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High temperature on-line monitoring of water chemistry and corrosion control in water cooled power reactors

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1995–1999

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HIGH TEMPERATURE ON-LINE MONITORING OF WATER CHEMISTRY AND CORROSION CONTROL IN WATER COOLED POWER REACTORS

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FOREWORD

This report documents the results of the Co-ordinated Research Project (CRP) on High-Temperature On-line Monitoring of Water Chemistry and Corrosion in Water Cooleed Power Reactors (1995–1999). This report attempts to provide both an overview of the state of the art with regard to on-line monitoring of water chemistry and corrosion in operating reactors, and technical details of the important contributions made by programme participants to the development and qualification of new monitoring techniques.

The WACOL CRP is a follow-up to the WACOLIN (Investigations on Water Chemistry Control and Coolant Interaction with Fuel and Primary Circuit Materials in Water Cooled Power Reactors) CRP conducted by the IAEA from 1986 to 1991. The WACOLIN CRP, which described chemistry, corrosion and activity–transport aspects, clearly showed the influence of water chemistry on corrosion of both fuel and reactor primary-circuit components, as well as on radiation fields. It was concluded that there was a fundamental need to monitor water-chemistry parameters in real time, reliably and accurately.

The objectives of the WACOL CRP were to establish recommendations for the development, qualification and plant implementation of methods and equipment for on-line monitoring of water chemistry and corrosion. Chief investigators from 18 organizations representing 15 countries provided a variety of contributions aimed at introducing proven monitoring techniques into plants on a regular basis and filling the gaps between plant operator needs and available monitoring techniques. The CRP firmly demonstrated that in situ monitoring is able to provide additional and valuable information to plant operators, e.g. ECP, high temperature pH and conductivity. Such data can be obtained promptly, i.e. in real time and with a high degree of accuracy. Reliable techniques and sensor devices are available which enable plant operators to obtain additional information on the response of structural materials in core and coolant circuits to changes in water chemistry. These have the potential for optimization of operational procedures and practices in the future.

The IAEA wishes to thank the participants and observers in the WACOL CRP and the members of the leading group for their project guidance and for their contribution to this publication. The leading group included J. Hickling, United Kingdom (measurements in BWRs), V. Kritski, Russian Federation (measurements in WWERs and RBMKs), J. Kysela, Czech Republic (measurements in primary side of PWRs), K. Makela, Finland (advancements in measurement techniques) and B. Stellwag, Germany (measurements in secondary side of PWRs). The IAEA officer responsible for this TECDOC was V. Onoufriev of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

CONTENTS

1. INTRODUCTION

1.1 Background to the WACOL Co-ordinated Research Project

Light and heavy water nuclear power reactors have three basic functional requirements:

- the structural integrity and operational status of the plant must be assured at all times;
- the plant design must permit access for operation and maintenance, taking into account the radioactivity which is present;
- the plant wastes must be controlled and disposed of safely, in compliance with established regulations.

The above requirements imply that the fuel cladding and the primary-pressure-boundary components are maintained intact. It is also necessary to minimise and control the generation of radioactive products and waste in the plant, as well as to keep deposits, which reduce heat transfer in the reactor core or steam generators, to a minimum. Water is the primary heat-transfer medium, and advances in coolant technology have played a vital role in ensuring safe, economic operation of various types of commercial reactors.

From 1986 to 1991 the IAEA carried out a co-ordinated research project (CRP) on water chemistry called WACOLIN (Investigations on Water Chemistry Control and Coolant Interaction with Fuel and Primary Circuit Materials in Water Cooled Power Reactors), which is documented in a programme overview [1] and in three volumes [2] describing chemistry, corrosion and activity-transport aspects of the subject. This programme clearly showed the influence of water chemistry on corrosion of both fuel and reactor primary-circuit components, as well as on radiation fields. It was concluded that there was a fundamental need to monitor water-chemistry parameters.

- in real time,
- reliably, and
- accurately.

This implies that efforts are required to obtain information "on-line" during all operating conditions of the plant (steady-state power operation, power transients, start-up and shutdown, etc.) in order to check

- that the plant is operating within its technical specifications,
- that it responds correctly to actions taken by the operating staff (e.g. when returning from transient to normal conditions), and
- that long-term trends, which may lead to operational malfunctions, are detected at the earliest possibility.

In a broader sense, such real-time information should lead to a deeper understanding of plant behaviour and to improved plant performance. Specifically, it can be used.

- to provide data for optimal control of plant operation (e.g. in terms of component reliability, reduction in primary-circuit corrosion, minimisation of activation products and dose rates, lower crud formation on fuel-elements, etc.) and
- to provide data for mathematical modelling and the development of expert systems.

At present, the water chemistry in power plants is monitored primarily either by on-line instruments in cooled sampling lines, or by taking samples from such lines at regular intervals and analysing them with off-line instruments. The disadvantages of this include:

- possible changes in the properties and composition of the water as a result of the sampling procedure,
- time delay in obtaining important information, and
- lack of completeness in the information obtained.

Many of these problems can be overcome by performing the measurements at high temperatures, i.e. without changing the physical and chemical state of the reactor water. In addition, it is often possible to assess directly, in situ, important effects of water-chemistry on material corrosion and radioactive transport. In recent years, a number of high-temperature (HT) monitoring devices have been developed and used in the laboratory, in pilot plants and test reactors, or even in commercial reactors. In 1994, the IAEA established the WACOL CRP (High-Temperature On-line Monitoring of Water Chemistry and Corrosion in Water Cooled Power Reactors) to facilitate such developments.

1.2. Objectives of the WACOL programme

The objectives of the WACOL CRP were to establish recommendations for the development, qualification and plant implementation of methods and equipment for on-line monitoring of water chemistry and corrosion. Approximately 20 participants from 13 countries provided a variety of contributions aimed at introducing proven monitoring techniques into plants on a regular basis and filling the gaps between plant operator needs and available monitoring techniques. Key stages in this programme of work were:

- identification of critical parameters,
- inventory of the status of present on-line monitoring techniques (laboratory, pilot plant, operating plant),
- proposal of new monitoring techniques with the potential for plant applications,
- recommendations for the preferred location of sensors and equipment,
- advice on instrument calibration and data validation,
- assessment of the relevance of the data to other locations in the plant (e.g. modelling).

1.3. Implementation of the WACOL programme

The first Research Co-ordination Meeting (RCM) on WACOL was held at University Park, Pennsylvania from October 16 to 20, 1995. The technical status of the programme at that time and the presentations from the meeting were summarised in a progress report (Annex 1), which was structured according to the format chosen originally for group discussion, namely consideration of eight specific types of on-line measurement:

- measurement of electrochemical potential (ECP),
- measurement of high-temperature (HT) conductivity,
- measurement of HT pH values (pH_T),
- measurement of dissolved gases and chemical species,
- particle measurement (optical methods),
- measurement of crack growth rate,

- measurement of electrochemical noise (EN),
- measurement of impedance.

Other methods were briefly examined. In each case, attention was paid to the technical justification and practical requirements of the technique, the current status/problems encountered were defined, and specific recommendations were made (see Annex 1).

When the 2nd RCM was planned at a consultants meeting in May 1997, it was considered necessary to adopt a more plant-oriented approach to the work, and this structure has been retained through to the present, final report on the WACOL programme. In essence, it was decided to consider the status of implementation of on-line monitoring according to the four following categories of plant:

- pressurised water reactors on the primary side
- pressurised water reactors on the secondary side
- boiling water reactors
- research reactors

with attention being paid separately to new methods which were still at the laboratory stage. In this context, the following categories were agreed upon to ensure uniform use of terminology:

- **Development** implies work on the technique itself, primarily in the laboratory
- **Qualification** means calibration/benchmarking of the technique is in progress
- **Implementation** means that the technique is actually being used to obtain data outside the laboratory
- **Routine use** implies that the end user (operator of test or power reactor) has adopted the technique.

The 2nd RCM on WACOL was held at the IAEA in Vienna from October 28 to October 30, 1997. It was attended by 20 representatives from 16 of the countries participating in the programme plus an additional observer from the UK. The technical status of the programme at that time and the presentations from the meeting were summarised in a progress report (see Annex 1).

The 3rd RCM on WACOL was hosted by VTT at the Dipoli Congress Centre in Finland from June 7 to June 10, 1999. 19 representatives from 15 of the countries participating in the programme, plus additional observers from Belgium, Germany, the UK and Japan took part at the meeting. The Italian delegate, who was prevented by illness from attending the meeting, submitted a written account of his work. Further details of the meeting are given in Annex 2.

This final report on the WACOL programme provides both an overview of the state of the art with regard to on-line monitoring of water chemistry and corrosion in operating reactors, and technical details of the important contributions made by programme participants to the development and qualification of new monitoring techniques.

2. STATUS OF ON-LINE MONITORING IN NUCLEAR PLANTS

A major part of the WACOL programme involved reviewing and updating the current status of various on-line monitoring techniques. Within the limits set by the knowledge and experience of the WACOL participants, the status of various on-line monitoring techniques can be summarised with regard to both commercial and test reactors as given in the following sections. Where a technique has been used in more than one country, the order of the sub-sections is alphabetical.

2.1. Pressurised water reactors on the primary side

Pressurised water reactors (PWR) include designs involving both light and heavy water as the reactor coolant/moderator. With the exception of primary water stress corrosion cracking (PWSCC) of Inconel 600 vessel head penetrations and steam generator (SG) tubing in some LWR designs, the PWR primary side has been relatively free from corrosion problems and the traditional, close control of water chemistry through variation of the boric acid/LiOH (or KOH) ratio, together with the addition of gaseous hydrogen, has been beneficial in controlling deposition and transport of crud. The major concern to date has been minimisation of fuel cladding corrosion (especially during longer cycles with higher burnup), although irradiation assisted stress corrosion cracking (IASCC) of core-shroud baffle bolts has recently been observed in some plants. Advanced water-chemistry modifications (e.g. addition of zinc) are also under active consideration with regard to minimising activity buildup.

2.1.1. In situ measurement of boron in PWRs

In situ measurement of boron is attractive primarily because of the increased use of (expensive) boric acid enriched in the B^{10} isotope in connection with advanced fuel-element designs. However it also represents an important safety enhancement, as it enables a more rapid response to disturbances. The measurement principle involves on-line determination of the B^{10} concentration via neutron absorption and commercially available units have been installed both in a German PWR [3] and in a Slovakian PWR (WWER type) [4,5]. In detail, the status is as follows.

2.1.1.1. Background

In nuclear power plants with pressurised water reactors, boric acid is added to the coolant to hold down excess reactivity. Natural boron contains about 20% by weight of the isotope B^{10}, which is a good neutron absorber. Boron concentration in the reactor coolant is reduced steadily with increasing burn-up. Uncontrolled addition of coolant with too high or too low a boron concentration would lead to a major operational upset, so that continuous monitoring of all systems containing reactor coolant is of central significance. This resulted in the following motivation for the development of a B^{10} instrumentation system:

- future planned operation of PWRs with enriched boric acid with a higher B^{10} content (use of chemical methods for measurement of B^{10} content in the coolant is not possible),
- control of inadvertent de-borating transients,
- backfitting and upgrading applications in existing plants,
- specific problem for the European Pressurised Reactor,

- general interest in boron instrumentation by operators of plants in Eastern Europe,
- application of a B^{10} instrumentation system for leak detection on systems containing boric acid.

2.1.1.2. Work done in the past and actual status

The requirements for a B^{10} instrumentation system were defined on the basis of the plant system and process engineering as follows:

- rapid qualitative measurement within <30 seconds,
- exact quantitative measurement (comparable with a titration) within 15 minutes,
- also has to be suitable for implementation on high-temperature piping and tanks in the equipment compartments,
- non-invasive system, so that no changes are required on systems to be instrumented,
- no additional exposure to radiation and hence no need for time-consuming licensing procedures.

The measurement technique is based on the absorption of moderated neutrons, which is a function of the B^{10} content of the absorbing fluid. The neutrons supplied, for example, by an AmBe neutron source pass through the boron-containing fluid, with the neutron fraction that is not absorbed then measured with the aid of suitably located counter tubes (see Fig. 1). Figure 2 shows an example for the results obtained during a reactor shutdown process.

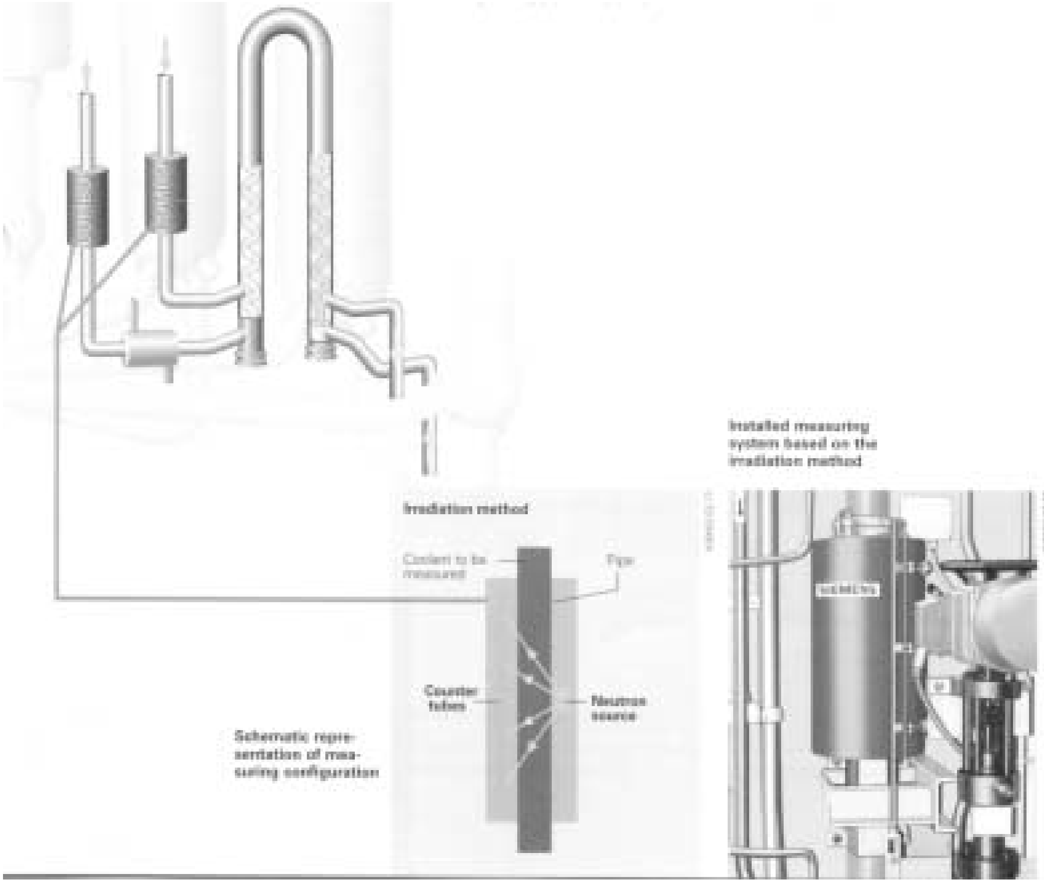


FIG. 1. Schematic of on-line boron measurement system.

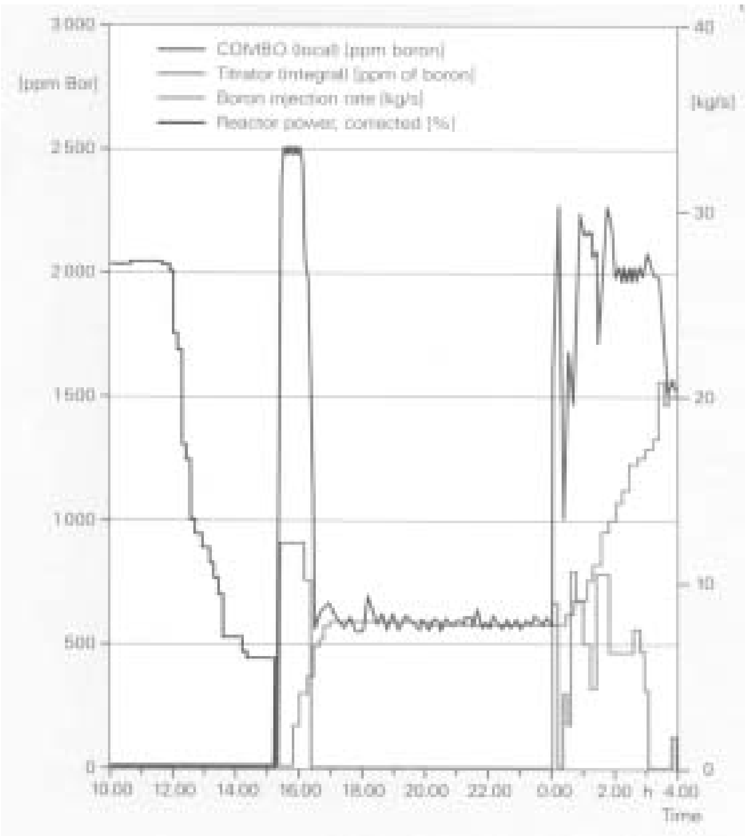


FIG. 2. Example of results of on-line boron measurement in relation to titrator signal, boric acid injection quantity and corrected reactor power during a plant shutdown transient.

2.1.1.3. Direction of future work

Following good operational experience in different PWRs, future work will be focused on the following items:

- further optimisation of the measuring geometry;
- simplification of the system design of boron containing systems by using direct continuous measurement of boron concentration;
- development of software modules with more sophisticated diagnostic function needed for the measurement itself and for the process where the boron measurement is being used;
- qualification of the hardware in order to be able to use the continuous boron concentration measurement for class 1 systems.
- development of a calibration system by using the same physical principle.

Beyond this, the vision for an advanced boron concentration measurement is:

- integration of the boron measurement in a reactivity surveillance system for reloading phase;
- optimisation of the procedures in case of operational transients;
- use of the boron measurement system for detection of fuel element leaks;
- detection of the water level in loop lines in case of LOCA.

2.1.2. In situ measurement of dissolved gases in PWRs

In situ monitoring for dissolved hydrogen (and oxygen) is of interest because of the time delay and possible absorption/desorption in the sampling line, and because of uncertainties in the radiolysis models with regard to the lowest possible concentration (desirable in order to reduce PWSCC susceptibility) that is still adequate to suppress oxygen formation during radiolysis in the core. Although development and qualification work on electrochemical sensors based on a solid-state electrolyte has been ongoing for many years [6], the sensor implemented for initial use in a heavy water reactor to measure dissolved hydrogen is based on a differential resistance Pd probe. While the possibility that such a probe could be used in reactor coolants has been known for some time, the detailed characterisation of the metal-coolant interactions and the qualification of a device to insert into the pressure boundary of a power reactor primary heat transport system (PHTS) have taken several years. The developments leading up to the hydrogen probe that is now installed at Point Leprau are summarised below.

2.1.2.1. Experimental work

The experimental Pd probe consists of Pd wire, about 1 mm in diameter, wound onto a ceramic (ZrO_2) insulator that is formed with a helical groove. Each end of the wire is brazed to two silver conductors, also about 1 mm in diameter, that penetrate the pressure boundary through a Conax fitting. The four-lead configuration, in which the silver conductors are at system temperature, allows in situ measurements to be made of the electrical resistance of the leads. In a typical experiment, the silver wire would contribute 2–6% of the overall sensor resistance as measured with a Keithley Multimeter.

The probe was tested in a small autoclave mounted in a high-temperature, low-volume flow loop. The autoclave and connections were situated in a temperature-controlled oven which permitted experiments to be done at temperatures up to about 585K. The loop was used to pump water, saturated in a feed tank with mixtures of hydrogen and argon at ambient conditions, through the autoclave at 10.8 MPa pressure or, when drained, to admit gas mixtures directly to the autoclave at pressures up to about 3 MPa.

In order to obviate the possibility that species other than hydrogen in the coolant (e.g. argon or water itself) could affect the response of the probe, diffusion-barrier sheaths were applied to the Pd wire of some sensors. A probe with a single-sheath barrier had a PTFE tube (wall thickness about 0.1 mm) heat-shrunk onto the wire, while a double-sheath barrier comprised the PTFE tube and a Pd tube (wall thickness about 0.15 mm) squeezed onto the outside.

A typical test series measured the responses of several probes (sheathed and unsheathed) to dissolved hydrogen in water at temperatures between 460 and 579K. The lower temperature was high enough to ensure a reasonable response time (< ~ 1h) of a double-sheathed Pd sensor while the higher temperature was just below the maximum (~ 583K.) that a PTFE sheath could withstand.

2.1.2.2. Sensor qualification

Fig. 3 presents the results of the test series as plots of resistance ratio (i.e. ratio of resistance of probe equilibrated with dissolved hydrogen to resistance of hydrogen-free probe) versus the square root of hydrogen partial pressure. At each temperature, a plot is nicely linear, reflecting the relationship:

$$\psi = 1 + k\, C_{H_2}^{1/2} \qquad (1)$$

where ψ is the resistance ratio, k is a constant and C_{H_2} is the concentration of dissolved hydrogen in water. This results from the resistance of Pd being a linear function of the contained hydrogen and the contained hydrogen itself following Sievert's Law and being proportional to the square root of the partial pressure of the hydrogen dissolved in water.

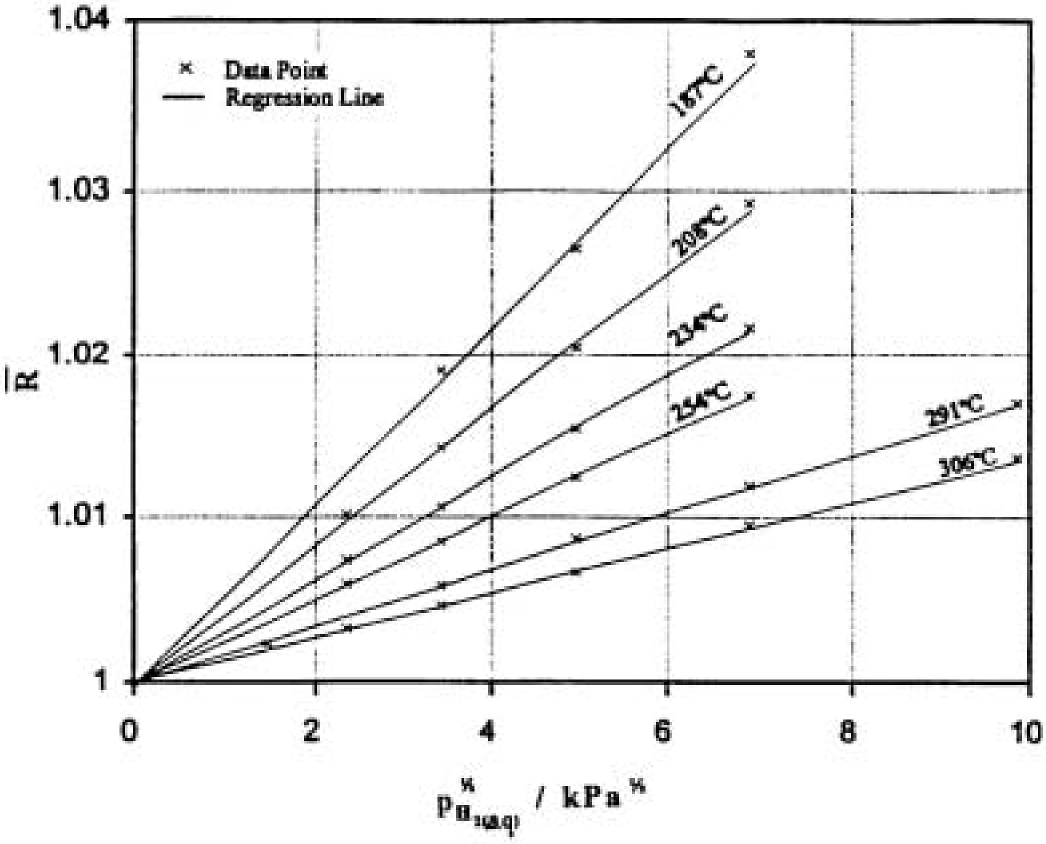


FIG. 3. Resistance ratio of Pd/H sensor: experiments in water at various temperatures.

An interesting development of the theory of hydrogen absorbed by Pd from solution in water and directly from the gas phase has been the use of the Pd resistance probe to determine the Henry's Law constant for hydrogen in water at high temperature [7]. Separate experiments for determining resistance ratio of a probe as functions of hydrogen concentration in the gas phase and dissolved in water can be carried out without having to equilibrate a gas with a solution and then sample and analyse both phases (at high temperature and pressure, such sampling is difficult). The Henry's Law constant is then a function of the k obtained from equation (1) applied to the liquid phase experiments and the equivalent constant obtained from the gas phase experiments. This measurement also avoids difficulties that can arise from effects of non-ideality in traditional experiments. Henry's Law constants determined by this method are 16–22% lower than those determined by traditional techniques in the temperature range 460–579 K.

2.1.2.3. Reactor application

The laboratory experiments indicated that Pd resistance probes for measuring hydrogen dissolved in reactor coolant had suitable sensitivity; unsheathed, or bare, probes gave a rapid response (<1 min.) to changes in concentration at high temperature and pressure, while probes with the double sheath of PTFE covered with Pd gave the most accurate measurements, particularly when impurities were present. Before a probe can be inserted into a reactor coolant system, however, it has to be designed, constructed and qualified to nuclear standards.

The major difficulty in nuclear qualification of probes that have electrical leads penetrating the pressure boundary is the design of the insulating pressure seal. Thus, while standard pressure tubing and Swagelok fittings of stainless steel, which were employed in the laboratory flow loop, are registered in the Canadian provinces of New Brunswick and Ontario as Nuclear Class 1 components, Conax seals are classed as non-nuclear. To overcome the difficulty, a seal that is a cross between a Conax and a Swagelok connector was designed, constructed and pressure tested. This CNER (Centre for Nuclear Energy Research) fitting has now been registered with the provinces of New Brunswick and Ontario as a Nuclear Class 1 component.

Fig. 4 is an overall diagram of the Pd resistance probe as manufactured and qualified for insertion in the primary coolant system of the CANDU reactor at Point Lepreau. Note that both the bare probe and the double sheath probe have similar construction -just the Pd wire presented to the coolant is different. It should be noted that the CANDU primary coolant is heavy water, D_20, and that although hydrogen gas is added to maintain a concentration within the specification of 3–10 cm^3 (STP)/kg D_2O it rapidly exchanges isotopically in the reactor core and effectively produces dissolved deuterium. Laboratory tests have qualified the probes for this system also.

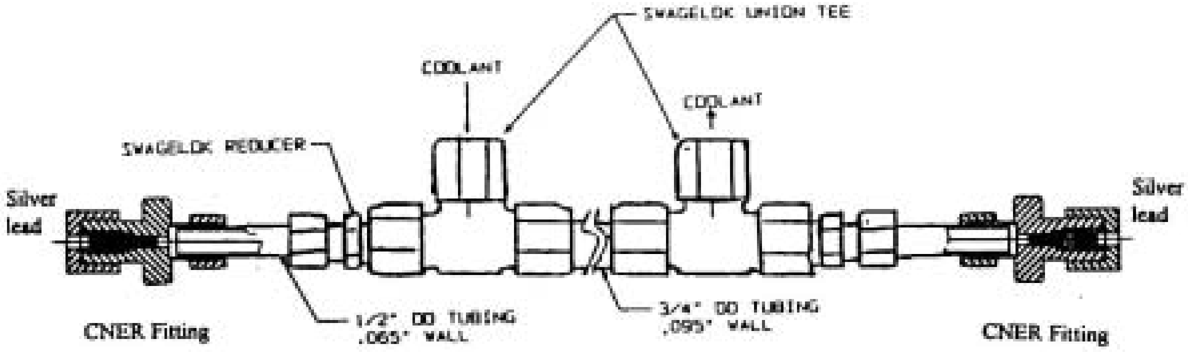


FIG. 4. Bare palladium and double-sheathed palladium probe for reactor installation.

The probe assembly ready for installation in the reactor is located in a by-pass circuit, taken off the reactor outlet header that feeds primary coolant to autoclaves that are used to test samples of system materials. The assembly fits between two isolation valves, and the whole installation has undergone rigorous seismic analysis as part of the qualification and approval procedures.

Overall, the development of the differential resistance Pd probe for measuring dissolved hydrogen or deuterium in reactor primary coolants has proceeded well and the qualification of a probe assembly for installation in an operating reactor marks a significant milestone.

Prolonged surveillance as the probes operate in the Point Lepreau primary coolant will indicate durability in the field and pinpoint any further development required to take the design beyond the prototype stage.

2.1.3. On-line monitoring of water chemistry and corrosion in the primary circuit of WWER plants

2.1.3.1. Experience in the Loviisa plant in Finland

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 [8]-Fig. 5. 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. During steady-state operation the ECP of construction materials at Loviisa unit 1 was close to $-0.740V_{SHE}$ as expected due to the hydrogen concentration of the coolant (35–45 $mlkg^{-1}$) 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. 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 [9].

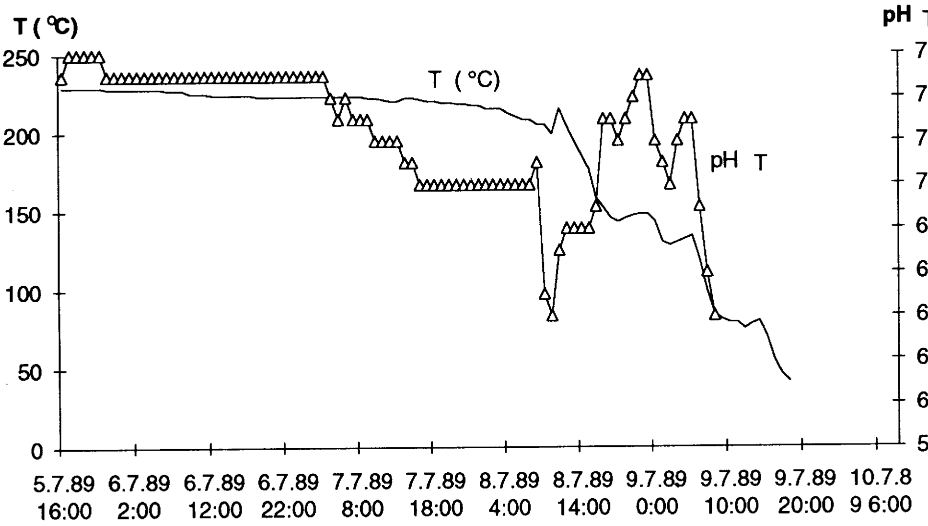


FIG. 5. The measured pH_T of the primary coolant and temperature during the shutdown at Loviisa 1 unit in 1989.

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. [10] 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 [11]. The additional follow-up measurements, which were carried out in the following years at Loviisa, confirmed the results discussed above. The changes in pH_T and ECP are rather small in the primary circuit during the steady-state conditions and therefore these measurements are followed up mainly during shutdown periods and other transient situations. Fig. 5 shows an example of this, taken from Ref. [12].

2.1.3.2. Ongoing work in Russia

Work has been ongoing for several years at VNIPIET in St. Petersburg, Russia to develop a system of on-line automatic chemical control and corrosion monitoring in the primary circuit of new-generation WWER type reactors. Fig. 6 shows sampling for on-line monitoring in the primary circuit of WWER reactors with the sequence of sensors and equipment. Table 1 shows recommended points for coolant chemistry control by the system of functional diagnostics. Table 1 presents the volume of coolant chemistry control in the primary circuit, while Table 2 describes coolant quality parameters and reasons for their control.

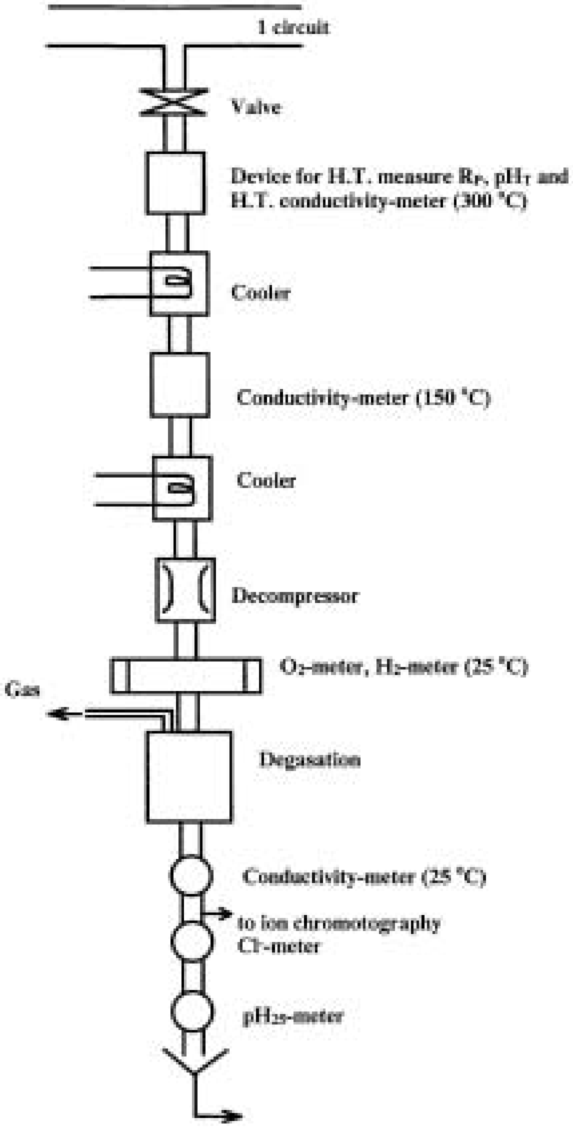


FIG. 6. Sampling loop for on-line monitoring in the primary circuit of WWER reactors with the sequence of sensors and equipment.

The choice of parameters to be controlled depends on the operation mode of reactor unit as well as their importance for water chemistry control and service performance of primary sensors. Depending of their design sensors now applied are subdivided into those operating at elevated temperature and pressure in the primary coolant circuit and those demanding temperature and pressure decrease and gas removal (see Table 1).

The system of automated chemical control and preparation of primary coolant samples should meet the requirements of a series of specifications and rules including an additional demand of limiting the water consumption for analyses and taking boron-containing samples in a special reservoir.

The sampling system is designed for taking steam and water samples from the primary circuit and their preparation (cooling, depressurization) before chemical analyses. Figure 1 shows the sequence of actuating the sensors and auxiliary equipment of the sampling loop. The parameters of experimental sensors are presented in Table 3. Some results of testing presented in Sections 3.2.5 and 3.4.4.

Table 1. System for coolant chemistry control in primary circuit of NP-640

Point of control	**Goals of determination**	**Control channel**
On pressure lines of circuit water circulation pumps	Major parameters of coolant corrosiveness	A, I, L
After water clean-up plant — 1	Plant efficiency	A, I, L
On make-up water line after pump	Make-up water characteristics	A, I
In pressuriser	Corrosiveness of medium	A
From high and low pressure CECS tanks	Purity degree of filling medium	L
In fuel-cooling pool	Compliance with water quality specifications	L
On pressure line of cooling-pool pump	Degree of cooling-pool water contamination	A
On feeding line of demineralised condensate (DC) to damper tank	Compliance of DC water with make-up water specifications	A
From line of containment-cooling channels	Composition of containment-cooling water	L
From condensate line of passive heat removal system	Composition and corrosiveness of filling water	A, L
Steam generator purging	Composition and corrosiveness of purging water	I, L

A: automatic channel 1 (on-line)
I: semiautomatic (waiting) mode of ion chromatography, channel 2
L: laboratory channel 3.

Table 2. List of primary coolant quality parameters

Parameter	**Reason for control**
pH_{25}	Together with the boron content, points to the excess or deficiency of the alkali cation sum and NH_3; characterises the NH_3 content in the coolant when (H_3BO_3+KOH) mixture is dosed to the primary circuit
PH_T	Departure from the specified range points to the increased probability of fuel failure, also the increase in corrosion product solubility and mass transport
Polarisation resistance, R_p and corrosion rate $I_k=b/R_p$	Points to the chemical stability of surface oxide films on the constructional materials of the primary circuits; is sensitive to coolant corrosiveness changes; allows rapid recording of this change and integral assessment of coolant chemistry
H_3BO_3	Its measurement is necessary to assess the compliance of the boron concentration in the coolant with the operating specifications
(K+Li+Na)	Together with the H_3BO_3 content, characterises the coolant quality; departure of H_3BO_3/(K+Li+Na) from an optimal ratio corresponds to pH change, also to increased corrosion and mass transport
NH_3	At the operating temperatures NH_3 is a source of H_3 and its concentration shows the extent to which the water coolant meets the requirement of reducing character
O_2	The growth of O_2 concentration beyond the specified value points to the danger of uniform and localised corrosion in the primary circuit constructional materials
H_2	Indicates the effectiveness of maintaining the reducing character of water coolant and suppression of water radiolysis. The increase or decrease in the H_2 content beyond the specified limits can stimulate corrosion and mass transport of corrosion products
N_2H_4	Is measured in the combination with the O_2 control in the make-up water to prevent excessive O2 ingress into the primary circuit
Cl	Is responsible for the corrosion of all constructional materials and pitting
F	Is responsible for the corrosion of all constructional materials
Na	The increase in Na content beyond the specified range in the filling and make up water contributes to radioactivity buildup during reactor operation and extends the shutdown period before repair
Fe	The Fe-content in the coolant serves an indicator of the coolant quality; high Fe concentrations point to intensive corrosion and mass transport which result in fuel deterioration and equipment surface contamination
Cu	Cu-content increase beyond the specified range in the presence of N_2H_4 and reducing conditions induces Cu deposition in metal form on the primary circuit surfaces, which creates conditions for pitting corrosion
Total specific activity of iodine isotopes	Characterises fuel cladding integrity and indirectly coolant quality in the operation period preceding the measurements
Oil	The increase of oil content in the make-up water cause deterioration of the filter operation in the water clean up plant. The products of its thermodegradation and radiolysis contaminate the coolant
θ	Together with the O_2 and Cl concentrations, helps to control the filter efficiency in the water purification system and to foresee the possibility of local corrosion

Table 3. Technical requirements for sensors and instruments for automatic chemical control in the reactor primary circuit

Measuring instrument Technical characteristics	**Conductivity meter**	**pH-meter**	**Cl-meter**	**O_2-meter**	**H_2-meter**	**PH_T-meter**	**Corrosion rate and electrical conductivity meter**
Function: measurement of water quality parameters	Electrical conductivity of liquid media	pH_{25}	Cl-ion content (Cl^-)	Oxygen content (O_2)	Hydrogen content (H_2)	PH_T	a) corrosion rate b) polarisation resistance (R_p), electrochemical impedance c) electrical conductivity
Units of measurement	mkCm/cm	pH	$mkgCl^-/kg$	$mkgO_2/kg$	$MkgH_2/kg$	pH	a) mm/y b) kOm-cm c) mkCm/cm
Limits of measurement	0–100	6–10	0–250	0–50	0–100	6–10	a) 0,001–10000 b) 0–200 c) 0–500
Measuring technique	Conductometric	Potentiometric		Ampermetric		Potentiometric	Conductometric
Sample preparation and use	a) cooling; b) depressurisation; c) sample disposal			a) cooling; b) sample return to circuit		sample return to circuit	sample return to circuit
Sample temperature, °C	20–40					150–300	20–300
Sample pressure, at.	1			circuit pressure			
Sample flow rate, kg/h	3			2–20			
Main reduced error,%	2,5	1	5	5	10	5	5
Output signal	(0–5) mA; (4–20) mA; digital binary-coded						
Metrological control by using	Standard solutions	Buffer solutions	Standard solutions	Special standard	Special standard	Buffer solutions	Equivalent cell

2.1.4. Corrosion potentials measured in the reactor water of a Swedish PWR

In-plant measurements were performed early on [13,14] in Ringhals 4, which is a 915 MW(e) PWR of Westinghouse design. A side-stream autoclave was used, installed as a by-pass in the primary coolant sampling system. Measurements were performed during steady reactor operation, during deliberate pH changes, and during start-ups and shutdowns.

The results from the measurements during steady-state reactor operation show that the corrosion potentials of the plant materials exposed, including nickel-base alloys, stainless steels, and a pressure vessel steel all coincide within a few mV with the potential of platinum, that is with the hydrogen equilibrium potential.

Over a 24 h period, the lithium hydroxide content of the reactor water was set at four levels. The response of the pH-changes on the electrode potentials was direct and in good agreement with calculated high-temperature pH-values. The results are illustrated in Fig. 7.

During start-ups and shut-downs of the reactor, the corrosion potentials differ significantly. The major changes from an electrochemical point of view occurred well below full reactor temperature.

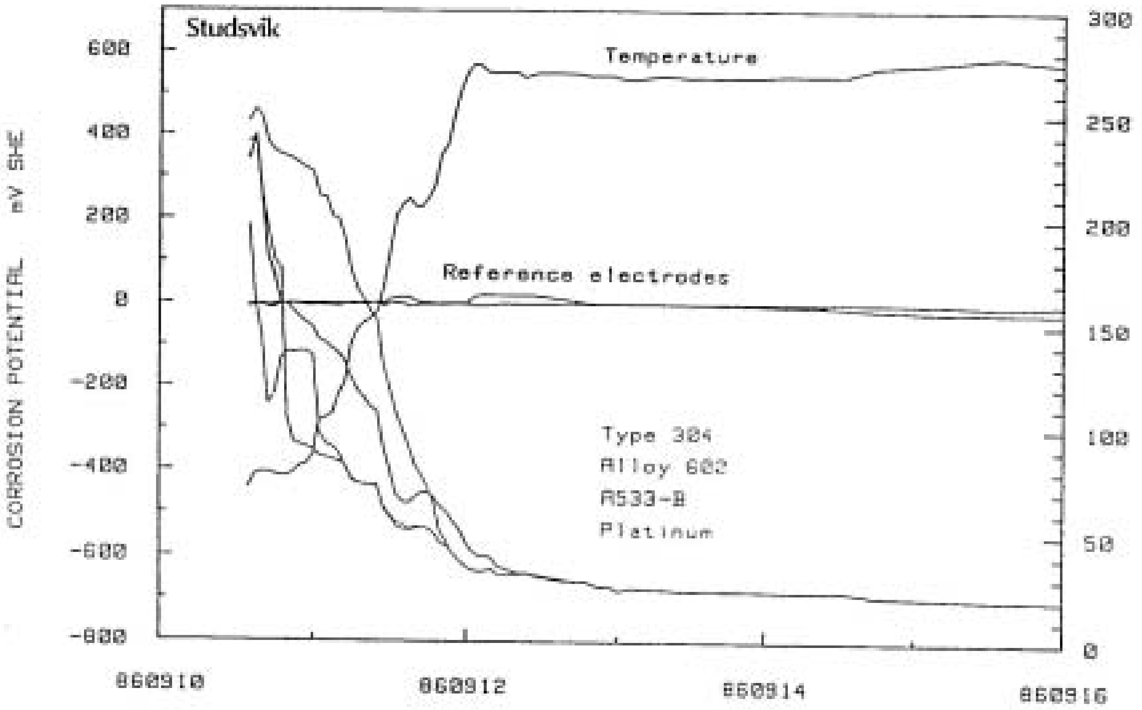


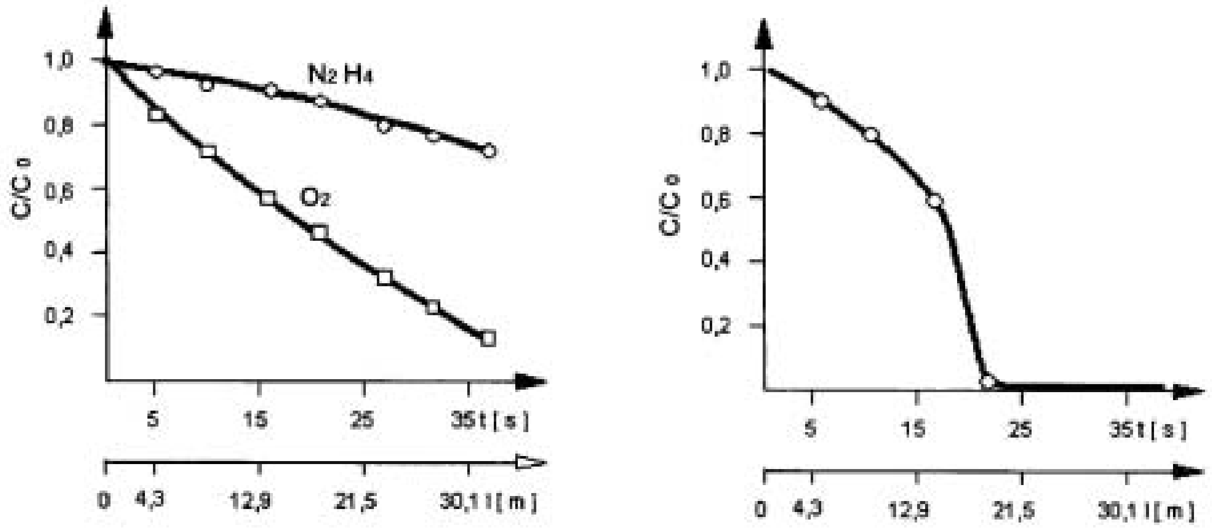
FIG. 7. Corrosion potentials in the primary water of a Swedish PWR during reactor start-up (1986).

2.2. Pressurised water reactors on the secondary side

On the secondary side of PWRs, high-temperature, on-line monitoring of water chemistry and corrosion is motivated primarily by the need to gain information so as to secure satisfactory operation of the steam generators (SG). For this purpose, monitoring of corrosion and redox potentials, oxygen, hydrazine, pH and perhaps other parameters, such as the state of oxide layers or the tendency for ongoing corrosion processes, can be considered. The key question is to determine how and where the monitoring should be performed (in the feedwater piping, side-stream autoclaves, or boilers with heated crevices, inside the steam generators themselves, or in the blow-down). For example, whereas high-temperature pH (pH_T) measurements in heated crevices are of definite interest, pH_T in feedwater is not required. In-pipe monitoring is generally preferable to monitoring in side-stream autoclaves because of the ever-present problems of changes in sampling lines (e.g. known inadequacy of oxygen monitoring in SG feedwater using long sampling lines [15] as shown in Fig. 8).

A further motivating factor is the need to ensure compatibility between SG and balance-of-plant chemistries. Experience with the following individual methods was considered in the WACOL programme:

- Redox and corrosion potential (ECP) measurements;
- PH_T measurements;
- high-temperature conductivity measurements;
- measurement of O_2 and other gases;
- heated-crevice tests in side-stream autoclaves;
- diagnostic systems for data acquisition and evaluation.



- *Left: inlet concentrations: O_2 = 20 ppb, N_2H_4 = 150 ppb, NH_3 = 1 ppm; tube preconditioned with oxygenated water.*
- *Right: inlet concentrations: O_2 = 40 ppb, N_2H_4 = 150 ppb; tube preconditioned with water containing hydrazine.*

FIG. 8. Laboratory data showing the change in concentration of species as a function of duration time (flow rate 35 l/h) and length of a preconditioned stainless steel sampling line of 4 mm internal diameter at 170 °C and 80 bar (after Haag et al.).

2.2.1. In situ measurement of potentials

Corrosion and redox potentials can be used as a global measure for oxidising and reducing species in the coolant (O_2, N_2H_4, etc.). Ultimately, implementation of the method may therefore enable measurement of such species (e.g. O_2 in final feedwater) to be discontinued. On-line measurement in final feedwater is thus a priority item here, both to ensure correct redox conditions in the SG and to optimise N_2H_4 dosing. ECP monitoring is thus of prime interest, both in bulk water and in heated crevices, but improved (more reliable) reference electrodes are required (in the latter case miniaturised).

Examples of operating experience gained in various countries are as follows.

2.2.1.1. ECP measurements in a Finnish reactor of WWER design

At the Loviisa WWER, the oxygen concentration in the feedwater is kept as low as possible (0.5 to 1.0 ppb) because the amount of reducing agent added (hydrazine) is not sufficient to scavenge possible oxygen from the water. However, it is known that even very low oxygen concentrations can lead to fairly high corrosion potentials on structural materials. To verify that reducing conditions do exist in the two SGs, on-line redox and ECP measurements were carried out in a flow-through cell attached to the sampling lines. An example of the results is shown in Fig. 9.

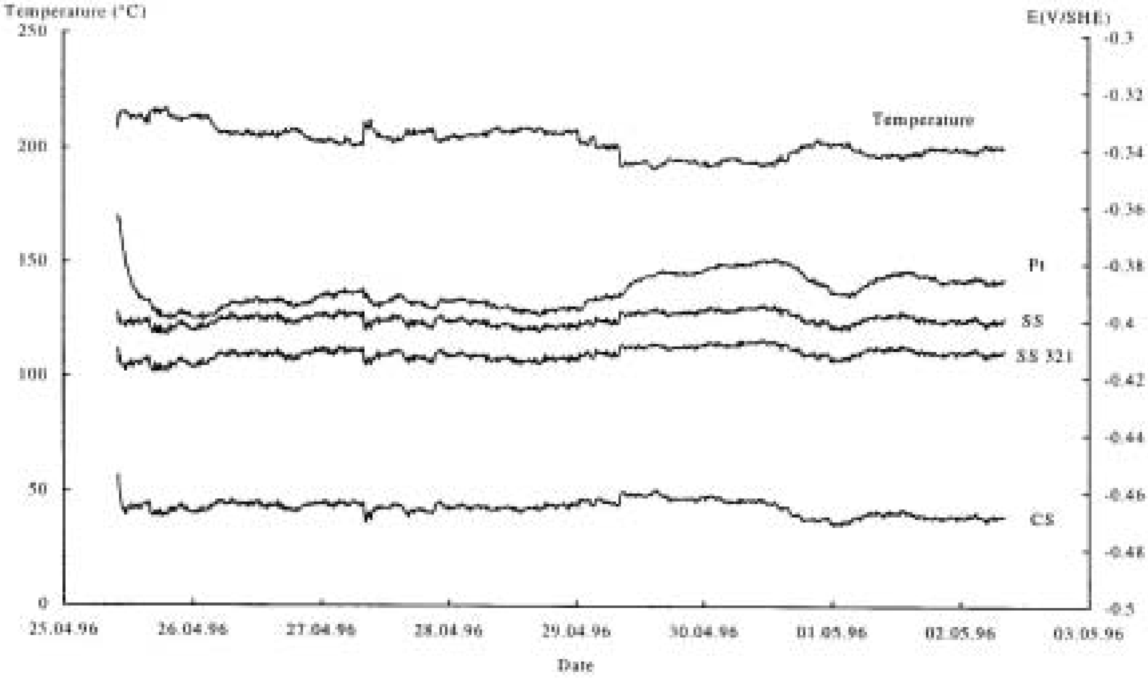


FIG. 9. Measured ECP values for various materials in the water coming from the hot end of one SG in a Finnish WWER plant.

The measured potentials indicate that the water chemistry environment in the different parts of the SGs is clearly reducing and only small differences can be observed between successive measurement locations. The ECP values of the typical structural materials differed to some extent due to the different oxides formed on the surfaces. As expected, the potential of the Pt electrode (redox potential) was highest, because of the catalytic properties of the surface.

During temperature fluctuations in the sampling line, the ECP values of the studied materials behaved differently. The potential of the carbon steel (CS) specimen changed more than the potential of the stainless steel (SS) alloys, clearly indicating that different oxide structures exist on the surfaces.

2.2.1.2. Potential measurements in a French reactor to assess the optimum hydrazine level to mitigate corrosion attack on SG tubing

ECP measurements were performed in 1997 by EDF (Generation and Transmission Division) at the PWR Golfech, which is a riverside plant. The objective was to evaluate the level of hydrazine in feedwater necessary to get a low ECP in the steam generator in order to mitigate intergranular attack/intergranular stress corrosion cracking (IGA/IGSCC). For this purpose, ECP measurements were performed on the secondary side at three points upstream of the steam generator, in feedwater and HP heater systems. The temperature ranged from 25 to 235°C. Oxide particles analyses were performed at these three points and in the steam generator blowdown.

The ECP measurements were made using a high-temperature reference electrode system (Ag/AgCl) from Studsvik (Sweden). Platinum electrodes were used to determine the redox potential, and carbon steel, 304 stainless steel and alloy 600 electrodes to determine the ECP values. The oxide analyses gave the total amount of iron (ICP measurements) and the magnetite/haematite ratio. The effect of hydrazine was studied in the range of 25–200 ppb, with the following major results:

A very low effect of the hydrazine level on the potential was observed. At 235°C, it was less than 30 mV in the range studied (Fig. 10). A negligible effect on the magnetite/haematite ratio was observed at the same time. The potential seems to be much more sensitive to oxygen variations, even if these are low.

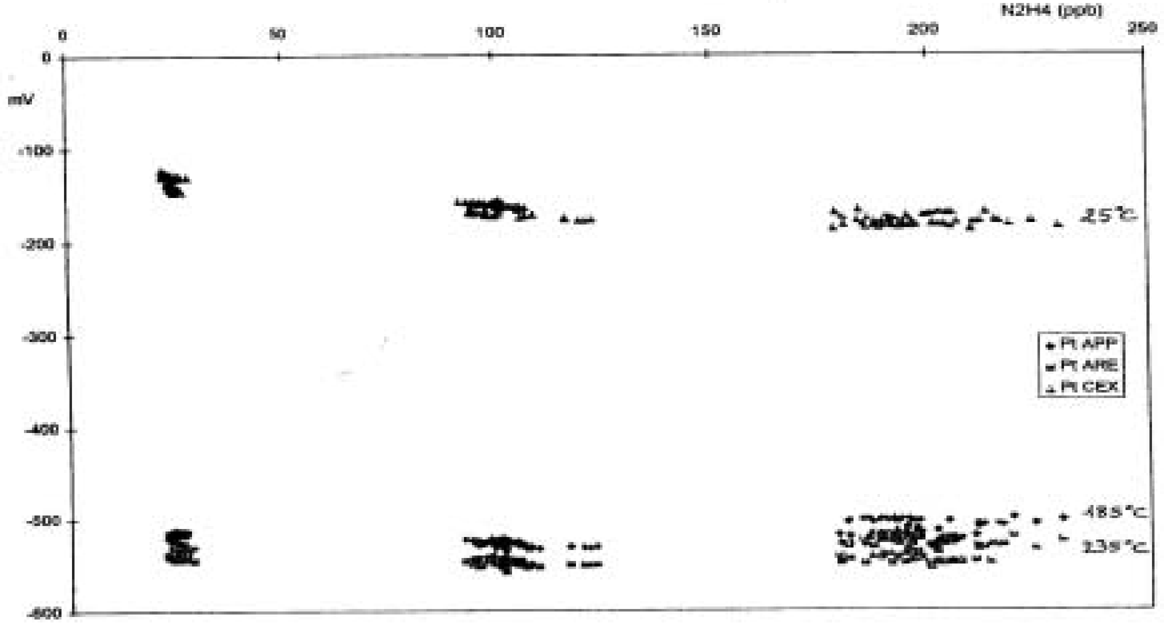


FIG. 10. Effect of hydrazine level on the redox potential (Pt electrode) in the secondary water of a French PWR at various temperatures.

These results, together with considerations of cost associated with high hydrazine levels and possible detrimental consequences on flow-assisted corrosion, led EDF to the decision that it was not justified to increase the hydrazine level above 100 ppb in plants with no copper alloys.

The ECP monitoring produced important data and allowed decisions to be made for plant secondary side chemistry. Some doubt still remains on the origin of unexpected. trends. However, in spite of the demonstration of usefulness, in-plant ECP measurements were judged to be expensive and time consuming, for proper interpretation. Thus, applications today will be limited to very specific campaigns. The next EDF project is ECP monitoring of steam generators blowdown in order to get information on redox potentials during hot and cold shutdown. A recommendation for the future is to develop integrated systems that make easier and cheaper the implementation of such monitoring.

2.2.1.3. Corrosion and redox potential measurements in two German reactors.

Routine measurements of electrochemical potential have been made at the Biblis A and B plants by Siemens and the plant operator (RWE) since 1985/1988. Originally, the main emphasis was on determining potentials directly within the SG tube bundle [16] using an external Ag/AgCl electrode and a long Luggin-Haber capillary, as shown in Fig. 11, as well as in the final feedwater heater. Fig. 12 illustrates the response of redox and ECP values to an interruption of hydrazine dosage.

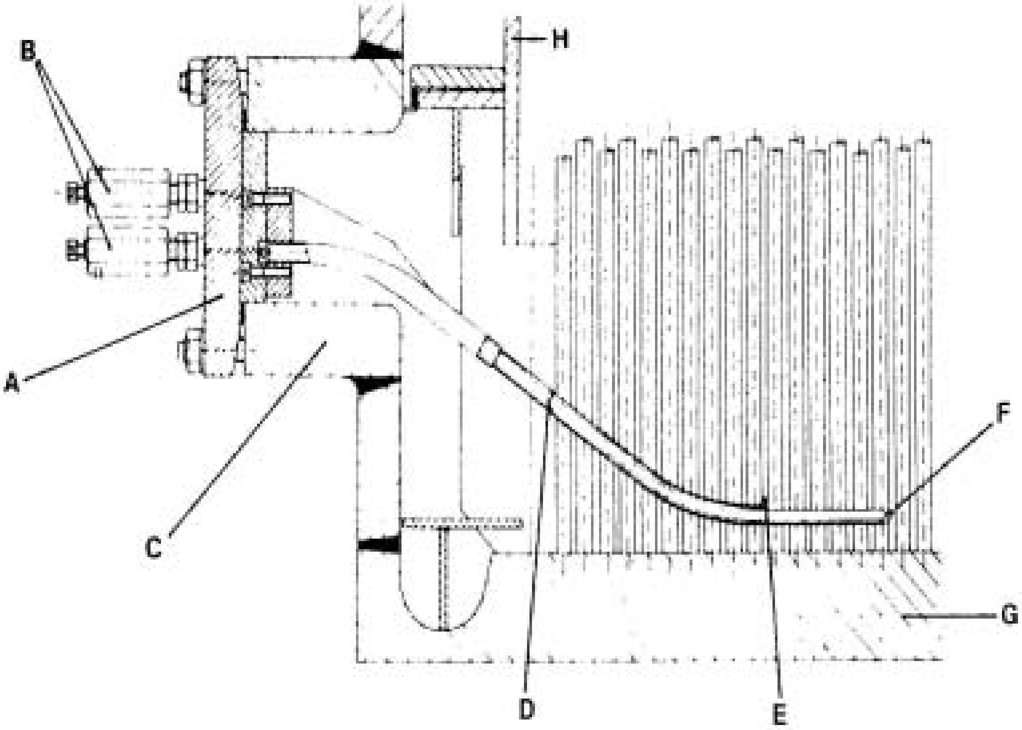


FIG. 11. Monitoring unit for the measurement of electrochemical potentials directly within the SG tube bundle of a German PWR.

Later work concentrated on measurements in final feedwater. The results confirmed that standard coolant sampling practice with long sampling lines and subsequent, continuous analysis of the sampled water at ambient temperature does not necessarily enable detection of oxidising conditions in system components. Significant increases in ECP values and redox potentials were sometimes recorded during plant operation, despite the fact that the oxygen concentration in samples from the final feedwater appeared to remain constant at the normal value of ca. 2 ppb. Further investigation showed that changes in true oxygen concentration up to less than 10 ppb can cause an increase in the measured potentials of ∅100 mV, even in the presence of relatively high hydrazine levels.

Reliability and long-term stability of the monitoring units has been excellent, with routine maintenance necessary only every two cycles. The recorded signals are checked by the shift personnel once per shift and by the plant chemists twice per day. Readings of the electrode potential > –150 mV_{SHE} must be reported for clarification of the causes.

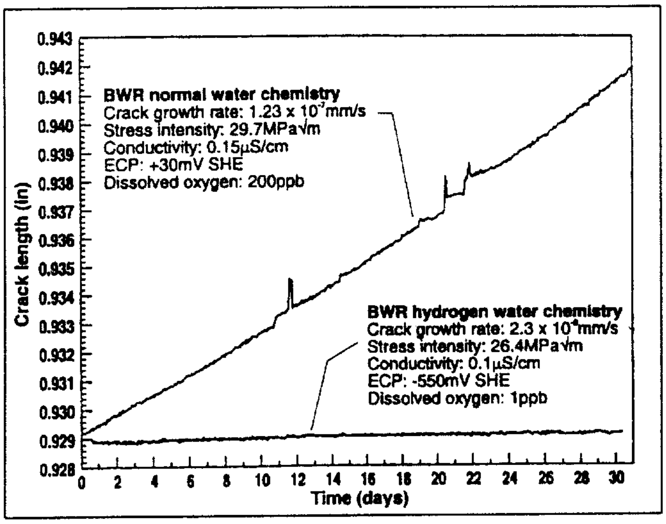


FIG. 12. Response of electrode potentials in the final feedwater heater (FWH) and SG tube bundle of a German PWR to interruption of hydrazine dosage.

2.2.1.4. Potential measurements in Swedish reactors

Studsvik Material AB has performed electrochemical monitoring in nuclear power plants since 1978. The in-plant monitoring was first performed with electrodes installed in side-stream autoclaves connected to the reactor systems by sampling lines. Later, in situ electrodes in the process piping have also been used. Much of this work on the secondary side at the Ringhals 3 and 4 PWRs has been published [17, 18].

Changes in redox potentials and water chemistry during an unintentional oxygen in-leakage, whilst the results of deliberate oxygen dosage to the sampling line (performed together with deliberate flow-rate changes to qualify the potential readings) are illustrated in Fig. 13. The electrochemical measurements clearly confirmed that, without on-line monitoring, oxygen transients can go undetected on the secondary side of PWRs [19].

2.2.1.5. Potential measurements in US reactors

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 operating power plants in the USA [20,21] and Europe. In the Commanche 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.

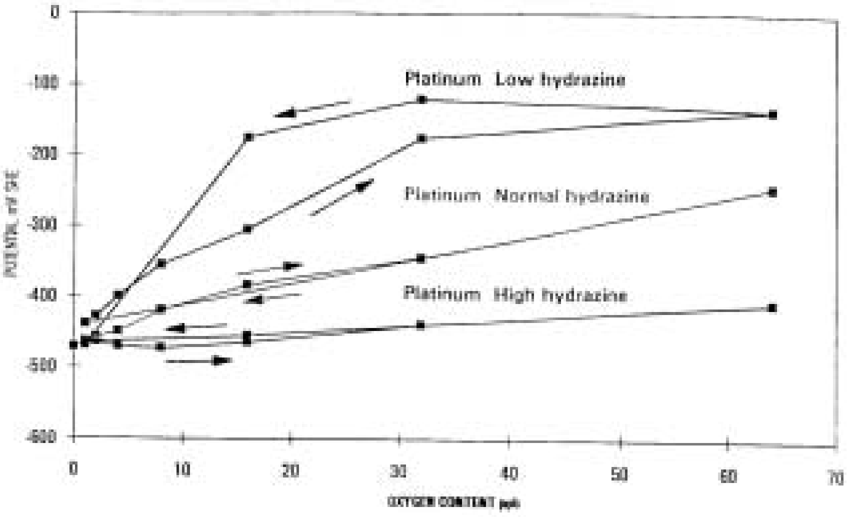


FIG. 13. Effect of oxygen dosage on the redox potential measured in a side-stream autoclave at a Swedish PWR. The arrows indicate measurement hysteresis effects.

The results clearly show that 30 μgkg^{-1} hydrazine is more efficient in decreasing the oxygen concentration in the feed water than 50 μgkg^{-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. 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 [22].

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.

2.2.2. In situ measurement of pH_T

Test measurements of high-temperature pH have been carried out on the secondary side in order to follow the effects of varying amine dosages [22], but the technique has not been adapted for routine use. Relevant measurements have also been made in geothermal applications [23] and fossil power stations (see, e.g. Sections 3.4.1 and 3.4.4).

2.2.3. In situ measurement of conductivity

HT measurement of steam conductivity (at an optimum temperature of around 150°C) has the potential to achieve better NH_3/N_2H_4 (and thus Ph) control on the secondary side of PWRs. Also, the lack of information on equivalent conductivities for many ionic species leads to difficulties in estimating true values of conductivity in the recirculating water at operating temperatures. However, RT measurements respond more sensitively to low levels of impurities.

Test measurements have been made at the Loviisa WWER in Finland [22] and in a variety of fossil power stations (see, e.g. Sections 3.3.2 and 3.3.3).

2.2.4. Heated-crevice tests in side-stream autoclaves

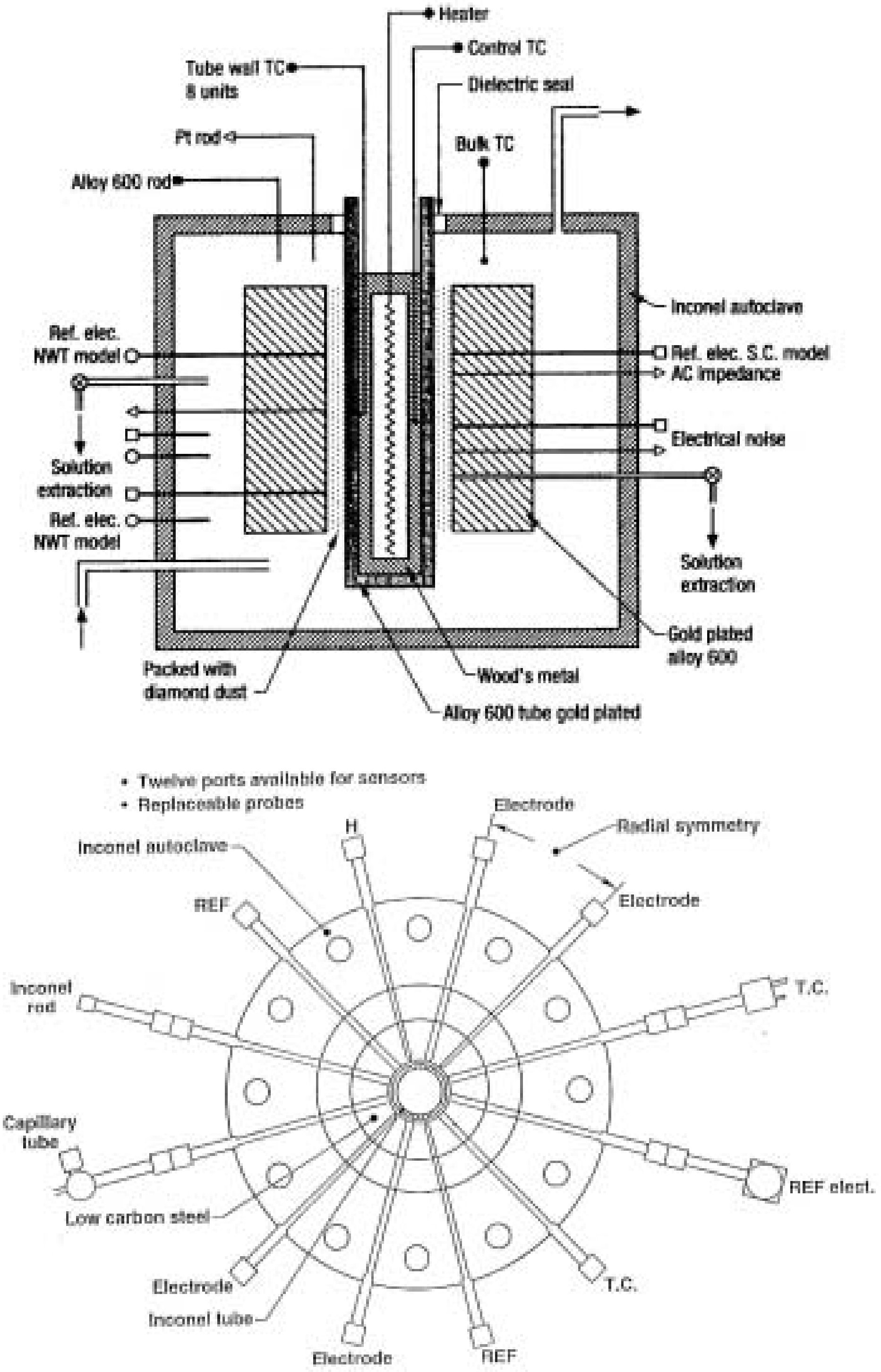
As an approach to obtaining a better understanding of how crevice chemistries relate to SG feedwater chemistry, an instrumented replica of a SG tube/tube support plate crevice has been constructed at the Rockwell Science Center in the USA under EPRI sponsorship [24] and recently installed in the blowdown line of a Japanese PWR. The system operates with simulated SG thermal conditions and is designed such that in situ measurements can be made of ECP values (crevice and free-span areas), temperature profiles, galvanic currents, AC impedance, electrochemical noise, Ph_T values, concentrations of specific ions, and incipient tube damage (see Fig. 14). In addition, the crevice solution can be extracted for analysis while the system is in a normal operating condition or analysed in situ using Raman spectroscopy.

Three different crevice configurations (open or packed, etc.) were examined during laboratory tests with NaOH solutions pumped through the autoclave. The results were in accordance with a model predicting that hideout reaches its equilibrium concentration when the boiling point elevation equals the available superheat within the crevice. The temperature profiles, which were monitored while sodium ions concentrated in the crevice, permitted the observation of the boiling to non-boiling transition at specific locations. An example of the data obtained is shown in Fig. 15.

With the installation of the system at Ohi 1 in 1997, heated-crevice devices have now left the development stage and are undergoing qualification.

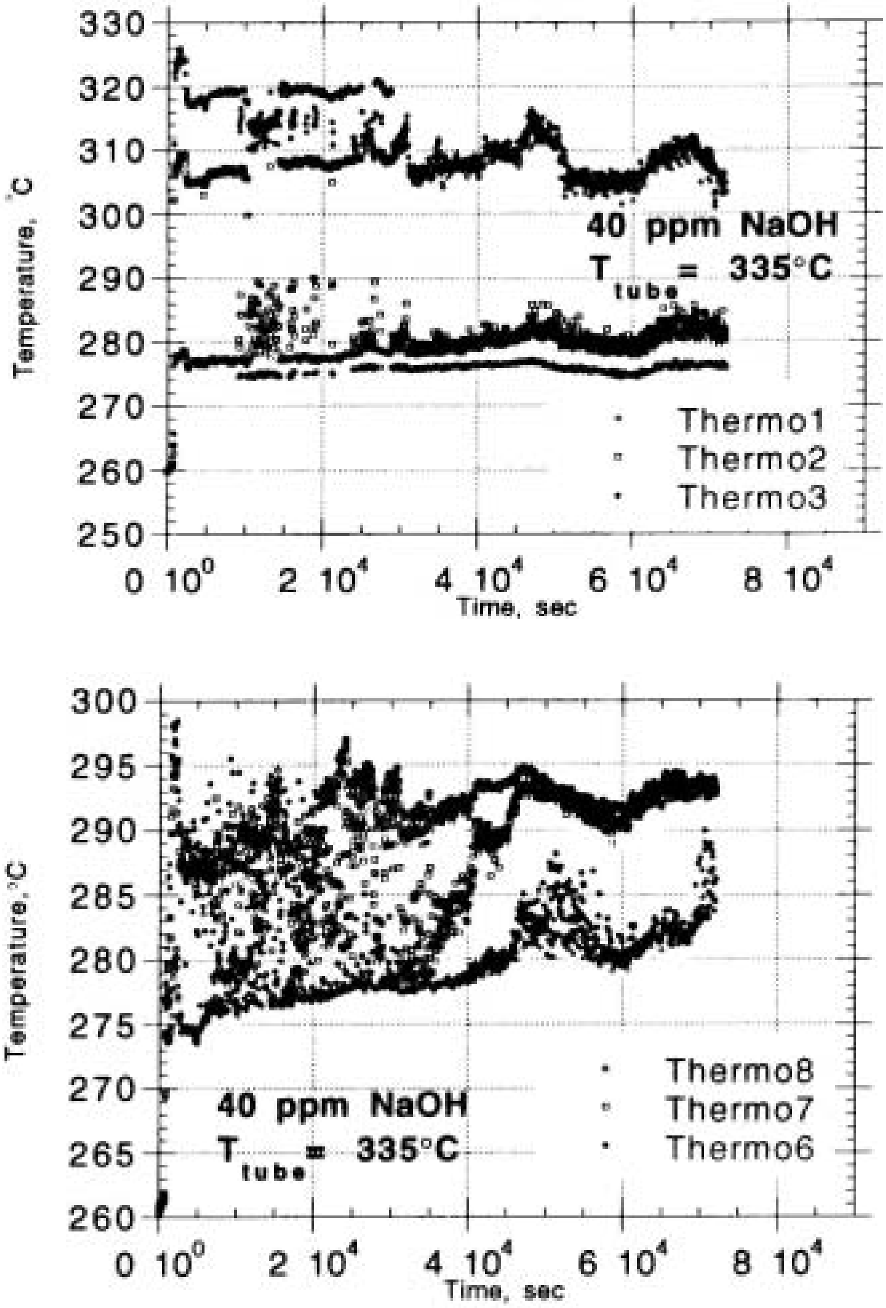
2.3. Boiling water reactors

Boiling water reactors are single-circuit units and include both the Western design (BWR) and the Russian RBMK reactor. BWRs have been severely affected by corrosion problems (primarily SCC) involving cracking of piping and, more recently, core internals (SCC/IASCC). Improvements in water chemistry have been the key to managing these problems in existing reactors and have thus provided an important driving force for implementing on-line monitoring. Continual reduction in impurity levels in the reactor coolant under normal water chemistry (NWC) now means that the majority of operating plants routinely achieve conductivities of around 0.1 μS/cm or better, a degree of purity which is very hard to simulate in laboratory autoclave experiments [25]. Since the introduction of hydrogen water chemistry (HWC) in the mid-Eighties, a powerful technique has become available to prevent SCC in most BWR components, even to the point of stopping the growth of existing cracks. This relies on adding gaseous hydrogen into the feedwater to scavenge oxygen (from radiolysis) in the downcomer region and thus obtain a reduction in the free corrosion potential (ECP) of austenitic materials (stainless steel and nickel-base alloys) to below the so-called protection potential (usually taken to be –230 mV_{SHE}). By its very nature, implementation of HWC lends itself to on-line monitoring by measurement of electrochemical potentials, and this now required of plant operators in the relevant EPRI water chemistry guidelines [26]. It can be regarded as a well-developed technology for out-of-core measurements, but opinions vary as to reliability, accuracy, and ease of conversion of data to the standard hydrogen scale, etc.



- *Once-through water-steam system*
- *Superheat cartridge heater*
- *Support plate, autoclave & tube electrically isolated*
- *Flexibility: tube, support plate & autoclave structurally independent; geometric configuration/crevice dimensions easily changed; open or packed crevice; open or closed bottom.*

Fig. 14. Conceptual design of heated crevice system: side (above) and top (below) views.



- **Thermal-Hydraulic Transitions**
  - **1 & 2 Steam Blanketed to Wetted**
  - **6 & 7 Steam Blanketed to Wetting & Drying to Wetted**
  - **8 Boiling to Wetted**
- **Electrochemical Potential**
  - **Invalid Measurement During Steam Blanketed, Boiling**
  - **Valid during Wetted, t > 5.5 X 10^4 sec**
  - **Δ ECP = 274 mV, 2.5 pH Units between Crev and Bulk**
- **[Na] Crevice = 2.8 X 10^5 ppm by Solution Extraction**
- **Ave BP Elevation of Tube Wall = 25°**
  - **Implies 3 X 10^5 ppm [Na] i.e., 30 w/o**

Fig. 15. Preliminary results from laboratory qualification of heated crevice device.

The second major driving force in improving BWR water chemistry has been to obtain a reduction in radiation fields and activity buildup. Unfortunately, use of HWC with high levels of injected hydrogen can lead to significantly increased N^{16} levels in the steam. In the last few years, a technique involving the treatment of reactor components with small amounts of noble metals (primarily platinum and rhodium) has been successfully implemented during plant shut down [27] so as to obtain catalytically active surfaces. This enables successful use of HWC at hydrogen levels which no longer increase radiation fields, but makes ECP measurement even more important. Improvements to in-core reference electrodes have been achieved, but routine, long-term monitoring experience is still needed and is the key to assessing to what extent HWC/NMCA can protect against SCC of reactor internal components.

2.3.1. In situ measurement of electrochemical potentials out of core

2.3.1.1. Corrosion and redox potential measurements in a German reactor

To study the environmental conditions which may result in IGSCC, and to determine the influence of radiolysis products on redox and corrosion potentials, two monitoring units were installed at the Gundremmingen B power station in 1996. Both are located in one of the two reactor water clean-up lines, but at distances of approximately 1 m and 17 m (in the flow direction) from the RPV. They incorporate an external Ag/AgCl reference electrode, as shown schematically in Fig. 16.

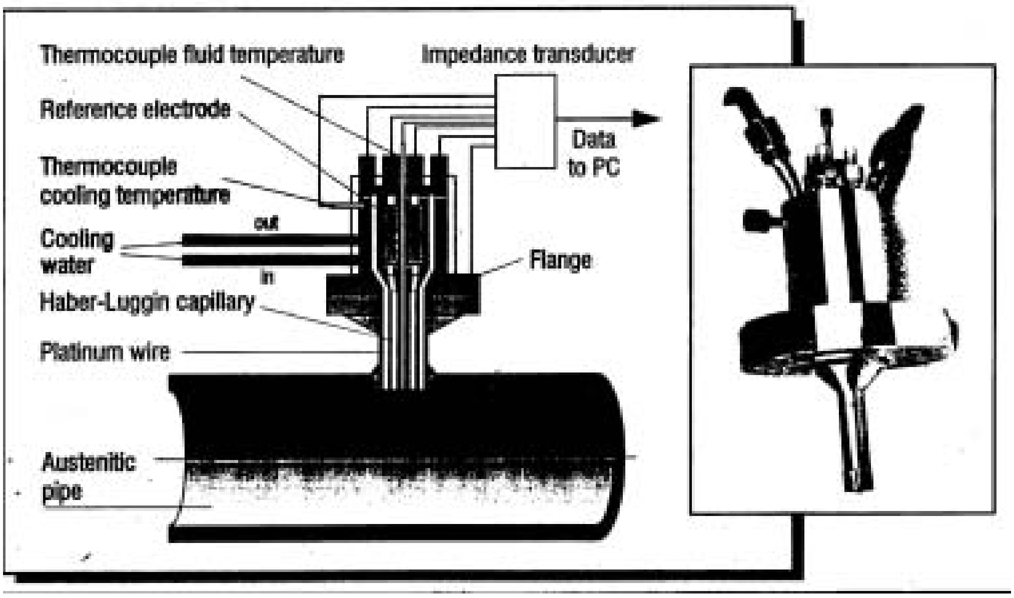


FIG. 16. Schematic diagram of probes installed in a German BWR.

Operation of the plant at full power operation and with a reactor water conductivity < 0.1 µS/cm and a flow rate of 1.2 m/s results in a corrosion potential of the piping material near the RPV of about 150 mV_{SHE} and in a redox potential of about 50 mV_{SHE}. At the inlet of the regenerative heat exchanger, the measured corrosion potential lies in the region of about 120 to 130 mV_{SHE}, the redox potential is –20 mV_{SHE}. The difference in potential as a function of measuring point is more pronounced for the redox potential than for the corrosion potential. The temperature of the reactor coolant, which can also influence the potential values for thermodynamic reasons and/or in transforming the measured values to hydrogen scale, is similar (approximately 250°C) at both installed locations. Independent of the measuring position, the redox potential is generally more negative than the corrosion potential of the piping..

Reduction of the power to less than approximately 75% results in a shift of both the redox and ECP to lower values. Fig. 17 shows the response of these potentials during a reduction of power to 40–50%. During this operational phase, the flow rate and the conductivity of the reactor water remained constant. Independent of the measuring position, the change of corrosion potentials is about 10 mV and the change of redox potentials is about 50 mV. An increase in potential values near the RPV can be observed if line 1 of the reactor water clean-up system is taken out of service, see Fig. 18. In parallel, the flow rate decreases immediately to zero. At the measuring locations the temperature decreased to 220°C near the RPV and to about 50°C near the regenerative heat exchanger. The redox and corrosion potential are influenced by temperature. Due to the very different temperatures at the measuring locations, comparison of potential values during this event is difficult. The shift in corrosion and redox potential can be caused by the temperature decrease and/or by the decrease in flow rate.

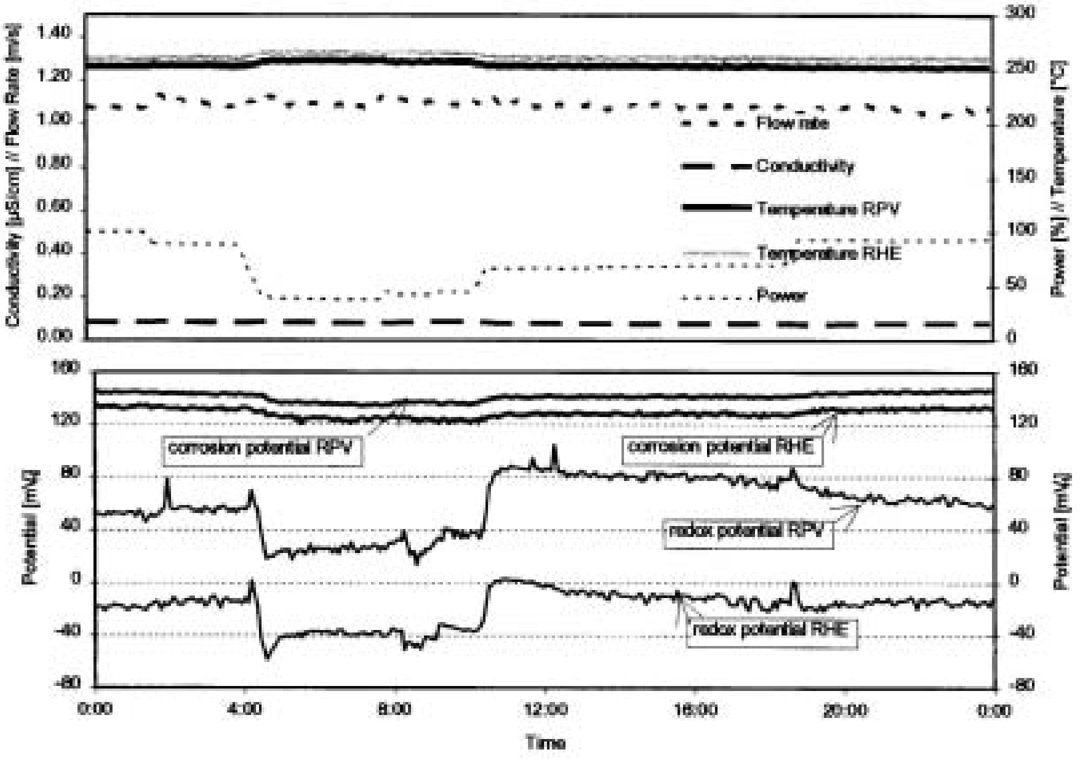


Fig. 17. Redox and corrosion potentials in a German BWR during a power reduction.

Percentage of reactor power, flow rate and the measuring locations influence the amount of radiolysis products in the fluid, which in turn affects the redox potential and the corrosion potential of the piping. The redox potential apparently reacts more sensitively to changes of these parameters and therefore to the partial decomposition of radiolysis products like H_2O_2 than the piping surface.

This behaviour can change if other phenomena become a more potential decisive factor. During operation of reactor coolant clean-up line 1, the condensate clean-up system was changed. This resulted in a small increase of conductivity up to 0.22 µS/cm for some hours.

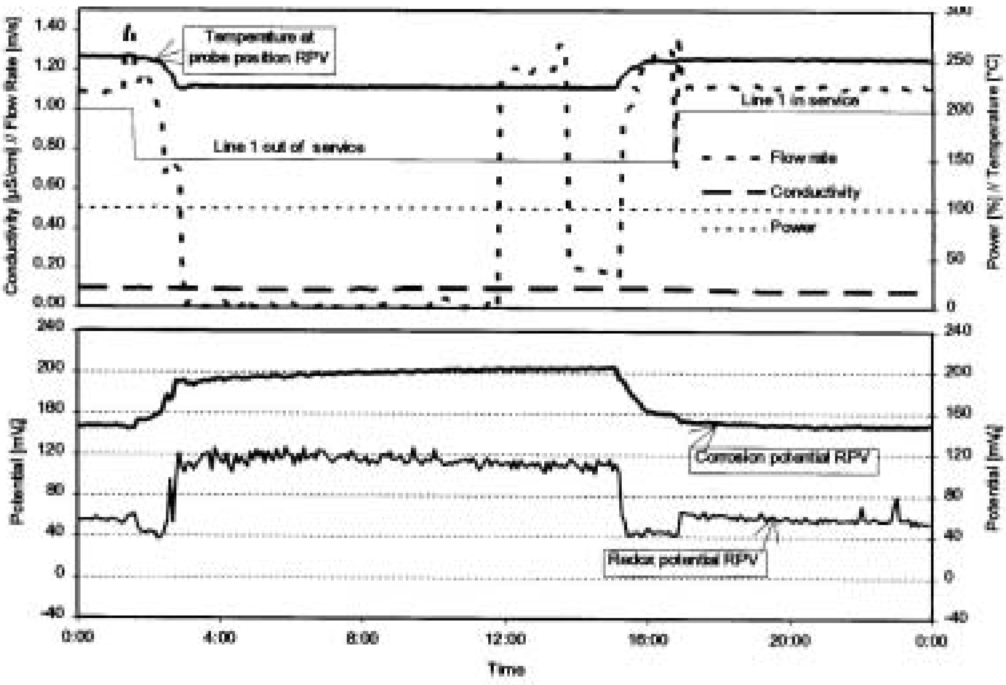


FIG. 18. Redox and corrosion potentials in a German BWR during reduced operational capacity of the reactor water clean-up system.

The response of the redox and corrosion potentials is shown in Fig. 19. Independent of the measuring location, both the redox and the corrosion potentials exhibit a shift to higher values. The shift of the corrosion potentials is more pronounced than the shift of redox potentials. When the conductivity decreased to normal values (0.09 µS/cm), the potentials also decreased to their previous steady-state values of conditions. The reason for this behaviour is not fully understood, but it may depend on the concentration of sulphate anion and the resulting concentration of hydrogen cations.

The monitoring units remained installed for more than one and a half years without maintenance service. Reliability and long-term stability of the electrodes were excellent.

2.3.1.2. Experience with ECP monitoring in Japan

Of the 28 BWRs in Japan, at least 12 had obtained experience of applying HWC by 1999. The factors considered to be of importance in making ECP measurements include:

- location of the monitoring probes
- design and manufacture of the reference electrodes
- choice of working electrode for the measurement (e.g. on coupon or component)
- effect of reactor design (dose and flow rates, etc.)

Details of some of the monitoring carried out to date are given in Table 4 and more details are to be found in the right column of this table.

Examples of the results obtained from ECP monitoring in some of the Japanese BWRs are shown in Figs 20–21. Even taking into account the differences in plant design, the consistency of the measurements is not yet considered satisfactory. Further work, in particular to combine monitoring with radiolysis modelling, is in progress.

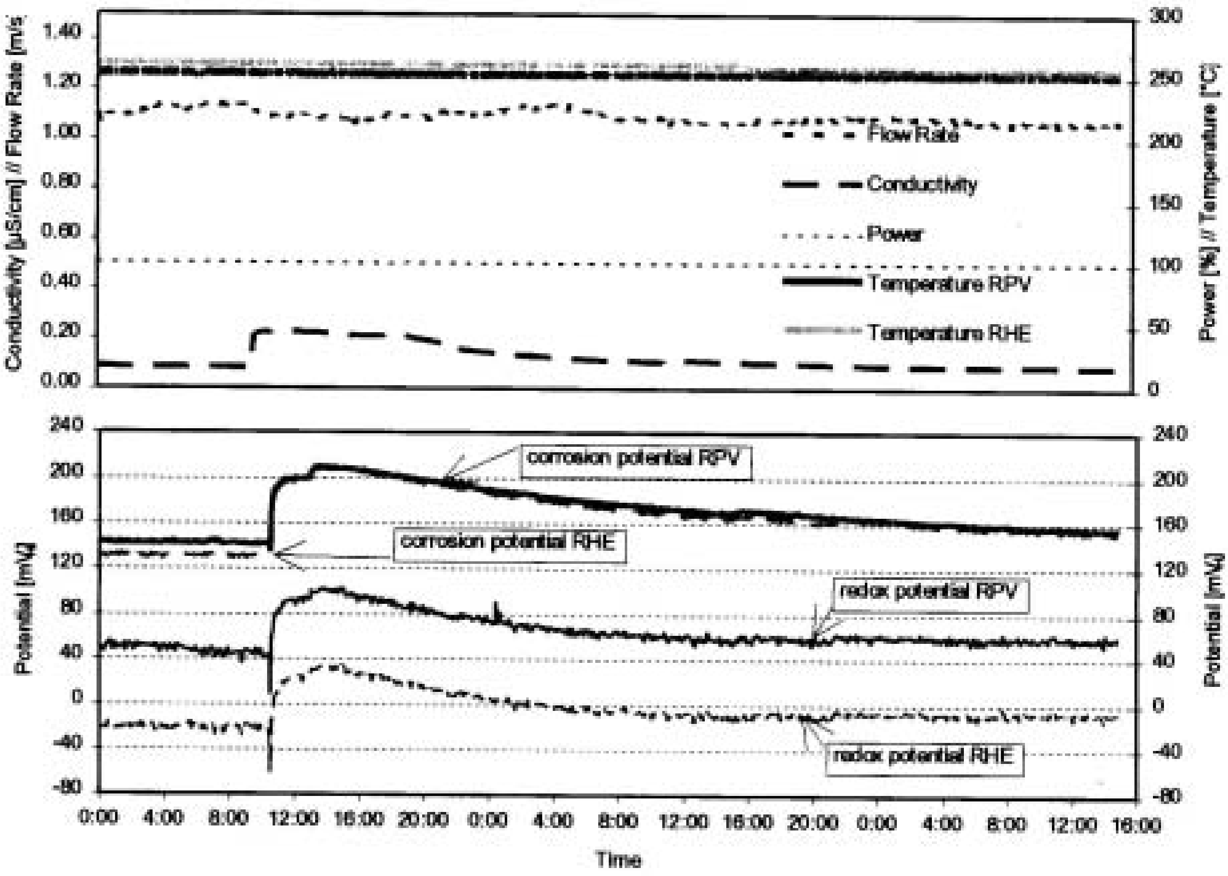


FIG. 19. Redox and corrosion potentials in a German BWR during a conductivity transient.

Table 4. Details of monitoring carried out in Japanese BWRs

Plant name	**Power MW(e)**	**Type**	**Year**	**Utility**	**Location**	**Monitoring techniques**	**Ref.**
Fugen	165	ATR	1984	JNC (ex PNC)	Autoclave (PCS)	ECP (Ag/AgCl) SSRT	[28]
Fukushima 1–3	784	BWR-4	1992	TEPCO	In-core (LPRM) Autoclave (RWCU)	ECP (Pt), ECP (Ag/AgCl) ECP (Cu/CuO), ECP (Ag/AgCl)	[29]
Fukushima 1–5	784	BWR-4	1995	TEPCO	Bottom drain line Autoclave (drain line)	ECP (Ag/AgCl) ECP (Ag/AgCl), CT	[30]
Tsuruga-1	357	BWR-2	1995	JAPCO	In-core (LPRM) Bottom drain line Autoclave (RWCU)	ECP (Ag/AgCl), ECP (Pt) ECP (Ag/AgCl), ECP (Pt) ECP (Ag/AgCl), SSRT/CT	[31] [32]
Tokai-2	1100	BWR-5	1997	JAPCO	Bottom drain line	ECP (Ag/AgCl), ECP (Pt) ECP (Fe/Fe_3O_4)	[29]
Simane-1	460	BWR-3	1997	CHUGOKU	Bottom drain line	ECP (Ag/AgCl)	[33]
Kashiwazaki Kariwa-7	1356	ABWR	1997	TEPCO	Bottom drain line	ECP (?), ECP (Pt)	[34]

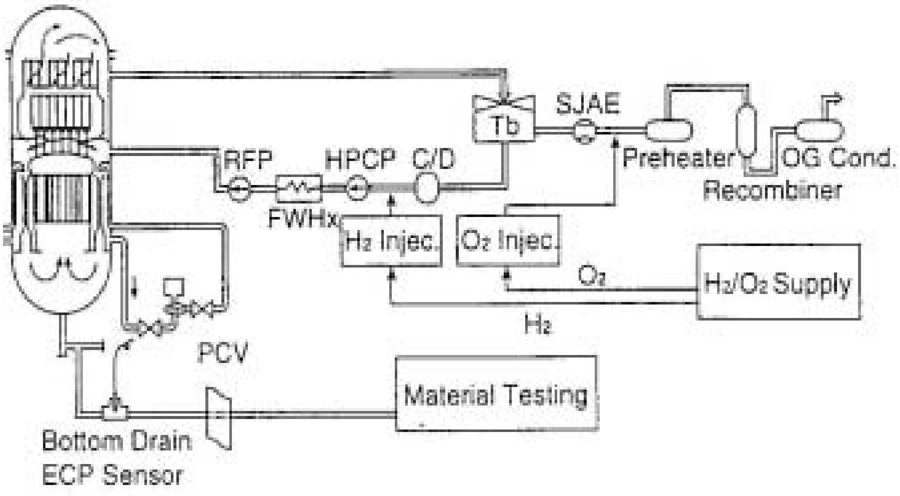


FIG. 20. Schematic diagram of monitoring locations at Fukushima 1–5 BWRs in Japan.

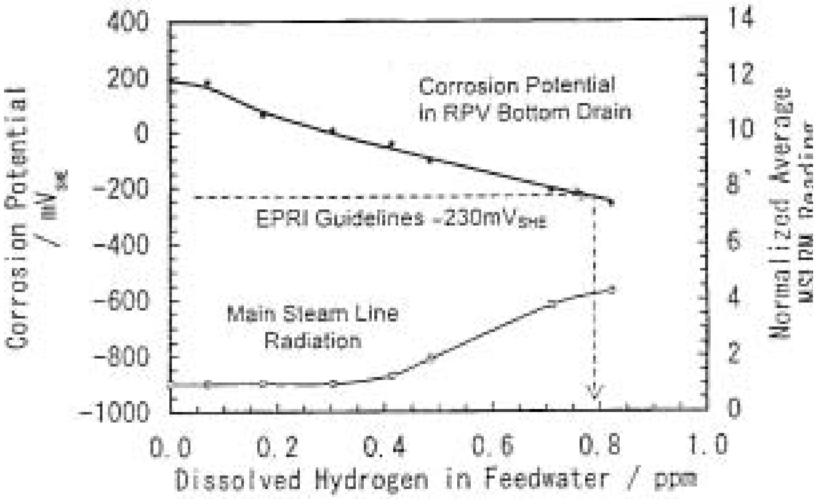


FIG. 21. Dependence of bottom-drain-line ECP at Fukushima on hydrogen injection rate.

2.3.1.3. ECP monitoring in Swedish BWRs

Studsvik Material AB has been involved in monitoring ECP and redox potentials in seven Swedish BWRs for many years (during NWC operation since 1978 and during HWC operation since 1981, with in situ electrodes being used since 1988). Much of this experience has been reported in the literature [35–39]. The technique is routinely used for HWC follow-up in all Swedish BWRs with external primary pumps, and measurement locations include both the main recirculation system and the residual heat removal (RHR)/reactor water clean-up (RWCU) systems. Both in situ electrodes and electrodes in side-stream autoclaves are used, and platinum has been found to be a reliable reference electrode during HWC.

For electrodes installed in the RHR/RWCU system, lifetimes of three years are verified, whereas replacement of electrodes in the main recirculation system is normally necessary after two years. Fig. 22 shows the arrangement for measurements in the Barsebäck 1 reactor using both in-pipe electrodes and side-stream autoclaves. An example of the data obtained during both HWC and NWC is given in Fig. 23.

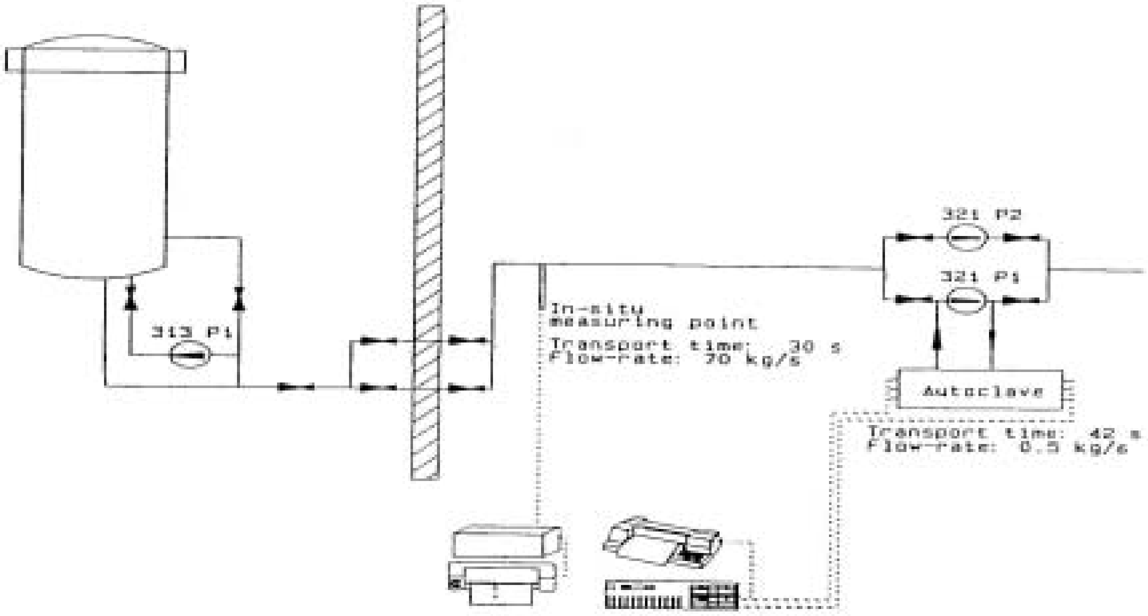


FIG. 22. Arrangement for ECP monitoring in the Barsebäck 1 BWR in Sweden.

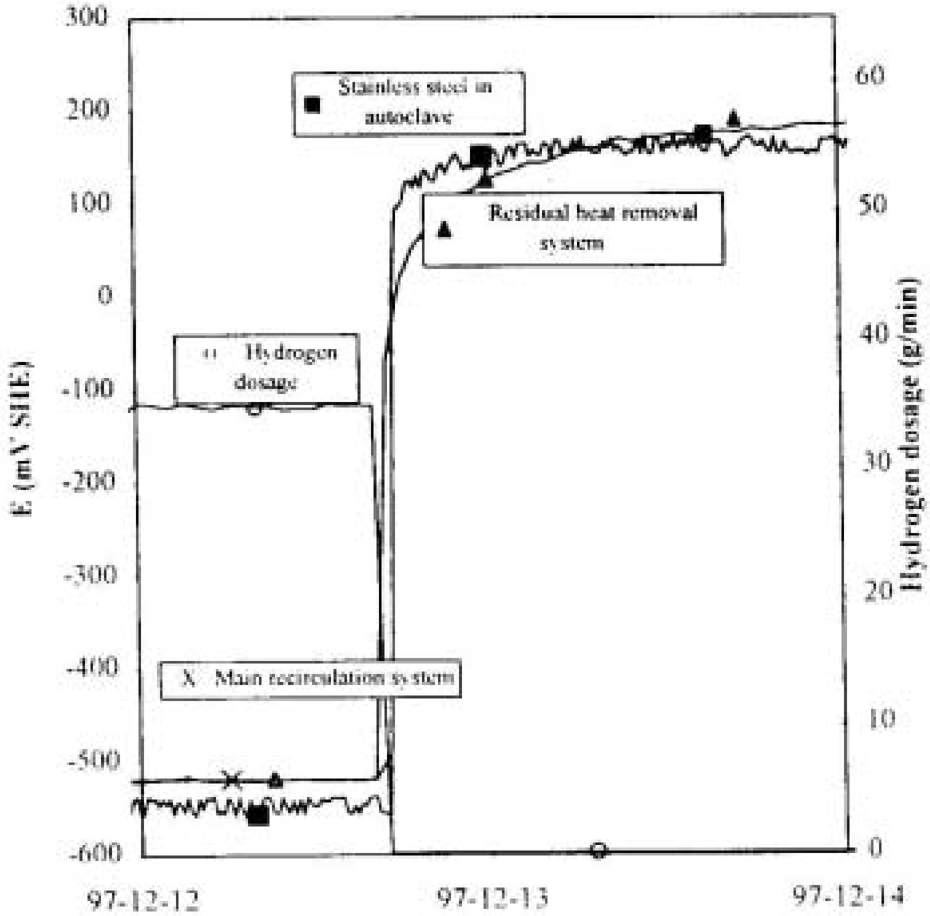


FIG. 23. ECP values measured during NWC and HWC in the Barsebäck 1 BWR.

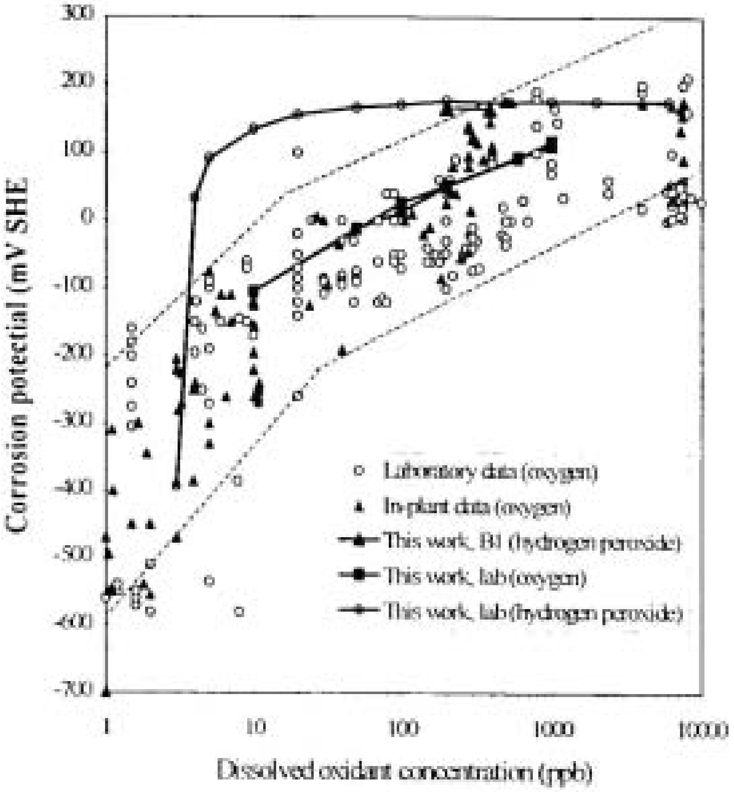


FIG. 24. ECP values for stainless steel measured in-plant and in laboratories versus the dissolved oxidant concentration.

Much attention has been paid in the Swedish work to understanding the influence of both probe design and measurement location on the measured potentials. Fig. 24 shows a comparison of the ECP values obtained in both American and Swedish plants as a function of the dissolved oxygen concentration. A further factor affecting, in particular, the comparison between plant and laboratory data is the presence of other oxidising species (primarily H_2O_2) from radiolysis in the plant systems.

Work is ongoing in Sweden to benchmark laboratory and plant measurements of ECP and to establish correlations with crack growth rate data.

2.3.2. Measurement of corrosion and redox potentials in-core

In-core measurements of potential were pioneered in America in the late Eighties as part of an integrated approach to monitoring for SCC [40] and have also been used sporadically in other countries, including Switzerland and Japan (see Table 4). The technique relies on the insertion of reference electrodes at several locations into one or more LPRM tubes within the core, usually together with comparison measurements in external piping. Fig. 25 illustrates a typical arrangement and Fig. 26 shows in-core data obtained from the Duane Arnold BWR before and after application of noble metal chemical addition in 1996.

Routine use of in-core ECP monitoring in commercial BWRs has been hampered by difficulties with the reliability of reference electrodes in high radiation fields, but work is ongoing to overcome this and alternative designs are also becoming available (see Sections 2.4.1 and 3.5).

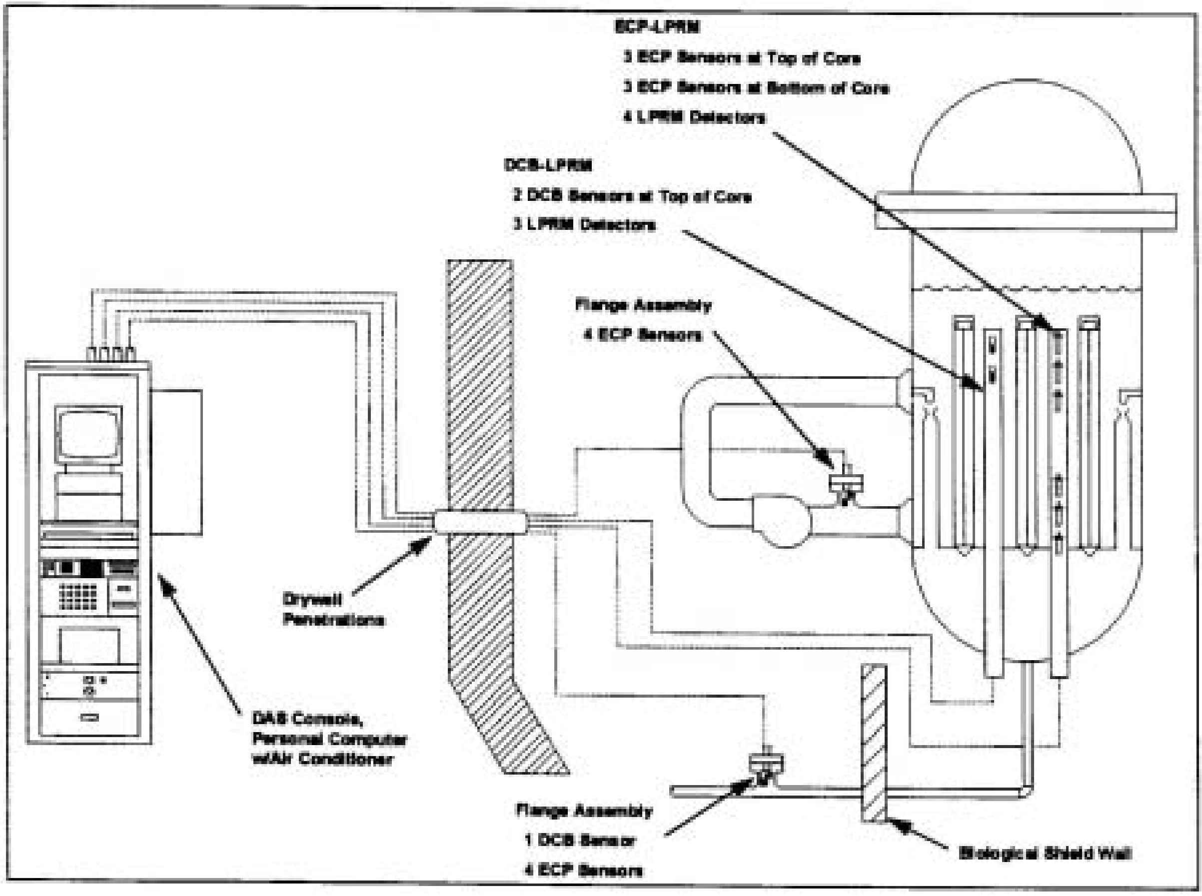


FIG. 25. Typical arrangement for comprehensive ECP monitoring in an American BWR.

2.3.3. On-line monitoring of activity buildup through gamma spectroscopy

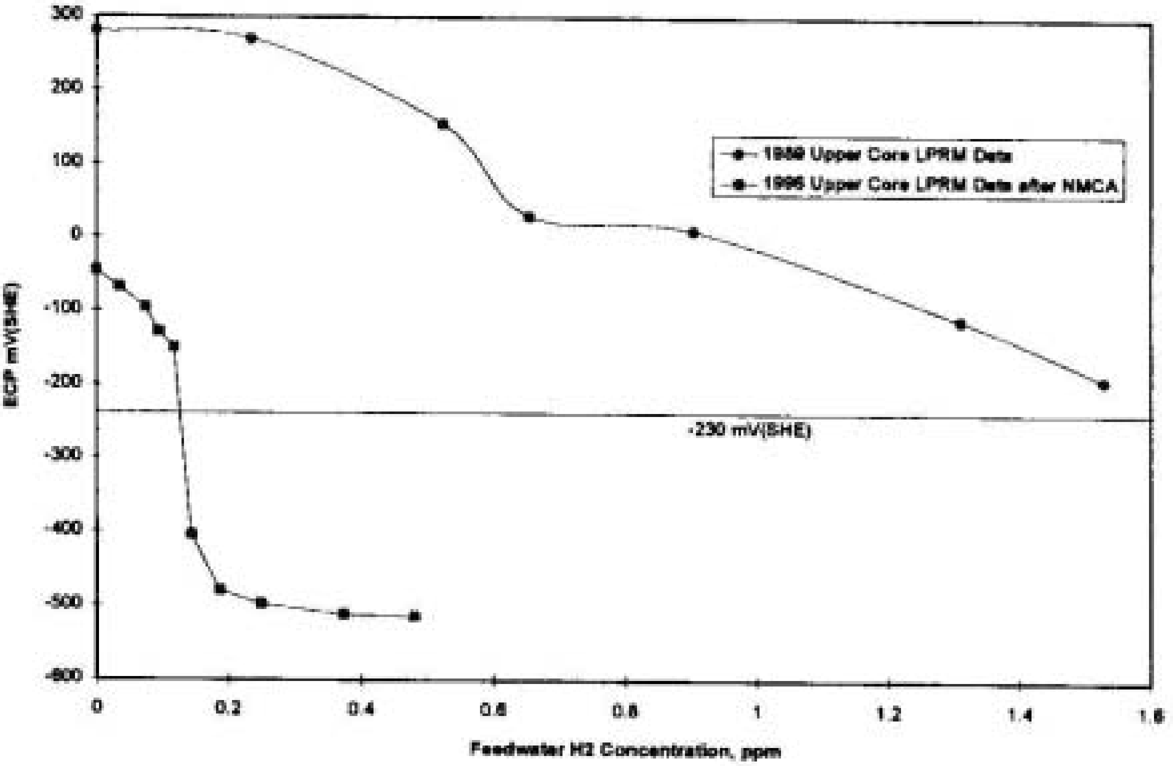
On-line monitoring of activity buildup has been pioneered at the Forsmark BWRs by Ullberg and co-workers, in part within the framework of the WACOL programme. The details are as follows.

Dose-rate measurements and gamma scans are performed each refuelling outage in Forsmark 1–3 and in most other BWRs. Interpretation of the results is made difficult by the low frequency of measurement. In particular, it is often impossible to answer questions such as:

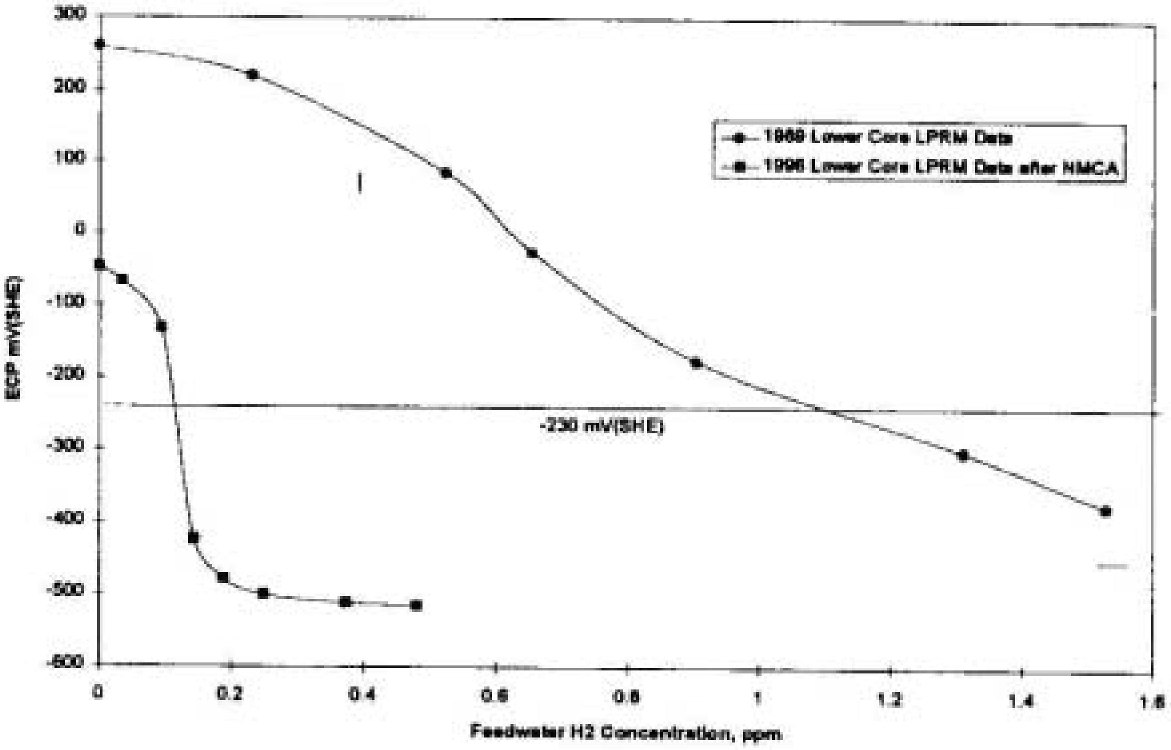
- what caused an increase/decrease of the dose rate?
- when did the increase/decrease occur?
- is the measured increase/decrease real, or is it an artefact?

Problems like these would be well addressed by on-line gamma scans, but for a long time on-line gamma scanning in BWRs was deemed not to be possible because of high background levels from short-lived activity in the reactor water, such as N^{16} with $t_{½} = 7.1$ s.

In 1996 it was found by G. Granath at Ringhals that very good data could be obtained for Co^{60} on a pipe in the RWCU system at some distance from the reactor. The transport time of the reactor water to the measuring point was 1 min, corresponding to eight half-lives for N^{16}.



Duane Arnold Upper Core - ECP Data



Duane Arnold Lower Core - ECP Data

FIG. 26. Results of in-core ECP monitoring at the Duane Arnold BWR before and after application of NMCA treatment (after Hettiarachi et al.).

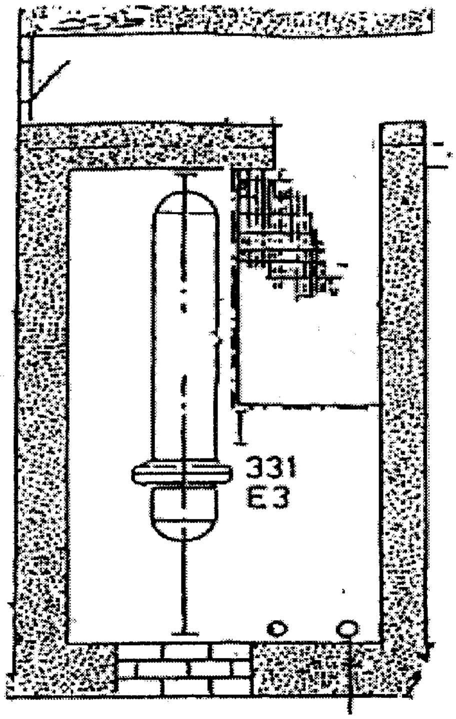


FIG. 27. Location of the OLA measurement system.

Useful data were also obtained for a number of other important nuclides, such as Co^{58}. The same type of on-line activity measurement was implemented in Forsmark 2 in 1998 using a measurement system called OLA (On Line Activity), which consists of a detector, associated electronics and a PC for data collection. The detector is situated in a passage in the reactor building, outside a shielded cell containing a heat exchanger and piping for the RWCU system. The detector monitors the activity on a vertical pipe in the cell through a hole drilled in the concrete wall, see Fig. 27. The pipe contains hot reactor water and the concrete wall acts as radiation shield. In the hole in the wall, there is a collimator and a background sample.

The OLA equipment collects one spectrum every four hours. The only required maintenance is replenishment of liquid nitrogen once a week. However, a considerable amount of work is necessary to process the raw data and to evaluate it. Some results obtained to date are as follows.

To reduce the risk of enhanced spacer shadow corrosion of the fuel cladding, iron has been injected into the feedwater of Forsmark 2 since November 1998. OLA has been used to study the effect of the modified reactor water chemistry on pipe surface activity. Iron injection caused similar, minor reductions of the levels of Co^{58} and Co^{60} and a major reduction of the level of Sb^{124} in the reactor water. In the middle of April 1999, NaOH injection (to be able to determine carry over by Na^{24} measurement) caused a temporary reduction of all three activated corrosion products.

Fig. 28 shows a significant reduction of the surface activity of Co^{58} and minor reduction of Co^{60}. (The figure shows untreated data for Co^{60} and a moving average over five data points for Co^{58}.) Both nuclides are, of course, chemically identical. Therefore, it is reasonable to attribute the different behaviour to the different half lives, 71 days and 5.3 years, respectively.

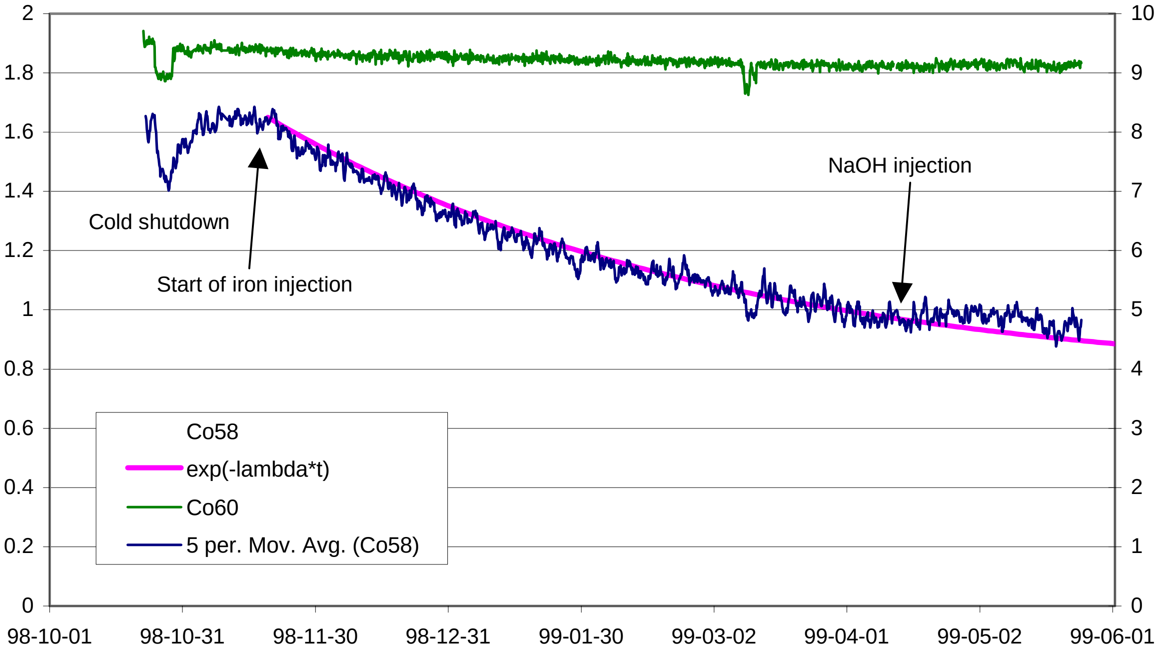


FIG. 28. Surface activity of Co^{60} (upper curve) and Co^{58} (lower curve) on RWCU pipe in Forsmark 2 since start of iron injection.

From previous experience, it is known that the residence time of Co^{60} and Co^{58} on system surfaces in Forsmark 2 is long. It is consequently reasonable to assume that the shortest time constant of the system is given by the half life of Co^{58}. An exponential function with the Co^{58} decay rate in the exponent is seen to fit the Co^{58} data well. From this fit we may predict that Co^{58} will eventually settle at a new level of approx. 45% of the original. The expected reduction of the surface activity is consequently greater than the reduction of the Co^{58} level in the reactor water. This indicates a lower deposition tendency of Co^{58} on system surfaces in Forsmark 2 when iron is injected. The decreasing trend seems to have been temporarily interrupted by the chemistry transient caused by NaOH injection in April 1999. From the chemical identity, we may predict that Co^{60} is also decreasing towards approx. 50% of the level in November 1998. The surface dose rate of the pipe will follow Co^{60}.

The experience at Forsmark enables the following conclusions and recommendations. Activity buildup in nuclear plants must be investigated at a high level of detail. This makes simulation in the laboratory extremely difficult. The data obtained demonstrate that subtle factors such as the balance of corrosion products, may have a profound effect on surface activity. The effect may also differ radically from one activated corrosion product to another. Direct study in-plant is therefore the preferred approach. To be able to relate cause and effect, it is necessary to have plant data of sufficient quality and frequency. It is obvious that the on-line data of Fig. 29 are an enormous improvement over the "once-a-year data". It is noteworthy that the significant advance described here did not require development of a single new component. Only judicious application of existing technology is involved.

A significant amount of manual work is currently required for processing of the raw data and for subsequent evaluation. Automatic evaluation is still some way off, due to limited knowledge, but processing of the raw data should be automated as far possible by further development of the software.

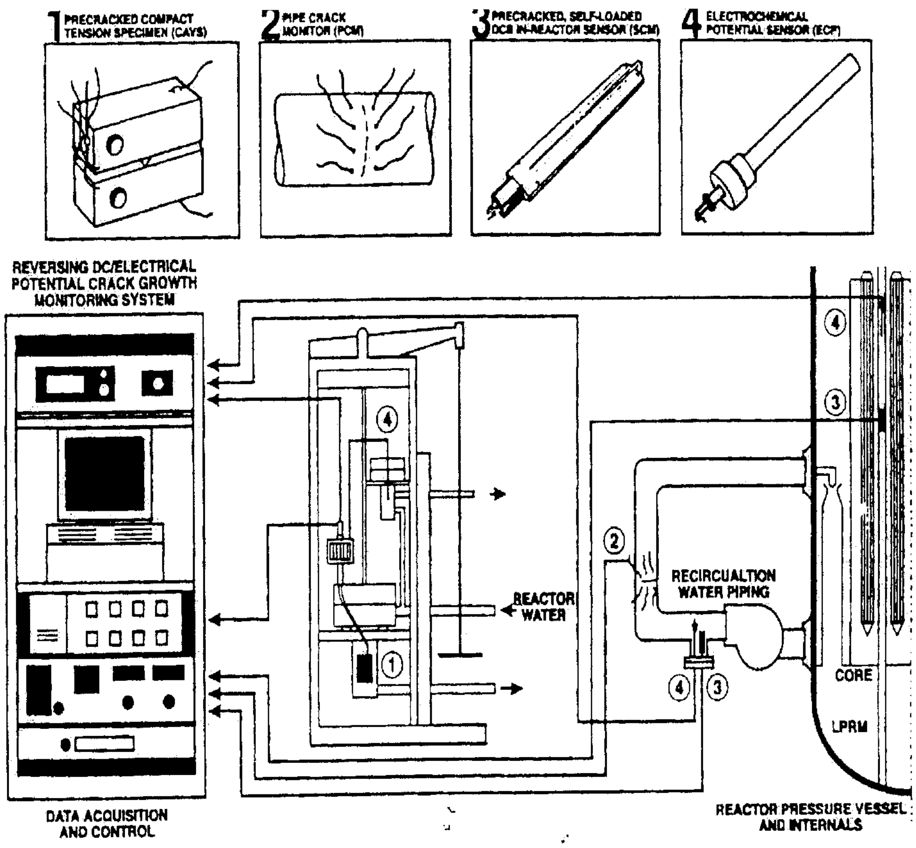


FIG. 29. Schematic diagram of technology in use for real-time monitoring of SCC behaviour in commercial BWRs (after Gordon & Miller).

2.3.4. On-line measurement of crack growth through SCC/IASCC

Given that a major motivation for on-line monitoring in BWRS is to improve the situation with regard to stress corrosion cracking of pressure-retaining and reactor-internal components, it is not surprising that attempts have been made to monitor cracking itself. Despite ongoing efforts (see, e.g. Section 3.1), no method is currently available for in situ detection of crack initiation. However, various methods for on-line monitoring of crack growth through SCC/IASCC have been in use for nearly 15 years. As shown schematically in Fig. 29, this has involved the use of crack depth determination through DC potential-drop on fracture mechanics probes both in external autoclaves (CT specimens) and within a LPRM in-core (DCB specimens), as well as directly by means of measurements on a section of cracked pipe.

Fig. 30 illustrates the type of data obtained from a commercially available so-called "crack-arrest-verification" (CAV) system and shows the effectiveness of HWC in stopping crack growth through IGSCC, even in a thermally sensitised stainless steel. Crack-growth monitors also provide real-time information on the effect of water chemistry transients, as shown in Fig. 31. Under irradiation in-core, the rate of growth is very much higher as a result of IASCC. If such in-core sensors are made of different test materials, the effect of alloy type and condition on IASCC behaviour can be monitored in situ.

Unfortunately, none of the WACOL participants had direct experience of the use of crack-growth-rate monitors in operating BWRs, but further information is available commercially.

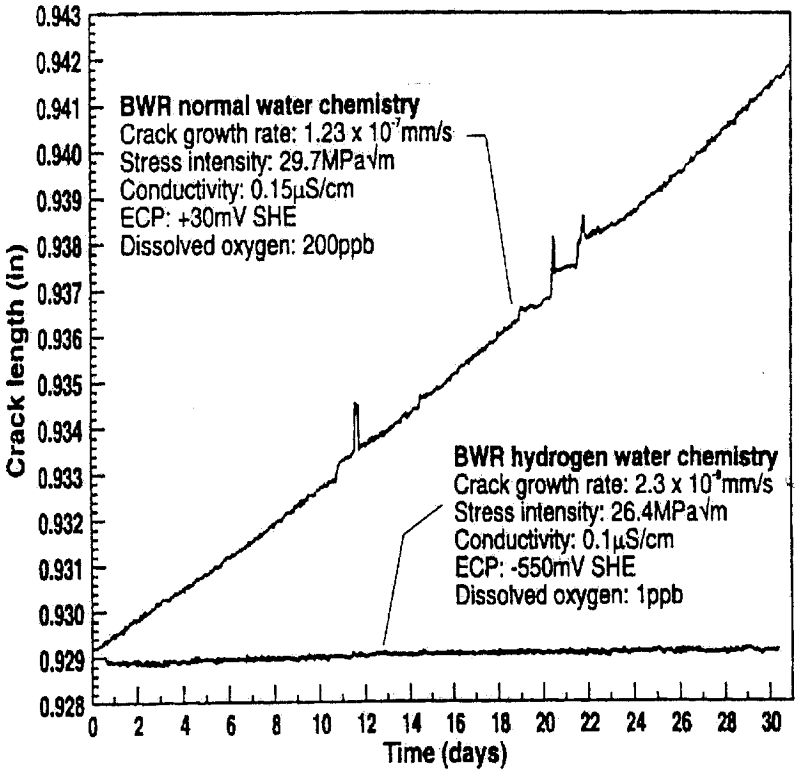


FIG. 30. Example for the effect of HWC in arresting crack growth: on-line monitor in the recirculation piping of a commercial BWR.

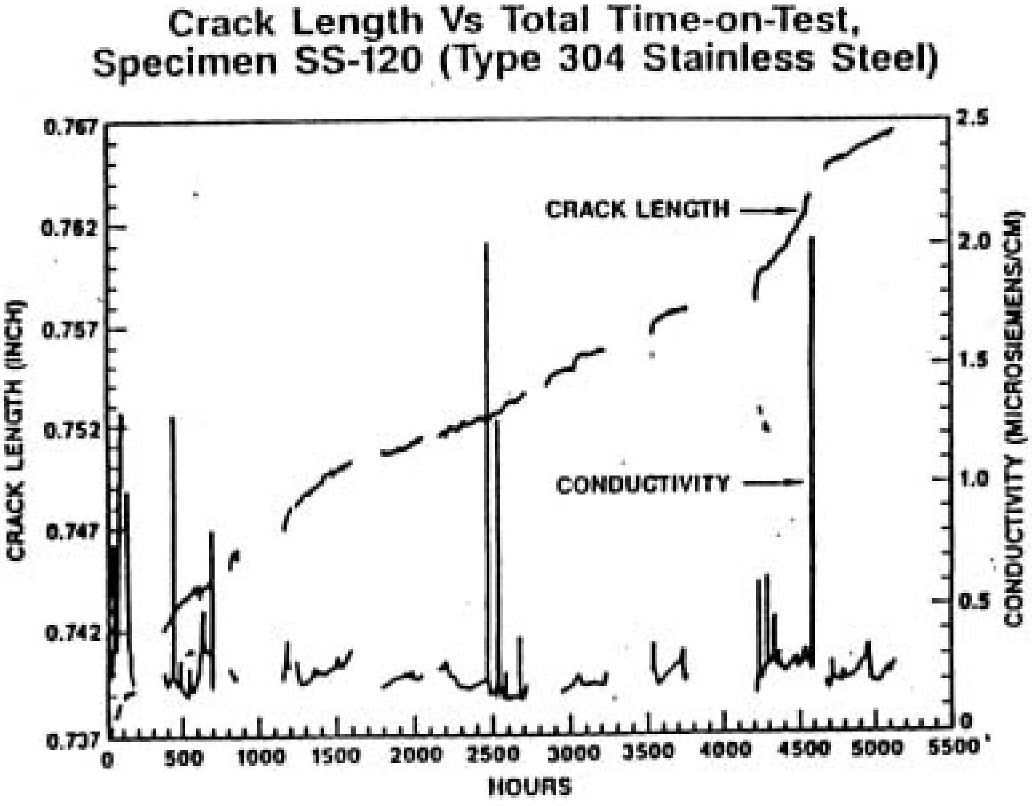


FIG. 31. Effect of conductivity transients on crack growth monitored on-line in a BWR.

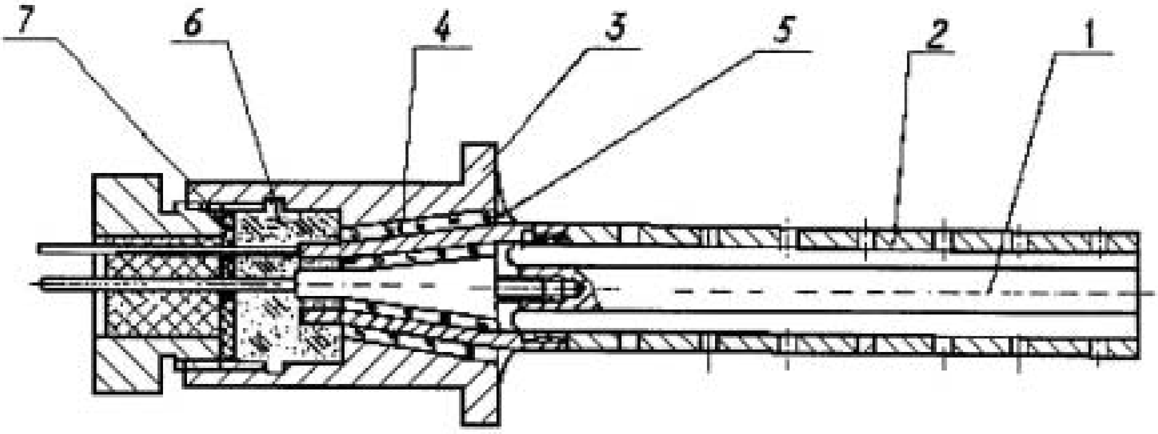


FIG. 32. Double-electrode metal-ceramic sensor [after Kritzky]:

1, 2: electrochemical samples (carbon or stainless steel); 3: stainless steel body; 4: metal to glass-ceramic (sital) seal; 5: ZrO_2 protective layer (plasma sprayed); 6: teflon seal; 7: Al_2O_3 support.

2.3.5. Measurement of corrosion rates by means of polarisation resistance in the feedwater of RBMK reactors

In the St. Petersburg laboratory, a device has been developed, which allows to determine corrosion rates of metals both in pure water and salt solutions. The design in based on measuring the polarisation resistance of a double-electrode flow detector and is meant to work up to 300 ^{0}C (see Fig. 32).

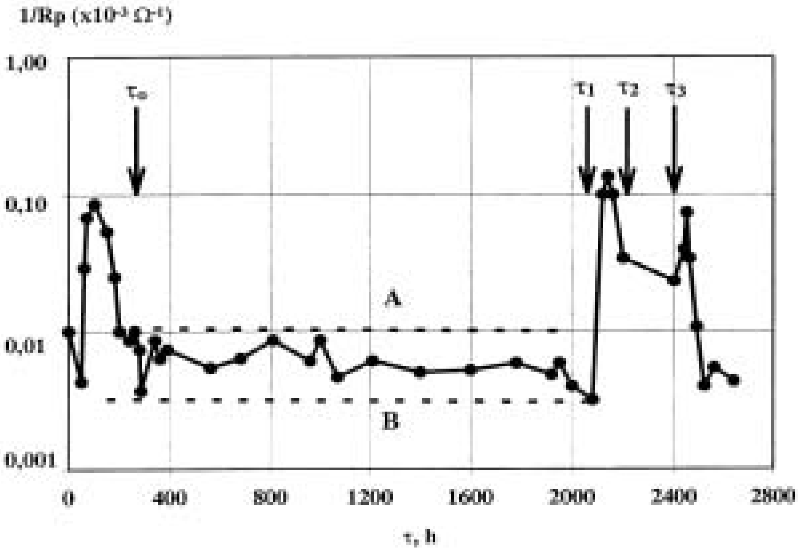
In view of the specific character of polarisation resistance measurements in desalted water, a pulse galvanostatic technique is used, which has been largely modified to reduce the single measurement time up to 10 min. Rp is obtained with frequency pulse technique, which consists of sequential measurements of voltage pulses at applying current pulses of selected frequency to the working electrodes of the detector. This method allows to suppress undesired effects of the polarisation current on the working electrodes. The use of the device for the pipe corrosion control is not restricted by the corrosion system parameters, since all the measurements are performed with the use of direct current of constant amplitude.

The method has a disadvantage, which is in the uncertainty of the constant "B". The constant "B" can be empirically defined as

B =÷mRp/St

where ÷m is sample mass loss, g; S is the sample area; t is time; Rp is the polarisation resistance in the course of the experiment. In practical terms the empirical determination of B allows more reliable calibration of the method. The deviation of the empirical "B" from calculated values may be caused by chemical corrosion which occurs in parallel with the electrochemical process.

The detector is placed on the bypass of a controlled pipe section, and the proportionality constant "B" is calculated after measuring corrosion rates and Rp during the period of the coupon exposure of ℑ500 h. Extended corrosion tests on carbon steel and type × 18H10T (18Cr10Ni1T) stainless steel over 2000 hours have shown that 99,6% correspondence can be achieved between electrochemical corrosion date and conventional weight-change techniques. Testing in the nuclear and heat power plant environments has confirmed the efficient and reliable work of the detector and the electronic system (see Fig. 33).



(τ_0) under normal operation following oxide film stabilisation; (τ_1) after shutdown and start of chemical passivation; (τ_2) during maintenance; (τ_3) at start-up. A, B indicate scatter band during normal reactor operation.

FIG. 33. Corrosion rate (polarisation resistance) of steel versus time in feedwater of an RBMK reactor.

2.4. Research reactors

2.4.1. In situ measurement of potential and dissolved gases

2.4.1.1. Data obtained at the Halden test reactor in Norway

Due to hydrogen addition (HWC) and application of the noble metal chemical addition (NMCA), only fairly low hydrogen concentrations are needed to obtain low enough a corrosion potential of core components during the fuel cycle. However, there are several unknown parameters in the core of BWRs such as water flow rates, radiation flux, dissolved hydrogen and oxygen concentrations, etc. A typical location where it is difficult to know accurately the water chemistry parameters is, for example, a core channel boiling region, where both hydrogen and oxygen are stripped from the liquid to the vapour phase. However, the concentration of hydrogen peroxide can remain high as a result of water radiolysis and therefore increases the ECP of the construction materials in this region. It is possible that neither HWC nor NMCA can provide sufficient decrease in ECP of construction materials simply because of very high oxidant concentrations and difficulty in achieving a stoichiometric excess of hydrogen. As the actual measurement of ECP in in-core location is of primary importance, the reference electrodes used in these measurements must be robust enough to be able to operate in high water flow rates and to sustain strong gamma and neutron fields. The expected service lifetime of these sensors is limited, currently ranging from a few weeks to 1.5 years. Therefore, the common practice has been to install several of these electrodes in the same location. This is not cost effective, but unfortunately, there are no other in-core electrodes currently commercially available. However, development work is going on in several research institutes to come up with a design, which can be used over several fuel cycles [41,42].

In the Halden test reactor, electrode development work has continued for several years along two parallel paths. One project has concentrated on developing suitable cable connectors to be used for the miniaturised in-core Pd reference electrode and other electrochemical sensors. The other project continued to verify and calibrate the in-core Pd reference electrode in an out-of-core test loop. In 1999 some electrodes were installed into an in-core location to obtain information about long-term stability under radiation.

In 1998, an electrically insulating leak tight connector (or seal) that was designed and developed at Halden, was qualified in out-of pile autoclave tests and subsequently installed in an in-pile test assembly for further performance evaluation through 1998 and 1999. In co-operation with VTT, Finland, the seal has also been used in the prototype of the miniaturised in-core palladium (Pd) reference electrodes, which have been tested in out-of-core BWR facilities. The results have shown that such an electrode can produce reliable and stable potentials even under highly oxidising environments, indicating that the shielding around the Pd electrode is good enough for protection against oxidising species present in typical BWR environments. However, the preliminary test results indicate that additional sets of calibration measurements are needed to verify more accurately the potential of the in-core electrode on the standard hydrogen scale. It is internationally agreed that the acceptable accuracy for a reliable electrode should be within + 25 mV during one year of operation.

The goal of the in-core Pd reference electrode development work is to produce a sensor which can be used for several years to give reliable reference values within + 40 mV of the true value. The sensor is expected to operate reliably for long periods, since it does not have any parts that can deteriorate and does not contain any fluids, only solid parts. The first BWR in-core measurements with the miniaturised in-core Pd reference electrode are to be started in mid-2001. This type of sensor has been exposed for 250 days of reactor operation in a PWR test rig without any sign of degradation. At the moment a Halden designed in-core Pt electrode (Pt 3 in Fig. 34) is placed into the BWR test rig together with two GE Reuter Stokes electrodes (Pt 1 and Pt 2 in Fig. 34). These electrodes have been exposed to 250 days of operation at full power and will be used at least for one more cycle of about 100 days. All electrodes correlate nicely to the changes in hydrogen content in the coolant as shown in the figure.

2.4.1.2. Data obtained at the NRI test reactor in the Czech Republic

A test facility for stress corrosion cracking of pressure vessel seals and in-core materials in BWR coolant and radiation condition was installed at the LVR-15 Rez research reactor. The facility involves high-pressure reactor water loop BWR-2 with two testing channels: one with radiation and the second comparative channel without radiation, both enabling 2 (2CT or 1CT) specimen loading. The loop operates at BWR coolant conditions and is equipped with in situ ECP measurement, conductivity and dissolved gases.

The ECP is measured by external Ag/AgCl reference electrodes located in three positions along the loop. BWR water chemistry is achieved by oxygen gas dosing to attain the same oxygen content and ECP as in a commercial reactor. Oxygen is dosed every hour and hydrogen concentration changes as a result of coolant radiolysis. Dependency of the ECP on oxygen concentration between 0.15 and 0.40 ppm at the temperature of 288 C was changed from +70 mV_{SHE} at 0.17 ppm of oxygen to +120 mV_{SHE} at 0.38 ppm at a hydrogen concentration of about 8 ppb.

Summary of ECP dependence on dissolved oxygen concentration over the period 1997 to 2000 is shown in Fig. 35. ECP gives very stable signals in long-term operation and showed good agreement with published data.

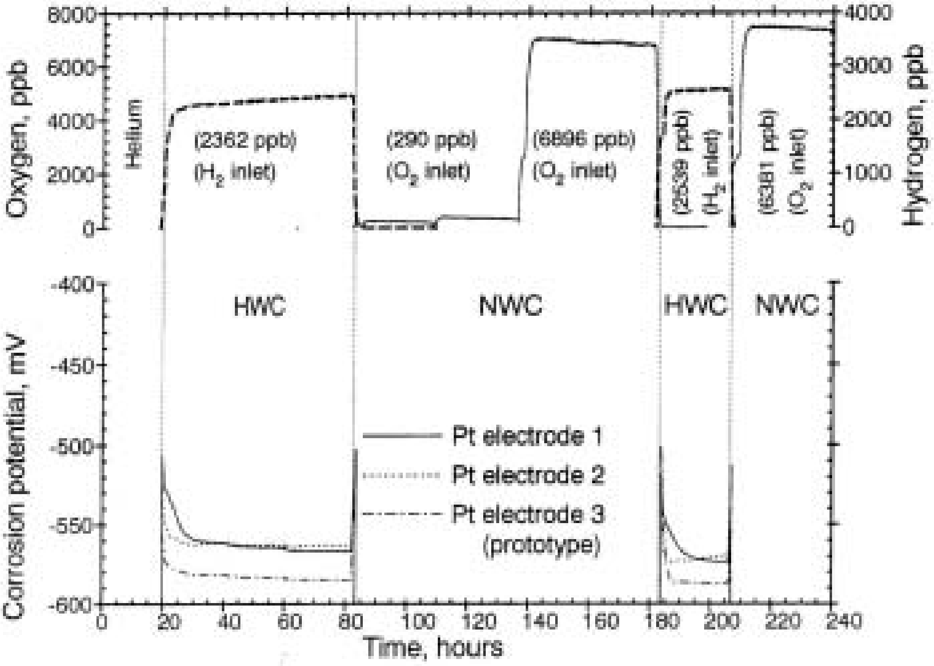


FIG. 34. Response of different types of Pt electrodes to switches in water chemistry in the BWR loop at the Halden reactor.

2.4.1.3. Data obtained at the Studsvik experimental reactor in Sweden

A new test facility for water chemistry and materials research in the Studsvik R2 reactor was put into operation in the mid-Nineties [43]. The facility is called the INCA-loop (IN-Core Assembly) and is especially designed for experiments during well controlled chemical conditions. The radiolysis of aqueous (non-boiling) solutions has been studied as a function of temperature. The neutron/gamma dose rate ratio was about 1.5 and the maximum total dose rate was about 10 w/g. Hydrogen was added in various amounts in order to determine the critical hydrogen concentration above which unacceptable amounts of oxidants would not be present. The effects of radiolysis were also calculated using a computer-based radiolysis model. The model utilises high-temperature G-values and rate constants, updated with recent literature data. However, due to insufficient experimental data, especially on high-temperature rate constants, the calculated results are associated with uncertainties. Thus, the experimental approach has been to start at a low temperature and then to gradually increase the temperature in subsequent experiments. Radiolysis is monitored by means of in-core corrosion potential measurements, using electrodes of the type shown in Fig. 36, and chemical monitoring in the loop outlet and inlet. An example of the type of data obtained is given in Fig. 37.

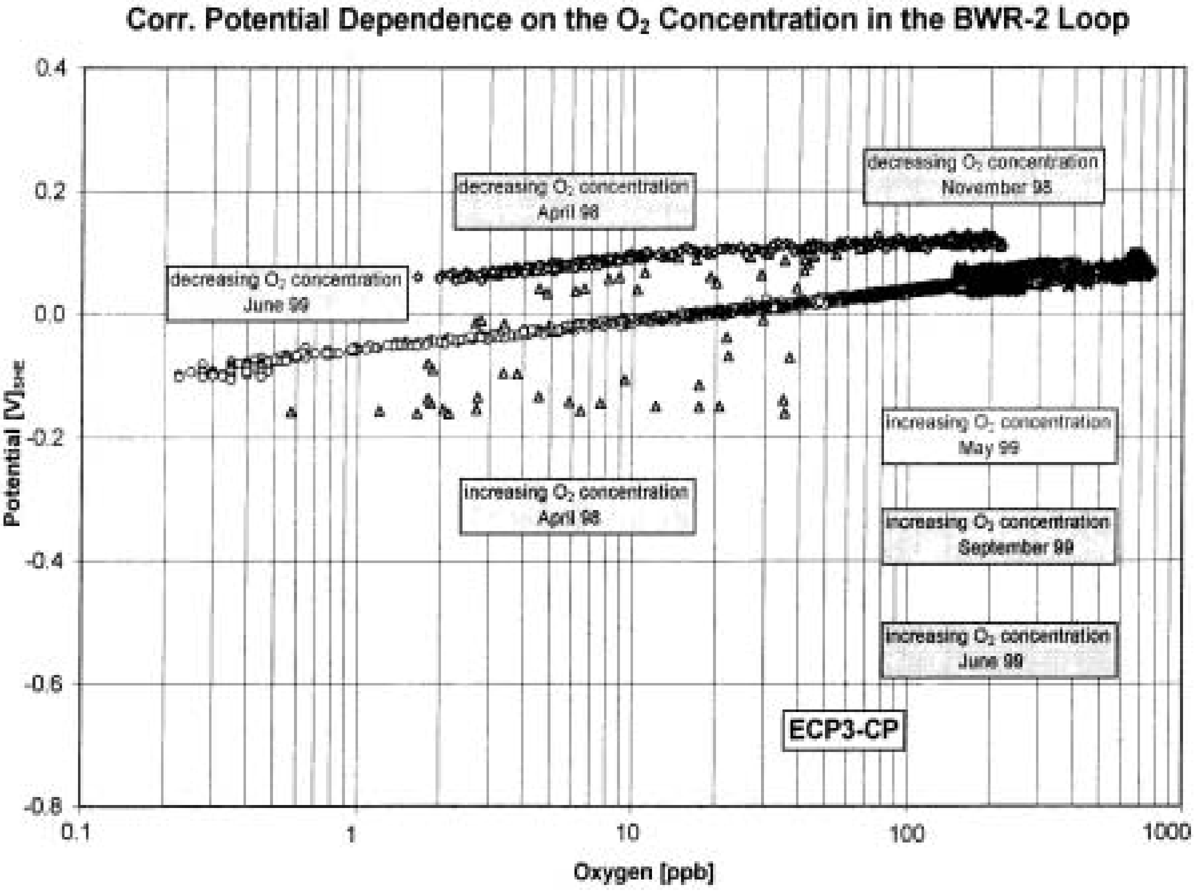


FIG. 35. Compilation of ECP data from a BWR loop at the NRI test reactor.

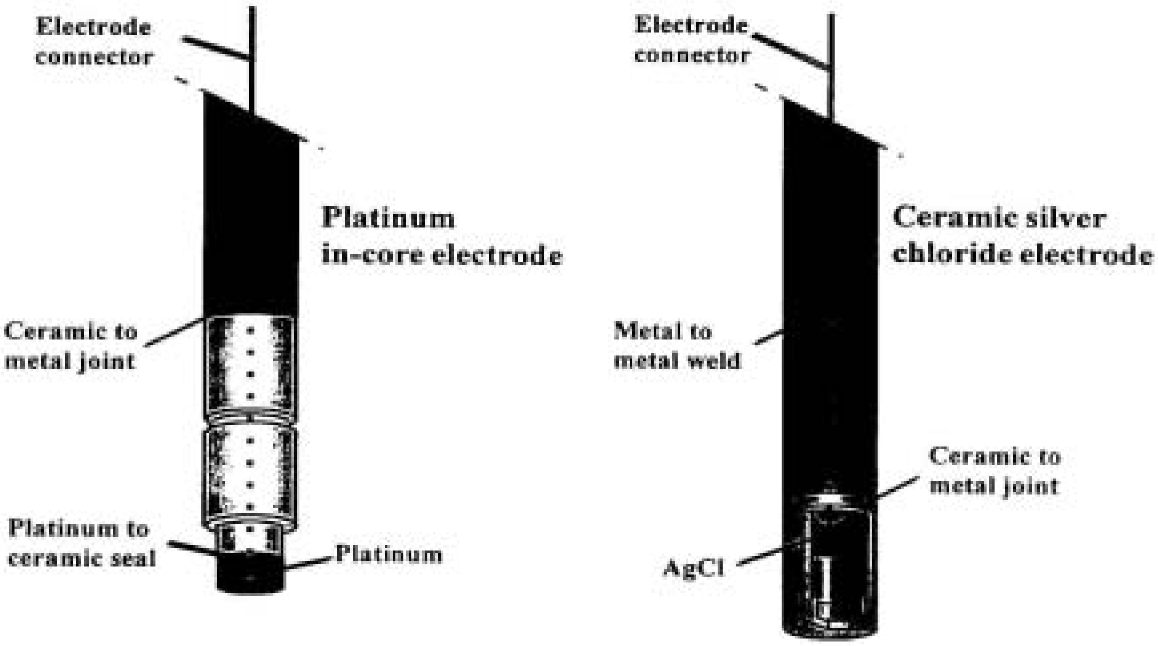


FIG. 36. Schematic drawings of in-core electrodes used at the Studsvik research reactor.

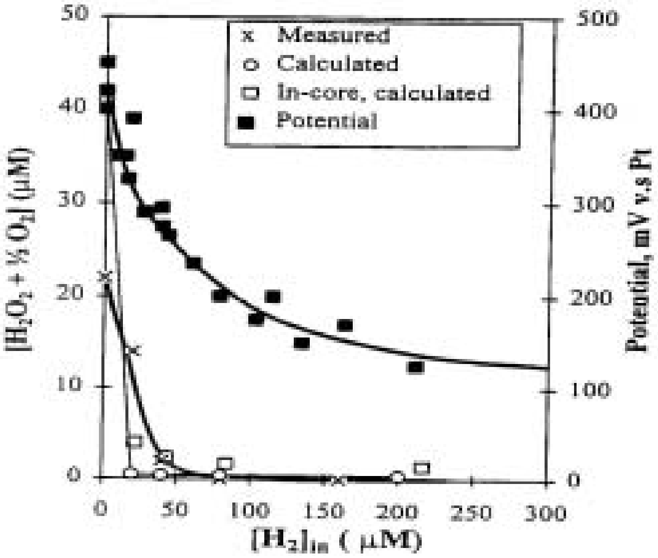


FIG. 37. Example of data obtained in the Studsvik research reactor at 150 °C: oxidant concentration and in-core ECP as a function of inlet hydrogen concentration.

2.4.2. On-line measurement of crack growth through SCC/IASCC

2.4.2.1. Data obtained at the Halden test reactor in Norway

An on-going OECD programme at the Halden reactor to study IGSCC and IASCC uses ¼" CT specimens, prepared with irradiated material inserts which are electron-beam welded into unirradiated carrier material, as shown in Fig. 38 and inserted, together with reference electrodes and thermocouples, into the in-pile BWR channel. The crack length in the individual specimens is measured with the DC potential-drop technique and an example of the on-line data obtained is shown in Fig. 39. Even under irradiation, HWC appears here to be successful in arresting earlier crack growth in a specimen of 304 stainless steel. Further details of the current status of the programme are given in [44].

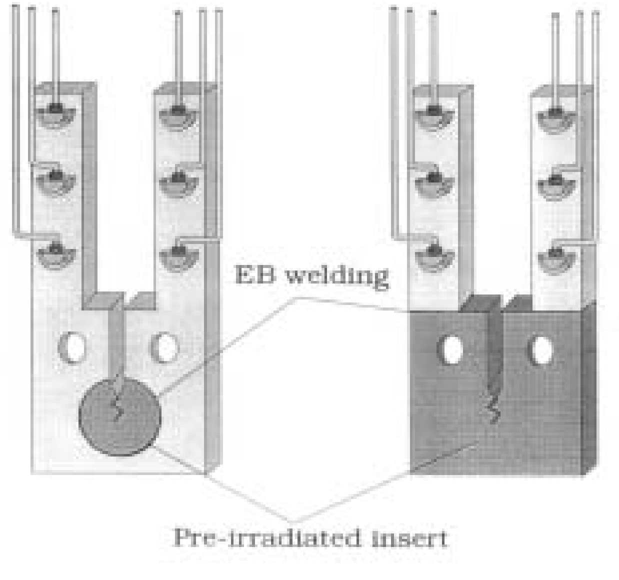


FIG. 38. Arrangement for studying IGSCC/IASCC at the Halden test reactor using miniature CT specimens instrumented by potential drop.

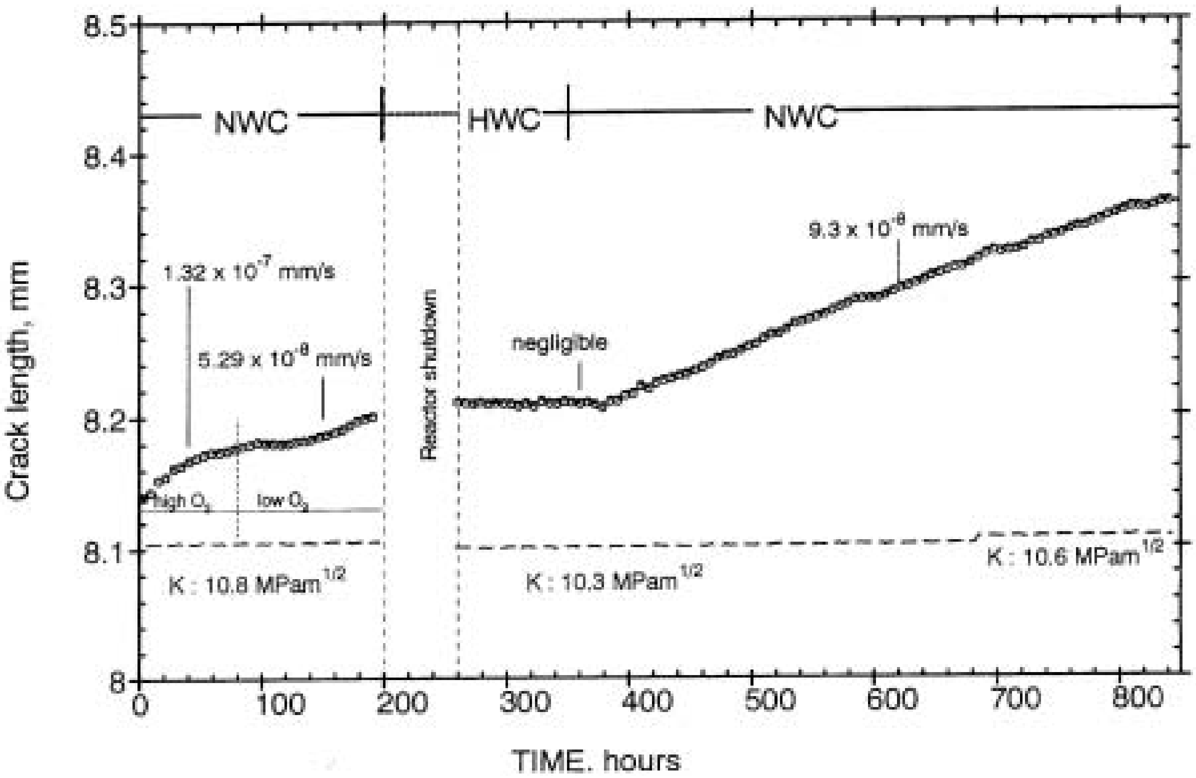


FIG. 39. Example of the on-line CGR data obtained in the BWR loop at the Halden test reactor.

2.4.2.2. Data obtained at the NRI test reactor in the Czech Republic

Stress corrosion cracking (SCC) of the low-alloy steel 22NiMoCr37 is being evaluated with the goal of determining crack growth rates in ferritic steel under conditions simulating closely the conditions of a BWR RPV under operation. An irradiation rig has been built for pre-irradiation of specimens to a fluence of 1.5 × 10^{18} n/cm^2 (E>1MeV). During the experiment, the specimens are loaded by cyclic and constant load. Crack growth is monitored by means of potential drop measurement and COD.

The principle test parameters monitored on line during the experiment are: load, COD, crack length, temperature, pressure, corrosion potential, oxygen and hydrogen content and, discontinuously, also hydrogen peroxide content.

Crack lengths are monitored by the reversed direct current potential drop technique (RDCPD). Two pairs of output probes are used in order to back up the measurement and to receive more precise data from each specimen. The resolution limit of RDCPD is better than 50 μm of crack length. Every specimen is also equipped with a COD sensor. The first results obtained from the in-pile and out-of-pile preliminary tests of unirradiated specimens are presented in [45] including detailed fractographic analysis of crack growth.

3. ADDITIONAL, SPECIFIC CONTRIBUTIONS TO THE DEVELOPMENT AND QUALIFICATION OF ON-LINE MONITORING TECHNIQUES BY WACOL PROGRAMME PARTICIPANTS

Many of the contributions provided by participants in the WACOL programme concerned the laboratory development and qualification of new methods for on-line monitoring, as listed in Annex 1 and indicated by the programme meetings described in Annexes 2, 3. In the following these are summarised, whereby both the order of the techniques considered, and the order of contributions to a particular technique, reflect the alphabetical order of the countries involved in the programme.

3.1. In situ detection of SCC crack initiation and growth

3.1.1. Work in progress at SCK/CEN in Belgium

Laboratory studies were recently started on the use of electrochemical noise (EN) to detect crack initiation under PWR conditions. The first probe design involved a pressurised tube surrounded by a platinum foil electrode (see Fig. 40, left), but this proved to have too high a capacitance. A modified design (see Fig. 40, right) was successfully used under simulated PWR conditions and examples of the initial results obtained are shown in Fig. 41. The ECP of stainless steel is not stress dependent below the yield strength, but plastic deformation can be detected both through a shift in DC potential and a reduction in the high-frequency component of the noise. Following development of a PWR-compatible electrical feedthrough, work is ongoing to test the technique in the Belgian BR2 research reactor.

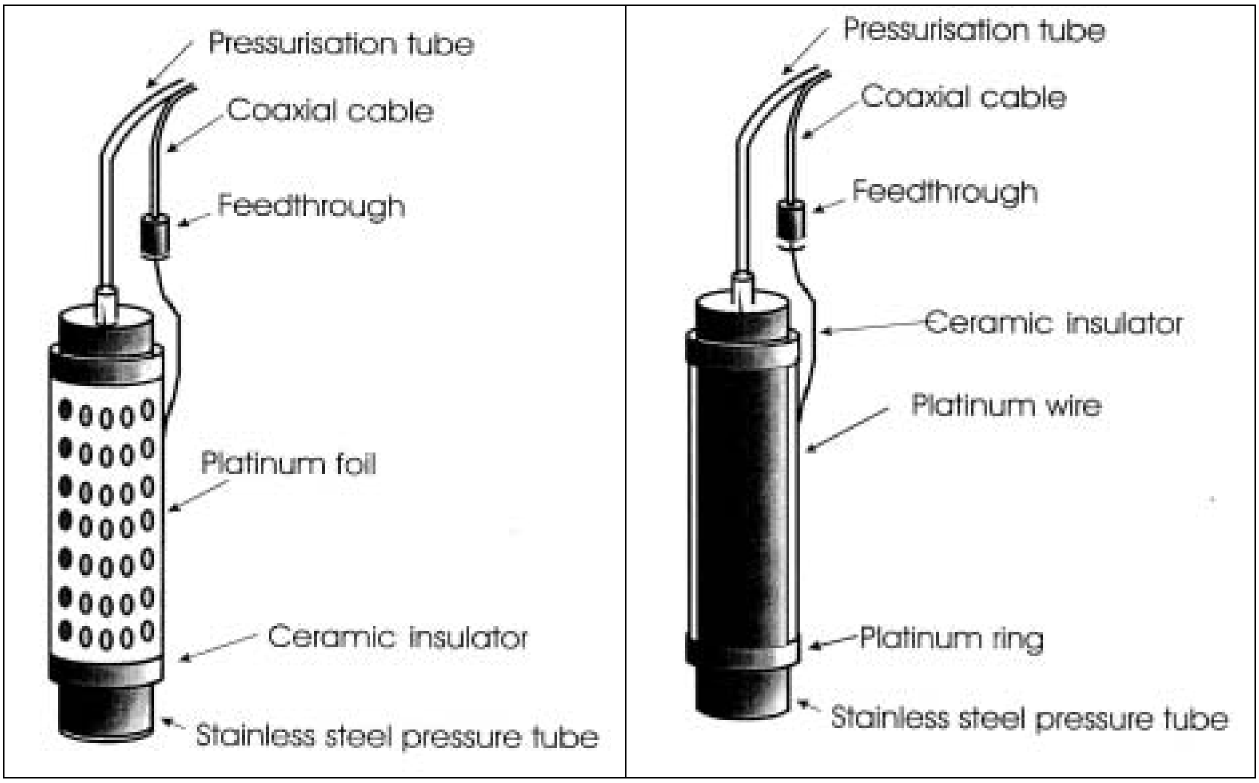


FIG. 40. First and second designs of the SCK-CEN electrochemical noise (EN) sensor for detecting crack initiation.

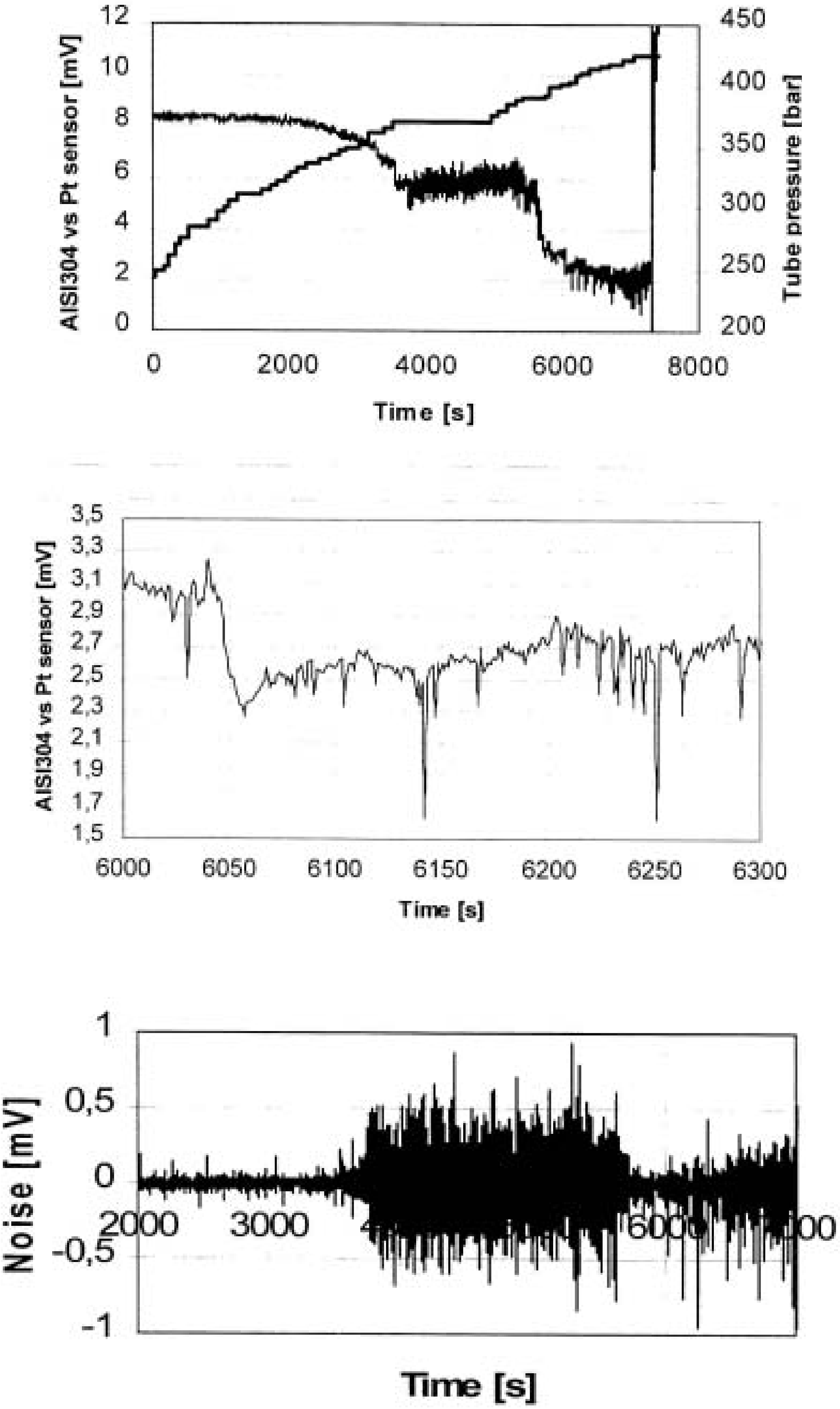


FIG. 41. Examples of initial EN results obtained under simulated PWR conditions.

3.1.2. Laboratory work at the China Institute of Atomic Energy

In the context of an Agency Research Contract, preliminary work has been carried out at the China Institute of Atomic Energy in Beijing to assess the use of EN techniques. Studies of pitting corrosion in room temperature chloride solutions and of SCC in boiling magnesium chloride at 143 °C were used to build up monitoring expertise.

3.1.3. Electrochemical studies at EdF in France

The electrochemical behaviour of Alloy 600 & 690 at 320–360 °C has been studied in laboratory autoclaves [46]. The first study aimed to progress on stress corrosion cracking (SCC) mechanisms understanding. The strategy was to assess if the electrochemical behaviour and repassivation kinetic of Alloy 600 & 690, in primary water at 320–360°C, were compatible with the predictions of different SCC models. The mechanisms assessed were Slip Step Dissolution model, Hydrogen Embrittlement, Internal Oxidation model and Corrosion Enhanced Plasticity Model. EdF studied the variation of electrochemical response as a function of H_2 overpressure and chromium content, using ECP measurements, I-E curves with ohmic drop correction (see Fig. 42) and measure of current responses during jumps of potential and Slow Strain Rate tests at various controlled potentials. The reference electrodes were external pressure-balanced electrodes.

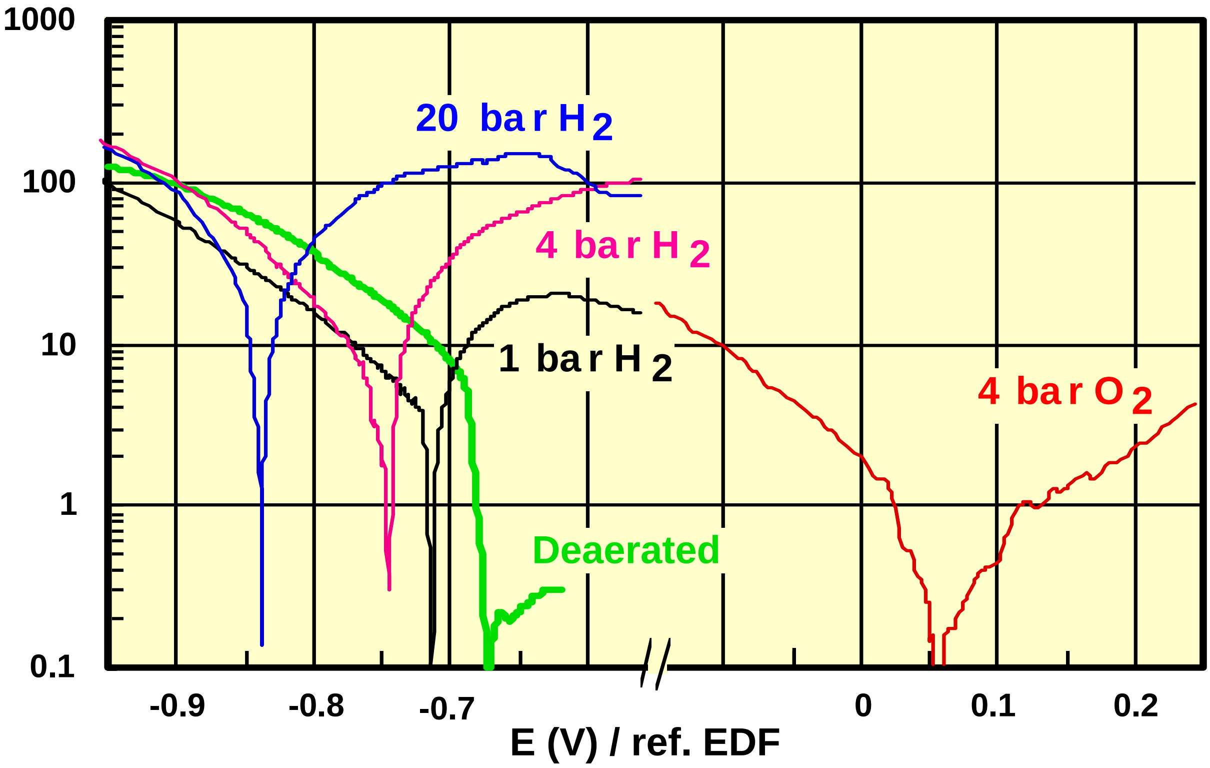


FIG. 42. I-E curves obtained at 360 °C in primary water on alloy 600, with various hydrogen or oxygen overpressures.

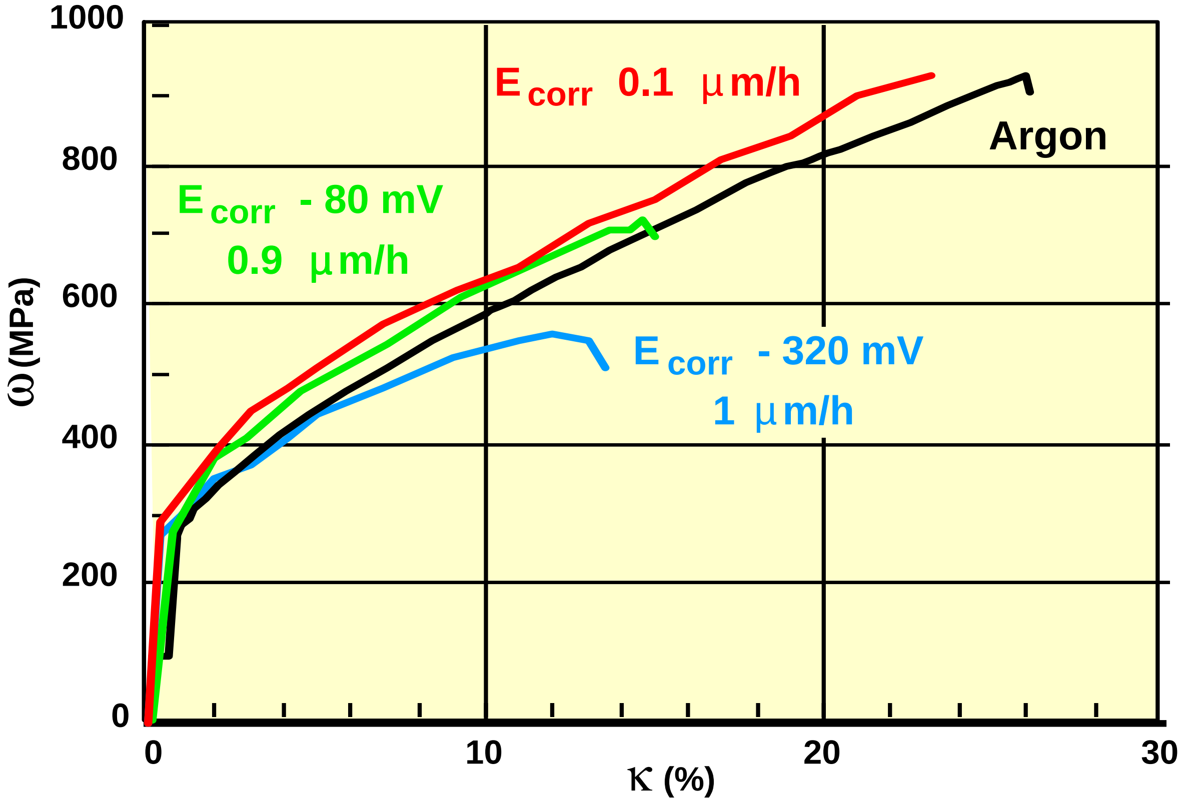


FIG. 43. Effect of cathodic potential on SCC of alloy 600 in 360°C primary water.

The major results were:

- a strong enhancement of SCC at cathodic potentials (see Fig. 43),
- very little effect of hydrogen overpressure on film stability or repassivation kinetics,
- no clear correlation between repassivation kinetics and SCC behaviour when the H overpressure or chromium content vary.

These results and others SCC tests and metallurgical examinations led to the conclusion that the dissolution model, the global hydrogen embrittlement model or the internal oxidation model were not able alone to explain the crack propagation. The corrosion enhanced plasticity model, a quite new model which is based on local interactions between corrosion, hydrogen and deformation, is more suitable [47,48].

This work was the first one at EDF with such a wide application of HT electrochemical monitoring. Such data acquisition and control were found to be very useful techniques. They were the only way to get the right information needed in this study. It would have been very difficult to advance in alloy 600 SCC mechanisms understanding without it. However, they need highly qualified staff for quality control and interpretation and are time consuming.

These techniques are now currently applied, when needed, in some of EdF's laboratory studies.

3.1.4. Use of electrochemical noise to detect SCC initiation in simulated BWR environments at CML (UK) and GE CRD (USA)

The objective of this research [49,50] was to investigate the use of electrochemical noise (EN) for detecting stress corrosion crack (SCC) initiation in boiling water reactor (BWR) environments. Initial experiments examined the response of thermally sensitised AISI Type 304 stainless steel (SS) in slow strain-rate tensile (SSRT) tests in oxygenated, 288°C/10.4 MPa water, a laboratory simulation of the normal BWR environment. This combination of specimen condition and geometry assured abundant nucleation of intergranular cracks, with controllable propagation and arrest via changes in either loading or environment. In the latter case, addition of gaseous hydrogen was used to simulate BWR hydrogen water chemistry (HWC) and lower the specimen potential into a non-cracking region.

The SSRT tests provided an ideal platform for optimising the electrochemical cell configuration, while establishing the nature of electrochemical potential and current noise (EPN and ECN) responses to crack initiation, propagation and arrest. The standard deviation of electrochemical potential, a measure of EPN amplitude, proved to be the best indicator of SCC initiation, as shown by the example in Fig. 44. However, the degree of correlation depended upon both the periodicity of the calculation and the electrode configuration. Further development work is expected to lead to a useful, in-plant sensor for real-time detection of SCC activity.

3.1.5. Development and qualification of electrochemical noise methods at PSU in the USA

Electrochemical noise corrosion sensors have been developed at Penn State University (PSU) and tested both in laboratory autoclaves and in various non-nuclear installations [51–53]. An example of the data obtained is shown in Fig. 45. They are considered to be effective in situ monitors, which provide a continuous measure of corrosion activity, but not corrosion rate.

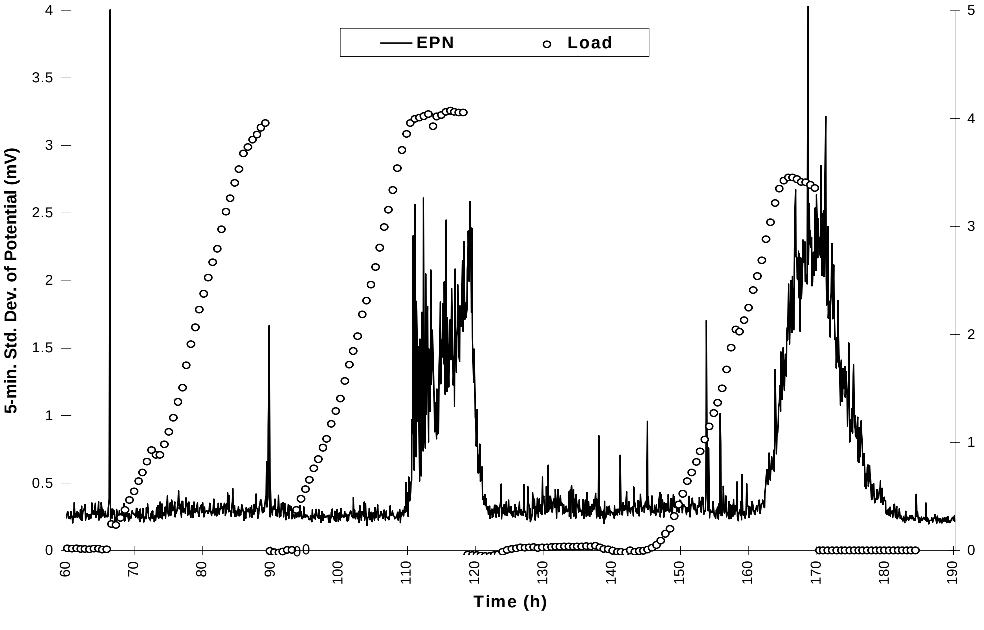


FIG. 44. Notched SSRT specimen, NWC: effect of periodic unloading on 5-minute standard deviation of corrosion potential.

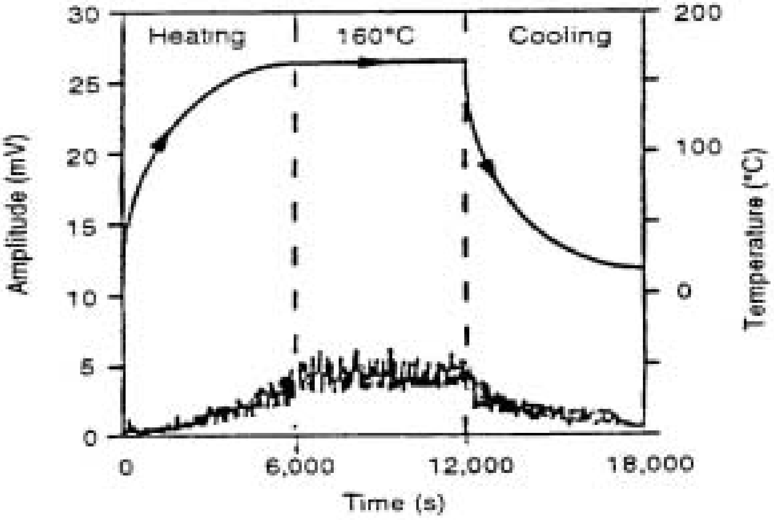


FIG. 45. Evolution of electrochemical noise induced by corrosion of carbon steel during a heating-cooling cycle.

3.2. Electrochemical measurement of dissolved gases

3.2.1. Development of amperometric microelectrodes at AECL in Canada

In contrast to conventional amperometric electrodes, amperometric microelectrodes exhibit certain unique characteristics that make them well suited as sensors in the dilute aqueous electrolytes. The heat transport systems (HTSs) of thermal power plants employ such electrolytes as coolants at elevated temperatures and pressures. Thus, amperometric microelectrodes are in principle well suited for the in situ monitoring of HTS coolant chemistry. The work reported in the WACOL programme referred to the experimental evaluation of a platinum microdisc electrode for one such application. An example of the type of data obtained is shown in Fig. 46. The results of these experiments demonstrate that microelectrodes can be used to monitor the concentration of dissolved oxygen in simulated HTS coolants at 150°C in the concentration range 10–1000 ppb [54].

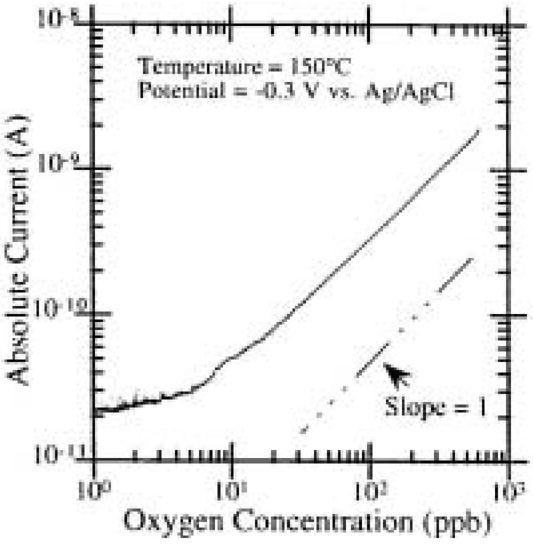


FIG. 46. Dependence of current generated by a platinum disc microelectrode upon dissolved oxygen concentration in an aqueous electrolyte at 150°C.

Measurements of open-circuit potential, commonly referred to as ECP, are currently being made from platinum electrodes installed in the HTSs of number of nuclear reactors. The availability of platinum microelectrodes capable of functioning under HTS conditions offers the prospect of replacing the conventional electrodes with microelectrodes. Such a strategy would allow the use of a variety of more advanced electrochemical techniques that involve the polarisation of the electrode from its open-circuit potential through the external application of potential. Thus, the utility of electrochemical monitors could be significantly enhanced for minimal additional expense while maintaining probe and system reliability.

3.2.2. Work carried out at VTT in Finland

Hydrogen fugacity can have a pronounced effect on many corrosion phenomena. Typically dissolved H_2 content in the primary is kept between 25–40 cc/kg H_2O, mainly in order to minimise general corrosion and to maintain reducing conditions in the core area. However, it has been shown that hydrogen influences the initiation and propagation of primary water stress corrosion cracking (PWSCC) e.g. of Alloy 600. If a threshold hydrogen content is found for this corrosion process to occur, there might be a need to be able to control the high temperature H_2 fugacity more accurately at high temperature.

Test experiments were performed to measure concentration of dissolved hydrogen in the primary circuit at the Loviisa WWER in Finland. These measurements were carried out using a pH_T — Pt electrode system. The basic design of the used yttrium-stabilised zirconia pH_T sensor is shown in Fig. 47. The operation of this measurement idea was verified at VTT re-circulation systems. At the same test a Pd–Ag tube electrode was used to follow the changes in hydrogen content in the high temperature water. Both systems followed the fluctuations in hydrogen concentration which were due to slow diffusion of hydrogen from the make-up water tank of the re-circulation loop (see Fig. 47). These changes were also confirmed by room temperature measurements with an Orbisphere hydrogen analyser. Both sensors reacted similarly to changes in hydrogen concentration. The differences in the absolute values shown in Fig. 48 result from the higher measurement temperature (320°C) for the Pd–Ag electrode compared with the pH_T sensor, which operated at 295°C.

3.2.3. Feasibility study on development of an oxygen sensor at Siemens in Germany

The main motivation for development of an in situ, on-line sensor for measurement of the concentration of oxygen in high-temperature water was to obtain additional and complementary information to corrosion and redox potential measurements. The development target is an integrated sensor device for on-line measurement of redox and corrosion potentials and oxygen. Moreover, an appropriate modification of the oxygen sensor may enable additional measurement of hydrogen peroxide.

The oxygen sensor is a spin-off of a device developed at Siemens for medical applications. The sensor is based on an electrode material which adsorbs oxygen selectively. The adsorbed oxygen can be reduced electrochemically either by means of a two or three electrode arrangement. The reference electrode used for the sensor device is the external Ag/AgCl-electrode. Exposure of the electrode to water at temperatures up to 350°C over time periods of weeks showed no degradation of the electrochemical properties of the material.

The adaptation of the electronic equipment for measurements in water of extremely low conductivity and the optimisation of the electrode arrangement in he device had to be carried out in iterative steps. Test results obtained with the optimised sensor and electronic equipment are plotted in Fig. 49. The test was carried out at 275°C with water with a conductivity at room temperature of 1.4 µS/cm, adjusted by addition of potassium sulphate. The test confirmed that the prototype is principally suited for the given purpose.

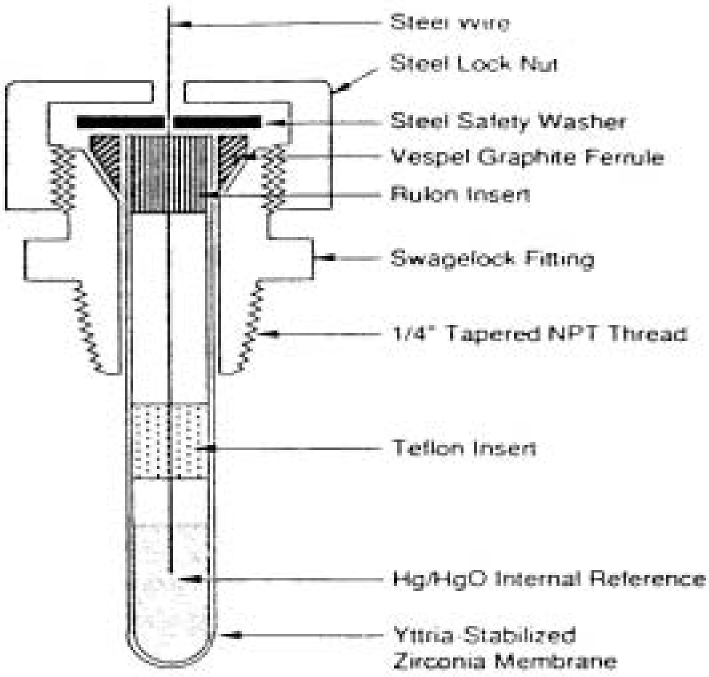


FIG. 47. Typical design of an yttrium-stabilised zirconia pH$_T$ sensor.

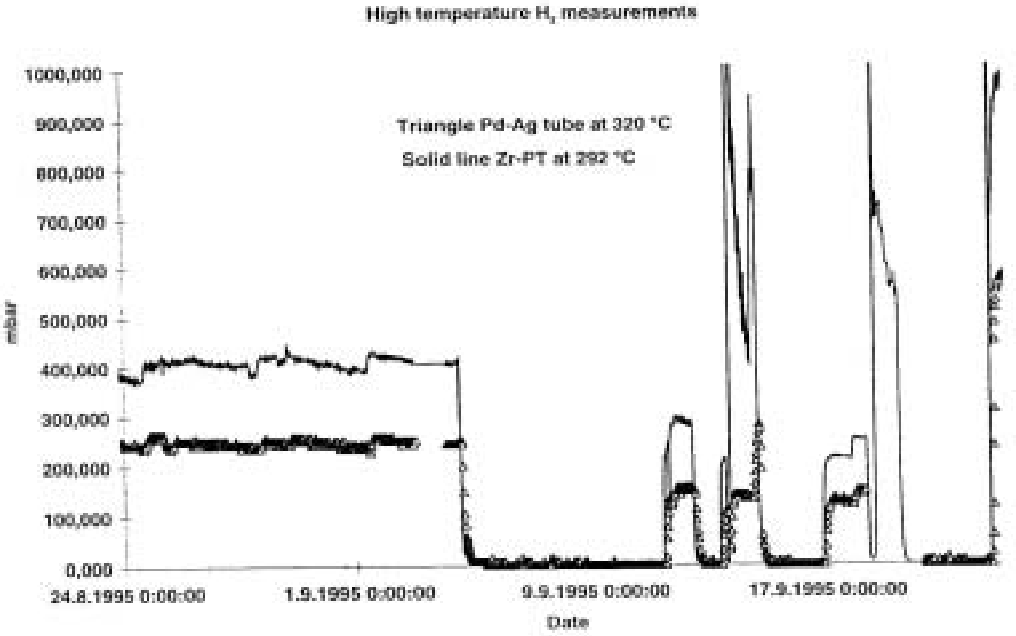


FIG. 48. Comparison of measurements of dissolved hydrogen in the primary circuit of a Finnish WWER made with a pH$_T$ sensor and a Pd-Ag membrane sensor.

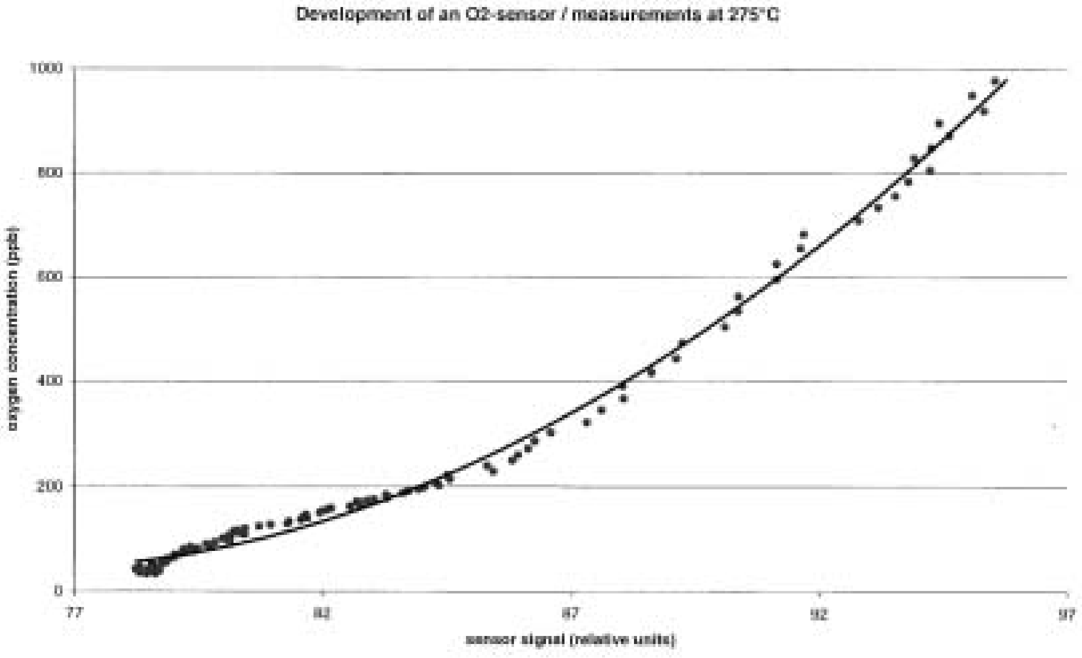


FIG. 49. Preliminary data obtained during development of a new oxygen sensor.

Future work must be directed at the design, calibration and qualification of an integrated oxygen plus redox and corrosion potential sensor for field application.

3.2.4. Development and qualification of H_2/O_2 sensors at PSU in the USA

Extensive laboratory work has been carried out at Penn State University on measurement of dissolved gases at high temperature in the course of development of a combination sensor (autocorrected for the pH of the solution) capable of measuring oxygen, hydrogen and redox potential simultaneously (see Fig. 50). The sensor is very resistant to corrosion through the use of yttrium-stabilised zirconia and platinum as constructional materials. The measurement accuracy is said to be 10 ppb within a temperature range of 25 to 450°C (for H_2) and 25 to 600°C (for O_2). Trials have been performed in various non-nuclear installations, including fossil power plants.

3.2.5. Monoblock of H2O/O2 sensors for on-line monitoring systems (VNIPIET, Russia)

Fig. 51 presents the scheme of monoblock-type of H_2 and O_2 sensors for on-line measurements. A dissolved oxygen (DO) and hydrogen (DH) meter is designed for continuous monitoring of these substances in the primary circuit coolant at excessive pressure of 0.5–1.0 Mpa that precludes gassing and provides representative sampling. The DO and DH meter consists of a flow-through chamber and membrane ommetric cells combined in a single SS block. Specifications of the meter with regard to hydrogen and oxygen are given in Tables 5 and 6, respectively.

Range switching is automatic on attaining 1,999 ppm at measured concentration increase and on attaining 1,00 ppm at concentration decrease.

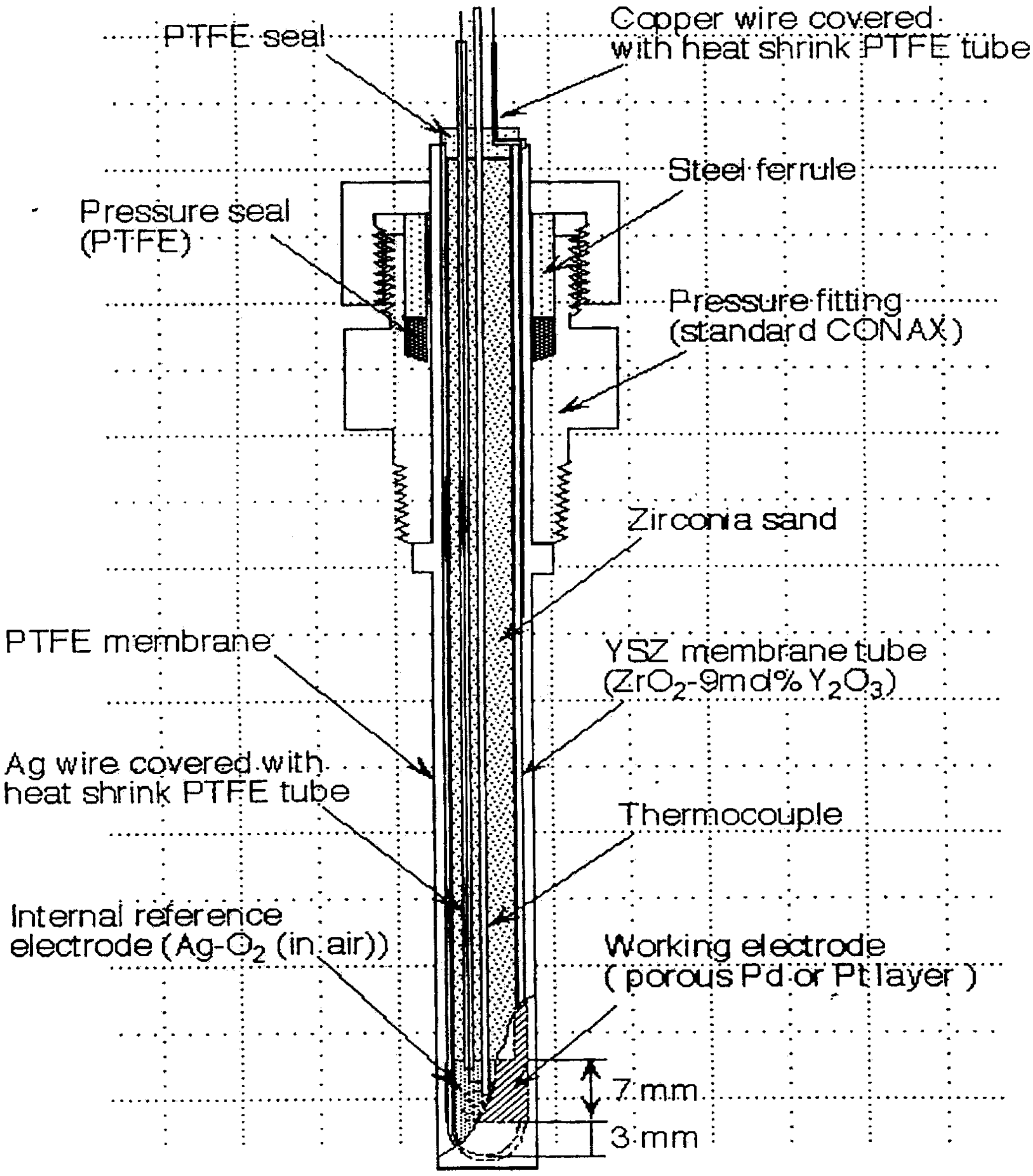


FIG. 50. Combination sensor developed at Penn State University for HAT measurement of dissolved gases and redox potential.

Table 5. Specification of the meter with regard to hydrogen

Range, ppm	Resolution, ppm	Acceptable basic error,% (analog display)
0–1,999	0,001	5
0–19,99	0,01	5

Table 6. Specification of the meter with regard to oxygen

Range, ppb	Resolution, ppb	Acceptable basic error,% (digital display)
1	2	3
0–19,9	0,1	± 10
0–199,9	0,1	± 5
0–1999	1	± 5
0–19,99	0,1	± 10

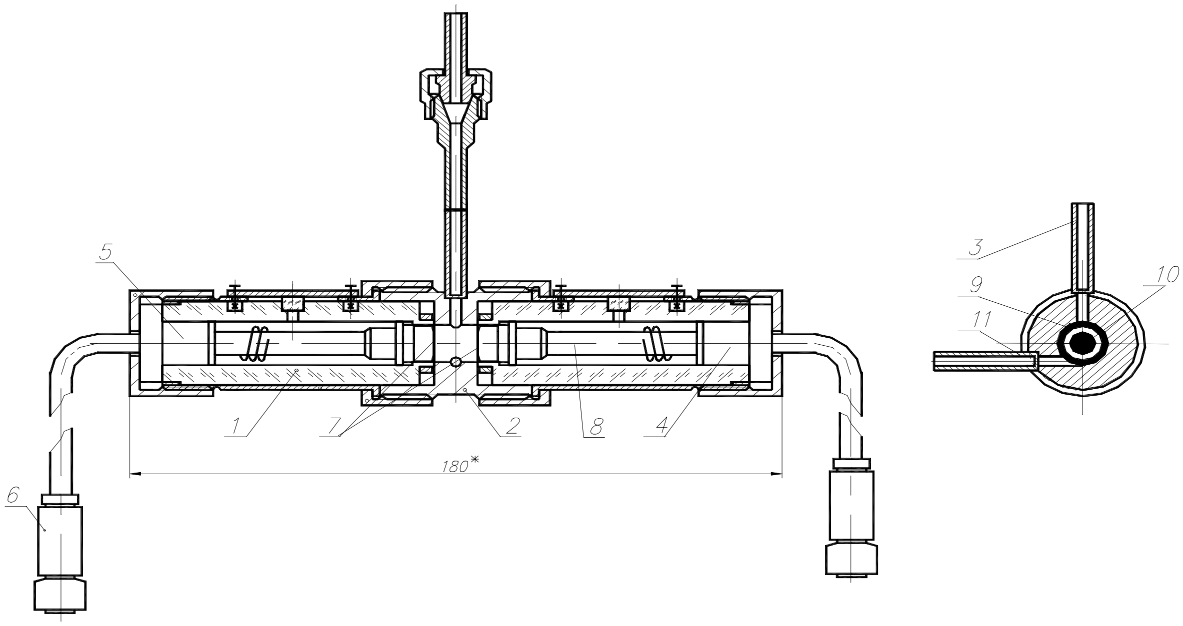


FIG. 51. Scheme of monoblock-type of H_2 and O_2 sensors for on-line measurements: 1: body of kettle, 2: flowing canal, 3: inlet tube, 4: O_2 –sensor, 5: H_2 –sensor,6: electric connector, 7: membranes, 8: reference-electrode, 9: protective electrode, 10: indicator electrode. 11: outlet tube.

Automatic temperature compensation is from 20 to 40°C. The complementary error from temperature measurement in a given range does not exceed the basic error. Response time for 95% accuracy is less than 3 minutes. Readiness time after prolonged de-energing of the cell is less than 2 hours. The temperature and pressure ranges of analyzed medium are 20–50°C. The DH measurement concept is based on the use of a membrane ommetric cell that presents a system indicating and an auxiliary electrodes separated from measured medium by a gas-tight membrane. EMF from an external power supply is applied between the electrodes.

Hydrogen diffuses through the membrane from the solution to the measuring electrode and is oxidized on it. The current in the measuring electrode circuit (I) (limiting diffusion current) is proportional to the DH (DO) concentration in the measured medium (C):

$$\mathbf{I=Io+S\cdot C}$$

The proportionality constant (S) is determined by calibrating the hydrogen (oxygen) electrode against solutions with the known DH (DO) concentrations prepared by water electrolysis technique. The zero signal of the cell (I) is set at cutting the measured medium flow through the chamber and is compensated. The protective electrode is meant for the decrease and stabilization of the zero signals. The results of metrological testing are presented at Fig. 52. The accuracy of measure at different ranges of concentration are variable, but not worse than 5–10%. This level of accuracy is more than sufficient for any NPP's applications in on-line monitoring systems. The monobloc of H_2 and O_2 sensors was install in the sampling loop.

3.3. In situ measurement of high-temperature conductivity

In addition to the following short reports, the reader is also referred to Sections 3.10.

3.3.1. Laboratory work at the China Institute of Atomic Energy

Laboratory work has been carried out under an Agency research contract to develop methods for on-line monitoring of aqueous conductivity. The initial approach involved a classical, parallel-plate cell and was tested at temperatures up to 90 °C. Later work concentrated upon the use of electrochemical coulostatic measurements, since these are rapid and do not involve applying a signal to the electrodes. The method is considered suitable for development as an on-line conductivity monitor.

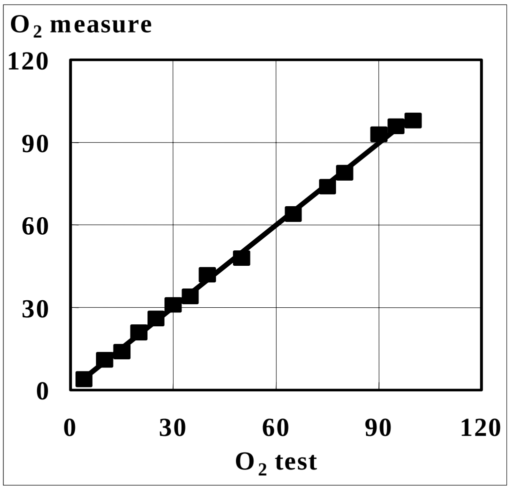


FIG. 52. Correlation between test and measure concentrations (ppb).

3.3.2. Evaluation of sensors at IRI in Japan

Work is ongoing at the Institute of Research and Innovation (IRI) in Japan to evaluate various types of HT water monitoring sensors now available and contribute to adjustment of the HT water database. For conductivity measurement, both a three-plate platinum sensor and a cell type sensor using gold plating have been examined. Fig. 53 shows the correlation between HT and RT measurements in various test solutions. It was concluded that there was little need for measurement of conductivity at operating temperatures.

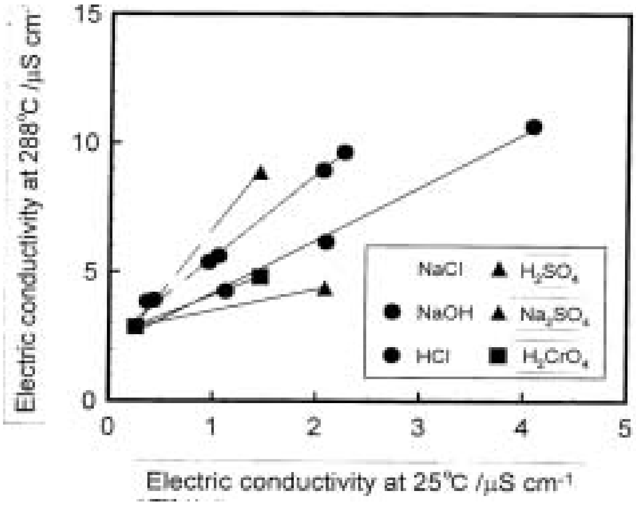


FIG. 53. Correlation between HT and RT conductivity as measured in various test solutions at IRI in Japan.

3.3.3. Development and qualification of HT conductivity sensors at PSU in the USA

HT conductivity measurements have been made at Penn State University and trials appear to have been performed in various fossil-fired power plants.

3.4. In situ measurement of high-temperature pH

In addition to the following short reports, the reader is also referred to Sections 3.10.

3.4.1. Evaluation of sensors at IRI in Japan

HT pH measurements have been made at IRI with a closed-end-tube type pH sensor using an yttrium stabilised zirconia (YSZ) membrane tube. As for HT conductivity, however, it was concluded that there was little need for measurement of pH_T.

3.4.2. Measurement of pH_T under simulated PWR primary circuit conditions in the UK

The UK Nuclear Safety Directorate (NSD) of the UK's Health and Safety Executive has commissioned a nuclear safety support study programme with the University of Newcastle Upon Tyne to investigate the values of K_w for water at high pressures and temperatures between 300 and 330 ^oC. Following an extensive literature review and some theoretical studies, the university concluded that there were significant uncertainties in the derived value of K_w under these PWR primary circuit conditions and recommended that an experimental programme be undertaken to assess the consequences of this uncertainty.

For the direct measurement of the pH of aqueous solutions under PWR primary circuit conditions, the University initially built and commissioned a rig based upon two PTFE pressure cells linked by a KCl solution. One cell contained the test solution and one a reference buffer solution. Each cell had a noble metal/metal oxide electrode inserted into the solutions and the EMF measured between the two electrodes was indicative of the pH difference between the reference and test solutions. Unfortunately, this equipment proved unreliable after repeated temperature and pressure cycling and so it was abandoned in favour of developing a pH measuring system based upon high temperature ceramic electrodes which could be inserted into a test facility belonging to the University's Corrosion Research Centre. Aqueous solutions, consisting of $LiOH/H_3BO_3$ or phosphate buffer were held at pressures up to 10.3 MPa and temperatures of 200–340^oC in the stainless steel autoclave of this facility.

The high temperature electrodes used in these experiments consist of YSZ ceramic thimbles packed inside with a metal/metal oxide internal reference and the outside in contact with the test solution in the autoclave. EMFs were measured against an Ag/AgCl external pressure balanced reference electrode which was contacted with the test solution through an aqueous KCl liquid junction. A Pt/H_2 electrode inserted into the test solution was used to provide a comparison with the pH values measured with the ceramic electrodes. This comparison electrode was viable because all of the test solutions were de-oxygenated and purged with H_2. Also, the Pt electrode was platinised using a special technique to render the Pt black layer resilient to temperature and pressure cycling.

Ceramic thimbles made by various manufacturers were tried and internal references tested included Ni/NiO, Co/Co_2O_3, Cu/CuO, Hg/HgO and Fe/Fe_2O_3. Stability of measured EMFs over time and response of electrodes to changes in solution pH (as a result of varying

$LiOH/H_3BO_3$ concentrations) and temperature were monitored. Hg/HgO and Fe/Fe_2O_3 filled thimbles showed required stability (after allowing for up to 10 hours for ceramic thimbles to become conditioned in the electrolyte solution) and Nernstian pH response. The response of two thimbles, packed with Fe/Fe_2O_3 internal reference, to pH change of phosphate buffer solution as its temperature changes over the range 200–340°C is shown in Fig. 54 and compared with the data of Le Peintre. The two electrodes gave good agreement with this data (and each other) over the temperature range 250°–280°C, but neither electrode responded well at temperatures below 250^0C, possibly because this is below the ceramic's optimum operating temperature.

Twin matched ceramic electrode experiments (i.e. using electrodes which were manufactured under rigorously controlled conditions so that they gave identical pH responses in the tests described above) were performed using ZDY-9 thimbles packed with Fe/Fe_2O_3. One ceramic electrode was contained in a HT-resistant Teflon heat shrink which was filled with phthalate pH buffer solution. A glass frit separated the phthalate from the phosphate buffer in the autoclave. A measured EMF of 320 mV would be expected between the two ceramic electrodes for a solution temperature of 270°C and values of this order were found. They remained stable over 35 hours at which time it is believed the Teflon compartment failed.

Further development work is needed to obtain ceramic thimbles which are capable of operation at lower temperatures (possibly based upon CeO_2 coated with YSZ), but the development of a practical system for the direct on-line measurement of the pH of coolant water in PWR primary circuits appears to be feasible.

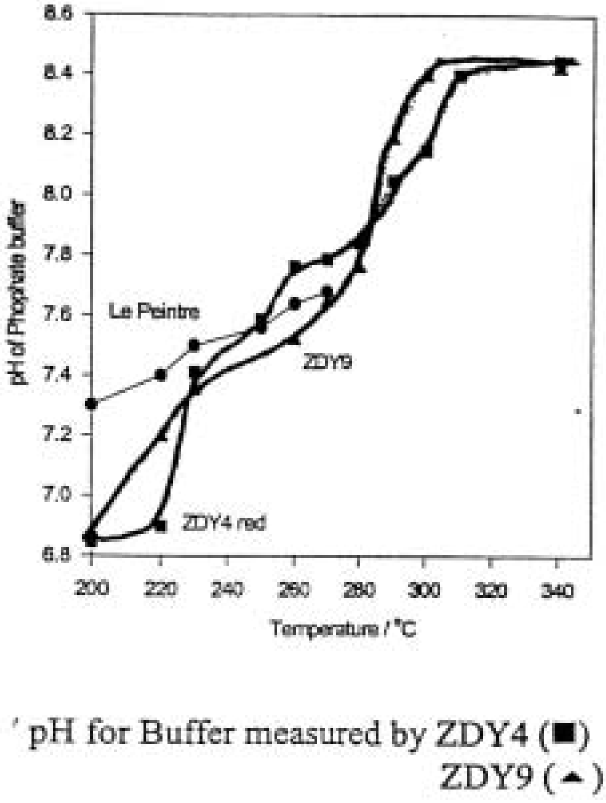


FIG. 54. Comparison of pH measurements from two sensors with literature data, as performed at the University of Newcastle, UK.

3.4.3. *Development and qualification of pH_T sensors at PSU in the USA*

Measurements of HT pH have been carried out for many years at Penn State University and the problems involved can be summarised as follows:

- The materials used for constructing high temperature parts of a hydrothermal electrochemical cell must be chemically and mechanically stable in high temperature and high pressure aqueous environments.
- The electrodes need to be sufficiently rugged to withstand high temperatures and pressures. Electroactive elements of the electrodes must be thermally and chemically stable at prevailing temperatures, so that the electrical potential of an electrochemical couple is well defined over the whole temperature range.
- For any reference electrode, the electrical potentials should be reproducible and reversible and should not exhibit any significant drifts over the entire range of operating conditions.
- The species conductances of the internal solution should be known so that the liquid junction potential in the system can be estimated reliably.
- The high-temperature reference systems should be available for calibrating non-primary pH sensors (e.g. glass electrode and W/WO_3 sensor), or assessing the viability and accuracy of primary pH sensors (e.g. H_2(Pt) electrode and YSZ pH sensors).

Recent work has concentrated on the very accurate measurement of HT pH for thermodynamic studies [55], using a flow-through cell, as shown in Fig. 55.

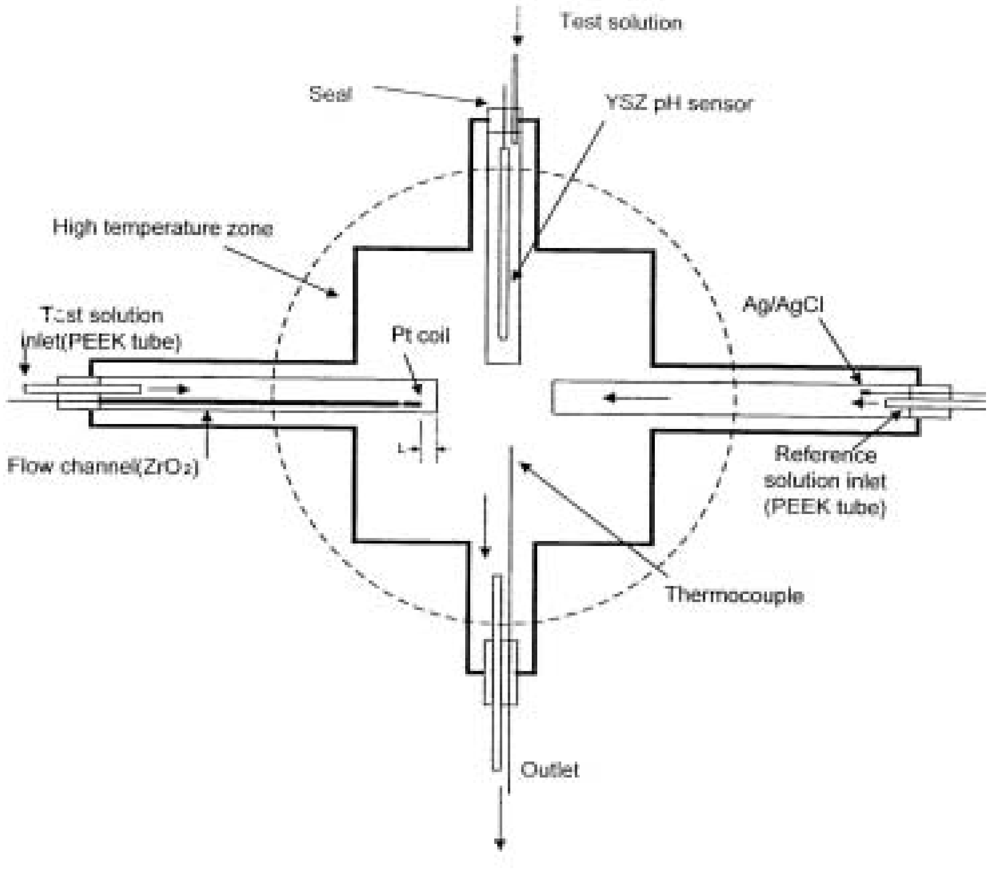


FIG. 55. Schematic design of a HT electrochemical cell for testing YSZ pH electrodes.

Trials using more conventional designs of sensor have been performed in various non-nuclear installations, including fossil power plants. The main practical emphasis at present appears to be on development of pH_T sensors for geothermal applications.

3.4.4. Sensor of pH_T measurement for WWER new generation

By applying thermocells in which an yttria-stabilized zirconia monocrystal tube of pH sensor and ligind-metal Bi-Pb/PbO pH electrode operate versus an external pressure balanced reference Ag/AgCl electrode, pH values of dilute aqueous solutions at temperatures from 150°C up to 300°C have been obtained. Comparison of the experimentally derived and theoretically calculated pH values, presented in Fig. 56, allows one to draw the conclusion that accuracy of ± 0,1 pH units can be achieved. This level of accuracy is more than sufficient for any industrial applications in power plant pH monitoring.

Because of lack of technical measuring aids, pH_T does not appear under standard control at domestic NPPs. pH of water solutions consisting of several components is a complex function of these components concentrations and dissociation constants thereof, depending on temperature. Therefore, it is difficult to judge about pH_{300} value of a solution of the same composition by pH_{25} value. In change of the component concentration relationship, first of all of H_3BO_3/O(K, Na, Li), pH_T value changes and corrosion products (CP), iron, nickel, cobalt solubility in different section of the circuit changes accordingly.

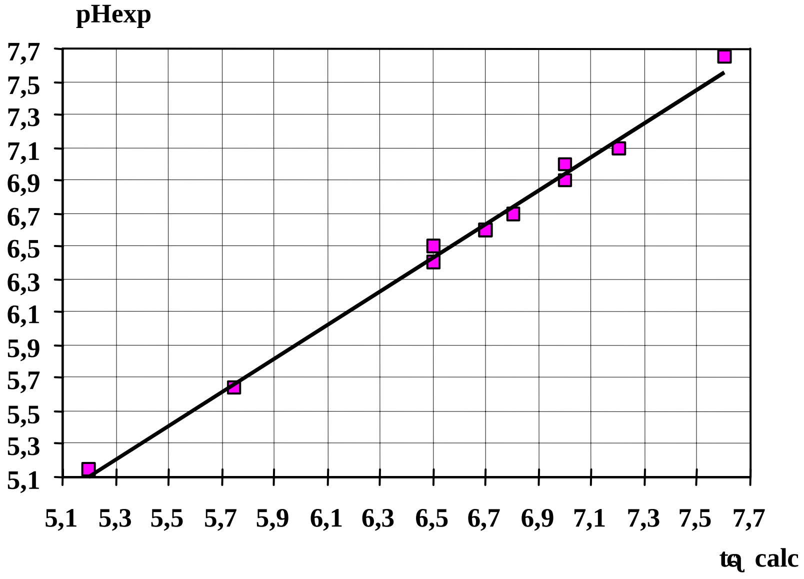


FIG. 56. Correlation between experimental pH_T and calculated pH for B-Li-Na-K solution (T=300 °C).

As there is no agreed-upon code of constants of water dissociation boric acid, potassium hydroxide and ammonia in temperature range 25–300°C, first of all it was necessary to check up pH_T calculation correctness. There are known experimental and calculational pH values for water solutions, containing NH_3, LiOH and H_3BO_3 in different proportions [56–58]. We have calculated pH_T values for the same solutions by the model [59] using interconsistent constants of H_3BO_3, LiOH, NH_3 dissociation.

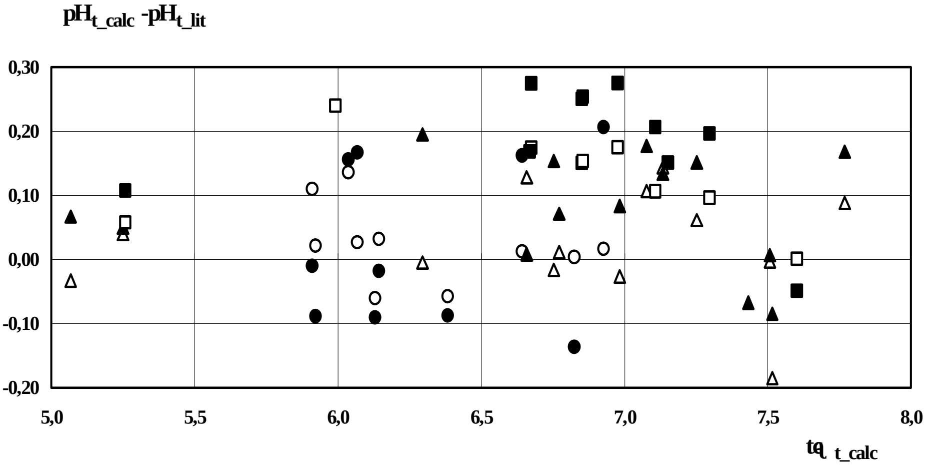


FIG. 57. Results of assessment of the calculated and experimental pH values coincidence.

Absolute disagreement of experimental and calculational values of pH_T and calculational pH_T values obtained does not exceed 0,3 (Fig. 57). Advantage of calculations, have performed, is absence of any systematical mistake as well, evidenced by discrepancy of pH_T values, we have obtained, and those of publications both in positive and negative regions (Fig. 57) [60].

3.5. In situ measurement of electrochemical potentials

In addition to the following short reports, the reader is also referred to Sections 3.10.

3.5.1. Evaluation of sensors at IRI in Japan

The programme of work on HT sensors at IRI includes examination of the effects of chemical additions (sulphate, chromic acid, etc.), dissolved oxygen, hydrogen peroxide and gamma irradiation on ECP of stainless steel. Both pressure-balanced external and internal reference electrodes (both of the Ag/AgCl type) are used. Examples of the data obtained are shown in Fig. 96. It is concluded that the effect of H_2O_2 on ECP of stainless steel differs from that of O_2 and that more data is needed here.

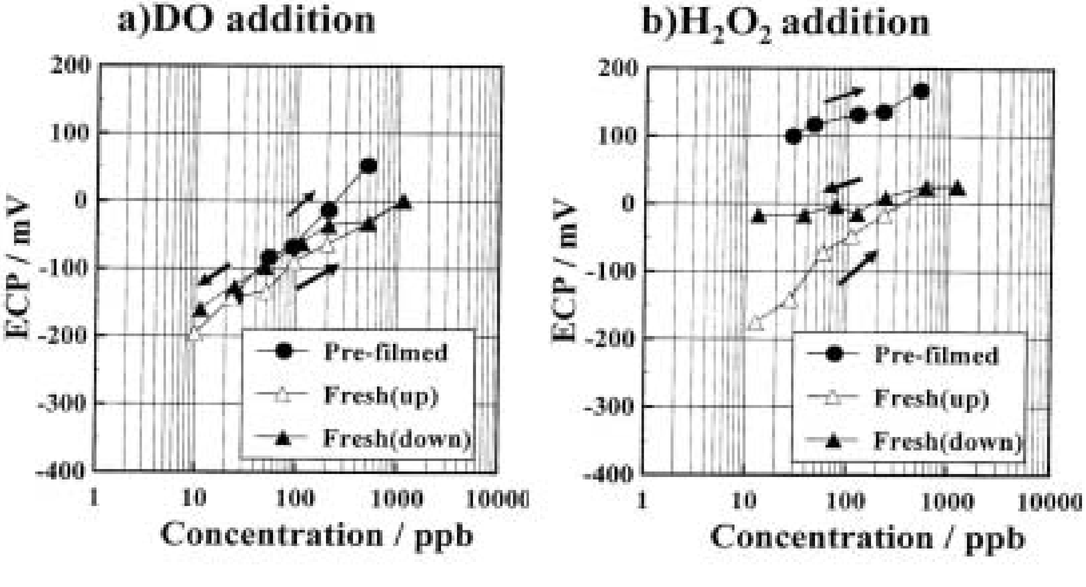


FIG. 58. ECP measurements at IRI in Japan: effect of variations in O_2 and H_2O_2 level.

3.5.2. *Development and qualification of reference electrodes at PSU in the USA*

D. D. Macdonald has been prominent in the development of HT reference electrodes for many years and work on improved designs is ongoing at Penn State University, with the emphasis now being on internal sensors. The requirements are summarised as follows:

- Thermodynamic viability (must be able to relate measured values to the SHE scale).
- Accuracy: ±1 mV is considered acceptable, but ± 0.1 mV would be preferred.
- Correction possible for the liquid junction potential and for the thermal liquid junction potential (Soret effect) with external reference electrodes.
- Rugged design for in-plant use.

PSU has been involved in ECP measurements at high temperature in both PWR and BWR plants, as well as in a variety of non-nuclear installations.

3.6. In situ measurement of corrosion rates

In addition to the following short reports, the reader is also referred to Sections 3.10.

3.6.1. *HT impedance measurements on Zircaloy at EdF in France*

The objective was to follow the corrosion in situ of Zircaloy 4, and to get information on the corrosion rate, the total thickness, and the inner dense layer thickness of the oxide. Special interest was directed to the period when the corrosion switch from a cubic to a pseudo-linear kinetics. The technique used was high temperature electrochemical impedance spectroscopy (EIS), in primary water at 350 °C (autoclave) with a two-electrode (Pt/Zr4) configuration. An example of the data obtained is shown in Fig. 59.

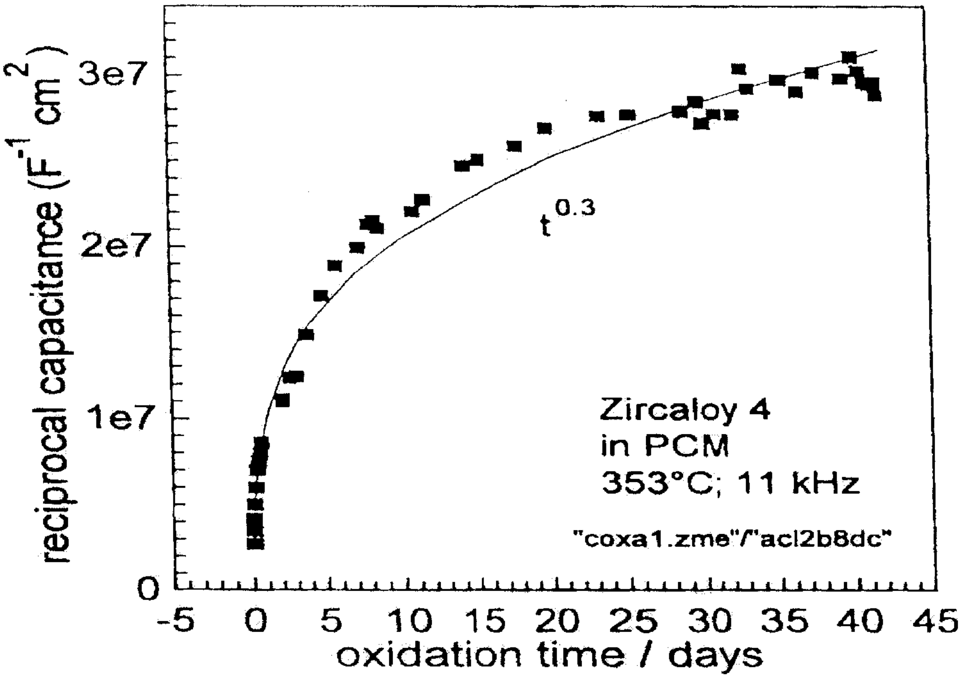


FIG. 59. In situ impedance monitoring at 350 °C of oxide growth on Zircaloy 4: reciprocal capacitance vs. time.

The main conclusion was that HT EIS measurements give very precise on-line information on what occurs at the metal interface. However, they are complex techniques, difficult for proper data acquisition and interpretation and needing specialists. Thus their use is still reserved to very specific needs and studies.

3.6.2. Development and qualification of impedance measurements at PSU in the USA

Impedance measurements in the broadest sense (i.e. including linear polarisation, AC measurements and special developments such as the contact electrical resistance technique discussed in the next section) have been studied for many years in an attempt to make in situ measurements of corrosion rates and are considered a valuable research tool in the laboratory. They have not been widely used for field measurements; however, primarily because data interpretation is complex and the techniques are difficult to apply with non-steady-state systems. They are also of limited use where localised corrosion is involved.

3.7. Characterisation of metal surfaces/oxide films

3.7.1. Development of controlled distance electrochemistry and contact electric resistance/impedance techniques at VTT in Finland

The models for HT 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. Thus 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. Therefore, controlled distance electrochemistry (CDE)- arrangement was developed at VTT during the 1990s to characterise the electronic properties of oxide films in aqueous high-temperature high-pressure environments. Due to the possibility to control accurately the distance between two electrodes, electrochemical measurements can be performed in poorly-conductive media such as BWR coolant. Application of the CDE-arrangement to various electrochemical measurements has already been described in several communications [61–65]. This experimental set-up is shown schematically in Fig. 60.

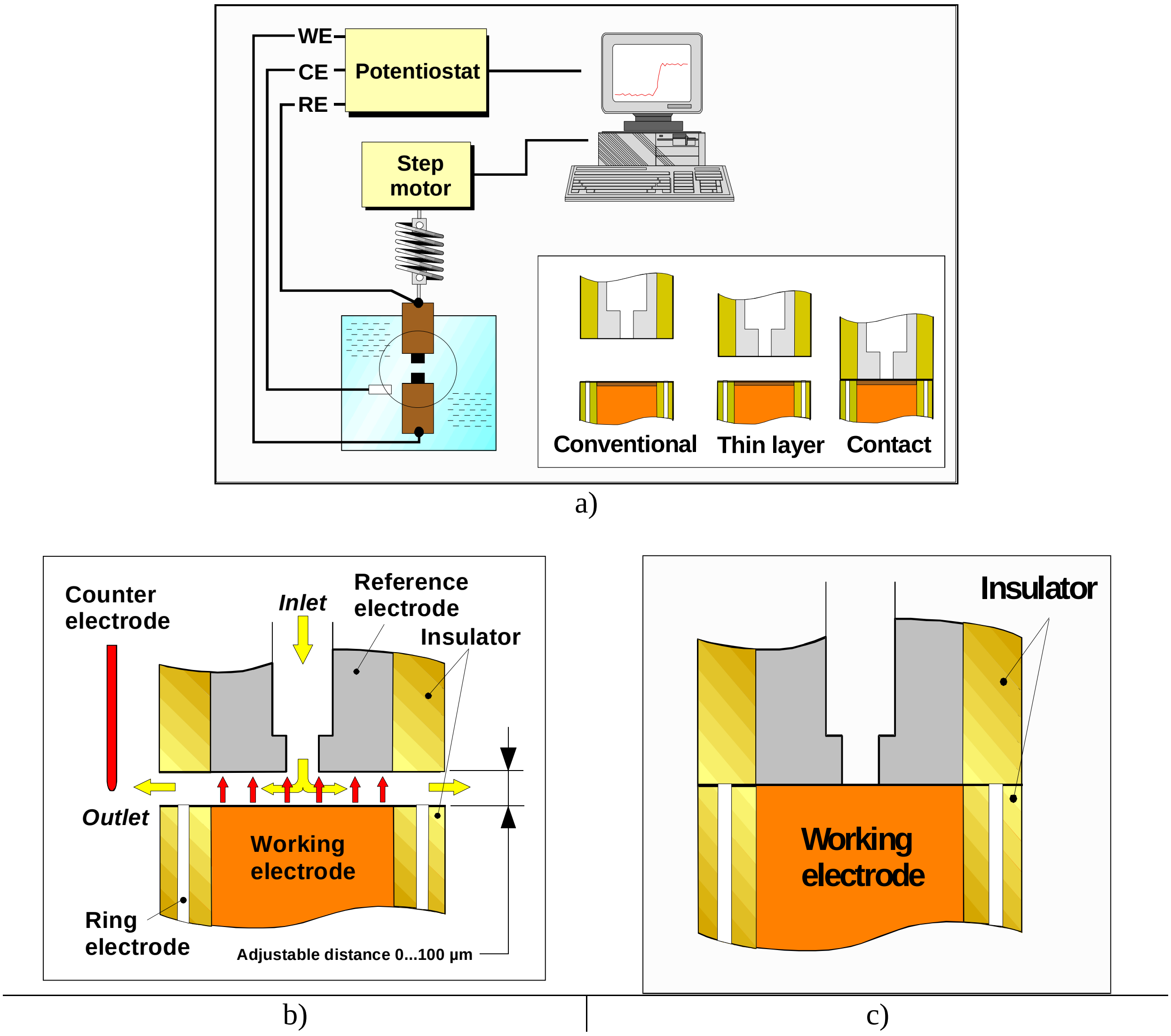
The CDE-arrangement can be employed for conventional electrochemical measurements, in which the gap between the working and reference electrodes may be large but more importantly for the following measurements:

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.
- Other controlled-potential and controlled-current measurements in low-conductivity aqueous environments.

Solid contact measurements

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



a)

b)

c)

FIG. 60. 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.

Wall-jet measurements

- Detection of soluble species released from the working electrode.

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. The oxide film forming on type 316 L stainless steel was characterised using the CDE-arrangement in high temperature fairly low conductivity water. The measurements were 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 T 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 hat two different types of charge carriers exist in the oxide film [66]. The CDE-arrangement was also used to study the properties of an anodic film on Fe in a nearly-neutral electrolyte at ambient temperature. The electronic resistance of the oxide film was roughly 3 T 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. 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). The calculated values indicate that 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, ($D_e >> D_i$) supports the assumption of the predominance of electronic conductivity over ionic conductivity in the passive film on iron.

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. The aim of the wall-jet measurements 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 [67,68]. The results obtained with the wall-jet arrangement show that the higher the Mo content of the alloy, the lower were the transpassive oxidation currents, 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. In addition 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 maintaining 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 might depend strongly on hydrodynamic conditions. It is likely that similar phenomena exist for other materials in other potential regions.

3.7.2. Use of the ultra thin layer activation technique at EdF in France

The objective was to check the predictions of some activity buildup computer codes and to improve the understanding of release phenomena in PWR primary water [69]. Tests were conducted on alloy 690 in 320–350 °C primary water in a loop called Boreal. A new and very sensitive monitoring technique (Ultra Thin Layer Activation technique (UTLA)) has been developed for in situ monitoring of release in the Boreal loop. This technique consists in indirect implantation of radioactive Co^{56}, using a cyclotron. A primary target of iron (Fe^{56}) is submitted to a proton beam and produces recoil implantation of Co^{56}, in a 25 cm long section of tube of alloy 600 or 690 which is settled below the iron sheet (the reaction is Fe^{56} + proton Ą Co^{56} +n). The alloy 690 tube is then introduced in the Boreal loop and the corrosion followed by gammametry. During the tests, the activity of Co^{56} was measured, corrected from the natural decay. This allows to detect loss of layers of 2 nanometers thick.

The adaptation of the UTLA technique to this range of sensitivity is itself a major result, and a condition to the success of the study [70]. The activation technique already existed but only as thin layer activation (TLA) technique. It uses direct activation of the sample by the proton beam instead of recoil implantation. A thicker implantation layer is then obtained and the resulting range of sensitivity is more than ***two orders of magnitude*** insufficient to follow the very low kinetics implied: in primary water, the alloy 600 steady-state corrosion rate is in the range of 0.1–1 micron by year. The UTLA technique is adapted to this range. The impedance measurements are more difficult and not applicable with hydrogen overpressure, since the corrosion rate measurement is noised with the H_2O/H_2 exchange current.

The loop was qualified in 1998 and the work is still in progress. The first tests have shown a good reliability and repeatability of measurements. They allowed to get the release kinetics, which is described by a law in the form of $R= At^b$ where b – 0.14–0.16. Another major result is the finding that the mass transfer conditions (i.e. water velocity) have very little or no effects on the release kinetics (Fig. 61). This result is in disagreement with most of the codes for activity buildup, and imply to modify the model on which they are based. In France, the reference code for CEA/EDF/FRAMATOME is Pactole, and an updating of its content is in progress [71].

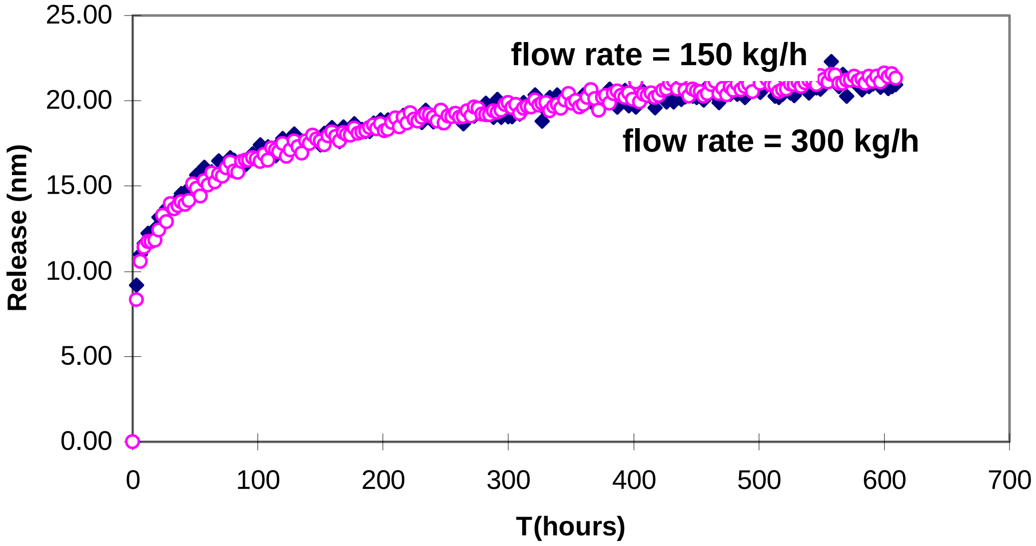


FIG. 61. Effect of mass transfer on alloy 690 release studied using UTLA.

It was concluded that the UTLA is a very powerful technique to get information at very low corrosion rates (<1 micron by year). Due to the very low activity implied, there is little constraint for safety.

3.7.3. Work on in-line, optical methods by the Institute of Nuclear Chemistry and Technology in Poland together with Paul Scherrer Institute in Switzerland

Work has been ongoing for some time in Poland and Switzerland on the development of optical methods for on-line monitoring [72–74]. One of the crucial points for reliable optical measurement of the growth of oxide films on metals in high-temperature water is the long-term stability of the window material in the presence of reactor coolant. The window should be transparent and has to form a pressure/temperature barrier for a long time. Simultaneously, the influence of ɔ-radiation on the UV-Vis-NIR light transmission of the window should be as small as possible.

Two potential window materials were selected and tested with regard to their suitability as an optical window for diffuse reflection spectroscopy (DRS), namely artificial sapphire and yttrium stabilised zirconia (see Fig. 62). DRS was then successfully applied to monitor in situ the early and advanced stages of the corrosion of stainless steel and Zircaloy under simulated BWR conditions. The measurements were carried out with a UV-Vis-NIR spectrometer connected to a flow-through cell by an optical fibre (see Fig. 63). In the cell the samples were illuminated through an optical window and the water from a nuclear reactor. Spectral investigations from 200 to 1000 nm wavelength allow in-line measurement of oxide layer thickness from some nanometers to the micrometer range.

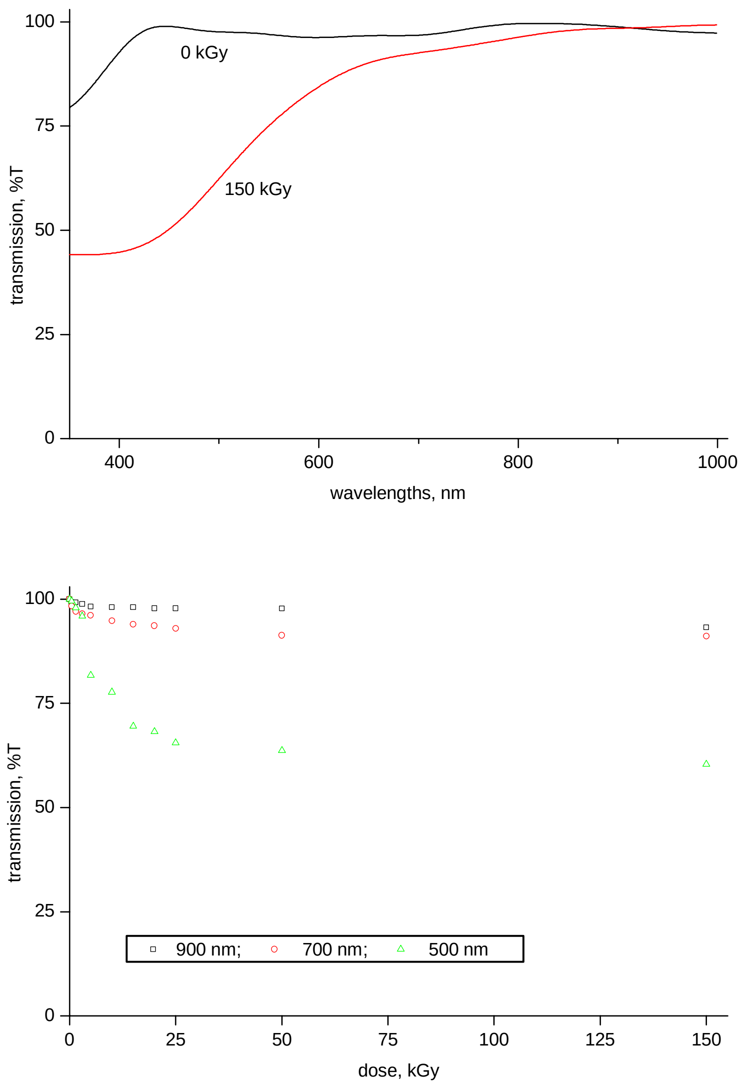


FIG. 62. Transmission spectra of the irradiated yttria stabilised zirconia in comparison with the non-irradiated material (upper plot) and changes of optical transmission with increasing ν-radiation dose (lower plot).

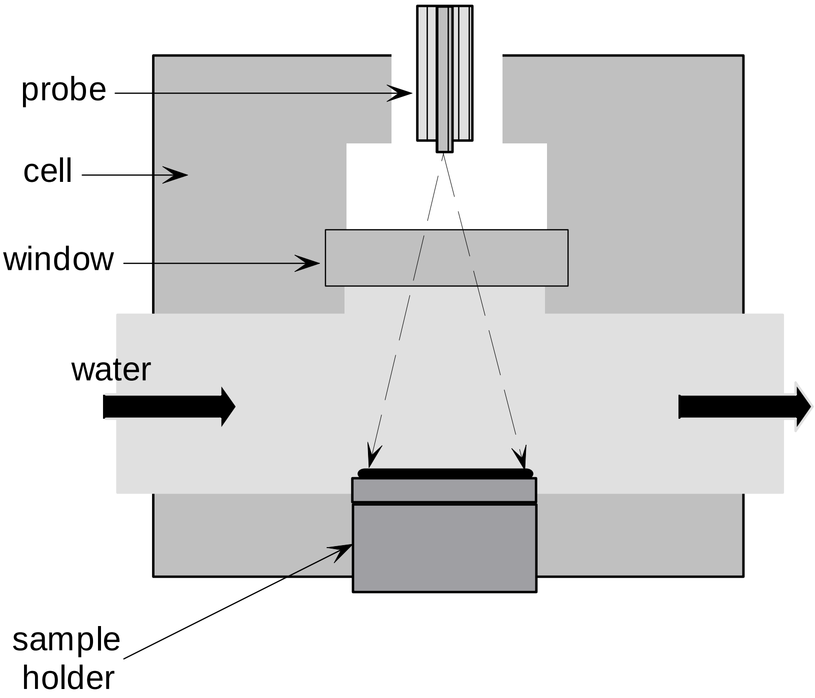


Fig. 63. Cross-section of the flow-through cell used for diffuse reflection spectroscopy measurement under simulated BWR conditions.

It was shown that the method allows non-invasive, continuous and no flow disturbing determination of thickness of the Zircaloy corrosion layer under BWR nuclear reactor conditions in their normal operating mode. The time necessary to record one spectrum is less than one minute, so the method seems to be especially efficient in the investigation of early stages of water induced corrosion. The method allows to study the oxide layer buildup over several weeks. Using a sapphire optical window the lower detection limit of the layer thickness is about 45 nm and the upper limit — about 1 μm.

The method allows precision of 5 (i/2) nm (where i stands for the order of interference) in measurement of the oxide layer thickness. The accuracy is controlled by the roughness of the surface of the oxide and also the exactness of the refractive index. It is about 3 nm. It was shown, that oxide layer buildup on the Zircaloy surface follows a power law with time. At temperature of 563 K (290°C) the suitable power is close to 2/3, while at 543 K (270°C) the power of 1/3 was found to be appropriate. The first one is consistent with the data which have been already proposed for the stainless steel, while the latter is consistent with the generally accepted model of corrosion of Zircaloy.

Diffuse Reflection Spectroscopy was further applied to investigate the action of an amphoteric redox reagent (H_2O_2) on a stainless steel surface, which leads to the buildup of specific resistant (passive) oxide layer. In the work done DRS was utilised in both in-line (using the sapphire window) and off-line modes. Within the investigated range of pH there is no distinct influence of the acidity of the oxidising solution on the thickness of the oxide layer. Independently of the H_2O_2 concentration, for the temperature of 400 K (i.e. about 130°C) process of buildup of the passive oxide layer on the surface of stainless steel is completed within 20 h. Increase of the H_2O_2 concentration from 0.001 M to 0.010 M, however, permits shortening of the coverage time to about 12 h. Desired thickness of the passive oxide layer, in turn, can be achieved only by changes of the temperature of the contacting solution.

In the initial stages of the process, when the passive oxide layer is not thick enough, absorption of light is the main effect taken into the account. According to the data presented in the paper, it was assumed that logarithmic dependence of the oxide layer thickness on the spectral reflectance, $d = a \ln(R) + b$, may be successively applied in the calculations. After a certain time, however, interferometric maxima appeared in the spectral region of 300 nm. It means that growth of the oxide layer approached to the thickness of about 50 nm and both phenomena, light interferometry and absorption, can be utilised simultaneously.

Registered spectra remain in sufficiently good agreement with these obtained from the analytical modelling using optical properties of hematite. Some influence of the chromite spectral reflection has been found, however.

3.8. Development of expert and diagnostic systems related to on-line monitoring of water chemistry and corrosion

3.8.1. Expert system for reactor chemistry developed by Siemens in Germany

3.8.1.1. Introduction

For computer-based water chemistry control a huge variety of different computer software is commercially available. In reality, most of this software has to be considered as data analysis and data acquisition systems (LIMS; Laboratory Information Management System) only.

The main distinguishing factor between data analysis and diagnostic systems is that analysis embraces all the activities performed by applying numerical mathematics in the broadest sense. In particular, this includes the calculation of characteristic parameters or set points, the comparison of set points with actual data and the detection of deviations and/or violation of limit values. Also included is the broad task of visualising information which has been measured or calculated. In addition to displaying numerical values in tables, for example, one of the main tasks is to present the information intuitively in optically enhanced graphics, trend plots and other presentation formats. The methodology is based on familiar, step-by-step solution procedures, i.e. algorithms. If the algorithms are known, they are relatively easy to implement in standard computer programs.

In addition to the tasks described above, diagnostic systems are expected to actually interpret the information, in order to assess a process in relation to particular properties and requirements. In analytical systems, this important task is left to the plant operators.

Diagnostic systems must also be capable of explaining the process used in deriving the diagnosis, so that the plant operator can understand it. Finally, the presentation of a forecast for subsequent process events, and the recommendation of countermeasures, are features which must be included in the performance spectrum. The above work is based mainly on mathematical logic, often combined with the processing of statements in (quasi-) natural language. Both technical and, especially, empirical knowledge, which cannot generally be expressed directly in algorithmic terms, are required from the human experts. A suitable method is to use a knowledge base in which the knowledge is formulated as rules.

For a long time, “diagnostics” was addressed to “the task of identifying possible malfunction causes from the incorrect behaviour of a component or system”. This definition can no longer be considered appropriate in many areas. A more up-to-date interpretation of the term is “preventive diagnostics” which detects and reports deviations, through continuous monitoring and assessment of events, prior to the occurrence of any damage or malfunction. This is the concept which is integrated into the DIWA diagnostic system. The computerised system DIWA (Diagnostic System of Water Chemistry) was developed for real-time diagnosis of chemical operating conditions as a basis for cost-effective, preventive maintenance.

3.8.1.2. Overall structure and operating principle of the expert system DIWA

One of the fundamental requirements for water chemistry control at power plants is to maintain the systems and components integrity. However, fast and comprehensive control of the water chemistry conditions is sometimes difficult, especially if only traditional water chemistry monitoring technologies are applied. To improve these conditions, the DIWA system has been developed to provide a real-time, on-line assessment of the water chemistry conditions. This diagnostic system can be easily customised to all types of thermal power stations. The knowledge base of the diagnostic system -which can be easily extended by the plant operator itself (learning system)- is integrated into the expert module and can be easily tailored to all types of water chemistry regimes. The expert module basically addresses to the following tasks:

- On-line acquisition of important chemical and thermodynamic parameters,
- Off-line acquisition of laboratory data,
- Calculation of reference values from measured data,
- Visualisation of data and reference variables in process displays,
- Freely configurable graphical display of data and reference variables,
- Data compression for reduced data volume,
- Plausibility checks,
- Comparison of actual data with setpoints (target, limit or control values), and
- Immediate indication of detected disturbances.

Special emphasis is placed on:

- Output of diagnoses (description, assessment),
- Recommendation for counteraction, and
- Time-based extrapolation of data for trend plots.

The overall structure of the system is shown in Fig. 64. The operating principle is evident from this diagram. After performing plausibility checks, calculations of characteristic and additional values, which cannot be measured directly, all of the measured data are directly accessible to the expert system database. From these values symptoms are derived by using fuzzy logic. This task is supported by the system's knowledge base.

After generating symptoms, the system accesses another part of the knowledge base where the rules of the expert knowledge are available. After running through all the rules, the expert system generates the diagnoses. Based on the symptoms within the rule base, the system calculates confidence factors for every diagnosis generated, which represent the safety level for the diagnosis. This workflow is directly related to the work a human being is doing as an expert.

All diagnoses which are created by the expert system are stored together with the related measured data within the expert system database. The user has access to the results via a graphical user interface.

The concept of the analytical part of the diagnostic system takes into account the fact that more than one input source can be available. In the case of power plant water chemistry control, it is normal that some of the measured data are collected via on-line sensors. Most of the data which have to be controlled are measured at the plant laboratories using special analytical methods and equipment, and therefore have to be input into the system "off-line".

The analysis part of DIWA performs the following tasks based on the specific data input:

- Plausibility check on all measured data. The data check is performed with respect to limit value violations, characteristic changes within the trend and their affinity in relation to other values. All results of these checks are stored in a quality identifier and are accessible to the diagnostic part of the system.
- Calculation of derived or not directly measurable values. This includes time and resource expensive numerical calculations of the distribution of major species and impurities within the several physical phases of the feedwater and cooling water, and estimates of characteristic values of major components (steam generator, condenser etc.).
- Derivation of statistical data of process monitoring (average, maximum and minimum values of important chemical measures, time range and distribution of limit value violations, monitoring of operational states etc.).
- Compression of the raw data material and transfer to the historical archive.

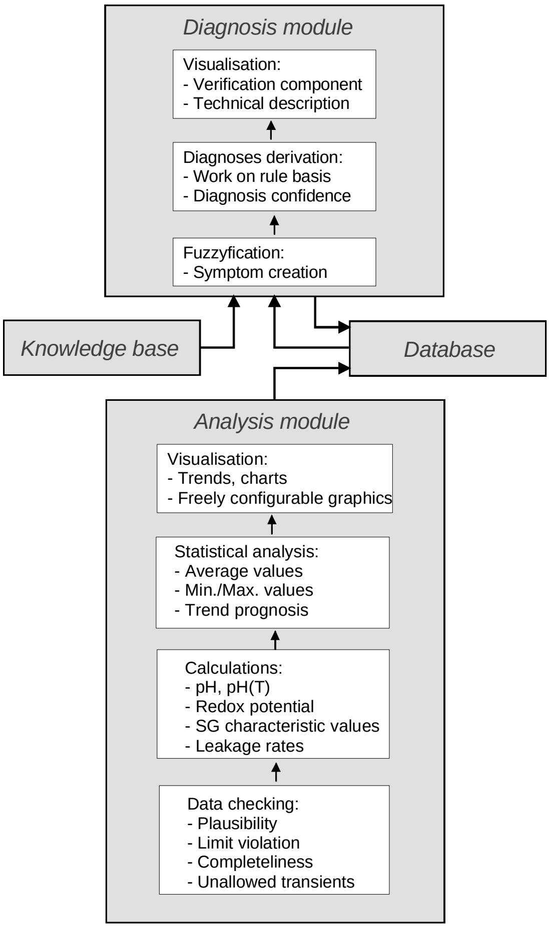


FIG. 64. Overall structure of the DIWA expert system.

The diagnostic system is built up around a plant-specific knowledge base which is designed for maximum flexibility and can thus be used for a variety of different applications in all types of power stations. The system capabilities can be adopted at any time to specific user requirements by installing additional on-line monitors and continuously incorporating new state of the art as well as additional plant-specific knowledge.

Once a diagnosis has been generated by the system, it will be shown in the Diagnosis Menu. In the diagnosis overview, information regarding date/time, confidence, confirmation and type of diagnosis are listed. In this menu a selection of diagnoses is possible to display only new, unconfirmed diagnoses or all diagnoses of a certain type (new and confirmed ones) or the last 200 diagnoses. This feature provides valuable information to the plant operator in assessment of the plant conditions, since also a trend prognosis for the next eight hours can be shown. This enables the operators to initiate necessary actions well before violating specifications or internal regulations.

For each type of diagnosis, additional information such as the technical description of the malfunction, recommendations for further checks and necessary actions to be initiated, is provided by the system. In addition, it will be documented which person recognised the diagnosis and which actions have to be initiated.

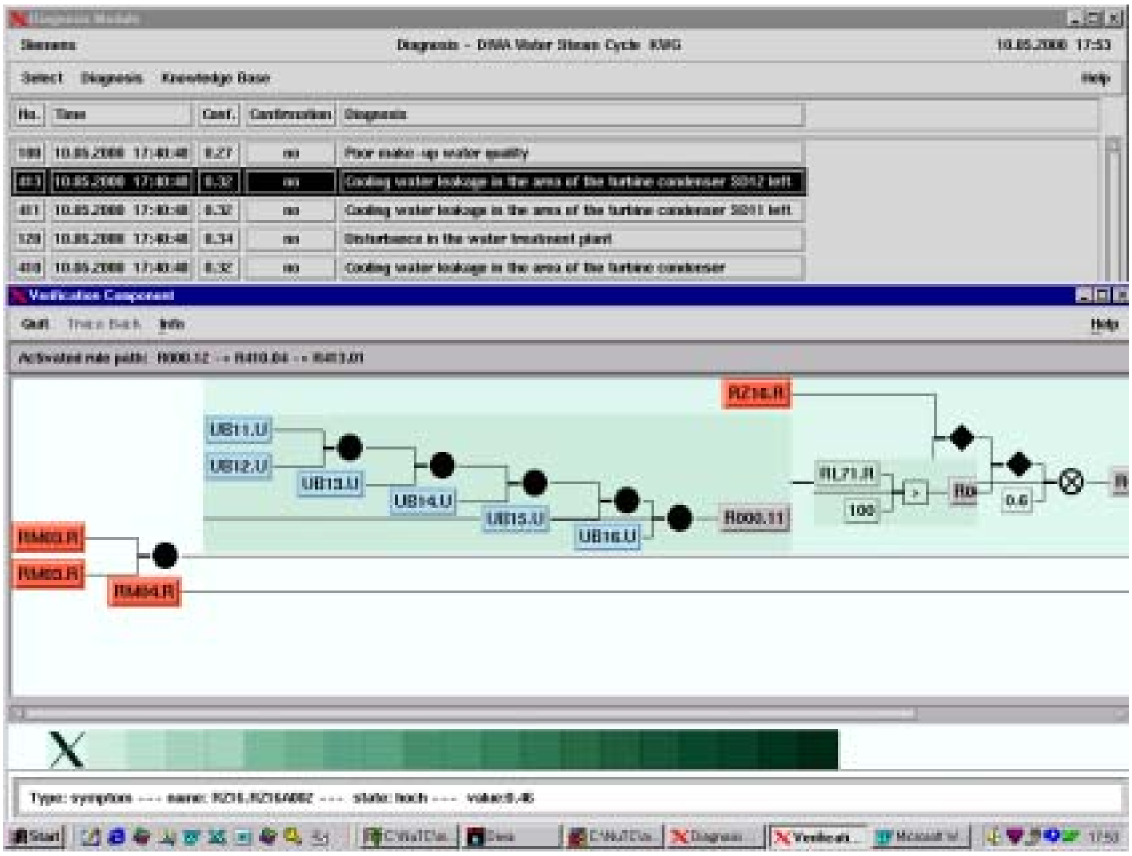
For performing a diagnosis, specific languages (PMCL and FCRSL) were designed to be used in combination with one another in order to construct on- and off-line expert systems. PMCL means “Port Measurement Computational Language” and FCRSL means “Fuzzy and Crisp Rule Specification Language”. PMCL covers the conventional, computational requirements of such systems. FCRSL, on the other hand, allows the implementation of a fuzzy and/or conventional, rule-based knowledge base within such systems. The notation in this language is quite similar to the formulation in natural language shown in the above example. The mechanism for integration of the rule into the program is to specify all rules in an external file-set (knowledge base). Rules can thus be edited as desired, without the need for reprogramming.

The verification component, with which the user can analyse the generated diagnosis, is an important component of the expert system. The complete rule tree involved in the diagnosis analysis is presented graphically on-screen. The rule-tree logic diagram shows the different rules, their logic and the symptoms (Fig. 65).

All graphic elements are mouse-sensitive: when the user positions the mouse on any of the symbols for rules, symptoms, operators or diagnoses, the associated values (names, states, weightings) are displayed. Elements are also highlighted in colour, wherever possible. Since the rule trees can, under certain circumstances, cover large areas and may not fit completely onto the screen, it is possible to expand and collapse rule symbols simply by mouse click. This enables context-sensitive navigation through the rule base, allowing the operator to concentrate on specific areas of relevance within the analysis.

With these features, the explanation component presents a powerful tool with which even less experienced users can rapidly trace the path of the diagnostic system from data measurement to the generation of the diagnosis, and thus pinpoint the causes.

Experience with the DIWA real-time diagnostic system has shown that it is a very useful tool for further improving the plant chemistry supervision concept, incorporating analysis and diagnostic elements into a conventional data acquisition system (LIMS). In this way, the quality assurance of the data acquired is improved, as well as the quality of the diagnosis, which can be performed more quickly and reliably. The diagnosis principle, based on an easily editable knowledge base which contains own and foreign knowledge and experience of many experts, is a valuable help to the chemistry and operating staff in preventing and correcting any chemistry perturbation which may jeopardise plant performance. Besides, it offers well organised data administration, enabling easy follow-up of the chemistry situation at any time. More details on the DIWA system are available in [75].



No.	Time	Conf.	Confirmation	Diagnosis
100	10.05.2000 17:40:48	0.27	no	Poor make-up water quality
413	10.05.2000 17:40:48	0.32	no	Cooling water leakage in the area of the turbine condenser S012 left
411	10.05.2000 17:40:48	0.32	no	Cooling water leakage in the area of the turbine condenser S011 left
120	10.05.2000 17:40:48	0.34	no	Disturbance in the water treatment plant
418	10.05.2000 17:40:48	0.32	no	Cooling water leakage in the area of the turbine condenser

FIG. 65. DIWA expert system: rule tree for condenser leakage.

3.8.2. Modelling work on reactor system behaviour at PSU in the USA

Macdonald and co-workers have worked on modelling both BWR and PWR systems for several years and the reader is referred to the recent literature (e.g. [76]) for more details on this.

3.8.3. Expert system for reactor chemistry developed by EPRI in the USA

In 1999, EPRI completed development of SMART chemWORKS^{TM,} a real time power plant chemistry monitoring and advisory system This system integrates chemWORKS^{TM}, EPRI’s family of chemistry codes with a plant data management system and a real time intelligence engine. The system has been installed by October 2000 at over 20 US plants, including BWRs and PWRs. More information is given in [77].

3.9. Concept and organisation of on-line monitoring water chemistry and corrosion for NPPs developed by VNIPIET, Russia

3.9.1. Concept

Work has been ongoing for several years at VNIPIET in St. Petersburg, Russia to develop a system of on-line, automatic chemical control and corrosion monitoring in the primary circuit of new-generation WWER type reactors. Furthermore, the need for a system of continuous water chemistry functional diagnostics and monitoring (SFDM) in RMBK reactors is dictated by the following considerations. First of all, the system provides for the control and prediction of cracking corrosion processes in the coolant circuit equipment, thus improving the operational safety of energy production. Continuous water chemistry monitoring extends the equipment life and the information on equipment physical condition allows to reduce the accident rate and frequency of necessary inspections. Also of great importance is the decrease of personal and environmental doses due to the reduction of the deposition rate of insoluble corrosion products with induced activity in the coolant lines. Owing to the specific character of the object of diagnostics (OD), namely the coolant passing through a series of functional groups of equipment, the water chemistry diagnostics and monitoring should be performed by an individual system integrated into the operation systems of NPP.

The diagnostics of reactor coolant quality is organised in 3 levels:

Level 1
Information system for collection of signals and routine data processing, providing warnings of departures from specification, etc.

Level 2
Diagnostic system enabling location of problem areas and identification of the causes of water chemistry disturbances, allowing advice to be issued to the operator.

Level 3
Prediction system for assessing the progress of corrosion and deposition, permitting calculation of radiation fields and doses, leading to recommendations during equipment and pipe inspection/repair.

The system of on-line, automated, chemical control and preparation of primary coolant samples relates to the 1st level. It is designed to provide the NPP personnel with the information on water quality and corrosion process which is necessary to reach adequate decisions for maintaining coolant quality within the specified limits and for safe and reliable operation of power equipment and pipelines.

Under normal operational conditions the system provides for:

- quick automated chemical control of the coolant quality parameters in the primary and secondary circuits, as well as prompt manual determinations (measurements);
- data reliability;
- representative samples;
- deeper, periodic control, giving an accurate account of the coolant composition and its constituents, dynamics of composition change with time, equipment corrosion, etc.;

- data collection (in the form of electronic signals) from primary sensors, data;
- processing in blocks and data transmission to the next level of water quality diagnostics (location of areas of departure from the specifications and issuance of advice to the operator);
- integration of the on-line data from sensors with normal laboratory measurements.

During reactor start-up and shutdown periods under normal operating conditions, the system gives an insight into the functioning of equipment and the coolant water quality of the primary and secondary circuits.

Collection of the information on coolant quality in the primary circuit is carried out by three channels:

- channel 1: continuous monitoring of the plant system condition (collection of data from the primary sensors) over a limited group of parameters;
- channel 2: periodic review of the system condition on evidence derived from the level 1 signals;
- channel 3: periodic review of the system condition with the maximum possible number of diagnostic procedures (full decoding of hand-taken samples) at much longer intervals, as compared to those in channels 1 and 2.

The information system as a whole continually accumulates chemical and corrosion monitoring data in real time and allows the input of data from additional (laboratory) chemical analyses of water samples. It tabulates and compresses the data, allowing easy production of daily summary reports, as required by the plant chemists, as well as issuing warning signals to the plant operator when parameters are outside the specified limits.

Representative samples are obtained by the use of special design and materials for sampling lines and reservoirs, coupled with special procedures for sample taking and storage. Table 1 (Section 2.1.3.2) shows the recommended points for coolant chemistry control by the system of functional diagnostics.

The choice of parameters to be controlled depends on the operation mode of the reactor unit as well as their importance for water chemistry control and service performance of primary sensors; see Table 2 (Section 2.1.3.2).

Depending on their design, the sensors now used are subdivided into those operating at elevated temperature and pressure in the primary coolant circuit and those demanding temperature and pressure decrease and gas removal (see Table 3 Section 2.1.3.2).

SFDM (system of functional diagnostics and monitoring) should also support operational decisions on accurate adherence to water chemistry specifications. The efficient interaction provides reliable and early detection of departures from water chemistry specifications, as well as quick detection of their cause and advice for their correction.

This is a multilevel distributed system with network connection between its components (see Fig. 66).

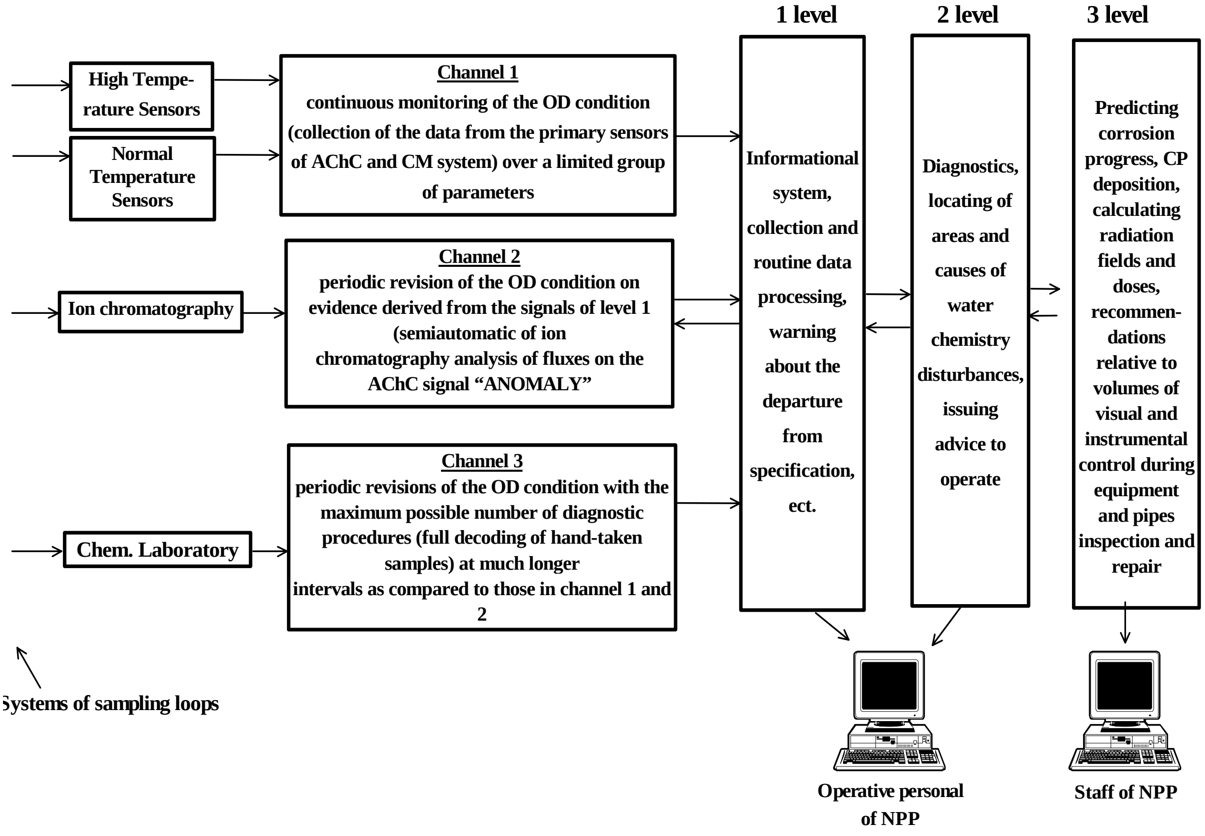


FIG. 66. Scheme of OD and SFDM system.

In addition to its direct functions SFDM the system collects, processes and stores data on water chemistry parameters and conditions coming from on-line and lab analyzers as well as information on the working conditions of NPP equipment coming from the controllers and computers of the operation systems. The system also documents information on water quality maintenance and departures from the specifications, and keeps archiving.

The typical main function of SFDM consists in the continuous monitoring of water chemistry parameters and the earliest detection of adverse trends and variations from specified conditions. The 2nd important function of SFDM consists in determining the causes of such variations and producing recommendations for their correction.

The fact of water quality impairment is established from diagnostic indices reflecting deviations beyond the specified ranges of water chemistry parameters, equipment operation conditions etc. These deviations are determined with methods applied in statistical control, among them the moving average for detecting rapidly developing deviations (with a period of several days to a week), and the cumulative sums method or control of correlation factor scatter for the deviations of medium and long-term duration.

The causes of deviations in water chemistry regime are searched with the use of a diagnostic model (DM), which correlates them with the diagnostic indices (symptoms) determined from current values of controlled process parameters.

DM is based on the graph of cause-effect relationships, obtained in analyzing expert, operational, theoretical and other information on processes occurring in the coolant and coolant circuit equipment [78]. Usually DM is presented as a matrix which relates causes to symptoms (the so-called "diagnostic matrix") and facilitates the search of disturbances along the vector derived for symptoms. However, the matrix presents low possibility for properly accounting for the quantitative effects of the causes on the extent of symptom manifestations. This difficulty hampers diagnostics and reduce its depth. To account for the quantitative effects corresponding weight coefficient, are introduced or fuzzy set apparatus is used.

To make the diagnostic more accurate the diagnostic matrix is complemented with another model, for example, a productive model, or stored images of concrete situations (fingerprints of disturbances- which are a set of parameters describing the disturbances). Theoretical knowledge in the form of mathematics models (for calculating water chemistry parameters at uncontrolled points or assessments of NH_3 content changes due to hydrazine decomposition and co on are also employed.

3.9.2. Description of the object of diagnostics (OD)

This section describes SFDM for NPPs with reactors of RBMK type (BWR).

The water coolant conductivity, pH and corrosion product concentrations are the main parameters which characterize the water chemistry [79].

The coolant quality indicators are classified as specified and diagnosed. The specified indicators set permissible levels of impurities for reliable and economic operation of power unit equipment during a designed service life period. Hence, surpassing this limit is considered as disturbance in water chemistry regime.

The diagnosed indicators serve for timely revealing tendencies toward disturbances in water chemistry (deviations in the specified indicators). The limits established for the diagnosed indicators represent expected values, deviations from which not being regarded as departure from normal operation conditions if the specified indicators limits are obeyed. However such deviations point to possible anomalies in the operation of the relevant technological systems and/or means of water chemistry control.

The diagnostics of the OD condition is carried out over a group of diagnostic parameters (indices). The information on the values and dynamics of these parameters is used by SFDM for defining the running OD condition, localizing OD failures, that have led to this condition, and prediction of failure development. The diagnostics of reactor coolant quality describe above.

3.9.3. SFDM description

The proposed system is based on the frame-production DM, which allows easy integration of different knowledge of deep (theoretical) and empirical (expert) ones. The frame includes a series of slots filled with knowledge and data related to a certain block of OD. The frames have a similar structure and are combined in a network, thus ensuring a comprehensive description of the complex OD.

The structure of FrB_i, frame which defines the *i*-block of OD, has the form (Table 7):

$$\mathbf{FrB_i = \{Name_i; Atr_i; St_i; Im_i; Dm_i; Cs_i; Rec_i; Pr_i; Conf_i; Next_i\}.} \quad (1)$$

The frame slots store the following information:

Name: the name of the OD block,

Atr: a list of diagnostic indices (symptoms) related to water chemistry disturbances in this block,

St: frame status (defined by scanning the diagnostic matrix located in the slot *Im* of the frame). The status may have the following meanings: *St=revealed, possible, unrevealed*. The situation status is defined by the procedure computing the value of the variable S, entering into the criterion which defined **St**:

$$\mathbf{S} = \sum_{j=1}^{K} \nu_j \Big/ \sum_{j=1}^{M} \nu_j \text{ , (2)}$$

where M is the total number of symptoms revealing disturbance, K is the real number of symptoms found in the process and related to a given disturbance (K and M are the parameters of the slot *Atr*), ν $(0<\nu<1)$ is the weight attributed to a given symptom and showing the degree of reflecting the disturbance (by this symptom) (similarly to the weights of influence in).

Depending on the numerical values of S the value of the slot St is defined as follows:

at S=0,85÷1,0 — St=revealed
at S=0,5÷0,85 — St=possible
at S<0,5 — St=unrevealed.

Im is diagnostic matrix for searching water chemistry disturbances related to a given block of the circuit. The matrix includes only the symptoms which are furnished with automatic instrumentation. The symptoms obtained in a laboratory are considered only in the production rules.

Dm is the base of production rules for refining possible water chemistry disturbances connected with a given block. The system uses a typical structure of production rules: the symptoms revealing the disturbance are listed through the conjunction D on the left side, while the right side contains addresses to the corresponding elements in the lists containing the causes of these disturbances, as well as the recommendations for their elimination (including necessary controls), forecasts of their progress (the list themselves are located in the slots Cs_i, Rec_i and Pr_i of the frame FrB_i).

Cs; Rec; Pr are the lists of water chemistry disturbances, recommendations for their elimination and forecasts of the situation progress, respectively.

Conf holds the information on the priority of possible water chemistry disturbances in the area of responsibility of the *i*-block. This allows giving preference to the disturbances of higher priority at the simultaneous occurrence of several disturbances (among them those which belong to different blocks), which should be eliminated by applying various (even mutually exclusive) controls.

Next is the address of the network transfer frame.

In the synthesis of DM the object was decomposed on the functional-territorial principle. The primary coolant circuit was divided into compact blocks — turbines, RCC, condensate polishing, CPS and drum-type separators. The blocks are characterized by a great number of specific disturbances of water chemistry. The concrete values of the model frame slots (attributes, diagnostic matrix, rules, ets) are defined by analyzing expert information. Studying the operating mode and expert information allowed to classify the water chemistry disturbances into 3 groups:

- those connected with changes in the operating conditions of the main circuit equipment;
- those connected with failures in measuring channels;
- those connected with chemistry parameters.

The algorithm of the SFDM function has a cycle character during the slots *Im* of the cycle frames containing diagnostic matrices are scanned in the sequence of their location in the DM network. If the fact of a disturbance (or unfavorable trend) is made evident, the frame is given a corresponding status and the possible causes of the disturbance are refined on the base of the productive rules located in the slot *Dm* of the frame. Appropriate recommendations are offered) to the personnel.

In such a manner water chemistry monitoring is performed not over all diagnostic indices but only these which are available by on-line measuring. The probability p_{oc} of the correct assessment of the water chemistry conditions is determined by an the entropy criterion $U(Sj)$. The latter characterizes the uncertainty of the OD condition, related to the monitoring of the symptom Sj:

$$U(S_j) = -\sum_{i=1}^{k} p_{ij} \mathrm{Log}_2 p_{ij}, \quad (3)$$

where p_{ij} is the probability of the apperance of the symptom Sj due to the presence of the i-disturbance (here, to a first approximation, the significance of all relations "disturbance-symptom" may be considered similar).

Then at the monitoring of N symptoms among M possible (considered in DM) indices the probability p_{oc} has the form:

$$p_{oc} = \sum_{j=1}^{N} U(S_j) \Big/ \sum_{j=1}^{M} U(S_j) = \sum_{j=1}^{N} U(S_j) \Big/ H_{tot}(M), \quad (4)$$

where $H_{tot}(M)$ is the total entropy related to OD at a given DM.

It is desirable to have the probability value $p_{oc} \in (0,5–0.7)$. Of essential importance is the definition of the permissible levels for the monitored water chemistry parameters — exceeding these should be considered as the sign of a disturbance. This function might be successfully fulfilled by the designed operational levels (which provide for safe operation during the designed NPP service life). The system of automated chemical control and preparation of primary coolant samples should meet the requirements of a series of specifications and rules, including an additional demand of limiting the water consumption for analyses and draining boron-containing samples into a special reservoir. The sampling system is designed for taking steam and water samples from the primary circuit and their preparation (cooling, depressurisation) before chemical analyses.

The sensors of the above system have been tested with units in VNIPIET (St-Petersburg) and PhEI (Obninsk). The system of synchronous data collection from 32 sensors and I and II channel data mixing has been tested at a thermal power plant (Kolenergo Co).

Table 7. Structure of the frame

Slots	Values
Frame`s name	Fr Bl 1 «Turbines installation»
Atr 1.1 Atr 1.2 Atr 1.3 . . . . Atr 1.8	Conductivity after ş ɩ ɼ -11 > norm Conductivity after ş ɩ ɼ -12 > norm Conductivity after ş ɩ ɼ -13 > norm . . . . Concentration of ʆ 2 after ş ɩ ɼ -24> norm
St 1	St 1=1/St 1=0
Im 1	Atr 1.1 1.2 1.3 1.4 . . . 1.8 S1 0 1 0 0 . . . 0 S2 1 0 0 0 . . . 0 S3 0 0 1 0 . . . 1 S4 0 0 0 1 . . . 0 . . . S8 0 0 0 0 . . . 1
Dm 1	S1 If *Atr 1.2*, then *Cs 20.2-1, Rec1, Pr* S2 If *Atr 1.1*, then *Lab1* If *Atr 1.1* and *Lab1=1*, then *20.1-1, Rec1, Pr* If *Atr 1.1* and *Lab1=0*, then *Cs 20.1-5.1, Rec2, Pr* ….. S8 If *Atr 1.8*, then *Cs 20.8-9, Rec1, Pr*
Cs 20.1-1 Cs 20.1-5.1 Cs 20.2-1 Cs 20.3-1 Cs 20.4-1 Cs 20.4-5.2 Cs 20.8-9	Suction of coolant sea water in ş ɩ ɼ -12 Pollutants in water after DBC Suction of coolant sea water in ş ɩ ɼ -11 Suction of coolant sea water in ş ɩ ɼ -12 Suction of coolant sea water in ş ɩ ɼ -14 Pollutants after CBO Suction of air in ş ɩ ɼ -24
Lab1 Lab2 ... Rec1 Rec2	Make the analysis on *Cl* after ş ɩ ɼ -12 Make the analysis on *Cl* after ş ɩ ɼ -14 ... Switch off the depressurized ş ɩ ɼ Switch off the faulty equipment
Pr1	
Conf	Conf *Cs1=1* Conf *Cs5.1=2* Conf *Cs5.2=2* Conf *Cs9=3*
Next Fr	FrBl2 «Condensate polishing system»

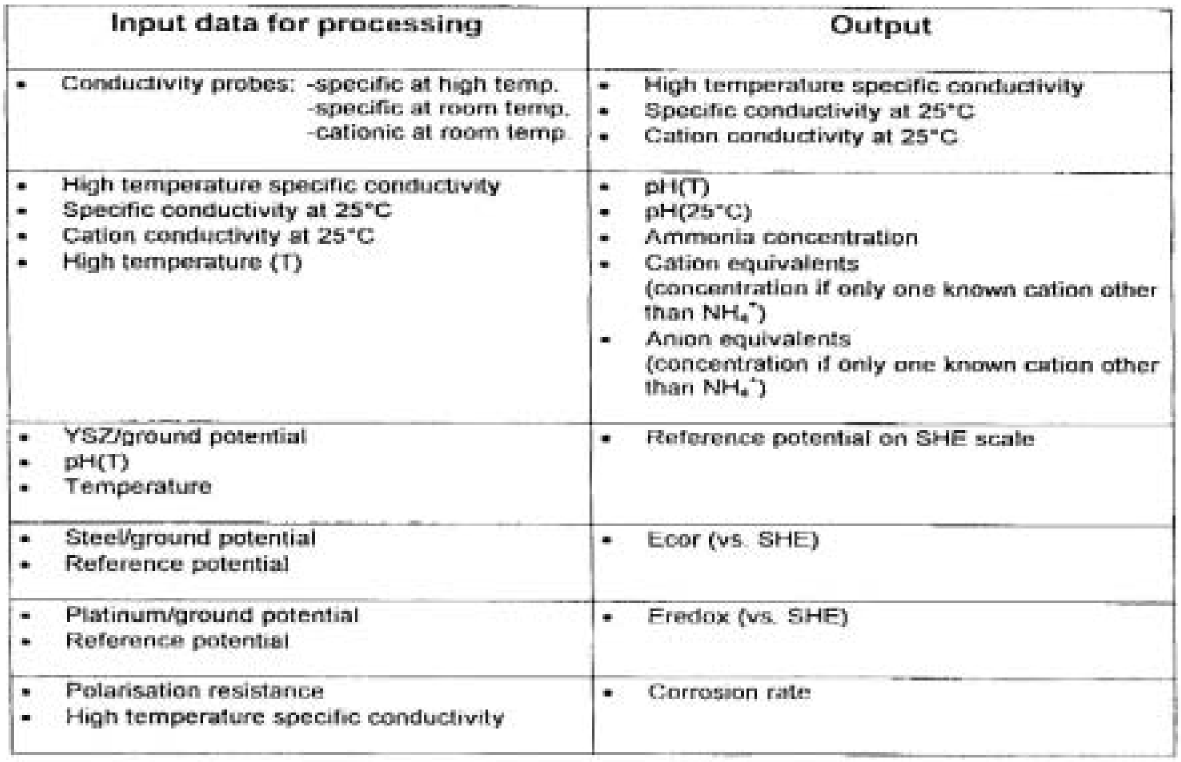
3.10. On-line monitoring of water chemistry and corrosion at conventional power stations by ENEL in Italy

ENEL has developed a comprehensive approach to on-line monitoring using electrochemical methods and has carried out both extensive laboratory work and measurements in several fossil-fired power stations (see Tables 8 and 9). Examples of the data obtained are given in Figs 67–68 and further details can be found in the literature (e.g. [79–81]).

ENEL concludes that monitoring of physio-chemical characteristics of operating fluids is a complex task to be necessarily performed to assure efficient, safe and economical plant operations, even if it represents a cost to optimise. Improvements are therefore to be carefully evaluated and very sound based on cycle chemistry knowledge to assure that the proper actions are implemented and the expected benefits will likely assure reasonable paybacks.

High temperature electrochemical methods have been proved to be very effective for this purpose and the results from ENEL applications to fossil units show the synergistic effect of applying this innovative monitoring technique and the related theoretical interpretation models for data processing: iron and copper alloys corrosion and corrosion products release to the operating fluid have been successfully predicted and monitored at different types of cycle chemistry (AVT and OT) and further correlation with plant operating conditions has been verified and explained on theoretical basis.

Table 8. Data treatment used recently by ENEL for on-line monitoring



Input data for processing	Output
▪ Conductivity probes: -specific at high temp. -specific at room temp. -cationic at room temp.	▪ High temperature specific conductivity ▪ Specific conductivity at 25°C ▪ Cation conductivity at 25°C
▪ High temperature specific conductivity ▪ Specific conductivity at 25°C ▪ Cation conductivity at 25°C ▪ High temperature (T)	▪ pH(T) ▪ pH(25°C) ▪ Ammonia concentration ▪ Cation equivalents (concentration if only one known cation other than NH_4^+) ▪ Anion equivalents (concentration if only one known cation other than NH_4^+)
▪ YSZ/ground potential ▪ pH(T) ▪ Temperature	▪ Reference potential on SHE scale
▪ Steel/ground potential ▪ Reference potential	▪ Ecor (vs. SHE)
▪ Platinum/ground potential ▪ Reference potential	▪ Eredox (vs. SHE)
▪ Polarisation resistance ▪ High temperature specific conductivity	▪ Corrosion rate

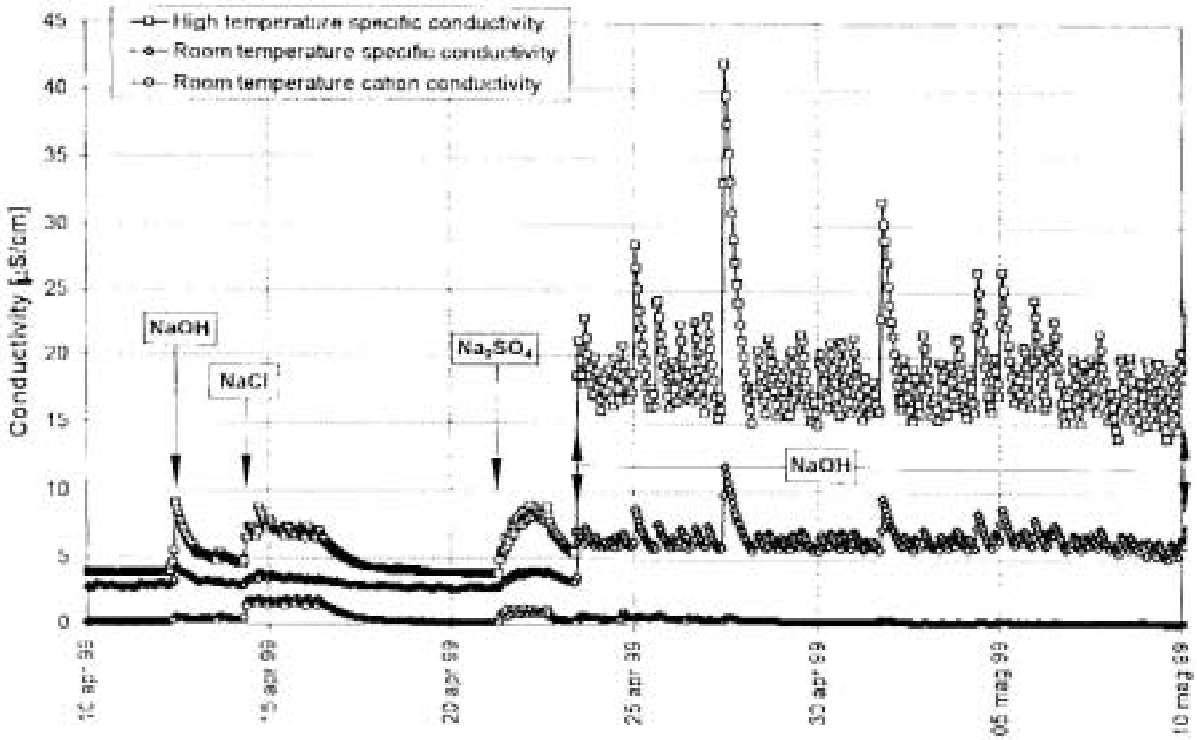


FIG. 67. HT and RT conductivity measurements at a fossil-fired Italian power station with AVT during investigations of the effect of impurity additions.

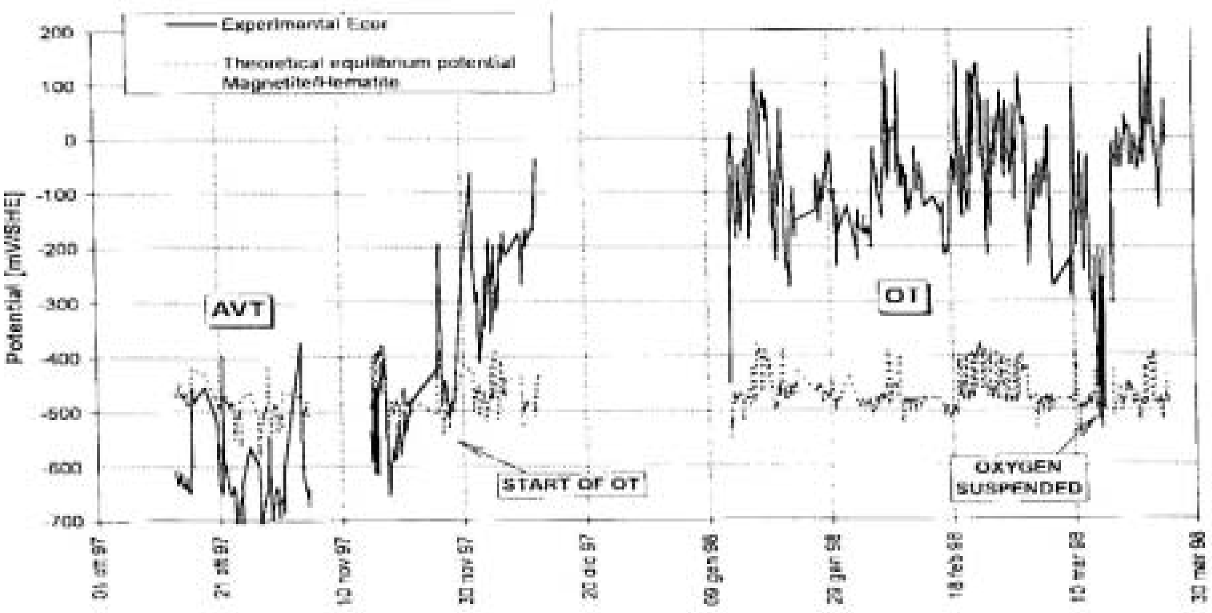
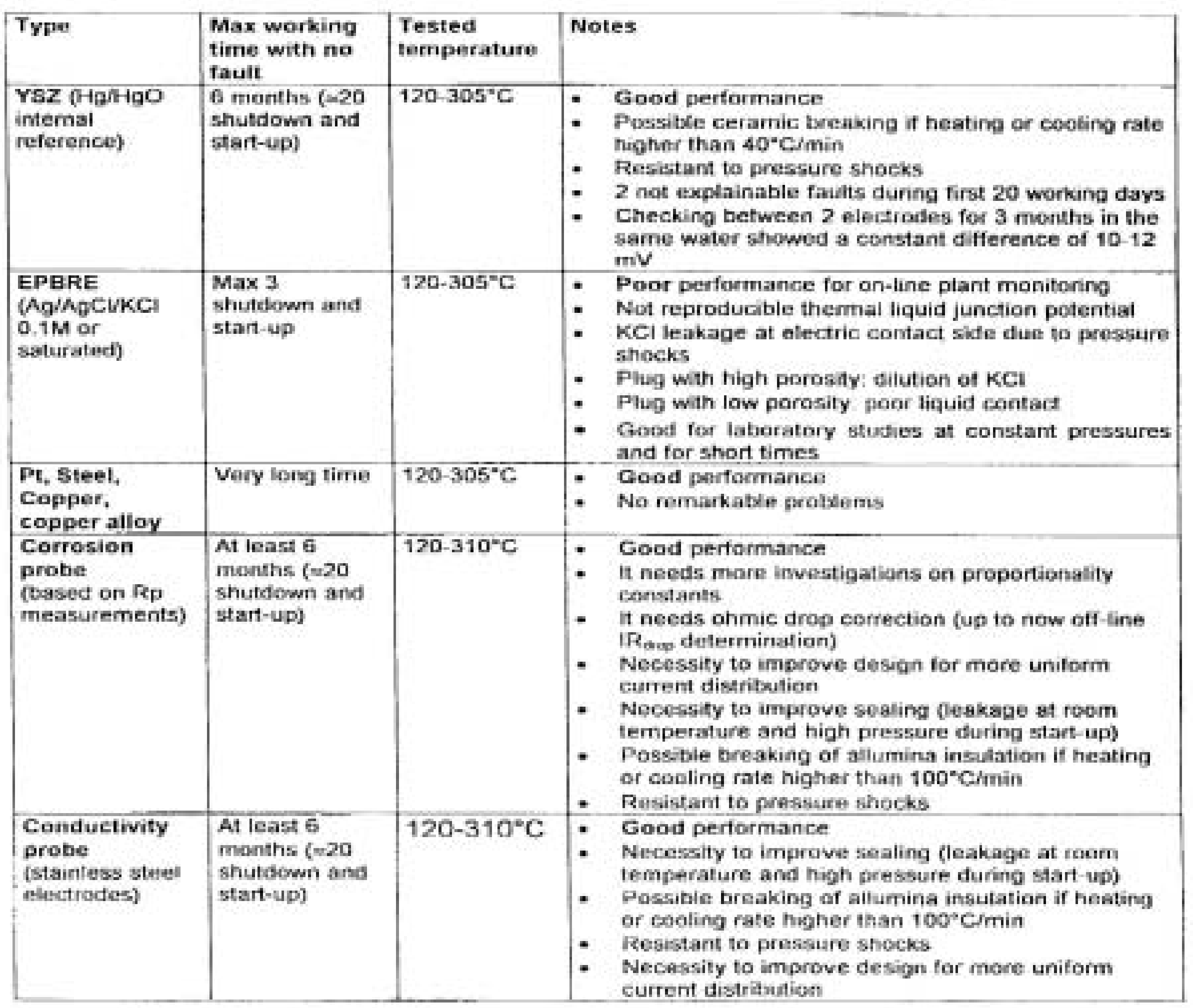


FIG. 68. ECP of low-alloy steel monitored at the boiler downcomer of a fossil-fired Italian power station firstly during AVT and then during oxygen treatment (OT).

4. CONCLUSIONS AND FUTURE DEVELOPMENTS

Until recently, the water chemistry in power plants has been monitored primarily either by on-line instruments in cooled sampling lines, or by taking samples from such lines at regular intervals and analysing them with off-line instruments. This approach has potential disadvantages associated with possible changes in the properties and composition of the water as a result of the sampling procedure, time delay in obtaining important information, and lack of completeness in the information obtained.

Table 9. Performance of on-line electrodes in monitoring by ENEL



Type	Max working time with no fault	Tested temperature	Notes
YSZ (Hg/HgO internal reference)	6 months (≈20 shutdown and start-up)	120-305°C	▪ **Good performance** ▪ Possible ceramic breaking if heating or cooling rate higher than 40°C/min ▪ Resistant to pressure shocks ▪ 2 not explainable faults during first 20 working days ▪ Checking between 2 electrodes for 3 months in the same water showed a constant difference of 10-12 mV
EPBRE (Ag/AgCl/KCl 0.1M or saturated)	Max 3 shutdown and start-up	120-305°C	▪ **Poor performance** for on-line plant monitoring ▪ Not reproducible thermal liquid junction potential ▪ KCl leakage at electric contact side due to pressure shocks ▪ Plug with high porosity: dilution of KCl ▪ Plug with low porosity: poor liquid contact ▪ Good for laboratory studies at constant pressures and for short times
Pt, Steel, Copper, copper alloy	Very long time	120-305°C	▪ **Good performance** ▪ No remarkable problems
Corrosion probe (based on Rp measurements)	At least 6 months (≈20 shutdown and start-up)	120-310°C	▪ **Good performance** ▪ It needs more investigations on proportionality constants ▪ It needs ohmic drop correction (up to now off-line IR_{drop} determination) ▪ Necessity to improve design for more uniform current distribution ▪ Necessity to improve sealing (leakage at room temperature and high pressure during start-up) ▪ Possible breaking of allumina insulation if heating or cooling rate higher than 100°C/min ▪ Resistant to pressure shocks
Conductivity probe (stainless steel electrodes)	At least 6 months (≈20 shutdown and start-up)	120-310°C	▪ **Good performance** ▪ Necessity to improve sealing (leakage at room temperature and high pressure during start-up) ▪ Possible breaking of allumina insulation if heating or cooling rate higher than 100°C/min ▪ Resistant to pressure shocks ▪ Necessity to improve design for more uniform current distribution

Such effects can be excluded a priori by performing the measurements in situ at high temperatures (HT), i.e. without changing the physical and chemical state of the reactor water. In addition, it is often possible to evaluate directly important effects of water-chemistry on material corrosion and radioactive transport. In the course of the WACOL CRP, an assessment was made of the extent to which such measurements have already been implemented in commercial and test reactors (see Section 2). Furthermore, close attention was paid to a variety of new techniques and sensors which are currently being developed (see Section 3). It is difficult to reach a clear consensus on the status of technology in this rapidly changing area, but the majority opinion of the WACOL participants was as follows.

The need for HT on-line monitoring on the *PWR primary side* has been less apparent than on the secondary side. Early measurements of electrochemical potential (ECP) in Sweden were discontinued. For the presently used PWR primary water chemistry with high hydrogen contents, electrochemical monitoring seems to be of limited practical value; the corrosion potentials coincide with the hydrogen equilibrium potentials and can be calculated. If considerably lower hydrogen contents were to be used in the future, in situ redox and corrosion potential monitoring would be helpful.

Although reliable HT pH sensors are available, their routine use on the primary side of PWRs would only be of value in transient situations, since the pH of the primary coolant is controlled very precisely during steady-state operation.

The only method in routine use in PWR plant at operating temperatures is in-line analysis for boron in primary coolant within the chemical and volume control system by neutron absorption. However, direct measurement of dissolved hydrogen is also being performed on a trial basis in a CANDU reactor (which uses heavy water).

The current status of monitoring efforts on the *PWR secondary side* is that ECP measurement, despite its long history, is still in the implementation stage and cannot yet be regarded as having attained widespread, routine use. Redox and corrosion potential measurements have often been carried out in commercial plants in various countries and reliable and robust sensors are available for in-plant installation, although laboratory "Round Robin" comparison tests have shown significant differences in the absolute value of the potential of the reference electrodes. The following aspects must be borne in mind with regard to more general implementation:

- It is an additional and new measurement parameter, i.e. there is no common reference in terms of specified values (normal values, target values, action values, etc.).
- Although having been frequently used in commercial plants, requirements on the measuring equipment have not been standardised.
- Price and other commercial aspects.

Other methods, such as HT pH and conductivity measurements, or heated-crevice tests in side-stream autoclaves, are used for special purposes. Direct measurement of corrosion phenomena (corrosion rate, oxide-film characteristics, cracking susceptibility etc.) has been studied in the laboratory, but it is not yet clear whether this will lead to plant implementation.

There has been more on-line monitoring performed in *BWRs* than in any other type of commercial reactor, driven primarily by the need to monitor improvements with regard to the stress corrosion cracking (SCC) behaviour of pressure-retaining and reactor-internal components. ECP measurement is the backbone technology for this, particularly in connection with the implementation of hydrogen water chemistry, which, by its very nature, lends itself to on-line monitoring. Installation of ECP sensors is then required of plant operators in the relevant EPRI water chemistry guidelines. It can be regarded as a well-developed technology, at least for out-of-core measurements, although opinions vary as to reliability, accuracy, and ease of conversion of data to the standard hydrogen scale, etc..

Despite ongoing efforts, no method is currently available for on-line monitoring of crack initiation through SCC. However, various methods for in situ determination of the tendency

for crack growth have been used in commercial reactors for nearly fifteen years, both in recirculation piping and side-stream autoclaves and, more occasionally, in-core (to monitor irradiation induced stress corrosion cracking (IASCC)). Such crack-growth monitors are able to provide valuable real-time information, e.g. on the effect of water-chemistry transients.
Optical methods and advanced electrochemical techniques (thin-film, contact electrical resistance, electrochemical noise, etc.) are proving very useful for mechanistic studies, but further development is required before their use as a plant sensor could be considered.

On-line monitoring of activity buildup using gamma spectroscopy has been successfully implemented in one BWR and appears to be a very promising technique.

In-core crack-growth-rate measurements are in use for IASCC studies at various *test reactors* and have also been performed in commercial plants, but they cannot yet be regarded as a routine monitoring tool. Various other monitoring techniques (ECP, in situ determination of dissolved gases, HT pH and conductivity, etc.) have also been studied in research reactors.

In the course of the WACOL programme, it became apparent that in situ monitoring is able to provide new and valuable information to plant operators. Such data can be obtained promptly (i.e. in real time) and with a high degree of accuracy. Reliable techniques and sensor devices are available which enable plant operators to obtain additional information on the response of nuclear plants to changes in coolant chemistry and the general behaviour of plant components and systems. These have the potential to permit optimisation of operational procedures and practices.

Despite the obvious benefits, the introduction of new and additional measurements in commercial plants is associated with additional work effort for the plant staff. Data must be collected, processed and evaluated. Moreover, the effects of operation of plant systems and subsystems on parameters such as corrosion and redox potentials can be rather complex, including temporary malfunctions. Full benefit from using on-line sensors in the real-time mode will only be obtained if sensor signals are collected and analysed with data acquisition and evaluation software in a computer-aided diagnosis system. Such intelligent systems have already been installed in commercial plants and the Agency is actively involved in ongoing developments in the context of a new CRP programme "DAWAC" (Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion Control in Water-Cooled NPPs).

ABBREVIATIONS

AC	alternating current
AVT	all volatile treatment
BAT	boric acid treatment
BOP	balance of plant
CAV	crack arrest verification
CDE	controlled distance electrochemistry
CDS	condensate demineralizing system
CEI	contact electric impedance
CER	contact electric resistance
CFD	condensate filter dimeneralizer
CP	corrosion product
CS	carbon steel
CW	condensate water
DAWAC	data processing technologies and diagnostics for water chemistry and corrosion control in water cooled reactors
DC	direct current
DEHA	diethylenhydrazineamine
DH	dissolved hydrogen
DIWA	diagnostic system for water chemistry (by Framatome-ANP, Germany)
DM	diagnostic model
DO	dissolved oxygen
DRS	diffuse reflection spectroscopy
DZO	depleted zinc oxide
EBA	enriched boric acid (treatment)
ECN	electric current noise
ECP	electrochemical corrosion potential
EDTA	ethylene diamine tetra acetic acid
EIS	electrochemical impedance spectroscopy
EMF	eletromagnetic force
EN	electrochemical noise
EPN	electric potential Noise
ETA	ethanolamine
FAC	flow assisted corrosion
FFCP	full flow condensate polisher
FW	feedwater
FWH	FeedWater heater
HT	high temperature
HTS	heat transport system
HWC	hydrogen water chemistry
IASCC	irradiation-assisted corrosion cracking
IGA/IGSCC	InterGranular Attack/InterGranular Stress-Corrosion Cracking
INCA	in-core assembly
LIMS	laboratory information management system
LOCA	loss of coolant accident
LOMI	low oxidation state metal ion (process developed by EPRI)
MCD	moisture separator drain
MPA	morpholine, ethanolamine and methoxyproPylAmine

MRC	molar ratio control
NMCA	noble metal chemical addition
NWC	normal water chemistry
OD	object of diagnostics
OLA	on-line activity (measurement)
OT	oxygen treatment
pH_{T}	high-temperature pH
RCCV	reinforced concrete containment vessel
PHTS	primary heat transport system
PTFE	polytetrafluorethylene
PWSCC	primary water stress-corrosion cracking
RDCPD	reversed direct current potential drop technique
Redox	reducing-oxidation
RHR	residual heat removal (system)
RPV	reactor pressure vessel
RT	room temperature
RWCU	reactor water cleanup (system)
SG	steam generator
SGBD	steam generator blowdown
SFDM	system of continuous water chemistry functional diagnostics and monitoring
SHE	standard hydrogen electrode
SS	stainless steel
SSRT	slow strain rate test
STP	standard temperature-pressure
TLEC	thin layer electrochemistry
UTLA	ultra thin layer activation (technique)
WACOL	high-temperature on-line monitoring of water chemistry and corrosion
WACOLIN	investigations on water chemistry control and coolant interaction with fuel and primary circuits materials in water-cooled power reactors
YSZ	yttrium stabilized zirconia

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Annex 1

PROGRAMME STATUS AT THE 1995 RCM IN PENN STATE UNIVERSITY, USA, AND LIST OF PRESENTATIONS MADE BY WACOL PARTICIPANTS

1. PROGRAMME STATUS

1.1. Measurement of electrochemical potential (ECP) — Task Leader: B. Stellwag

1.1.1. Technical justification

- corrosion processes are electrochemical in nature;
- ECP relates to potential/pH diagrams which provide thermodynamic background;
- connection between damage and ECP has been established;
- control of ECP may allow operation within a regime which minimises damage (e.g. ECP is specified in EPRI guidelines for BWR operation with hydrogen water chemistry);
- important for radiation field control;
- chemistry monitoring alone may be insufficient (e.g. to secure reducing conditions in critical areas on the secondary side of PWRs);
- determination in plant permits link-up with a large amount of R+D (laboratory) work where ECP was measured/controlled;
- ECP allows the calibration of damage models (if hydrodynamics and surface condition of the measured surface are well defined).

1.1.2. Practical requirements

- may be different in PWR primary, PWR secondary and BWR environments;
- lab requirements may sometimes be more severe (e.g. PWSCC experiments at up to 360 °C);
- possibly different requirements for out-of-core and in-core measurements (reference electrode (RE) must be Teflon free in-core);
- need, if possible, a RE which will produce data on a thermodynamic scale (SHE);
- long-term stability (>= 1 year) with drift better than accuracy;
- accuracy after conversion to SHE (minimum requirement of ± 25 mV);
- ability to calibrate (and re-calibrate) inside or outside plant (use multiple electrodes?);
- leak-tightness (pressure-retaining boundary), ruggedness (mechanical stability) and acceptability of materials of construction (e.g. Teflon) are key issues;
- must withstand temperature and pressure fluctuations/shocks;
- use of chloride-containing filling solution is not really an issue because of minute volume, unless fixed arbitrarily by authority requirements (need to inform plant personnel better);
- measurement location is critical: preferably in situ (difficult if corrosion conditions are localised); when ex-situ (e.g. side-stream autoclave), back calibration with an appropriate model is required.

1.1.3. Current status/problems encountered

- External, pressure-balanced Ag/AgCl RE:
  - 4 various designs have been used in plant (e.g. filling solutions from sat. KCl to pure water);
  - 4 locations include BWR, PWR secondary and primary sides, but not, of course, in-core;
  - 4 several types are commercially available (e.g. NWT, VTT, Studsvik, Siemens, GE);
  - 4 calibration to thermodynamic scale possible if thermal liquid junction potential is reproducible;
  - 4 dilution of filling solution through loss of KCl affects accuracy;
  - 4 high resistance across junction can cause problems with stray currents in low-leakage designs;
  - 4 differences of opinion on long-term stability (majority thinks 1 year possible);
  - 4 quasi-calibration (cross-checking) possible;
  - 4 EPRI source book available (primarily BWR) + newer EPRI report (Millett) on PWR.

- Internal Ag/AgCl RE:
  - 4 used succesfully in lab and plant (including in-core measurements);
  - 4 some concerns on stability (e.g. influence of redox reactions).

- Internal Pt or Pd RE:
  - 4 not a true reference electrode;
  - 4 ability to convert to thermodynamic scale, stability, accuracy etc. all depend on the immediate environment;
  - 4 encouraging results reported from Halden on a Pd electrode with a sintered Pt shield and internal hydrogen charging (VTT design).

- Other internal reference electrodes:

  - 4 Ytrium stabilised zirconia functions as a pseudo-reference electrode when the pH is known;
  - 4 this has been used in plant without encountering ceramic cracking or ceramic-metal brazing problems.

1.1.4. Specific recommendations

- need to develop a solid-state RE so as to obtain reproducible thermal liquid junction potentials;
- Teflon-free electrodes with improved irradiation resistance required in-core;
- longer-term stability needs to be improved;
- will require individual calibration standards for different plant locations.

1.1.5. Written submissions from participants

- B. Stellwag (Germany): "ECP monitoring in NPP coolant systems";
- K. Mäkelä (Finland/Norway): "High temperature in-line ECP measurements";

- D.D. Macdonald, et al. (USA): "Development of sensors for in situ monitoring of corrosion and water chemistry parameters for the electric power utility industry";
- D.D. Macdonald, et al. (USA): "Monitoring corrosion and chemistry phenomena in supercritical aqueous sytems";
- S.N. Lvov, D.D. Macdonald (USA): "Estimation of the thermal liquid junction potential of an external pressure balanced reference electrode";
- D.D. Macdonald, M. Urquidi-Macdonald (USA): "On the interpretation of ECP data from boiling water reactors operating under hydrogen water chemistry conditions";
- J.K. Pettersen (Norway): "Development of in-core miniature ECP sensor";
- G. Perboni, M. Broglia (Italy): "Validation of electrochemical systems for on line monitoring of steam generator water in operating conditions";
- K. Mäkelä, et al. (Finland): "The effect of the new feedwater distributor design on the impurity concentrations in one of the Loviisa 2 unit steam generators";
- A. Molander, B. Rosborg (Sweden): "In plant redox and corrosion potential monitoring".

1.2. **Measurement of HT-conductivity** — Task Leader: K. Mäkelä

1.2.1. Technical justification

- lack of dissociation constants for chemical species (proper models, e.g. for stress corrosion cracking, use HT data in calculations and laboratory tests should include HT conductivity measurements);
- avoidance of distorting effects of long sampling lines, such as reactions between chemical species and sampling line walls or corrosion products, etc.;
- may enable greater precision (e.g. for control of NH_3 dosage);
- improved control of crevice chemistry in laboratory work (link to modelling);
- lack of information on equivalent conductivities for most ionic species (leads to difficulties in estimating (modelling) the true “resistance” of environments at high temperature).

1.2.2. Practical requirements

- same requirements on leak-tightness and mechanical/thermal stability as for reference electrodes (see Section II.1.2);
- should not be affected by absorbed corrosion products (electrode fouling) or polarisation (from the measurement itself);
- long-term stability.

1.2.3. Current status/problems encountered

- has been used extensively in laboratories and test reactors (Finland, Sweden, USA);
- has been used in conventional power plant in feedwater during all volatile treatment (AVT);
- has been used in PWRs on the secondary side;
- was used by ABB in the reactor water of BWRs (recirculation loop) for up to 2 years in the Eighties;
- BWR use discontinued because of lack of apparent advantages (with current water chemistry practices, HT conductivity measurement does not give additional information due to the higher background conductivity);

- problems have occurred with deterioration of the insulation and electrode fouling (latter may be mitigated by 4-electrode design).

1.2.4. *Specific recommendations*

- plant-specific comparison is required between low and high temperature data;
- for the PWR secondary side, HT conductivity measurements can be used to verify the calculated high temperature values;
- examine possible use for determination of local conductivities (e.g. in crevices);
- re-assess for BWRs if water chemistry is changed from ultra high purity water.

1.2.5. *Written submissions from participants*

- K. Mäkelä (Finland/Norway): "High temperature in-line conductivity measurements";
- V.G. Kritsky, et al. (Russia): "Concept of organizing automated primary coolant chemistry control at NPPs of new generation with VVER-640 type reactors";
- L.B. Kriksunov, D.D. Macdonald (USA): "Advances in measuring chemistry parameters in high temperature aqueous systems".

1.3. **Measurement of HT pH values (pH_T)** — Task Leader: K. Mäkelä.

1.3.1. *Technical justification*

- deposition of dissolved corrosion products depends on pH_T of the coolant and therefore this is an important parameter to know and follow;
- stability of metal oxides does not only depend on ECP but also on pH_T, thus linking pH_T to activity buildup;
- on-line measurements do not suffer from sampling-line effects and can be used to indicate possible transients faster than calculated pH_T values (which are always based on grab sample analysis);
- measurement of pH_T for localised chemistries (e.g. in crevices on the PWR secondary side) could be a powerful tool to control/avoid corrosion damage.

1.3.2. *Practical requirements*

- same requirements on leak-tightness and mechanical/thermal stability as for reference electrodes (see Section II.1.2);
- accuracy of the measurement depends on the accuracy of the associated reference electrode (detection limit for pH sensor itself is ±0.05 pH units);
- required accuracy will depend upon the exact application/situation: currently power plants operate with narrow range pH_T control, which requires knowledge of pH_T within 0.2 pH units. Therefore accuracy of the measurement should be significantly better than this. However, in crevices, e.g. ± 0.5 pH units would be excellent!

1.3.3. *Current status/problems encountered*

- has been used in PWRs on primary side. However, since the pH_T of the primary coolant is controlled very precisely during *steady state operation*, calculated values are at least as good as pH_T measurements. Additional information was obtained upon plant shutdown;

- has been used in PWRs on secondary side to follow the changes in pH_T during dosage of different amines;
- has been used in-core in BWRs as a quasi reference electrode;
- has been used extensively in laboratories (including simulated crevice situations) and test reactors.

1.3.4. Specific recommendations

- for PWRs on the primary side, attention should be concentrated on *transient situations*, since it has been shown during shutdown that pH_T measurements were more sensitive to the changes in water chemistry parameters than the RT measurements;
- because oxide properties also depend on $pH_{T,}$ and since decomposition of different amines on the secondary side of PWRs can be plant specific, additional information may be obtained by using high temperature measurements in some circumstances;
- with current water chemistry practices in BWRs, high temperature pH_T measurements do not give additional information, because it is possible to calculate accurately the pH-value of high purity water as a function of temperature. However, if BWR water chemistry is changed, the importance of in-line pH_T measurements should be re-evaluated;
- possibility of useful crevice measurements should be actively pursued (miniaturisation required).

1.3.5. Written submissions from participants

- K. Mäkelä (Finland/Norway): "High temperature in-line pH measurements";
- V.G. Kritsky, et al. (Russia): "Concept of organizing automated primary coolant chemistry control at NPPs of new generation with VVER-640 type reactors";
- D.D. Macdonald, et al. (USA): "Development of sensors for in situ monitoring of corrosion and water chemistry parameters for the electric power utility industry";
- D.D. Macdonald, et al. (USA): "Monitoring corrosion and chemistry phenomena in supercritical aqueous sytems";
- L.B. Kriksunov, D.D. Macdonald (USA): "Advances in measuring chemistry parameters in high temperature aqueous systems";
- K. Ishigure, et al. (Japan): "Measurements of pH in high temperature water using commercial YSZ sensor system";
- G. Perboni, M. Broglia (Italy): "Validation of electrochemical systems for on line monitoring of steam generator water in operating conditions".

1.4. **Measurement of dissolved gases and chemical species** — Task Leader: H.-P. Alder

1.4.1. Technical justification

- as for reference electrodes, require water chemistry regime to prevent damage and these measurements may replace or complement ECP in some systems (e.g. CANDU primary circuit);
- important for radiation field control;
- needed for modelling work (feedback to R&D).

1.4.2. Practical requirements

- long-term stability (1 year);
- accuracy ±2%.

1.4.3. Current status/problems encountered

- HT H_2 sensor has been used in PWR and will be used in CANDU;
- O_2 sensor is used in laboratories but not at sufficiently high temperatures. Significant R&D effort is required here;
- some ideas exist for a H_2O_2 sensor.

1.4.4. Specific recommendations

- measurement of the concentration of oxidising species (e.g. H_2O_2) is urgently required for modelling work;
- need sampling lines which do not change radiolysis product concentrations;
- O_2 measurements should be attempted in the condenser and feedtrain (e.g. deaerator).

1.4.5. Written submissions from participants

- H.-P. Alder (Switzerland): "Review of the role and analysis of radiolysis products in the boiling water reactor";
- D.D. Macdonald, et al. (USA): "Development of sensors for in situ monitoring of corrosion and water chemistry parameters for the electric power utility industry";
- D.D. Macdonald, et al. (USA): "Monitoring corrosion and chemistry phenomena in supercritical aqueous sytems";
- T.-K. Yeh, D.D. Macdonald (USA): "Modeling materials damage in the BWR heat transport circuits";
- K. Mäkelä (Finland): "High temperature in-line O_2/H_2 measurements";
- J. Kysela, J. Srank (Czech Republic): "Testing of high-temperature sensor for water chemistry monitoring";
- L. Yang, et al. (Canada): "Palladium resistance probe for monitoring dissolved hydrogen in the primary CANDU coolant".

1.5. **Particle measurement (optical methods)** — Task Leader: H.-P. Alder

1.5.1. Technical justification

- optical methods can be applied for several purposes (e.g. to determine surface condition of austenitic materials, organic carbon concentration, particle measurement);
- useful for investigation of activity transport and deposition (e.g. when materials change polarity).

1.5.2. Practical requirements

- not yet clarified.

1.5.3. Current status/problems encountered

- promising results achieved in laboratory studies.

1.5.4. Specific recommendations

- continuation of research effort.

1.5.5. Written submissions from participants

- H.-P. Alder (Switzerland): "Non-invasive monitoring of LWR water chemistry by optical methods";
- L. Fuks (Poland): "Materials for in situ monitoring of light water reactor (LWR) chemistry by optical methods".

1.6. **Measurement of crack growth rate** — Task Leader: J. Hickling

1.6.1. Technical justification

- direct measurement of damage due to stress corrosion cracking (SCC) and/or corrosion fatigue (CF) if mechanical loading conditions are appropriate;
- allows real-time verification of system integrity and determination of safety margins (e.g. success of damage-prevention strategies such as HWC in BWRs, avoidance of undue conservatism associated with some lab data);
- permits direct assessment of the effect of plant transients and can contribute to a plant life extension strategy;
- allows verification of modelling work (e.g. identification of "weak points");
- can be used for assessment of alternate materials.

1.6.2. Practical requirements

- measurement must be reliable and representative (material condition, mechanical loading, chemistry and hydrodynamics of environment, etc.);
- sensitivity of physical crack length determination must be high to separate out transient effects;
- monitoring system must not intefere with plant operation (e.g. loose-parts concerns, etc.).

1.6.3. Current status/problems encountered

- extensive experience in laboratories and test reactors;
- routinely used in BWRs (commercial systems available);
- development and optimisation still ongoing (particularly for in-core IASCC applications);
- difficulties have been experienced in installing sensors in the appropriate positions;
- data evaluation is complex and may lead to "false alarms" in terms of actual component behavior (e.g. methods take no account of crack initiation behaviour, crack geometry in sensor may not be realistic, data may exhibit considerable scatter, etc.);
- in situ measurements are considered expensive by plant operators.

1.6.4. Specific recommendations

- examine improved sensor geometries to better simulate real cracks (i.e. give less conservative cracking response);
- investigate complementary techniques to monitor crack initiation;
- emphasise the "educational" aspects of such measurements for plant operators (i.e. they make improvements in plant operation "visible").

1.6.5. Written submissions from participants

- J. Hickling (UK): "Recent work in the field of on-line corrosion monitoring with particular reference to the detection of environmentally assisted cracking (EAC)";
- D.D. Macdonald, et al. (USA): "Theoretical estimation of crack growth rates in type 304 stainless steel in BWR coolant environments";
- J.K. Pettersen (Norway): "In-core crack growth rate sensors".

1.7. **Measurement of electrochemical noise (EN) —** Task Leader: J. Hickling.

1.7.1. Technical justification

- a genuine "real-time" technique which is basically simple and highly sensitive;
- minimally intrusive (sensors are robust and do not need a true RE);
- potentially suitable to monitor the *initiation* of damage;
- can provide information on *localised* corrosion processes (e.g. pitting, cracking);
- may give mechanistic information with more sophisticated signal analysis.

1.7.2. Practical requirements

- choice of appropriate hardware (sensors, instrumentation) and data-evaluation software;
- access to relevant locations in plant.

1.7.3. Current status/problems encountered

- commercial systems available;
- used successfully in situ at various locations in fossil plants and in conventional areas (e.g. cooling-water heat exchangers) of nuclear plant;
- on-line monitoring for atmospheric corrosion (inc. SCC) of structural materials carried out long-term in the calandria vault of a CANDU reactor;
- used to verify absence of corrosion during decontamination/steam generator (SG) cleaning operations in PWRs;
- extensive lab. studies for nuclear applications (e.g. SG crevice corrosion, SCC in BWRs) ongoing;
- resistance encountered to wide-scale use in the nuclear field for a number of reasons (e.g. lack of acceptance of theoretical basis for the measurement, difficulties in data handling and signal interpretation etc.).

1.7.4. Specific recommendations

- standardisation needed in measurement techniques and signal processing(ASTM efforts in progress here);
- further research, including application of sophisticated techniques such as pattern recognition, neural networks, fuzzy logic, etc. should be encouraged to provide the end-user with more assistance in data interpretation;
- use of the technique in a test reactor should be supported.

1.7.5. Written submissions from participants

- J. Hickling (UK): "Electrochemical noise";
- D.D. Macdonald, et al. (USA): "Development of sensors for in situ monitoring of corrosion and water chemistry parameters for the electric power utility industry";
- D.D. Macdonald, et al. (USA): "Monitoring corrosion and chemistry phenomena in supercritical aqueous sytems";
- C. Liu, et al. (USA): "Electrochemical noise analysis for monitoring corrosion activity in SCWO systems";
- C. Liu, et al. (USA): "Probing corrosion activity in high subcritical and supercritical water through electrochemical noise analysis".

1.8. Measurement of impedance — Task Leader: D.D. Macdonald

"Impedance" is used here in its broadest sense, i.e. covering the linear polarization method, AC measurements and special developments such as the "Contact Electric Resistance" (CER) technique. The latter formed the main focus of discussion at the CRM, as reflected in the following.

1.8.1. Technical justification

- impedance measurements provide fundamental electrochemical information, since all corrosion phenomena involve interaction between the surface and the environment. At the moment both the scientific understanding of corrosion processes and the engineering practices of corrosion control in power plants can benefit considerably from the development of in situ, on-line instruments capable of characterising the surface films on constructional materials.
- the specific CER technique has been developed to measure the electric resistance of surface films, which is a basic physical parameter widely used in different applications for characterisation of materials.

1.8.2. Practical requirements

- the general material requirements for CER measurements are the same as for reference electrodes;
- the technique can be used up to a maximum operational pressure of 300 bars and a temperature of 1000 °C;
- the accuracy of the measurement is 10^{-9} T, which has been shown to be equivalent to 0.03 monolayers in thickness of the surface layer in the case of copper metal.

1.8.3. Current status/problems encountered

- impedance measurements generally are a valuable research tool in the laboratory, but have not been widely used for field measurements, primarily because data interpretation is complex and the techniques are difficult to apply with non-steady-state systems. They are also of limited use where localised corrosion is involved. However, the paper by Kritsky gives information on their use for corrosion rate measurements on carbon and stainless steels in the feedwater train of a RBMK-type reactor;

- the CER measurement technique has been used in simulated nuclear environments in the laboratory within the following research areas:
  - monitoring of oxide growth on fuel cladding materials in both PWR and BWR environments;
  - characterisation of the oxide on fuel cladding after a four year in-plant service;
  - determining the effect of Zn injection on properties of the oxides on different PWR primary loop materials;
  - analysing the effect of water chemistry variables (B, Li, SO_4^{2-}, H_2, ...) on the electric properties of the surface film on Alloy 600;
  - characterisation of the surface films on Alloy 600 from different crevice environments of a steam generator;
  - assessing the effect of potential inhibitors for IGSCC on the surface films on Alloy 600.
- CER measurements at the plant have been performed in other industrial areas and negotiations are presently underway with two nuclear utilities.

1.8.4. Specific recommendations

- The CER technique appears especially promising and further development is encouraged, particularly in the following areas:
  - activity buildup (including the effects of Zn additions);
  - monitoring decontamination processes;
  - investigating SCC susceptibility of Alloy 600 SG tubing;
  - optimising PWR secondary water chemistry.

1.8.5. Written submissions from participants

- V.G. Kritsky (Russia): "Brief report on impedance and polarization technique";
- U. Ehrnstén, et al. (Finland): "Characterisation of material behavior by means of simultaneous monitoring of water chemistry and of surface film electric resistance";
- J. Piippo, et al. (Finland): "Influence of zinc on properties and growth of oxide layers in simulated primary coolant".

1.9. Other methods — Task Leader: J. Kysela

The following techniques were included in a general discussion at the end of the CRM of other methods to improve corrosion and coolant technology control:

- **on-line analyzers for various species** (to avoid problems with sampling techniques and location, length and size of sampling lines, delay in obtaining data and discrepancies caused by different off-line analytical procedures);
- **ion chromatography** (in particular for measurements of corrosion products);

- **determination of organic carbon concentration** (e.g. as related to QA procedures involving analytical methods for make-up water);
- **gamma spectrometry** (e.g. for continuous measurements on primary piping).

Further consideration of these methods is expected during the course of the WACOL CRP.

1.9.1. Written submissions from participants

- M. Ullberg (Sweden): "Why monitor chemistry and corrosion?";
- W. Metzner, B. Stellwag (Germany): "Advanced on-line chemistry monitoring concept".

2. OVERALL LIST OF WRITTEN SUBMISSIONS REFERENCED

- B. Stellwag (Germany): "ECP monitoring in NPP coolant systems";
- K. Mäkelä (Finland/Norway): "High temperature in-line ECP measurements";
- D.D. Macdonald, et al. (USA): "Development of sensors for in-situ monitoring of corrosion and water chemistry parameters for the electric power utility industry";
- S.N. Lvov, D.D. Macdonald (USA): "Estimation of the thermal liquid junction potential of an external pressure balanced reference electrode";
- D.D. Macdonald, M. Urquidi-Macdonald (USA): "On the interpretation of ECP data from boiling water reactors operating under hydrogen water chemistry conditions";
- J.K. Pettersen (Norway): "Development of in-core miniature ECP sensor";
- G. Perboni, M. Broglia (Italy): "Validation of electrochemical systems for on line monitoring of steam generator water in operating conditions";
- K. Mäkelä, et al. (Finland): "The effect of the new feedwater distributor design on the impurity concentrations in one of the Loviisa 2 unit steam generators";
- A. Molander, B. Rosborg (Sweden): "In plant redox and corrosion potential monitoring";
- K. Mäkelä (Finland/Norway): "High temperature in-line conductivity measurements";
- V.G. Kritsky, et al. (Russia): "Concept of organizing automated primary coolant chemistry control at NPPs of new generation with VVER-640 type reactors";
- D.D. Macdonald, et al. (USA): "Monitoring corrosion and chemistry phenomena in supercritical aqueous sytems";
- L.B. Kriksunov, D.D. Macdonald (USA): "Advances in measuring chemistry parameters in high temperature aqueous systems";
- K. Ishigure, et al. (Japan): "Measurements of pH in high temperature water using commercial YSZ sensor system";
- K. Mäkelä (Finland/Norway): "High temperature in-line pH measurements";
- H.-P. Alder (Switzerland): "Review of the role and analysis of radiolysis products in the boiling water reactor";
- T.-K. Yeh, D.D. Macdonald (USA): "Modeling materials damage in the BWR heat transport circuits";
- K. Mäkelä (Finland/Norway): "High temperature in-line O_2/H_2 measurements";
- J. Kysela, J. Srank (Czech Republic): "Testing of high-temperature sensor for water chemistry monitoring";
- L. Yang, et al. (Canada): "Palladium resistance probe for monitoring dissolved hydrogen in the primary CANDU coolant";

- H.-P. Alder (Switzerland): "Non-invasive monitoring of LWR water chemistry by optical methods";
- L. Fuks (Poland): "Materials for in-situ monitoring of light water reactor (LWR) chemistry by optical methods";
- J. Hickling (UK): "Recent work in the field of on-line corrosion monitoring with particular reference to the detection of environmentally assisted cracking (EAC)";
- D.D. Macdonald, et al. (USA): "Theoretical estimation of crack growth rates in type 304 stainless steel in BWR coolant environments";
- J.K. Pettersen (Norway): "In-core crack growth rate sensors";
- J. Hickling (UK): "Electrochemical noise";
- C. Liu, et al. (USA): "Electrochemical noise analysis for monitoring corrosion activity in SCWO systems";
- C. Liu, et al. (USA): "Probing corrosion activity in high subcritical and supercritical water through electrochemical noise analysis";
- V.G. Kritsky (Russia): "Brief report on impedance and polarization technique";
- U. Ehrnstén, et al.: "Characterisation of material behavior by means of simultaneous monitoring of water chemistry and of surface film electric resistance";
- J. Piippo, et al. (Finland): "Influence of zinc on properties and growth of oxide layers in simulated primary coolant";
- M. Ullberg (Sweden): "Why monitor chemistry and corrosion?";
- W. Metzner, B. Stellwag (Germany): "Advanced on-line chemistry monitoring concept".

Annex 2

PROGRAMME STATUS AT THE 1997 RCM IN VIENNA, AUSTRIA, AND LIST OF PRESENTATIONS MADE BY WACOL PARTICIPANTS

1. STATUS OF ON-LINE MONITORING IN THE CONTEXT OF THE WACOL PROGRAM

1.1. PWR primary side

With regard to the technical motivation for on-line monitoring in PWR plants on the primary side, the following conclusions can be drawn:

Direct oxygen monitoring is of interest because the existing measurement off-line does not correspond to the real conditions in the primary circuit (time delay in sampling line, absorption and desorption in the line can falsify the data). Furthermore, it would enable detection of oxygen spikes during system feeding.

Direct hydrogen monitoring is also of interest because of the time delay in the sampling line. Furthermore, there are uncertainties in the radiolysis models as to the lowest possible hydrogen concentrations which are necessary to suppress oxygen formation.

pH_T measurement is attractive in optimising water chemistry for control of activity buildup.

On-line measurement of the actual ^{10}B concentration in the primary coolant is an attractive water chemistry control feature.

Monitoring (e.g. investigation and evaluation of IASCC, PWSCC and Zircaloy corrosion by electrochemical and other methods) is desirable to follow the corrosion of structural materials.

Investigation of the corrosion layer and activity transport (e.g. by electrochemical and surface measurement techniques) is required to reduce activity buildup.

Overall, however, it is more difficult to persuade PWR operators of the need for monitoring here than on the secondary side.

1.2. PWR secondary side

On the secondary side of PWRs, it seems fair to state that high-temperature, on-line monitoring of water chemistry and corrosion is motivated primarily by the need to gain information so as to secure satisfactory operation of the steam generators. For this purpose, monitoring of corrosion and redox potentials, oxygen, hydrazine, pH and perhaps other parameters, such as state of oxide layers or tendency for ongoing corrosion processes, can be considered. The key question is to determine how and where the monitoring should be performed (in the feedwater piping, side-stream autoclaves or boilers with heated crevices, inside the steam generators themselves, or in the blow-down). E.g. whereas pH_T measurements in heated crevices are of definite interest, pH_T in feedwater is not required. In-pipe monitoring is generally preferable to monitoring in side-stream autoclaves because of the ever-present problems of changes in sampling lines (e.g. known inadequacy of oxygen monitoring in SG feedwater using long sampling lines).

A further motivating factor is the need to ensure compatibility between SG and balance-of-plant chemistries.

ECP monitoring is of prime interest, both in bulk water and in heated crevices, but improved (more reliable) reference electrodes are required (in the latter case miniaturised). On-line measurement in final feedwater is probably a priority item here, both to ensure correct redox conditions in the SG and to optimise N_2H_4 dosing.

HT measurement of steam conductivity (at an optimum temperature of around 150 °C) would bring advantages by achieving better NH_3/N_2H_4 (and thus pH) control.

The current status of monitoring efforts on the PWR secondary side is that ECP measurement, despite its long history, is still in the qualification stage and cannot be regarded as having attained routine implementation. Incorporation of on-line data into an integrated, computer-aided diagnosis system may be advantageous here. With the recent installation at Ohi 1, heated-crevice devices have just left the development stage and are undergoing qualification.

1.3. BWR

Stress corrosion cracking (SCC) problems in boiling water reactor plants are an important driving force for implementing on-line monitoring: of the ten presentations in the BWR session, four were related to the measurement of electrochemical corrosion potential (ECP) in operating reactors and three others to ECP measurements in test reactors. With regard to ECP monitoring in-core, it appears that this is still at the development stage, with an accurate, long-term measurement capability under irradiation not yet available.

Concerning ECP measurements outside the reactor pressure vessel, a number of electrode designs are commercially available and have been implemented in operating plant. Sometimes, the reference electrodes are actually primary pH electrodes, which make use of the virtually constant pH in the BWR coolant to provide measurements of ECP and redox potential. The main concern being addressed is correct implementation of hydrogen water chemistry (HWC) in those plants which have chosen to go to this as a SCC counter-measure. However, several participants also regarded such measurements as of more general value as a complement to the conventional determination of water chemistry, particularly with regard to the effects of transient conditions. Opinions were divided with regard to the present reliability of such ECP measurements in operating BWRs: the Japanese delegate, in particular, reported that the experience to date in his country was unsatisfactory. In the discussion, it was suggested that a "Round Robin" test of commercially available electrodes under realistic BWR conditions might be of considerable value here.

Several delegates commented that although ECP was clearly the dominant monitoring technique at present in BWRs, it was only of real use in conjunction with modelling activities. Opinions varied as to the status of these: apart from difficulties associated with inputting correct flow dynamics, there is a lack of fundamental electrochemical data (e.g. for exchange current densities on oxide-covered surfaces). It was suggested that the application of neural networks would be of value in improving present ECP and radiolysis models.

Several presentations in the BWR session described on-going development work in connection with other techniques for the mitigation of SCC. Electrochemical noise is being used in an attempt to develop a sensor to determine crack initiation times. Measurements of crack growth rate on actively loaded, pre-cracked, fracture mechanics specimens are already routinely performed in plant using bypass autoclaves. Work is also ongoing at two test reactors to make similar measurements available in-core for monitoring irradiation assisted SCC.

The second main issue driving on-line monitoring development in BWRs is activity buildup. One participant described the successful use of continuous, on-line, gamma spectroscopy at an operating reactor to understand water-chemistry effects. He commented, however, that more information is needed on actual corrosion rates to relate to the modelling of activity buildup. A novel optical technique for monitoring oxide layer growth on-line is currently under development as part of the WACOL program and may eventually be able to provide such information. Other relevant measurements currently being studied in the laboratory include the determination of contact resistance and electrochemical impedance at oxide-covered surfaces.

In general, it appears that high temperature pH and conductivity monitoring is not actively being pursued for BWR applications.

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- R. Riess, F. Roumiguiere (Germany): "Technical Review of Aims and Scope of WACOL Program".
- J. Kysela (Czech Republic): "Technical Motivation for On-line Monitoring in Plant: PWR Primary Side".
- R. Van Nieuwenhove (Belgium): "Sensor Development Work at the Corrosion Group of SCK/CEN".
- D.S. Mancey (Canada): "Monitoring with Microelectrodes".
- F. Jiang, D.R. Morris, D.H. Lister, J.M. McInerney (Canada): "Electrochemical Sensor for Monitoring Hydrogen and Oxygen in Water at High Temperature".
- L. Yang, D. Sun, D.S. Mancey (Canada): "A Palladium Probe for Dissolved Hydrogen in the Primary Heat Transport Coolant of CANDU Reactor".
- K. Mäkelä, et al. (Finland): "Oxide Films in High Temperature Aqueous Environments".
- D. Noel (France): "Several Techniques of Monitoring in PWR Primary Side".
- F. Roumiguiere, et al. (Germany): "COMBO — Continuous Boron Concentration Measuring System".
- V.G. Kritski, et al. (Russian Federation): "Technical Motivation for On-Line Monitoring in NPP".
- Molander, B. Rosborg (Sweden): "Electrochemical Monitoring" (Part I).
- H. Starkie, et al. (United Kingdom): "The Direct Measurement of the pH of Aqueous Solutions under PWR Primary Circuit Conditions".
- D.D. Macdonald (USA): "Measurement of [H_2] and [O_2]".
- R. Kilian, et al. (Germany): "Corrosion and Redox Potential Measurements in German Pressurised and Boiling Water Reactors.
- D. Noel, et al. (France): "Secondary Water".
- G. Perboni (Italy): "Applications of High Temperature Electrochemical Techniques to Power Plants".
- Molander, B. Rosborg (Sweden): "Electrochemical Monitoring" (Part II).
- D.D. Macdonald (USA): "Sensors for Chemical and Electrochemical Measurements in Power Plant Coolant Circuits".

- J.B. Lumsden (USA): "Steam Generator Monitoring using a Heated Crevice Model".
- J.B. Lumsden, et al. (USA): "Hideout in Prototypic Tube/Tube Support Plate Heated Crevices", Proc. 8th Int. Symp. on Env. Degr. of Materials in Nuclear Power Systems — Water Reactors, Pub. ANS (1997) 108–112.
- F. Roumiguiere, W. Metzner (Germany): "DIWA — The Siemens Expert System for Chemistry Diagnosis in PWR Plants.
- Z. Pingzhu, H. Shilin, Z. Weiguo (China): "High Temperature On-Line Monitoring of Conductivity and Electrochemical Noise — On-Line Monitoring Aqueous Solution Conductivity".
- M. Ullberg (Sweden): "On-Line Monitoring of Activity Build-Up.
- L. Fuks (Poland): "Materials for In-Situ Monitoring of Light Water Reactor (LWR) Water Chemistry by Optical Methods".
- K. Ishigure (Japan): "Current Activities of Researches, Development on Water Chemistry Monitoring in Nuclear Reactor Systems in Japan".
- Molander, B. Rosborg (Sweden): "Electrochemical Monitoring" (Part III).
- Beverskoeg (Norway): "In-pile Crack Growth Monitors used in Halden IASCC Test Programmes".
- K. Mäkelä (Finland): "In-Core Pd Reference Electrode Development Work in 1996–1998".
- J. Kysela (Czech Republic): "Nuclear Research Institute Experience in High Temperature On-Line Monitoring of Water Chemistry and Corrosion".
- J. Hickling (United Kingdom): "Use of Electrochemical Noise to detect Stress Corrosion Crack Initiation in Simulated BWR Environments".

Annex 3

PROGRAMME STATUS AT THE 1999 RCM IN ESPOO, FINLAND, AND LIST OF PRESENTATIONS BY WACOL PARTICIPANTS

1. STATUS OF ON-LINE MONITORING IN THE CONTEXT OF THE WACOL PROGRAM

1.1. *PWR primary side — Task Leader: J. Kysela*

The status here was summarised in terms of both development of methods and implementation in the following tables:

Table 1. PWR primary side — methods (status as of June 1999)

METHOD	COUNTRY												
	Belgium	Canada	Czech Rep.	Finland	France	Germany	Japan	Norway	Russia	Sweden	Switzerland	UK	USA
ECP				X						X			
HT pH				X				X	X	X		X	
HT conductivity			X	X					X				
Oxygen		X				X			X				
Hydrogen		X							X				
Boron			X			X			X				
Particles											X		
Radioactivity buildup				X	X					X			
Crack growth	X							X					
Noise	X												
Impedance				X									
Others													

Table 2. PWR primary side — implementation (status as of June 1999)

METHOD	STANDARD	SPECIAL	LOCATION
ECP		X	Side stream
HT pH		X	Side stream
HT conductivity		X	Side stream
Oxygen (HT)	X		Primary circuit
Hydrogen (HT)	X		Primary circuit
Boron	X		Primary circuit
Particles		X	Primary circuit
Radioactivity buildup		X	Side stream (Primary circuit)
Crack growth		X	Side stream
Noise		X	Side stream (Primary circuit)
Impedance		X	Side stream

1.2. ***PWR secondary side —*** *Task Leader: B. Stellwag*

Main topics of the session were:

- Redox and corrosion potential measurements
- HT pH measurements
- HT conductivity measurements
- Measurement of O_2 and other gases
- Diagnostic systems for data acquisition and evaluation.

Redox and corrosion potential measurements have been carried out in commercial plants in various countries, e.g. France, Germany and Sweden. Diagnostic systems are also already implemented in various plants. The other methods are either used for special purposes, e.g. heated crevice tests in side-stream autoclaves, or are still at the development stage (e.g. O_2 sensors). It was generally agreed that reliable and robust sensors are available for in-plant installation. It was also pointed out, however, that Round Robin tests have shown significant differences in the absolute value of the potential of the reference electrode.

Discussion of the advantages and disadvantages of permanent use of the various sensors as standard instrumentation yielded the following results. Corrosion and redox potential measurements are recommended for "special purposes". The audience also expressed the opinion that the method has the perspective to be used as a standard measurement parameter for characterisation of the properties of final feedwater. The following aspects must be born in mind with regard to general implementation:

- It is an additional and new measurement parameter, i.e. there is no common reference in terms of specified values (normal values, target values, action values, etc.).
- Although having been frequently used in commercial plants, requirements on the measuring equipment have not been standardised.
- Price and other commercial aspects.

These facts do not permit immediate use of corrosion and redox potential measurements as standardised, permanent instrumentation for on-line, real-time surveillance of the coolant quality in PWR steam-water cycles. Further experience must be gathered prior to inclusion of this measurement parameter into specifications. The corrosion potential can be used as a global measure for oxidising and reducing species in the coolant (O_2, N_2H_4, etc.). Ultimately, implementation of the method may therefore enable measurement of such species (e.g. O_2 in final feedwater) to be discontinued.

The other measurement parameters and sensors discussed should be used only for special purposes. The introduction of new and additional measurements in commercial plants is associated with additional work effort for the plant staff. Moreover, the effects of operation of plant systems and subsystems on corrosion and redox potentials can be rather complex, including temporary malfunctions. Full benefit from using on-line sensors in the real-time mode will only be obtained if sensor signals are collected and analysed with data acquisition and evaluation software. Such intelligent systems have already been installed in commercial plants.

*1.3. **BWR —** Task Leader: J. Hickling*

The results of the BWR session can be summarised as follows:

- On-line monitoring of activity buildup has been successfully implemented in one plant.
- Optical methods have been successfully developed in the laboratory environment, but no plant experience is available.
- Oxygen/hydrogen sensors are available, but optimisation and further development is desirable.
- Advanced electrochemical techniques (thin-film, CER, EN, etc.) are proving very valuable for mechanistic studies, but further development is required for use as a plant sensor.
- Crack-growth-rate measurements are in use for IASCC studies at a test reactor and have also been performed in commercial plant, but they cannot (yet?) be regarded as a routine monitoring tool.

ECP MEASUREMENT IS THE BACKBONE TECHNOLOGY:

- It will be required even more in the future (noble metals).
- It is a well-developed technology for out-of-core measurements, but opinions vary as to reliability, accuracy, ease of conversion to the SHE scale, etc.
- An independent comparison of reference electrodes from different vendors (Round Robin at a BWR plant) would be desirable.
- Improvements to in-core reference electrodes have been achieved, but routine, long-term measuring experience is still needed. This is the key to assessing to what extent HWC/NMCA can protect against SCC of core components.

2. OVERALL LIST OF WRITTEN SUBMISSIONS REFERENCED

- J. Kysela (Czech Republic): "On-line monitoring in PWR plants, primary side (overview)".
- R. Van Nieuwenhove (Belgium): "Electrochemical noise measurements under PWR conditions".
- D.H. Lister, et al. (Canada): " The monitoring of dissolved gases in high-temperature water".
- D.S. Mancey (Canada): " The use of microelectrodes for the in-situ monitoring of the chemistry of aqueous coolants in heat transport systems of nuclear reactors".
- K. Mäkelä (Finland): " Changes in oxide films on stainless steel during a fuel cycle in a VVER plant".
- D. Noel (France): "EdF WACOL activity report 1995–1999: Electrochemical behaviour of alloy 600, 690 at 320–360 C".
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- W. Metzner (Germany): Siemens work report NW-C/99/E029 "Advanced on-line chemistry monitoring concept: In-situ measurement of boron in PWRs
- H. Starkie, et al. (United Kingdom): " The direct measurement of the pH of aqueous solutions under PWR primary circuit conditions".
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- T. Gaudreau (USA): "EPRI's heated crevice monitor"
- G. Perboni (Italy): "ENEL experience on high temperature electrochemical techniques applied to power plants".
- M. Ullberg (Sweden): "On-line monitoring of activity build-up.
- L. Fuks (Poland): "Materials for in-situ monitoring of light water reactor (LWR) water chemistry by optical methods".
- C. Degueldre (Switzerland): "In-line diffuse reflection spectroscopy study of the oxide layer build-up on stainless steel and zircaloy under BWR conditions".
- B. Stellwag (Germany): Siemens work report NW-C/99/E029 "Advanced on-line chemistry monitoring concept: ECP and oxygen sensors".
- J. Kysela (Czech Republic): " NRI experience in high-temperature on-line monitoring of water chemistry".
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- K. Mäkelä (Finland): " Optimisation and application of electrochemical techniques for high temperature aqueous environments".
- K. Hiroishi (Japan): " Current status of the application of high temperature monitoring systems in Japanese BWR"
- S. Ono (Japan): " ECP, pH and conductivity measurement in high-temperature water
- B. Beverskog (Norway): " Irradiation assisted stress corrosion cracking programme ".
- V. Kritski (Russian Federation): " Monobloc of H2/O2 sensors for on-line monitoring systems"
- B. Rosborg (Sweden): " Electrochemical monitoring in nuclear power plants".
- J. Hickling (UK): " Does noble metal technology present new or additional challenges to on-line monitoring in BWRs?"
- T. Saarion (Finland): " Oxide films and stress corrosion cracking".
- S. Lvov (USA): " Problems of high temperature pH measurements".
- H. Shilin (China): " On-line monitoring of resistance of solution aqueous at high temperature".
- V. Kritski (Russian Federation): " Water chemistry functional diagnostics and monitoring system for NPP with RBMK reactor".

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