high temperature

environments. The work has resulted in an international patent application, PCT/FI98/00627.

- Contact electric impedance and resistance measurements enabled the quantitative prediction of ionic and electronic properties of oxide film on iron.
- The developed wall-jet configuration based on the CDE-arrangement can be used to qualitatively detect soluble species both at room temperature and at elevated temperatures.

7. Conclusions

Different corrosion phenomena may have a serious impact on construction materials employed in high-temperature aqueous environments. To be able to mitigate the risk of detrimental corrosion phenomena of structural materials, a mechanistic understanding of the contributing processes is required. This thesis describes the development and application of different electrochemical techniques in order to obtain information about processes affecting the oxidation behaviour of typical construction materials in operating nuclear power plants. The main conclusions of this work are as follows:

- High temperature electrodes provide sufficiently reliable and accurate information about different operational environments both in operating power plants and in laboratory conditions.
- Even though water chemistry has an impact on all aqueous corrosion phenomena in power plants, detailed information about factors affecting phenomena like activity build-up and stress corrosion cracking cannot be obtained solely from parameters like pH_T and ECP.
- A more comprehensive understanding is needed of oxide film structures and their electronic and ionic transport properties in high temperature aqueous solutions. The CDE-arrangement developed during this thesis enables the use of a combination of different electrochemical techniques to characterise these oxide film properties under relevant conditions.
- The benefits of high temperature electrochemical measurements are rather limited if they are not properly used in models describing high temperature oxidation of construction materials.

If these different electrochemical techniques are to be used routinely in power plants they should be simpler in design and have lower operating, capital and maintenance costs. Until this is achieved, these techniques will be used only during special campaigns. However, the data obtained during the special campaigns can be used to benchmark the expert systems providing more accurate predictions of effects of operational conditions on material behaviour in locations where in-line monitoring is not practical or is too expensive.

References

1. Berge, J.P. What are today's choices for PWRs water chemistry. Proceedings of JAIF International Conference on Water Chemistry in Nuclear Power Plants – Water Chemistry '98, Kashiwazaki, Japan, 13–16 October, 1998. Pp. 7–12.
2. Millet, P.J. and Wood, C.J. Recent advances in water chemistry control at US PWRs. Proceedings of JAIF International Conference on Water Chemistry in Nuclear Power Plants – Water Chemistry '98, Kashiwazaki, Japan, 13–16 October, 1998. Pp. 19–24.
3. Niedrach, L.W. J. Electrochem. Soc., 127 (1980), p. 2122.
4. Tsuruta, T. and Macdonald, D.D. J. Electrochem. Soc., 128 (1981), p. 1199.
5. Tsuruta, T. and Macdonald, D.D. J. Electrochem. Soc., 129 (1982), p. 1221.
6. Macdonald, D.D. and Hettiarachchi, S. J. Electrochem. Soc., 131 (1984), p. 2206.
7. Hettiarachchi, S., Kedzierzawski, P. and Macdonald, D.D. J. Electrochem. Soc., 132 (1985), p. 1866.
8. Danielson, M.J., Koski, O.H and Myers, J. J. Electrochem. Soc., 132 (1985), p. 296.
9. McKubre, M.C.H. and Madou, M. Probes for corrosion-related variables in LWR coolant. EPRI NP-5372, Palo Alto, 1987.
10. Lvov, S.N., Gao, H. and Macdonald, D.D. J. Electroanal. Chem., 443 (1998), p. 186.

11. Hettiarachchi, S., Mäkelä, K. and Macdonald, D.D. Development of solid state reference electrodes and pH sensors for monitoring nuclear reactor cooling water systems. Proceedings of JAIF International Conference on Water Chemistry in Nuclear Power Plants, Tokyo, Japan, 22–25 April, 1991. P. 349–354.
12. Hettiarachchi, S., Macdonald, D.D., Song, H. and Mäkelä, K. AIChE Symp. Ser., 278 (1990), p. 54.
13. Seyes, A.A., van Haute, A.A. and Fujii, T. The value of the external diffusion potential in corrosion experiments at high temperature introduction of a thermal diffusion coefficient. Corrosion, Houston, 1977. P. 467.
14. Macdonald, D.D., Scott, A.C. and Wentreck, P. J. Electrochem. Soc., 126 (1979), p. 908.
15. Macdonald, D.D., Scott, A.C. and Wentreck, P. J. Electrochem. Soc., 126 (1979), p. 1618.
16. Danielson, M.J. Corrosion, 39 (1983), p. 202.
17. Bogaerts, W.F. and van Haute, A.A. J. Electrochem. Soc., 131 (1984), p. 68.
18. Hettiarachchi, S., Mäkelä, K., Song, H. and Macdonald, D.D. J. Electrochem. Soc., 139 (1992), p. L3.
19. Mäkelä, K., Hettiarachchi, S. and Macdonald, D.D. Development of reference and pH sensors for monitoring high temperature water chemistry parameters in nuclear power plants, Proceedings of 12th Scandinavian Corrosion & EUROCORR'92, Espoo, Finland, 31 May – 4 June 1992. Pp. 155–167.
20. Hettiarachchi, S., Song, H., Mäkelä, K., Emerson, R. and Macdonald, D.D. Development of pH and reference electrodes for use in supercritical water. Proceedings of international conference on measuring waterborne trace substances, Baltimore, USA, 1990. 18 p.

21. Aaltonen, P. Mäkelä, K., Järnström, R. and Kvarnström, R. Shutdown water chemistry and dissolution of activated corrosion products at Loviisa 1 PWR. Proceedings of 12th Scandinavian Corrosion & EUROCORR'92, Espoo, Finland, 31 May – 4 June, 1992. Pp. 77–87.
22. Berry, W.E. and Diegle, R.B. Survey of corrosion product generation, transport and deposition in light water nuclear reactors. EPRI NP-522, Palo Alto, 1979.
23. Sandler, Y.L. Corrosion, 35 (1979), p. 205.
24. Llovet, R., Kormuth, J.W., Lillo, E.F., Boronat, M. and Ortega, A. Shutdown chemistry in Spanish plants. Proceeding of sixth conference on water chemistry for nuclear reactor systems, Bournemouth, Great Britain, October 12–15, 1992. Pp. 67–73.
25. Mäkelä, K., Aaltonen, P. and Järnström, R. Shutdown water chemistry and dissolution of corrosion products at Loviisa 1 PWR. PWR Plant Chemist's Meeting, San Diego, USA, 1992. 14 p.
26. Pashevich, V. I. Therm. Eng., 31 (1984), p. 595.
27. Pashevich, V. I. Therm. Eng., 32 (1985), p. 27.
28. Kysela, J., Jind Rich, K., George, G., Kelm, H., Nebel, D., Schlenkrich, H., Herold, C. and Schönherr, M. Influence of hydrazine and higher pH on the corrosion product layer of austenitic steel. Proceedings of water chemistry of nuclear reactor systems 5, Bournemouth, Great Britain, October 23–27, 1989. Pp. 97–104.
29. Brunning, J., Cake, P., Harper, A. and Sims, H. E. Some observations on hydrazine and ammonia based chemistries in PWRs. IAEA technical committee meeting on influence of water chemistry on fuel cladding behaviour, Rez, 1993.

30. Yurmanov, V.A., Mamet, V.A., Shestakov, Yu.M. and Amosov, M.M. Water chemistries in VVER reactors. IAEA technical committee meeting on influence of water chemistry on fuel cladding behaviour, Rez, 1993.
31. Beyer, W., Stellwag, B., Wieling, N. and Doerr, A. On-line monitoring of electrode potentials in the steam generator of a PWR. 3rd International Symposium on the Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors. Traverse City, USA, 30 August – 3 September, 1987. Pp. 173–182.
32. Mäkelä, K. Secondary side ECP monitoring. EPRI's PWR Secondary Water Chemistry Training and Optimization Workshop, San Antonio, USA, 11–13 July, 1994. 15 p.
33. Mäkelä, K., Laitinen, T. and Buddas, T. The effect of new feed water distributor design on the impurity concentrations in one of the Loviisa 2 unit steam generators. Proceedings of water chemistry of nuclear reactor systems, 7. Vol. 1, Bournemouth, Great Britain, 13–17 October, 1996. Pp. 364–370.
34. Molander, A., Rosborg, B., Anderson, P.O. and Bjornkvist, L. Electrochemical measurements in secondary system of Ringhals 3 PWR. Proceedings of water chemistry of nuclear reactor systems, 6. Vol. 2, Bournemouth, Great Britain, 12–15 October, 1992. Pp. 228–234.
35. Kassen, W.R., Seager, J.S., Beichel, K.E. and Millet, P.J. On-line electrochemical potential monitoring in the feed water at the St. Lucie 2 PWR. Proceedings of conference on chemistry in water reactors: operating experience & new developments, Nice, France, 24–27 April, 1994. Pp. 638–641.
36. Fox, M.J. A review of boiling water reactor water chemistry. NUREG/CR-5115, ANL-88-42, R5. Washington: US Nuclear Regulatory Commission, NRC FIN A2212, 1989.
37. Wood, C.J. BWR Water Chemistry Guidelines – 1993 Revision, Normal and Hydrogen Water Chemistry. EPRI TR-103515, Palo Alto, USA.

38. Andresen, P.L. Effect of noble metal coating & alloying on the stress corrosion crack growth rate of stainless steel in 288°C water. Proceedings of Sixth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, San Diego, USA, 1–5 August, 1993. Pp. 245–253.
39. Indig, M.E. and McIlree, A.R. Corrosion, 35 (1979), p. 288.
40. Macdonald, D.D. Corrosion, 48 (1992), p. 194.
41. Lin, C.C. and Smith, F.R. Decomposition of hydrogen peroxide at elevated temperatures. EPRI NP-6733, Palo Alto, 1990.
42. Nelson, J.L. and Andresen, P.L. Review of current research and understanding of irradiation-assisted stress corrosion cracking. Proceedings of fourth international symposium on environmental degradation of materials in nuclear power systems-water reactors, Monterey, USA, 25–29 August, 1991. Pp. 10–26.
43. Jones, R. BWR Hydrogen Water Chemistry Guidelines: 1987 Revision. EPRI NP-4947SR. Palo Alto, USA: EPRI, 1988.
44. Cowan, R.L. The mitigation of IGSCC of BRW internals with hydrogen water chemistry, Proceedings of water chemistry of nuclear reactor systems, 7. Bournemouth, Great Britain, 13–17 October, 1996. Pp. 196–206.
45. Cowan, R.L., Hettiarachchi, S., Hale, D.H. and Law, R.J. Electrochemical corrosion potential monitoring in boiling water reactors. Proceedings of JAIF International Conference on Water Chemistry in Nuclear Power Plants – Water Chemistry '98, Kashiwazaki, Japan, 13–16 October, 1998. Pp. 419–425.
46. Yeh, T.K. and Macdonald, D.D. Predictions of enhancing hydrogen water chemistry for boiling water reactors by general catalysis and general inhibition. Corrosion 96, USA, Paper 96124.

47. Kim, Y.J. and Andresen, P.L. Application of insulated protective coating for reduction of corrosion potential in high temperature water. Corrosion 1996, USA, Paper 96105.
48. Robertson, J. Corros. Sci., 29 (1989), p. 1275.
49. Robertson, J. Corros. Sci., 32 (1991), p. 443.
50. Lister, D.H. and Davidson, R.D. Corrosion product release in light water reactors. EPRI NP-6512, Palo Alto, 1989.
51. Lister, D.H. Activity transport and corrosion processes in PWRs. Proceedings of sixth conference on water chemistry of nuclear reactor systems, 6. Bournemouth, Great Britain, 12–15 October, 1992. Pp. 49–60.
52. Riess, R., and Stellwag, B. Effects of zinc on the contamination and structure of oxide layers. Proceedings of water chemistry of nuclear reactor systems, 7. Bournemouth, Great Britain, 13–17 October, 1996. Pp. 573–582.
53. Lin, C.C and Smith, F.R. BWR cobalt deposition studies: Final report. EPRI NP-5808, May. Palo Alto, USA: EPRI, 1988.
54. Saario, T., Laitinen, T. and Piippo, J. Mat. Sci. Forum, 289–292 (1998), p. 193.
55. Bojinov, M., Laitinen, T., Mäkelä, K., Saario, T. and Sirkiä, P. A combination of AC impedance and DC resistance techniques to study corrosion in high temperature aqueous environments. Proceedings of the 4th International Symposium on Electrochemical Impedance Spectroscopy, Rio de Janeiro, Brazil. 2–7 August, 1998. Pp. 393–395.
56. Bojinov, M., Laitinen, T., Mäkelä, K., Saario, T., and Sirkiä, P. A novel technique for electrochemical measurements in low conductivity environments. EUROCORR'98, Utrecht, The Netherlands, 28 September – 1 October, 1998. 6 p.

57. Bojinov, M., Laitinen, T., Mäkelä, K., Mäkelä, M., Saario, T. and Sirkiä, P. Advanced electrochemical techniques for power plant use. EUROCORR '99, The European Corrosion Congress, Aachen, Germany, 30 August – 2 September, 1999. 17 p.
58. Stimming, U. and Schultze, J.W. *Electrochim. Acta*, 24 (1979), p. 859.
59. Searson, P.C., Latanision, R.M. and Stimming, U. *J. Electrochem. Soc.*, 135 (1988), p. 1358.
60. Koenig, U. and Schultze, J.W. *Solid State Ionics*, 255 (1992), p. 53.
61. Koenig, U. *Materials Sci. Forum*, 79 (1995), p. 192.
62. Buechler, M., Schmuki, P., and Boehni, H. J. *Electrochem. Soc.*, 144 (1997), p. 2307.
63. Vetter, K.J. *Electrochim. Acta*, 25 (1971), p. 1923.
64. Kirchheim, R. *Corros. Sci.*, 29 (1989), p. 183.
65. Castro, E.B. *Electrochim. Acta*, 39 (1994), p. 2117.
66. Cahan, B.D. and Chen, C.-T. *J. Electrochem. Soc.*, 129 (1982), p. 921.
67. Guo, W.-P., Tomoe, Y., Imaizumi, H. and Katoh, K. *J. Electroanal. Chem.*, 95 (1998), p. 445.
68. Bojinov, M., Fabricius, G., Laitinen, T., Mäkelä, K., Saario, T., Sundholm, G. *J. Electrochem. Soc.*, 146 (1999), p. 3238.
69. Bojinov, M., Fabricius, G., Laitinen, T., Mäkelä, K., Saario, T. and Sundholm, G. *Electrochim. Acta* (2000, in print)

70. Bojinov, M., Laitinen, T., Saario, T. and Fabricius, G. Mechanism of transpassive corrosion of chromium in neutral aqueous solutions. EUROCORR'97, The European Corrosion Congress, Trondheim, Norway, 22–25 September, 1997, Vol II. Pp. 617–622.
71. Bojinov, M., Fabricius, G., Laitinen, T. and Saario, T. Transpassivity mechanism of metals and alloys studied by AC impedance, DC resistance and RRDE measurements. *Electrochim. Acta*, 44 (1999), pp. 4331–4343.

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Series title, number and report
code of publication

VTT Publications 415
 VTT-PUBS-415

Author(s) Mäkelä, Kari			
Title Development of techniques for electrochemical studies in power plant environments			
Abstract <p>The properties of the oxide films on the engineering alloys used as construction materials in power plants change as a result of exposure to aqueous environments. The susceptibility of the materials to different forms of corrosion is influenced by the properties of these oxide films. The structure and electrochemical properties of the oxide films are in turn dependent on the applied water chemistry. Therefore, water chemistry control has been used in minimising the impact of different corrosion phenomena in operating power plants. Since there is not only one ideal operational specification for all light water reactors, individually designed water chemistry programs are needed to take into account plant-specific design features and particular problem areas. The applicability of alternative water chemistry practices require fast and reliable in-line electrochemical techniques to monitor possible changes in the oxidation behaviour of nuclear power plant materials.</p> <p>This thesis summarises the work done at the Technical Research Centre of Finland over the past 10 years to increase the knowledge of factors affecting the oxidation behaviour of construction materials in aqueous coolants at high temperatures. The work started with the development of electrodes for measurement of high temperature water chemistry parameters such as pH and the corrosion potential of construction materials. After laboratory testing these electrodes were used both in test reactors and in operating nuclear power plants. These measurements showed that high temperature water chemistry monitoring may be more accurate than corresponding room temperature measurements, particularly during transient situations. However, it was also found that understanding the processes taking place within and on oxide films requires a combination of electrochemical techniques enabling characterisation of the electronic properties of these films. This conclusion resulted in development of a controlled-distance electrochemistry arrangement. The arrangement was used to obtain data on different transport processes in the oxide films exposed to aqueous solutions. The information was then used to model the oxidation behaviour of construction materials in these solutions.</p>			
Keywords power plants, corrosion, nuclear reactors, water chemistry, high temperature, oxide films, properties, electrodes, electrochemistry			
Activity unit VTT Manufacturing Technology, Materials and Structural Integrity, Kemistintie 3, P.O.Box 1704, FIN-02044 VTT, Finland			
ISBN 951-38-5571-6 (soft back ed.) 951-38-5572-4 (URL: http://www.inf.vtt.fi/pdf/)		Project number V9SU00120	
Date June 2000	Language English	Pages 46 p. + app. 128 p.	Price D
Commissioned by Technical Research Centre of Finland (VTT), Ministry of Trade and Industry (KTM), Radiation and Nuclear Safety Authority (STUK), OECD Halden Reactor Project			
Series title and ISSN VTT Publications 1235-0621 (soft back ed.) 1455-0849 (URL: http://www.inf.vtt.fi/pdf/)		Sold by VTT Information Service P.O.Box 2000, FIN-02044 VTT, Finland Phone internat. +358 9 456 4404 Fax +358 9 456 4374	