



**FIELD EXPERIENCE WITH ADVANCED METHODS OF
ON-LINE MONITORING OF WATER CHEMISTRY AND
CORROSION DEGRADATION IN NUCLEAR POWER STATIONS**

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Abstract

Retrospective off-line inspections of the cumulative effects of corrosion damage do not hold the key to maximum reliability and availability of nuclear power stations. They cannot provide meaningful control, because "control" implies feedback within a time scale effective in stopping the problem. For maximum control, real-time, on-line feedback is required. Taking account of this fact, advanced methods for on-line, in-situ water chemistry and corrosion monitoring in nuclear power stations have been developed during the past decade. The terms "on-line" and "in-situ" characterise approaches involving continuous measurement of relevant parameters in high temperature water, preferably directly in the systems and components and not in removed samples at room temperature. This paper describes the field experience to-date with such methods in terms of three examples:

- (1) On-line water chemistry monitoring of the primary coolant during shutdown of a Type VVER-440 PWR.
- (2) Redox and corrosion potential measurements in final feedwater preheaters and steam generators of two large KWU PWRs over several cycles of plant operation.
- (3) Real-time, in-situ corrosion surveillance inside the calandria vault of a CANDU reactor.

The way in which water chemistry sensors and corrosion monitoring sensors complement each other is outlined: on-line, in-situ measurement of pH, conductivity and redox potential gives information about the possible corrosivity of the environment. Electrochemical noise techniques display signals of corrosion activity under the actual environmental conditions.

A common experience gained from separate use of these different types of sensors has been that new and additional information about plants and their actual process conditions is obtained. Moreover, they reveal the intimate relationship between the operational situation and its consequences for the quality of the working fluid and the corrosion behaviour of the plant materials. On this basis, the efficiency of the existing chemistry sampling and control system can be checked and corrosion degradation can be minimised. Furthermore, activity buildup in the primary circuit can be studied.

Further significant advantages can be expected from an integration of these various types of sensors into a common water chemistry and corrosion surveillance system. For confirmation, a complete set of sensors will be installed in the near future in a loop of a test reactor operated with PWR primary coolant chemistry. The purpose of these investigations is to obtain a better understanding of activity build-up on materials as a function of the coolant chemistry.

1. Introduction

The quality of the working fluid is of prime importance for the reliability and availability of power stations. Surveillance of the working fluid in steam power stations relies in essence on standard water sampling practice: water samples are withdrawn from relevant plant systems and components, cooled and continuously or discontinuously analysed with respect to certain important parameters, such as pH value, conductivity, concentration of impurities, etc. . Specified water quality levels must be maintained. In case of excursions from the specified values, actions must be taken.

Water sampling and analysis practice has been successfully used for decades. It is an indispensable tool for the plant chemist.

Considered from the viewpoint of chemical engineering, sampling lines represent chemical reactors. Depending on the layout, temperature and operation mode of

these chemical reactors, the chemistry of the water flowing through the tube can be considerably affected:

- (1) At high temperatures, chemically active species in the fluid, such as oxygen, hydrogen peroxide or hydrazine can react with the tube walls of the sampling lines.
- (2) Corrosion products can be deposited and reentrained during sampling.
- (3) The process of cooling the water samples can alter the solubility and valency of dissolved substances. In addition, it is associated with a change in the pH value of the fluid.

As a consequence, the interpretation of water chemistry data requires considerable expertise on the part of the plant chemist even in case of optimum layout and operation of the sampling systems.

Taking account of these facts, advanced methods for on-line, in-situ water chemistry and corrosion monitoring in steam power stations have been developed during the past decade. This paper describes the field experience to-date with such methods in terms of three examples:

- (1) On-line water chemistry monitoring of the primary coolant during shutdown of a Type VVER-440 PWR.
- (2) Redox and corrosion potential measurements in final feedwater preheaters and steam generators of two large KWU PWRs over several cycles of plant operation.
- (3) Real-time, in-situ corrosion surveillance inside the calandria vault of a CANDU reactor.

The measurements have been already described in detail elsewhere [1], [2],[3], [4]. Purpose of this paper is not to summarise their results. Instead, an attempt is made to trace out common features and inherent benefits of on-line, in-situ water chemistry and corrosion monitoring in power stations. The terms "on-line"

and "in-situ" characterise approaches involving continuous measurement of relevant parameters in high temperature water, preferably directly in the systems and components and not in removed samples at room temperature.

2. On-line Monitoring of Primary Coolant Chemistry during Shutdown of a Type VVER-440 PWR

2.1 Requirements to PWR Primary Coolant Chemistry

The chemistry of the primary coolant of PWRs has to fulfil various major requirements:

- Reactivity control. Chemical shim is usually achieved by dosing boric acid into the coolant.
- Minimisation of release, transport and deposition of corrosion products in the primary circuit. These processes are very important for activity build-up in the system. It is effected by an alkaline water treatment and reducing conditions. Lithium or potassium hydroxide are used as alkalisating agents. Hydrogen or ammonia are added to maintain low redox and corrosion potentials. Ammonia decomposes in the radiation field under formation of hydrogen.
- Compatibility of chemistry to structural materials and fuel cladding.

Reactivity control and thus the concentration of boric acid in the coolant is a function of the burnup of the fuel.

Metal release rates depend on the pH value, temperature and corrosion potential and are material specific. Widely used plant materials for nuclear power stations are austenitic stainless steels, nickel base alloys and cobalt base alloys, which are used for hardfacings. Generally, for minimisation of release, transport and deposition of corrosion products, an elevated pH value of the coolant is favourable [5], [6]. The optimum pH value depends on the major construction

materials used in the considered power station. It may thus slightly differ from plant to plant.

In contrast to minimisation of activity build-up which is achieved by high pH values, advanced fuel element concepts (longer cycles, higher burn-up, increased power) impose a limitation on the use of alkalising agents, especially lithium hydroxide. For steam generators tubed with the nickel base alloy I 600, an influence of the lithium concentration of the coolant on primary water stress corrosion cracking is currently being debated.

The primary coolant chemistry in PWRs is therefore subjected to conflicting demands.

On-line water chemistry and corrosion monitoring enables prompt recording of the response of plant systems to variations in water chemistry. Critical parameters can be identified, yielding the clue to an understanding of the underlying mechanisms. Equipment for measurement of high temperature water chemistry parameters and the concentration of corrosion products has been installed in the Loviisa 1 and 2 nuclear power stations. Results obtained with this equipment are described in the following section.

2.2 On-line Monitoring of Primary Coolant Chemistry during Shutdown of a PWR

The shutdown of PWRs is characterized by large chemistry and temperature gradients. This section concentrates, therefore, on measurement data obtained during a shutdown of Loviisa 1 nuclear power station. Each of the six primary loops of this Type VVER 440 PWR is equipped with coolant cleaning systems. The continuous coolant cleaning system consists of two independent ion-exchanger lines operating under full system pressure at temperatures below 100°C. One is a mixed - bed filter and the other is a cation-anion filter.

The reactor pressure vessel is weld clad with austenitic stainless steel. Primary coolant piping and steam generator tubing are also made of austenitic stainless steels similar to Type AISI 321. Fuel cladding is a zirconium alloy. Nickel and cobalt base alloys are usually not used in Type 440 VVER PWRs.

The corrosion potential of austenitic stainless steel, the high temperature pH value pH_T and the temperature were continuously monitored. Electrodes and sensors were installed in a cell which was connected to a sampling line coming from the RPV core near to the reactor water inlet. The temperature in the cell during power operation was 240°C. The reactor water inlet temperature is 267°C.

Corrosion and redox potential measurements in reactor water of a PWR were also performed by A. Molander et al.[7].

The concentration of soluble corrosion products was measured on-line with ion chromatography using the same sampling line. In addition grab samples were taken at regular intervals from the standard sampling system during shutdown. Conventional water chemistry analyses at room temperature were carried out every two hours during the shutdown.

The variation of the water chemistry parameter during shutdown is shown in Fig. 1. Four operation phases can be distinguished. They are also indicated in Fig. 1:

- (A) Stoppage of ammonia dosage and subsequent start-up of the primary water clean-up system.
- (B) The reactor reaches a subcritical state.
- (C) Boration of the primary water.
- (D) Reactor water temperature decreases below 120°C and degasification is started.

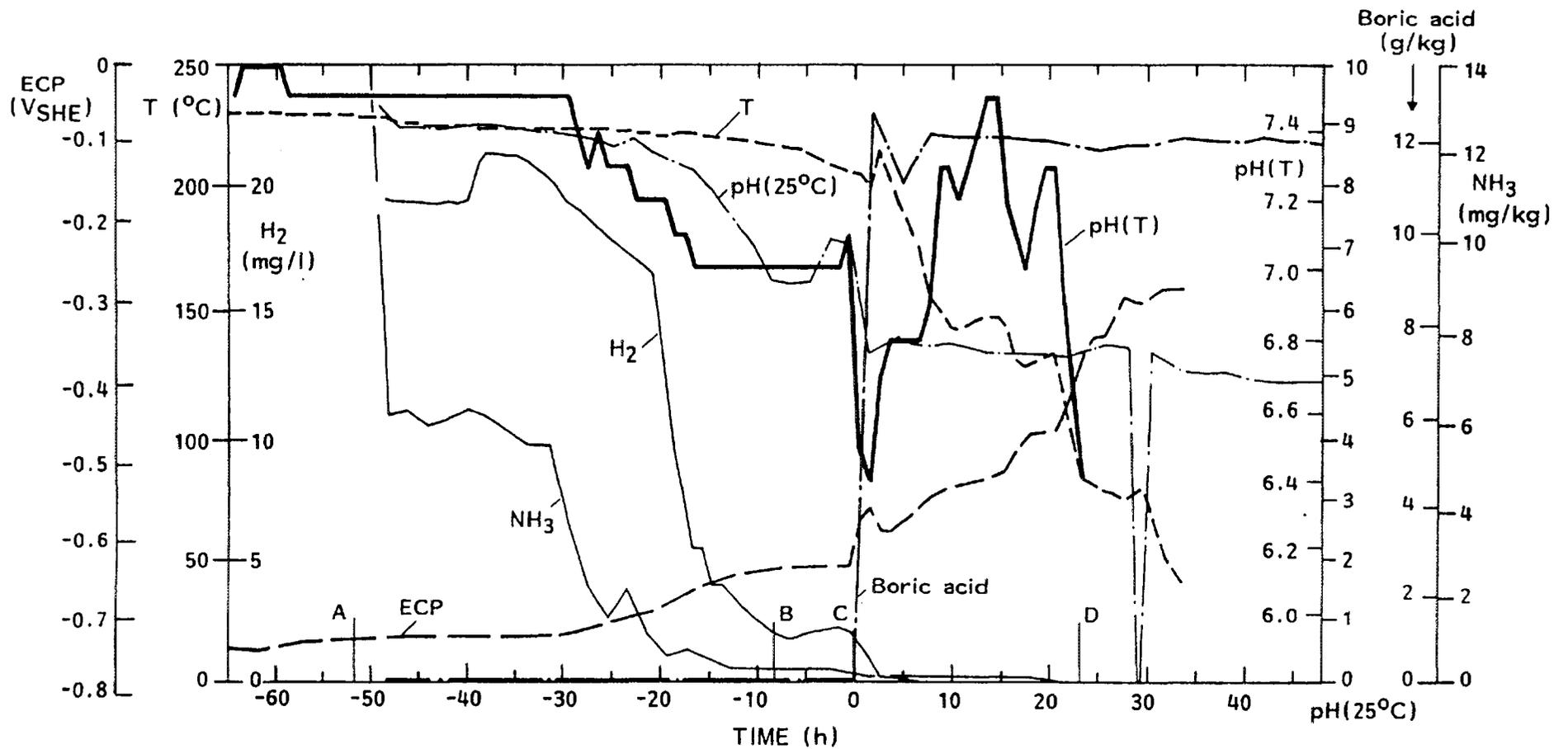


Figure 1 Variation of water chemistry parameters in the primary system during shutdown of the plant.

- Phase A: Stoppage of NH₃ dosage, subsequent start of clean-up system.
- Phase B: Subcriticality of reactor.
- Phase C: Boration of the primary water.
- Phase D: $T_{\text{Reactor}} < 120^{\circ}\text{C}$, start of degasification

The stoppage of ammonia dosage and the subsequent start-up of the clean-up systems is associated with the removal of ammonia and other water treatment chemicals (potassium hydroxide, total alkalinity, i.e. $K^+ + Na^+ + Li^+$).

Therefore, both pH_T and pH_{RT} decrease. Since hydrogen is produced through radiolytical decomposition of NH_3 , its concentration decreases in parallel. As a consequence of the decrease in both pH and H_2 concentration the corrosion potential increases from ca. - 740 mV_{SHE} to ca. - 640 mV_{SHE}.

Phase B (reactor reaches a subcritical state) is characterised by the constancy of water chemistry conditions.

Boration of the system and the following operation period (Phase C) is associated with pronounced fluctuations in the chemistry parameters. The temperature decrease during this phase is ca. 100°C. Upon boration, the high temperature pH_T value decreases rapidly to 6.4. The room temperature pH_{RT} value drops simultaneously to 5.5 and then remains more or less constant. However, the high temperature pH_T value fluctuates significantly between 7.5 max. and 6.4 min.. These fluctuations were associated with simultaneous variations in the coolant temperature and the flow rates in the clean-up systems. The fluctuations in the high temperature pH_T value are ascribed to the capture of boric acid by the ion exchangers and the simultaneous release of basic anions. The effect apparently depends on the flow rate in the clean-up system.

Boric acid is a weakly dissociating substance. Dissociation thus decreases with temperature. This is not the case for strongly dissociating substances, such as potassium and lithium hydroxide. As a consequence, mixed solutions of these substances with concentrations typical for primary coolant are slightly acidic at room temperature. With increasing temperature, such solutions become alkaline. The measured significant differences between pH_T and pH_{RT} are therefore related to the temperature dependent dissociation behaviour of boric acid and

alkalising agents in primary coolant. In addition, actual changes in the coolant composition tend to level out during sampling.

The continuous increase in corrosion potential during this operation period is ascribed to the decreasing coolant temperature.

The final shutdown phase (Phase D, reactor coolant temperature lower than 120°C and degasification) results in a further increase in the corrosion potential. The final value of - 260 mV_{SHE} corresponds roughly to the equilibrium value of the hydrogen electrode in boric acid at the given pH_{RT} value.

Corrosion product release during shutdown of the plant is shown for nickel and cobalt in Fig. 2. The release characteristics of manganese followed the pattern observed for nickel. The dissolution behaviour of iron was similar to cobalt.

A first dissolution peak of all cations was induced by the boration of the system. During the following temperature decrease and pH_T fluctuations the various metal cations showed a different response. Release of the various cations always closely followed the variations in the pH_T. In the case of nickel and manganese, release behaviour was also influenced by variations in the corrosion potential. In the case of cobalt and iron, variations in the corrosion potential were of minor importance. Instead, temperature variations were revealed to be essential for cobalt and iron release.

The results of the simultaneous measurements of high temperature water chemistry parameters and concentrations of corrosion products dissolved in the primary coolant revealed that the release of metal cations is closely linked to pH_T, temperature and corrosion potential.

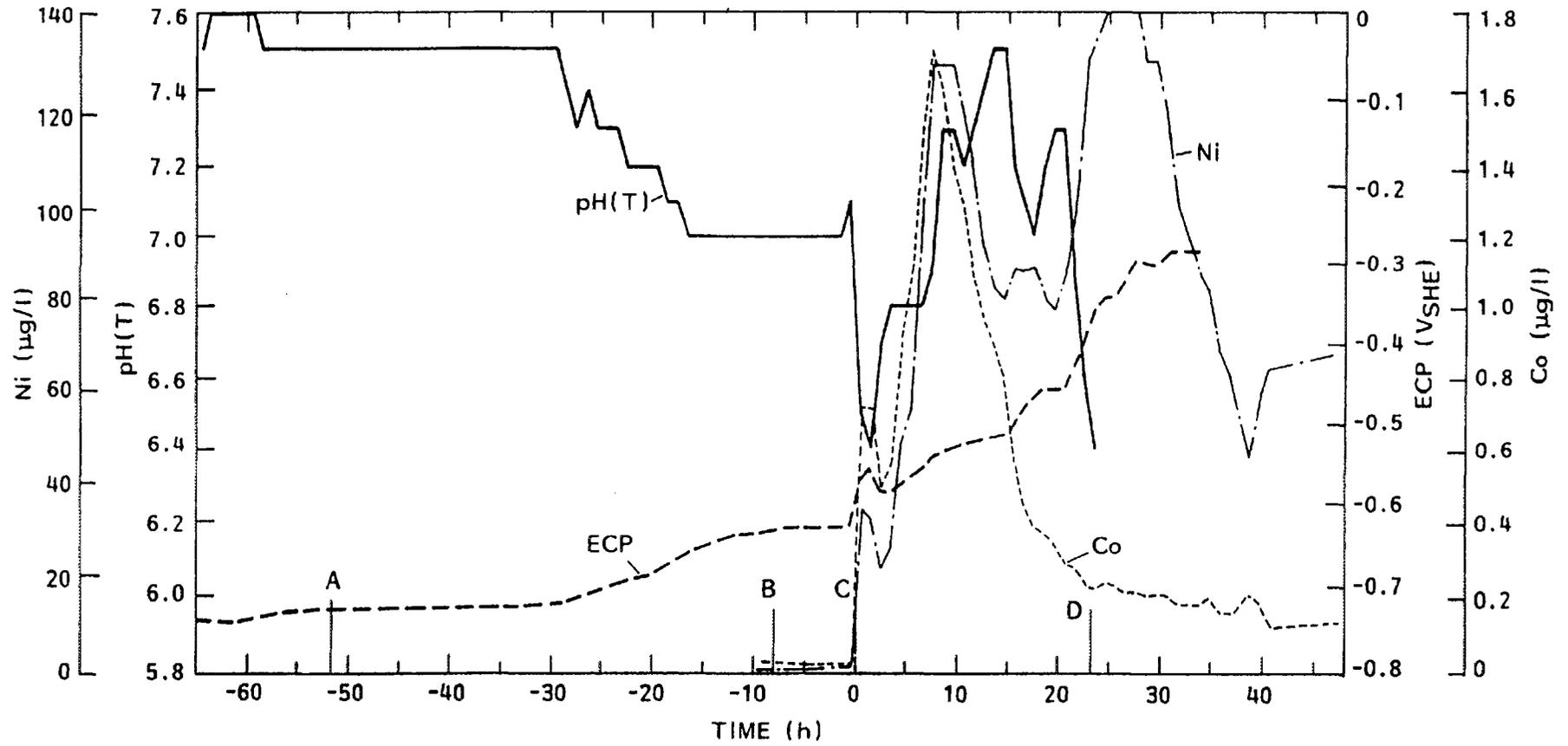


Figure 2 Release of metal cations into the primary coolant during shutdown of the plant.

Moreover, these parameters turned out to be intimately related to plant operation practice. In particular, actual flow rates through the clean-up systems revealed to be of major importance. The induced fluctuations in the high temperature pH_T value were not displayed by the room temperature pH_{RT} value. In order to understand the causes for the observed pH_T fluctuations, the role of the clean-up system and the process taking place during shutdown must be studied in more detail.

2.3 Conclusions

Altogether, on-line water chemistry monitoring indeed gave the clue to a better understanding of release of activated corrosion products not only for this particular power station but also in terms of basic processes.

The consequences for improvement of the shutdown practice can be briefly summarised using the term "soft shutdown". Soft shutdown practice has been developed for boiling water reactors and aims at avoiding pronounced gradients in terms of pressure, temperature and water chemistry. The results obtained in Loviisa 1 show that such features must be also taken into account in pressurised water reactors. It is apparent that on-line water chemistry monitoring is an important tool for the study of such practices in PWRs.

On account of the positive experience with the on-line monitoring system in Loviisa 1, such equipment was also installed in Loviisa 2. It has been used since then routinely for evaluation of the water chemistry in both plants.

3. On-line, In-Situ Monitoring of Corrosion and Redox Potentials in Steam Generators and Feedwater Heaters of PWRs

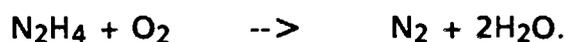
3.1 Requirements to PWR Water/Steam Cycle Chemistry

In order to protect components of water/steam cycles against corrosion, design and sound materials selection are backed up by suitable chemical feedwater conditioning practices to maintain specified water quality levels. Specifications for steam generator feedwater only permit extremely low levels of impurities. In the event of malfunctions in the condensers, however, salts and oxidants in the feedwater can be entrained into the steam generator and accumulate in pockets of zero flow. The spectrum of water quality which can be encountered in nuclear steam generators can therefore range from extremely pure to heavily contaminated water. Reducing water conditions must prevail if the safety margin with regard to corrosion mechanisms such as pitting and stress corrosion cracking is to be maintained.

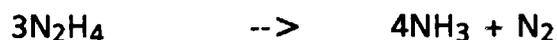
Potential oxidants in steam generator water are dissolved copper species and oxygen. Copper compounds are released from turbine condensers and feedwater heater tubes and transported into the steam generators in stations equipped with copper alloys in these components. As already mentioned, air and thus oxygen may be drawn in by leaking turbine condensers.

Widespread water treatment practice is to add hydrazine N_2H_4 to the fluid.

Hydrazine is a reducing agent. It scavenges oxygen according to



The thermal decomposition of hydrazine to ammonia



provides volatile alkalisation of the fluid in the circuit.

Under oxidizing conditions N_2H_4 is electrochemically oxidized, e. g.



Typically, reactions involving hydrazine under the conditions concerned are irreversible. The kinetics of these reactions are dominated by catalytic effects, being additionally influenced by factors such as temperature, pH value, etc.. Depending on the layout, temperature and operation mode of sampling lines for final feedwater, consumption of hydrazine and oxygen can be considerable. Examples are given in Figs. 3 and 4.

Oxidising conditions in steam generators thus cannot be ruled out on the basis of measurement of the concentration of hydrazine and oxygen concentration in water samples withdrawn from final feedwater. For reliable detection of

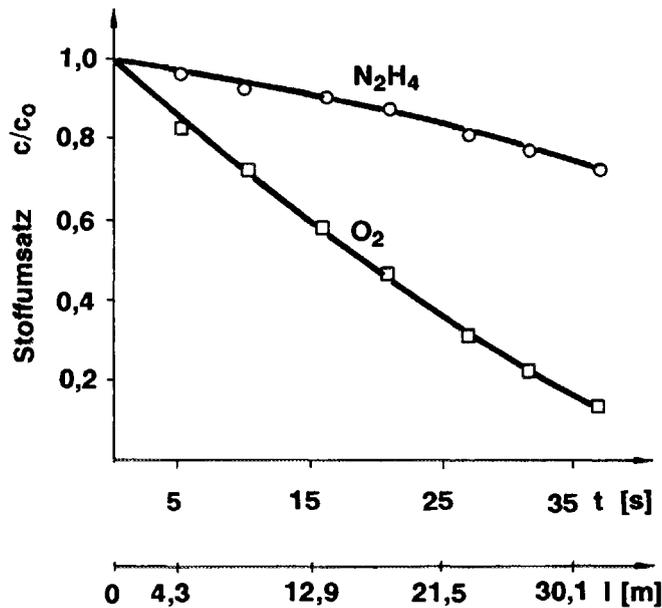


Figure 3 O_2 and N_2H_4 concentration in water flowing through a tube as a function of the tube length.

Test conditions: Tube material austenitic stainless steel, inner diameter 4 mm, water flow rate 35l/h, test temperature 170°C, pressure 80 bar,
 $C_{O_2} \sim 20$ ppb; $C_{N_2H_4} \sim 146$ ppb,
 $C_{NH_3} \sim 1$ ppm at inlet.

Prior to the test, the tube was operated with oxygenated water ($C_{O_2} \sim 400$ ppb).

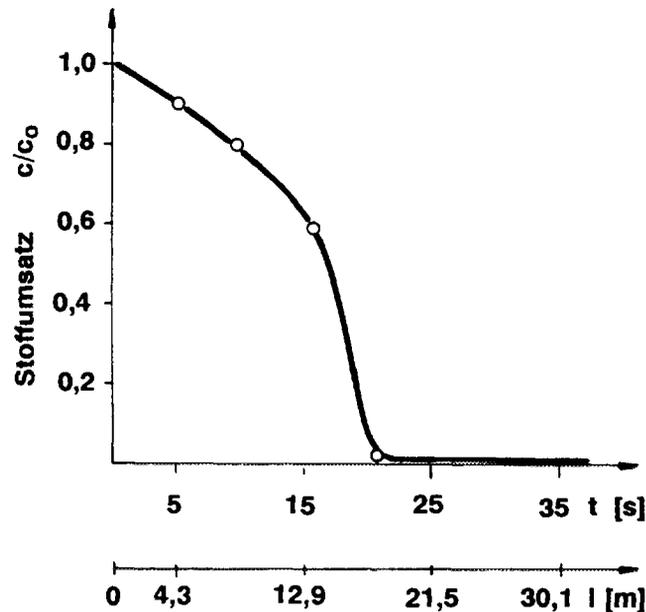


Figure 4 O₂ concentration in water flowing through a tube as a function of the tube length.

Test conditions as described in Fig. 3 with the following exceptions: Prior to the test the tube was operated with water containing hydrazine ($C_{N_2H_4} > 100$ ppb, $CO_2 = 0$ ppb). The test was performed with water, containing 40 ppb O₂ and 105 ppb N₂H₄ at the tube inlet.

oxidising conditions in the steam generator recirculating water, electrode potentials must be measured in-situ.

3.2 Corrosion and Redox Potential Measurements in Steam Generator Circulating Water and Final Feedwater

A monitoring unit for measurement of electrode potentials which was installed in the tube bundle of steam generator of the 1204 MW Biblis A PWR is shown in Fig. 5. Its design is described in detail elsewhere [2], [3].

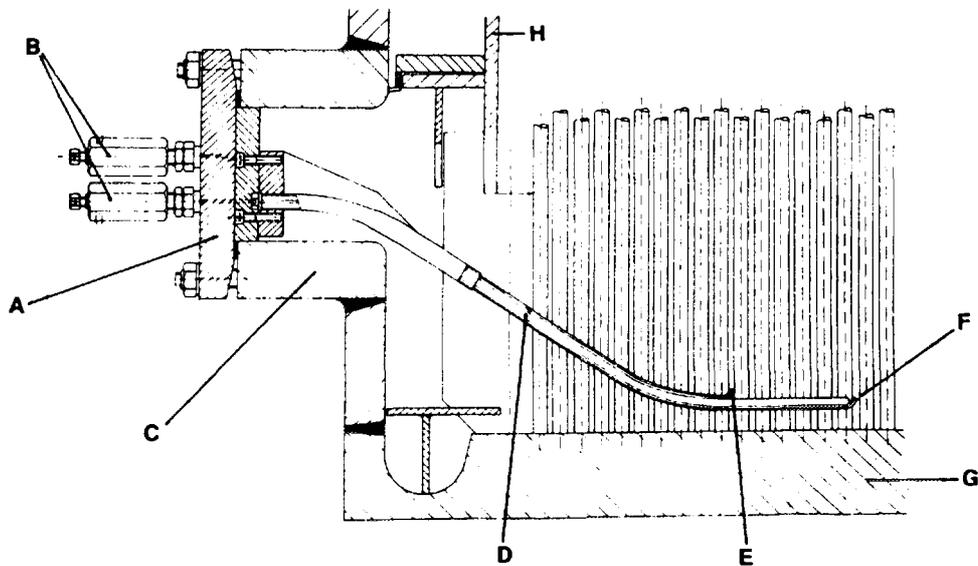


Figure 5 Monitoring unit A for the measurement of electrode potentials in the tube bundle (side view). The unit consists of a handhole cover preassembled with casings for the electrodes B and probes D for the measurement of potentials at locations E and F ca. 50 mm above the tubesheet G.

C denotes the handhole, H the shroud.

In addition, monitoring units of similar design have been installed in final feedwater heaters upstream of the steam generators. Measurements have been taken since 1985. Experience gained from use of these monitoring units is described in terms of various examples.

The response of electrode potentials to stoppage of hydrazine dosing of the fluid and the decrease in hydrazine content is shown as a function of time in Fig. 6.

An increase in electrode potentials is observed during this period.

Changes are pronounced in the feedwater heater (cf. curve 6 in Fig. 6). In steam generator water the effect is less pronounced for various reasons:

- (1) The buffering capacity of the large water reservoir in the steam generator levels out short-term changes in water chemistry.

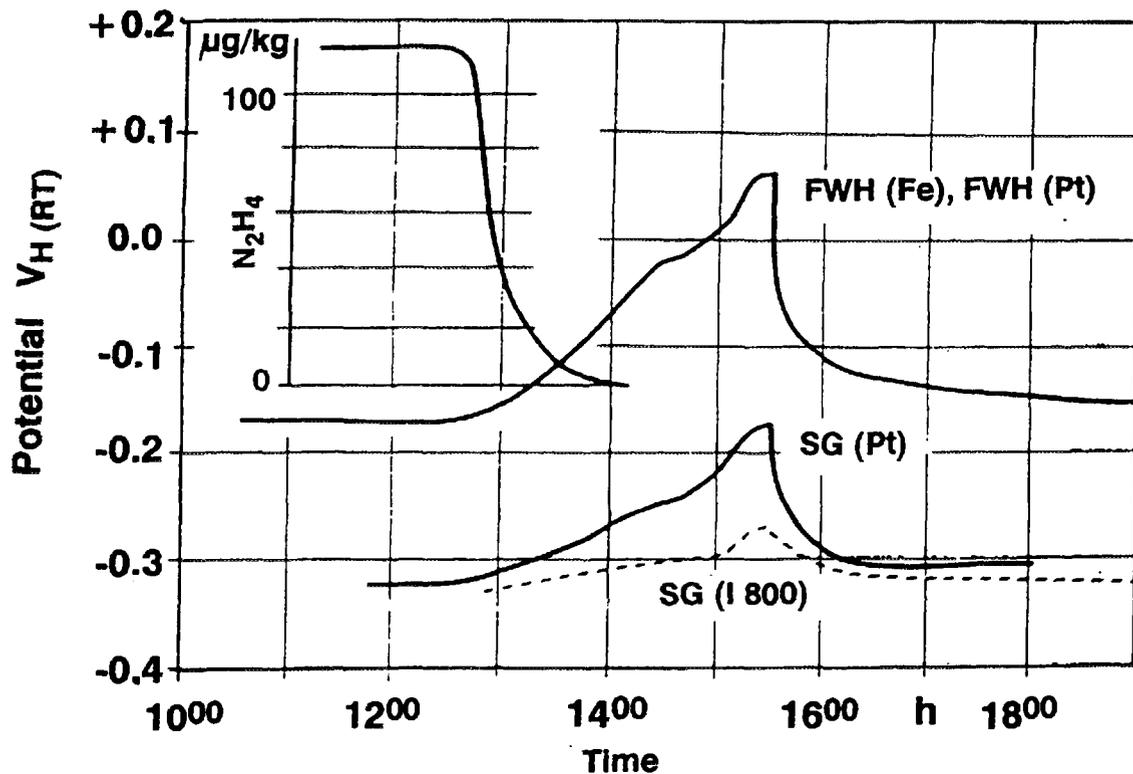


Figure 6 Response of electrode potentials to stoppage of hydrazine dosing of the fluid and decrease in the hydrazine content as a function of time (Insert).

- (2) The rate of reaction of O_2 with N_2H_4 increases significantly with temperature.
- (3) The steam generator acts as a deaerator. O_2 has a significantly higher volatility than N_2H_4 and is therefore preferentially carried into steam. It should be noted that in case of dissolved copper compounds, opposite behaviour must be expected.

The oxygen concentration measured in water sampled from the high pressure heater with the standard plant sampling system was less than 2-3 $\mu\text{g}/\text{kg}$ and constant during this period. The steam-water circuit of this plant is not equipped with copper base alloys. Copper species can be therefore ruled out as oxidants.

In Fig. 7 the response of electrode potentials during cleaning of the turbine condenser water boxes is shown. This results in an increased oxygen content in the steam condensate as displayed. The electrode potentials follow the measured oxygen concentration, although the hydrazine concentration in feedwater was 130 $\mu\text{g}/\text{kg}$ and constant during this time period. The oxygen concentration in the water sampled from the high pressure heater remained constant at 2-3 $\mu\text{g}/\text{kg}$. This example shows that an abundance of hydrazine does not necessarily exclude anodic excursions of electrode potentials within steam generators.

Steady state corrosion potentials of Alloy 800 steam generator tubes measured as a function of hydrazine concentration in the final feedwater are shown in Fig. 8. A hydrazine concentration $>50 \mu\text{g}/\text{kg}$ in the final feedwater is apparently sufficient to maintain reducing water conditions in the associated steam generator.

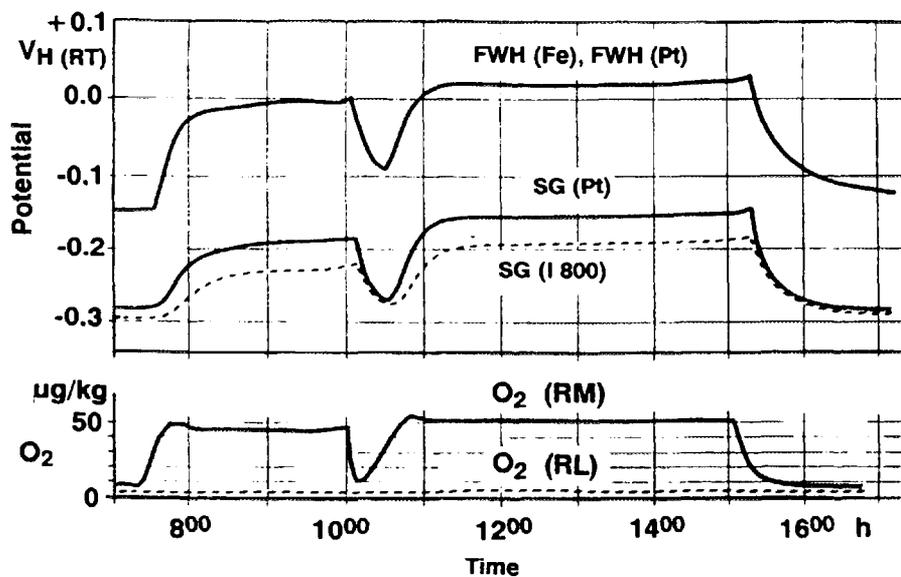


Figure 7 Electrode potentials measured as a function of time and oxygen concentration in the main condensate (bottom diagram) during successive cleaning of two of the water boxes of the turbine condensers.

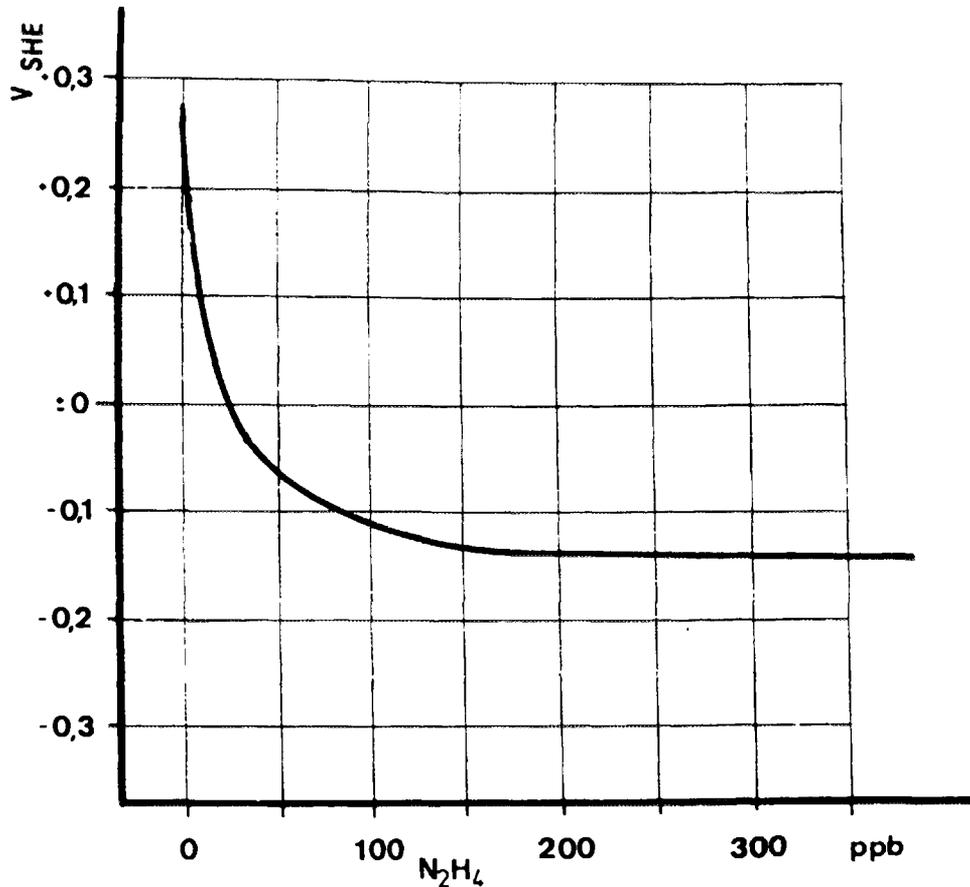


Figure 8 Steady state potentials of austenitic Alloy 800 steam generator tubes measured as a function of the hydrazine concentration in the final feedwater.

3.3 Consequences

The required minimum hydrazine concentration depends on the plant specific situation, i. e. concentration of potential oxidants such as copper compounds and/or oxygen. It can be determined reliably only by on-line electrode potential measurements. Electrode potential measurement units can be further used for detection of the sources of oxidant ingress into the feedwater system. The described examples also show that on-line monitoring can be used to check the efficiency of the normal plant water chemistry sampling system.

With respect to hydrazine dosing it has to be borne in mind that an abundance of hydrazine is associated with high ammonia concentrations in the water-steam

circuit. This may cause increased ammonia corrosion of copper base alloys. In addition, ammonia discharge with waste water has been limited by law. Such conflicting demands can be satisfied with on-line monitoring units: they allow optimisation of the chemistry in water/steam cycles and control with respect to corrosion degradation and environmental requirements.

As in the case of Loviisa 1 and 2, monitoring units have been installed on account of the positive experience gained in Biblis A in the second unit of the Biblis power station (Biblis B PWR with 1300 MW). The monitoring units have been routinely used for evaluation of the quality of the final feedwater by the plant operation personnel.

4. Real-Time, In-Situ Corrosion Surveillance Inside the Calandria Vault of a CANDU Reactor

4.1 Background

Corrosion processes in aqueous solutions are normally of an electrochemical nature, i.e. they are associated with the transport of metal ions across the electrically charged metal-solution interface. The resulting charge transfer current is a direct measure of the corrosion rate, which is an indirect function of the corrosion potential. These two parameters, the corrosion current and the corrosion potential, are directly related to the onset of corrosion attack in plant materials and its subsequent intensification.

The use of on-line measurement of corrosion potentials for analysis of corrosion product release and for optimization of water chemistry has been described in Sections 2 and 3. The corrosion potential was measured in these cases using a reference electrode, i.e. on an absolute potential scale.

The anodic corrosion current cannot be directly accessed with simple measuring techniques, since it is balanced by a cathodic reduction current of the same size, i.e. there is no external current flow. However, it has been found that nominally identical electrodes normally have differing balances of anodic and cathodic activity and hence take up slightly different corrosion potentials. The open-circuit voltage between "identical" electrodes can be measured in a non-perturbative way using a high impedance voltmeter. The apparently random fluctuation of the voltage as a function of time is typically in the millivolt range and is described as electrochemical potential noise.

Short-circuiting two such "identical" electrodes with a zero resistance ammeter results in a fluctuating galvanic current, (so-called electrochemical current noise). Current noise signals are typically in the range of 1 μ A or less.

Using appropriate equipment, current noise and potential noise can be registered simultaneously as an indication of surface condition. Continuous in-situ measurement of these parameters enables real-time identification of the onset and intensification of corrosion. This is the principle of the electrochemical noise (ECN) techniques. If necessary, the ECN measuring method can be complemented by perturbative techniques, such as electrochemical impedance spectroscopy (EIS) or determination of linear polarisation resistance (LPR). In the case of uniform corrosion, ECN and EIS measuring methods enable determination of actual corrosion rates. Furthermore the initiation of localized corrosion processes, such as pitting or crevice corrosion, stress corrosion cracking, etc., can be monitored. Under favourable conditions, the rate of growth of pits or stress corrosion cracks can also be estimated. Applied together, these techniques provide a comprehensive tool with which to determine the rate and mode of corrosion attack. For brevity, the reader is referred with respect to details to the literature [9], [10].

Two features are essential for successful on-line corrosion surveillance with the described techniques:

- Design of the corrosion sensors (multi-electrode probes).
- Processing and analysis of the measurement signals.

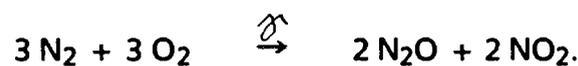
The corrosion sensors must be designed to take account of the corrosion mode which is to be expected. E.g., stressed specimens are required, if the occurrence of stress corrosion cracking is suspected. Creviced specimens enable detection of the onset and growth of crevice corrosion, etc.. The design of the corrosion sensors must also take into account the corrosive environment in the considered plant, which can, e.g., result from a condensate film or deposits on heavily fouled heat exchanger tubes. Last not least, it has to be ensured that variations of the corrosivity of the operating environment are correctly detected by the plant sensors. Considerable experience is therefore necessary to design corrosion sensors adequately and to select an appropriate location for installation.

The random fluctuations of ECN recorded with corrosion sensors are characteristic for the mode of corrosion attack encountered. Different modes of corrosion attack are associated with different signal patterns, which can be therefore used as a "finger-print", indicating, for instance, uniform corrosion, pitting, crevice corrosion or stress corrosion cracking. Moreover, signal patterns of the various modes of corrosion attack vary as a function of the actual status or progress of degradation. In addition to adequate design of corrosion sensors, processing and analysis of recorded data is a key feature of ECN techniques. As a consequence, accurate and effective on-line corrosion surveillance can be achieved only on the basis of modern instrumentation together with sophisticated data processing and analysis techniques.

4.2 Application Example

Characteristic features of on-line corrosion surveillance using ECN techniques are now described in terms of measurements in a nuclear power station. The measurements were performed in the calandria of a pressurized heavy water reactor (PHWR) of the pressure tube type [4]. The general features of this type of reactor are shown in Fig. 9. The calandria vault contains the fuel channel assemblies and subsystems of the heavy water moderator system and consists of concrete walls through which all coolant piping must pass. The calandria vault concrete walls, floor and roof, are cooled by a biological shield cooling system. Such cooling is necessary to limit the maximum concrete temperature to 54°C and to minimise thermal movement of the vault concrete. An additional water cooled thermal shield is provided to attenuate the higher flux in certain locations of the calandria. Major construction materials in the calandria include carbon steel and low alloy steels. The calandria vault in the nuclear power station considered has inside dimensions of approximately 6 m width, 10.7 m length, a height of 16.7 m and a free volume of 625.6 m³ which is filled by nominally dry air. However, as a result of sporadic leaks, for instance through the piping of the biological shield cooling system, the vault air may reach high levels of humidity. The radiolysis of moist air in the calandria vault results in the production of nitric acid by the following reactions:

Nitrogen oxides are produced by radiolysis of nitrogen and oxygen which results in a large number of radicals:



With the addition of water to dry air, nitric acid is produced based on the following reaction step:



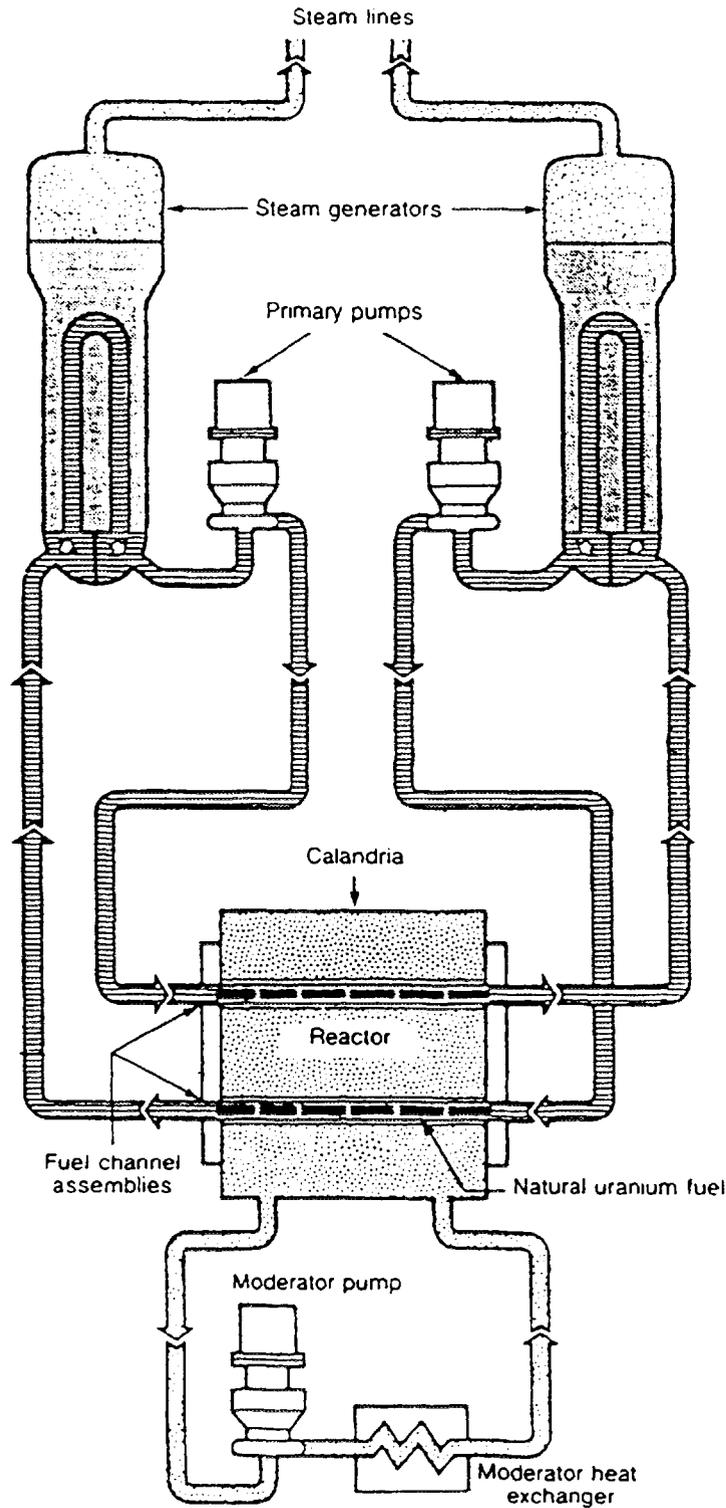


Figure 9 CANDU nuclear steam supply system. The fluids, represented by different types of shading, are (from top to bottom): light water steam, light water condensate, heavy water coolant, heavy water moderator (from [8]).

The presence of nitric acid has been detected by analysis of vault sump drain samples (measured pH values of 3.2 to 4.8).

In addition, visual inspections of components revealed the local presence of dust-like particles. Samples of dust and loose debris were retrieved, using remotely controlled tooling. Chemical analysis also indicated presence of NO_3^- and a minor amount of calcium (2 - 10 wt. pct.). The presence of calcium can be related to release from the concrete walls of the vault. Thus, the possibility of the formation of concentrated aqueous nitrate solutions within a vault with a high relative humidity cannot be totally excluded. Concentrated nitrate solutions can induce stress corrosion cracking in carbon steels, so that concerns were expressed regarding the integrity of all exposed carbon steel components under such conditions.

On-line corrosion surveillance using ECN techniques was implemented in the calandria vault with the following objectives:

- To monitor continuously the corrosion status of carbon and low alloy components.
- To correlate corrosion behaviour with changes in environmental conditions.
- To assess the effects of remedial actions.

Two corrosion sensors were installed in the vault, each consisting of five different materials to be monitored. The top surfaces of the corrosion sensors were covered with a layer of dust and loose debris, which had been retrieved during previous inspections. The deposits favour the absorption of moisture from the environment. In part, stressed sensors were used, since occurrence of stress corrosion cracking in carbon and low alloy steels in the polluted environment could not be completely excluded. Electrical connections were made with radiation resistant sheathed and insulating cables.

The corrosion surveillance system was operated via remote control. The system logged corrosion data 24 hours a day with a data storage capacity for 56 weeks. Data were taken once per hour.

A combination of zero resistance ammetry, impedance spectroscopy and ECN was employed.

In the case of uniform corrosion, the corrosion rate i_{corr} can be estimated from impedance spectroscopy and ECN measurement data. The charge transfer resistance R_{ct} obtained from impedance spectroscopy measurements is proportional to the corrosion rate i_{corr} , i.e.

$$i_{corr} = B'/R_{ct}.$$

The constant B' is a modified Stern-Geary value. i_{corr} is converted to a corrosion rate using Faraday's Laws.

In case of ECN measurements, estimates of the rate of uniform corrosion are obtained in an analogous method to that used for impedance. In this case ECN resistance R_n is calculated by:

$$R_n = V_n/I_n$$

where V_n , I_n are the potential and current standard deviations.

The degree of localisation of corrosion (DoL) provides an indication of the stochastic distribution of microscopic events from current noise (I_n) and the root mean square of the current (I_{rms}):

$$DoL = I_n/I_{rms}.$$

For uniform corrosion the DoL is typically 1×10^{-3} . In the case of localised corrosion (e.g. pitting, crevice corrosion or stress corrosion cracking) the raw data typically exhibit stochastic transients and the DoL value can approach unity.

Zero resistance ammetry (ZRA) was used for measurement of the galvanic coupling current.

In addition to on-line corrosion measurements with these methods, dewpoint measurements were taken at other locations in the vault.

For brevity, this paper concentrates on measurement data from one of the low alloy steels over a time period of three months (from September to November 1991).

Before the time period considered, the vault environment was dry with negligible corrosion. A significant bioshield cooling supply leak of 10 kg per hour was reported by the staff of the plant on September 30. After a period of about one month, the leak was repaired on November 2.

Figure 10 shows the analysed ECN data measured for September. An increase in corrosion rate and a decrease in DoL is observed in the course of September 26. The mean coupling current, measured with ZRA, increases in parallel (Fig. 11). The data unequivocally signal the onset of increased, uniform corrosion as a consequence of the in-leakage of cooling water into the vault.

The second sensor detected the leak one day later. The delay showed that the location of the leak was closer to the first sensor.

The leak could only be detected with other methods four days later. The equivalent water loss into the vault area during this time was approximately 960 kg.

In October, uniform corrosion continued (Fig. 12). ECN data indicate maximum rate estimates of 0.1 mm per year. Corrosion rate estimates from impedance

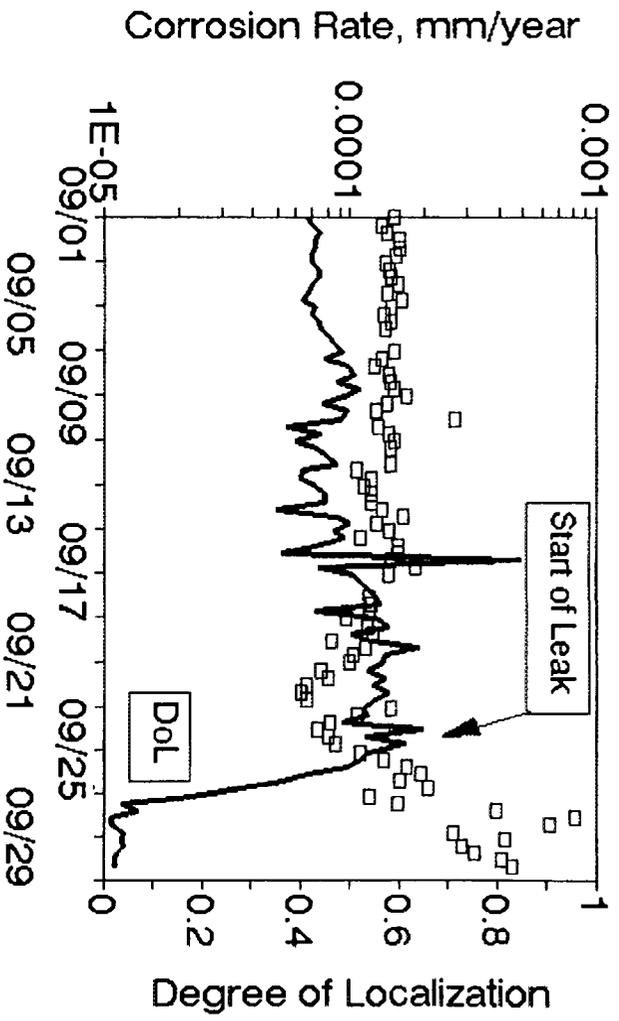


Figure 10 ECN corrosion rates and degree of localisation measured during September, 1991.

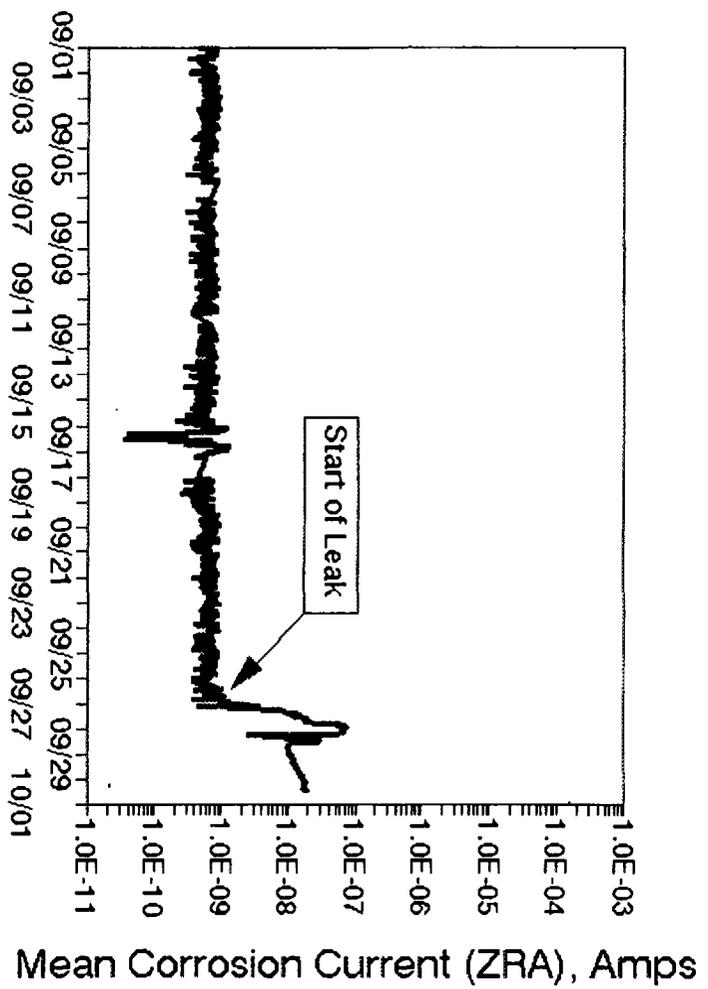


Figure 11 Increase in the mean coupling current, measured using ZRA, during September 1991.

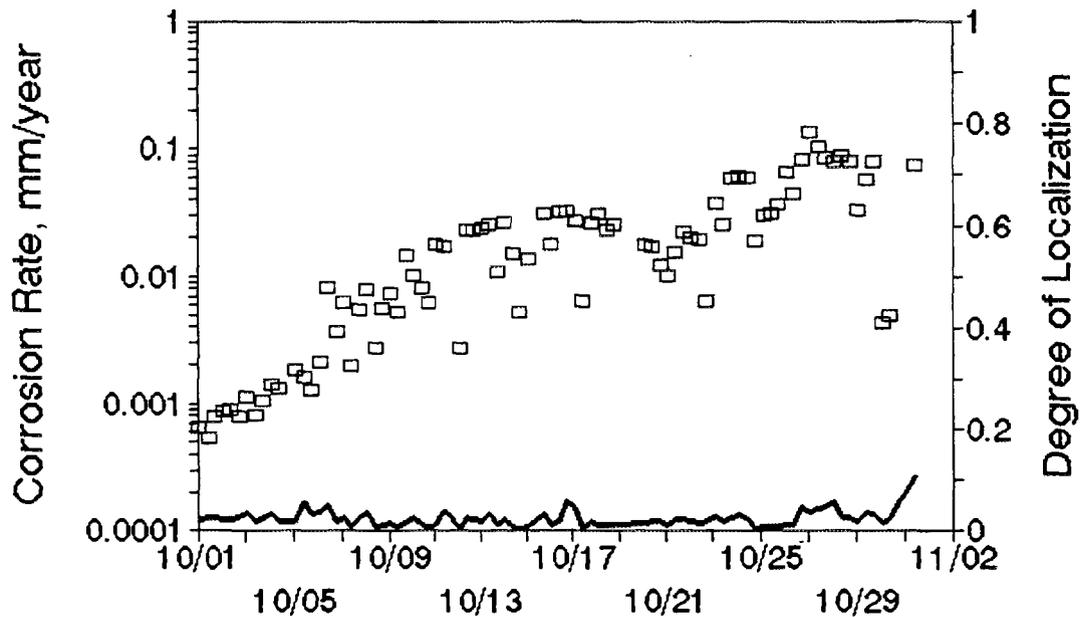


Figure 12 ECN corrosion rates and degree of localisation measured during October 1991.

spectroscopy were in good agreement with ECN corrosion rate data. Mean coupling currents achieve maximum levels of about 1×10^{-6} A (Fig. 13). These values must be compared to values of 1×10^{-9} A measured during initially "dry" condition levels.

The leak was sealed on November 2. This was associated with an immediate decrease in the mean coupling current to 1×10^{-7} A (Fig. 14). ECN corrosion rate estimates decreased in parallel by one order of magnitude. However, the corrosion activity did not return to the extremely low levels of early September for various reasons:

- Although the leak was sealed, the relative humidity in the vault did not immediately decrease to the initial, very low value.
- The film of corrosion product formed on the surface of the sensor favoured the retention of absorbed moisture.

These effects were expected. However, corrosion activity had been substantially mitigated and continued to decrease subsequently.

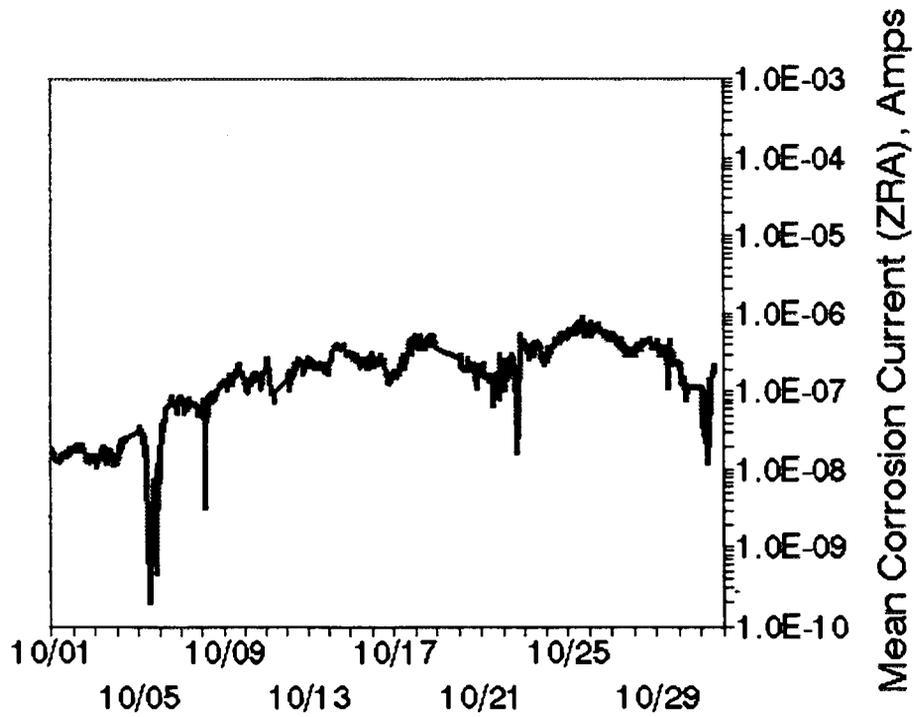


Figure 13 Mean coupling current measured during October 1991.

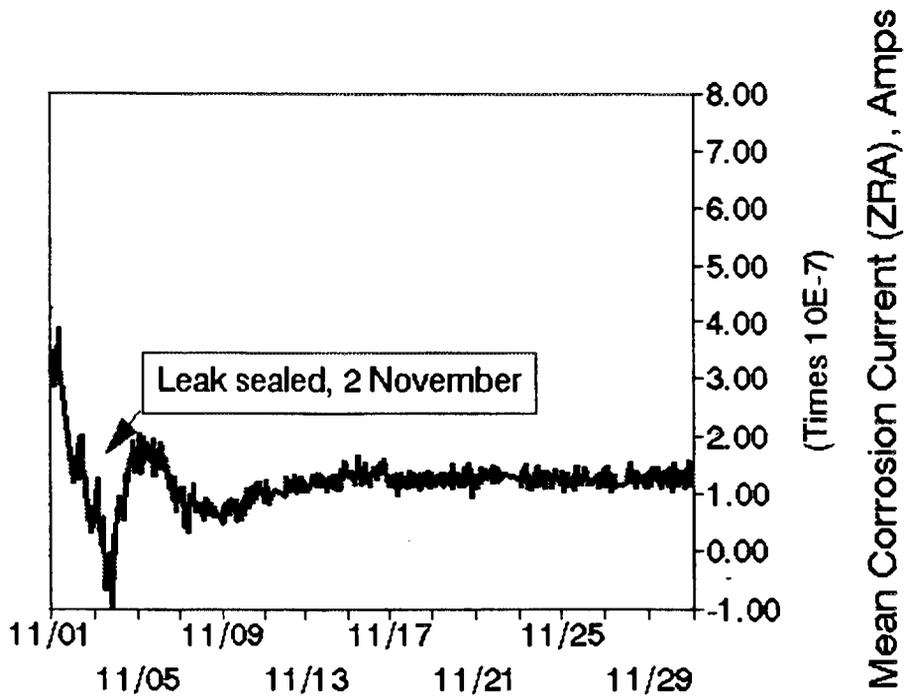


Figure 14 Mean coupling current measured during November 1991.

The analysis of the recorded ECN measurement signals gave no evidence for stress corrosion cracking. Based on these results, the integrity of carbon and low alloy steel components in the vault was clearly maintained.

4.3 Concluding Remark

In summary, the corrosion surveillance system has proved successful for monitoring variations in low levels of uniform corrosion in acidic humid atmospheres inside the reactor vault. The system had a fast response time for the identification of water leaks and provided corrosion data for the selected materials in real time. The general corrosion behaviour of materials is indeed affected by changes in vault moisture, but no evidence for stress corrosion cracking was observed. The system thus assisted the operator of the nuclear power station to verify the continued safe corrosion status of the facility.

The evident advantages of on-line corrosion surveillance have been outlined using an application case from the nuclear industry. However, the described corrosion surveillance systems have also been used with great success not only in the fossile power industry, as well as in chemical/petrochemical and refining industries and in systems for oil and gas production [11], [12]. Such approaches are now being adopted for permanent plant installation with the ultimate goal of full integration into plant control and measurement systems.

5. Discussion and Future Activities

Sound design and adequate selection of construction materials, in combination with suitable water treatment practices, ensure the reliable operation of nuclear power stations with high availability.

For existing facilities in the nuclear industry, targets such as reduction of radiation exposure levels and higher burn-up of fuel, etc. are gaining in importance. An attempt has been made to outline major advantages in using on-line monitoring sensors in plant systems for water chemistry and corrosion surveillance in order to achieve such targets. Two types of sensors were used:

- (1) Sensors for on-line, in-situ measurement of water chemistry parameters, namely pH value and redox potential. Use of these sensors was backed up in Loviisa 1 by conventional and advanced water chemistry analysis techniques, yielding information about actual concentrations of water treatment chemicals (H_3BO_3 , NH_3 , H_2 , O_2 , N_2H_4) and various metal cations dissolved in the coolant.
- (2) Sensors for measurement of corrosion parameters, such as corrosion potential, current and potential noise, coupling currents, impedance spectroscopy response.

Both corrosion properties and response of the involved materials and water chemistry parameters must be understood in order to optimise features such as release, transport and deposition of corrosion products and to ensure trouble-free operation of plant systems. Further significant advantages can be expected to accrue from an integration of the various types of sensors described into a common water chemistry and corrosion surveillance system. Experience will be gained in the near future with a complete set of the described sensors. These will be installed in a loop of a test reactor operated with PWR primary coolant chemistry. The goal of these investigations is a better understanding of activity build-up on various materials as a function of the coolant chemistry. For this purpose, the physicochemical properties of the fluid will be recorded concurrently with characterisation of the properties of oxide layers using corrosion surveillance instrumentation. Development of sensors for in-situ H_2 and

O₂ measurement is also in progress. Depending on the state of development, installation in the loop may be possible.

Notwithstanding these ongoing activities, the experience described from separate use of these different types of sensors with for different purposes shows that new and additional information about plants and their actual process conditions was obtained in each case. Moreover, the intimate relationship between the operational situation and its consequences for the quality of the working fluid and the response of the plant materials was revealed. Advanced on-line, in-situ sensors for water chemistry and corrosion surveillance are clearly very important for a better understanding of plants and their actual process conditions, since in-plant conditions and process control can be optimised. Optimisation of plant operation is, indeed, a prerequisite in order to fulfil the increasing and more stringent demands being made upon existing facilities in the nuclear industry.

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