

***Data processing technologies
and diagnostics for water
chemistry and corrosion control
in nuclear power plants (DAWAC)***

*Report of a coordinated research project
2001–2005*



IAEA

International Atomic Energy Agency

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DATA PROCESSING TECHNOLOGIES AND DIAGNOSTICS FOR WATER CHEMISTRY
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FOREWORD

This report presents the results of the Coordinated Research Project (CRP) on Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion Control in Nuclear Power Plants (DAWAC, 2001–2005). It provides an overview of the methods for development, qualification, and implementation of data processing technologies for water chemistry and corrosion control. Such processes include data collection, data evaluation, diagnostics and assessment, provision of calculation modules and supports the expert systems. These systems are needed to have full benefit from using on-line sensors in real time mode when sensor signals, and other chemistry and operational data, are collected and continuously analysed with data acquisition and evaluation software. Both data acquisition systems and intelligent water chemistry diagnostic systems have already been installed in some commercial plants.

The DAWAC CRP is a follow-up to the WACOL (High Temperature On-line Monitoring of Water Chemistry and Corrosion Control in Water Cooled Power Reactors) CRP (1995–1999). The WACOL CRP, described on-line monitoring techniques for control of water chemistry parameters and corrosion conditions and firmly demonstrated that in situ monitoring was 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 from 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 major objective of the DAWAC project was to improve the data processing technologies and diagnostics for water chemistry and corrosion control in nuclear power plants. In the framework of this CRP, water chemistry specialists from 18 nuclear utilities and research organizations representing 16 countries exchanged experience in the collection and evaluation of water chemistry and corrosion data in nuclear power plants and in the development of diagnostic and assessment systems to advise the operators on the status of the plant. Technical knowledge was acquired in the following major areas:

- Water chemistry control techniques (grab sampling, on-line monitoring, data collecting and processing, etc);
- Plant chemistry and corrosion diagnostics;
- Plant monitoring (corrosion, chemistry, activity);
- Plant chemistry improvement (analytical models and practices).

The CD-ROM attached to this TECDOC includes the report itself, detailed progress reports of three research coordination meetings (Annexes I–III) and the final country reports.

The IAEA wishes to thank the participants and observers of the DAWAC CRP and the members of the leading group for the project guidance and for their contribution to this publication. The leading group included F. Nordmann (diagnostic systems for water chemistry control: development and practices), K. Makela (methods of on-line water chemistry monitoring and control), V. Kritsky and I. Smiesko (water chemistry and corrosion control in WWERs and RBMKs). The IAEA officer responsible for this publication was V. Onufriev of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

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CONTENTS

1. INTRODUCTION.....	1
1.1. Water Chemistry management at NPPs and DAWC CRP	1
1.2. Link between DAWAC CRP and previous IAEA water chemistry projects	2
1.3. Specific research objectives of the DAWAC CRP.....	4
2. IMPLEMENTATION OF THE DAWAC PROJECT	6
2.1. Participants/contributions to the DAWAC project.....	6
2.2. Short summary of the 1st RCM.....	9
2.3. Short summary of the 2nd RCM	9
2.4. Short summary of the 3rd RCM	10
3. APPROACH TO WATER CHEMISTRY AND CORROSION CONTROL	13
3.1. Major purposes of water chemistry control.....	13
3.2. Off-line (grab) sampling.....	18
3.3. On-line monitoring	19
3.4. Data storage	22
3.5. Data processing, trending and analysis.....	22
3.6. Quality assurance of data.....	28
3.7. Updating chemistry specifications	29
4. PLANT OPERATION SUPPORT.....	32
4.1. Need for on-line analysis.....	32
4.2. Diagnostic approach	34
4.3. Methodology.....	34
4.4. Users of diagnostic results.....	44
4.4.1. Operators — Users of diagnostic results.....	45
4.4.2. Chemistry staff	45
4.4.3. Plant management	47
4.5. Limitations and perspectives of expert systems use.....	49
5. PLANT CHEMISTRY IMPROVEMENTS	52
5.1. R&D support	52
5.1.1. Water chemistry studies carried out at Institute for Nuclear Research (INR) in Romania	52
5.1.2. Water chemistry studies carried out at Institute for Nuclear Research and Nuclear Energy (INRNE) in Bulgaria.....	53
5.1.3. Primary water chemistry R&D carried out at the NRI Rez, Czech Republic	53
5.1.4. Water chemistry studies carried out at VVT, Finland.....	57
5.1.5. Development of method for defining optimum pH-ECP for corrosion control at CRL in Canada	59
5.1.6. Laboratory work and recommendations on corrosion monitoring at the China Institute of Atomic Energy	61
5.1.7. Corrosion monitoring in CANDU reactor from Cernavoda NPP Unit #1 in Romania	62
5.2. Development of models.....	63
5.2.1. Modelling of electrochemical potential (ECP).....	63
5.2.2. Corrosion control.....	67

5.2.3. Life time prediction — Russian approach.....	68
5.2.4. Analytical models within ChemAND to predict performance degradation	70
5.2.5. Plant verification	72
6. RECOMMENDATIONS ON MONITORING.....	75
6.1. Chemistry monitoring.....	75
6.2. Radioactivity monitoring.....	78
6.3. Fuel failure estimation from coolant activity and its possibility to implement in diagnostic systems.....	79
6.4. Corrosion monitoring	81
6.4.1. Electrochemical corrosion potential (ECP) monitoring in Swedish BWRs.....	81
6.4.2. Further development of on-line HT sensors for ECP measurements	83
7. CONCLUSIONS AND FUTURE DEVELOPMENT	84
7.1. General considerations	84
7.2. Current status of chemistry monitoring and associated data processing support.....	84
7.3. Expert system expectations and limitations	84
7.4. Recommendations for further development	85
REFERENCES.....	87
ABBREVIATIONS.....	93
CONTRIBUTORS TO DRAFTING AND REVIEW	95
PARTICIPANTS IN THE COORDINATED RESEARCH PROJECT	97

CONTENTS OF THE CD-ROM

Final country reports

ANNEX I: Report of the 1st Research Coordination Meeting of the Coordinated Research Project on Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion in Nuclear Power Plants (DAWAC) 20–23 November 2001, Smolenice, Slovakia

ANNEX II: Report of the 2nd Research Coordination Meeting of the Coordinated Research Project on Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion in Nuclear Power Plants (DAWAC) 26–29 November 2002, Prague, Czech Republic

ANNEX III: Report of the 3rd Research Coordination Meeting of the Coordinated Research Project on Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion in Nuclear Power Plants (DAWAC) 23–27 August 2004, Beijing, China

1. INTRODUCTION

1.1. Water chemistry management at NPPs and DAWAC CRP

More than 95% of the nuclear power in the world is derived from water cooled reactors. In nuclear power plants water is used in primary circuits, secondary circuits (PWRs and PHWRs) and in a number of auxiliary systems. Water may be an aggressive medium especially at high temperature when in contact with structural materials. This means that the reliability of many nuclear power plant systems (fuel, steam generators, etc.) is dependent on the water chemistry during normal operations, startups, shutdown and abnormal operation cases. Advanced water chemistry specifications have been developed for the existing water-cooled reactors; however, there is still some room for improvement. Water cooled power reactor experience shows that even under normal operating conditions, some undesirable effects can occur: corrosion, erosion or deposition of corrosion products on heat transfer surfaces.

Chemistry control in nuclear reactors is important at least from four different angles, namely: (a) material integrity, (b) plant radiation levels (c) deposit buildup and (d) safety. The basis of chemistry control is operational experience, laboratory tests, corrosion and release data and the transport and deposition of crud/corrosion products under operating conditions. The chemical control in nuclear reactors consists of two essential parts:

- Chemicals added to counteract the harmful effects of products generated by radiolysis, to adjust the pH to the value corresponding to a low corrosion rate of structural materials and also to compensate the acidity variations due to chemical shim;
- Minimization of the concentration of chemical impurities, which catalyse the degradation of material, coolant and protective oxide coatings.

Water chemistry strongly influences the operational safety of reactors in the following ways:

- By potentially affecting the integrity of the barriers containing radioactivity such as fuel clad and primary circuit materials;
- By affecting the out-of-core radiation fields, which in turn influence man rem budgeting;
- By affecting formation of deposits, which may cause heat transfer degradation and enhance localised corrosion processes.

Good control of water chemistry can significantly reduce both above-mentioned problems and consequently improve the plant safety. The importance of the role of the chemistry management in the nuclear power plants has been recognized many years ago. Water chemistry management in the nuclear power plants can be applied to mitigate the corrosive environments inherent in plant operation. There are some chemistry requirements in PWRs and BWRs Water Chemistry Guidelines, Technical Specifications, Fuel Warranty, Water Quality Specifications and so on to keep the reliability of nuclear power plants operation. It is important that the chemistry program must ensure compliance with the above requirements. The chemistry management systems have been developed to support and assess the correct chemistry implementation in the nuclear power plants. The systems can provide effective and sophisticated functions such as data acquisition, evaluation, analysis, calculation, trending reporting, and so on. The systems can contribute to confirm the chemistry reliability of the nuclear power plant operation.

The results of the DAWAC CRP published in this TECDOC cover the following issues relative to water chemistry management at NPPs:

- Continuous monitoring of process conditions, recognition of disturbances and unfavorable trends in the water chemistry regime, diagnostics of their causes and certain recommendations for personnel;
- Control and diagnostics of disturbances related to equipment operation and causing deviations in water chemistry parameters, also of disturbances in measuring channels;
- Support for solving operational problems in maintaining water chemistry conditions within specified intervals;
- Prediction of chemistry evolution may support timely and optimized countermeasures implementation.

1.2. Link between DAWAC CRP and previous IAEA water chemistry projects

Research on coolant-component interactions was carried out in the framework of the former Coordinated Research Projects (CRPs) on Investigation of Fuel Cladding Interaction with Water Coolant in Power Reactors (CCI, 1981–1986) [1], on Investigations on Water Chemistry Control and Coolant Interactions with Fuel and Primary Circuit Materials in Water Cooled Power Reactors (WACOLIN, 1987–1991) [2-4] and on “High Temperature On-line Monitoring of Water Chemistry and Corrosion” (WACOL, 1995–2000) [5].

Five subjects of major importance were identified in the CCI CRP in view of the future trends for reactor operating conditions: increased performance, better fuel utilization, flexibility of operation, reliability and safety. These subjects were proposed as main concerns for the new WACOLIN CRP. The objective of this project was to produce a manual about reactor water chemistry in nuclear power plants. The influence of water chemistry on fuel and reactor primary circuit corrosion, and on radiation fields, was clearly shown in this project. Results of the WACOLIN CRP were published in 1993 as the Technical Reports Series “Coolant Technology of Water Cooled Reactors: An Overview” [6]. Corrosion control and activity buildup depend upon the physicochemical parameters of the coolant. In the conclusions of the WACOLIN CRP, one important issue was identified to be the high-temperature, on-line monitoring of water chemistry and corrosion. The need to monitor and control water chemistry parameters in real time, reliably and accurately is therefore of fundamental importance.

The objectives of the WACOL CRP (1995–2000) were to establish recommendations for the development, qualification and plant implementation of methods and equipment for on-line monitoring of water chemistry and corrosion. The project was 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 purpose of on-line monitoring in operating power plants is to obtain information during all operating conditions (steady state, transients, startup and shutdown). This type of monitoring gives even more accurate results if the measurements are performed at high temperatures without changing the physical and chemical status of the reactor water. One conclusion drawn from the WACOL project was that based on information gathered with monitoring techniques, it can be checked:

- Whether the plant is operating within the technical specifications;
- How plant responds to measures taken by the staff, e.g. to return from transients to normal conditions; and
- If there are any long-term trends which may lead to abnormal conditions.

In a broader sense, this 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 plant control, to provide data for mathematical modelling, and to maintain conditions with minimum materials corrosion, and thus:

- To assure component reliability and to extend their life;
- To minimize crud formation on fuel rod cladding so as to achieve high fuel burnup and longer fuel cycles;
- To minimize the formation, transport and deposition of activation products, therefore, leading to a decrease in local radiation dose rates;
- To minimize radioactive wastes.

Full benefit from using on-line sensors in the real-time mode will, however, only be obtained if sensor signals, and other chemistry and operational data, are collected and continuously analysed with data acquisition and evaluation software. Both, data acquisition systems and intelligent water chemistry diagnostic systems have already been installed in some commercial plants.

Modified and new water chemistry regimes have presently been applied in operating plants and other ones are considered for future implementation in order to reduce activity buildup, to be able to use extended fuel cycles (higher burnup), and to apply effective remedies for existing corrosion problems (plant life extension). Examples are zinc dosage in PWR and BWR plants, noble metal addition in BWRs, hydrazine dosage to primary coolant in WWER plants, optimization of pH and B/alkaline ions ratio in primary coolant with regard to high fuel enrichment and extended fuel cycles, and others. There is a need to quickly identify unexpected behaviour and to avoid possible detrimental side effects when applying such advanced water chemistries. New data processing technologies, in combination with conventional analysis techniques or new sensors, offer the means for achieving a more reliable database and faster feedback to follow the influence of advanced or proven water chemistry regimes.

A tentative outline of the basic structure of a data processing and diagnostic system is shown in Figure 1. Chemistry and radiochemistry data measured with conventional or advanced methods and sensors, as well as plant data (such as temperatures, mass flow rates, and other thermo-hydraulic and operational data) are normally collected with a data acquisition system. Data processing usually includes plotting of the measured values and applying plausibility checks. Plausibility of data can be confirmed, for instance, by a cross check or consistence check with other measured data, or by a comparison with values calculated with an independent set of input parameters.

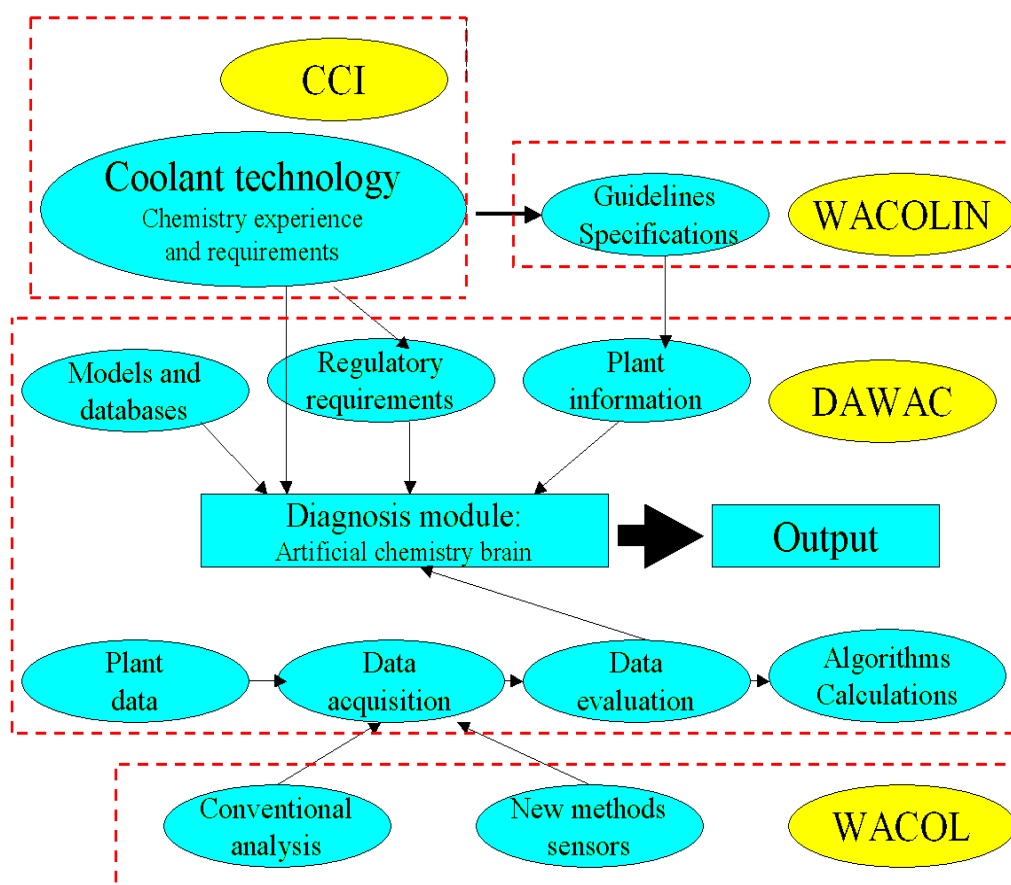


FIG. 1. Main areas covered by the IAEA CRPs: CCI, WACOLIN, WACOL and DAWAC.

The diagnosis module (“the artificial chemistry brain”) is the key component of water chemistry and corrosion control expert systems. It contains the general chemistry experience and requirements as well as the additional plant-specific information. This so-called knowledge base should be expandable to allow regulatory requirements, corrosion degradation data bases/design curves, or sophisticated predictive codes to be included or updated. Such sub-routines will facilitate evaluation of component reliability and condition-based component maintenance, and contribute to plant life extension.

The knowledge base stored in the diagnosis module should enable prompt display of chemistry anomalies, which may affect the corrosion performance of components or other chemistry-related plant performance factors. It should further give information about possible causes for the detected anomaly and recommendations for possible countermeasures, and should indicate the relative importance, urgency and consequences of the identified chemistry anomaly.

1.3. Specific research objectives of the DAWAC CRP

The specific research overall objective of the DAWAC CRP, as agreed in the beginning of the project was to set up methods for development, the qualification, and the nuclear power plant commissioning of data processing technologies for water chemistry and corrosion control including data collection, data evaluation, diagnostics and assessment, provision of

calculation modules and support the expert systems. The following areas were defined for contributing to the project:

Data collection:

- Field evaluation of advanced on-line and in-situ sensors, like ECP, pH, etc. that have reached the stage of installation in an operating reactor (follow-up to the WACOL CRP),
- Comparison with other, more conventional on-line instruments in cooled sampling lines or off-line analysis techniques applied to grab samples,
- Other relevant experience and know-how with regard to data collection.

Data processing and evaluation:

- Experience with data evaluation systems from operating plants (so-called laboratory information and management systems, LIMS). LIMS helps to manage laboratory work and to coordinate on-line and off-line data;
- Data analysis: experience with algorithms and calculation routines for calculation of chemistry parameters (e.g. ECP in BWRs, pH in PWR primary coolant, etc.). Comparison with measured values, plausibility checks.

Diagnostics, assessment:

- Establish recommendations for the basic structure of an intelligent system for diagnosis of water chemistry and corrosion control;
- Expand and define the knowledge base for the different types of light water reactors under the aspects of:
 - In Situ measurements,
 - The kind of anomaly,
 - The relative importance, urgency and consequences;
- Experience gathered with interpretation of data in terms of system behaviour. Link between monitoring, observed phenomena and underlying processes;
- Trend analyses, predictions: mathematical modelling and calculation modules to resolve various corrosion-control items, like erosion corrosion, fouling of PWR steam generators, crud accumulation in the reactor core, inter-granular stress corrosion cracking of BWR stainless steel components.

2. IMPLEMENTATION OF THE DAWAC PROJECT

2.1. Participants/contributions to the DAWAC project

17 organizations from 16 countries representing equal mix of utilities, fuel vendors and research organizations joined their efforts in this project. Table 1 presents names of chief investigators, their organizations, title of their contributions at the 1st, 2nd and 3rd meetings and relation to the objective of the project (1- Processing and diagnostic systems for water chemistry control; development and practices; 2- Methods of on-line water chemistry monitoring and control; 1-2- mix of 1 and 2), and title of the agreement or contract. The major part of the reports (29 contributions) is devoted to diagnostics, 14 contributions to on-line monitoring and 6 contributions cover both. Detailed list of participants and observers to the DAWAC CRP is given at the end of the report.

Table 1. Participants/contributions to the DAWAC CRP

Chief Investigator	Organization	Title of the contributions at the 1st, 2nd and 3rd meetings	Title of agreement/contract
I. Dobrevsky	INRNE, Bulgaria	1-2. Optimization of WWER water chemistry guidelines; modelling of activity build-up in primary circuit	Approaches for the improvement of the water chemistry and corrosion control praxis and its assessment in Kozloduy NPP
		1-2. Optimization of WWER water chemistry guidelines; modelling of activity build-up in primary circuit	
		1-2. Impact of power transient conditions on Hide-out and Hide-out return processes in WWER SGs	
C. Turner	CRL, Canada	2. ChemAND™ uses models and blocks for chemistry parameters control, SG fouling control, SG crevice chemistry, steam cycle chemistry, Hideout Return Analysis	Chemistry monitoring and diagnostics of CANDU reactor systems
		2. Update of ChemAND™ System, Gentilly-2 experience	
		2. Update of ChemAND™ System-minimization of corrosion rate	
Hu Shilin/ Zhang Weiguo	CIAE, China	1. Monitoring of electrochemical noise on localized corrosion (Lab work)	High temperature on-line monitoring of water chemistry and corrosion
		1. Monitoring of electrochemical noise on localized corrosion (Lab work)	
		1. Monitoring of electrochemical noise on localized corrosion (Lab work)	
M. Zmitko	INR, Czech Rep.	2. Alpero Semi-Expert Water Chemistry Control System for CHEMIS Information System for Temelin NPP	Semi-expert system for primary waste water chemistry control and diagnostics
		1. Water chemistry and corrosion monitoring during hot rests of Mochovce and Temelin NPP	
		1. Effect of preconditioning on activity build-up in primary circuit of Temelin NPP	

Chief Investigator	Organization	Title of the contributions at the 1st, 2nd and 3rd meetings	Title of agreement/contract
K. Makela	VTT, Finland	1. HT measurements in primary circuits of BWRs and WWERs	In-line high temperature water chemistry measurements under primary circuit conditions in operating BWR and PWR
		1. HT measurements in primary circuits of BWRs and WWERs-to correlate activity build-up and water chemistry parameters	
		1. Fe content in the feed water for WWER SGs-role of the solubility of iron oxides on harmful deposits in SGs	
F. Nordmann	EDF, France	2. EdF approach for WC control in PWRs	Data processing technologies and diagnostics for water chemistry and corrosion control in NPPs in France
		2. On line monitoring and Merlin data bank in French PWRs	
		2. Optimized monitoring control and diagnostics for a safe, efficient and improved plant operation	
J. Schunk	Paks NPP, Hungary	1. Medium term experiences with in-situ gamma-spectrometry of the primary loop transport processes at Paks NPP	Evaluation and analysis of data from in-situ gamma-spectrometric measurements versus operational parameters
		1. Evaluation and analysis of data from in-situ gamma-spectrometry SG measurements versus operational parameters	
		1. Measurement of surface contamination of uranium/transuranium on fuel assemblies, spectrometry measurements on SGs and ion exchange column	
S. V. Narasimhan	BARC Facilities, India	2-1. Development of an Expert System and implementation of on-line measurement methods in Indian reactors	High temperature on-line monitoring of some chemistry parameters and development of an expert system for primary system chemistry of BWRs and PHWRs
		2. Water chemistry monitoring and diagnosis in PHWRs. Control parameters, Techn. Spec, action levels	
		2. Water chemistry monitoring and diagnosis in PHWRs. Establishment of universal database in India for PHWRs and diagnosis modules for "Wise Plant Chem" system	
Uchida	Tohoku University Japan	2. Anomaly diagnosis system of structural materials in BWRs based on water chemistry data	Diagnostics and assessment sub-programme
		2. Water chemistry data acquisition, processing, evaluation and diagnostic systems in LWRs – Latest experience with Japanese LWR plants	
		2. Water chemistry data acquisition, processing, evaluation and diagnostic systems in LWRs – Future improvement of plant reliability and safety	
I. Pirvan	INR, Romania	2. Overview of Romanian program to investigate corrosion of CANDU-6 PHT structural materials	Monitoring of water side corrosion of CANDU 600 primary circuit components
		2. Chemical control and assessment of corrosion, deposition and release of corrosion products in the primary circuit of CANDU-6 PHWR	
		2. Development of informative system for water chemistry and corrosion assessment in primary circuit of CANDU-6 reactor	

Chief Investigator	Organization	Title of the contributions at the 1st, 2nd and 3rd meetings	Title of agreement/contract
V. Kritski	VNIPIET, Russian Federation	2. Modular diagnostic system for evaluation of quality and water chemistry control at NPPs	Data evaluation and diagnostic systems for water chemistry in NPPs
		1-2. Development of control system for cracking prevention of near-steam zone of pipeline Du300	
		2. The data evaluation and diagnostic systems for water chemistry in NPPs	
I. Smiesko	Bohunice NPP, Slovakia	2. NPP Bohunice-Chemistry Information System Introduction to neural networks Specification and experiences with collecting data from on-line analysers of chemical parameters and diagnostics chemistry regime in NPP Mochovce	Investigation of neuro-fuzzy methods applicability in water chemistry expert systems
		2. Use of PEANO module for diagnostic of water chemistry. First test at real plant chemistry data	
		2. Results of continued tests of PEANO module applicability for water chemistry diagnostics	
M. Ullberg	Studsvik Nuclear AB, Sweden	1-2. Limitations of HWC models	Data management and operating experience with in-situ sensors for corrosion monitoring in NPPs
		2. Beyond EXCEL-Analysis of crud data	
		2. Computer-added monitoring of the secondary site chemistry in Ringhals PWR	
A. Masko A. Arkhyenko	Ministry of Fuel and Energy, Ukraine	2. Chemical technologies and life management of Ukrainian NPPs	Chemical technologies and life management of Ukrainian nuclear power reactors of WWER type
		2. NNEGC “Energoatom” activity on the organization and improvement of the chemical control in Ukrainian NPPs	
		2. Ukraine NNPGC “Energoatom” - Improvement of the water chemistry and control systems	
D. MacDonald	PSU, USA	1. Techniques for monitoring the chemistry and electrochemistry of supercritical aqueous systems	Development of high temperature chemistry and corrosion sensors
		1. Controlling IGSCC in BWR coolant circuits	
		1. The Impact of Water Radiolysis on the ECP in PWR Primary Coolant Circuits	
T. Gaudreau N. Delse	EPRI, USA	No contribution	Intelligent water chemistry diagnostic systems (SMART ChemWORKS)
		2. On-line chemistry monitoring and diagnostics using SMART ChemWorks™	
		2. A practical view of SMART ChemWorks™, an on-line diagnostic monitoring system, after 150 plant years of experience	
W. Metzner P. Zeh	Framatome -ANP (Areva), Germany	2. Diagnostic System for WC control DIWA	Diagnostic systems for WC control
		No contribution	
		2. Fuel failure estimation from coolant activity to implement in diagnostic system	

Short summaries of three research coordination meetings (RCMs) are given below to describe the implementation of the project.

2.2. Short summary of the 1st RCM

The 1st RCM was held at Smolenice, Slovakia, November 20–23, 2001. The technical status of the programme at that time and the presentations from the meeting were summarised in a detailed progress report (Annex I), which was structured according to the format chosen originally for two group discussion:

- Session I: Diagnostic systems for water chemistry control: development and practices;
- Session II: Methods of on-line water chemistry monitoring and control.

Meeting's results achieved and recommendations are given below. Results obtained were evaluated by all participants as very positive ones, especially in the areas of data analysis and diagnostics and, to a lesser extent, in data collection area. Directions of future activities in the area were discussed and agreed upon for each participating organization. Participating organizations agreed that major directions of the co-operation effort in this Project would include:

- In data collection - minimization of data volume with strong prioritisation of data to be measured on-line; search for optimal combination of on-line measured data and laboratory measured data; modernization of measurement methods and equipment; comparison of theoretical models and measurement results;
- In data evaluation and processing area - clarification of the list of chemical parameters to be measured and then-processed; optimisation of data format and volume to be submitted to diagnostic part; further development of data handling blocks of the Expert System; progress in water chemistry codes;
- In data diagnostic area - definition of the borderline between R & D activities in water chemistry monitoring area and actual plant needs in water chemistry expert systems; extension of system's performance and capabilities in the direction of: alarm signal→ advice to operator→ self-education; optimal architecture of Expert's Systems for plants with different reactor types and of different age.

2.3. Short summary of the 2nd RCM

The 2nd RCM was held at Prague, November 26–29, 2002. The technical status of the programme at the time and the presentations from the meeting were summarised in a detailed progress report (Annex II), which was structured in exactly the same way as the 1st RCM.

According to the different presentations and experiences, it is now obvious that plant data acquisition through databases is almost mandatory, and particularly when a utility or an organism is in charge of several units in operation. In this case, such a centralized data bank allows gathering all relevant data and comparison between data from one unit to another. Then this allows trending the data and evaluating if they look satisfactory or not. These practices now seem efficient and correctly settled to plant needs and proper operation.

Then, investigation on chemical parameters is also useful in order to optimize chemistry in operation, and thus to decrease corrosion, activation and transport process. One example was given on the way to decrease deposits of crud on the fuel elements and to look at the influence of operating chemical parameters on the crud composition and stability which will be one of the ways to avoid fuel degradation, axial offset anomalies and to minimize corrosion product activation. The other example dealt with the way of optimizing hot functional tests, in terms

of duration and chemical conditions in order to get more stable oxide, and thus to decrease their release and activation during following power operation, in connection to adequate operating conditions such as purification rate.

More questionable is the use of diagnosis expert systems which are used in some cases in order to give to the plant staff the action to take, based upon operating chemical values and more or less sophisticated tools which may, for example, compute the chemical condition in areas of restricted flow, where concentration process will occur. Based on the calculated chemistry (alkalinity, redox potential, soluble corrosive compounds concentration, etc) the expert system will give the decision to the plant staff if operation may or not continue.

The discussion was summarized with the following diagram, on the data processing, which should be based on the necessary and sufficient parameters, which will allow the plant staff to take the appropriate decision (Fig. 2).

Even though all of the papers were really interesting, they have only a little use for daily operation in plants. The results presented in the numerous papers may be readily used by experts as tools to understand how plant components behave under given water chemistry conditions. However the experiences gained in laboratory tests and campaigns at plants should not be lost, but incorporated somehow to existing data collecting and diagnostic systems. Only this way the information can be indirectly utilised in such a manner by operators, which may lead to longer lifetime of the plant components.

In the area of water chemistry monitoring and control, the relevant question that needs to be answered is the following: The amount instrumentation needed in the future? The general consensus was that not too much because that would lead to too many data points to be followed and then again not too few, because one does not want to compromise the accuracy of the water chemistry control. However, this issue will be discussed in more detail in the next meeting. In addition, a question was also raised: Are there some new monitoring techniques needed to ensure safe operation of the plants (like Li monitor being developed at EdF, need for sensor to be used directly in SG crevice)? Again more detailed discussion will be carried out during the next workshop.

2.4. Short summary of the 3rd RCM

The 3rd meeting of the DAWAC project was held in Beijing, August 23–28, 2004. The technical status of the programme at the time and the presentations from the meeting were summarised in a detailed progress report (Annex III), which was structured like previous reports. The key points have been highlighted at the end of this 3RD DAWAC meeting as following:

Insufficient correct updating of chemistry specifications

It appeared from the diagram reported in conclusion at the end of the 2nd DAWAC meeting report, that after the 1st step (plant data collection and history, future data, operational diagnosis), the 2nd step (research, data analyses, experiments, models validation), the 3rd step is more and more insufficient. It corresponds to the need for updating the chemistry specification based on high level expert with enough background to take into account materials and design evolution, plant experience feedback, R&D laboratory results and models, international data.

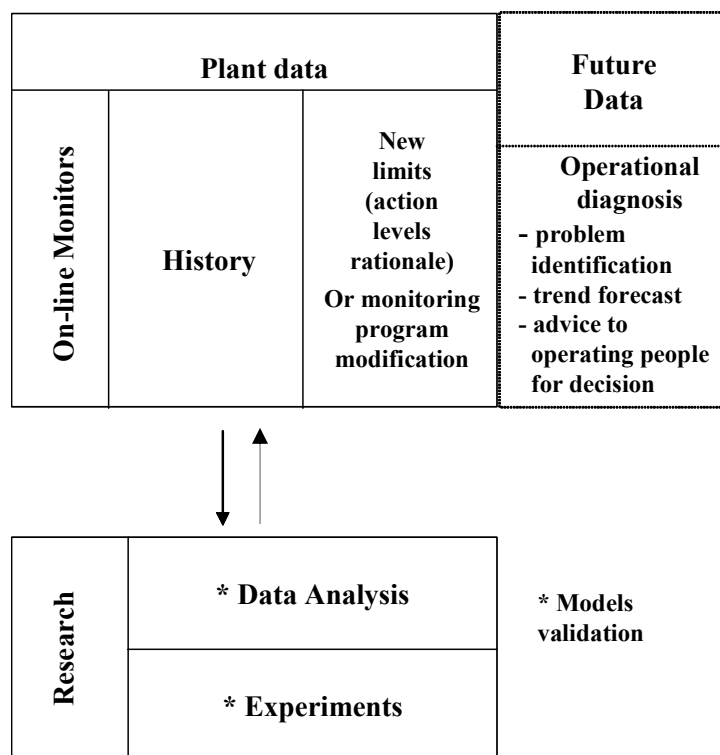


FIG. 2. Diagram of data processing based on the necessary and sufficient parameters, which may allow the plant staff to take the appropriate decision.

Limitation of using expert systems

It is recognized that if expert systems may be of great help for some chemists, particularly young and overloaded ones, they may not replace the need for experienced chemists able to evaluate the origin of specific situations and take the appropriate decision of corrective action.

It seems that there is rather an increasing lack of high-level experts than of expert systems. The expert systems will be used either for diagnosis or as an additional tool for data handling.

Various potential organizations

The need to handle the 2 types of tasks:

- (a) Decision on plant chemistry operation, and
- (b) Long term evaluation, studies and chemistry specification updating,

may rely on various potential organizations which should properly answer to these two tasks.

The expert systems or external help may contribute to decrease the load of the plant chemist for (a) tasks in most frequent cases but not in all the unexpected situations. The R&D people, the models and plant tests may contribute to tasks (b) for which the experts may be located in a central organization, particularly for large utilities.

Need for data handling

The need for on-line monitors for the important parameters associated with efficient data storage and trending is completely agreed by all the participants. It is not any more suitable not to have such systems.

Several participants considered that there are many data but not always properly evaluated. Thus, if during a plant test of R&D, a huge number of data has to be gathered, for normal plant operation, it seems advisable to focus on the number of necessary parameters and correctly analyzing their results for taking the correct action, when necessary. Additional data may be stored for a future potential need if this is not detrimental for gathering and evaluating those data that are of utmost importance.

High temperature on-line monitoring

The need for low temperature on-line monitors (sodium, conductivity...) for the important parameters associated with efficient data storage and trending is completely agreed by all the participants. It is not any more acceptable not to have such systems.

But the need for sophisticated high temperature on-line monitors should be only recommended for performing R&D or plant test in order to support the (b) work category defined in above point 3. A typical example is the ECP which will be used to define the correct ECP value associated to some chemical added in the system and thus to define the specified range of the chemical in order to mitigate the various potential risks of corrosion for the different materials that are present.

Then, the use of such high temperature on-line sensors is considered as a R&D tool, of high technology, requiring the presence of a highly experienced expert in this field to appropriately interpret the results that is not compatible with the normal work of a plant chemist.

International experience exchange

It has been pointed out that the need for cross checking plant data and experience feedback as well as evaluation for updating chemistry treatment and specification requires high level experts who may hardly be present in all the utilities for all the considered field of concern.

Thus, for example, a regular meeting for WWER NPPs chemists may be considered for more efficiently improving the chemistry in the various countries.

Proposal for new coordinated research project (CRP)

In the end of the meeting participants of the DAWAC CRP prepared recommendation on initiation of new CRP on Optimisation of water chemistry to ensure reliable water reactor fuel performance at high burnup and in ageing plant (FUWAC). Proposal is given in the end of Section 7.

3. APPROACH TO WATER CHEMISTRY AND CORROSION CONTROL

3.1. Major purposes of water chemistry control

The most important roles of cooling water of light water reactors are as energy transporting medium and neutron moderating medium. With light water as coolant in nuclear power plants, the resulting high temperature water causes corrosion of structural materials, which leads to adverse effects in the plants, e.g. increasing shutdown radiation, generating defects in materials of major components and fuel claddings, and increasing the volume of radioactive waste sources.

In order to control the adverse effects, it is essential to understand corrosion behaviour of structural materials and then to control them in both systems. Corrosion behaviour is strongly affected by the combinations of water qualities and materials. In order to minimize the adverse effects, optimal water chemistry control has been proposed as shown in Figure3 [7].

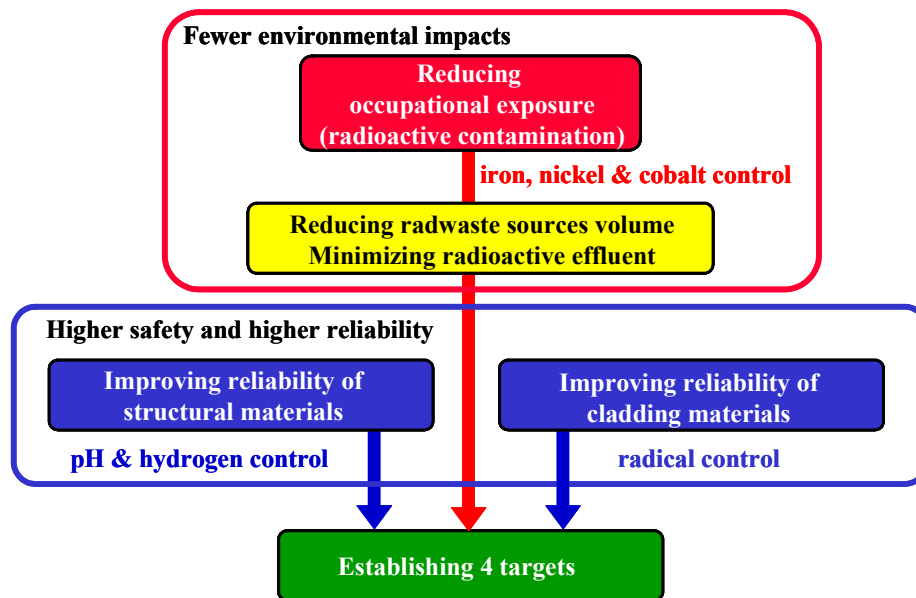


FIG. 3. Optimal water chemistry control (BWR and PWR plants – [7]).

Cooling systems, major components and water chemistry differ in BWR and PWR plants. Procedures to measure water chemistry are also different in both reactor systems. At the same, common points in both reactor systems should also be discussed from the viewpoints of water chemistry data acquisition systems. Examples of water chemistry data acquisition systems for Japanese BWR and PWR plants are given in Figs. 4 and 5 [8, 9]. Many other plants are using similar systems modified with regard to the particular needs.

Importance of water chemistry data in BWR [8] and PWR plants is summarized in Tables 2 and 3, respectively.

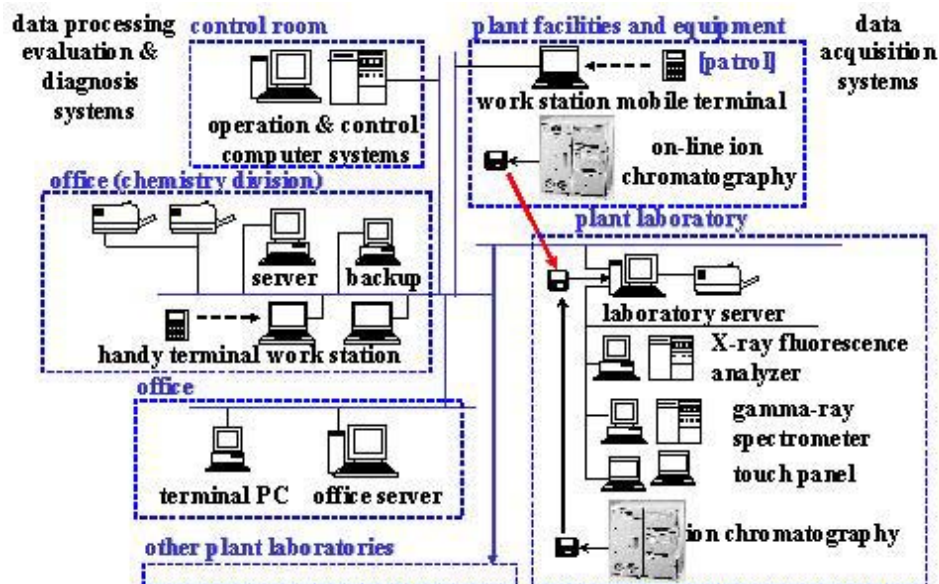


FIG. 4. Water chemistry data acquisition systems (Japanese BWR plants.) [10]

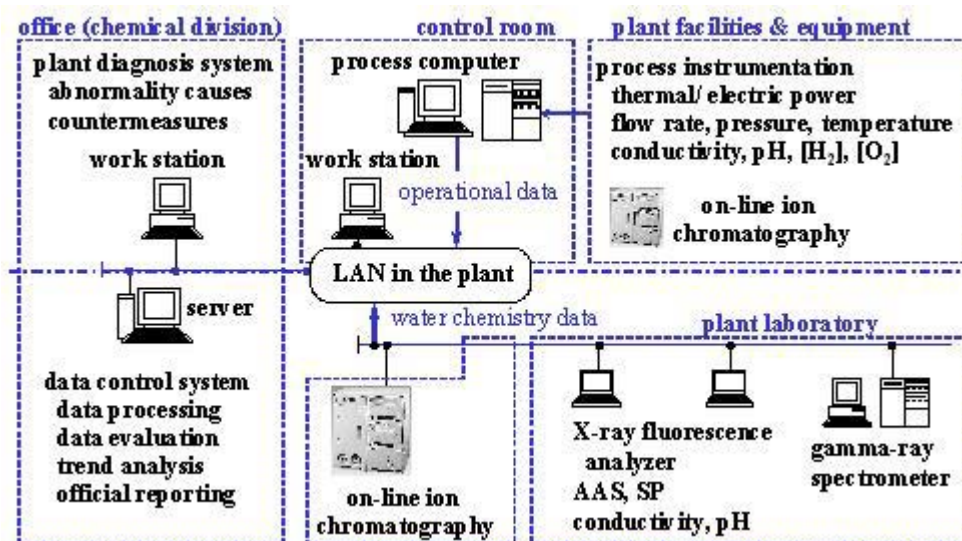


FIG. 5. Water chemistry data acquisition systems (Japanese PWR plants.) [10]

Table 2. Interaction of water and materials (BWR) [10]

Water chemistry factors [operational data]	1) Dose rate reduction	2) Fuel integrity	3) Structure integrity
Macroscopic factors			
pH [6 - 8]*	♣ high pH decreases ⁶⁰ Co release from fuel deposits	♥ high pH promotes zircaloy corrosion	♣ small effect around neutral pH
* room temperature pH	♥ small effect with the range	♦	♥ crack depth is increased cond.
Conductivity [0.1 - 0.3 μS/cm]	♦ few data	♦	♥ low ECP mitigates IGSCC
ECP [-150 - +100 mV]			
Radiolytic sepecies			
H ₂ [~10ppb]	♣ high [H ₂] enhances ⁶⁰ Co release from fuel deposits	♥ high [H ₂] promotes hydrogen pickup by zircaloy	♦ hydrogenation
O ₂ [~200ppb]	♥ low [O ₂] enhances ⁶⁰ Co zircaloy corrosion	♥ high [O ₂] promotes	♥ low ECP mitigates IGSCC
H ₂ O ₂ [~300ppb]	♥ H ₂ O ₂ prevent corroison	♦ H ₂ O ₂ promotes Zr corrosion	♥ crack growth is increased
Metallic sepecies			
Fe [~1ppb]	–	♣ thick deposits promote zircaloy corrosion	–
Cr [~1ppb]	♥ increased pH decreases ⁶⁰ Co release from fuel deposits	♥ higher [Cr ₆ ⁺] promotes corrosion	♥ higher [Cr ₆ ⁺] promotes IGSCC
Zn [<1ppb]	♥ Zn moderates ⁶⁰ Co deposition on pipes	♥ few data	♥ Zn mitigates IGSCC
Alkali metals [<1ppb]	♣ high pH causes low ⁶⁰ Co corrosion	♥ high [Li] promotes	♦
Radioactivity			
⁶⁰ Co, FP [~1Bq/ml]	♣ high [⁶⁰ Co] causes dose rate	♣ fuel defects cause high [FP]	♣ high dose rate obstructs inspection & maintenance
ECP: electrochemical corrosion potential ♣ : quantified and mechanism known ♣ : effects of the factor known but not quantified FP: radioactive fission products ♥ : quantified but mechanism not known ♦ : effects of the factor not known IGSCC: intergranular stress corrosion cracking – : small effect			

Table 3. Interaction of water and materials (PWR) [10]

Water chemistry factors [operational data]	1) Dose rate reduction	2) Fuel integrity	3) Structure integrity
Macroscopic factors			
pH [6.8-7.2]*	♣ high pH decreases ⁶⁰ Co & ⁵⁸ Co generation on fuel surfaces	♦	♣ high pH moderate corrosion
* high temperature pH	♦	♦	♦
Conductivity [<30mS/cm]	♦ few data	♦	♦
ECP [not measured]			
Radiolytic sepecies			
H ₂ [~2,000ppb]	♦ high [H ₂] increases ⁵⁸ Ni(⁵⁹ Co) deposition on fuel surfaces	♥ high [H ₂] promotes hydrogen pickup by Zr	♦ high [H ₂] promote PWSCC
O ₂ [<5ppb]	♥ small effect with the range	♥ small effect with the range	♥ small effect with the range
H ₂ O ₂ [<1ppb]	♥ small effect with the range	♥ small effect with the range	♥ small effect with the range
Metallic sepecies			
Ni [~1ppb]	–	♣ thick deposits promote zircaloy corrosion	–
Zn [<50ppb]*	♥ Zn moderates ⁶⁰ Co deposition on pipes	♥ few data	♥ Zn mitigates IGSCC
* Zn injection	♦	♥ high [Li] promotes PWSCC of Ni base alloy	♦
Alkali metals [<1ppb]			
Li [0.7-2.2 ppm]	♦ few data for simple effect	♣ high [Li] promote corrosion	♦ few data for simple effect
B [0-2,500 ppm]	♦ few data for simple effect	♣ high [B] moderate corrosion	♦ few data for simple effect
Radioactivity			
⁶⁰ Co, FP [~Bq/ml]	♣ high [⁵⁸ Co] causes dose rate	♣ fuel defects cause high [FP]	♣ high dose rate obstructs inspection & maintenance
ECP: electrochemical corrosion potential ♣ : quantified and mechanism known ♣ : effects of the factor known but not quantified FP: radioactive fission products ♥ : quantified but mechanism not known ♦ : effects of the factor not known PWSCC: primary water stress corrosion cracking – : small effect			

There are some gaps between the measured water chemistry data and information to understand plant conditions and interactions between materials and cooling water, which are shown in Table 4 [10].

Table 4. Gaps between desired information and measured data (Beyond water chemistry data) [10]

Desired information to understand in-plant phenomena	Measured WC data in plants	Major measures to bridge the gaps
Corrosive conditions [H ₂ O ₂ , O ₂ , H ₂]	• Measured [O ₂ , H ₂]	• Theoretical models for water radiolysis • HT O ₂ sensors • ECP sensors
Crevice water chemistry	• Bulk water chemistry	• Theoretical crevice radiolysis models • Theoretical & empirical models for impurity concentration in crack tip
Crack propagation rate	• Crack growth rate in simulated condition	• HT crack growth rate sensors • Theoretical & empirical models for crack propagation rate
Soluble and insoluble metallic species	• Saturated concentrations along sampling lime	• Solubility analysis & deposition/release analysis along sampling lime • High temperature conductivity sensors
High temperature pH	• pH at cooled water	• Theoretical evaluation • HT pH sensors
Properties of oxide film on sampled specimens	• Characterization of oxide film	• Theoretical oxidation models • HT impedance sensors • HT: high temperature

In nuclear power plants, there are in principle two types of water chemistry control methods:

- Off-line (grab) sampling, i.e. a sample taken manually and then analyzed in the laboratory (see section 3.2);
- Continuous on-line (or in-line) monitoring with several advantages (see section 3.3).

Systems of data processing technologies, diagnostics of water chemistry and corrosion control requires sophisticated set-up for each individual plant. Data processing begins with plant data collection. The collection of the information on the coolant quality in circuits is carried out by three channels [10]:

- Channel 1: continuous monitoring of the primary/secondary water chemistry condition (collection of the data from the laboratory analyses of grab sampling and on (in)-line primary sensors of chemistry and corrosion monitoring systems) over a limited group of parameters;
- Channel 2: periodic revision of the primary/secondary water chemistry condition on evidence derived from the "ANOMALY" signals of channel 1;
- Channel 3: periodic revisions of the primary/secondary water chemistry 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 provides representative samples, expeditious control and reliable analytic results.

The term "representative" sample implies the invariability of composition during sampling, sample storage and transportation before making measurements with methods, demanding coolant parameter decrease. The representative sample is obtained by use of special design and materials for sampling probes and reservoirs coupled with special procedures at sample taking and storage. Examples of locations for on-line monitoring and sampling in Japanese BWRs are shown in Figure6 [10].

Locations for on-line monitoring and sampling in Japanese PWRs are shown in Figure 7.

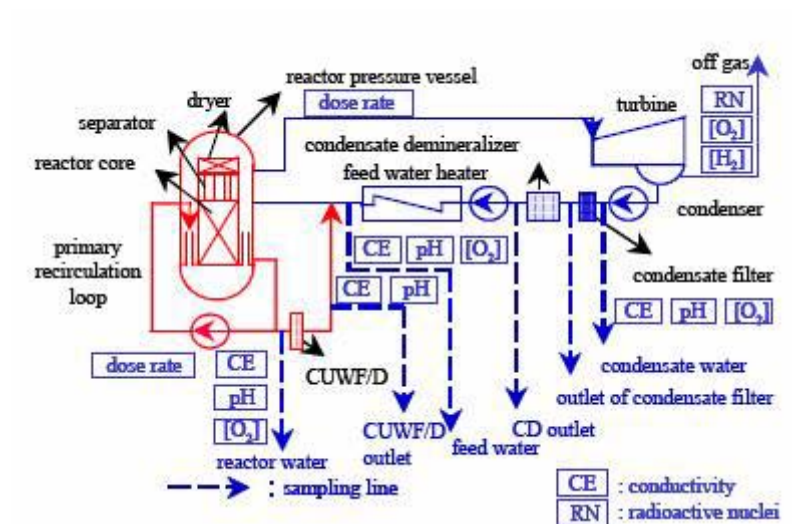


FIG. 6. Possible locations for on-line monitoring and grab sampling at Japanese BWR plants [10].

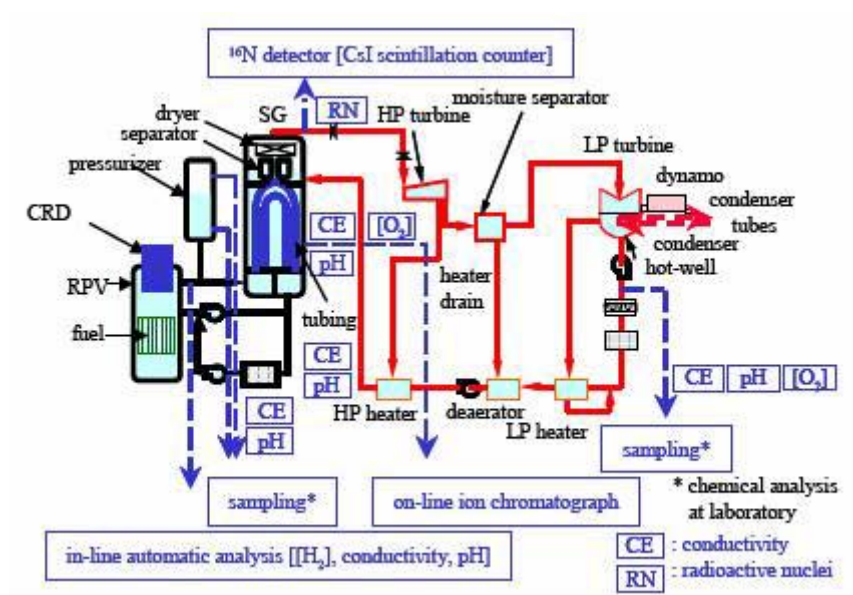


FIG. 7. Possible locations for on-line monitoring and grab sampling at Japanese PWR plants [10].

Chemistry and radiochemistry data measured with conventional or advanced methods and sensors, as well as plant data (such as temperatures, mass flow rates, and other thermo hydraulic and operational data) are normally collected with a data acquisition system. Data processing usually includes plotting of the measured values and applying plausibility checks. Plausibility of data can be confirmed, for instance, by a cross check or consistence check with other measured data, or by a comparison with values calculated with an independent set of input parameters.

3.2. Off-line (grab) sampling

Grab sampling requires adequate sampling system, which is generally provided within plant engineering design. Sampling lines have to be adequately flushed/drained before sample is taken to assure its representativity. Sampling and all further sample handling must be done with adequate care to avoid sample contamination, especially in the case when trace concentration of different species (like sodium or chloride) is to be measured.

Even with on-line monitoring instrumentation available, grab sampling and laboratory analysis is often used for verification of on-line monitor data. Generally grab sample data due to their low frequency generation are not very convenient as principal data in water chemistry diagnostics, but in many cases they serve as supplemental data, which may significantly weaken or strengthen fidelity/credibility of diagnoses.

On-line monitoring is the generally preferred method, but at least in the following cases grab sampling should be performed:

- When no on-line monitor is available for a chemical parameter of sufficient importance (e.g. lithium albeit some is under development in France) [11];
- When the required frequency of analysis would induce more time for on-line monitor maintenance than for grab sampling and analysis (e.g. once a week frequency, diagnostic parameter);
- When the volume of the system does not allow on-line monitoring continuous flow (e.g. safety tank kept filled);
- In some cases, when the economical situation is not favourable to the on-line monitor and if the required frequency does not require a frequent value;
- Or in a very few other cases, when the reliability or sensitivity or adequacy of the on-line monitor is not as good as the laboratory method.

There are very few parameters, which cannot be measured by grab sample method, like low conductivity, cation conductivity, corrosion rate, polarization resistance etc. due to disturbing effect of sample/air contact.

Laboratory analytical data can be collected by the laboratory automation system (LAS). The system is developed for the purpose to collect chemistry analysis data easily, correctly and effectively. The LAS is constituted of the combination of chemical analyzers such as X ray fluorescence, Ge(Li) detector NaI detector, spectroscopic analyzer, ion chromatography, conductivity meter, pH meter and so on. Figure 8 shows the outline of the LAS [12].

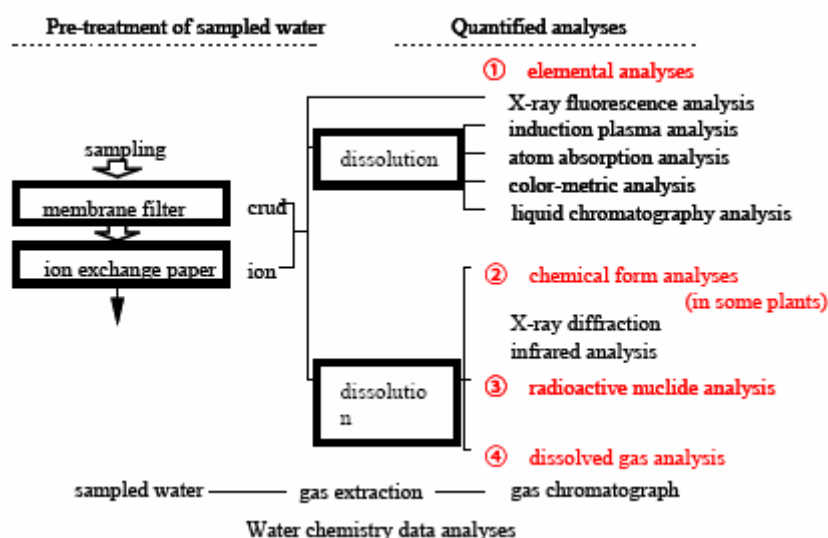


FIG. 8. Chemical analyses off-line sampling [12].

3.2.1. Management of chemistry analysis program in the laboratory

The chemistry analysis schedule and items are registered in the chemistry management system and should be included in a data bank. The chemistry analysis data are input into the laboratory server computer. The input data can be confirmed by the laboratory server.

3.2.2. On-line collection of laboratory chemistry data

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.

Depending on their design the 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.

3.2.3. Analysis operation support

The chemistry analysis manual and procedures of the chemical analysers must be available to the chemists (see section 4).

3.3. On-line monitoring

On-line monitoring is one of alternative technical solutions used for monitoring of chemical parameters at nuclear power unit. Major features of the on-line water and in-line chemistry monitors and process monitors to obtain water chemistry and concerned data are summarized in Table 5 [12].

Table 5. Major on-line water chemistry sensors [12]

Measured items	Detectors	Principles	Remarks
Temperature	Thermocouple	Seebeck effect	HT
Pressure	Diaphragm type pressure gauge	Pressure transducer	HT
Flow rate	Orifice type pressure gauge	Pressure difference	HT
Conductivity	Conductivity detector	Electric resistance	RT
Dissolved O ₂	Oxygen detector	Polarographic	HT, RT
Dissolved H ₂	Hydrogen detector	Polarographic	HT, RT
pH	Glass electrode	Potential drop caused by pH difference	RT
Cl ⁻ ions	Cl detector	Cl ion electrode	RT
Turbidity	Light detector	Light penetration/reflection	RT
Dose rate	Dose rate detector	Ionization, luminescence	RT

RT: room temperature; HT: high temperature

On line monitoring has several advantages when compared to grab sampling:

- High frequency of data generated allows early detection of anomalies;
- Assures surveillance also in period between two manual samplings when short-term events may occur;
- On-line analyzers are often more sensitive than laboratory analysis;
- Risk of sample contamination and human errors is reduced;
- Some parameters even cannot be measured by grab sampling and laboratory analysis (especially very low concentrations);
- There is an immediate indication in control room in case of large deviation for important parameters requiring an immediate action, which may include the shutdown of the unit. Thanks to on-line monitor's redundancy, the plant operators do not wait for validation of the large pollution by grab sampling before deciding to shut down the unit. This avoids material degradation and pollution of the system, which would require more cleaning time before following startup. Moreover, there is not chemist on shift in many nuclear power plants (like in French plants) during normal power operation, under normal circumstances;
- The trending of small pollution is possible when it is close to the detection limit or blank variation with grab sampling. This makes possible detection and fixing of small pollution;
- The reduced time and money demand;
- The plant chemists will have time to concentrate their effort on studying the results and will be more inclined to take the appropriate remedial actions.

To take advantage of on-line monitors, reliability and accuracy must be assured. This is done through:

- Selection of proper parameters to be monitored (simple measurement preferred);
- Selection of verified instruments – laboratory and field testing;
- Appropriate field care (calibration, maintenance);
- Redundancy of on-line monitors.

Extent of monitoring must be evaluated with respect of particular parameter importance, potential possibility of grouping of samples (stream sequencing), instrument price, operational expenses and technical care. On-line monitoring is the generally preferred method, but of course, it should not be systematically applied and grab sampling should be carried out in several cases discussed in Section 3.2.

For EDF, such a monitoring policy is based on a Central Laboratory in Chinon NPP which qualifies the on line monitors which may be used in French plants to be sure of the validity of the results under all circumstances. Then, a policy for calibration and maintenance of on-line monitors has been established [13].

In order to determine water quality of BWR primary cooling water, e.g., pH, conductivity and oxygen concentrations, cooling water to be measured is cooled down for application of proven type on-line sensors. For more detailed measurement for concentrations of chemical elements and radionuclide, cooled and depressurized water is sampled and brought to chemical laboratory in the plants for chemical analysis and radioactive nuclide analysis.

In order to determine water quality of PWR primary and secondary cooling water, e.g., hydrogen and oxygen concentrations, pH and conductivity, cooling water to be measured is cooled down and depressurized for application of proven type on-line sensors as like as BWRs. For more detailed measurement for concentrations of boron, lithium and other anions and cations, cooled and depressurized water is sampled for chemical analysis and radioactive nuclide analysis.

It is easy how to take data from the on-line monitors into the computer systems; water chemistry data from the sampled water used to be inserted into the computer system by plant chemists through keyboard entry. Large improvements have been reported in the latest plants on automatic analysis of chemical and radioactive nuclide data. Chemical species and radioactive nuclides collected on membrane filters are analyzed by X ray fluorescence analyzer and gamma ray spectrometer, respectively, and then the measured data are transferred from the analyzers to the computer system directly [12, 14].

On-line ion chromatographs have been applied in some plants for fully automatic data acquisition for the concentrations of anion and cation species, where the data are transferred to the laboratory data server [15, 16].

The IAEA report on High Temperature On-line Monitoring of Water Chemistry and Corrosion Control in Water Cooled Power Reactors 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 important contributions made by CPR WACOL participants to the development and qualification of new monitoring techniques [5].

3.4. Data storage

Chemistry monitoring may generate different amount of data depending on the complexity of the plant, extent of on-line monitoring and data pre-processing system. Many systems have been developed and implemented worldwide for handling of these considerable data volumes along with progress of hardware and software capabilities, starting from simple spreadsheet and database applications to sophisticated and tailored systems with many processing and presentation capabilities. One of the problems resulting from very fast development of the computerized world is to maintain compatibility and retrievability of data both from data format and storage media used point of view. Such a necessity especially in the large data volumes may require data re-storage operations when either hardware is no more available for reading particular storage media or software becomes non functional due to operating systems or other software environment upgrades. In such a case, conversion of the data into newly designed information systems has to be performed often by development of devoted conversion applications. This may not be necessarily trivial task due to different system architectures. Historical chemistry data importance is more and more pronounced in connection with plant life management and plant life extension activities.

Over the last five years, the cost of storing large volumes of data has significantly decreased due to the advances in hard drive and computer memory technology. The methods of storage have also proven to be robust and reliable, such that great volumes of data can be stored without much risk of data loss. For example, plants that use SMART ChemWorks store an average of 80 data points, with approximately 20 of those points being recorded every five minutes and the remainder once a day [17]. This data is kept on EPRI solutions servers, with data dating back to 1998. Even with the low cost and high reliability of data storage, there are still a number of issues that need to be considered. These factors are discussed briefly in the following section.

Another issue that must be considered is the time that it takes plant personnel to collect the data that is being stored. Although data storage is now inexpensive, it still takes up substantial amounts of plant personnel time to collect the data. Plant personnel need to evaluate which data is important to collect, which data may need to be collected only during certain circumstances, and which data is unnecessary. Nevertheless, if data is collected, in most circumstances it may be worthwhile to store that data because of the relatively cheap cost to do so. If data is very frequent, plant personnel may choose to store only an average data point (i.e. for a parameter that is measured constantly, a daily average may be calculated and stored). However, since it is unknown as to what problems may arise in the future and what data would be useful to solve those problems, it is suggested that historical data records are kept.

3.5. Data processing, trending and analysis

Large amounts of data are generated by chemistry monitoring from both grab samples and on-line monitors. These data must be effectively processed to provide graphical representations, statistical evaluations, trending and more complex calculations, as required. Initially, data-processing systems were based on the capabilities of spreadsheet calculations, but even with the development of standard templates, this interactive data processing was quite time intensive for the user. Therefore task-specific solutions have been developed, either as stand-alone modules or as more complex data management systems.

For example, in Slovakia at the Bohunice Nuclear Power Plant (NPPs), a mainframe alphanumerical terminal with a COBOL programming language-based application was

introduced in 1986 to provide a data collection system for the analysis of grab sample data. This user-unfriendly system was replaced with a simple Foxbase-type application in 1990 using personal computers operating on a local area network. Following step by step upgrades to a FoxPro client server environment, this software was replaced at the end of 1999 by an ORACLE-based application because of Y2K incompatibility. Since this transition, all Czech and Slovak NPPs are now using the same information system [18, 19]. Although the basic functionalities have remained unchanged, user-friendliness interface and quality control of the data have increased significantly. The present system offers the following capabilities:

- Automated job planning, depending on the status of plant systems (different sampling and analysis requirements for start up, steady state, shutdown, outages);
- Action levels and alarms automated control and alerting by a plant system schematic view and a separate text window;
- Graphic visualization by predefined single or batch graph generation modes;
- Statistical processing covering all typical statistical calculations;
- Calculated parameters, investigation of mutual parameter interdependencies;
- Quality assurance modules (e.g., calibrations, quality control charts).

In Figures 9 and 10 some examples of application are given.

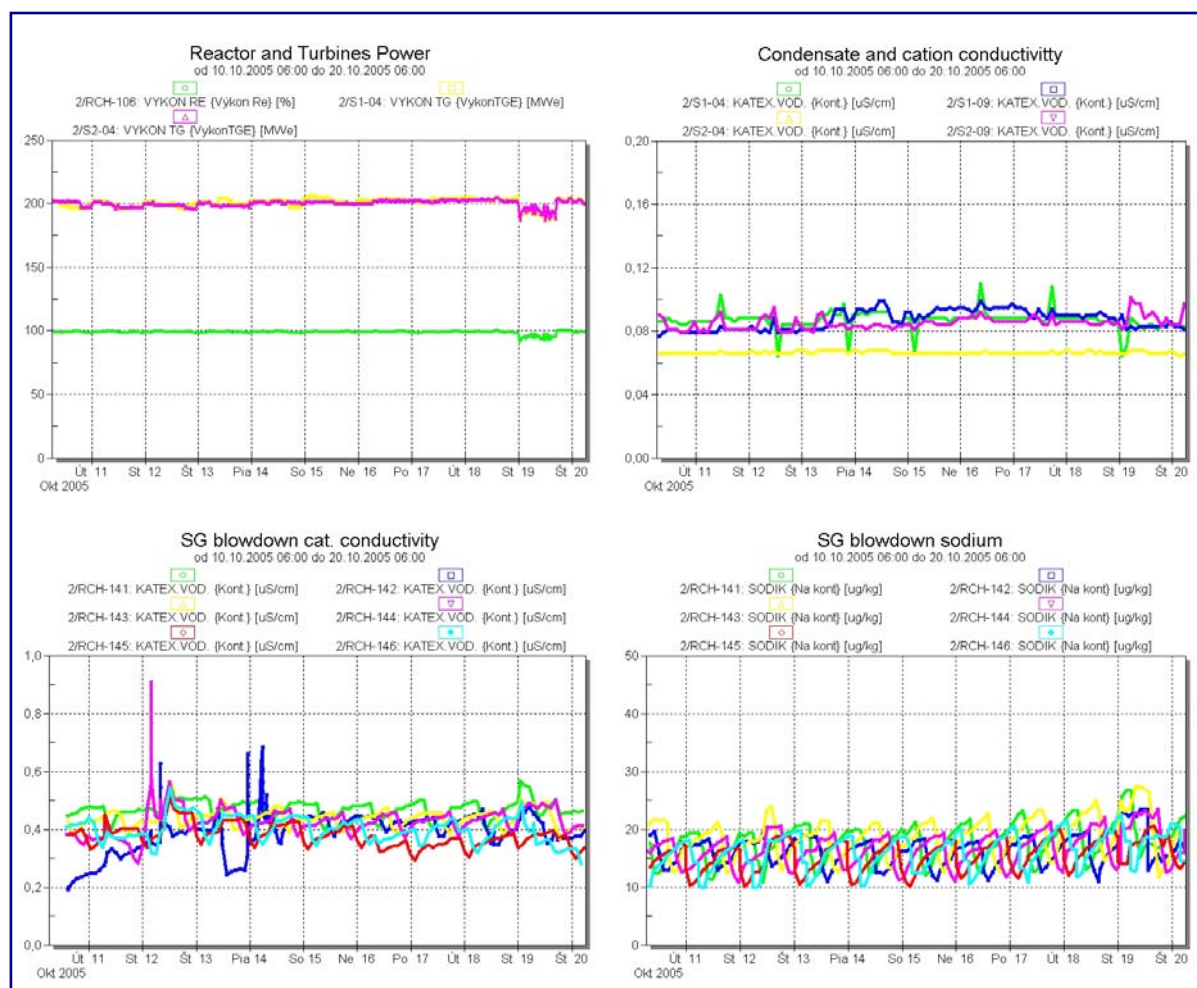
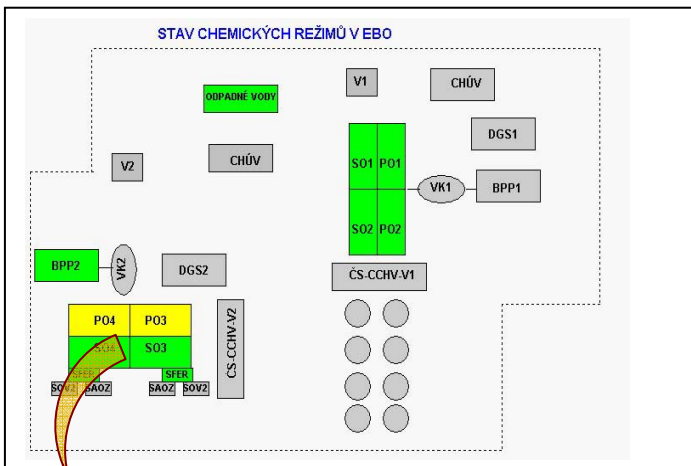


FIG. 9. Trending of secondary water chemistry.

Overall Status of Plant Water Chemistry



Analytical results

	K.BORITA	N2H4.H2O	K
	g/kg	g/kg	g/kg
2/RCH-170	46.3	10	106.4

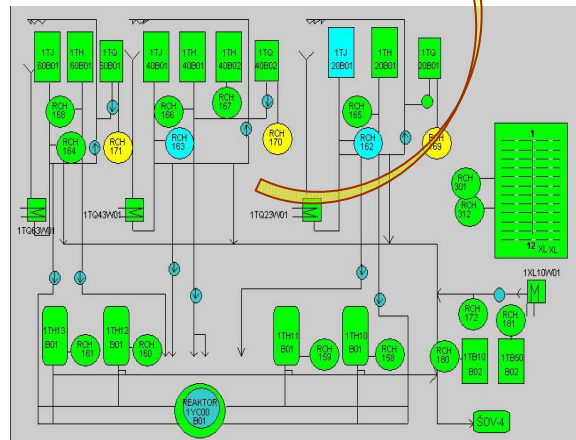
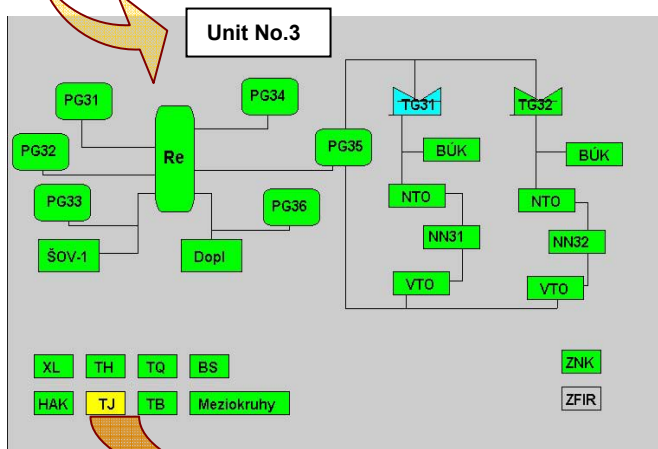


FIG. 10. Overview of plant chemistry status.

Atomic Energy of Canada Ltd. has developed a commercial system for monitoring, diagnostics and analysis of plant chemistry data known as ChemAND® [20]. Specific features of ChemAND include:

- Trending of plant chemistry data;
- A Status Panel to provide warnings and alerts when chemistry parameters are trending out of specification;
- Function-based displays of plant chemistry data to facilitate problem identification;
- Calculation and reporting of chemistry-related performance indices;
- Integration of plant data with sophisticated models for prediction and analysis;
- Easy configuration management of the software to a specific plant.

ChemAND has been in operation at the Gentilly-2 nuclear generating station since January 2002, following a 2-year period of development and field trial. ChemAND combines

chemistry data from on-line monitors with ‘grab sample’ data from the Chemistry Information Management System (CIMS) and stores the data in a dedicated data historian for plant chemistry. These data can be quickly retrieved to facilitate the comparison of historical data with current trends. The Status Panel, see Figure 11, is modelled after the hard-wired ‘tiles’ found in conventional plants and is designed to run as a stand-alone application on the user’s desktop. Each major system is assigned one tile in the status panel. If any parameter in a given system is out of specification or is forecast to be trending out of specification within a prescribed period of time the tile will change colour. Different colours are used to indicate different levels of alarm. Selecting a tile that is in alarm pulls up a list of parameters in alarm for that particular system. Selection of a parameter from the alarm list pulls up a function-based display showing other parameters that correlate with the out-of-spec condition. This is a useful diagnostic aid that helps the plant chemistry staff to readily diagnose the cause of the problem.

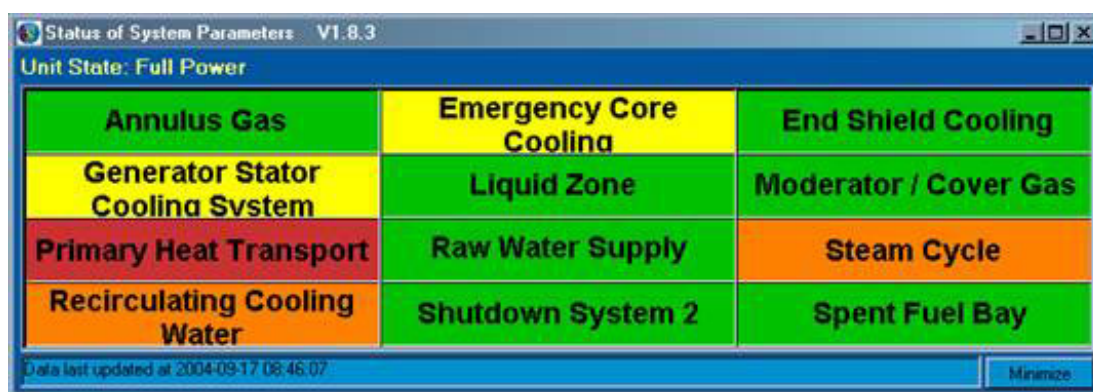


FIG. 11. Status Panel showing the status of chemistry parameters in selected systems [20] where: Green – OK; Yellow – high parameter trend rate; Orange - warning; Red – parameter out-of-specification.

Figure 12 shows a function-based display from the Steam Cycle entitled “Monitoring for Condenser Leak”. This particular display shows trends for on-line condensate Na^+ together with Na^+ , Cl^- , SO_4^{2-} and cation conductivity for the steam generator (SG) blow down. Simultaneous increase of the magnitude of all 5 parameters is an easily recognized fingerprint for a condenser leak. Hence, the situation that caused the alarm associated with the function-based display in Figure 11 was quickly diagnosed as a drift in the calibration of the on-line Na^+ analyzer because the other 4 parameters that correlate with a condenser leak were not trending in the same way. ChemAND also performs simple calculations, such as leak rate based on impurity concentration, ion exchange efficiency and correlations between pH, conductivity and the concentration of alkalizing agent, in order to assist staff in their efforts to monitor chemistry performance.

There are 3 analytical models in ChemAND that are interfaced with chemistry data which can be used to investigate the impact of process conditions on system performance. (Two of these are described in more detail in Section 5.) One of the models, ChemSolv™, is used to predict the concentrations of chemicals used in the all-volatile treatment (AVT) chemistry control program at selected locations throughout the steam cycle, the crevice chemistry in the SG based on the blow down chemistry, and the electrochemical potential of the SG tubes. A second model in the steam cycle, SLUDGE™, predicts the rate of boiler fouling and the deposit distribution within the SG as a function of operating conditions, e.g., feed water iron concentration and blow down rate. SLUDGE tracks deposit inventory as a result of both start

up and full-power operation, and predicts when to clean and where to inspect. A third model being developed for ChemAND is a combined iron-transport and activity transport model for the primary reactor coolant circuit. This model can be used, for example, to assess the effectiveness of operational changes made to the purification system on the buildup of radiation fields at the reactor face.

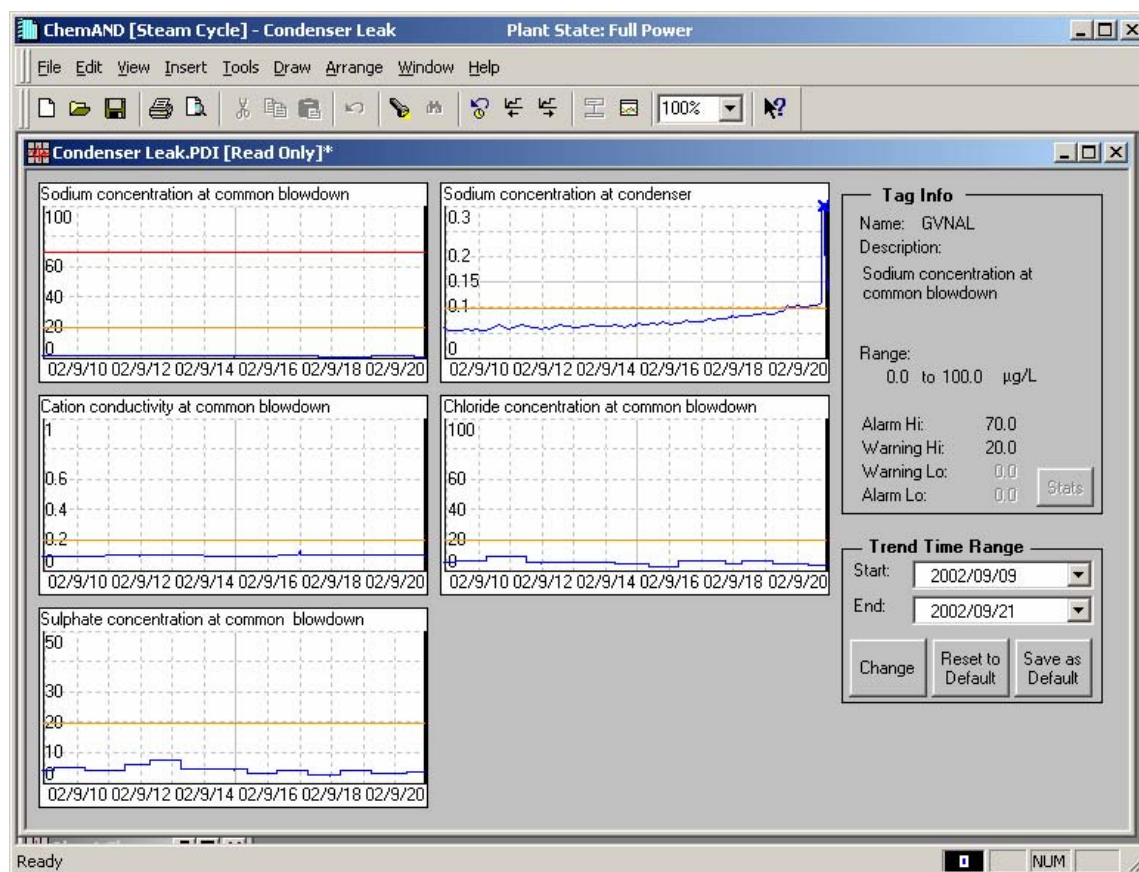


FIG. 12. Function-based display “Monitoring for Condenser Leak” in ChemAND [21].

Another feature of ChemAND that provides a significant savings in time is the automated calculation of chemistry performance indices. These calculations include the WANO chemistry performance index as well as chemistry and safety performance indices mandated by the regulatory authority and station-specific performance indices reported to plant management.

In 1998, EPRI released the first version of its online diagnostic monitoring software called SMART ChemWorks™. SMART ChemWorks (SCW) integrates a plant’s chemistry data management system (CDMS) and a real-time intelligence engine to perform virtual sensing, identify normal and upset conditions, and evaluate the consistency of on-line monitor and grab sample readings. The system also performs diagnostics to identify the cause of chemistry upsets using a “virtual fingerprinting” technique. SCW uses a patented technology that employs plant-specific data, analytical and artificial intelligence models to determine the chemical state of the steam cycle. The objective of SCW is to monitor chemistry 7 days per week/24 hours per day with minimal utility resources. More information is available in [22].

In terms of the data processing, trending, and analysis that SCW performs on incoming data, there are two main elements, statistical analysis, and calculation of “virtual sensors.” SCW performs four types of statistical analysis on incoming data:

- Out of Confidence Interval tests if the current value is outside the 95% confidence interval for this parameter. This test is positive when the current value for the parameter is 1.96 or more standard deviations away from the mean. This test is used to evaluate whether the change in a measurement is normal noise or if it is statistically significant;
- Spike in Data tests if the current value represents a spike. This test is positive when the value of the current point is several standard deviations away from the mean. The number of standard deviations away from the mean is configurable, and typically set to five;
- Fast Evolution tests if there is a continuous change of the parameter in one direction. This test is positive when the last four measurements all indicate a change in the same direction (e.g. increasing or decreasing in value). In order to filter out noise, there is another condition: the first and fourth measurements must be several standard deviations away from each other. The number of standard deviations is configurable, and typically set to three;
- Slow Evolution tests if the mean value of the parameter is changing in one direction over time. This test compares the mean value of three sets of measurements of a given parameter. Typically, this is configured so that the last thirty measurements are divided up into three groups of 10 measurements. (Ten measurements per group, spaced ten measurements apart). This test is positive when the three mean values all indicate a change in one direction. In order to filter out noise, there is another condition: there must be at least one standard deviation's difference between each of the three mean values.

SCW also calculates “virtual sensors.” The system continuously runs a full steam cycle chemistry simulator with measured data used as the known inputs. With measured data, such as impurity and chemical additive concentrations in locations such as the condenser or feed water, virtual sensors are calculated in the rest of the steam cycle from which it may be difficult to obtain samples. Virtual sensors encompass conductivities and low and high temperature pH values, in addition to impurity and chemical additive concentrations in locations such as feed water, steam generator blow down, blow down demineralizer effluent, main steam lines, main steam reheater drains, heater drain tanks, condensate pump discharge, and condensate demineralizer effluent.

By having SMART ChemWorks compare virtual sensor calculations with online instrument readings, plants can verify that instrument readings are correct or identify suspect results, such as an instrument that needs calibration or other maintenance. For example, in the past one US plant performed theoretical calculations of ammonia, ETA, pH, and conductivity at feed water, steam generator blow down, and condensate to verify instrument readings. Figure13 presents examples of calculated data by virtual sensors [22, 23].

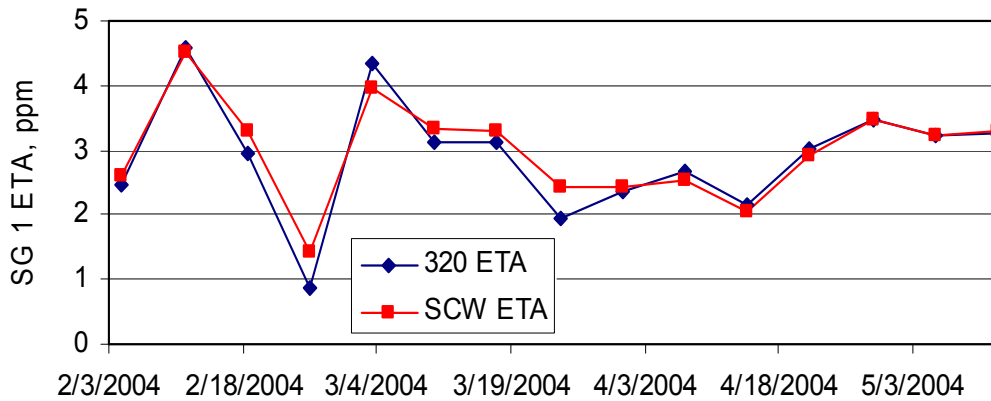


FIG. 13. Improved ETA virtual sensors [22].

Other additional types of analysis that SCW is capable of include calculation of primary pH at temperature, primary lithium and boron control bands, primary to secondary leak calculations via off-gas system analysis, tritium analysis, blow down system calculations, and/or main steam calculations, and calculations of performance indicators.

3.6. Quality assurance of data

The most important roles of cooling water of light water reactors are as energy transporting medium and neutron moderating medium. With light water as coolant in nuclear power plants, the resulting high temperature water causes corrosion of structural materials, which leads to adverse effects in the plants, *e.g.*, increasing shutdown radiation, potentially generating defects in materials of major components and fuel claddings, and increasing the volume of radioactive waste sources [7, 24–26].

In order to control the adverse effects, it is essential to understand corrosion behaviour of structural materials and then to control them in both systems. Corrosion behaviour is much affected by the combinations of water quality and material properties. In order to minimize the adverse effects, optimal water chemistry control has been proposed.

Cooling systems, major components and water chemistry differ in BWR and PWR plants. Procedures to measure water chemistry are also different in both reactor systems. At the same, common points in both reactor systems should also be discussed from the viewpoints of water chemistry data acquisition systems. Example of locations for on-line monitoring and sampling for Japanese BWR and PWR plants are given in Figures 6 and 7.

In order to evaluate plant condition by using water chemistry data, two points should be carefully considered. The first point is quality assurance of water chemistry data and the other is bridging the gaps between desired information and measured data. Evaluation should be based on reliable data. For this, quality assurance of water chemistry data is essential. Standardization of data acquisition procedures is required to obtain qualified data, where sampling location & periods, sampling procedures and analytical instruments to determine chemical and radioactive components, calibration procedures for the instrument and their frequencies, training of plant chemists and documentation guides are clearly defined.

At the same time trace ability of water chemistry data is required. For this, standard procedures for document management should be established. Major organizations for water chemistry standard are summarized in Figure 14.

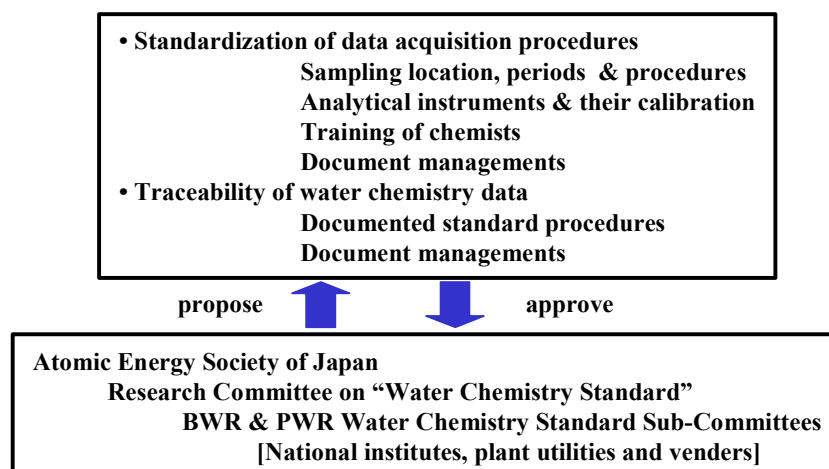


FIG. 14. Quality assurance of water chemistry data (example of Japan [10, 25-26]).

3.7. Updating chemistry specifications

The updating process of chemistry specifications is closely related to the plant chemistry improvement detailed in Section 5. Updating chemistry specifications should be done:

- Either when a specific event is occurring that shows the inadequacy of the present chemistry specifications,
- Or on a regular basis in the frame of the permanent improvement of applied chemistry and control.

The main reasons for updating the chemistry specifications for a specific event are:

- A new corrosion phenomenon,
- A new type of pollution identified as detrimental,
- The need to optimize and decrease radiation dose rates, impact on the environment, risk of corrosion and associated failure.

However, it appears also the need to regularly update the chemistry specifications according to:

- Plant operation feedback with encountered experience on safety issues, materials behaviour, corrosion, dosimetry, wastes and effluents release to the environment,
- Design modification or new materials,
- Chemistry treatment optimization,
- Laboratory Research and Development methods results,
- List of input data and potential impact of the modification,
- Tests performed in operating units for chemistry improvements,
- International plant feedback and other information,
- New regulation and recommendations (e.g. OSART, IAEA...),
- Operating costs and availability optimization.

The chemistry specifications should be thoroughly and carefully prepared before application, meaning they should be defined for at least several years. The revision process should include an evaluation of the new project by a team including at least a staff of engineering, design and operating people. Then, the chemistry specifications of PWR NPPs may be directly applied on a permanent basis on all the units of a utility or on one or a few units as a trial phase after which the new chemistry specification may be re-evaluated and again updated.

In the past, modification of chemistry specifications mainly focused on safety improvements, dose rate mitigation (e.g. lithium/K in RCS), secondary circuit treatment optimization (amines, hydrazine) and steam generator degradation which has been abnormally important in the case of Alloy 600 MA tubing.

There have been many cases for which the chemistry specifications had to be conservatively revised without adverse side effect. In a very few cases, the reverse trend was applied (e.g. silica limit and its impact on zeolite hard deposit on fuel cladding). But, the key chemistry parameters related to plant safety, availability and material behaviour are those at steam generator blow down. Due to this complicated situation and important impact, more and more stringent chemistry specifications have been applied at steam generator blow down in many countries, and particularly in those with Alloy 600, very sensitive to Stress Corrosion Cracking. Those improvements of chemistry specifications have been unable to mitigate the corrosion and many plants replaced their steam generator with resistant tubing (Alloy 690 or 800). Thus, it is also advisable, when a new and resistant material has been selected, to evaluate a relaxation of chemistry specifications severity.

Table 6. Some parameters values of SG blow down chemistry and action "levels" in specifications of different countries

№	Action "levels"	PWR, France [27]		PHWR, India [28]			WWER-1000, Russia [29-31]		
		χ , $\mu\text{S/cm}$	Na, ppb	χ , $\mu\text{S/cm}$	Na, ppm	Cl, ppm	χ , $\mu\text{S/cm}$	Na, ppb	Cl, ppb
1	2	3	4	5	6	7	8	9	10
1	Normal operation	<0.5	<3	<25	≤ 0.5	<1	≤ 5	≤ 300	≤ 100
2	Permissible operation with no time limit	<1	<10	-	-	-	-	-	-
3	1 month 360 h [28]	0.6-1.0	10-20	-	-	-	-	300-500	-
4	1 week [26,28] 240 h [27]	<4	<50	25-50	0.5-2	1-5	5-9	500-1000	100-300
5	24 h	≤ 7	≤ 150	50-150	2-5	5-10	9-15	1000-1500	300-500
6	Emergency shutdown (1-5 h)	>7	>150	>150	>5	>10	>15	>1500	>500

The large difference in values of water chemistry parameters for various reactor types (even under normal operation) can be explained by the use of different steel, alloys and distinction between steam generators thermo-technical characteristics. However, analysis of data from Table 6 makes it possible to detect the uniform approach when permissible deviations of water chemistry parameters are established to ensure the NPP's reliability and safety (see Sections 4.4.3 and 5.2.3).

The chemical environment in BWR primary water is established by four independent processes:

1. The combined effect of boiling and radiolysis results in a steady state concentration of O_2 , H_2 and H_2O_2 . The actual concentration of these species around the circuit varies, but the net result is a very oxidizing environment unless modified by chemical additions;
2. The feed water composition establishes the mass of impurities input into the primary circuit;
3. The size and efficiency of the reactor water cleanup system entering via the feed water;
4. The efficiency of deposition of insoluble (and some soluble) species on boiling fuel surfaces determines the concentration of insoluble species in the coolant and their deposition rate on out of core surfaces. It is the challenge of the BWR operator to balance these processes to optimize the performance and longevity of his unit.

BWR chemistry is indeed a delicate balance. Although high purity of both the feed water and reactor water is desired, certain impurities are actually beneficial and these must be controlled within fairly strict ranges to optimize operation. The desired concentrations of these beneficial impurities are quite low, in the parts per billion range, but when in balance, they can make large, beneficial impacts on key operating parameters.

Utilities periodically change specifications to follow to the Optimum Water Chemistry (OWC) strategy. OWC strategy is to keep all impurities to a minimum except the feed water additives iron, zinc, oxygen and hydrogen, which are all controlled for a beneficial effect.

4. PLANT OPERATION SUPPORT

4.1. Need for on-line analysis

The rapid growth that on-line analysis has experienced over the past years may be attributed to the need to improve process control and to optimise manpower. As shown in the previous Section, the evolution of computer technologies has made it possible to compile and construct expert systems for such complicated fields as chemistry management in the nuclear power plant. The chemistry expert system has two functions viz. predictive diagnosis and root cause investigation.

The diagnosis function can detect indications of chemistry anomalies by chemistry data processing and evaluation as mentioned below in Section 4.3. When the chemistry changes are detected, the causes of chemistry transients and anomalies will be inferred and estimated using a diagnostic matrix. The diagnostic matrix is constituted by the relationships between the chemistry anomalies and plant operation and chemistry parameters. Each parameter is considered to add some weight according to the influence of the individual chemistry anomaly and transient.

Immediate investigation and countermeasures against chemistry anomalies are required. In addition, high similarity and accuracy are desired in the methods of investigation and taking countermeasures. The modular structure of water chemistry expert system might be seen in Figure 15 [30–31].

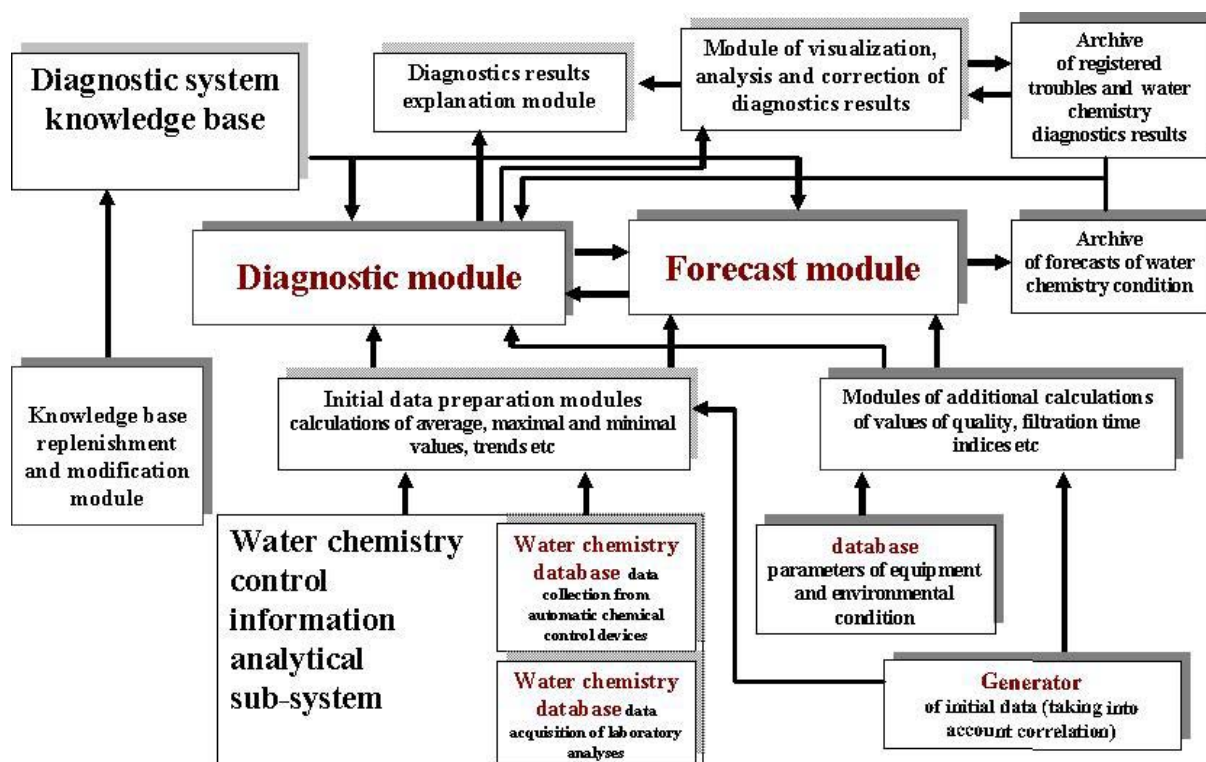


FIG. 15. Modular structure of expert system for diagnostics of water chemistry condition [30–31].

The basic functions of the system for data acquisition and processing are:

- The acquisition of important chemistry and process parameters, their processing, storage and display;
- The comparison of the measured parameters with the standard values;
- The generation of alarms when the set-points are either reached or approached;
- The diagnostic analysis for revealing the causes of deviations from controlled chemistry parameters in order to timely warn the operators about the requested corrective actions.

The expert function will be implemented by processing the chemistry parameters using logic algorithms, which will take in consideration the various parameters involved in the deviations. Warning of the operators about the chemistry parameters changes, their causes and necessary corrective actions shall be made in real time, if necessary, particularly, in relation to safety related parameters (boric acid concentration) or in case of sensitive equipment to be protected (steam generators).

The proposed improved chemistry monitoring system is determined by the nature of equipment to be protected in the primary and secondary circuits, and by the events that could lead to chemistry deviations detrimental for this equipment. This will lead to the choice of the most relevant chemical parameters to be monitored in those systems and to the additional equipment and sampling points necessary to achieve the requested protection.

The following equipment is considered critical in terms of safety and operation of the PWR units and must be protected against chemistry parameters deviations:

Primary circuit: Fuel Assemblies;
 Steam Generators.
Secondary circuit: Steam Generators;
 Turbine including condenser.

The following events could potentially lead to chemistry deviations, which could be detrimental for the above equipment:

Primary circuit:

- Inadequate boric acid concentration control;
- Inadequate hydrogen and oxygen control;
- Inadequate alkalinity control;
- Inappropriate ion-exchange resins operation (regeneration, cleaning, loss of resins);
- Out of specification make-up water.

Secondary circuit:

- Condenser in leakages;
- Excessive oxygen ingress;
- Poor quality of make-up water;
- Inappropriate operation of condensate polishing system and SG blow down water purification plant (regeneration, cleaning, loss of resins);
- Excessive ingress of corrosion products into steam generators, mainly from the two-phase flow equipments and lines.

4.2. Diagnostic approach

Several chemistry parameters are measured during the course of reactor operation. Chemical additives and ingressed impurities constitute these chemical parameters. There are also indicative parameters like specific conductivity, pH, electrochemical potential etc., which vary with changes in concentration of chemical species. A good diagnostic approach should consider the variations in all the chemistry parameters and substantiate them through chemical equilibria. The ultimate purpose of diagnostic approach is to identify the root cause of violation in the most important chemical constituents of a given system. The importance of the chemical constituents arises from only two criteria namely safety and economics of the plant operation. Consistency of a data set is equally important to avoid misinterpretation due to spurious fluctuations. Apart from consistency, time dependant variation in the chemical constituents as a function of reactor operating parameters like temperature, purification flow, make-up rate is also very relevant for the purpose of root cause analysis.

Monitoring systems of water chemistry generally provide extended data sets, which may serve as basis for adequate chemistry evaluation, negative trends early identification and prompt countermeasure implementation.

Such a diagnostic system may consist of several modules performing following different tasks:

- Check of the data plausibility – all data are evaluated respecting some rules and interdependencies, wrong (non plausible) data may be excluded from further processing or replaced by the calculated data;
- Evaluation of chemistry, identification of deviation causes – kind of root cause identification (leaks, pollutions, material degradation, mistaken manipulations etc.) – so called system diagnosis;
- Advisory function – verification of diagnosis (if needed), proposal of countermeasures for mitigation of the consequences;
- Prediction of trends, estimation of material corrosion behaviour, deposit formation trends etc. – based on the theoretical models, laboratory and experimental loop tests, operational data etc.

Both categories have some advantages and disadvantages indicated in Table VII.

4.3. Methodology

4.3.1. WSCL, India [28]

From the point of view of interaction between structural material and high temperature water/steam, the chemical constituents and its threshold limits are defined in terms of action levels. This is based on R&D work carried out in the laboratory. Threshold limit in concentration is prescribed for continuous exposure during the lifetime of reactor operation. After giving due weight age for instrumentation and calibration uncertainties, significant variation in the most important chemical constituents should be viewed as initiation of an unusual event, which can trigger the diagnosis process.

Table VII. Advantages and disadvantages of deterministic and probabilistic approaches.

	Deterministic approach	Probabilistic approach
Advantages	<ul style="list-style-type: none"> • Well understood process • Clear rules definition • High fidelity of the trend forecasts • Even not yet experienced events can be described with sufficient accuracy • Tuning of the system is more easy 	<ul style="list-style-type: none"> • Do not require full understanding of the process • Early identification of sensor malfunction • Possibility of replacement of wrong data • System may understand and recognize scenarios influenced by the parameter not included in the input data sets
Disadvantages	<ul style="list-style-type: none"> • Lack of knowledge to cover all potential problems • Some models may be very complex and not easy to implement in the in the plant system 	<ul style="list-style-type: none"> • Some systems may require thorough training of all scenarios • Non trained scenarios (events) may be not recognized • System architecture is very much bound to system configuration, (input parameter data sets) so even small change in the configuration may cause diagnosis becomes weak or even useless • Lower fidelity of trend forecasts

Several systems of both categories are now successfully implemented in the plant chemistry supervision or are tested on real plant data.

The standard diagnosis process itself constitutes an established co-relation in magnitude and direction between one or more interlinked chemical parameters in that system. These co-relations are built in the form of “rules”. For one or more combination of such rules, the cause for violation is prepared before hand with due weight age for operational experience. Such system is made available to the code in the form of a look-up table. Subsequent to identification of the root cause, chemical equilibria relevant to that system is reviewed in the context of the concentration of different parameters within the experimental uncertainties. The rate of change of concentration of all the chemical constituents is computed from the time of first detection. Similar variation is also computed for the time zone before the first detection. The assumption here is that they could have been in the concentration of chemical constituents without exceeding a critical limit. Analysis of this time zone will confirm such a variation provided analytical methods permit reliable quantification. The variation in the approaches by different participants was only minimal. Specific mention should be made with reference to the approach presented by Smiesko based on Neural Network. In this methodology, different scenarios of chemistry violation in terms of perturbation in chemical concentration identified with a root cause are prepared. The system chemistry is compared with these scenarios on a continuous basis by a code (after thorough training of the neural network module).

4.3.2. EPRI, USA [22, 23]

The diagnostic approach that is taken by EPRI's SMART ChemWorks™ (SCW) software (background to SCW given in Section 3.5) is to remotely and automatically process all incoming plant data, monitor a deviation from normal chemistry, and notify plant personnel if abnormal chemistry conditions are observed. Many of the utilities that are currently using this system already have a chemistry data management system that centralizes on-line readings as well as manually entered grab sample analysis results. In this case, an interface program is used which queries the chemistry data management system on a regular basis (i.e. once per minute) and a small file is produced which contains the latest values for the information required by SCW. This file is then sent to a central location, using FTP over a secure Internet connection. At other plants where the in-line data is from a different source, or where no data management system is being used, a slightly modified methodology is used.

Once the data file is received, the intelligence engine assesses the data, looking for bad sensors, making calculations, and diagnosing the system chemistry. The ChemWORKS Plant Chemistry Simulator is a core component in the model-based SMART ChemWorks system. The simulator is a deterministic model that describes material balance constraints, multi-component equilibrium and kinetic processes throughout the steam cycle. Custom set-up of the simulator requires a detailed description of the piping components in the system, including fluid flow and thermal conditions as well as all major interconnections between piping systems. SCW runs the simulators continuously using the continuously updated data feed. The incoming data is evaluated for inconsistencies. Bad monitors are identified and data from bad sensors is removed from further consideration. Data, which has become outdated, is given less importance than newer data for the purpose of diagnosing the system.

The filtered data is then used to perform calculations that produce species distribution around the steam cycle along with the resulting pH and specific and cation conductivities. These data may be output for any location, producing what is called a "virtual sensor." In addition to virtual sensing, system monitoring and diagnostics are continually performed to determine the state of the plant. The incoming data are continually evaluated using pattern recognition techniques to determine if the plant is running in the normal mode. If a chemistry upset does occur, this evaluation process will search a library of 'fingerprints' of known upset scenarios to determine what type of condition is most likely causing the abnormal chemistry.

A scenario is a condition that could occur in the plant. For example, Baseline Condition is a scenario describing normal chemistry, while Condenser Leak or Resin Intrusion are scenarios describing abnormal conditions which can be detected by SCW through continual monitoring of normally collected data. In SCW, each scenario has a fingerprint. A fingerprint can be thought of as a set of characteristics that describes each scenario uniquely. For example, in the PWR secondary system version of SCW, the chemistry conditions (i.e. species concentrations, pH and conductivities) at eight locations in the secondary plant are used to form the fingerprint for each scenario. When the incoming data, which is comprised of measured chemistry conditions at these locations and has its own fingerprint, is compared to the library of scenario fingerprints, an assessment can be made as to how well the incoming data fingerprint matches each of the scenario fingerprints. The scenario fingerprint with the best match to current data describes the most likely cause of any chemistry upset being observed.

For example, one of the scenarios frequently detected is condenser in leakage. This is an example from one plant. At approximately 15:00 on May 3, 2000 a small condenser leak

began to increase during power operation. Figure 16 shows the sodium concentration in the steam generator blow down.

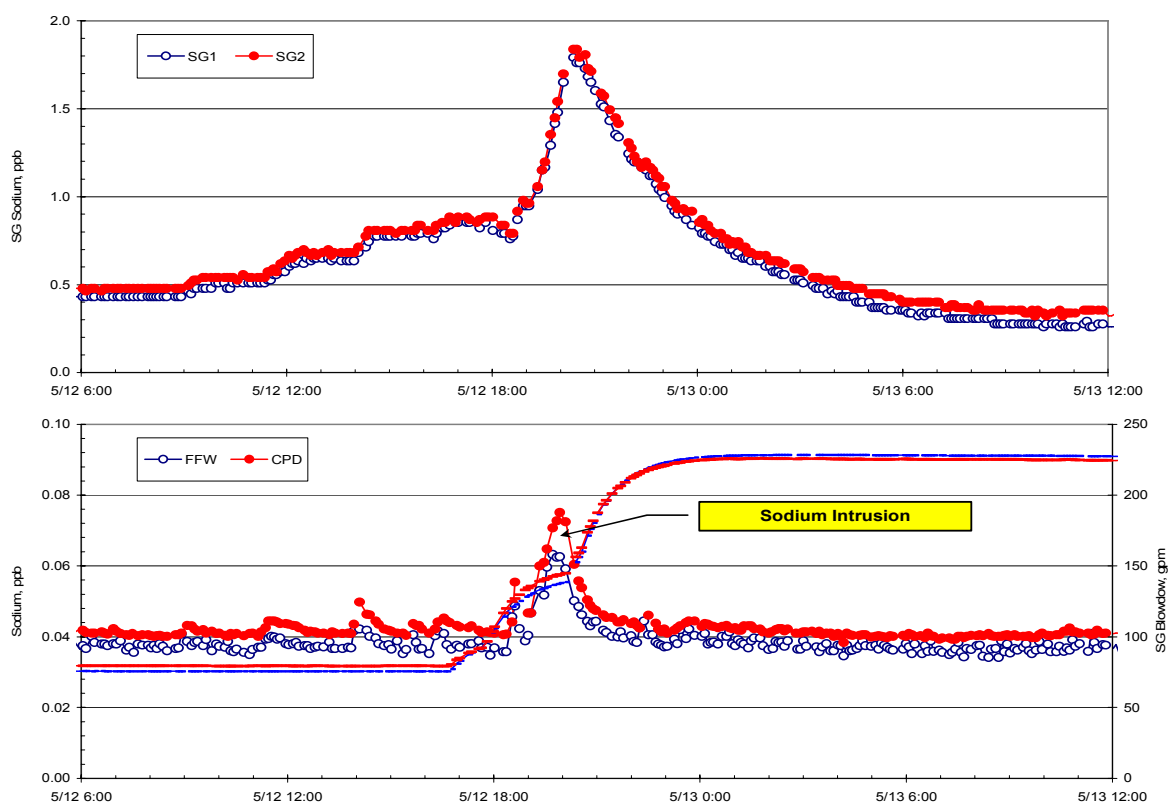


FIG. 16. Sodium intrusion [22]

As the condenser leak began, the SMART chemWORKS diagnosis went from predicting normal chemistry with a high confidence, to predicting a small condenser leak with a high confidence. An alert was sent at 15:58 and as corrective actions were taken, SMART chemWORKS returned to diagnosing Normal Chemistry. At this plant, chronic low levels of leakage exist, and the sensitivity has been adjusted to account for this baseline leakage.

4.3.3. EdF, France [13]

Several chemical parameters are measured during normal power operation: chemical additives, impurities or indicative parameters like total conductivity or pH.

Then, diagnostic measurements should be done in specific cases:

- When pollution is present and if the normal on-line monitors have been unable to identify its origin. In most cases, the on-line monitors will easily and hopefully quickly identify the origin of the pollution, allowing the plant staff to take the appropriate remedial action, as defined by the chemistry specifications (e.g. a condenser leak, which represents the most frequent case). But in some other rare cases, very unusual pollution may occur and would require a diagnostic approach. In this case, additional measurements of either other parameters or other sampling points of already measured parameters will help to identify the origin of the deviation. Such example that occurred in operating Nuclear Power Plants are: the use of a wrong

reagent to fill the tank from which the reagent is injected in the system, a contaminated reagent, abnormal system connections during specific cases of operation (mainly during transients);

- When a test is performed for improving the plant chemistry, as explained in Section 5c. In this case, during the testing period, sophisticated diagnostic approach will allow a thorough evaluation of the chemistry conditions. Such diagnostic may include very specific measurements that are difficult or expensive or detrimental (e.g. associated dosimetry) to carry out under normal operation condition. The main examples are redox electrochemical potential, corrosion products in the primary coolant, various oxidation contributors of corrosion products (e.g. magnetite, hematite, Cu^0 , Cu^I , Cu^{II}) in the steam-water system;
- When an abnormal event is occurring in the operating unit: e.g. CIPS (crud induced power shifts, also named by some people Axial Offset Anomaly, AOA), high radioactivity.

Decision to shutdown the plant can be effectively implemented by the indications from several reliable on-line monitors. This is an over simplified approach in which it is presumed that the predetermined parameters will be the only control parameters. Only a short diagnosis is anticipated at the time of shutdown, but no grab sampling is previously required when the action level implies an immediate shutdown (the most frequent case is a condenser leak which is easily diagnosed). Subsequent analysis of related parameters may lead to diagnosis of the root cause of the failure. Such a system is conducive for industrial application and can be tackled with less trained manpower. This approach is being practiced in France. French have also advocated periodic technical specification revision and special campaigns in plants for validation of new chemistry domain.

4.3.4. Diagnostic system for water chemistry control (DIWATM) [32]

FRAMATOME ANP developed an expert / diagnostic system for monitoring the plant water chemistry (DIWATM).

The expert system performs basically the following tasks:

- Centralized data collection of chemistry and chemistry-related parameters;
- Calculation of derived parameters (e.g. reference values, mass balances, trends, etc.) from the acquired data;
- Cross check between measured and calculated parameters, verification of data consistency (plausibility control of the acquired information), diagnosis of sensor problems;
- Logic linking of the acquired and verified information (inference) by means of a knowledge base, to obtain a diagnosis, with indication of kind of anomaly, degree of credibility, priority, origin and possible remedies, and generation of group as well as specific alarms.

This is achieved by applying advanced software techniques including client-server design and the use of fuzzy logic for the processing of uncertain knowledge within the expert system. The diagnosis module consists of a knowledge base, which is able to interpret the symptoms and to derive diagnoses. The knowledge base reflects all known plant situations, depicting all relevant plant chemistry anomalies.

The diagnoses knowledge base is prepared by experienced plant chemistry experts, and may be adapted to the specific characteristics of the plant.

Brief description of DIWA™ system function real time on-line data acquisition.

All of the on-line measured values (i.e. all of the measured values, which are detected with the help of sensors and passed through to various MCMS and I&C) are put into the DIWA system as one general data stream. It has no interest for DIWA, which MCMS detects the data. DIWA defines a general unified data format for all steps of transmission and identification of the on-line measured values. The identifiers of the individual measured values are based on the Plant - Identifier System for I&C. The transmission standard is based on an Ethernet connection (Hardware) and TCP/IP (transmission software protocol). The online data will be processed by a Unix based system, which does guarantees the real time operating system at least.

The database (dB) is developed for a real-time online data acquisition system, which is essential to process the high rate of plant data and data evaluation.

Acquisition of laboratory data

The off-line data acquisition is a DIWA separated software because it has to fulfill not only the function of data acquisition but also as laboratory information and management system (LIMS). LIMS as a time-independent off-line system is using a rational dB. The laboratory measured data which are required for DIWA system (for example for high diagnoses confidence), will be transferred directly (see Fig. 17).

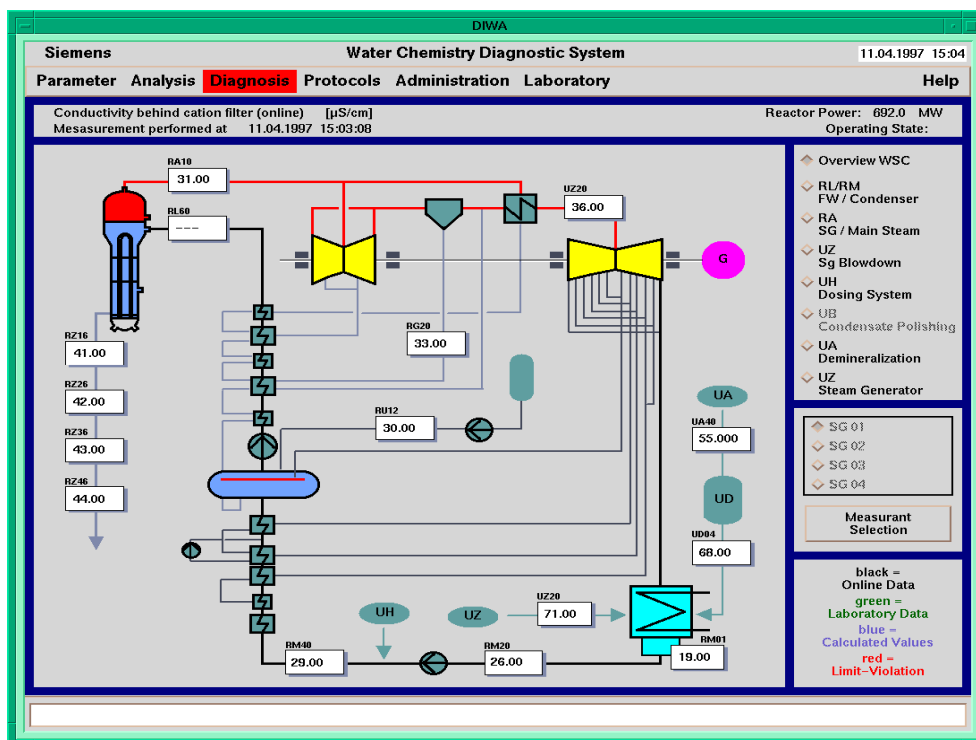


FIG. 17. Steam water cycle display [32].

What are done: plausibility checks; calculation of reference variables from measured data; long term storage of the main measured data and reference variables for subsequent analysis; data back up archives; comparison of actual data with set points.

Guideline values are defined for many chemistry parameters in the steam water cycle. Measured values outside the guideline values indicate a disturbance of the chemical conditions and require the initiation of countermeasures, depending on the size of the deviation (e.g. action level 1, 2, or 3). DIWA provides the possibility to use several different guideline values. If one of these values is exceeded, the following actions are performed:

- Color coding of the measured values on the process displays and in tables,
- Entry of the event in the logbook.

Usually the diagnostic system of DIWA will be activated and consequently countermeasures will be initiated long before major excursions of chemical values occur.

Presentation of measured data and reference variables in process displays including: graphics; time-based extrapolation of curves for trend plots; information on the operating state. The broad task of visualizing information, which has been measured or calculated is obvious for the DIWA system.

The main distinguished factor of the system is that analysis embraces all the activities performed by applying numerical mathematics in the broadest sense. In particular, this includes the calculation of characteristics parameters or set points, the comparison of set points with actual data, and the detection of deviations and limit violations. In addition the displaying numeric 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.

Functioning of diagnostics

There is immediate signaling of detected disturbances. The on-line data, which are measured and processed at real time are collected continuously in fixed measuring cycles.

The diagnostics module monitors chemistry based on measured and calculated values as well as rules stored in the knowledge base. If a new diagnosis is generated, the diagnostics button of the process display is displayed in red and the information will signal at the control room panel.

Selecting the Diagnostics menu item opens the diagnostics window, in which the diagnoses are listed in table form. The following information is given:

- Diagnosis number: The diagnosis is stored in the knowledge base under this number;
- Time: Current time is displayed for diagnoses, which have not yet been acknowledged. The time of acknowledgement is shown for acknowledged diagnoses;
- Confidence: Depending on the diagnosis, the confidence is a measure of the magnitude of the disturbance or of the probability, that the disturbance has occurred;
- Confirmation: yes/no. It can be used as logbook and documentation for diagnostics related instructions;
- Diagnosis text: brief description of diagnosis counteractions.

Individual diagnoses can be selected and diagnostics menu item can be used to display information. The verification of the diagnosis is represented by a graphical rule tree. The trend of determined confidence and diagnoses relevant measurements are shown in form of diagrams. Editing of knowledge base (description, explanation, countermeasures, recommendations, assessment); printout of logs and hard copies.

4.3.5. Slovakia [18, 19]

The Halden Reactor Project code called PEANO was used in Slovakia as one of probabilistic approaches for water chemistry diagnosis. Detailed monitoring of related chemistry parameters gives extended data sets, which may serve as a basis for adequate chemistry evaluation. There is further justification for diagnostic system due to destaffing trends worldwide which can partially offset the non-availability of chemists. The probabilistic diagnosis approach itself is thought off closer to reality than the deterministic approach.

Probabilistic approach (also called as neuro/fuzzy logic based system) does not require full understanding of the process, can indicate unrealistic data due to sensor malfunction and extraneous influences not listed in input data sets. However, this approach suffers from the need to give extensive training of all scenarios, requires voluminous data sets and it is system configuration specific. PEANO software has been tested on plant with satisfactory results (see Fig. 18, 19).

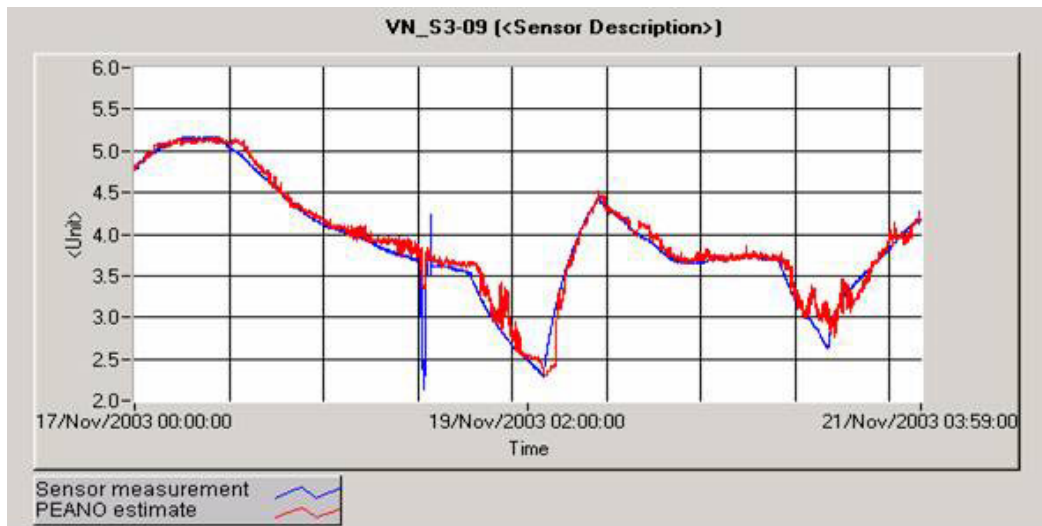


FIG. 18. The correlation of signals - sensor measurement and PEANO estimate [18].

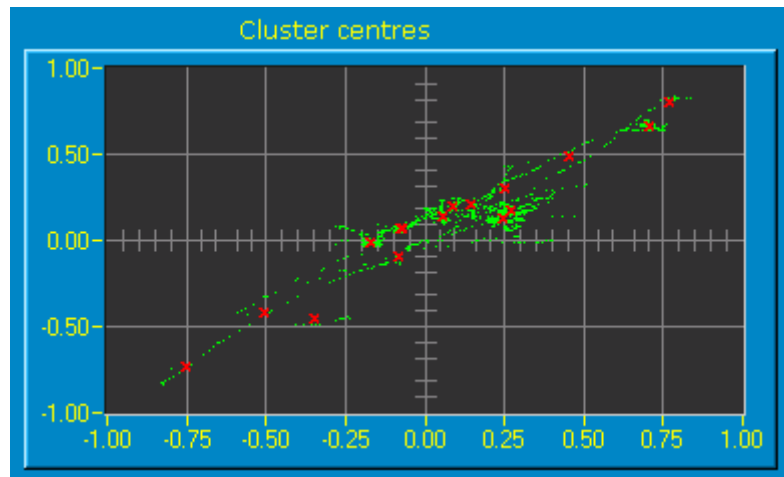


FIG. 19. The partition of data into fuzzy clusters depending on time delay implemented into data processing [18,19].

4.3.6. Russian Federation [30, 31]

One of the most significant advantages of **RF expert system is a WCh diagnostics model** which is based on diagnostic matrices and refining productive rules with the use of fuzzy logic. Due to the use of frames, the diagnostic model provide more extended and various knowledge of water chemistry and because of applying construction of production rules the logical structure and a possibility to use the fuzzy logic instrument are realized which allow to numerically evaluate confidence of the diagnosis produced. Such an approach allows identifying and analyzing a complex of causes of disturbance in WCh status.

Except two above mentioned information sources this system collects **processed statistical data**, which can be used later for prediction, generation of disturbance archives, correction of diagnoses and simulation.

The simulation model of the process is built based on accumulated statistical data and reflects a probable object status that had already taken place over the data accumulation period. The presence of this simulation model in the system allows refining diagnoses derived from the basic model.

The simulation model of some processes, which use statistical data about quality indices values, is accomplished with the application of nonparametric statistical techniques and neuron-network techniques of automatic classification and based on correlation analysis techniques.

By now, the Russian have developed an algorithm of water chemistry simulation. The performance of this algorithm was tested by simpler simulation of RCC (the Forced Recirculation Coolant Circuit) water chemistry.

The use of above techniques allows implementing such important functions of the diagnostics and monitoring systems like a virtual sensor, data recovery in case of measurement channel failures.

A specially developed **knowledge acquisition module** is used to enter new knowledge into diagnostics model and to revise available data.

The list of diagnostic indices is renewed and edited, criterion and threshold values are set of them, lists of faults, recommendations and additional questions are prepared against specially developed patterns based on structured knowledge (Fig.18).

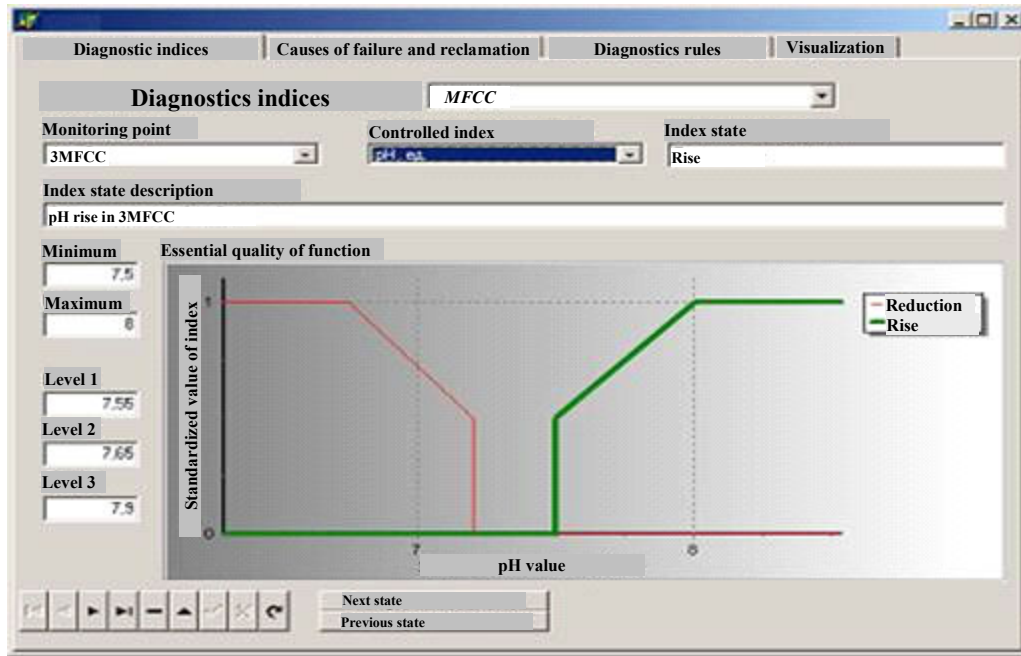


FIG. 18. Setting threshold and criterion values for diagnostic parameters.

The link between diagnostic indices and proper diagnoses is established by introducing construction of (diagnostic) rules, which are prepared and entered into the knowledgebase with a special logic-programming language (Fig. 19). Links within the model are set when preparing diagnostic rules on the screen with necessary fuzzy coefficients.

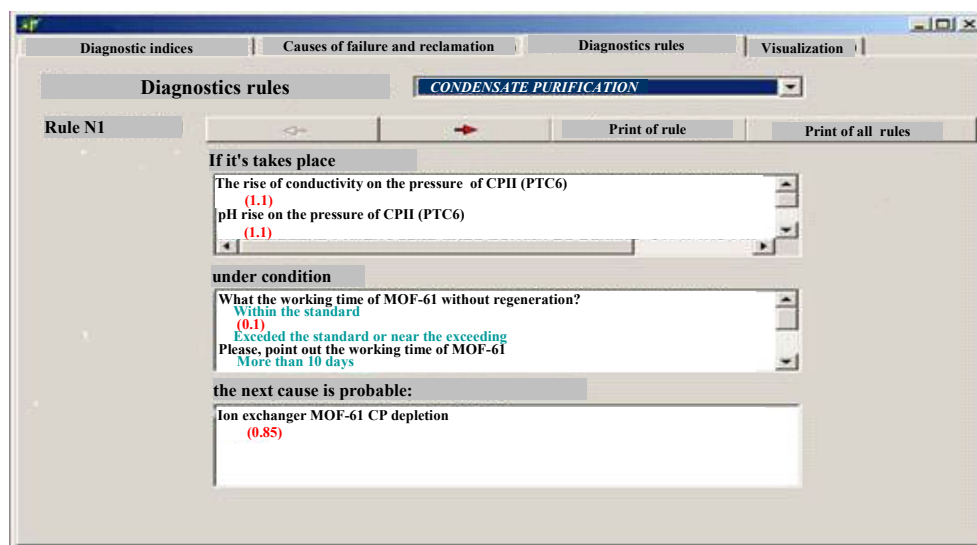


FIG. 19. Formation of diagnostic (construction) rules [31].

Data entry into diagnostics system database by the use of knowledgebase adjustment module is adapted to the operating personnel (process engineers of the chemical workshop). The inclusion of this module in the system's structure substantially extends system's possibilities for training and adaptation.

4.4. Users of diagnostic results

Section 3 indicates what type of monitoring and measurements (on-line monitoring and grab sampling) should be done. Section 6 indicates what ways can be followed to develop and complete knowledge module. After having explained in which cases a diagnostic measurement is useful, this Section describes the various users of the diagnostic results.

Chemistry expert system

The evolution of computer technologies has made it possible to compile and construct expert systems for such complicated fields as chemistry management in the nuclear power plant. The chemistry expert system has two functions viz. predictive diagnosis and root cause investigation.

Predictive diagnosis function

The predictive diagnosis function can detect indications of chemistry anomalies by chemistry data treatment and evaluation as mentioned above in Section 4.2. When the chemistry changes are detected, the causes of chemistry transients and anomalies will be inferred and estimated using a diagnostic matrix. The diagnostic matrix is constituted by the relationships between the chemistry anomalies and plant operation and chemistry parameters. Each parameter is considered to add some weight according to the influence of the individual chemistry anomaly and transient. The diagnostic parameters and their weight have been selected based on empirical knowledge and experiences.

Root cause investigation

Immediate investigation and countermeasures against chemistry anomalies are required. In addition, high similarity and accuracy are desired in the methods of investigation and taking countermeasures. Empirical knowledge, technologies and experiences are needed to investigate root causes and provide adequate countermeasures.

The expert systems to investigate root causes and provide countermeasures have been developed as follows:

- (1) Investigation of reactor water quality changes;
- (2) Countermeasures against cooling (raw/sea) water leakage in the main condenser;
- (3) Evaluation of reactor water cleanup system performance;
- (4) Leakage evaluation in the primary containment vessel.

Reporting

The chemistry reports may vary by pattern and format, for example, daily, weekly, monthly, quarterly and annual reports. These may be not only typical but also may be temporary formats, which contain many tables and figures. To provide the chemistry reports, the chemistry management system is very effective.

Calculation

For chemistry management in the nuclear plant, it is necessary to calculate and estimate chemistry data. The following calculation functions have been provided in the chemistry management system:

- (1) Theoretical calculation of conductivity and pH based on ion impurities concentrations;
- (2) Simulation of reactor water quality changes when RWCU is isolated and feed water quality changes;
- (3) Simulation of reactor water quality changes at the cooling water leakage in the main condenser;
- (4) Evaluation of fission products release pattern.

Education and training

The system has some education and training functions. These functions can be useful for inexperienced chemists.

4.4.1. Operators — Users of diagnostic results

The first general users of chemistry results should be the operators in control room who have to decide of a potential immediate action, particularly in the presence of high and unacceptable pollutions that may require an immediate shutdown. But in general, it is advisable that the plant operators get a clear answer to such actions thanks to on-line monitor indications without having the necessity to establish a diagnosis before taking an immediate action. The typical case is a large condenser leak for which the condenser and the steam generator blow down on-line monitors give enough reliable confirmation of pollutions through on-line monitor redundancy. Thus, the operators will be able to take the decision of the action, particularly if an immediate shutdown is required. Although there could be some uncertainty on the origin of the pollution, the chemistry specification clearly indicate what action to take, according to the chemistry parameters values, and the plant operators should not have to further investigate before applying the requires action.

4.4.2. Chemistry staff

Chemistry staff can use diagnostic system as a tool for fast orientation in the plant chemistry deviations, but still – expertise of knowledgeable and experienced chemist must be of higher level (reliability). It is chemistry staff who should supervise effectiveness of diagnostic system and who should initiate system modification and tuning if necessary. Consequently, in most cases, the diagnostic should be made by the chemistry staff, which will:

- Define the required action (that may be proposed to the plant management or operator responsible), if it is not an immediate one already taken by the plant operator, such as an immediate shutdown as explained above;
- Define the origin of the abnormal situation, if the normal monitoring and sampling was insufficient to draw a clear conclusion;
- Define the strategy to be proposed to the responsible persons to recover from the situation (e.g. leaking condenser tube to be plugged and when, need to search for an air ingress in the condenser, replacement or regeneration of an ion exchanged resin bed).

Thus, in most cases, the first users of a diagnostic results will be the chemistry staff. It is true, for example, also for SMART ChemWorks™ (SCW). The software could be useful for operators and plant management, but efforts to introduce SMART ChemWorks into the daily procedures of operators and plant management have been minimal to date. One of the most utilized features of SCW is also one of the simplest features. Plant personnel find the alerting feature of SCW very helpful. Plant personnel can be alerted on any incoming parameter with a variety of alerting limits. Examples include:

- Condensate Pump Discharge (CPD) Sodium > 0.5 ppb;
- Feed water Hydrazine < 8 * CPD Oxygen;
- CPD O₂ > 10 ppb;
- Steam Generator Blow down (SGBD) Chloride > 2.5 ppb;
- SGBD Cation Conductivity > 1 µS/cm.

The combination of alerting functionality and the capability of SCW to detect early warnings of abnormal chemistry conditions allows chemistry staff to focus on issues that need immediate attention, rather than spending a large portion of time simply monitoring chemistry. SCW monitors chemistry for the chemistry staff and alerts staff as soon as there is any indication that a chemistry excursion may be underway (see table 8 and Fig.20).

Table 8. SCW Gives Early Warnings [22-23].

Chemistry Event at US Plant	
Way of Analyses	What do operators
Sodium concentration started increasing at blow down ~5/12/2004 09:00 hours	SCW's first alert Issued 'SG2 Na >0.75 ppb' alert at 14:35 hours on 5/12
No changes were observed in blow down cation conductivity levels	SCW's second alert Issued 'SG1 Na >0.75 ppb' alert at 14:52 hours on 5/12
Brief minimal increases of sodium levels were observed at feed water and condensate	SCW Engineer Support Sent an Email to plant chemistry group regarding to the sodium ingress at 14:58 hours on 5/12 Plant started increasing blow down flow at 17:00 hours on 5/12
Operating with a normal blow down flow	

SCW also improves the availability and ease of viewing chemistry data for chemistry staff, because it makes chemistry data available through a secure web browser. With the aging workforce and the concomitant loss of experienced chemistry staff, many of the smaller plants only have one or two members of the staff who have enough experience to deal with chemistry events. In the case that there is a chemistry event while that person(s) is offsite, the person will very easily be able to log on to SCW through an Internet browser and see all the pertinent chemistry data for his plant. That person will then be able to quickly instruct other plant personnel, given the information from SCW. In the cases where minutes matter, use of SCW may help chemistry staff mitigate the more serious effects of chemistry events.

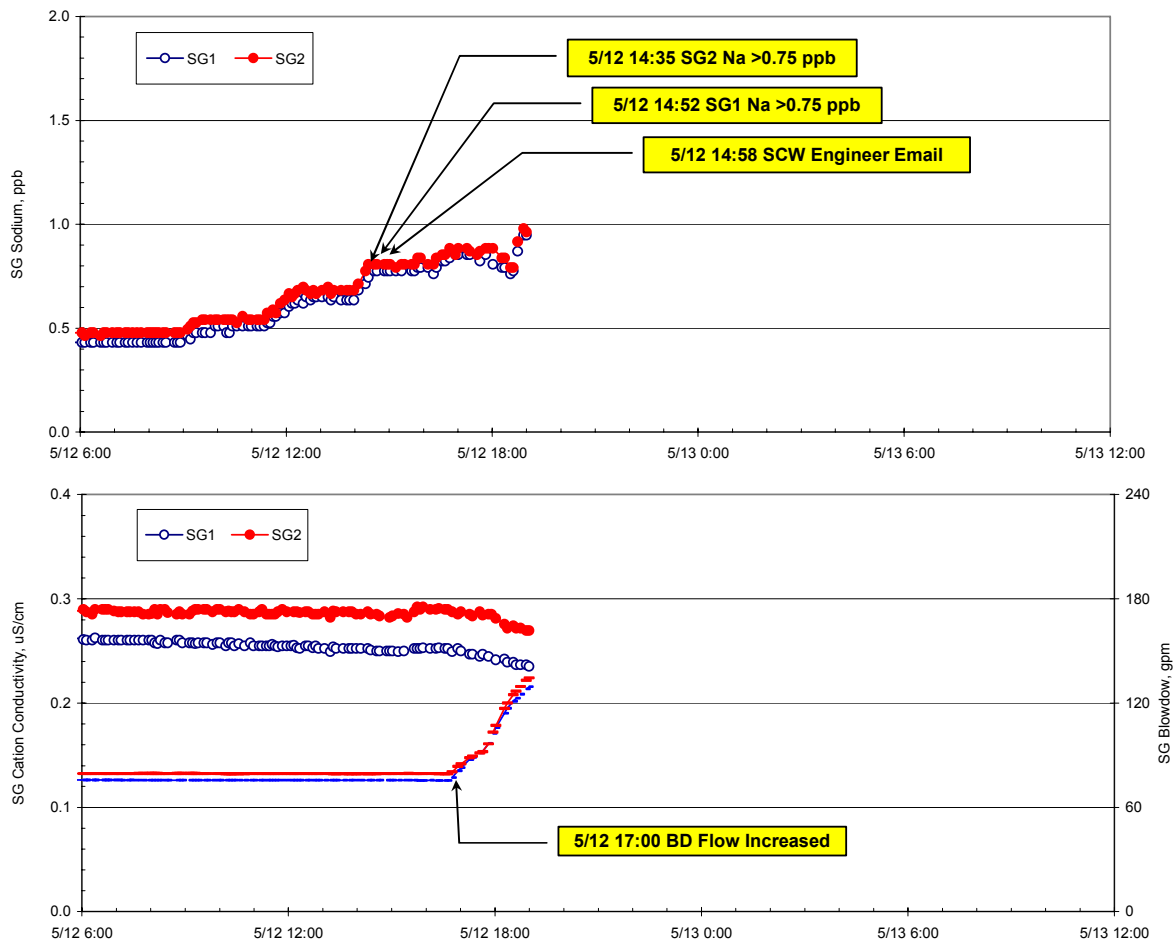


FIG.20. SCW gives early warnings [22].

Although SCW is currently not often used by operators or plant management, there are some aspects of the application that would be useful. Operators could use the reporting feature of SCW, which is similar to that of AECL's ChemAND software. Reports for different types of chemistry excursions could be created and operators could be instructed on what actions to take during those different scenarios. Plant managers may also find the calculations of chemistry performance indicators helpful. During large chemistry events, they may also find that the availability of data through SCW will allow a better understanding of the event and what their staff is doing to mitigate consequences.

4.4.3. Plant management

Very often management at nuclear power plant is either ignorant or misinformed of the importance of on-line monitoring in the process. It is important that management is made aware of the long-term benefits of on-line monitoring, since failures due to improper chemical control may take many years to manifest themselves. Without continuous monitoring and effective data capture and processing, it is not possible to assess the current or predict the long-term performance of the plant and without the support of management no on-line analysis programme will be effective. It is therefore the duty of the power plant chemist to keep management informed with respect to the chemical health of the plant and to promote the need and benefits of on-line analysis. Management support is essential if on-line

monitoring programmes are to be extended or upgraded to ensure continued trouble-free plant operation.

Plant management is not direct user of system outputs, at this level consequences of some chemistry deviations and excursions can be demonstrated with use of diagnostic system (if system capabilities allow it), which may serve as support for important and strategic management decisions.

When a safety issue is related to the abnormality, the decision will be clearly taken according to the technical specifications. But, out of an action required by the technical specifications, the final decision of the action to undertake is generally under the plant management responsibility when there is a consequence on, availability, dosimetry, environment and costs or when a balance has to be made between several options with an impact on the above consequences. Nevertheless, the plant management decision should be based on the diagnostic evaluation of the chemistry staff.

Main important parameters that influence on service life of the equipment of nuclear power plants, formation of deposits on fuels and accumulation of activity are concentrations of aggressive impurities, electric conductivity of water, pH value and concentration of corrosion products in the coolant.

The number of types of equipment components of nuclear power plants, sudden failures of which should be prevented, is tremendous. The study of the flow of failures intensity of separate equipment components taking into consideration variety of possible mechanisms of generation and development of defects is not effective due to complicity of conducting proving experiments [33-34]. The long-time predict module is based on quantitative evaluation of the influence of parameters of water chemistry on service life of different equipment components of nuclear power plants by implementation of the chemo metric method of analysis. The chemo metric analysis is a kind of the system analysis, which is based on the search of functional interrelations in a certain system. In the Russian case the process circuits of reactor unit of nuclear power plants can be regarded as systems.

Within the limits of the chemometric analysis data included in reports on failures of equipment and the results of regular chemical monitoring of the coolant agent of process circuits of the reactor block of nuclear power plants are regarded as the database of a passive experiment [33-34]. Water-chemistry parameters of process circuits are interrelated physically and are checked regularly by independent channels. It makes it possible, on the one hand, to check the reliability thereof and, on the other hand, to use them for general description of situations regarding service life of various equipment components assuming functional similarity in generation and development of a defect. In this case service life characteristics of equipment component are the response function, e.g. the flow of failures, intensity, and the results of regular measurements of parameters of the water-chemistry are the argument.

When applying the chemometric method of analysis it is expedient to use dimensionless values normalized by a certain rule [33-34]. E.g. values may be normalized as the difference between the current value of the magnitude to be converted and its average values in the sample for a certain time period divided by the difference between the maximal and minimal values in this sample. Normalizing makes it possible to compare parameters having different dimensions of quantity and incomparable numerical values and to objectively compare parameter values of similar reactor blocks with different variation intervals of these parameters. Besides the chosen method of normalization enables to exclude mechanisms of initialization and development of a certain defect.

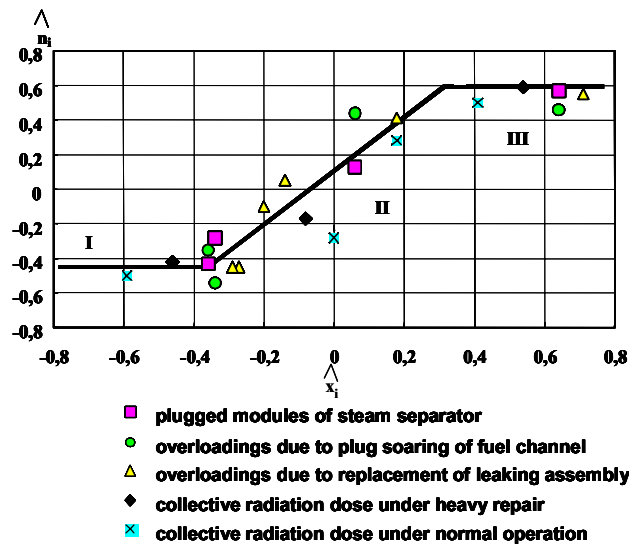


FIG. 21. A correlation between normalized values of indices of RBMK-1000 equipment reliability collective dose and normalized values of iron corrosion product release with feed water [32].

$$\hat{n}_i = \frac{n_i - \bar{n}}{n_{\max} - n_{\min}}; \quad \hat{x}_i = \frac{x_i - \bar{x}}{x_{\max} - x_{\min}}, \text{ where } \frac{n}{\tau} \sim \dot{V} - \text{speed produced of defects,}$$

where indexes max and min - intervals board of parameters; x_i, n_i – carriers, \bar{x}, \bar{n} - average value of parameters.

Three areas can be singled out conditionally in Figure8 and interpreted in the following way:

1. High purity area of the coolant, hence the influence of the coolant on service life of equipment components of nuclear power plants is insignificant, in this case service life of equipment during operation is mainly determined by properties of the material of the equipment and the level of loads, assigned by the structure concerned and specified in the project;
2. Area of correlation between service life characteristics of equipment and characteristics of the coolant;
3. Area of inadmissible reduction of service life of equipment components of nuclear power plants, in this case the site personnel takes active arrangements to replace defective equipment, changes structural material or the design of equipment.

4.5. Limitations and perspectives of expert systems use

Despite the need for on-line analysis identified above, it must be considered that too complicated system may not be beneficial due to increased failure rate of its constituents. Earlier attempts at on-line chemical analysis were both costly and non reliable. Successful instrumental laboratory techniques taken into the field failed dismally and instruments were rapidly destroyed by the harsh industrial environment and inadequate control of the physical variables of flow, pressure and temperature. The track record of on-line analysis was far from example with the arena being littered with the carcasses of so many black boxes and the science obtained a bad name. Although on-line analysis systems have become very sophisticated over the past decades, it should not be forgotten that this instrumentation is merely an extension of laboratory apparatus and requires the same care. The major difference

is that the field-mounted instrument usually has many more built-in features, such as automatic calibration, alarms and remote recording facilities. Furthermore, the monitor is expected very often to operate reliably and trouble-free for 24 hours a day, 365 days a year, without maintenance and need of calibration.

For a sampling and sample conditioning system to operate correctly, selection of components is of primary importance because of the high pressures and temperatures experienced in the Nuclear Power Plant cycle, therefore certified and therefore costly components must be installed to control and regulate these energies.

Different reasons for the failure of on-line analytical systems have been identified and are listed below:

- Inadequate sampling and sample conditioning;
- Incorrect equipment for the measurement, i.e. not "fit-for-purpose";
- Ignorance, i.e. inadequate understanding or Interpretation of the philosophy of on-line analysis;
- Lack of training;

- Inadequate maintenance;
- Disregard by (or misinformation to) management with respect to the importance of the on-line analytical instrumentation.

In general, maintenance should follow the manufacturer's guidelines in the instruction manual for the equipment, e.g. routine (in many cases preventive) replacement of filters, seats, pump, tubes etc. The on-line analyser should be treated with the same care as the analytical instruments in the laboratory, i. e. similar preparation of reagents and calibration solutions, frequency of calibration and verification. Sample conditioning equipment should be kept in optimum condition to prevent damage to the on-line monitors owing to excursions in pressure, temperature and flow. Analysers should not be exposed to harsh environmental conditions, e.g. extreme conditions of ambient temperature and humidity. Correct selection of the monitoring instrumentation is essential and will prevent many of the failures experienced.

The need for on-line monitoring in the power plant will continue. The following statement clearly defines the future need. There is a continuously increasing tendency to exhibit confidence in the automation of power plant. It is identified that as a result conclusion:

- Staff may be reduced, which includes chemists and instrumentation technicians;
- Higher availability of technical installations may be realised, which without question, includes continuous on-line analytical measurements;
- Investment may be optimised, i.e. the utilisation of instruments, offering the most benefits but excluding superfluous features, to its full capacity;
- In order to fulfil the demands placed on effective automation, provision must be made for measuring equipment which:
 - Delivers trustworthy results, within the specified physical/chemical constraints,
 - Complies with the minimum operational, maintenance, and repair costs,
 - Conforms to the requirements and needs of power plant operation.

It is recognized that if expert systems may be of great help for some chemists, particularly young and overloaded ones, they may not substitute fully experienced chemists able to evaluate the origin of specific situations and take the appropriate decision of corrective action. Therefore increasing lack of high-level experts is kept along with the need of expert systems.

The expert systems or external support may contribute to decrease the load of the plant chemist for decision on plant chemistry operation tasks in most frequent cases but not in all the unexpected situations. The R&D people, the models and plant tests are still necessary to contribute to tasks such as long term evaluation, studies and chemistry specification updating for which the experts may be located in centralised organizations.

The need for on-line monitors for the important parameters associated with efficient data storage and trending is completely agreed by all participants of the DAWAC CRP. It is not any more suitable not to have such systems. Several participants considered that there are many data but not always properly evaluated. Thus, if during a plant test of R&D, a huge number of data has to be gathered, for normal plant operation, it seems advisable to focus on the number of necessary parameters and correctly analyze their results for taking the correct action, when necessary. Additional data may be stored for a future potential need if this is not detrimental for gathering and evaluating those data that are of utmost importance.

The need for low temperature on-line monitors (sodium, conductivity...) for the important parameters associated with efficient data storage and trending is completely agreed by all the participants. From other side, the need for sophisticated high temperature on-line monitors should be only recommended for performing R&D or plant test in order to support the long term evaluation, studies and chemistry specification updating work category defined in above. A typical example is the ECP, which will be used to define the correct ECP value associated to some chemical added in the system and thus to define the specified range of the chemical in order to mitigate the various potential risks of corrosion for the different materials exposed.

Then, the use of such high temperature on-line sensors is considered as an R&D tool, of high technology, requiring the presence of a highly experienced expert in this field to appropriately interpret the results that are not compatible with the normal work of a plant chemist.

5. PLANT CHEMISTRY IMPROVEMENTS

5.1. R&D support

DAWAC project participants unanimously agreed that expert systems are not able to replace experienced chemists in evaluating the origin of specific situations and taking the appropriate decision of corrective action. The expert systems will be used either for diagnosis or as an additional tool for data handling (see Sections 3 and 4). In practice, there is some need to handle two types of R&D support:

- a. Decision on plant chemistry operation,
- b. Long term evaluation, studies and chemistry specification updating.

The expert systems or external help may contribute to decrease the load of the plant chemist for (a) tasks in most frequent cases but not in all the unexpected situations. The R&D people, the models and plant tests may contribute to tasks (b) for which the experts may be located in a central organization, particularly for large utilities.

Some results of water chemistry and corrosion related studies conducted at the Institute for Nuclear Research (Romania), Institute for Nuclear Research and Nuclear Energy (INRNE) in Bulgaria and Nuclear Research Institute (NRI) in Czech Republic.

5.1.1. Water chemistry studies carried out at Institute for Nuclear Research (INR) in Romania [35-37]

To understand the contribution of water chemistry in initiation of some accelerated corrosion processes, intensive studies were executed at INR. Thus, to investigate the influence of water chemistry (pH, O₂ dissolved, Cl⁻, F⁻) on corrosion of some structural materials (carbon and martensitic steels, Zr and Ni alloys) and to establish the maximum permissible values, corrosion experiments by static autoclaving and electrochemical methods were performed.

The excessive lithium hydroxide concentrations raising the pH above 11.5 accelerate the pre-transition corrosion rate and oxidation of Zr alloys [35], because of the possible formation of lithium zirconate.

Also, the pH increase to 11.5 by adding LiOH resulted in appearance of some localized corrosive attacks on martensitic steel samples [36]. Attacks were observed linked to non-metallic inclusions or intermetallic precipitates.

The concentration of dissolved oxygen is a factor of the great importance for corrosion of structural materials. An acceleration of Zr-2.5%Nb alloy corrosion at oxygen concentration above 0.1ppm O₂ was observed, accompanied with the formation of porous thick oxide films and of larger and more numerous hydrides.

Presence of a higher oxygen concentration can result in pitting corrosion on carbon steel [37].

The contamination of the primary coolant with more than 0.2ppm Cl⁻ and more than 0.1ppm F⁻ accelerated the oxidation and hydriding of Zr alloys.

Therefore, taking into account the contribution of water chemistry on structural materials corrosion, the following water chemistry regime must be maintained in a pressurized heavy water reactor (PHWR)-CANDU:

- An alkaline reducing chemistry by lithium hydroxide ($0.4 \div 1.1 \text{ mg Li/kgD}_2\text{O}$) for obtaining of $\text{pH} = 10.2 \div 10.8$,
- Hydrogen gas addition ($3 \div 10 \text{ ml H}_2/\text{kgD}_2\text{O}$) to suppress formation of oxygen,
- Cl^- concentration $< 0.2 \text{ mg/kgD}_2\text{O}$, and
- F^- concentration $< 0.1 \text{ mg/kgD}_2\text{O}$.

5.1.2. Water chemistry studies carried out at Institute for Nuclear Research and Nuclear Energy (INRNE) in Bulgaria [38, 39]

The practice of Kozloduy NPP experiences that the reactor long time operation with 50% power is not an exception. As a consequence, decrease of both inlet coolant temperature to 260°C and outlet coolant temperature to 273°C is observed. Under these conditions the real coolant's high-temperature pH-values decrease by $0.3 - 0.4$ in comparison with the pH-values corresponding to the coolant's temperature at 100% power. These lower coolant's pH-values should increase of the primary circuit's stainless surfaces corrosion processes and also the increase of the corrosion product's concentration in a coolant. This will accelerate the activity build-up on the circuit's surfaces. The above-mentioned situations require that the certain parameters like high-temperature pH-values should be adjusted for different reactor operation conditions.

It is generally known that concentrations of specific salts (ions) in the steam generators water considerably decrease during operation due to hide – out effect, and during shutdown they increase again due to hideout return. The experience of Kozloduy NPP WWER-1000 shows that at transient conditions (with more than 20 % of power change), both effects are observed. However, it was observed, that changes in power during transition conditions are always accompanied by a change of Na^+ and Cl^- ions, but often this change is in atypic reverse order: by power decreasing the concentrations of Na^+ and Cl^- decrease and by the next increasing of the power the concentrations of these ions increase.

5.1.3. Primary water chemistry R&D carried out at the NRI Rez, Czech Republic [40]

5.1.3.1. WWER primary coolant technology

As in PWRs, WWER's chemistry has to ensure alkaline reducing conditions in the primary system during the normal operation. Several modifications of WWER primary coolant chemistry which differ in the way how the boron-potassium coordination is controlled during the cycle (standard and modified chemistry) and in way how hydrogen is produced and maintained in the coolant (ammonia, hydrazine and hydrogen chemistry) have been developed and applied.

In the beginning of 90s, instead of the “standard water chemistry” has been developed and introduced “modified water chemistry” which ensures the constant pH_T and stable physical-chemical conditions during the whole reactor cycle what should reduce radiation fields. The choice of the optimal pH_T was a result of the plant data analysis as well as of the mathematical modelling. For WWER-440 units the pH_{300} in range of $7.1-7.3$ and $7.0-7.2$ for WWER-1000 was chosen as an optimum. This type of water chemistry has been introduced at

many plants (e.g. Dukovany and Temelín in the Czech Republic, Bohunice in Slovakia, and at Russian and Ukrainian plants). At the same time, utilities specify different maximum potassium level allowed (20 ppm at the Czech, Russian and Ukrainian units; 16.4 ppm at Bohunice). Boron/potassium co-ordination for the standard and modified chemistries is given in Figure 22.

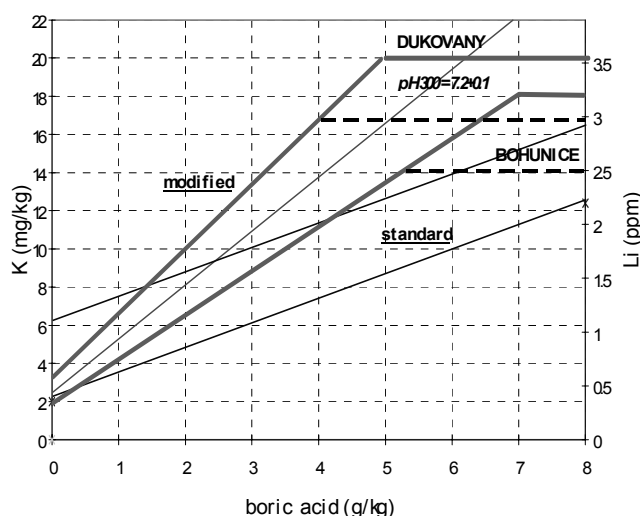


FIG. 22. Boron/potassium co-ordination for the standard and modified chemistries

Taking into account obtained operational experience in WWER units as well as the best world practice the WWER Primary Water Chemistry Guidelines have been developed in the Czech Republic by NRI Rez. The Guidelines formulate requirements for the primary water chemistry parameters (control and diagnostic parameters) and their monitoring, including appropriate action levels for start up, nominal operation and shut down (see Tables 9, 10).

Table 9. WWER water chemistry specification for reactor power operation (control parameters)

Control parameter	Sampl. Frequency	Typical value	Action level		
			1	2	3
Chlorides, ppm	3xWeek	<0.05	-	>0.1	>1.0
Fluorides, ppm	3xWeek	<0.05	-	>0.1	>1.0
Sulphates, ppm	3xWeek	<0.05	-	>0.15	>1.0
Oxygen, ppb	OLM	<5	>5	>10	>100
Hydrogen, Nml/kg	OLM	20-40	<20; >40	<10; >50	<5
Total alkalinity as potassium, mmol/kg	3xWeek	Related to pH ₃₀₀	-	>0.5	-
pH at 300°C	calculation	7.1-7.3 ¹⁾ 7.0-7.2 ²⁾	<7.1; >7.3 <7.0; >7.2	<6.9; >7.5	-

¹⁾ for WWER-440 units

²⁾ for WWER-1000 units

OLM – on-line monitoring

Table 10. WWER water chemistry specification for reactor power operation (diagnostic parameters)

Diagnostic parameters	Sampling frequency	Typical value
pH at 25°C	1xDay	5.7-10.2
Conductivity, $\mu\text{S}/\text{cm}$	1xDay	25-125
Boric acid, g/kg	1xDay	As required for reactivity control
Ammonia, ppm	1xDay	>5
Suspended solids, ppm	1xWeek	<0.1
Silica (SiO_2), ppm	1xWeek	<1.0

5.1.3.2. Inner surfaces passivation during the plant commissioning

Two units of WWER-440 at NPP Mochovce in Slovakia and two units of WWER-1000 at NPP Temelín in the Czech Republic were commissioned in past years. The hot functional tests (HFT) were conducted at controlled primary water chemistry with the aim to develop a protective passive film on the primary circuit surfaces. Special water chemistry guidelines were developed and implemented at this period. Also, some surveillance samples (corrosion coupons) were placed into the primary circuit and subsequently analyzed to obtain information about characteristics of the formed passive film.

Water chemistry specification for the HFT stage of both WWER-440 and 1000 is given in Table 11.

Table 11. Water chemistry specification for period of HFT of WWER-440 and WWER-1000 units

Parameter	Limit	Note
pH @ 25°C	5.6-7.5	Before KOH dosing
pH @ 25°C	9-10.5	After KOH dosing
pH @ 300°C (calculated)	6.9-7.5	After KOH dosing
Cl^- and F^- , ppm	<0.1	
K^+ , ppm	2-5	After KOH dosing
O_2 , ppm	<0,02	At >120°C
SiO_2 , ppm	<0,2	
Suspended solids, ppm	<0,2	
H_2 , Nml/kg	2-5	Expected level

The hot functional tests with the controlled passivation stage have been applied at NPP Mochovce, units 1 & 2 (EMO-1 and EMO-2), and at NPP Temelín, units 1 & 2 (ETE-1 and ETE-2).

It was identified that corrosion layers in Temelín units consist of two spinels with different lattice parameters. Elemental composition of corrosion layer corresponds to formulas from $(\text{Ni}_{0.05}\text{Fe}_{0.8}\text{Cr}_{0.15})_3\text{O}_4$ to $(\text{Ni}_{0.1}\text{Fe}_{0.6}\text{Cr}_{0.3})_3\text{O}_4$. In all cases, the coupons were covered by a layer of loose crud that was formed by small, well-developed crystals of 1-2 μm size (see Fig.23). Thickness of this crud layer differed from case to case and lay typically in range of 1-3 μm .

Well-developed passive film was observed only on coupons from Temelín units. In Mochovce the passive film thickness was below a resolution limit of SEM (0.1 μm). A typical view of passive film is shown in Figure 24. It can be seen that the passive film has a rather uniform and compact structure with typical thickness of $0.6\pm 0.1\ \mu\text{m}$.

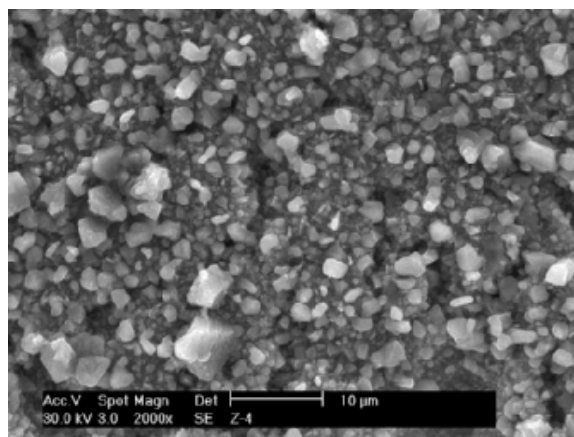


FIG. 23. A typical view of corrosion layer covering an outer surface of the surveillance coupons

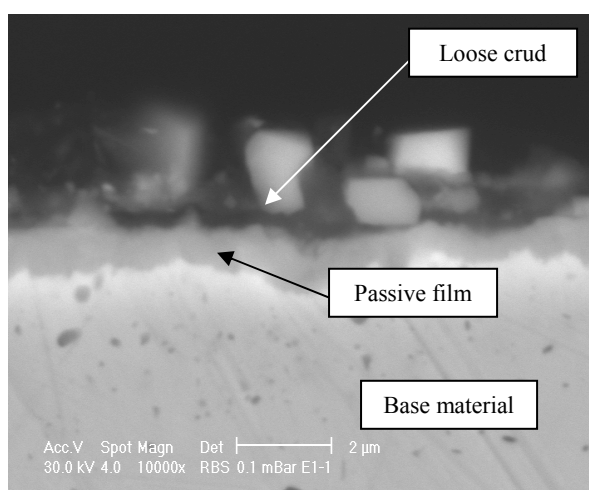


FIG. 24. Typical view of cross section of corrosion layers formed on surveillance coupons from ETE-1 and ETE-2 units. Passive film is apparent below the layer of loose crud.

After passivation performed during HFT at EMO-1, EMO-2 and ETE-1 units, both the surface and coolant activities differ significantly in the case of Mn^{54} and Co^{58} . These radio nuclides produced from Fe by nuclear reaction of $\text{Fe}^{54}(\text{n,p})\text{Mn}^{54}$ and from Ni by reaction of $\text{Ni}^{58}(\text{n,p})\text{Co}^{58}$ provide direct information about the efficiency of the passive film on the inner surfaces. It is believed that radiation situation observed in these units is closely connected with the passivation stage performed during the hot functional tests. The way in which the units were operated during the reactor cycles was rather similar and cannot be a reason for the different radiation situation. Passivation in the case of EMO-1 lasted relatively short time and due to technical problems the purification system was in operation only for a limited time. This is assumed to be as a main reason for the worse radiation situation at EMO-1 unit. Corrosion products released massively into the coolant during passivation stage had not been

removed and during the subsequent operation of the reactor they were activated and redistributed around the primary circuit.

5.1.4. Water chemistry studies carried out at VVT, Finland [41, 42]

Dissolved oxidising species which increase the corrosion potential (ECP) of the construction materials may enhance the risk of localised corrosion occurring in steam generator (SG) components in pressurized water reactors (PWR). Aggressive anions like sodium, chlorides, sulphates and fluorides in the secondary side water may increase the risk of detrimental corrosion reactions. These ionic impurity ingresses can be produced by a poor make up water quality, a major leakage of ion exchange resins into the secondary side water or by in-leakage of cooling water into the system. If Fe-rich large deposits (sludge piles) are formed in the steam generator, the enrichment of different impurities in these regions of restricted flow may occur and form locally aggressive environments which have been found to lead to intergranular attack in connection to stress corrosion cracking of the steam generator tubes. Within these sludge piles pH of the water may also change significantly. The magnitude of the changes largely depends on the type of the impurity ingress into the secondary side. Laboratory tests have shown that a rapid damage of tubes occurs if acidic (or alkaline in other laboratories) crevice conditions are formed near the tube surface.

The typical appearance of the sludge pile material taken from a SG at Loviisa unit 1 is shown in the photographs in Figure 25. The shape of the sludge pile material closely resembles the shape of the SG tube surface. The diffractogram measured from the sample was similar to that of the standard reference diffractogram of magnetite.

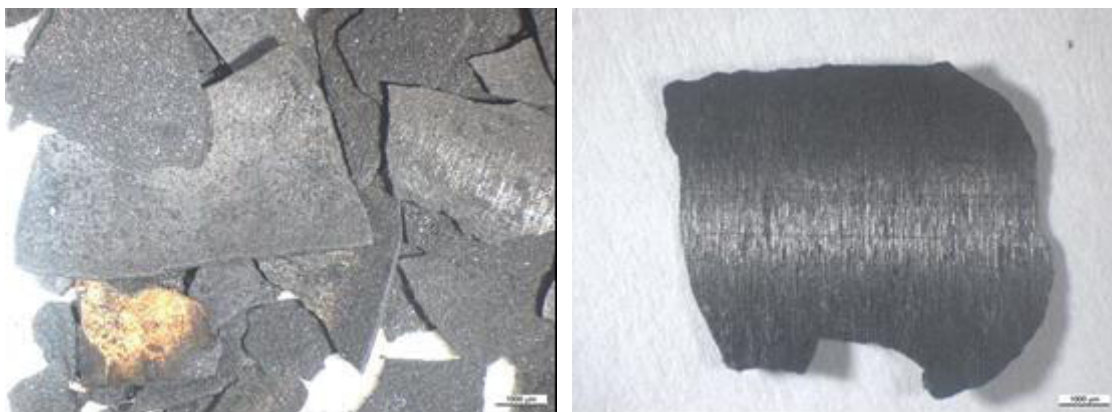


FIG. 25. Photographs of the sludge pile material removed from SGs at Loviisa unit 1.

Siemens Nuclear Power GmbH has developed the **COMSY** software system (Condition Oriented Ageing and Plant Life Monitoring System) to be used for managing the ageing and service life of mechanical components in energy producing power plants. Such software enables also the implementation of targeted maintenance programs at the plants. The program consists of several modules and can be customised to specific needs of individual power plants. The software discussed in some detail in this paper has been tailored according to the specifications provided by Fortum Power and Heat Oy to model the components and water chemistry regimes used in the secondary side at Loviisa nuclear power plant.

In a rough analysis, the heat balance diagram of the water/steam cycle in the power plant is modelled using graphical tools. This module creates basic data structure of the virtual power

plant allowing an analysis of different water chemistry conditions existing in the secondary side.

The flow sheet gives pH (RT) values, amount of mass flow and oxygen content of the water in different parts of the secondary side at Loviisa NPP. This information together with the data of material compositions of different components can be used to assess the areas where iron oxides are mainly released into the secondary side water and transported to the steam generators. The accuracy of this type of a theoretical approach can be evaluated by comparing the "modelled" values with the weekly laboratory analysis results of Fe and Cu contents done from the secondary side coolant at the plant.

At Loviisa the secondary side water chemistry (low AVT with hydrazine additions) is controlled using on-line measurement instruments as well as carrying out the analysis of grab samples taken from different parts of the system [41,42]. Figure 26 shows the locations of these different sampling points. The analysis results give an overall picture of Fe and Cu contents in the coolant throughout the secondary system and can be used as an input data to defining the factors that may play an important role in their transport into the steam generators.

Figure 26 also shows the content of iron in the water at Loviisa 1 unit in generator system measured at 6 different sampling points during one fuel cycle.

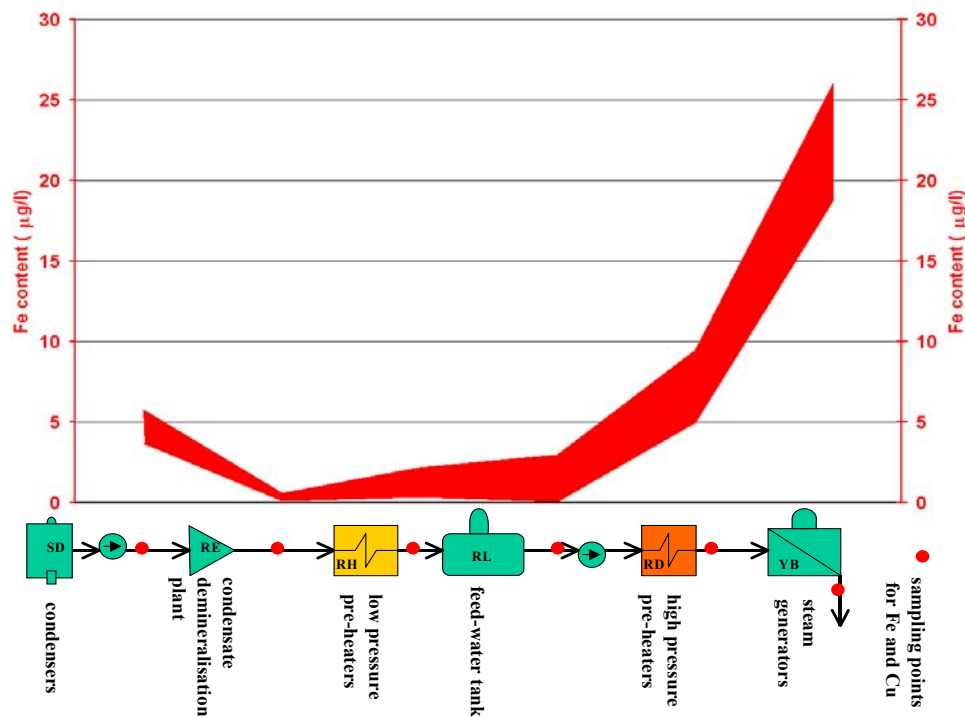


FIG. 26. Concentration of Fe in different parts of the secondary side at Loviisa 1 unit during one fuel cycle in generator system. The bandwidth shows the calculated average values \pm the standard deviation [42].

The highest Fe contents in the water have been measured at steam generator blow down and the lowest ones downstream of the condensate demineralisation plant. The first clear increase in iron content in the water is after the high-pressure pre-heaters. The increase in the Fe

content occurs between the feed water tank and these pre-heaters. Likely sources are the carbon steel joints to the high-pressure pre-heaters. However, a major source for iron in the feed water must be the piping between the feed water pumps and high temperature pre-heaters. Role of hydrazine in reducing the iron dissolution rates needs to be looked into as well as the effect of the hydrazine injection location on iron release rates.

5.1.5. Development of method for defining optimum pH-ECP for corrosion control at CRL in Canada

A method of corrosion mitigation is described here whereby water chemistry specifications are selected to maintain the material of interest within an acceptable range of pH and electrochemical corrosion potential (ECP). The optimum range for the ECP can be deduced from features of the potentiodynamic polarization curve of the material at the pH of interest. The optimum pH-ECP (electrochemical corrosion potential) zone within which the corrosion rate of metals and alloys is minimized can be determined; therefore, from potentiodynamic polarization scans at selected values of pH_T at the temperature of interest [43, 44]. A schematic of the anodic branch of a polarization scan for a typical structural material is shown in Figure 27. Although not all alloys will behave as illustrated in Figure 27, it is instructive to review the features and discuss what information they convey about the response of the material to an oxidizing environment.

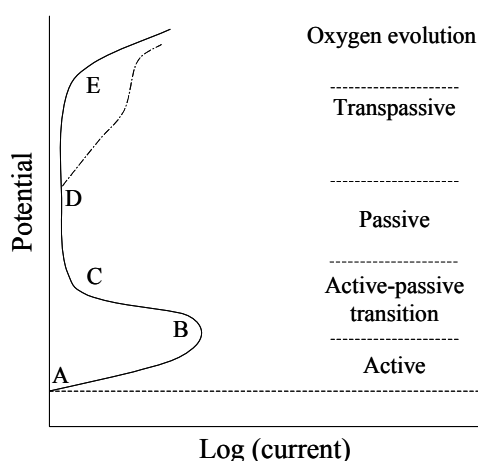


FIG. 27. Representation of the anodic branch of a potentiodynamic polarization scan.

For potentials from A to B the current increases with increasing potential, and the alloy is said to be undergoing active corrosion. At B, a protective oxide film starts to form on the surface that tends to retard the corrosion process, hence this potential region is called the active-passive transition. Increasing the potential from B to C results in complete formation of the passive or protective film, and the current flow decreases significantly. The current remains relatively low and insensitive to increases in potential until the potential reaches E, the pitting potential, at which point the protective film breaks down, giving rise to severe localized attack in the form of pits. On the reverse scan, repassivation of the material occurs at a potential D known as the protection potential. Provided the potential remains below D, new pits will not initiate and existing pits will not grow. The region between potentials at C and D is called the passive regime.

Polarization scans of the type shown in Figure 27 are typically obtained from relatively large electrodes of polycrystalline material, with the dimensions of the electrode far exceeding the dimensions of the individual grains. Because the grain boundary tends to be more active than

the body of the grain, the polarization scan for just the grain boundary will be shifted to lower (i.e. more negative or active) potentials than the polarization scan for the body of the grain. Thus, holding a material at a potential near B can result in preferential dissolution of the grain boundaries [45], a form of localized corrosion known as intergranular attack (IGA). In the presence of a sufficiently high residual or operating stress, the material will be susceptible to intergranular stress corrosion cracking (IGSCC). A similar situation prevails for crevice regions; the potential in the crevice is more negative (more active) than is the potential outside of the crevice [43]. Thus, potentials in the vicinity of B can lead to crevice or under - deposit corrosion as well. To minimize corrosion degradation, therefore, the local chemistry environment must be such that the material adopts an ECP that is in the passive region. For potentials outside of the passive region, the material may experience high rates of either general or localized attack [44].

Application of the methodology discussed above is illustrated for minimizing corrosion degradation of Alloy 800 SG tubing during normal operating conditions. The optimum pH-ECP zone for Alloy 800 at 300°C is shown in Figure 28 [44]. From the Figure 28, the optimum range of ECP for Alloy 800 in a Pb - free environment at 300°C is from -700 to -300 mV (SHE) for pH_T ranging from 5.6 to 8.9. The range of acceptable ECP is reduced in the presence of Pb, which is why Pb should be eliminated as much as possible from the plant environment. Note that silica has a beneficial effect by inhibiting the Pb-induced corrosion at the lower potential region of the optimal zone. The presence of 100 $\mu\text{g/kg}$ hydrazine results in a free-span ECP of approximately -600 mV (SHE) for Alloy 800NG at 300°C, which is about 100 mV above the recommended lower limit for a Pb-free environment, and just below the lower limit for a heavily Pb-contaminated environment unless the crevice pH_T is greater than 6.5. A lower hydrazine concentration in the SG, e.g., in the range 25 to 50 $\mu\text{g/kg}$, would raise the ECP to a value above -600 mV (SHE), and is closer to what is considered to be the optimum concentration for hydrazine required to minimize corrosion degradation of the SG tubes.

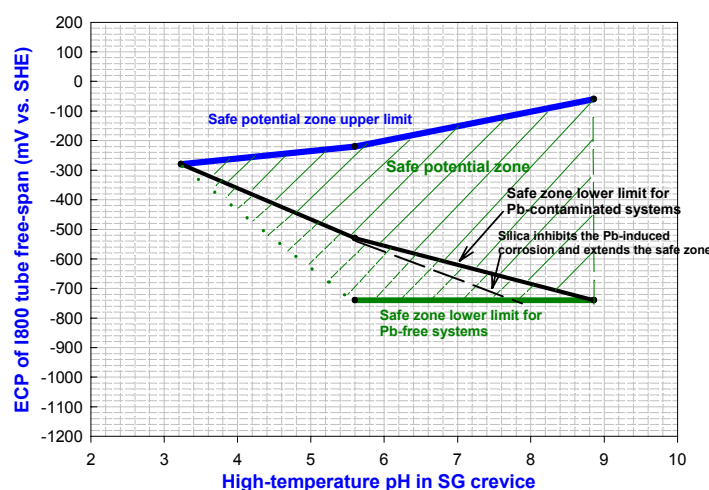


FIG. 28. Optimal ECP/pH zone for Alloy 800 free span tubing at 300 °C [44].

5.1.6. Laboratory work and recommendations on corrosion monitoring at the China Institute of Atomic Energy [46, 47]

Under an IAEA research contract, preliminary laboratory work has been carried out at the CIAE in Beijing to develop methods for on-line monitoring of aqueous conductivity, pitting corrosion and SCC. The first part of the work concentrated upon the use of electrochemical coulometric measurements, which is now considered suitable for development as an on-line conductivity monitor; Another part of the work concentrated on assessing the use of electrochemical noise (EN) measurement techniques of pure iron in the mixture solution of inhibitor and sodium chloride was investigated; the SCC behaviour of 18-8 stainless steel in boiling 42% magnesium chloride was also studied. Studies of pitting corrosion in room temperature chloride solutions and of SCC in boiling magnesium chloride at 143°C were used to buildup monitoring expertise. The test material is 316 stainless steel. On-line monitoring of electrochemical current/potential noise during pitting corrosion and during slow strain rate tests (SSRT) showed clear indications of pit initiation and growth in NaCl and MgCl₂ solutions (example is shown on Figure 29). However during SSRT tests it is very likely that not all measured signals originated from the crack tip. It is quite possible to have current peaks due to the oxide film rupture in some other parts of the surface.

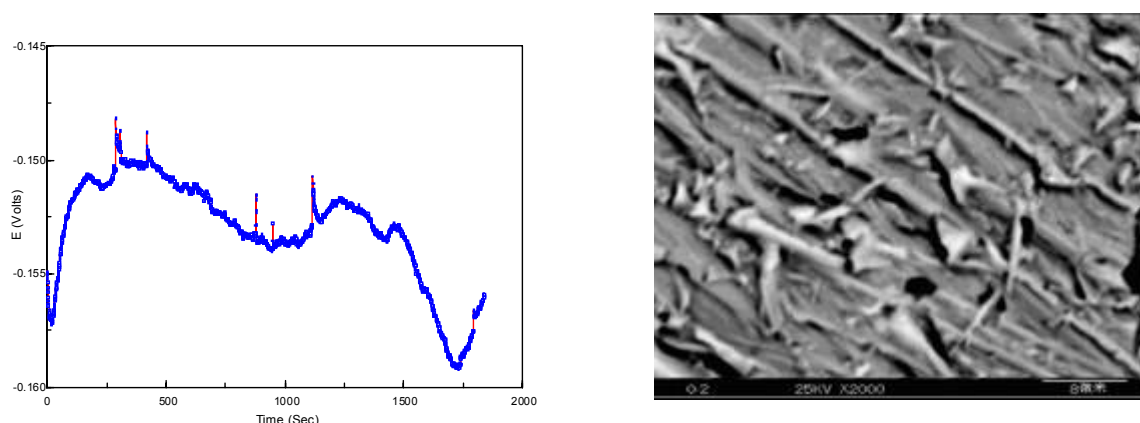


FIG. 29. EN diagram and SEM photograph of cracking surface of the specimen after test in 3.5% NaCl solution.

Some basic work has just been finished and some of the tests were carried out under simulated conditions of NPP. According to the obtained experimental data, the EN technique and high temperature conductance measurements seemed to be efficient methods for on-line monitoring of corrosion in NPP. It is strongly suggested the above-mentioned methods should be applied in NPP for further research. It is expected that research work listed below will be performed soon:

1. Relation between electrochemical noise and initiation and propagation of SCC of stainless steel;
2. Relation between initiation of SCC of stainless steel and water chemistry condition;
3. Analysis of electrochemical noise by power spectral density.

5.1.7. Corrosion monitoring in CANDU reactor from Cernavoda NPP Unit#1 in Romania [48, 49]

To monitor the effects of operating chemistry on the corrosion and the build-up of activity on some structural materials and to show important effects in the field of activity transport, one Autoclave System (Y₁-Y₄) is assembled in by-pass of CANDU-6 Primary Heat Transport System (PHTS) at Cernavoda-NPP, Unit 1 [49].

The Autoclave System consists of four autoclave circuits (Y₁-Y₄), one from the reactor outlet header to the boilers (Y₁ or Y₄) used to measure corrosion in the reactor outlet conditions (310⁰C) and one from the circulating pump discharge to the reactor inlet header (Y₂ or Y₃) used to measure corrosion in the reactor inlet conditions (260⁰C), on each of the two PHT loops.

The corrosion analysis of the coupons from PHTS autoclaves has been performed after different stages during commissioning (Hot Conditioning, Hot Performance and Loss of Class IV test) and after different exposure times in normal operation.

The data concerning the characterization and the corrosion analysis of coupons from different materials were stocked in „CNE Coroz Test” database [49]. The analysis of the coupons after different exposure times in autoclaves allowed to determine the corrosion rate, deposition and releasing of corrosion products, as well as characteristics of corrosive films formed on carbon, martensitic and stainless steel, zirconium alloys (Zircaloy-4 and Zr-2.5%Nb) and nickel alloy (Incoloy-800).

Thus, by corrosion analysis of carbon steel coupons generalized corrosion rate was determined [48] as shown on Figure 30.

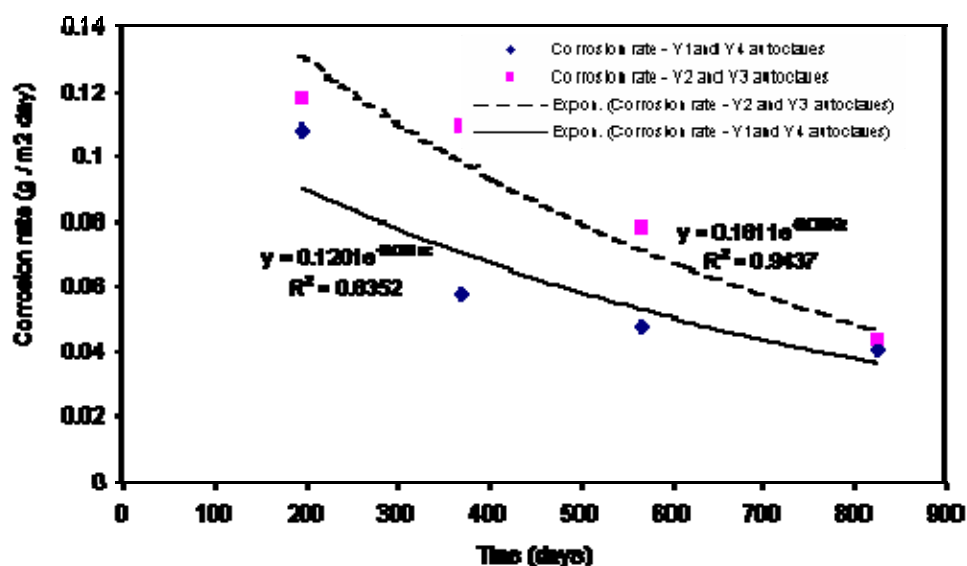
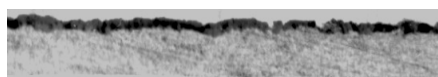
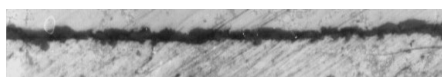


FIG. 30. Kinetics of the corrosion rate on carbon steel SA 106 gr. B coupons.

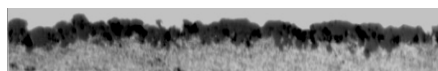
The corrosion products release rate and corrosion rate, for carbon steel SA 106 gr. B, decreased, while the exposure time increased. The bigger values for these rates, especially at the beginning, were obtained on coupons exposed in Y₂ and Y₃ autoclaves. Corrosive films are shown in Figure 31.



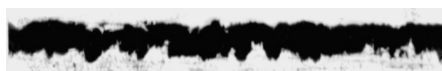
197 exposure days



371 exposure days



568 exposure days



825 exposure days

FIG. 31. Microscopical aspect of corrosive films on carbon steel SA 106 gr. B coupons (x500).

The deposits of corrosion products were in the shape of magnetite crystalides and their density increased with exposure time.

5.2. Development of models

There are a number of situations when modelling can significantly supplement or extend the information that is available directly from measurements. Examples of such situations include:

- The quantity of interest is not directly accessible,
- The quantity of interest is difficult and/or expensive to measure,
- The quantity of interest varies with location and modelling is necessary to get an overview of the variation.

Some examples of such situations in BWRs and PWRs are given below.

5.2.1. Modelling of electrochemical potential (ECP) [10]

Hydrogen peroxide is an important oxidizing species in BWR reactor water (RW). At high temperatures, hydrogen peroxide decomposes heterogeneously (i.e. on surfaces). As a consequence of this behaviour, the decomposition is slow in large diameter piping in the reactor, typically a factor of two in 100 m of a diameter 100 mm pipe. In small diameter (6 mm) sampling lines, however, the hydrogen peroxide concentration is typically reduced by a factor of two in less than 3 m. Therefore, it is not possible to determine the level of hydrogen peroxide by sampling the RW. Instead, the level of hydrogen peroxide has to be modelled. First, the generation by radiolysis of the coolant in the reactor core has to be calculated using a radiolysis code. Then, the heterogeneous decomposition in various parts of the reactor system has to be modelled.

The electrochemical potential (ECP) is an important parameter with regard to corrosion, e.g. intergranular stress corrosion cracking. It is well known that the risk of IGSCC is greatly reduced if the ECP is reduced. Therefore, in many BWRs hydrogen is added to the feed water to lower the ECP in at least parts of the reactor system. To be able to control the hydrogen injection rate, it is vital to know the ECP at some critical locations, such as the recirculation piping and the lower plenum. The ECP is very sensitive to mass transfer limitations and to decomposition of hydrogen peroxide. Therefore, it has to be measured in-situ. From a practical point of view, this can be done only at a very limited number of points, typically one

or two. This means that the ECP at other locations of interest has to be modelled. This is challenging, since the modelling result is sensitive to the input data, some of which are difficult to obtain with a high degree of accuracy. However, at least the broad picture of ECP level variations in the reactor circuit can be modelled.

5.2.1.1. Water radiolysis model for BWRs

The outline of the one of the models is shown in Figure 32 [50]. Non-linear rate equations are calculated to obtain the concentration distribution on radiolytic species in whole primary coolant [6]. The gap between the measured ECP and effective oxygen concentration ($[O_2]_{eff} = [O_2] + 0.5[H_2O_2]$) is explained by the contribution of H_2O_2 on effective oxygen contribution especially at high H_2 injection rate and on ECP [51-53].

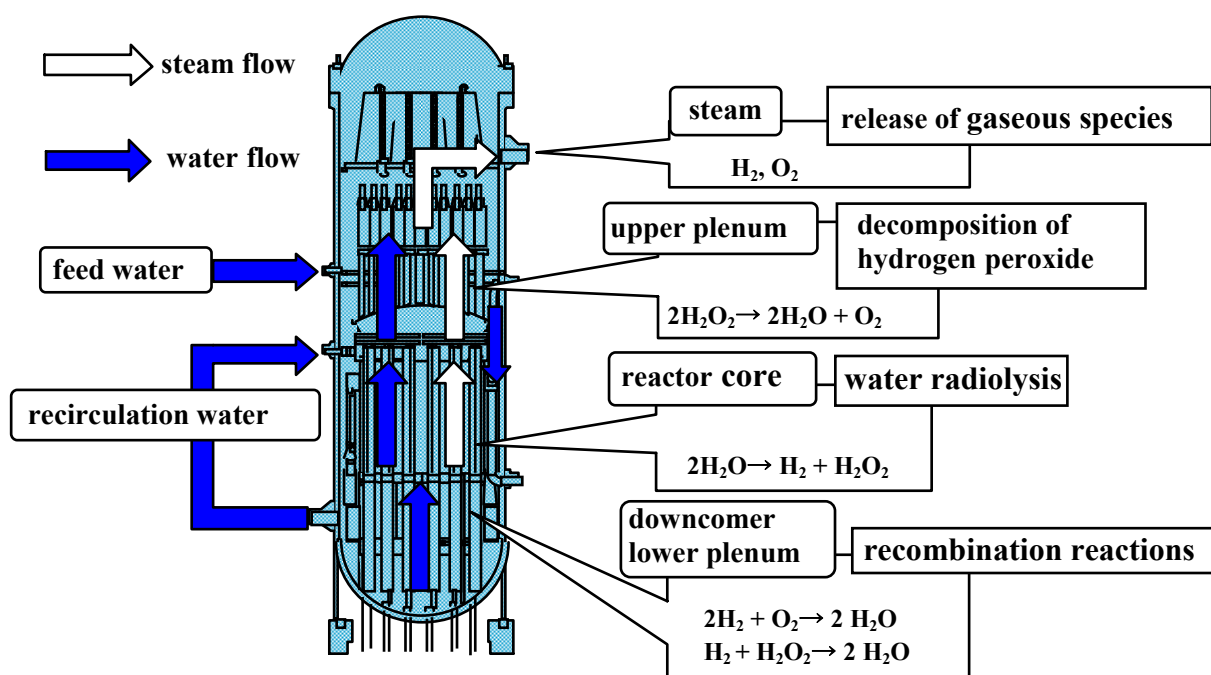


FIG. 32. Water radiolysis model for BWR.

5.2.1.2. Crevice radiolysis model

The concentrations of radiolytic species in a crack tip under non-irradiation condition are so low to reduce local ECP to -600mV-SHE , while under irradiation condition the concentrations are rather high as a result of direct generation oxidising species in the crack tip and then the local ECP is higher than that under non irradiation condition. Crevice radiolysis model has been developed in order to estimate local ECP in a crack tip, Figure 33 [54]. Radiolytic specie's concentrations, ECP and then crack growth rate have been calculated and results published in [55].

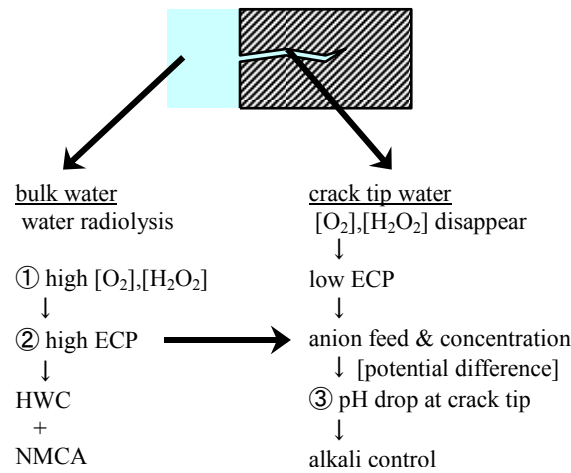


FIG. 33. Crevice radiolysis model.

5.2.1.3. Water radiolysis model for PWRs

In PWR primary coolant, sufficient amount of H_2 has suppressed O_2 concentration to avoid problems related to corrosion. Recently, it was reported that PWSCC of Ni-base alloy was caused by H_2 in the coolant. In order to avoid PWCC, optimization on H_2 concentration has been requested and a water radiolysis model for PWRs has been developed. PWR radiolysis model is much simpler than that for BWRs because transfer of radiolytic species from water phase to steam phase is not considered, but prior to radiolysis calculation, high temperature pH determined by Li and B concentrations should be calculated and irradiation effects of α rays from $^{10}B(n, \alpha)^7Li$ reaction as well as γ rays and neutrons should be considered [14]. Application of high temperature G-values to the PWR radiolysis model is shown in Table 12. The calculated results of the PWR radiolysis model are summarized in Figure 34. They are used to determine $[H_2]$ to suppress $[O_2]$ based on data at ambient temperature, but recombination reaction between H_2 and O_2 is accelerated at elevated temperature and lower $[H_2]$ is expected to suppress $[O_2]$ [56].

Table 12. Number of molecules or atoms of defined species generated by absorption of 100 eV energy of α , γ and neutron radiation

Species	BWR (285°C)		PWR (350°C)		
	γ -rays	neutrons	γ -rays	neutrons	α -rays
e^-	3.50	0.60	3.565	0.662	0.152
H	0.90	0.50	0.927	0.453	0.199
H^+	3.50	0.60	0.612	1.278	1.974
H_2	0.60	1.50	3.565	0.662	0.152
H_2O_2	0.55	1.14	0.542	0.836	1.104
HO_2	0.00	0.04	0.000	0.050	0.300
OH	4.50	1.70	4.632	1.849	1.191
OH^-	0.00	0.00	0.000	0.000	0.000

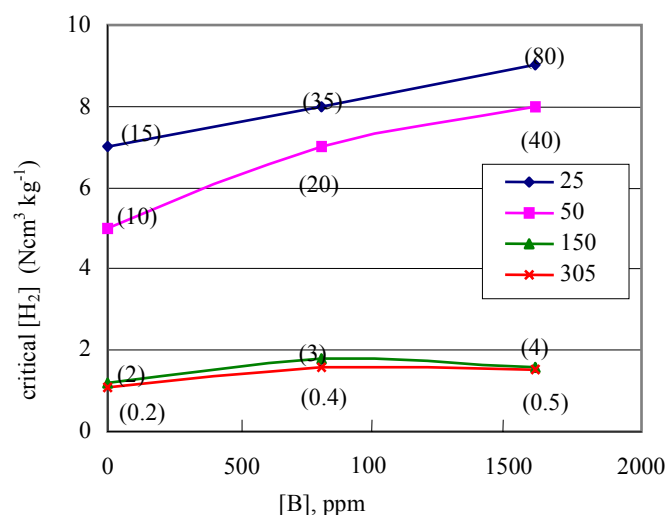


FIG. 34. Calculated results of water radiolysis model for PWRs:
critical $[H_2]$: minimum $[H_2]$ to reduce $[O_2]_{eff}$ to less than 1 ppb or to minimum
 $[O_2]_{eff}$; $[O_2]_{eff}$ for the critical $[H_2]$.

5.2.1.4. Crevice pH evaluation for SG tubing

One of the key issues for integrity of steam generators (SG) tubing is to determine local pH in crevices between tubing and tube support plate. Even if the steam generator tubing has been replaced with tubing made of corrosion resistant materials, continuous attention should be paid to Stress Corrosion Cracking (SCC) of tubing, especially in the crevice region.

From evaluation of corrosion of steam generator tubing, it was concluded that both higher and lower pH values enhanced SCC. In order to prevent SCC of steam generator tubing, pH in the steam generator secondary water, especially that in the crevice, should be controlled in the suitable range from pH300C 5 through 9. It is not so difficult to control pH300C of bulk water in the optimal range. However, control of pH in the crevice water is difficult. In order to control the crevice pH300C in the optimal range, the pH300C in the crevice water is calculated by using the measured concentrations of ionic species in the bulk water and their concentration factor in the crevice water obtained from mock-up experiments [57].

5.2.1.5. The impact of water radiolysis on the ECP in PWR primary coolant circuits.

A chemistry/radiolysis/mixed potential model has been developed by Macdonald's group to calculate radiolytic species concentrations and corrosion potential at closely spaced points around the primary coolant circuit of a pressurized water reactor (PWR). The pH, as a function of temperature of the coolant, is calculated at each point of the primary loop using a chemical equilibrium model. The radiolysis model is a modified version of the code developed to previously model the radiochemistry and corrosion properties of boiling water reactor (BWR) primary coolant circuits by Macdonald [58]. The modifications include additional species and reactions taken from other models [59-62] for describing the radiolysis of water.

The model offers the possibility of choosing up to 48 different sets of reactions when calculating species concentrations. The set of 34 reactions used to calculate the ECP in a BWR by Macdonald was completed up to 48 reactions. Six different modified subsets were obtained from that original set as indicated in [63]. In paper [63] authors explore (1) the impact of choosing different sets in the calculation of the ECP and (2) the impact on the ECP calculations when 14 additional authors' data for the 48 reactions were used (in addition to the original 34 reaction sets used by Macdonald and the set of 48 reactions obtained by adding 14 additional reactions to the original 34 reactions set; data on the 48 reactions from the 14 authors was compiled. The radiolytic yields for the primary species (14 different species as this paper we selected to work with the set shown in [64]). It is important to recognize the dictions due to the fact that we currently have electrochemical kinetic data for only a limited number of redox species (H_2 , O_2 , H_2O_2) on Type 304 SS, so only this substrate could be modeled with respect to the ECP. However, it is believed that Type 304 SS serves as a good analog for other stainless steels and, perhaps, for nickel-based alloys, such as Alloys 600 and 718, as well, because all chromium-containing alloys appear to form passive films that are essentially Cr_2O_3 having same thickness at any given potential.

The impact of the various reaction sets and rate constant values on the calculated ECP for primary coolant circuit components in a hypothetical PWR under normal (full power) operating conditions was explored. Results are a warning to researchers on the importance to consider the appropriate set of reactions and the appropriate values for the corresponding rate constants.

The essential requirement is, therefore, that the model accurately predicts the concentrations of the most abundant species, not that it predicts the concentrations of all species accurately. However, given an accurate model, we are aware that the accuracy of the results will strongly depend on the accuracy of the inputs and parameters used in the model. Authors [63] explored the importance of having an accurate set of reactions and the corresponding rate constants and activation energy and obtaining accurate values for the radiolytic yields of the species considered (G-values). Authors shown how the calculated ECP depends on using a "correct" reaction set; and stress the importance of continuing studies aimed at developing more viable water radiolysis models.

5.2.2. Corrosion control

The PWR secondary side normally uses an all volatile treatment (AVT) to control corrosion. Many plants use hydrazine to reduce the oxygen level and ammonia to raise pH. A very low level of oxygen in the water has a favourable effect on the corrosion rate of carbon steel, especially on flow assisted corrosion (FAC). However, oxygen is believed to have a potentially detrimental effect on the steam generators. To satisfy both requirements, oxygen and hydrazine have to be carefully controlled. The problem is that low levels of oxygen in the feed water are impossible to monitor, due to a heterogeneous reaction between oxygen and hydrazine in the sampling line. (The situation is analogous to the heterogeneous decomposition of hydrogen peroxide mentioned above.) Thus, the oxygen level has to be modelled. The best way to do this may be to use electrochemical kinetics to model the heterogeneous reaction of oxygen and hydrazine (mixed potential model). Today, a homogeneous reaction of oxygen and hydrazine is normally assumed in models.

More generally, monitoring of the secondary side chemistry in a PWR using AVT is limited by available resources and the number of sampling points. A model can greatly increase the amount of information obtained. An example is the *Steam ChemCalc* used at Ringhals NPP

[65]. This model is based on a combination of thermodynamics relationships and mathematical models for the plant equipment. An example of the modelling of a steam generator is shown in Figure 35.

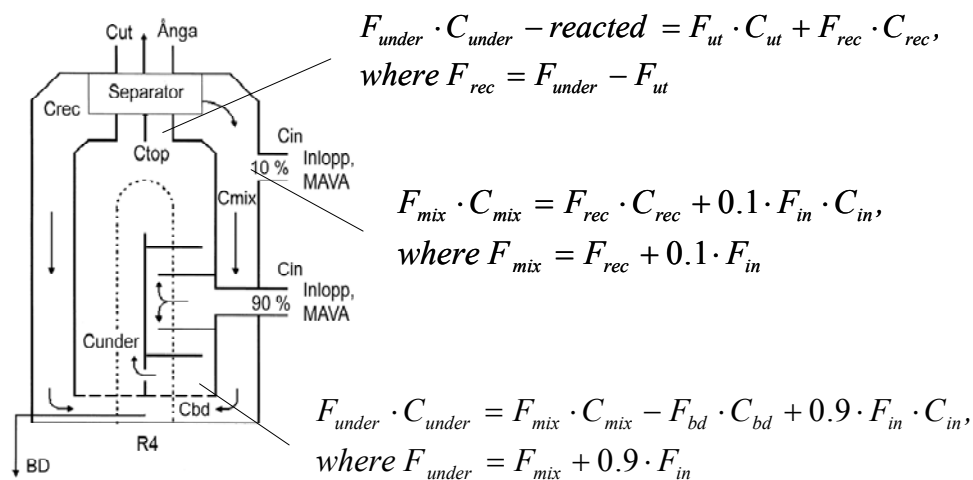


FIG. 35. Steam generator model.

The present chemical modules in the *Steam ChemCalc* allow calculation of the following parameters:

- Oxygen
- Hydrazine
- Ammonia
- Acetate
- Formate
- pH
- Conductivity
- Acid conductivity

The model calculates important chemistry parameters in 50-60 nodal points. Thus, by interpolating and extrapolating data from the sampling points, using the computer model, it is possible to greatly increase the amount of information available to the plant chemists.

5.2.3. Life time prediction – Russian approach [66-67]

An important program of chemistry and corrosion evaluation has been implemented in order to help the staff in charge of chemistry control and maintenance. The tool is able to predict, evaluate and thus avoid the risk of corrosion in case of chloride presence by establishing the relation between SCC and chloride concentration.

$$\tau_{SCC} = \tau_0 + \alpha \cdot [Cl^-]^{-n}, \quad (1)$$

where τ_0 – incubation period; n – coefficient; $n \approx 1$ in the presence of dynamic loads, $n > 1$ when chemical parameters play essential part in crack initiation, $n \approx 1,5$ under data processing of test results of static load specimens [66], $[Cl^-]$ – chloride concentration in blow down. Coefficient

α in equation (1) represents threshold of total chloride amount (or more exactly, total amount of anions) passed through SG, exceeding which leads to SCC of cold header and tubes of WWER-1000 SG.

Analysis of data from table 6 (Section 3.7) revealed similar for all NPP's secondary circuits relationship between permissible operation time for different action levels and “normalised” associated water chemistry action level values.

Normalisation is done by dividing particular action level value by value, below which operation time is not limited. **The prediction module for short time** uses information about variations of all the diagnostic indices in complex. In course of the first stage of its performance, an express-prediction of individual indices value variations is built. Conventional extrapolation is used as a prediction technique in the prediction module. Figure 36 presents an example of predicting on oxygen concentration value before deaeration as of December 31, 2002 against 50 previous values.

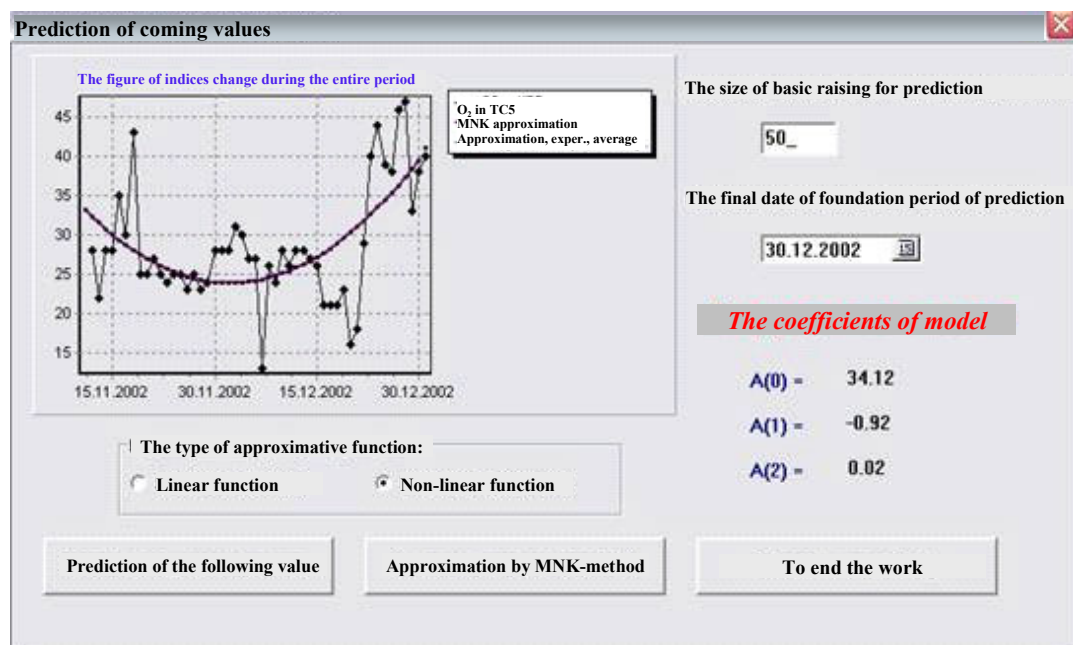


FIG. 36. Building express-prediction by extrapolation technique.

A general prediction of the WCh status is made based on individual predictions against indices. In its performance, this module triggers the diagnostics module whose performance results, in this case, are recorded in a special WCh status prediction file. The verification of a prediction entered by the user is recorded in prediction and fault files and are used by the system in making new predictions and updating diagnoses.

In making long term predictions, the system uses algorithms and the exponential smoothing technique as it allows assessing parameters of the trend, which define a more general tendency.

As an example, the correlation between permissible operation time of SG and “normalised” concentrations of Na is shown in Figure 37. As shown there, the lines, which correspond to

values for various types of NPPs, practically coincide, and dependence is expressed by equation (2), practically coincided with equation (1).

$$\tau_{\text{permissible}} = \tau_0 + \beta \cdot \left(\frac{x_i}{x_0} \right)^n, \quad (2)$$

where $n \sim 1, 5-2, 0$.

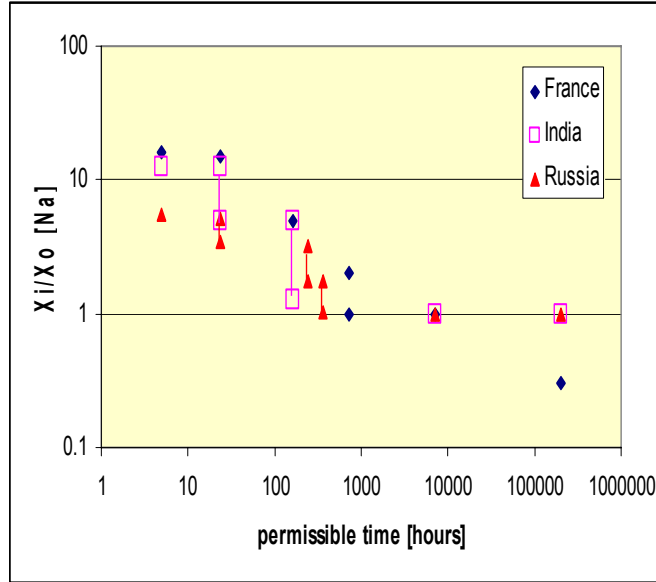


FIG. 37. Correlation between normalized values of Na content in SG blowdown water and permissible operational time related to action levels (by specifications of countries) under corresponding water chemistry deviations.

Thus, to make a conservative evaluation of WWER-1000 steam generator residual life, plant management can use formula (3) (proposed by in [34]), based on operating experience [66-67] and confirmed by normative documents [29-30].

$$\tau_{\text{RL}} = \tau_{\text{ass}} - \frac{\sum (\Delta x_i)^n \Delta \tau_i}{(x_0)^n} \quad (3)$$

where τ_{RL} – residual life, τ_{ass} – design life time of SG, $\Delta \tau_i$ – time intervals, when current value of parameter x_i is observed, x_0 – normative value of parameter, $n \sim 1, 5$.

This diagnosis model allows determining the residual time of operation before failure, to predict the risk and to determine the situation of abnormal operation and the appropriate corrective action to be applied, if necessary.

In order to evaluate plant condition by using water chemistry data, two points should be carefully considered. The first point is quality assurance of water chemistry data and the other is filling the gaps between measured data and desired information. In order to bridge the gaps between measured data and desired information, interactions between water and materials in the plants should be understood clearly.

5.2.4. Analytical models within ChemAND to predict performance degradation

One of the functions of AECL's chemistry monitoring system, ChemAND [20-21], is to interface plant chemistry data with analytical models to assess the effect of operating

conditions on factors that may affect performance degradation. Two models related to corrosion degradation are incorporated into the current version of ChemAND to predict the effect of operating conditions on: i) chemistry throughout the steam cycle, including the crevice regions at the steam generator (SG) tube/tube support intersections, ii) the rate of deposit buildup and deposit distribution within the SG. Deposit buildup in the SGs is related to the effectiveness of the corrosion control program for the steam cycle, and fouling of the SGs produces regions where aggressive chemistry conditions can develop that lead to localized corrosion, so the application of these two models to chemistry and fouling control in the steam cycle is synergistic. Each model can be run using input data from the chemistry monitoring system or with user-defined input to assess particular operating scenarios. This modelling capability is especially important for assessing the impact of transient conditions, e.g. startups, shutdowns, and other events that may cause systems to be temporarily pushed outside of their recommended operating regimes, on factors that ultimately effect performance degradation of key components within the plant.

ChemSolv™ is the model used to calculate chemistry throughout the steam cycle. ChemSolv solves a set of differential equations based on mass and charge balance to determine the chemistry at a number of nodes throughout the system [68]. The equations take account of reactions that are at thermodynamic equilibrium as well as those that do not reach thermodynamic equilibrium because the reaction kinetics are too slow, e.g., the reaction between hydrazine and oxygen in the feed water system. An output screen from ChemSolv showing the calculated high-temperature pH at selected nodes throughout the steam cycle is shown in Figure 38. Other parameters that can be displayed on the output screen include pH of the neutral point, the concentration of hydrazine and dissolved oxygen, and the concentration of volatile amines used for pH control. This application of ChemSolv is useful for optimizing steam cycle chemistry with respect to the pH in critical locations, such as reheater drain, the shell-side of feed water heaters, the steam generator and the final feed water.

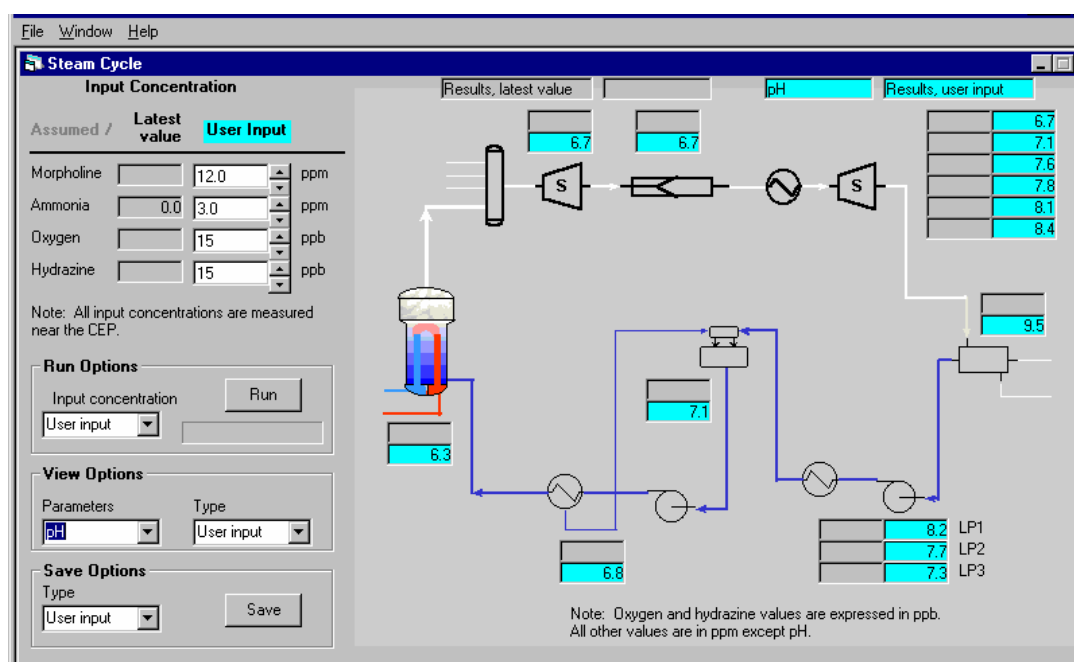


FIG. 38. Output screen from ChemSolv showing high-temperature pH calculated at selected nodes throughout the steam cycle.

A second application of ChemSolv calculates chemistry conditions that result from the build-up of non-volatile impurities within flow-occluded regions in the steam generator, such as the crevices at tube/tube-support intersections. The pH in these locations is determined by the composition of the solution that remains in equilibrium with the compounds that have precipitated as a result of boiling within the crevice [69]. The composition of the solution being drawn into the crevice is given by the concentrations of impurities in the SG blow down. This application of ChemSolv can be used to assess the impact of chemistry transients, such as can occur during startup or shutdown of the reactor or as a result of the transport of impurities to the SG following a condenser leak or a water treatment plant excursion, on crevice chemistry and, consequently, the future performance of the SG tubes.

ChemAND also incorporates a SG fouling model, SLUDGE™, to track the rate of deposit build-up and deposit distribution throughout the SG during normal operation as well as during startup, when feed water concentrations of corrosion product are often elevated as a result of ‘crud bursts’ originating from somewhere in the feed train. SLUDGE [70] includes mechanisms for deposition, removal and deposit consolidation to predict the build-up of deposit on the tube bundle and tube sheet, as well as the fraction of in-coming corrosion product that is removed with the blow down. This latter feature can be used to assess the impact of operational changes, such as a change in blow down rate or the use of water-treatment additives that have been shown to reduce the rate of fouling under SG operating conditions [71-72]. By reporting both average tube-bundle deposit mass and details of the deposit distribution, SLUDGE can be used to advise the operations staff when to clean and where to inspect.

5.2.5. Plant verification

It has been seen that plant chemistry can be further improved and that the first steps of this improvement are the R&D laboratory tests and, frequently, model developments. Once this has been defined, it is necessary to check in a plant the proposed improvement in order to check in real conditions what has been proposed from laboratory conditions and/or evaluated from models. The main reason for such plant verification is to gather detailed information for adequately defining the conditions under which the improvement has to be implemented and the relation between the exact selection of the improvement and the plant design or characteristics.

The reason for this verification is that during laboratory tests, the representative design of the plant may need to be checked. Moreover, the improvement depends on these design characteristics, which may vary from plant to plant.

Then, another need for plant verification is to do it thoroughly with many measurements and then, once the new chemistry has been validated, it may be normally applied with a limited number of monitoring, comparable to what was done before the improvement. Thus, the impact of the increased load of work will be limited to the plant verification duration.

Finally, in some but not all cases, the feasibility and ease of use may also be checked. Since this may look more or less clear, a few examples will better clarify what is needed for plant verification in case of chemistry improvement.

5.2.5.1. Example 1. Primary coolant

One of the key option for the primary water chemistry improvement is the optimisation of the pH_T and the corresponding alkaline reagent(s) concentration(s) for minimizing transport of radioactive corrosion products (Co...) and subsequent dose rate index.

Several codes are applied to define this chemistry, laboratory tests are performed to check if this chemistry does not induce any corrosion of the materials in presence, and then it is applied. But, before extending it to all the plants of the same design, it may be advisable to check in a couple of units:

- If the results in dose rate index are matching the expectation,
- If there is no adverse effect on materials during operation, including the fuel behaviour.

During this plant verification, detailed activity measurements will be done in various parts of the primary coolant. Corrosion products investigation may be done. Once this new chemistry, which in many cases consists in increasing the pH_T , has been validated, it may normally be applied to the other plants with similar design and fuel.

5.2.5.2. Example 2. Steam water system

One of the key tasks for the secondary chemistry improvement is the optimisation of the pH, amine selection and reducing reagent concentration. The objective is the limitation of corrosion of the various structural materials, the minimization of environmental impact and finally the operating costs.

After laboratory studies on corrosion rate (mainly erosion-corrosion of carbon steel, corrosion product transport and deposition), the codes can be used to calculate the chemistry in various parts of the system and see if it will be appropriate for the various components.

Then, the new chemistry can be applied in a unit with many measurements including alkalising reagent concentration, $\text{pH}_{25^\circ\text{C}}$ in various locations of the steam-water system, suspended solids concentration and composition (e.g. hematite versus magnetite), decomposition products, if necessary. Environmental and cost impacts, as well as ease of implementation, must be also considered (e.g. resin behaviour and duration, pH stability).

For example the first experimental application of advanced amine – morpholine on the units of the type WWER was conducted in 1998-2001 years on the unit No 3 of South Ukrainian (SU) NPP. The experience of the chemistry improvement at the unit No 3 SU NPP testifies that complex approach to introduction of new chemical technologies, diagnostics of water chemistry and corrosion control leads to the upgrading of safety and reliability of NPPs. This work was performed for the secondary circuit and resulted in:

- Concentration of the dissolved oxygen in condensate has been reduced from 30-35 ppb to 2 -10 ppb;
- Concentration of iron oxides in the feed water of steam generators (SG) has been reduced by 50 %;
- The amount of corrosion product deposited in SGs has been reduced;

- The $\text{pH}_{25^{\circ}\text{C}}$ rate of the blow down water of SGs have been increased from 7.5-8.2 up to 8.8-9.2;
- The number of newly appeared SG tube defects started to decrease;
- Operating costs have been reduced by 100,000 \$/year for one unit due to reduction of chemical reagents consumption.

Now this experience is extended to other six units of the type WWER [73].

6. RECOMMENDATIONS ON MONITORING

6.1. Chemistry monitoring

Many of the plants do not employ chemists on shift. Some basic information about the water chemistry should therefore be provided on the automated basis. Therefore parameters of highest priority (control parameters in the water chemistry specification) should be monitored continuously by the direct measurement or indirect method (calculation from other parameter(s)). Selection of parameters for continuous monitoring should reflect principal construction material corrosion behaviour should be made with respect of their importance and of the availability of reliable and sufficient accuracy.

Simple and reliable instrumentation should be preferred and sufficiently field test proven instrument should be installed.

One of the most common and reliable instruments are conductivity monitors used either directly or in connection with cation exchanger sample pre-treatment. They represent general look to the system and provide warning about any deviations. In many cases this parameter offers some other possibilities - like calculation of pH, ammonia, amine concentrations. In some circumstances temperature compensation method should be carefully selected.

Other reliable monitors are available for sodium, boron, oxygen and hydrogen concentration monitoring. Monitoring system should be designed in a way that it allows cross check (verification of particular signal plausibility from other monitors data).

Acquisition and data processing system for all chemistry monitors signals should be installed either as autonomous system or within the plant process-monitoring computer. Data after verification should be checked against alarm levels carefully selected for each particular case to provide early alerting of expected negative events. Chemistry data must be supplemented by the operational data, which may be determining for chemistry in some cases (power transients, equipment scheduled cycling etc.) Processing of the data should be made prior to output on the final information panel for shift operation personnel in order to minimize information burden from one side, from other side to provide as condensed and clear information as possible. Such a system will build trust of operators in its supportive diagnostic capability.

Other monitors can be used to provide chemists by the information about auxiliary systems operation without interference to shift personnel.

For parameters with no reliable and economically feasible continuous monitoring instrumentation available, grab sampling should be preferred method of monitoring. Sampling should be done with adequate frequency.

Each type of control defined in the chemistry specification for normal power operation of nuclear power plants should be associated with expected and/or limit values. This means that no monitoring is requested for research purposes if it is not associated with an action in case of deviation. Moreover, the number of monitored parameters is limited to what is necessary so that the plant chemists' staff may concentrate on reliable measurements and spend more time on the various ways to achieve a good chemistry rather than spending time to redundancy of

monitoring. Of course, in case of abnormal or specific situations, additional monitoring for diagnosis purpose is requested.

In addition to previous explanation, the need to focus on a limited number of on-line monitoring points is due to the fact that if too many data are transmitted to the staff in charge of plant operation, the immediate decision will be too difficult to take.

Thus, the optimum situation seems to correspond to:

- A very limited number of on-line monitors with data transmitted to control room and from which the operators may decide to normally continue the plant operation, to shutdown the unit within a short term, to ask the chemist on call to more thoroughly evaluate the situation or to ask to the designed staff to take a corrective action. Example: sodium at SG blow down, boron concentration, oxygen in condensate water;
- Other on-line monitors which have to be used by the chemist for checking if all the key parameters are correct, either related to pollution, which do not require an immediate shutdown, or to conditioning optimization. Example: cation conductivity in steam, hydrazine in feed water;
- Grab sampling for other parameters, which do not require on-line monitoring, as explained in Section 3.2.

More generally, the decision for selection of grab sampling or on-line continuous monitoring is discussed in Sections 3.2 and 3.3.

Examples of possible water chemistry data acquisition systems for BWR and PWR plants are compared in Figs 4 and 5 and major procedures for water chemistry data analysis are summarized in Figure 6 (Section 3.1) [9-10].

Data from the on-line monitors can be easily transferred into the computer systems; water chemistry data from the grab sample analyses are inserted into the computer database by plant chemists. Large improvements have been reported in the latest plants on automatic analysis of chemical and radioactive nuclide data. Chemical species collected on membrane filters are analyzed by X ray fluorescence analyzer, and then the measured data are transferred from the analyzers to the computer system directly (Fig. 8). Accumulated data are stored in a host computer (data server) allowing easy observation of plant water chemistry.

Many kinds of high temperature sensors have been developed for direct measurement of plant performance and water qualities (Table 13). Only a few of them have been applied to operating power plants [14]. Table 14 lists high temperature sensors applied at operating plants. Most of them are sensors for structural material integrity tests. High temperature reference electrodes for electrochemical corrosion potential measurements and contact tension specimens for crack propagation measurements are applied for task force of hydrogen water chemistry [58].

In order to obtain a reductive environment and thus mitigate secondary side corrosion of steam generator tubing, the optimum hydrazine content in the secondary system of PWR should be discussed based on ECP measurement. However, ECP measurement is carried out only in a very few units. Once the optimum hydrazine condition is defined, the plant staff will only routinely monitor hydrazine and ECP measurements can be terminated. Instead of direct ECP measurement, a combination approach of concentration measurement of anions and cations with ion chromatograph and empirical calculation based on crevice concentration

factors and pH evaluation has been successfully applied to determine the corrosive conditions at the tubing and the crevice between the tubing and the supporting plate.

Table 13. High temperature water chemistry sensors [10]

Measured Items	Detector	Principle	Application
1) Water chemistry:			
a) Dissolved O ₂	Pressure balance type O ₂ detector	Membrane + polarography	Lab
b) Dissolved H ₂	Pressure balance type H ₂ detector	Membrane + polarography	Lab
c) Conductivity	Pd wire type H ₂ detector	H ₂ absorption + electric resistance	Lab
	Coupled electrodes detector	Alternative impedance	Lab
	Triple electrodes detector	Alternative impedance	Lab
d) pH	ZrO ₂ type pH sensor	Ion electrode	Lab
	TiO ₂ type pH sensor	Flat band potential	Lab
2) Interaction between water and materials:			
a) Electrochemical corrosion potential (reference electrode)	External type electrode (Ag/AgCl)	Ion electrode	Reactor
	Internal type electrode (Ag/AgCl)	Ion electrode	Reactor
	Internal type electrode (Fe/Fe ₃ O ₄)	Ion electrode	Reactor
	Internal type electrode (Ni/NiO)	Ion electrode	Reactor
b) Corrosion rate	DC corrosion detector	Terfel plot	Lab
	AC corrosion detector	Board diagram	Lab
c) Crack growth rate	CT specimen	Potential drop measurement	Reactor
	DCB type crack growth detector	Potential drop measurement	Reactor
Lab: used only in laboratory experiments; Reactor: applied in operating plants			

Table 14. High temperature sensors for BWR water chemistry monitoring [10]

Plant	Power (Mwe)	Reactor type	Utility	Sensor Location	Monitor/Test
Fugen	165	ATR	JNC	AC	ECP1/SSRT
Fukushima 1-3	784	BWR-4	TEPCO	LPRMH	ECP1, ECP2
				AC	ECP1, ECP3
Fukushima 1-5	784	BWR-4	TEPCO	BD	ECP1
				AC	ECP1/CT
Tsuruga-1	357	BWR-2	JAPC	LPRMH	ECP1, ECP2
				BD	ECP1, ECP2
				AC	ECP1, SSRT/CT
Tokai-2	1,100	BWR-5	JAPC	BD	ECP1, ECP2
Shimane-1 Kashiwazaki Kariwa-7	460	BWR-3	Chugoku	BD	ECP4
	1,356	ABWR	TEPCO	BD	ECP1, ECP5
Abbreviations: AC: autoclave; BD: bottom drain; LPRMH: local power range monitor housing; ECP1: ECP(Ag/AgCl); ECP2: ECP(Pt); ECP3: ECP(Cu/CuO ₂); ECP4: ECP(Fe/Fe ₃ O ₄); ECP5: type not reported; SSRT: Slow Strain Rate Test, CT: Compact Tension.					

6.2. Radioactivity monitoring

Results of activity monitoring are used for several different purposes [74, 75]:

- Monitoring of the status of fuel cladding integrity through activity of fission products and transuranium elements;
- Monitoring of injected chemicals through their activation products, if this applies;
- Monitoring of impurities through their activation products, if this applies;
- Monitoring of corrosion and deposition processes through activated corrosion product;
- Monitoring of purification facilities performance;
- Monitoring integrity of systems;
- Monitoring activity of releases.

Activity monitoring is generally made by grab sampling which is simple, quite accurate but has also some disadvantages, like:

- Difficulties in the separation of the gaseous radio nuclides (noble gases);
- Disability for measurement of short time radionuclides activity.

Another alternative is represented by the continuous activity monitoring which can be done on the basis of simple total activity measurement (monitoring of system integrity) or on the more sophisticated spectroscopic approach (^{16}N monitoring using low/moderate resolution spectrometry or primary coolant on-line gamma spectrometry using HPGE detectors). This monitoring is in principle semi-continuous because certain counting time is always required. Defects of SG tubing, if some defects occur in tubing unfortunately, are monitored by ^{16}N detection at the main steam line. A couple of CsI scintillation counters are on operation at the main steam lines to monitor the surface dose rates at the main steam piping and their gamma ray spectra, which are affected by ^{16}N increase through the tubing defects, Figure 39 [9].

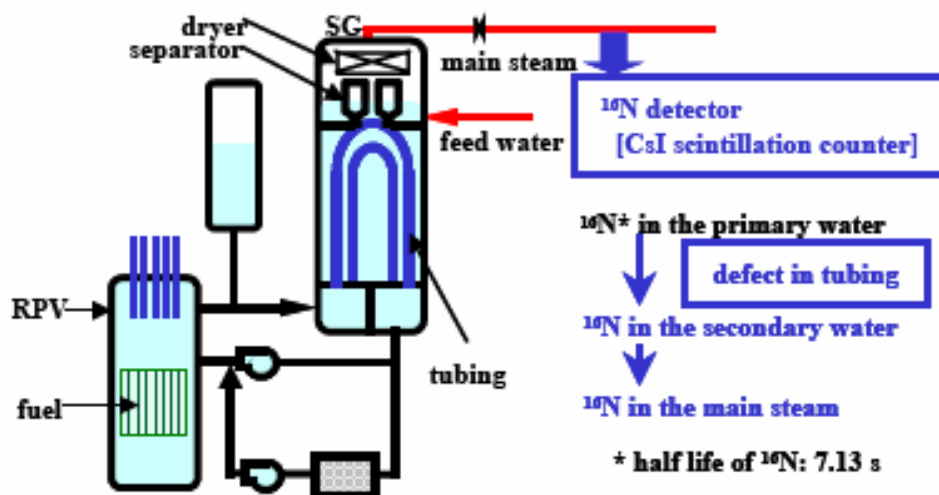


FIG. 39. On-line monitoring of SG tubing defects [9].

ECP (electrochemical corrosion potential) can be measured in several locations in the primary coolant at elevated temperature and extrapolated to the location of interest to evaluate the target structures. Conductivities and pH are measured at room temperature and their effects on

the materials should be considered by extrapolating them to those at the elevated temperature. One of the most important radiolytic species, H_2O_2 , which cannot be measured in the sampled water, should be determined by the theoretical water radiolysis model along with O_2 and H_2 at the location of interest.

Major gaps between the desired information to understand the phenomena and measured data are shown in Tables 2 and 3 (Section 3) with the major measures to bridge the gaps.

On-line gamma spectrometry was successfully implemented at several reactors offering following possibilities:

- Monitoring of the status of fuel cladding integrity through activity of fission products and transurans – noble gases due to simple transport mechanism (diffusion) offer higher sensitivity and easier interpretation of measured data being not disturbed by the superposition of several different processes;
- Monitoring of injected chemicals through their activation products in some cases – potassium concentration at WWER reactors – possibility of cross check with chemistry monitor data;
- Monitoring of impurities through their activation products in some cases – chlorides, sodium concentration can be monitored through activity of ^{38}Cl , ^{24}Na – possibility of cross check with chemistry data;
- Monitoring of corrosion and deposition processes through activated corrosion product. At BWR plants, radioactive nuclides collected on membrane filters are analyzed by semiconductor type gamma spectrometer, and then the measured data are transferred from the analyzers to the computer system directly;
- Monitoring of purification facilities performance. Contact dose rate of piping of BWR primary cooling system is monitored, even during plant operation period, at reactor water cleanup line by semiconductor type gamma ray spectrometer with thick tungsten made collimator and radiation shields.

Primary coolant gamma spectrometry generates very complicated spectra therefore high quality of detectors, electronic modules and spectra processing software is necessary. This option represents for chemistry monitoring certain comfort, but combined with monitoring of some other systems and stack releases activity it may become a very complex diagnostic tool for radiation protection purposes as well.

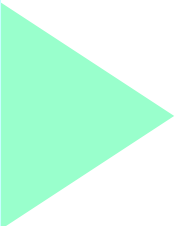
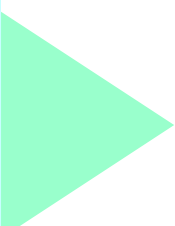
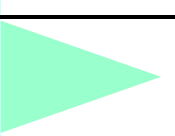
A very special kind of radioactivity measurement is implemented at different plants in order to follow corrosion in primary coolant and deposition processes on primary surfaces. This in-situ gamma spectrometry is carried out regularly during refuelling outages. Based on the results and detailed evaluation of them consequences on system integrity status, corrosion problems and radioactivity transport processes can be drawn.

6.3. Fuel failure estimation from coolant activity and its possibility to implement in diagnostic systems [75]

Aim of expert/diagnostic system giving information of the occurrence and situation of fuel rod defects during power operation.

Method operation is evaluation of the trend of fission product concentration in primary coolant and/or off gas.

Table 15. Fuel Failure Estimation Information got from different radionuclides.

<ul style="list-style-type: none"> Fission noble gases Xe-133, Xe-135 Kr-85m, Kr-87 		<ul style="list-style-type: none"> Occurrence of defect Number of defects Size of defects
<ul style="list-style-type: none"> Iodine und Caesium I-131, I-133 Cs-134, Cs-137 		<ul style="list-style-type: none"> Size of defects Development of defect Contact with water Burnup
<ul style="list-style-type: none"> Neptunium Np-239 		<ul style="list-style-type: none"> Size of defects Fuel release

Possibilities of an expert / diagnostic system:

- Distinction between intact core and core with defective fuel rods;
- Estimation of the date of defect initiation (especially at the first incident of the cycle);
- Estimation of tramp uranium from short living radionuclides, as I-134, Xe-138.

Restrictions of an expert / diagnostic system:

- Total number of defective fuel rods;
- Distinction between primary and secondary defects;
- Type of defect;
- Burn up of defective fuel rods;
- Estimation of the date of defect initiation in case of several incidents during the cycle.

The implementation of fuel failure estimation in an expert / diagnostic system is a good tool but cannot substitute the experience of experts (see Fig. 40).

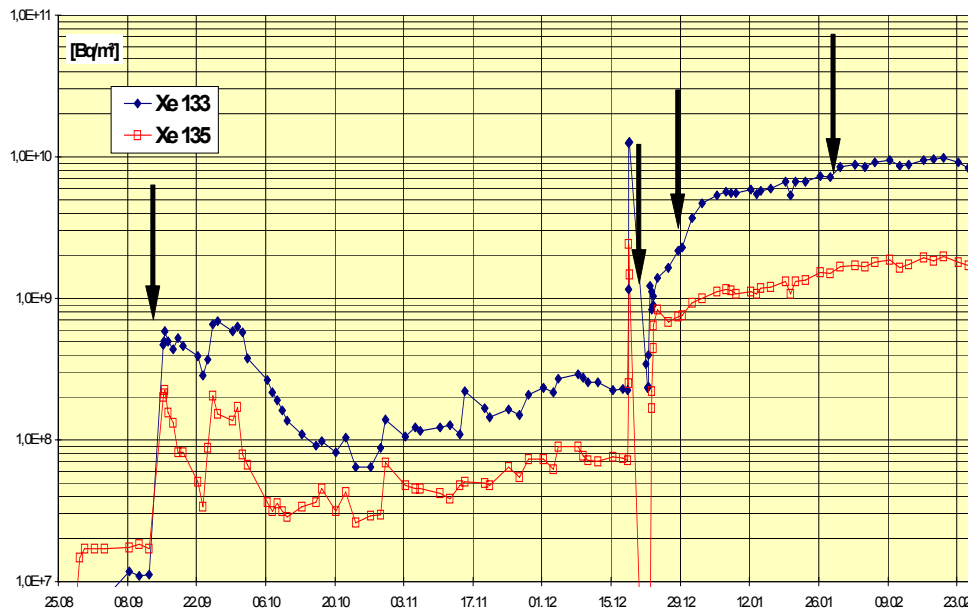


FIG. 40. Defect detection by Xe133 and Xe135.

6.4. Corrosion monitoring

6.4.1. Electrochemical corrosion potential (ECP) monitoring in Swedish BWRs [76]

Many BWRs have applied hydrogen water chemistry (HWC) to reduce IGSCC. The objective of HWC is to reduce the electrochemical potential (ECP) in (parts of) the reactor system to below -230 mV SHE, which is a generally accepted threshold value for IGSCC. HWC is achieved by injecting hydrogen into the feed water.

An immediate problem is how much hydrogen to inject. It is sometimes thought that HWC can be modeled and that the amount of hydrogen to inject can be determined from the model. While it is true that HWC can be modeled, it also true that the modeling results are very sensitive to the input data to the model. Unfortunately, some of the most critical input data varies during operation and is difficult to calculate with the required degree of accuracy. This is the dose rate in the downcomer. HWC relies on radiation induced recombination in the downcomer. The dose rate is the most important parameter for the recombination process, besides the hydrogen injection rate.

The importance of the dose rate can be inferred from Figure 41. The figure shows the hydrogen injection rate in a Swedish BWR as a function of time. This BWR has an in-situ Pt reference electrode in the recirculation piping. This electrode is used to control the hydrogen injection rate. The governing principle is to keep the ECP of the recirculation piping at -250mV SHE. It is apparent from the figure that there are very significant long-term variations in the hydrogen injection rate necessary to maintain a constant ECP.

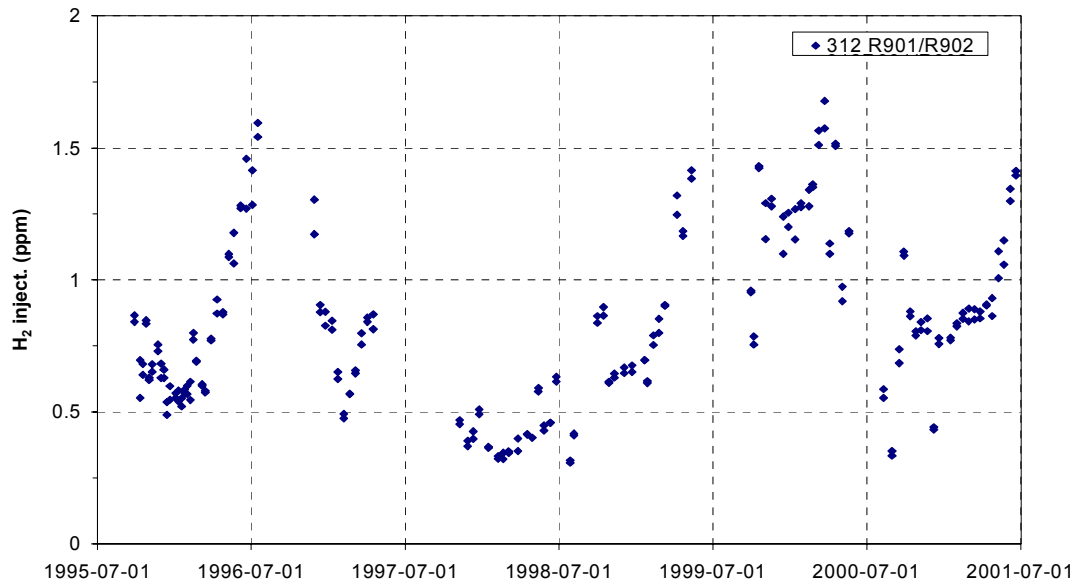


FIG. 41. Hydrogen injection rate necessary to maintain an ECP of -250 mV SHE over time.

One of the main reasons for the long-term variations in Figure 38 is varying relative power level in the fuel bundles in the core periphery. The variation of this parameter during the same period as in Figure 41 is shown in Figure 42.

In general, the dose rate in the down comer decreases during each cycle. However, there are also variations from one cycle to another. A very long term trend is that the dose rate in the down comer slowly decreases with time as more advanced fuel designs are introduced. The leakage of neutrons from the core is reduced.

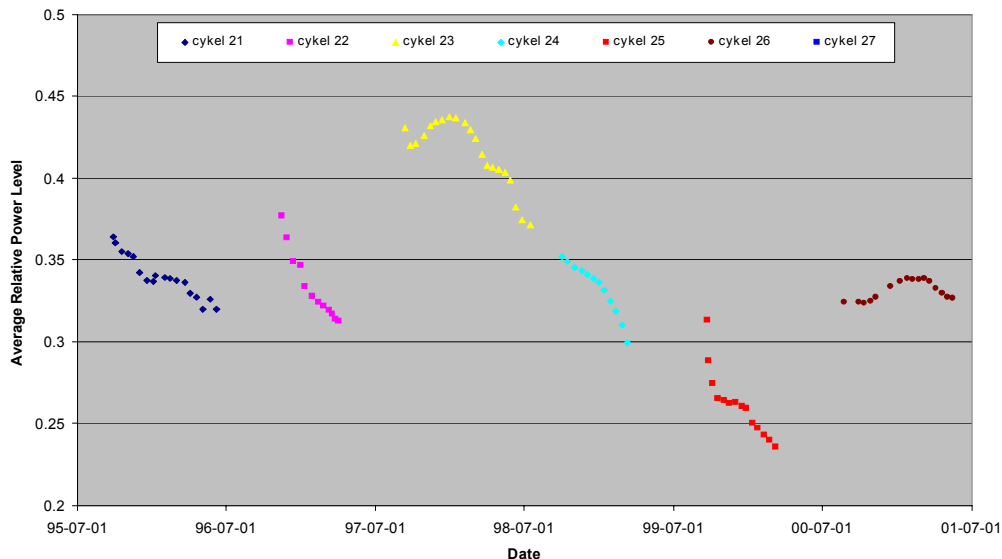


FIG. 42. Average relative power level of the fuel bundles in the core periphery of the same reactor as in Figure 38.

The obvious conclusion is that it is very difficult to forecast the hydrogen injection rate necessary to maintain HWC. Therefore, ECP monitoring is strongly recommended in BWRs applying HWC.

6.4.2. Further development of on-line HT sensors for ECP measurements [77]

Corrosion Monitoring System (CMS) has been developed for an operative estimation of the influence of the coolant quality and water chemistry of multiple forced circulation circuit of RBMK-1000 on the material condition of austenitic pipelines, including welded seams in all operation modes: hydro-testing, startup, normal operation conditions, etc.

For better understanding the influence of water chemistry on IGSCC in RBMK-1000 units, measurement and evaluation of ECP and water chemistry has been initiated at unit 3 LNPP. Three in-pipe electrodes are connected to the sampling line from the drum separator. A hydrogen, oxygen and conductivity measuring loop is installed after cooler and depressor valve in electrodes pipe as shown on Figure 43.

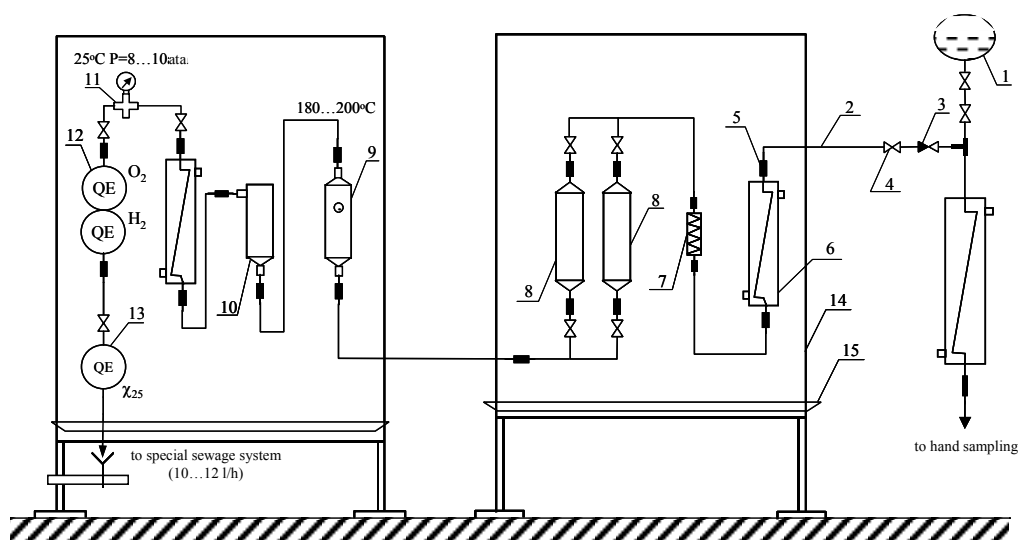


FIG. 43. Hydraulic hookup diagram of the "Corrosion measurement loop" with instrumentation elements

1 – drum separator, 2 – pulse pipes, 3 – disconnecting device, 4 – bellows valve, 5 – connection sphere on the cone, 6 – cooler, 7 – screw-regulator of flow rate, 8 – mechanical filter, 9 – sensor of electrochemical corrosion potential, 10 – sensor of polarization resistance, 11 – pressure regulator, 12 – measuring instrument of concentration H_2 , O_3 , 13 – conductometer, 14 – box, 15 – collection of leakages

7. CONCLUSIONS AND FUTURE DEVELOPMENTS

7.1. General considerations

The DAWAC project considered development and implementation of Data Processing Technologies for Water Chemistry and Corrosion Control at NPPs including data collection, data evaluation, diagnostics and assessment and provision of calculation modules as constituents of water chemistry expert systems. Water chemistry expert system is expected to perform following major tasks: prompt personnel alerting in case of water chemistry deviation, anomaly cause identification and trends prediction.

These systems were found necessary to have full benefit from using on-line sensors in the real-time mode when sensor signals, and other chemistry and operational data, are collected and continuously analysed with data acquisition and evaluation software. Both, data acquisition systems and intelligent water chemistry diagnostic systems have already been installed in some commercial plants.

7.2. Current status of chemistry monitoring and associated data processing support

- Low temperature on-line monitors (sodium, conductivity...) for the important parameters are considered as essential for satisfactory plant chemistry surveillance. Their data are supplemented by appropriate grab sample analyses;
- The data collection and evaluation tools are used more and more extensively in nuclear power plants. The main driving factors for their implementation have been cost reduction and more efficient utilisation of the collected data from the process instruments, particularly when a utility is in charge of several units in operation. In this case, such a centralized data bank allows gathering all relevant data and comparison between data from one unit to another. Therefore utilisation of such systems should be encouraged for further improvement the chemistry control and can be considered as mandatory requirement for newly commissioned plants;
- Several water chemistry expert systems are under development and some of them are already used by the utilities. Based on the calculated chemistry (alkalinity, redox potential, soluble corrosive compounds concentration, etc.), these systems are helping to the plant staff in operation;
- Specific In Situ high temperature monitors are considered preferably as a tool for R & D in order to optimize chemistry condition to be specified in nuclear power plants (NPP), but in some circumstances they can be found very beneficial when used in the NPPs under normal operating conditions.

7.3. Expert system expectations and limitations

The chemistry expert system consists of several modules, two of them having key roles. The diagnostic module ("the artificial chemistry brain"), contains logic algorithms derived from design, chemistry operating experience, regulatory requirements and complementary plant-specific information. So-called knowledge base module contains different corrosion degradation data bases/design curves, or sophisticated codes. Both modules are periodically updated with new requirements and new information from both R&D and industrial experience feedback.

The use of expert system in the future will be preferred mainly by NPPs where:

- Significant data volumes are generated and cannot be easily handled by the plant chemist;
- Staff is not full time available to define the cause and remedy to any abnormal situation in chemistry;
- The expert system or external help may contribute to decrease the load of the plant chemist for tasks in most frequent cases but not in all the unexpected situations;
- The expert systems may be of great help for some chemists, particularly young and overloaded ones.

Despite of above summarized benefits, such systems will still have limitations due to following reasons:

- Operating practice shows that expert systems are not able to replace fully experienced chemists in evaluating the origin of specific situations and taking the appropriate decision of corrective action;
- The second limitation is the lack of data allowing accurate modeling (e.g. local chemistry according to the concentration process).

7.4. Recommendations for further development

- Chemistry monitoring exhibits increased preference of on-line monitoring over grab sampling for important chemistry parameters. Such a process must be carefully reviewed and on-line/grab sampling chemistry monitoring ratio should be optimised with regard to plant design, staffing and necessary external support;
- Architecture of the expert system should allow customisation for particular plant design, current configuration and age;
- System should be designed to allow enhancement of its performance and capabilities by the self learning function;
- There is not sufficient experience accumulated from use of chemistry expert systems so far, so no judgement can be made about best methodology approach, therefore combination of different methods – fuzzy logic, neural networks, analytic models is being believed will give best results;
- Consideration should be given to modifications of chemistry database in order to keep historical data retrievability and compatibility with changes of both hardware and software environment due to rapid development of computer technologies;
- The balance between R & D activities in water chemistry monitoring area and actual plant needs should be established. The experience gained in extensive laboratory tests and campaigns at plants should not be lost, but either safely preserved for future needs or incorporated into expert system modules;
- It may be concluded from the DAWAC project results, that with continuous progress of the 1st step (Plant data collection and history, future data, operational diagnosis) and the 2nd step (research, data analyses, experiments, models validation), the 3rd step (update of water chemistry specifications) needs to be also developed correspondingly. It corresponds to the need for updating the chemistry specification based on high-level experts with sufficient background to take into account materials and design evolution, plant experience feedback, R&D laboratory results and models, international data;
- Water chemistry determines the behaviour of core and circuit materials, and influences the plant operation through transport and deposition of corrosion products including crud on the fuel. Aging facilities have been operated in various water chemistry regimes.

- Optimisation and control of the current water chemistry can help minimise problems with deposit buildup and control operational exposure;
- With regard to above mentioned facts, DAWAC group considers as useful to extend the basic lines of previous water chemistry focused CRPs for current reactor core operational parameters taking into account high burnup, the use of mixed cores and plant ageing. International cooperation on Optimisation of Water Chemistry to ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plant might be conducted in the future with consideration of the following issues and remedies:
 - Understanding the causes and mechanisms of crud deposition on fuel and its composition, which can cause crud induced power shifts (CIPS, previously called AOA) or localised clad corrosion for high burnups and also for advanced water chemistry regimes (noble metals or zinc addition, etc) and “old” units;
 - Materials behaviour at high burnup, also for “old” units, including:
 - Fuel rod claddings,
 - Other materials (Inconel, Stainless Steel);
 - Remedies by chemistry optimisation for high burnups, mixed cores and plant ageing:
 - Concentration and type of alkaline reagent,
 - Hydrogen concentration and production mode (direct injection or through NH_3),
 - Fuel cleaning (chemical cleaning, ultrasonic leaning),
 - Decontamination and post-decontamination water chemistry treatment,
 - Enriched boron-10 addition (EBA).

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ABBREVIATIONS

AC	alternate current
AVT	all volatile treatment
BAT	boric acid treatment
BOP	balance of plant
CAV	crack arrest verification
CDE	controlled distance electrochemistry
CDMS	chemistry data management system
CDS	condensate demineralizing system
CEI	contact electric impedance
CER	contact electric resistance
CFD	condensate filter demineralizer
CIMS	chemistry information management system
CP	corrosion product
CPD	condensate pump discharge
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
EDF	Eectricité De Fance
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	feed water
FWH	feed water heater
HT	high temperature
HTS	heat transport system
HWC	hydrogen water chemistry
IASCC	irradiation-assisted stress corrosion cracking
IGA/SCC	intergranular attack/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
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
OWC	optimal water chemistry
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	reduction-oxidation
RHR	residual heat removal (system)
RPV	reactor pressure vessel
RT	room temperature
RWCU	reactor water cleanup (system)
SCC-	stress-corrosion cracking
SCW	SMART ChemWorks TM
SG	steam generator
SGBD	steam generator blow down
SFD	system of functional diagnostics
SFDM	system of continuous water chemistry functional diagnostics and monitoring
SHE	standard hydrogen electrode
SMART	ChemWorks TM -SCW
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
WANO	world association of nuclear plant operators
WCh	water chemistry
YSZ	Yttrium stabilized Zirconia

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