IAEA-TECDOC-1666

Optimization of Water Chemistry to Ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plant (FUWAC)

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OPTIMIZATION OF WATER CHEMISTRY TO ENSURE RELIABLE WATER REACTOR FUEL PERFORMANCE AT HIGH BURNUP AND IN AGEING PLANT (FUWAC)

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2011

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IAEA, VIENNA, 2011
IAEA-TECDOC-1666
ISBN 978-92-0-120510-0
ISSN 1011-4289

Printed by the IAEA in Austria
October 2011

FOREWORD

This report presents the results of the Coordinated Research Project (CRP) on Optimization of Water Chemistry to Ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plants (FUWAC, 2006–2009). It provides an overview of the results of the investigations into the current state of water chemistry practice and concerns in the primary circuit of water cooled power reactors including:

- corrosion of primary circuit materials;
- deposit composition and thickness on the fuel;
- crud induced power shift;
- fuel oxide growth and thickness;
- radioactivity buildup in the reactor coolant system (RCS).

The FUWAC CRP is a follow-up to the DAWAC CRP (Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion Control in Nuclear Power Plants 2001–2005). The DAWAC project improved the data processing technologies and diagnostics for water chemistry and corrosion control in nuclear power plants (NPPs). With the improved methods for controlling and monitoring water chemistry now available, it was felt that a review of the principles of water chemistry management should be undertaken in the light of new materials, more onerous operating conditions, emergent issues such as CIPS, also known as axial offset anomaly (AOA) and the ageing of operating power plant.

In the framework of this CRP, water chemistry specialists from 16 nuclear utilities and research organizations, representing 15 countries, exchanged experimental and operational data, models and insights into water chemistry management.

The CD-ROM attached to this IAEA-TECDOC includes the report itself, detailed progress reports of three Research Coordination Meetings (RCMs) (Annexes I–III) and the reports and presentations made during the project by the participants.

The IAEA wishes to thank the participants and observers of the FUWAC 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, K. Makela, V. Kritsky, V. Onufriev, I. Smiesko, K. Vonkova, and J. Schunk. The IAEA officer responsible for this publication was J. Killeen of the Division of Nuclear Fuel Cycle and Waste Technology.

CONTENTS

1. INTRODUCTION

1.1. Water chemistry management at NPPs and FUWAC CRP

More than 95% of the nuclear power in the world is derived from water cooled reactors. In such reactor systems, water is used in primary circuits, secondary circuits Pressurized Water Reactors (PWRs) and Pressurized Heavy Water Reactors (PHWRs) and in a number of auxiliary systems. Water can be an aggressive medium especially at high temperature when in contact with structural materials. This means that the reliability of many NPP systems (fuel, steam generators, etc.) is dependent on the water chemistry during normal operations, startup, shutdown and abnormal operation conditions. Advanced water chemistry specifications have been developed for the existing water cooled reactors, but here is still room for improvement, particularly as fuel duty and burnups have increased, with new materials and enhanced requirements for reactivity control. There is also the further complication that these specifications have changed over time and many older plants will have experienced operation with several different chemistry regimes.

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 six different perspectives: material integrity, plant radiation levels, deposit build-up, fuel performance, environmental impact and safety.

The basis of chemistry control is operational experience, laboratory tests, corrosion and release data and information on the transport and deposition of crud/corrosion products under operating conditions. 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 reactivity control.
- Minimization of the concentration of chemical impurities, which may enhance 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-Sievert budgeting;
- by affecting formation of deposits, which may cause heat transfer degradation, flow measurement problems, enhance localised corrosion processes or localised reactivity problems.

A good understanding of the effects of water chemistry on plant components can support improvements to operating practices and help ameliorate any problems arising from changes in plant operation, such as fuel burnup or heat rating. It can also compensate for ageing effects within the plants, particularly due to conditioning to previous water chemistry regimes.

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

Research on coolant-component interactions has been carried out in the framework of four previous CRPs:

- Investigation of Fuel Cladding Interaction with Water Coolant in Power Reactors (CCI, 1981–1986) [1].
- Investigations on Water Chemistry Control and Coolant Interactions with Fuel and Primary Circuit Materials in Water Cooled Power Reactors (WACOLIN, 1987–1991) [2]–[4].
- High Temperature On-line Monitoring of Water Chemistry and Corrosion (WACOL, 1995–2000) [5].

- Data Processing Technologies and Diagnostics for Water Chemistry and Corrosion Control in Nuclear Power (DAWAC) – Report of a Coordinated Research Project 2001–2005 (DAWAC, 2001–2005) [6].

The first of these, the CCI CRP, considered the basic water chemistry in NPPs and at the end of the project five subjects of major importance were identified: increased performance, better fuel utilization, flexibility of operation, reliability and safety. These topics became the main concerns for the WACOLIN CRP, where the objective was to produce a manual of water chemistry in the primary circuit of NPPs. The influence of water chemistry on fuel and reactor primary circuit corrosion, and on radiation fields, was clearly shown in this project. Corrosion control and coolant activity were seen to depend upon the physicochemical parameters of the coolant. Among 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 was seen to be of fundamental importance.

The objectives of the subsequent WACOL CRP (1995–2000) were therefore 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 which did not use such technologies on a routine 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 ensure the availability of appropriate 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. The WACOL project demonstrated that in-situ monitoring was able to provide additional and valuable information to plant operators, e.g. electrochemical corrosion potential (ECP), high-temperature, pH and conductivity. Such data could be obtained promptly, i.e. in real time and with a high degree of accuracy. Reliable techniques and sensor devices are available which enable plant operators to obtain additional information on the response of structural materials in core and coolant circuits to changes in water chemistry. Based on the information gathered with such monitoring techniques operators can confirm:

- 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.

However, full benefit from using on-line sensors in the real-time mode can only be obtained if sensor signals and other chemistry and operational data were to be collected and continuously analysed with data acquisition and evaluation software. That recommendation led to the DAWAC project.

The major objective of the DAWAC project was to improve the processing technologies and diagnostics for water chemistry and corrosion control in NPPs. In the framework of this CRP, participants exchanged experience in the collection and evaluation of water chemistry indicators and corrosion data in NPPs and in the development of diagnostic and assessment systems to advise the operators on status of their plant. Acquired technical knowledge covered the following major areas:

- optimal 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).

On the basis of the accumulated experience in chemistry monitoring, there was an increased preference for on-line monitoring over grab sampling for important chemistry parameters. The on-line/grab sampling chemistry monitoring ratio was carefully reviewed and optimised with regard to plant design, staffing and necessary external support. The best methodological approach to the architecture of an expert water chemistry system was found to be a combination of different methods – fuzzy logic, neural networks and analytic models. The balance between research and design (R&D) activities in the water chemistry monitoring area and actual plant needs was established. The experience gained from extensive laboratory tests and campaigns at plants has been retained for future needs and incorporated into expert system modules.

It was concluded from the DAWAC project results, that with continuous progress in plant data collection and operational diagnosis and with advances in research, data analysis, experiments and model validation there is a need to update water chemistry specifications based on expert advice taking account of materials and design evolution, plant experience feedback, R&D laboratory results and models and international operational and experimental data. This recommendation has led to the present FUWAC project.

1.3. Research objectives of the FUWAC CRP

The overall objectives the FUWAC CRP, as agreed in the beginning of the project, included monitoring, maintaining and optimising the water chemistry regime in the primary circuit of water-cooled power reactors, taking into account high burnup operation, mixed cores and plant aging. The main research objective was to understand the causal mechanisms for the following issues:

- deposit composition and thickness on the fuel;
- CIPS and power limitation;
- fuel oxide growth and thickness;
- corrosion related fuel failure;
- Crud Induced Localized Corrosion (CILC);
- radioactivity build-up in RCS.

Areas covered by participants during the project included:

- The influence of plant design. Various reactor designs were considered, PWR and WWER, BWR and RBMK, and CANDU. Also considered were the appropriate cladding, spacer grid, steam generator and reactor pressure vessel materials taking into account current and proposed fuel burnup and cycle length.
- The influence of reactor age, fuel tramp contamination, fuel duties, neutron flux profile, sub cooled boiling, radiochemistry results linked to activity release and build-up, fuel cleaning and RCS decontamination.
- The influence of operating parameters, including burnup and enrichment, cycle length, load follow, transients and fuel element cycle number.
- The important chemical parameters, including the type and concentration of boron and alkaline reagent, pH, hydrogen, oxygen and some others.
- The role of chemical additives/advanced water chemistry regimes on fuel (deposits and corrosion).
- The role of important operational regimes, e.g. shutdown processes, on fuel (deposits and corrosion) and dose accumulation.

2. IMPLEMENTATION

2.1. Participation

Fifteen organizations from fifteen countries representing a broad mix of utilities, fuel vendors and research organizations joined their efforts in this project. Table 2.1 presents the names and countries of the chief scientific investigators at the start of the project, their organizations, and the title of their contribution. Proposals included laboratory experiments, theoretical assessments and power plant feedback covering coolant chemistry (CC) parameters, their influence on oxidation of primary circuit components and crud deposition, mitigation and consequences, including issues such as dose control and CIPS. The Republic of Korea joined the project after it began and their team is included in Table 2.1.

All the reports and presentations given by the participants are contained in the CD appended to this document.

Table 2.1. FUWAC PARTICIPANTS

Country	Name of chief scientific investigator	Institute	Title of project
Bulgaria	Mr. I. Dobrevski	Institute for Nuclear Research and Nuclear Energy (INRNE)	WWER-1000 Coolant Chemistry Improvement for Extended Fuel Cycles
Canada	Mr. D. H. Lister	University of New Brunswick	Laboratory Studies of In-core Corrosion Product Transport and Deposition in PWR Primary Coolant
China	Mr. ShiLin Hu	China Institute of Atomic Energy	The Influence of Water Chemistry with High Lithium on Fuel Crud Build-up
Czech Republic	Mr. M.Zmítko, Ms K. Vonkova	Nuclear Research Institute Řež plc	The Role of the Coolant Chemistry and Decontamination on Formation of Corrosion Product Deposits on the Fuel Cladding and on the Out-of-core Surfaces
Finland	Ms. L. Heikinheimo, Mr P. Kinnunen	VTT Technical Research Centre of Finland	Role of Alkaline Reagent and Alloying Elements in the Pre-transition Oxidation of Zr-alloys in Simulated PWR and WWER Conditions
France	Mr. F. Nordmann, Ms A. Tigeras	Electricité de France – CEIDRE	Optimization of Water Chemistry Technologies to ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plants (FUWAC)
Hungary	Mr. J. Schunk	Paks NPP	Analysis of Corrosion and Fissionable Product Particles in Primary Coolant
India	Mr. S.V. Narasimhan	Water and Steam Chemistry Division, BARC	Studies on Flow Accelerated Corrosion, (FAC) Metal Ion Passivation Techniques for Water Chemistry Management»
Japan	Mr S. Uchida	Japan Atomic Energy Agency (JAEA)	Optimization of Water Chemistry to ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plants (FUWAC)
Republic of Korea	Mr. W-Y Maeng	Korea Atomic Energy Research Institute (KAERI)	The Effects of Water Chemistry (pH, H_2 on Crud Deposition in PWR
Romania	Ms. I. Pirvan	Institute for Nuclear Research	Corrosion Behaviour of Zircaloy-4 Alloy Cladding of CANDU Advanced Fuel for High Burn-up
Russian Federation	Mr. V. Kritsky	VNIPIET	Decontamination and Post-decontamination Water Chemistry Treatment
Sweden	Mr. J. Chen	Studsvik Nuclear AB	Exchanging of our Knowledge in the Field of Optimization of Water Chemistry to Ensure Reliable Water Reactor Fuel Performance at High Burnup and in Ageing Plant (FUWAC) 2006–2010
Sweden	Mr B.Beverskog	Forsmark NPP	Axial Offset Anomaly PWR Fuel Crud
Ukraine	Mr. I.Petelguzov	National Science Centre, Kharkov Institute of Physics and Technology	Analytical and Experimental Research of Water Chemistry Impact on Corrosion Processes of Ukrainian WWER-1000 Core Materials
United States of America	Mr. S. Hettiarachchi	GE Energy, Nuclear	Advances in Water Chemistry Technologies and Management to Ensure Reliable Fuel Performance at High Burnup and in Ageing Plants

2.2. Short summary of the 1st RCM

The 1st RCM was held at Vienna, Austria, 4th–6th July 2006. A full summary of the meeting is given in Annex I. Following the participant's presentations, discussion sessions were held to allow a sharing of concerns and ideas, and to attempt to optimize the sharing of effort in the CRP to maximize the benefit for all the participants.

The first discussion session considered the topic of crud transportation and composition. The discussion focused on the nature of the crud, and what were the characteristics of cruds that were capable of inducing CIPS or AOA in NPPs. It was noted that soluble species may not be seen in post irradiation examination and there are crud releases (bursts) on shutdown in both BWR and PWR plants due to chemistry changes. It was also noted that RBMK plants have similar cruds and that WWER plants tend to have more magnetite and less nickel in the crud than PWRs. The Hungarian representative noted that a study in Hungary showed that the oxide layer on WWER fuel was changed by the decontamination process and was very similar to PWR crud, but that no CIPS had yet been observed.

Consideration was given to the composition of the steam generators and it was noted that WWER plant had 18/10 steel steam generators, and there was therefore less nickel in the coolant. It was also noted that WWER used potassium rather than lithium for pH control and that differing solubilities might affect crud compositions. The correlation between CIPS and steam generator tube material was recognized, with plants with steam generators manufactured from alloys 690 and 800 less likely to give rise to CIPS and some believed that nickel enrichment in the crud was necessary for CIPS, and that perhaps bonaccordite or a crud with a high specific surface area was necessary e.g. needles.

Another issue was that power plants operated at an oxygen potential that was close to the $Ni/NiO/Ni_xFe_{(3-x)}O_4$ phase boundaries, and that perhaps CIPS plants were operating in the more oxidizing conditions. A Swedish representative noted that many species have been found on filters including iron, iron/chromium/nickel iron/chromium oxides and also needle like NiO after peroxide injection. Silicates had also been found. It was asked if the chemical form of the cruds can change when on the fuel surface and exposed to a temperature flux and noted that radiotracer measurements can demonstrate ×3000 concentration of species in a crud oxide. The discussion on CIPS cruds included recognition that hideout return can be very slow and that crud density can be important. There was disagreement as to the importance of physisorption of nickel or boron in deposits and one participant felt that the lithium concentration in crud spinels could be important. This was usually experimentally difficult to determine by Scanning Electron Microscope with Energy-dispersive X-ray Spectroscopy (SEM/EDS), as lithium is not seen by X-Ray fluorescence techniques.

The discussion then focused on experimental techniques to determine the boron and lithium in crud, and it was noted that a very high concentration of B was needed for reliable detection by SEM/EDS. However, the detection of small concentrations of B and Li can be readily made by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Differences between WWER and PWR cruds were discussed and loop tests were discussed.

A final discussion session focused on issues concerning experimental techniques and problems in relating such experiments with plant data. The challenge was seen to be how to make representative crud out of reactor. The participants exchanged information on the differences between the various reactor systems and the crud types seen, noting high concentrations of hematite particulate in BWR due to the oxidizing conditions, whereas the conditions were less stable in WWER, in CANDU the issue of mass transfer due to fluid shear stress was highlighted. The crud bursts in PWR on shutdown and the levels of particulate and soluble species at startup and during transients were described.

Autoclave facilities were described that were able to simulate PWR crud, in particular the chimney structure and with a ratio of Ni/Fe ratio of around 1.5. A threshold thickness of crud of 20 μm was noted as necessary for an CIPS type of crud. It was noted that Calloway had had the most extensive experience with AOA and they would be asked to provide detailed information to assist experimental simulation of their crud.

The effects of zinc additions were discussed and it was noted that there were concerns that zinc injection early in cycle could enhance the probability of CIPS.

Overall, the main topic of concern was seen to be deposition on fuel which had the potential to cause localized power shifts.

2.3. Short summary of the 2nd RCM

The 2nd RCM was held at Chennai, India, December 11th–14th 2007. A full summary of the meeting is given in Annex II.

The participants gave presentations of their work to date and discussed issues and concerns for the second half of the CRP. The following areas of interest were covered:

2.3.1. AOA/CIPS

The influence of structural materials, particularly steam generator tubing:

- It was concluded that Ni, either as Ni metal or Ni oxide, is one important cause of CIPS.

The influence of water chemistry:

- Several parameters that may have an impact on CIPS have been identified:
    - pH selection with Ni solubility.
    - Use of enriched 10B (EBA).
    - K vs. Li for pH regime.
    - Importance of H2 concentration.
    - Silica and other compounds (Al) effect.
    - Zinc injection.

Design and operation; fuel cycle options:

- fuel options (cycle length and enrichment);
- temperature;
- operating conditions and options;
- core design – sub-cooled nucleate boiling (SNB): is not seen as a key parameter at this time.

2.3.2. Decontamination

This is a way to remove crud and deposits in the primary coolant for decreasing future occupational exposure from dose rates and future risk of CIPS associated with corrosion product transport. However, such an operation is time consuming, expensive, includes several risks of corrosion and induces a large quantity of undesirable liquid wastes. It is important to fully evaluate the advantages and drawbacks of such an operation before applying it.

This has been mainly a WWER issue, while the CIPS and dose rates mitigation has mainly been a problem for PWRs. Thus, a clarification on this decontamination, its purpose and how to decide to apply it or not is of great importance in the FUWAC project.

2.3.3. Fuel cladding corrosion

Several important presentations of this second FUWAC meeting dealt with fuel cladding corrosion which is a crucial issue regarding safe operation of NPP The following parameters were evaluated:

- Cladding material.
- Core characteristics: these are burn up, temperature, heat flux, SNB.
- Chemistry:
    - pH selection with Ni solubility.
    - K versus Li.
    - Radiolysis, hydrogen.
    - BWR; NWC, HWC, noble metal.
    - Zinc, noble metal.

2.3.4. Dose rate mitigation

Material selection is not covered by the FUWAC project. Chemistry does have an impact on dose rate, and is related to corrosion product transport and CIPS phenomenon.

- K versus Li and pH.
- New fuel and fuel cycle options with, in some cases, higher boron concentration at beginning of cycle (BOC) can affect dose rates.
- Zinc addition, noble metal.

2.4. Short summary of the 3rd RCM

The 3rd RCM was held at Turku, Finland, 15th–18th September 2009. A full summary of the meeting is given in Annex III.

The participants presented their final reports, and discussed the main issues that had arisen during the project. The main topics discussed were:

- Corrosion products.
- Crud composition and impact of CIPS.
- Fuel investigations.
- Decontamination – passivation.
- Chemical additives.
- NPP feedback on CIPS.

The information from the Electricité De France (EDF) units with various steam generator tubing materials shows that there is no difference in CIPS results on units with steam generators made from Alloy 600 or Alloy 690, although these materials have different Ni contents. The variability of Ni is a known parameter on crud deposits which have caused CIPS. The Korean units with 690 steam generator tubing do not have CIPS but the experienced feedback is insufficient to draw any firm conclusions. When EDF units switched from 12–16 months fuel cycles, no CIPS was observed. In the absence of stretch out, the increasing probability of CIPS is explained by the absence of corrosion product elimination and higher boron concentration. It was suggested by the Canadian representative that a parametric study of Ni/Fe ratio and the relation to the corrosion products and crud composition should be carried out.

A discussion took place for defining what may be considered as a CIPS/AOA. The Russian representative considers that AOA means a difference of at least 3% between the measured and theoretical flux. The French member claimed that very few assemblies in EDF units have such a deviation.

The Hungarian member confirmed that decontamination is a maintenance action that should be avoided as much as possible.

The participants reviewed the original purpose of the project and the outcome for each of them. All had benefited from the exercise, but it was felt that the issues surrounding crud and CIPS were still not completely understood and that further work in the area was still warranted.

3. CHEMISTRY

3.1. Description

3.1.1. PWR

The primary water of a PWR contains boron as boric acid in order to control the core reactivity through neutronic absorption of ^{10}B. Even though boric acid is weakly dissociated, particularly at high temperature, an acidic environment is unacceptable since it increases the general corrosion of materials in its presence, with the consequence of high activation and transport of corrosion products in the system.

Thus an alkaline reagent (lithium hydroxide) is added in the water in small quantities to achieve a slightly alkaline pH at operating temperature which minimizes corrosion, solubility and transport of activated corrosion products.

The Table 3.1 and Table 3.2 indicate the main radioisotopes produced by activation of corrosion products, and their half-life. Table 3.1 reports those obtained from activation of the base metals of the components, stainless steels or nickel base metals. Table 3.2 reports those obtained from activation of small quantities of elements which are present in specific components but are highly activated.

TABLE 3.1. MAIN ISOTOPES FROM ACTIVATION OF BASE METALS CORROSION PRODUCTS IN A PWR

Stable isotope	^{58}Ni	^{54}Fe	^{58}Fe	^{50}Cr
Radioactivated isotope	^{58}Co	^{54}Mn	^{59}Fe	^{51}Cr
Half-life	71 d	312 d	45 d	28 d

TABLE 3.2. MAIN ISOTOPES FROM ACTIVATION OF HIGHLY ACTIVATED METALS IN A PWR

Stable isotope	^{59}Co	^{109}Ag	^{121}Sb	^{123}Sb
Radioactivated isotope	^{60}Co	^{110m}Ag	^{122}Sb	^{124}Sb
Half-life	5.3 y	250 d	2.7 d	60d

Natural Li is not used since it contains too high a proportion of ^{6}Li, which is activated into undesirable tritium. Instead, lithium enriched to over 99% of ^{7}Li is used. In WWER, another alkaline reagent, potassium hydroxide, is generally added instead of lithium. Nevertheless, lithium-7 is produced in situ from the neutronic reaction ^{10}B $(n,\alpha)^{7}$Li.

Finally, hydrogen, directly added through a gas pressure or coming from radiolysis decomposition of ammonia in the WWER design, is present to counteract radiolytic decomposition of water into oxidizing compounds and oxygen, which are not compatible with the presence of stainless steel, in the circuit, which are sensitive to cracking corrosion at high temperature in presence of oxygen and chloride

The ^{10}B concentration is imposed by the core characteristics and design and by the fuel burn up. Natural boron only contains about 20% of ^{10}B, the useful isotope in neutronic absorption. This means that the required total boron content at the start of a cycle usually lies within the range 1000–2000 ppm B and progressively decreases throughout the fuel cycle as the fuel burn up increases. At the end of the fuel cycle, the boron concentration reaches a few ppm or is close to zero.

Consequently, to maintain the optimum high temperature $pH_{300°C}$ also requires a decreasing lithium concentration throughout the fuel cycle.

Calculation codes as well as feedback experience have led to the choice of a $pH_{300°C}$ of $\approx 7.2 \pm 0.2$ to minimize (i) the solubility and corrosion of the surfaces of the main components in the primary system, (ii) the difference of solubility and thus of transport of radioactivated isotopes in the various parts of the system at different temperatures, typically in the range 270–325°C for a standard 1000 MW PWR. The curve of lithium concentration following the decrease of boron content in French units is shown in Fig. 3.1. The modified chemistry that is applied in some French units and which is similar to that used in PWRs in other countries is shown in Fig. 3.2.

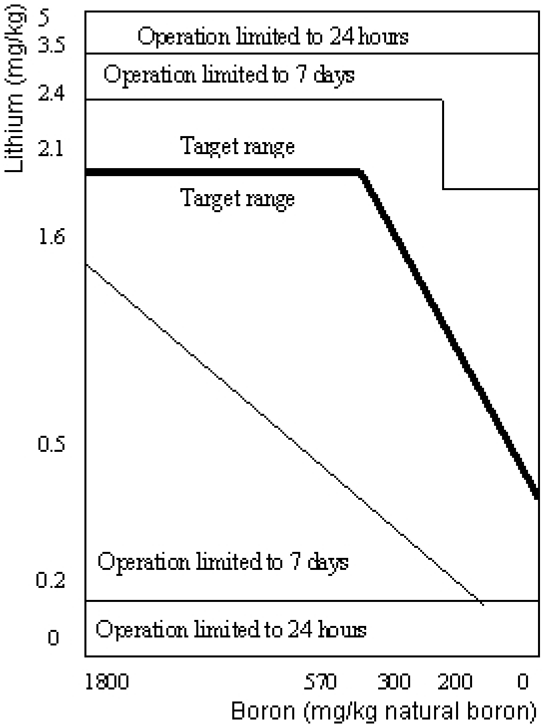


FIG. 3.1. Boron-lithium curve along the fuel cycle of a French PWR [7].

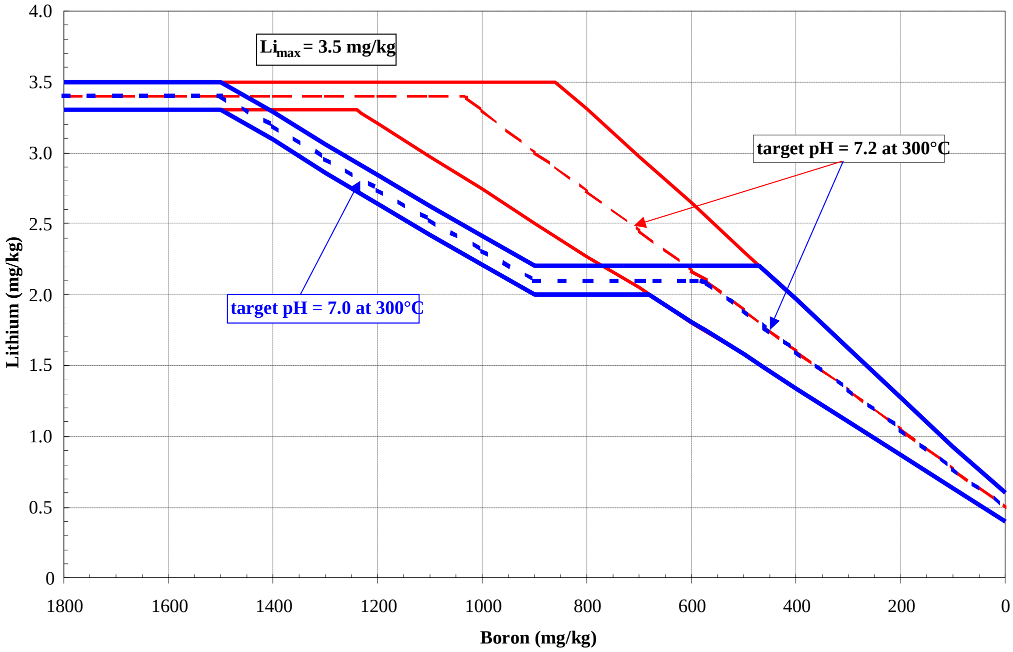


FIG. 3.2. French considered 'modified chemistry' (lower curve), 'high lithium' chemistry (upper curve) [8].

The lithium concentration corresponding to the required pH and the BOC boron concentration ranges from 5–10 mg/kg.

Concentrations of 0.5 mg/kg Li with a few mg/kg B are low enough not to cause any problem, but, at the BOC, a 1300 mg/kg boron content with, for example, a lithium concentration of around 4 mg/kg is likely to induce significant concentrations and precipitation conditions, on the fuel even if nucleate boiling at the cladding surface is avoided. Lithium concentration has to be limited to avoid too high a local concentration on the fuel cladding, with subsequent corrosion. Similarly, a too high boron concentration may increase the risk of precipitation leading to the safety concern of axial flux anomalies and inadequate control and monitoring of the core fission.

Further such deposition on the fuel will increase nucleate boiling conditions which should not exist in a PWR primary system as it is does in a BWR. Finally, there is the additional risk of allowing other compounds to precipitate in this deposit with consequences on corrosion, thermal transfer or radioactivation.

Consequently, in most cases, lithium concentration has been limited to 2.2 mg/kg mainly to avoid fuel cladding corrosion, based on fuel vendor restrictions, leading to low $pH_{300°C}$ and non optimized control of corrosion products activation and transport near BOC.

Some utilities have already started to increase the maximum lithium content up to 3.5 mg/kg, corresponding to a $pH_{300°C}$ at the beginning of the fuel cycle of almost 7.0, which is more or less acceptable, but with increasing burnup of the fuel, longer fuel cycles, less frequent shutdowns for refuelling and maintenance, the boron concentration has to be higher at the beginning of the fuel cycle and the $pH_{300°C}$ can be insufficient, even with 3.5 mg/kg Li.

One solution, already applied in some European PWRs (Germany, Switzerland), is to use enriched boric acid (EBA) with a higher proportion of ^{10}B. As an example, if only 40% of ^{10}B instead of 20% as in natural boron is used, the total boron concentration is halved and a concentration of 2.2 mg/kg Li becomes satisfactory for pH control.

The benefit of such EBA use will initially be in obtaining the optimum $pH_{300°C}$ at any moment, with minimized dose rates from activated corrosion products, but a second purpose will be the limitation of boron deposition with its consequences described above.

Parameters other than boron and lithium specified in the primary coolant under normal operating condition are listed in Table 3.3.

It should be noted that the specifications of silica have been modified to take into account the experience of units with zinc injection and duty level. Nickel concentration is also monitored and there are defined thresholds for units with zinc injection (Table 3.4)

TABLE 3.3. PRIMARY SYSTEM LIMITS UNDER NORMAL OPERATION [9]

Parameter	Unit	Expected value	Limit value	Monitoring frequency
Oxygen	mg/kg	< 0.010	< 0.10	No (H_2 only)
Hydrogen *	ml/kg	25–35	20–50	On-line
Chloride *	mg/kg	< 0.05	< 0.15	1/week
Fluoride *	mg/kg	< 0.05	< 0.15	1/week
Sulphate *	mg/kg	< 0.05	< 0.15	1/month
Sodium *	mg/kg	< 0.1	< 0.2	1/month
Silica	mg/kg	< 0.6	< 1.0	1/month
Calcium	mg/kg	-	< 0.05	1/month
Magnesium	mg/kg	-	< 0.05	1/month
Aluminium	mg/kg	-	< 0.05	1/month

** Parameter included in technical specification for safety.*

Table 3.4. PRIMARY SYSTEM LIMITS FOR SILICA AND NICKEL WHERE THERE IS ZINC INJECTION [10]

Parameter	Unit	Expected value	Limit value	Monitoring frequency
Silica	mg/kg	< 0.6	< 1.0, 1.5 or 2 dependent on fuel supplier and duty level	1/month without zinc injection, 1/week at BOC with zinc injection
Nickel	mg/kg	< 0.003	< 0.006 (low duty plants) < 0.003 (high duty plants)	For units with zinc injection 1/month or 1/week depending on zinc injection phase

One of the ways to mitigate activation of cobalt is to replace it by zinc in the surface composition. Thus, a few µg/kg of Zn is already added to the coolant in some countries (e.g. France, Japan) or considered as a key option in other countries.

The oxygen limit is not included in technical specifications since it is not controlled under normal operating conditions. The required limit is achieved through the presence of hydrogen. However, oxygen is controlled and monitored during shutdown after peroxide injection and before and during start up, with hydrazine addition for its elimination.

The limits for oxygen, chloride and fluoride are based on the risk of Stress Corrosion Cracking (SCC) of stainless steels at high temperature. Chloride and fluoride limits have been settled a long time ago and have not been modified since, there is neither difficulty to maintain them at any time nor any corrosion problem associated with the limit values. With the primary circuit under pressure, there is almost no possibility for contamination, except under transients or through resins. EDF in France uses only qualified nuclear grade resins and does not regenerate them, avoiding any risk of contamination in the primary system, nuclear auxiliary or secondary systems.

The limits for silica, aluminium and magnesium have been set by the risk of forming zeolite (hard deposits) with low solubility, on the fuel, which would decrease the heat transfer, increase the surface temperature and potentially cause deterioration of the cladding. The silica limit is less stringent than the one for the other elements since it is more difficult to keep a low value for silica which is less purified through resins and more frequently present in the system. If silica is present without the other elements, the risk of forming zeolite is negligible.

At this time, no abnormal contamination has occurred in the primary system and no major degradation has been observed. However, Alloy Inconel 600 is highly sensitive to SCC, even in pure water. SCC is the main weakness of many PWR units with a Western design of steam generators including Alloy 600 Mill Annealed (MA). In countries with Alloy 600 MA, the tubing has been affected on the primary side by Primary Water Stress-Corrosion Cracking (PWSCC) or secondary side by Intergranular Attack/Stress Corrosion Cracking (IGA/SCC). Consequently, most PWRs with Alloy 600 MA steam generators have already replaced their steam generators or will do so in the near future. Alloy 800 selected by the German or Alloy 690 (selected in almost all new PWR units started after 1990 or in most of steam generator replacements after 1990) are not sensitive to this type of degradation.

3.1.2. WWER

Different water chemistries are recommended for the WWER-440s and WWER-1000s to reflect their different operating temperatures (265–295°C vs. 289–322ºC). Also the boron-potassium coordination control during the cycle differs with respect to the use of standard or modified chemistry. pH control is carried out in different ways at individual stations using a combination of potassium hydroxide addition and potassium removal using cation ion exchange resins in the Primary Circuit Purification System SVO-1 and the Letdown Clean-up System SVO-2.

Standard water chemistry was developed in late 1970s and was designed to produce a nominally constant high temperature pH of $pH_{260°C}$ 7.3 at 270°C. pH was calculated according to the Meek method which is now known to give an error in high-temperature pH_T determination - nevertheless this type of boron/potassium control is still used at some WWER plants.

Modified water chemistry was introduced in the beginning of 1990s. This water chemistry ensures a constant pH_T and stable physical-chemical conditions during the whole reactor cycle which should reduce radiation fields. The choice of the optimal pH_T was a result of plant data analysis as well as mathematical modelling. For WWVER-440 units, the pH_{300} is in the range of 7.1–7.3 while 7.0–7.2 was chosen as the optimum for WWER-1000. This type of water chemistry has been introduced at many plants (e.g. Dukovany and Temelín in the Czech Republic, Bohunice in Slovakia, Kozloduy in Bulgaria and at Russian and Ukrainian plants). At the same time, utilities specify different maximum potassium level allowed (20 mg/kg at the Bulgarian, Czech, Russian and Ukrainian units; 16.4 mg/kg at Bohunice).

Boron/potassium co-ordination for the standard and modified chemistries of WWER-440 and WWER-1000 units is given in Figs 3.3–3.4. Typical high-temperature pH during the reactor cycle for the standard and modified chemistries are shown in Fig. 3.5.

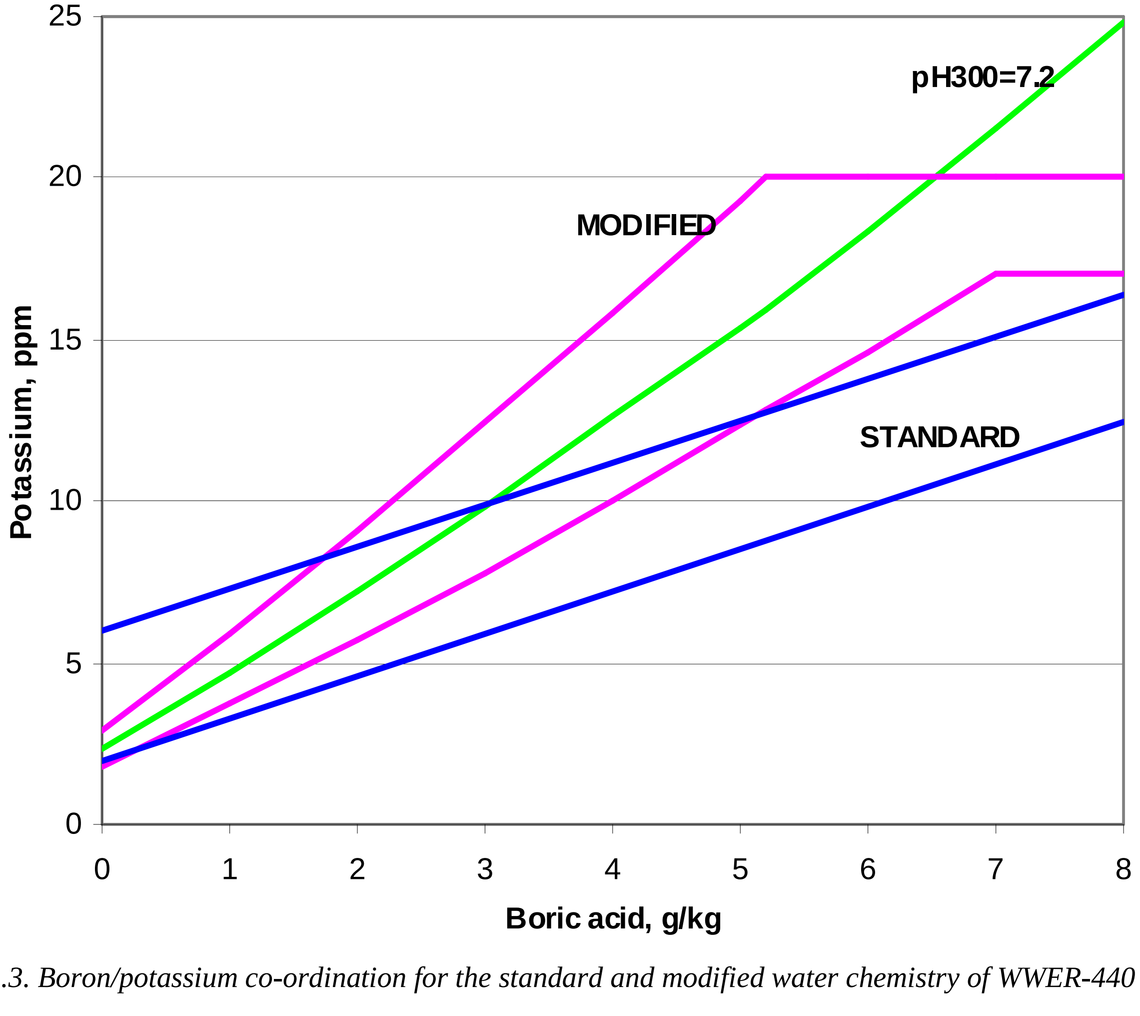


FIG. 3.3. Boron/potassium co-ordination for the standard and modified water chemistry of WWER-440 units.

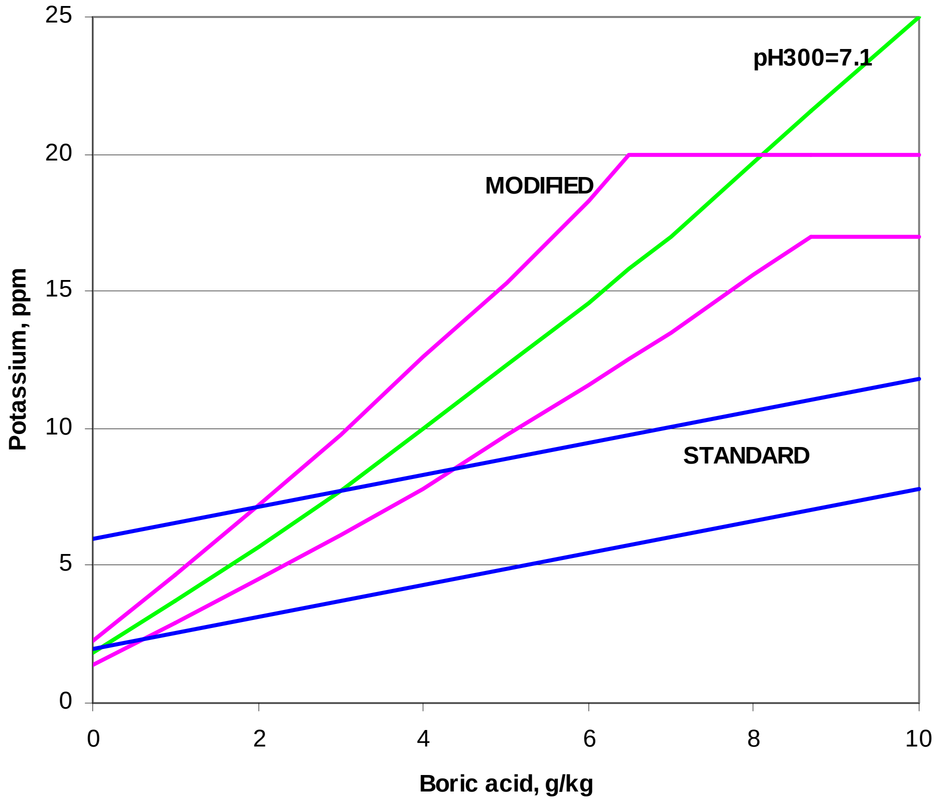


FIG. 3.4. Boron/potassium co-ordination for the standard and modified water chemistry of WWER-1000 units.

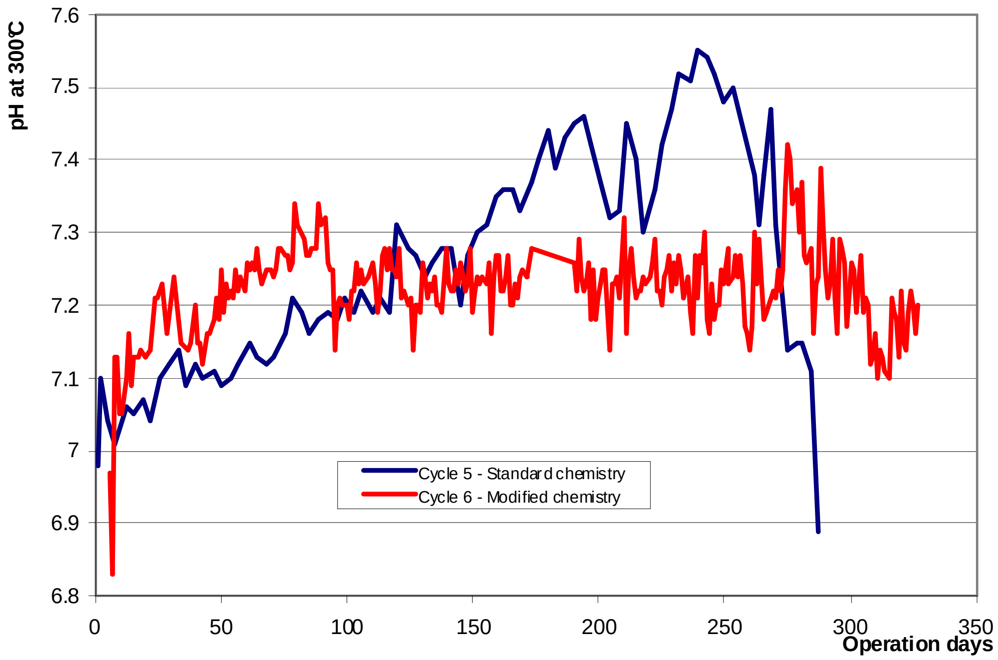


FIG. 3.5. Typical pH$_{300}$ of standard water chemistry and modified water chemistry during a reactor cycle (WWER-440 unit).

The specific features of the WWER-1000 units in Bulgaria:

- Steam generators are with austenitic stainless steel 08Cr18Ni10Ti tubing.
- Steam generators are with horizontal straight tubing.

- Fuel cladding material is Zr-1%Nb (Zr1Nb) alloy–recent trade name E110.
- Neutron absorbers are dissolved boric acid (with natural ^{10}B content) in the coolant and solid burnable neutron absorber Gd_2O_3 integrated in the fuel.
- Potassium hydroxide is used as the pH control agent in the coolant. The high temperature coolant value of $pH_T = pH_{300}$ is the main criteria determining the quantity of the applied alkalising reagent, necessary for the neutralization of boric acid in coolant. The values of pH_{300} are required to be in the range of $pH_{300} = 7.0$ and $pH_{300} = 7.2$ for the entire operation. All the various areas of operation are shown in Fig. 3.6.
- The build-up of lithium (^7Li) is based on the neutron reaction: $^{10}B\ (n, \alpha) \rightarrow\ ^7Li\ (n, \alpha)$.
- The necessary quantity of hydrogen in the primary circuit is generated through NH_3 radiolysis.

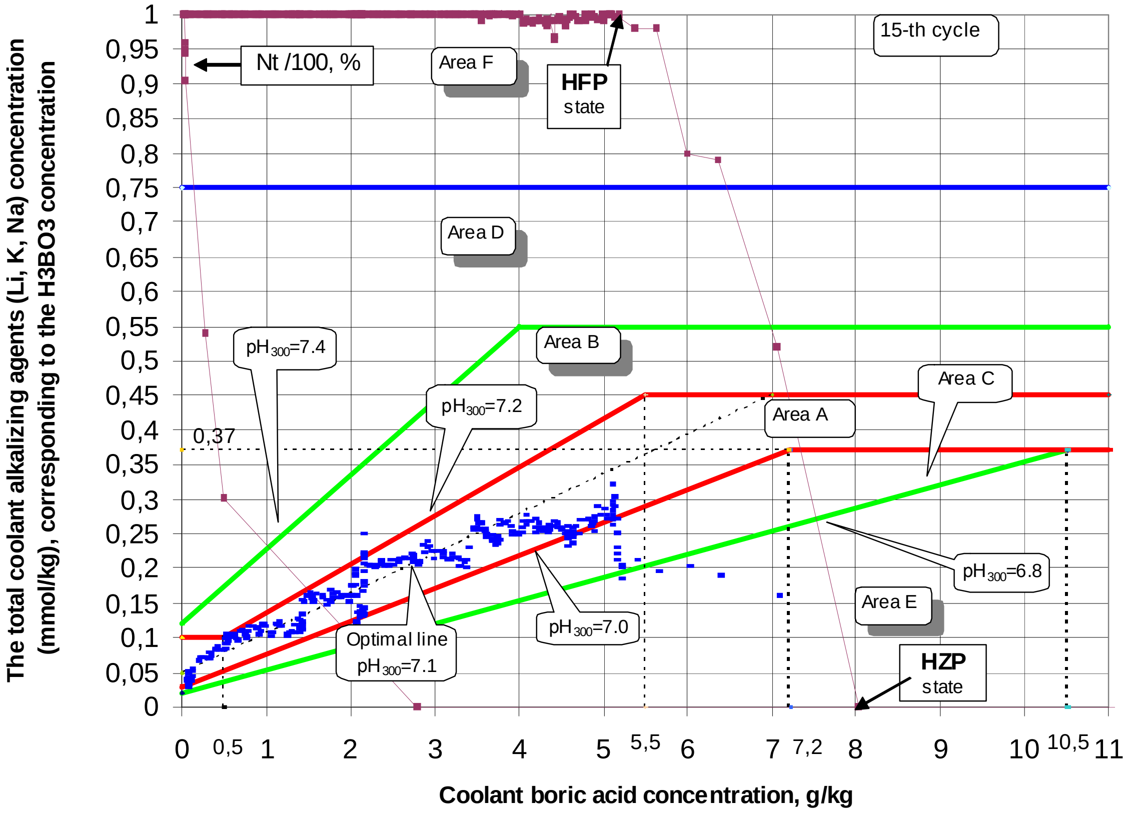


FIG. 3.6. Coolant water chemistry. Plant data for Cycle 15 at Kozloduy NPP unit 5 [11].

pH_T deviation from the optimal value towards acid or alkali region, variation of soluble gas concentration or temperature fluctuations are accompanied by changes in the solubility of the products of iron corrosion, which increases iron, nickel and cobalt mass transfer. Excess of alkali agents (alkalization) in the coolant promotes failure of zirconium cladding.

The two main tasks of water chemistry control in the primary coolant circuit are:

- ensuring corrosion resistance of fuel assembly (FA) and equipment materials–those of steam generators, pipelines, etc.;
- ensuring minimum doserate.

The majority of the impurities in the primary coolant circuit are generated as a result of corrosion of structural materials, leaking fuel cladding and, to a lesser extent, from impurities from filter materials.

In the case of oxygen presence in the makeup water, hydrazine-hydrate is introduced. At temperatures above 150°C it interacts with oxygen, but under the impact of ionizing irradiation in the presence of oxygen traces nitrates and nitrites can be formed. This process is most likely during reactor start-up, therefore, this is done under ammonia-potassium conditions, ammonia binding nitrogen-containing anions.

For periods of operation at power, the dissolved hydrogen concentration is in the range of 2.7–5.4 mg/dmi (30–60 nml/kg). After introduction of new standards, the maximum permissible concentration of oxygen dissolved in the coolant was reduced from 0.01 mg/dm^3 (10 µg/kg) to 0.005 mg/dm^3 (5 µg/kg). Maintenance of the standard oxygen concentration is achieved by addition of ammonia > 5 mg/dm^3.

The relation between hydrogen and ammonia is shown in Fig. 3.7.

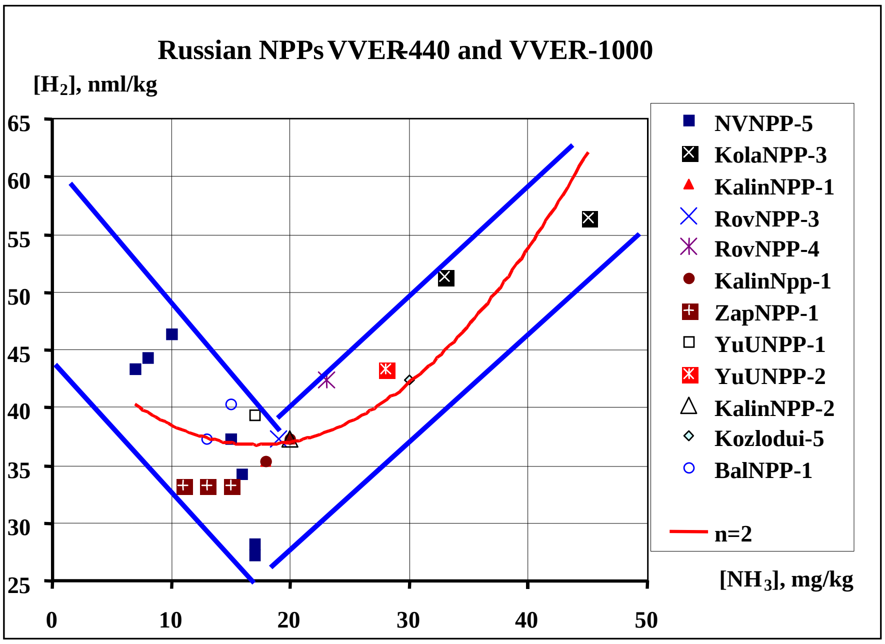


FIG. 3.7. Hydrogen/ammonia ratio at Russian NPPs with reactors WWER-440 and 1000.

Under the considered conditions, radiolytic synthesis of hydrogen from ammonia follows the reaction:

$$2NH_3 \rightarrow 3H_2+N_2 \tag{3.1}$$

Thus, for a stoichiometric reaction, 17.6 kg of hydrogen are formed for every 100 kg of ammonia added to the coolant.

Analysis of operational data from South Ukraine and other WWER-1000 NPPs demonstrates that it is ammonia injection into the primary coolant that accounts for the largest amount of corrosion-active impurities. Corrosion resistance of zirconium alloys decreases with increased concentrations of such contaminants as chlorides, fluorides, and sulphates. Unlike ammonia and hydrazine-hydrate solutions, injected gaseous hydrogen is virtually free of corrosion-active impurities. Based on the maximum values of impurity concentrations, injected ammonia can deliver up to 140 g of sulphates, 28 g of chlorides, 7 g of iron, and 14 g of heavy metals to the primary circuit annually. If hydrazine is used as a corrective additive instead of ammonia, the amounts of impurities delivered can be up to 400 g of sulphates, 400 g of chlorides, 40 g of iron, and 160 g of heavy metals.

Thus, in the Ukraine replacement of ammonia dosing with gaseous hydrogen injection will significantly decrease the quantities of harmful impurities delivered to the primary circuit and reduce their corrosion effects on the primary-circuit structural elements.

The use of ammonia at Zaporozhe as a corrective additive in the primary circuit increases ion load on cation-exchange filters of water cleanup facilities and decreases their filtration cycle, which complicates the use of non-recoverable ion-exchange resins. In evaporators ammonia, due to its high volatility, ends as condensate in the cleaned up environment. During cleanup the ammonia condensate on the ion-exchange resins transfers to regeneration solutions which deliver it again to evaporators. This circulation of ammonia in the cleanup system increases the amount of regeneration solutions, and thus of liquid radioactive waste (LRW).

The fuel cycle currently operated in Ukraine's NPPs does not require EBA. For mixed oxide fuel (MOX), the use of EBA will become necessary; therefore the question has to be investigated in order to be prepared for its implementation if required by new cycles.

The cost of boric acid enriched with ^{10}B is around 500 times higher than of acid with the natural concentration of boron isotopes. However, Emsland NPP (Germany, 1400 MW) uses EBA with 28% ^{10}B enrichment, and its losses are about 12 kg/year, which is around 800 times smaller than for a WWER-1000 case for a similar fuel cycle, which shows the economic inefficiency of its use. It should also be noted that Ukraine does not have the capacity to produce enriched ^{10}B. Zaporozhye NPP has used about 60–90 tonnes of boric acid in each of the past 7 years.

The use of EBA as a way of enhancing the primary CC is not a promising line of development for Ukrainian units. In case of nuclear fuel with a higher enrichment, MOX fuel and implementation of longer fuel cycles, the predicted boric acid concentration required to maintain the controlled reactor sub-criticality will increase and eventually reach a value which cannot be compensated with alkaline additives without a risk of damaging fuel rods or generating crud depositions on their surface.

3.1.3. BWR

The chemistry of BWR primary water is determined by:

- soluble/insoluble impurities in the feedwater;
- species (O_2, H_2 and H_2O_2) generated by the radiolysis of water in the reactor core;
- deposition and release of soluble/insoluble species on fuel;
- and removal of reactor water impurities through the clean-up system.

The challenge faced by the BWR industry is to balance these processes to maintain water chemistry within operating guidelines to optimize the performance of the BWR. Typically, BWR primary water is largely oxidizing due to the presence of O_2 and H_2O_2 in the reactor water. The oxidizing nature of the water increases the ECP measured against a standard hydrogen electrode (SHE) of internal metal surfaces in the positive direction that in turn makes materials susceptible to intergranular SCC. Table 3.5 summarizes an example of typical water chemistry parameters employed by BWRs

TABLE 3.5. A TYPICAL OPTIMUM WATER CHEMISTRY (OWC) SPECIFICATION FOR BWRS [12]

Feedwater		Reactor Water	
Conductivity (µS/cm)	< 0.065	ECP (V (SHE))	< -0.230
Total Iron (ppb)	0.5–1.5	Sulphate (ppb)	< 5
Oxygen (ppb)	20–50	Chloride (ppb)	< 5
Copper (ppb)	< 0.05	Conductivity (µS/cm)	< 0.08
Zinc (ppb)	< 0.6	Cobalt-60 (µCi/kg)	< 0.05
Hydrogen addition	Yes	Zinc (ppb)	5–10
		Copper (ppb)	< 0.5

Basically, the Optimum Water Chemistry (OWC) strategy is to keep all impurities to a minimum except the desirable feed water additives such as iron, zinc, oxygen and hydrogen, which are all controlled for a beneficial effect. The BWR water chemistry of currently operating plants may have some variations to those listed in Table 3.5 depending on specific plant operating requirements and improvements.

Conductivity is a quantitative measure of the soluble impurity level in BWR water. After intergranular SCC was observed in welded austenitic stainless steel piping circuits in the late 1970s, it was realized that reducing the impurity content of reactor water would help mitigate intergranular SCC. There has been a steady improvement of fleet conductivity in BWRs beginning in 1982. Currently, the fleet average reactor water conductivity is about 0.085 µS/cm. This improvement was made possible by improving the quality of the reactor feedwater and improving the performance and the capacity of the clean-up system. However, the presence of low conductivity is necessary, but not a sufficient condition to minimize intergranular SCC.

Common BWR structural materials such as Type 304 and 316 stainless steels, and nickel alloys have exhibited SCC in BWR environments due to high temperature and highly oxidizing conditions prevailing in BWR water. The oxidizing nature of the BWR environment is largely due to the presence of oxygen and hydrogen peroxide. Oxygen is generated by the radiolysis of water, and H_2O_2 is generated by the recombination of hydroxyl radicals that are also generated by the same radiolytic process. The low volatility of H_2O_2 makes the BWR water net oxidizing, thus increasing the ECP of structural materials exposed to the BWR environment. Typical ECPs of reactor internal components could be in the range of +100 to +250 mV (SHE) due to the presence of the above oxidizing species, [13]. Radiolysis of water also generates hydrogen, however, because of the higher volatility of hydrogen, it makes little impact on the overall oxidizing conditions of the BWR water phase. Furthermore, the oxidizing condition within the BWR also varies from location to location depending on the overall neutron and gamma dose rates at each location as well as the water flow velocities. As an example, recirculation system H_2O_2 concentration is typically less than that in the core regions due to the efficient decomposition of H_2O_2 on metal surfaces, as well as recombination of H_2O_2 with H_2 by gamma induced catalysis.

Structural materials in BWRs operating under normal water chemistry conditions (NWC) exhibit high ECP values in the range +100 to +250 mV (SHE). High ECPs increase the propensity for intergranular SCC of nickel weld metals and stainless steels especially in the weld heat affected zone of BWR welds and materials. A practical and system-wide SCC mitigation solution available for operating BWRs is to modify the water chemistry, i.e. lower the ECP of reactor internal components.

Currently, all 34 US BWRs, 14 Japanese BWRs and 6 European BWRs employ hydrogen injection into feedwater (HWC) to mitigate intergranular SCC of reactor internals by suppressing radiolytically generated oxidants.

In addition, a majority of the US BWRs, a few Japanese BWRs and a few European BWRs now employ NobleChem^{TM} in combination with low HWC that improves the effectiveness of recombination of H_2 and oxidants to achieve low ECPs. Typical NobleChem^{TM} applications (injection of noble metals into the reactor water) are performed just prior to an outage at a temperature of 240–290°F (116–143°C). NobleChem^{TM} has been further developed so that noble metals at very low concentration can be injected into the coolant while the plant is operating at full power. This process is called On-Line NobleChem^{TM} or OLNC, and is applied at a reactor water temperature of 530–540°F (277–282°C). The advantage of NobleChem^{TM} or OLNC is that they require very little hydrogen addition in to the feedwater (0.15–0.35 ppm) to achieve low ECPs, thus minimizing operating dose rate concerns. However, there are dose rates concerns and the addition of depleted zinc oxide (DZO) into the feedwater is one of the possible counter measure against drywell dose rate increases.

Conclusions on advantages of On Line Noble Chemistry (ONLC) in BWR units for mitigating Crack Growth Rate of SCC on different materials are:

- Combination of DZO and NobleChem^{TM} is more effective in dose rate reductions.
- Noble Metal Addition lowers ECP and Crack Growth Rates.
- On-Line NobleChem^{TM} lowers ECP and Crack Growth Rates.
- On-Line NobleChem^{TM} releases activation corrosion products from surfaces resulting in lower dose rates.
- There is no impact on fuel performance.

With OLNC, Fe_2O_3 is transformed into Fe_3O_4. ONLC has been applied on two Swiss units and 4 US units. It could be considered for WWER as an alternative to switching from ammonia to hydrogen. The typical reactor water platinum concentration during an OLNC has been in the range of 20–100 ppt.

The NMCA technology in combination with low hydrogen addition has lowered the ECP of plant materials below the SCC mitigation potential with no long-term increase in main steam line radiation (MSLR) fields, and has also helped to lower the drywell dose rates when DZO is used along with NMCA. A total of 33 BWRs are currently using this technology worldwide.

During the qualification testing program of NobleChem^{TM}, it was noted that the Pt + Rh treated surfaces incorporated significantly less ^{60}Co on their surfaces than the untreated controls when tested in zinc containing water at a molar ratio of $H_2/(O_2 + ½ H_2O_2) > 2$.

3.1.4. RBMK

The common water chemistry of NPPs with RBMK and BWR does not imply any alkaline reagent addition and the plants operate with a pH_{25} of the coolant close to neutral (6.5–8.0). The maintenance of water chemistry conditions at such NPPs to norms and standards is ensured by the effective operation of reactor water and condensate cleanup systems and the use of corrosion-resistant materials.

The main sources of impurity ingress to the reactor circuit are the following:

- leakages in the condenser;
- corrosion of structural materials, especially during the start up and shutdown periods;
- organic and chemical reagents (drainage equipment and hydraulic systems, cooling systems, etc.);
- ion-exchange resins (leakages, resin aging, etc.).

In Table 3.6–3.7, the operation standards for the coolant quality at NPPs with RBMK-1000 and RBMK-1500 are presented.

TABLE 3.6. *OPERATION STANDARDS OF THE COOLANT QUALITY FOR RBMK-1000 REACTORS*

Parameter	Water of the multiple forced circulation circuit		Turbine condensate after condensate cleaning		Feed water		Saturated steam, controlled parameters
	Rated parameter	Limit value of controlled parameter	Rated parameter	Limit value of controlled parameter	Rated parameter	Limit value of controlled parameter	
pH at 25°C	6.5–8.0	-	-	6.8–7.1	-	6.8–7.1	-
Electrical conductivity at 25°C, µS/cm	<1.0	-	<0.1	-	-	<0.1	-
Chloride-ion +fluoride-ion, µg/kg	<100	-	-	<10.0	<4	-	-
Hardness, µg-equ./kg	<5	-	-	<1.0	-	<1.0	-
Silicic acid, µg/kg	-	500–1000	-	-	-	-	5–10
Oxygen, µg/kg	-	<50	-	<10	<10	-	-
Sodium, µg/kg	-	-	-	<3	-	-	-
Products of Fe corrosion, µg/kg	-	<50	-	<10	<10	-	-
Products of Cu corrosion, µg/kg	<20	-	<2	-	-	<2	-
Oil content, µg/kg	<200	-	-	-	-	<100	-

TABLE 3.7. STANDARDS OF THE COOLING WATER QUALITY AND CONTROLLED PARAMETERS OF WATER CHEMISTRY FOR RBMK-1500 OPERATION AT POWER LEVEL ABOVE 500 MW FOR EACH TURBINE

	Water of the multiple forced circulation circuit		Turbine condensate after condensate cleaning		Feed water		
Parameter	Rated parameter	Limit value of controlled parameter	Rated parameter	Limit value of controlled parameter	Rated parameter	Limit value of controlled parameter	Saturated steam, controlled parameters
pH at 25°C	6.5–8.0	-	-	6.8–7.1	-	6.8–7.1	-
Electrical conductivity at 25°C, µS/cm	<1.0	-	<0.1	-	-	<0.1	-
Hardness, µg-equ./dm^3	<5	-	-	<0.2	-	<0.2	-
Sodium concentration, µg/dm^3	-	-	-	<3	-	-	-
Oxygen concentration, µg/dm^3	-	-	<50	-	<15	-	-
Oil concentration, µg/dm^3	<100	-	-	-	-	<100	-

The impurity content in the reactor water is mainly determined by the quality of feed water and operation of water cleanup systems of the multiple forced circulation circuit, and condensate feed circuit.

The content of corrosion products and impurities in feed and reactor water is considered to be one of the most important parameters affecting sedimentation on fuel elements and activity accumulation in BWR circuits. Correspondence of the feed and reactor water quality to the standard indicators is controlled with regular analysis of water samples.

The ionic conductivity of water is the most important characteristic that determines the impurities content in water. The ionic conductivity of high-purity water is about 0.1 µS/cm. In BWR-type reactors in the stationary operation mode the ionic conductivity of reactor water usually does not exceed 0.2 µS/cm, and of the feed water ~0.1 µS/cm.

The pH value is also an important parameter. Simultaneous monitoring of pH and ionic conductivity allows estimating the quality of water chemistry conditions in boiling reactors.

Another parameter of the quality of water chemistry conditions, characterizing the process of corrosion, is iron concentration in the coolant.

The control over corrosion products (especially Fe) content in the coolant is necessary primarily to evaluate sedimentation on the fuel elements. Reduction of corrosion products content permits to minimize the sedimentation and sediment activity. Radioactivity accumulation on the pipeline surfaces outside the core represents the main problem for the water quality maintenance in BWR-type reactors.

At steady state operation of RBMK-1000 type reactors, corrosion products concentration is within the range of 2–20 µg/kg (by iron). Corrosion products concentration in the water of the multiple forced circulation circuit is in equilibrium with the balance of iron inflow and sedimentation. Generalization of the available data shows that an increase of iron concentration in feed water leads to a growth of iron concentration in the reactor water.

At the Russian RBMK reactors a number of traditional measures are taken to reduce iron content in feed water, and consequently, in the reactor water:

- Manufacturing of equipment parts and tube still of condenser heaters of a corrosion-resistant alloy.
- Application of full-flow condensate cleaning.

Corrosion of tubes and shells of low-pressure heaters, pipelines and other elements of the condensate-feed circuit of NPPs with RBMK-1000 does not restrict their reliability and service life.

Nevertheless, iron ingress into the multiple forced circulation circuit is still considerable, and results in corrosion products sedimentation on fuel element surfaces and the necessity of periodical decontamination of the nuclear plant equipment.

3.1.5. PHWR

In the primary heat transport system (PHTS) of CANDU reactors, heavy water is used both as coolant and moderator. The use of heavy water in CANDU circuits is an added incentive to strive for optimum control. The operation parameters for the heavy water used as coolant are: inlet temperature 265ºC (11.2 MPa) and outlet temperature 310ºC (9.89 MPa). The cooling water is in contact with different materials and their corrosion behaviour is much affected by water qualities.

In order to minimize the adverse effects, an optimal chemistry control has been proposed. Objectives of chemistry control are: minimize the degradation of the diverse system materials, minimize transport of radioactivity and prevent fouling of the core by magnetite deposition. These objectives are achieved by respecting PHTS chemistry specifications in normal operation, presented in Table 3.8.

The aggressiveness of PHTS water is reduced by controlling dissolved oxygen content, pH, impurities, radioactive crud and fission products.

TABLE 3.8. PHTS CHEMISTRY SPECIFICATION IN NORMAL OPERATION

Parameter	Type	Specification range (Desired range)	Rationale
Dissolved deuterium	Control	3–10 ml/kg (3–7 ml/kg)	Lower to prevent radiolytic oxygen formation. Upper to minimize deuterium pick-up Zr-alloys.
Dissolved oxygen	Diagnostic	<10 mg/kg	Minimize Zr-Nb alloy corrosion. Minimize pitting corrosion of carbon steel and cracking of stainless steel. Minimize activity transport through minimizing crud formation. Minimize corrosion of Incoloy-800.
pH_a	Control	10.2–10.8 (10.2–10.4)	Lower limit is set to: minimize deposition of magnetite in core. Upper limit set to: minimize Zr-alloys and martensitic steel corrosion and minimize FAC of carbon steel.
Conductivity	Diagnostic	8–25 μS/cm (8–20 μS/cm)	Used in conjunction with pH_a readings.
Lithium ion	Diagnostic	0.4–1.1 mg/kg (0.5–0.7 mg/kg)	Used in conjunction with pH_a readings.
Chloride ion	Control	<200 μg/kg (<50 μg/kg)	Minimize pitting corrosion of Zr-alloys, carbon and martensitic steel. Minimize cracking of stainless steel.

The corrosion rates of Zr alloys (fuel sheaths and pressure tubes) and of carbon steel (feeders and headers) are significantly enhanced in presence of dissolved oxygen.

Oxygen production reaction:

$$OD + D_2O_2 \rightarrow DO_2\,; \quad OD + DO_2 \rightarrow O_2 + D_2O; \quad DO_2 + DO_2 \rightarrow O_2 + D_2O_2 \qquad (3.2)$$

The operating objective is to maintain the concentration of dissolved <10 μg O_2/kg D_2O. Production of oxygen is suppressed by the addition of extra deuterium to the coolant. Thus, the addition of gaseous hydrogen to the PHTS coolant creates, by isotopic exchange, the concentration of dissolved deuterium necessary to minimize the production of dissolved oxygen without causing unacceptable downgrading of the heavy water.

Chain reaction to remove oxygen and peroxide:

$$OD + D_2 \rightarrow D + D_2O; \quad D(e_{aq}) + D_2O_2 \rightarrow OD + D_2O; \quad D(e_{aq}) + O_2 \rightarrow DO_2 \qquad (3.3)$$

Reaction (3.3) is made to go ‘faster’ than reaction (3.2) by adding excess deuterium so oxygen will not be formed.

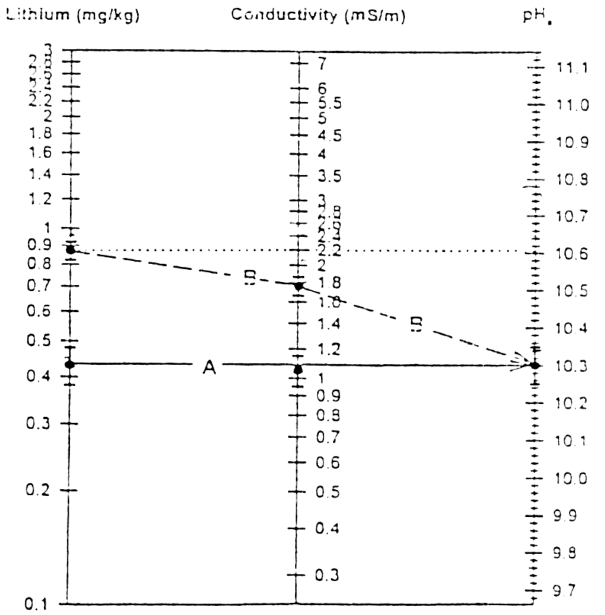
$$k_{33}[D_2] >>> k_{32}[D_2O_2], \qquad (3.4)$$

where k_{xx} is the rate constant associated with the appropriate reaction.

A high concentration of dissolved deuterium should be avoided to minimize any potential for dissolved deuterium to accelerate the formation of zirconium deuterides in any inadvertently overstressed regions of the pressure tubes. There is a critical deuterium concentration (CDC) required to suppress oxygen formation. Dissolved deuterium specification is 3–10 ml/kg.

The pH value in accordance with AECL specification is $10.2 < pH_a < 10.8$.

The pH_a of the PHTS coolant is controlled by the concentration of LiOD by using a Li^+/OD^- form ion exchange resin (pH_a is the reading on a pH-meter calibrated in light water buffers. All at 25°C; $pH_a = pH + 0.463$). A pH_a value must be correlated to $[Li^+]$ and to the ionic conductivity: $pH_a \leftrightarrow [Li^+] \leftrightarrow$ conductivity, Fig. 3.8.



pH	$[Li^+]$ (μg/kg)	Conductivity (mS/m)
10.8	1.37	3.44
10.4	0.55	1.37
10.2	0.34	0.86
10	0.22	0.55

Line (A) is an example of a correlation indicating pH_a, is a valid number;
Line (B) is an example of a correlation indicating contamination of the HTS coolant;
Line (---) indicated the pH_a, calculated from the Li^+ concentration.

FIG. 3.8. Correlation of PHTS data for $[Li^+]$, conductivity and pH_a at 25°C.

There is a narrow band of pH values: $10.2 < pH_a < 10.4$, within which the PHTS operates optimally. At Cernavoda NPP Unit#1, one main issue for PHT chemistry control is to reduce the pH value from 10.2–10.8 to the optimum range: 10.2–10.4 [14]. This desired range (Fig. 3.9) is set to minimise Zr-alloy corrosion/deuteriding, minimize the Flow Accelerated Corrosion (FAC) rate of carbon steel outlet feeders and avoid deposition of magnetite in the reactor core, i.e. the ‘solubility’ of magnetite must be normal, increasing across the core.

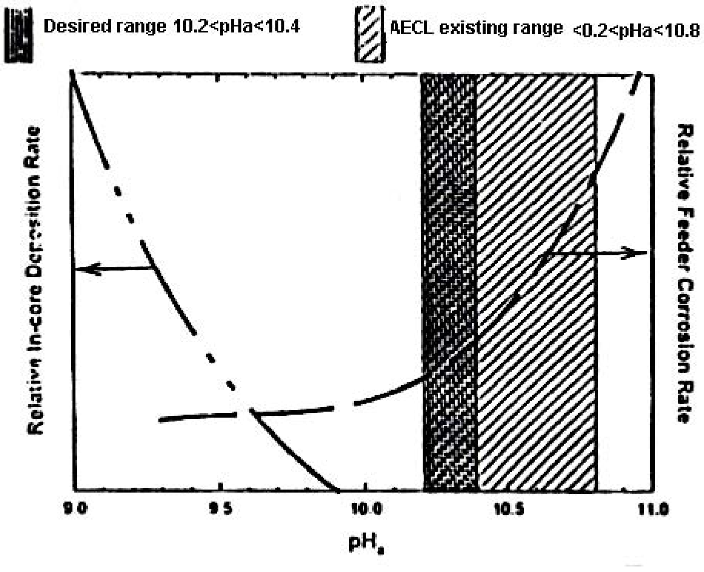


FIG. 3.9. Schematic illustration of proposed pH$_a$ region for HTS coolant to reduce feeder wall thinning of outlet feeders.

The production rate of radioactive materials is minimized by: operating with a low concentration of dissolved oxygen, which is maintained by hydrogen addition to the PHT water; continuous steady state operation with no thermal, hydraulic or chemical transients; operating at pH values above 10.2 and operating with a minimum number of defective fuel bundles.

PHWRs in India are tube type reactors, having 306 Zircaloy-2/Zr-Nb alloy pressure tubes. They are horizontally positioned in the calandria vessel made of stainless steel. This vessel holds the moderator heavy water. Each pressure tube is connected to the steam generator through the carbon steel feeders on both sides of the horizontal core. The feeders then transfer the coolant to the two carbon steel headers on either side. Thus, carbon steel feeders constitute an important component of the primary coolant system in PHWRs. The tubes in the steam generator are made of Incoloy 800. Thus, the three major materials in the PHTS of PHWRs are Carbon steel (1500 m^2), Incoloy (8000 m^2) and Zircaloy (6000 m^2).

Indian PHWRs have a separate moderator and coolant system. The primary heavy water (D_2O) coolant is operated in the temperature 250–300°C and at pressures between 87–92 kg/cm^2 in single phase in the 220 MWe and 540 MWe reactors. The coolant pH$_a$ is specified to be in the range 9.5–10.5 but mostly operated in the range 10.0–10.5, which is adjusted using LiOD and hydrogen is maintained in the concentration range of 3–10 ml/kg D_2O to achieve a reducing condition. The PHT storage tank also has a nitrogen cover gas (instead of He in some plants). Hydrogen gas is injected into the feed water under high pressure.

Since PHWRs practice online refuelling, the concept of fuel cycle does not arise. However it is to be noted that a fresh bundle stays in the core for an average time of 2–3 years, and may reside at different locations in the core.

The chemistry maintenance in the PHTS is to meet the following objectives:

- Minimise the corrosion release of materials from PHTS surfaces especially carbon steel (CS) feeders and Incoloy800 tubes.
- Minimise the deposition of crud on fuel surfaces and steam generator tube surfaces.
- Minimise the build up of radioactivity on out of core system surfaces.

The coolant is maintained under reducing conditions by dissolved hydrogen. In reactors where PHTS storage tank contains N_2 as cover gas, some quantity of dissolved nitrogen enters the coolant. As dissolved nitrogen is exposed to core radiation, it is also playing a role in the inhibition of radiolytic decomposition of water mediated through the probable formation of ammonia.

3.2. Discussion

WWERs are using potassium hydroxide rather than the lithium hydroxide used in PWRs with two main advantages:

- cost limitation by avoiding the use of enriched ^{7}Li;
- higher solubility of K as compared to Li, with lower risk of precipitation and axial offset anomalies.

But there is one constraint with K, necessity to monitor K + Li for the pH control since ^{7}Li is anyhow produced from ^{10}B. In addition, Na being present as an impurity of K it is also monitored.

Quality standards for WWER and PWR reactors are presented in Table 3.9.

TABLE 3.9. SUMMARY OF WATER CHEMISTRY STANDARDS FOR THE PRIMARY COOLANT CIRCUIT PWR

Parameters	EPRI (USA)	Westing-house (USA)	VGB (Germany)	Siemens-KWU (Germany)	J-PWR (Japan)	EdF (France)	WWER 440/ 1000	WWER 440 (Finland)	New project (Russia)
Lithium hydroxide	0.2–2.2	0.7–2.2	0.2–2.2	0.2–2	0.2–2.2	0.45–2.2			
Potassium hydroxide	-	-	-				2–26.5#	2–22#	2–26.5#
Ammonia	-	-	-				>5	>5	>5
Hydrogen	2.2–4.5	2.2–4.4	1–4	2–4	2.2–3.15	2.2–4.4	2.7–4.5	2.2–4.5	2.7–5.5
Oxygen	<0.01	<0.005	<0.005	<0.005	<0.005	<0.1	<0.01	<0.01	<0.005
Chlorides	<0.15	<0.15	<0.2	<0.02	<0.05	<0.15	<0.1	<0.1	<0.1
Fluorides	<0.15	<0.15	-	-	<0.1	<0.15	<0.05	<0.1	<0.05
Dissolved iron	-	-	-	(<0.05)	-	-	-	-	
General iron	-	-	(<0.01)		-	-	<0.2	-	
Sulphates	0.1	-	-	-	-	-			
Silica	-	<0.2	-	(<0.5)	-	<0.2	-		
Solid particles	0.35	<1	-	(<0.1)	<0.5	<1	-	-	
Aluminium	-	<0.05	-	-	-	<0.1	-	-	
Calcium	-	<0.05	-	-	-	<0.1	-	-	
Magnesium	-	<0.05	-	-	-	<0.1	-	-	

Western standards for the primary coolant circuit of PWR-type reactors provide for water chemistry conditions controlled by additives of H_3BO_3, LiOH, H_2 and N_2H_4, H_2O_2 if necessary. The standards are all the time improved depending on the plant power, materials used and the accumulation of data on the mechanisms of corrosion, mass transfer and accumulation of radioactivity. The latest recommendations provide for the maintenance of the ‘coordinated’ water chemistry with pH_T value variation depending on the fuel cycle.

Although the aims and objectives pursued WWERs in Ukraine and PWRs are the same, the ways and means of achieving them are different.

To offset and control reactivity, WWER and PWR reactors use boric acid diluted in the primary coolant, which requires pH correction with alkaline additives. For pH correction PWRs inject LiOH only during reactor startup, as long-term reactor operation produces Li through neutron capturing by ^{10}B, which is used to control the neutron flux. In WWERs pH is corrected through continuous injection of potassium hydroxide, KOH. The amounts of alkalis injected into the coolant are different too. For example, the Emsland NPP, where ^{10}B-EBA acid is used, consumes 1 kg of lithium hydroxide per year per 1400 MW unit, whereas Zaporozhe with a WWER-1000 1300 kg of potassium hydroxide.

The experience of enhancing western PWRs chemistry has led the Ukraine to consider that it may be possible to decrease the dose rates and radioactive waste by changing WWER primary CC along the following lines:

- replacement of ammonia injection with gaseous hydrogen injection;
- zinc injection;
- application of boric acid enriched with ^{10}B isotope.

The Emsland NPP, which has implemented gaseous hydrogen injection and has been utilizing boric acid enriched with ^{10}B isotope, annually generates no more than 10 m^3 of vat residue of LRW with 25% concentration of salts. ZNPP generates over 100 m^3 of LRW vat residue per unit with the same salt concentration.

Ten years of zinc microinjections at the Biblis NPP allowed reducing primary-circuit equipment activity by 10–15% a year.

To suppress generation of radiolysis oxidation products, PWR inject gaseous hydrogen, whereas WWER inject ammonia. Ammonia injection into the coolant brings additives capable of getting activated in the reactor. Presence of considerable concentrations of ammonia in the primary coolant reduces the exchange capacity of the water cleanup system (WCS) filters, requiring frequent regenerations and leading to increased amounts of LRW. The amount of radioactive waste at Ukraine's NPPs is one order higher than at NPPs with PWRs. The use of ammonia to control hydrogen concentration during reactor startups and transients complicates maintenance of controlled oxygen concentrations, since hydrogen production is proportional to the neutron flux in the core.

In the past, few years Ukraine has been aspiring to diversify its nuclear fuel and to operate mixed cores with fuel assemblies of various suppliers, each with its own inventory of structural materials. Westinghouse fuel has been operated and has demonstrated good corrosion resistance in PWRs. PWR imposes stricter requirements compared to WWER, in terms of coolant quality indicators (oxygen, iron, chlorides, sulphides, carbon).

Unlike PWR-type reactors, in BWR's because of coolant boiling in the core, it is impossible to introduce noticeable amounts of salt reagents to the coolant. Therefore, regulation of the reactor water quality is achieved by maximum decrease of impurities content in feed water

4. CORROSION PRODUCTS

4.1. Formation

4.1.1. Light water reactor processes

Primary circuit materials undergo general corrosion in high temperature, deoxygenated, neutral or mildly alkaline solutions to form thin oxide films. Corrosion products are formed by the release of metal-oxide ions, colloids and particles, they are typically comprised of iron and nickel oxides with small amounts of manganese, chromium, and traces of cobalt.

Steel corrosion usually results in formation of a two-layer oxide film. Some outer layer dissolves and is carried over to the coolant. At the same time, the dissolved components of the outer layer precipitate on the oxide film surface. In case of corrosion resistant steels, the inner layer is an iron-chromium-nickel spinel (iron chromite) enriched in chromium and depleted in iron and nickel compared to the chemical composition of the main metal. The outer oxide layer is an inverted iron-and-nickel spinel (partly substituted magnetite) with an insignificant quantity of chromium and traces of other transition metals. Chromium remains in the inner oxide layer, since it has low solubility in the coolant in reductive conditions.

The formation of an adherent oxide layer and the dissolution of some part of the metal into the circulating coolant (corrosion release) are caused by corrosion. Corrosion release follows similar time dependence to corrosion itself. Inner chromium-rich oxide layer has low cation diffusion coefficients and thus control iron and nickel transport from the metal surface to the outer layer and their dissolution into the coolant. Diffusion and corrosion release rates reduce also as the inner layer thickness increases with time.

The corrosion process in stainless steels is non-uniform. A significant impact on the rate and mechanism of oxidation is exerted by the chemical composition of the environment and availability of oxidizing components. The kinetics of corrosion behaviour of sample weight gain is also significantly impacted by the initial treatment of the sample surfaces. Upon exposure of more than several thousand hours, the corrosion rate is 0.001–0.005 mg/(dm^{2}h). Ukrainian research demonstrates that corrosion processes on stainless steels are usually coincident with weight losses. This indicator, however, has irregularities, i.e. after specimen weight loss, the weight can increase and then decrease again. A typical function of stainless steel weight change versus time during their testing in autoclaves in the environment simulating the composition and parameters of the WWER-1000 coolant is provided Fig. 4.1. The results of laboratory autoclave research demonstrate that the corrosion rate of stainless steel 08Ch18N10T is about 0.001 mg/(dm^{2}h).

Corrosion processes on reactor steels lead both to formation of an adhesive (tightly adherent to the surface) oxide layer and to dissolution of some oxide layer in the circulating coolant flow. The process of corrosion products carryover to the coolant is characterized by the same time dependence as the general corrosion process. It is caused by low cation diffusion factors for the chromium-enriched inner oxide layer which controls iron and nickel mass transport processes from metal to the outer oxide layer, as well as their dissolution in the coolant. As the inner layer becomes thicker with time, the diffusion rate and the carry-over rate of the corrosion products decreases. According to experimental research, less than half of the maximum possible total thickness of oxides tends to transfer from surfaces to the corrosion environment. The least soluble products remain in the inner oxide layer.

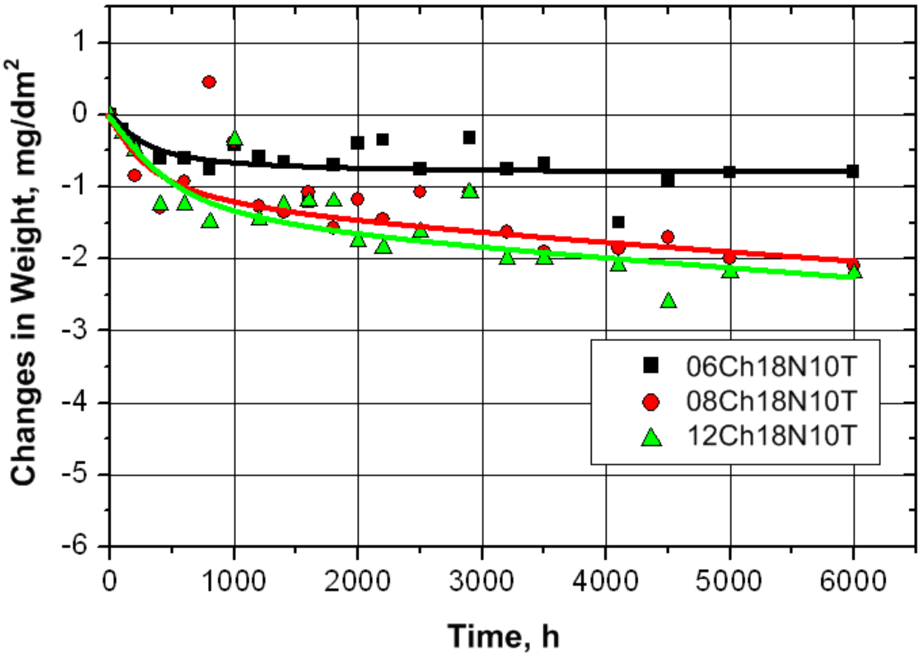


FIG. 4.1. The function of weight changes in stainless steel specimens versus time during their testing in water simulating WWER-1000 coolant composition at a temperature of 350°C and a pressure of 16.5 MPa [15][16].

Thus, the rate of corrosion products carryover to the coolant is related to the general corrosion rate, which explains the similar nature of their kinetic dependencies. For the corrosion resistant steel 08Ch18N10T this value is 30–60% of the corrosion rate. During laboratory tests this value was about 30% of the corrosion rate for the experimental steel types. Although the corrosion rate in most processes of corrosion products transfer reduces with time relative to the initial level, there always is a tendency towards a constant oxide layer formation rate. Ultimately, the equilibrium rate of corrosion products transfer to water becomes equal to their removal by the coolant cleanup system and deposition on the fuel.

The rate of corrosion processes in corrosion resistant steels is a function of temperature, oxidation-reduction conditions, and pH$_t$. Fig. 4.2 shows the function of changes in iron concentration versus temperature in the reactor's primary coolant after high-temperature titanium and ion-exchange filters (during reactor cooldown).

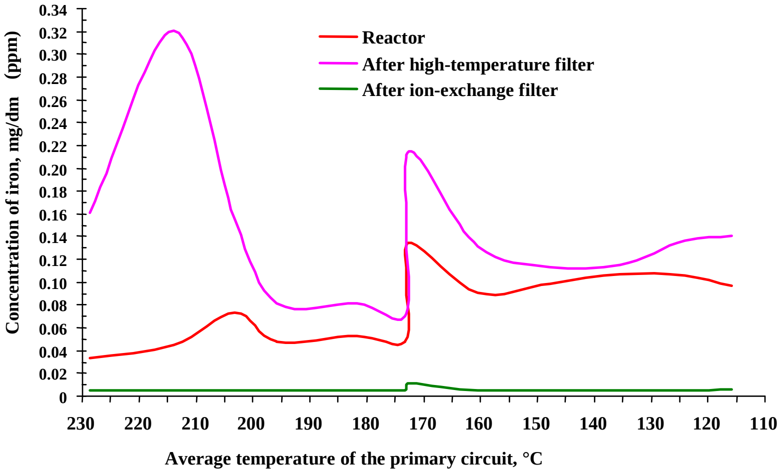


FIG. 4.2. The function of iron concentration in the primary coolant (in the reactor and after high-temperature titanium and ion-exchange filters) during reactor shutdown.

The corrosion rate of corrosion resistant steel depends on the final machining of surfaces which results in surface micro roughness and changes in the surface properties. Mechanical treatment or polishing increases the size of surface micro roughness and leads to sub-surface damages. This intensifies the rate of diffusion on the grain boundaries causing increased corrosion rate and oxide layer. A finer surface treatment, such as electrolytic polishing, does not produce sub-surface damages and ensures formation of a thin and uniform chromium-enriched layer. This causes low corrosion rate and formation of thin oxide films.

In-pile loop tests were carried out on the RVS-3 loop (PWR loop with 2 channels: active, inactive) at Řež to investigate the effect of the primary chemistry on the surface potential. ‘Standard Water Chemistry’ and ‘Hydrazine Water Chemistry’ primary chemistry conditions were studied via measuring of the redox potential both in-core and out-of-core at 290–300ºC and 230–268ºC, respectively. No change in redox potential was observed on changing from ‘Standard Water Chemistry’ to ‘Hydrazine Water Chemistry’ and, further, that the surface potentials were almost the same as was obtained with hydrogen gas additions.

These results suggest that the surface potential is always close to the hydrogen line and that hydrazine has no significant impact on the surface potential. Since the data from Paks show that hydrazine operation is accompanied by an increase in the steady-state ammonia and hydrogen concentrations, whilst at the same time there are only µg/kg concentrations of hydrazine present, the results suggest that factors other that the hydrazine concentration could be responsible for any improvement obtained with hydrazine dosing.

Corrosion rate examination was carried out during the same test program (‘Standard Water Chemistry’ v. ‘High pH Chemistry’ v. ‘Hydrazine Water Chemistry’) on the RVS-3 loop. Specimen corrosion rates were not much affected by the different chemistries, although those inferred from loop decontamination data suggested that the corrosion rate was lowest for the ‘Hydrazine Water Chemistry’ and highest for the ‘High pH’ chemistry. Similar results were found from direct corrosion tests of primary system reference samples at Kola, Zaporozhe and Novovoronezh, where the stainless steel corrosion rate was shown to be lower in case of ‘Hydrazine Water Chemistry’ than for the ‘Standard Water Chemistry’.

Another experimental programme carried out on RVS-4 loop at NRI Řež investigated corrosion behaviour under modified water chemistries: ‘Standard Water Chemistry’, ‘Hydrogen Water Chemistry’, ‘Elevated Ammonia Water Chemistry’ and ‘Standard Water Chemistry with Zinc Dosing’. Water chemistry parameters, volume and surface activities and corrosion layers were monitored and examined. Global results from this experiment led to recommendations of ‘Hydrogen Water Chemistry’ as well as ‘Elevated Ammonia Water Chemistry’ for WWER units. Both regimes showed lower volume activities as well as lower corrosion layers. Experiment results favoured elevated hydrogen level, which was provided either by higher ammonia or direct hydrogen dosing. Elevated hydrogen inhibits corrosion products’ content and in consequences also mitigates crud layers and leads to lower dose rates. The lowest surface activities were measured for ‘Elevated Ammonia Water Chemistry’. On the other hand, zinc dosing had detectable positive impact on activities spikes during shut-downs.

Swedish studies showed that PWR operations, such as shutdown and H_2O_2 injection, may have some impact on the characteristics of corrosion products of stainless steels and nickel based alloys. During the shutdown operation, the changed redox potential of reactor water and temperature may change the stability of some corrosion products. The injection of hydrogen peroxide may also change the characteristics of corrosion products. Table 4.1 shows the composition of corrosion products during shutdown and H_2O_2 injection.

TABLE 4.1. THE PHASE COMPOSITION OF CORROSION PRODUCTS COLLECTED FROM PRIMARY WATER: (LEFT) THE PHASE COMPOSITION OF CORROSION PRODUCTS COLLECTED FROM PRIMARY WATER DURING SHUTDOWN PERIOD, (RIGHT) SHOWS THE PHASE COMPOSITION OF CORROSION PRODUCTS COLLECTED DURING H_2O_2 INJECTION PERIOD

Phase	Size (nm)	Abundance	Determined with	Phase	Size (nm)	Abundance	Determined with
Ni (metal)	Ø50	<5%	EDS	Ni (metal)	150	<5%	EDS
Fe_3O_4	Ø50	<10%	SAED + EDS	$NiFe_2O_4$	35	<5%	SAED + EDS
$NiFe_2O_4$	Ø200	<5%	EDS	Fe_2O_3	50-250	≈20%	SAED + EDS
$(Cr_xNi_yFe_z)_3O_4$ (x,y=0.1-0.3; z=0.5-0.8)	Ø20	≈80%	SAED + EDS	$(Cr_xNi_yFe_z)_2O_3$ (x,y=0.1-0.3; z=0.5-0.8)	50-150	≈80%	SAED + EDS
$Fe_{0.4}Ni_{0.1}Cr_{0.5})_2O_3$	Ø20	<5%	SAED + EDS				

Note*:* Selected Area Electron Diffraction (SAED), Energy Dispersive Spectrometry (EDS).

4.1.2. PHWR plant processes

The pH_a of the coolant controls the solubility of magnetite. Computation of solubility of magnetite at the temperature of operation of coolant system indicated that if the pH_a of the coolant is reduced by 0.2 pH units, the dissolved iron value decreases by a factor of two thereby correspondingly reducing the FAC rate. However, this has to be experimentally proved. Reducing the pH_a of the coolant increases the chances of crud deposition on fuel and pressure tube surfaces. Thus, the requirement of low pH and minimization of deposits on the fuel surfaces are mutually opposed to each other. Hence, a balance has to be achieved between these two opposing factors.

On carbon steel feeders and headers of the primary heavy water coolant systems of PHWRs and under the reducing condition, magnetite (Fe_3O_4) is the dominant corrosion product. Magnetite is observed not only over the carbon steel, it is observed over the steam generator tube surfaces and over core Zircaloy surfaces including fuel surfaces. Presence of other elements especially nickel modifies the composition of deposits present in the steam generator surfaces to Nickel ferrite ($Ni_xFe_{(3-x)}O_4$) which can also get transported to core Zircaloy surfaces to a smaller extent in PHWRs. Antimony also has been observed to get transported and deposited in core Zircaloy surfaces causing radiation field problem during shut down. However, its chemical concentration is expected to be very small.

In the recent past it has been observed that the outlet carbon steel feeders are undergoing wall thinning due to enhanced flow in comparison to the corrosion rate observed in headers and other low flow areas. The wear rate is further enhanced in some specific location like the first bend in the feeder, near places where localized weld burs etc exist. In these places excessive local turbulence occurs and enhances the wear rate considerably due to FAC. This wall thinning is a cause of concern as the rate of corrosion is more than the corrosion allowance assumed during design.

Typical wear rates encountered in the actual plants have been measured between 49 μm/year and 156 μm/year. It should be noted that these are best estimates and not necessarily the actual values because the initial wall thickness data was not available at the time of computation.

Hence, frequent wall thinning measurements of the feeder elbows are being carried out to predict residual life of the feeder for regulatory purpose. Thus, there is an interest to relook at the chemistry specifications of the heavy water primary coolant and also to investigate the feasibility of adding a passivating metal ion to control both the radiation field build-up and flow accelerated corrosion. The changes in the chemistry condition of the coolant might alter the deposition behaviour of crud on the fuel.

Since it is relatively difficult to obtain field data on wear rates as a function of position in the pipe in order to predict the residual life of a pipe, it is necessary to estimate the life by computation and modelling. It calls for validation of the measured wear rate data under simulated condition with the model. An attempt was made to measure the wear rate in ring specimens under simulated conditions. A typical result from such an experiment is given below (Fig. 4.3–4.4)

The experiments were carried out under simulated conditions with ring specimens made of carbon steel. The wear rates are measured by gravimetric estimation of the ring and hence represent the average across the ring.

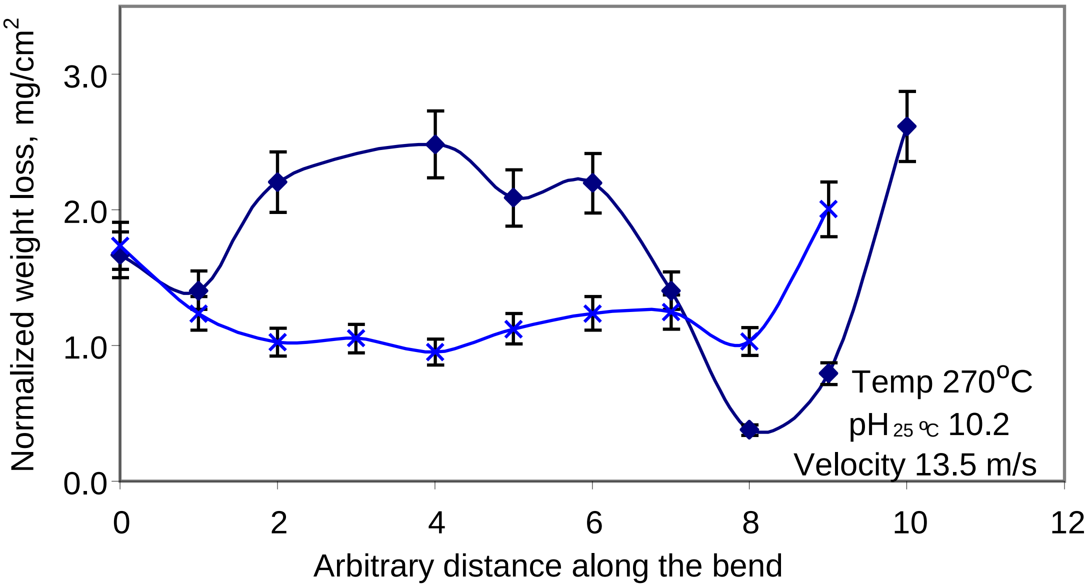
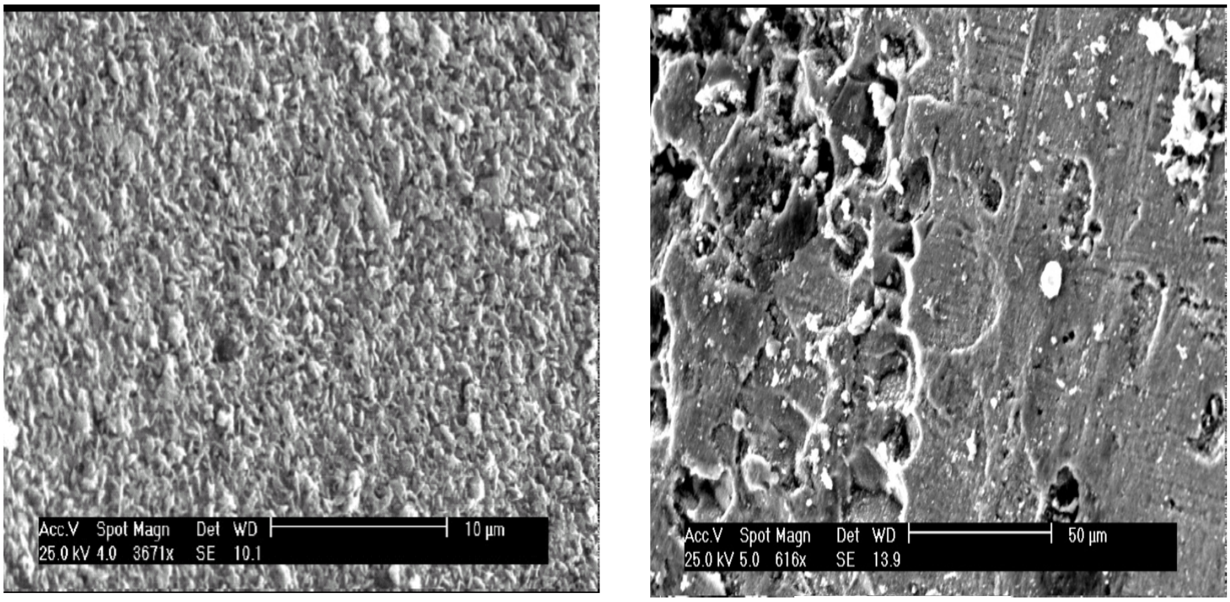


FIG. 4.3. Normalized weight loss on carbon steel specimens.



Straight ***Bend Section***

FIG. 4.4. Photo-micrographs indicating the presence of typical scallops characteristic of FAC. Magnesium was present in the coolant to the extent of 20–50 ppb and its incorporation in the deposited oxide film could be clearly seen. The additional benefit given by the incorporation of Mg for the reduction in FAC wear rate, if any, is being evaluated.

4.2. Steam generator tubing

The source of Ni in PWR primary circuits is mainly the Ni-based alloy steam generator tubing, which generally represents about 75% of wetted surface area (at WWER steam generator tubing material is stainless steel as are the other reactor construction materials – piping, vessel). Corrosion of steam generator tubing, as the main area contributor, therefore, determines the corrosion deposits and its consequences (e.g. CIPS, filter activity).

There are three main Ni-based alloys used in PWR as steam generator tubing: Alloy 600, Alloy 690 and Alloy 800. These alloys supplied by different manufacturers may have been processed with different heat treatments and therefore, exhibit different microstructures, which might alter the characteristics of any oxide film formed under high-temperature environments.

The Canadians investigated samples of various steam generators tubing from three manufacturers for their metallurgical properties, namely Vickers hardness and grain size analysis. It was found that cold-drawn (CD) samples are the hardest, whereas mill annealed (MA) and thermally-treated (TT) samples have similar hardnesses. Alloy 600 exhibits the smallest grain size of about 10 µm while the grain sizes of Alloy 690 and Alloy 800 are between 15 µm and 35 µm. It is evident that compared with MA and CD samples, grain boundaries of etched TT samples are sharp and clear, indicating a more complete elemental precipitation in the alloy. The relationship between grain size and heat treatment of alloys cannot be clearly seen. The ultimate goal of the analyses was to correlate the metallurgical properties with the characteristics of the oxide formed under simulated PWR primary coolant conditions in the laboratory. The loop tests carried out by the Canadian team did not show any relation between the steam generator tubes heat treatment and the grain size, but the steam generator material gave different results with smaller (10 µm) and harder grain sizes for Alloy 600 (high Ni content) compared with Alloy 690 or 800 (15–35 µm). The corrosion product transport has been evaluated in the loop and will continue with longer duration to get more representative results.

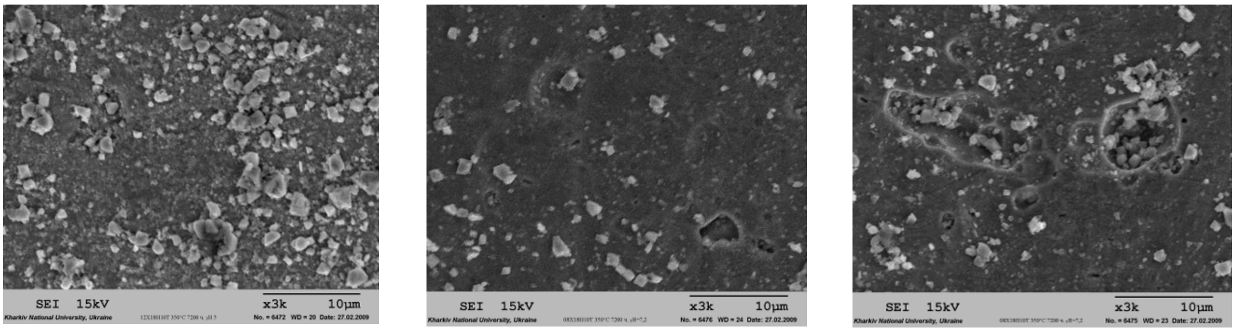
In general, it is significant that the characterization of the steam generator materials reveals no obvious differences attributable to the three manufacturers that would lead to different behaviour on exposure; however, different heat treatments by a manufacturer may or may not produce different grain sizes and only CD material exhibits a different, higher, hardness. More experimental runs in simulated PWR coolant are needed to obtain definitive correlations between oxide characteristics and alloy microstructure.

Ukrainian laboratory studies of steel demonstrate the same situation as in the reactor: formation of an outer oxide layer occurs with precipitation of corrosion products onto the oxide film surface from the corrosion environment into which they were previously transferred. The surfaces of the 08Ch18N10T and 12Ch18N10T steel specimens oxidized at 350°C and 16.5 MPa in the environments provided in Table 4.2 are shown in Fig. 4.5 [15].

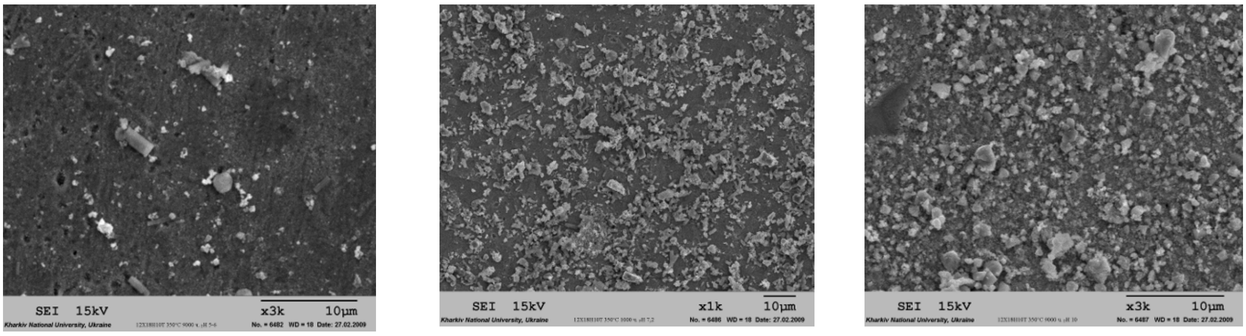
TABLE 4.2. COMPOSITION AND PH VALUE OF THE WATER ENVIRONMENT FOR AUTOCLAVE TESTS

Additives	Environment No. (Chemical composition)		
	1	2	3
pH*	6.0	7.2	10.0
H_3BO_3 g/dm^3	5.0	3.11	1.2
KOH g/dm^3	0	0.025	1.2
NH_4OH mg/dm^3	1.4	5.6	14.0

** pH measurements were done at room temperature.*



a) (pH=6), 08Ch18N10T b) (pH=7.2), 08Ch18N10T c) (pH=10), 08Ch18N10T

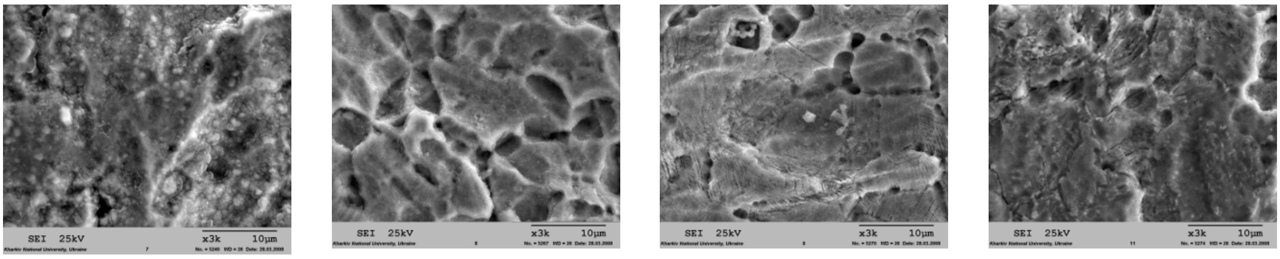


d) (pH=6), 12Ch18N10T e) (pH=7.2), 12Ch18N10T f) (pH=10), 12Ch18N10T

FIG. 4.5. Surface of oxidized 08Ch18N10T and 12Ch18N10T steel samples after oxidation in composition environments (pH = 6.0; 7.2; 10.0) at 350°C and 16.5 MPa for 7200 hours.

The research into effects of surface treatment on corrosion kinetics showed that for the investigated steel types in conditions simulating WWER-1000 coolant environment and parameters, the lowest corrosion rate was observed on the samples subjected to electrochemical surface polishing. A higher corrosion rate is typical for etched surfaces and the highest for those mechanically treated. These studies are of interest, as surface treatment can be the reason for a relatively thicker oxide layer on the crudely treated surfaces of the primary circuit steel compared to a very thin inner oxide layer on the smooth surface.

An interesting result was obtained during investigation into corrosion resistance of stainless steels preliminarily oxidized for 3500 hours with subsequent removal of oxide films [15] using a variant of chemical deactivation technology of primary circuit equipment [17]. The appearance of samples at each stage of oxide film removal is provided in Fig. 4.6.



a *b* *c* *d*

FIG. 4.6. Surface of 08Ch18N10T stainless steel samples preliminarily oxidized for 3,500 hours in the environment simulating WWER coolant at a temperature of 350°C and a pressure of 16.5 MPa after various stages of oxide film removal: a) Oxidation in the water solution of KMnO4;b) Etching for 4 hours (4±1 g/kg EDTA, 1± 0,2 g/kg H3Cit); c) Etching for 4 hours (6±1 g/kg EDTA, 1,6± 0,4 g/kg H3Cit); d) Passivation for 10–12 hours (0,25…0,35 g/kg N2H2, 0,15…0,25 g/kg NH3).

Plots of stainless steel sample weight changes after chemical treatment of the sample surfaces (using a variant decontamination technology) versus time after their oxidation at a temperature of 350°C and pressure of 16.5 MPa in the water environment of composition 2 (with pH=7.2) [15] are presented in (Fig. 4.7). The corrosion kinetics of samples treated according to the above mentioned technology of chemical decontamination (based on sample weighing) shows a positive weight gain.

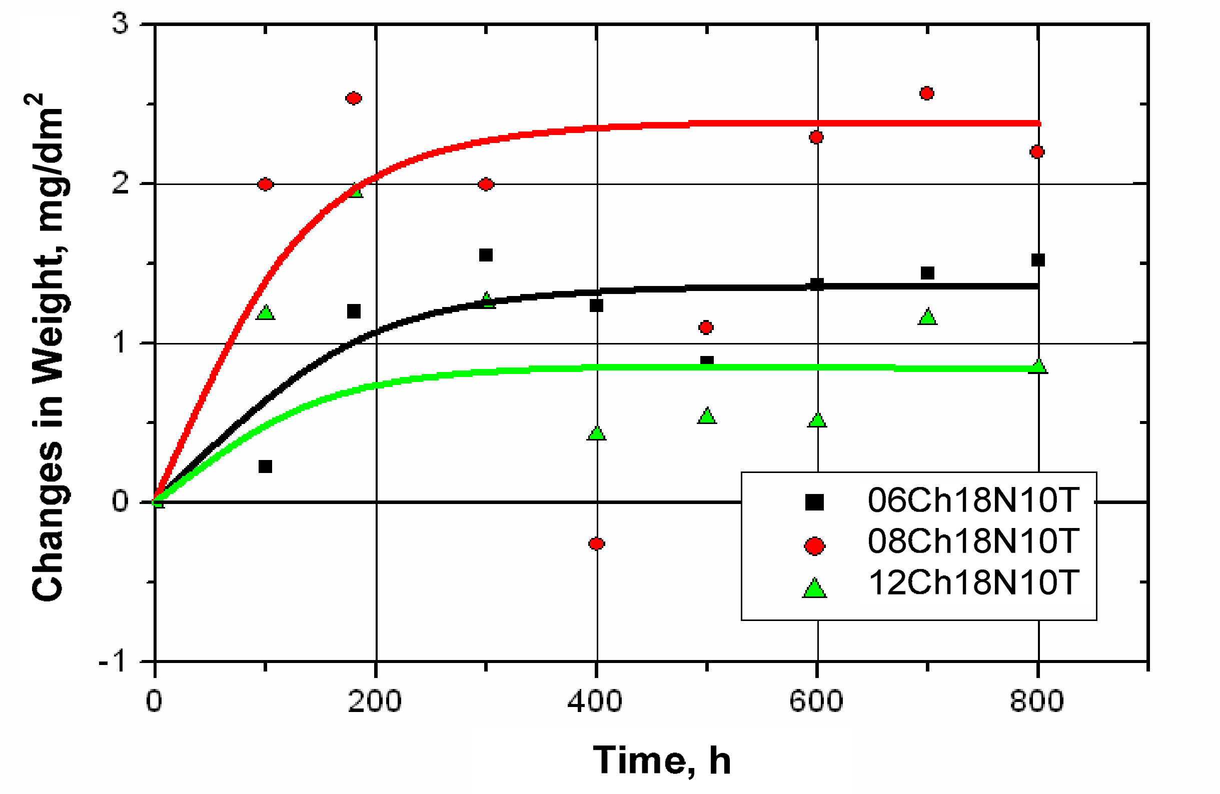


FIG. 4.7. The functions of stainless steel samples' weight changes after chemical treatment of the sample surfaces (using the deactivation technology) versus time after their oxidation at a temperature of 350°C and environment pressure of 16.5 MPa in the water environment of Composition 2 (with pH=7.2) [15].

In-pile loop tests at the Nuclear Research Institute Řež in the Czech Republic have also been carried out to examine the effect of CC on the corrosion rate of steam generator tubes SS material. These showed that specimen corrosion rates were largely unaffected by the different chemistries. However, the corrosion rate for steam generator tube samples was affected by the surface finish and was the lowest for electropolished surfaces and the highest for grit-blasted surfaces.

4.3. Dose rate concern

Non-radioactive corrosion products form as a result of oxidation of primary circuit construction materials. Some of these corrosion products are released and are transported by the coolant and redeposit throughout the primary system. These metallic non-radioactive corrosion products become radioactive by absorbing fast or thermal neutrons in the reactor core. Activated corrosion products move throughout the primary circuit and redeposit on ex-core components’ surfaces, resulting in increased radiation fields and personnel exposure.

In operation mode the main effect is caused by γ-irradiation, its contribution usually amounts to 90% of the external dose. Analysis of the radioactive sources at Russian plants indentify the main contribution to the personnel exposure during repair works as ^{60}Co, ^{51}Cr, ^{59}Fe and ^{58}Co. Iron is the main component of corrosion products coming into the reactor core with feed water. It plays an important part in the transfer, sedimentation and activation of Co that makes the greatest contribution to the radiation dose from the pipelines.

Table 4.3 shows the correlation between the dose rate and group dose at NPPs for a BWR reactor of 1100 MWe.

TABLE 4.3. CORRELATION BETWEEN THE DOSE RATE AND COLLECTIVE EXPOSURE (MEAN VALUES)

Dose rate, mSv/h	Collective exposure, pers.- Sv/year
0.20	0.6
0.30	1.6
0.50	2.6
0.55	4.0
1.00	5.1
1.25	6.2

Taking into account the personnel coefficient (1 person/MW) and doses allowed by the sanitary standards, the collective dose at NPPs with RBMK is ten times higher.

Fig. 4.8 illustrates the correlation between annual amount of iron introduced with the feed water to the multiple forced circulation circuit and the collective dose at an RBMK-1000 power unit.

FIG. 4.8. *Collective dose (man-rem per GW×hour, 1 rem = 0.01 Sv) at the power unit with RBMK-1000 versus annual amount of iron (kg/year) brought with the feed water to the multiple forced circulation circuit. The white dots represent 'major repair' and the black dots 'normal operation'.*

Material selection, the importance of nickel and its release and activation into ^{58}Co, the presence of cobalt and its activation into ^{60}Co, the presence of antimony in pump sealing and of silver in various components were not covered by the Russian report.

4.3.1. Zinc and noble metal addition

Many PWRs add or are considering the addition of zinc for dose rate mitigation. There has been a clear demonstration of the benefit in many cases of zinc addition which has been evaluated within the framework of the FUWAC project for PWRs. Such an addition has not yet been applied to WWERs but it is a potential improvement.

Similarly, noble metal addition has been studied for BWR and zinc injection is being evaluated for CANDU.

WWER

Ukraine is considering zinc injection in its WWER plants. Zinc injection significantly reduces the rate of corrosion processes in the primary circuit. Zinc, having a lower cohesive energy in spinels than cobalt, preferentially embeds into oxide films, preventing radioactive cobalt from participation in the processes. This leads to a considerable reduction in activity from the PWR primary circuit equipment, since up to 90% of the total activity arises from the activity of cobalt isotopes. In WWERs, cobalt activity accounts for less than 50% of the total activity, therefore zinc injection does not produce an equally visible and quick effect compared to PWRs. However, the average dose rate from primary-circuit equipment increases with time, leading to a requirement for measures to reduce the average dose rates or at least to stabilize them.

The use of zinc injection at the Biblis NPP allowed an annual 10% reduction in the dose rates from the equipment. Considering that the composition of structural materials at the Biblis NPP and the Zaporozhe NPP differs in concentration of nickel and cobalt, this technology is expected to be less efficient for reduction of dose rates at WWER NPPs. On the other hand, if this optimization results in stabilization of dose rates, the benefits of its use will increase significantly.

There is an unresolved issue related to the effects of zinc on the operation of high-temperature titanium filters in WWER which are not used in the coolant cleanup system in PWRs.

BWR

In BWRs, the use of higher feedwater hydrogen concentrations (1.6–2 ppm) called moderate hydrogen water chemistry (MHWC) results in two undesirable side effects:

a) increase in radiation levels in the main steam lines due to the conversion of ionic forms of N-16 to more volatile chemical species under reducing conditions, and
b) increase in drywell dose rates due to the mobilization of Co-60 from fuel crud that subsequently deposits on out of core piping surfaces.

Despite these deficiencies, eight US BWRs are still operating with MHWC. These plants have employed shielding to minimize MSLR fields and adopted the addition of DZO into the feedwater as a counter measure against drywell dose rate increases. Three of these 8 BWRs will be applying On-Line NobleChem^{TM} in the near future.

Feedwater hydrogen addition raises the concentration of ^{60}Co in the reactor water by a factor of up to 2 or higher. Under the reducing conditions of HWC, the stable form of the outer oxides on stainless steel and fuel deposit surfaces change from the hematite form (Fe_2O_3) to the magnetite form (Fe_3O_4). It is believed that this restructuring results in the release of ^{60}Co and other activated corrosion products and also an elevated incorporation rate of activated corrosion products into the restructured oxide. By maintaining a reactor water zinc concentration of 5–10 ppb, the reactor water ^{60}Co level can be reduced by a factor of 2–5. Zinc in the reactor water promotes the formation/conversion of Fe_2O_3 oxide to a zinc containing spinel of the form $ZnFe_2O_4$. The zinc also occupies sites in the spinel lattice favoured by cobalt. Thus, the actual concentration of Co (and ^{60}Co) in new corrosion films is reduced. This behaviour occurs in both non-hydrogen addition plants and HWC plants.

Although zinc addition lowers the ^{60}Co concentration, the ^{64}Zn content of natural elemental zinc (about 48%) can activate to ^{65}Zn, an isotope almost as energetic as ^{60}Co. To mitigate this effect, zinc isotopically depleted in ^{64}Zn is utilized for feedwater zinc injection. The zinc is added to the feedwater in the form of ZnO and if the ZnO is isotopically depleted it is called DZO.

PWR

Zinc injection in PWR is generally in the form of $C_4H_6O_4Zn_2H_2O$, called depleted zinc acetate (DZA). EDF began zinc injection in 2004 at Bugey 2 and in 2006 at Bugey 4.

The evolution of dose rates are illustrated in Figs 4.9–4.11 [18]. It is noted that after the first cycles, there is not a clear effect of zinc but after the third cycle of injection a reduction is observed (of about 15% depending on circuits). In addition, the Bugey demonstration has shown the benign effect of zinc on components, materials, effluents, wastes and fuel.

Based on the Bugey results and on the international feedback, EDF decided in 2008 to implement zinc addition on additional units, not only to control contamination and dose rates but also to manage a potential AOA risk on future core designs and to mitigate PWSCC.

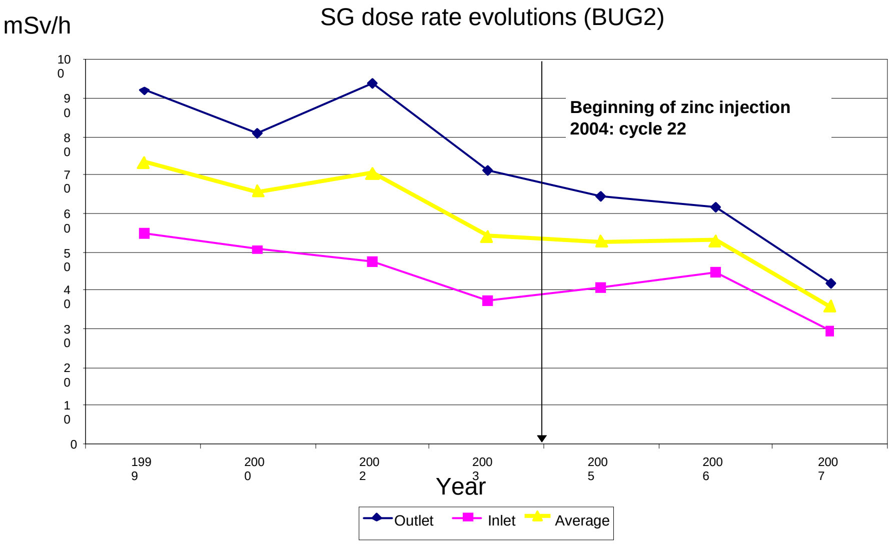


FIG. 4.9. *Steam generator dose rate evolutions at Bugey 2.*

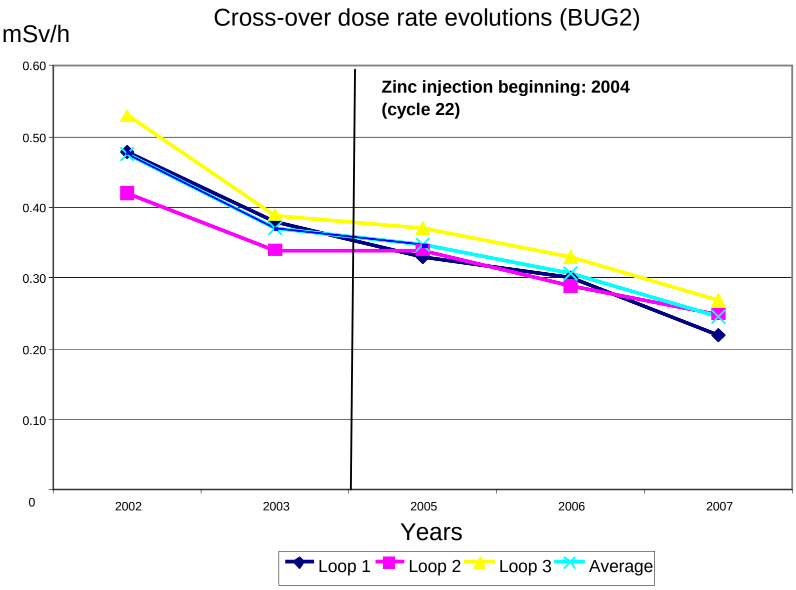


FIG. 4.10. *Dose rate at the crossover legs at Bugey 2.*

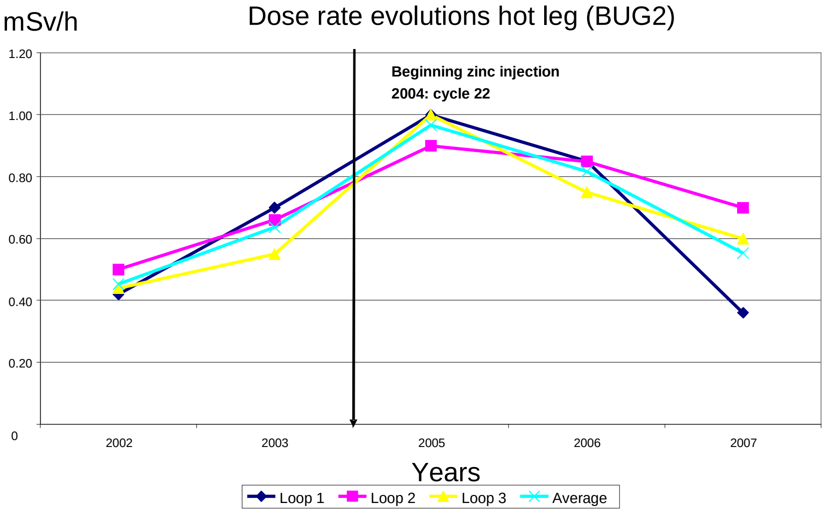


FIG. 4.11. Dose rate at the hot legs at Bugey.

During the first cycles of zinc injection, the potential increase of corrosion products and transition metals in primary coolant (due to the cobalt replacement by zinc) may increase the crud deposition and the risk of CIPS for a high duty plant. However, international feedback and French experience show that activity increase in the primary coolant is not observed in all the plants and even if an increase occurs, the correct monitoring and operation within specifications assure the absence of any negative impact on fuel [10].

The fuel examinations conducted at Bugey confirm the international results:

- flux maps do not show any indication of AOA;
- oxide measurements carried out on Zircaloy-4 alloy are similar to those from other cycles without zinc;
- visual examinations do not show any particularity;
- no fuel failures associated with crud corrosion have been detected during cycles with zinc.

EDF is working on the elaboration of guidelines for units with zinc injection, taking into account the particular operation with load following, the chemistry and radiochemistry conditions of the units and the fuel risk. Information about these guidelines is to be provided in reference [10]. The parameters to monitor are Zn, Ni and Si with a frequency adapted to the period of injection and the risk of CIPS. EDF is carrying out an exhaustive study of parameters to determine the main factors to evaluate the actual risk of CIPS in a plant with zinc injection:

- CIPS history of the unit;
- corrosion product inventory;
- fuel management: length of cycles, power of assemblies, boron concentration;
- operational conditions in previous cycles: stretch out.

Since 1994, international PWR feedback shows the absence of any negative impact of zinc addition on fuel. The initial hypothetical risks have not been observed. On the contrary, if zinc injection is carried out according to the specifications, zinc addition is considered as a possible action to mitigate the CIPS risk.

- Zinc injection contributes to reduce the source term due to a general reduction of corrosion of reactor materials and consequently any crud should be reduced after some cycles of injection.
- Visual inspections show that, in the presence of zinc, the crud is relatively uniform from top to bottom of the rods. Without zinc, the crud deposition is higher at the top of rods where the power is more significant and sub-nucleate boiling may occur.

4.4. NPP feedback

4.4.1. NPP in Hungary

The behaviour and residence time of corrosion particles in reactor core was evaluated and determined using appropriate analytical and radioanalytical methods. The increased corrosion product transport after extensive steam generator decontamination was followed and it was recognised that this process stabilised and returned back to its original low level.

Based on residence time determinations, it was also concluded that the direction of transport is to the core and deposition on steam generators and other surfaces is limited. These conditions have to be maintained by the appropriate operation practice and water chemistry regime.

There are two points that require further effort to clarify and understand:

a) An appropriate decontamination or oxide removal process is necessary that will not adversely affect the oxide layer structure on primary surfaces, mainly on steam generator heat transfer tubes.
b) In order to determine basic causes of AOA a wider scope should be considered other than pure chemical reasons (e.g. hydraulic, material concepts, reactor physics and construction).

The forms, characterisation and sorption of transuranic (TRU) particles were also investigated and determined.

It was revealed that 50–80% of these particles are bonded on SS surfaces within 30 hours by surface complexation processes. It was also found that corroded surfaces bound TRU radionuclides better than non corroded ones. These results were effectively used in re-starting our Unit 2 following the severe incident in 2003. Results may also be used during normal operation – even with failed fuels – to take into consideration and elucidate/investigate the effect of surface contamination of TRU particles.

4.4.2. NPP in the Ukraine

The WWER plants in the Ukraine maintain stable primary CC conditions which enables the fulfilment of its functions to suppress the formation of radiolysis oxidation products and to ensure the design corrosion resistance of structural materials of fuel rods and fuel assemblies

The main disadvantage of the WWER primary CC is high consumption of chemical agents and, consequently, production of large quantities of radioactive waste. The bulk of this waste is boric acid and alkaline metals which are used for coolant adjustment, as well as regeneration solutions.

Technical factors allow a conclusion that at the first stage of CC-1 optimization, replacement of ammonia injection with injection into the coolant of pure gaseous hydrogen is the most promising line of development for Ukraine's NPPs. A tangible effect is also expected after successive implementation of a set of measures to optimize CC-1 aimed at mitigating the main shortcomings of the WWER CC-1 technology. A comprehensive CC-1 optimization will allow using standard FA structural materials during transition to longer fuel cycles and higher fuel burnups.

Another problem in WWER is the increased dose rates from primary-circuit equipment due to long-term operation of the ageing NPPs. For example, the average dose level of the primary-circuit equipment in the steam generator hot headers for Zaporozhie-5 increased 3.4 times (from 4.5–15.4 mSv/hour) from 2001–2006 (Fig. 4.12). It causes a need to take measures aimed at reducing or at least stabilizing the dose rates from the primary-circuit equipment.

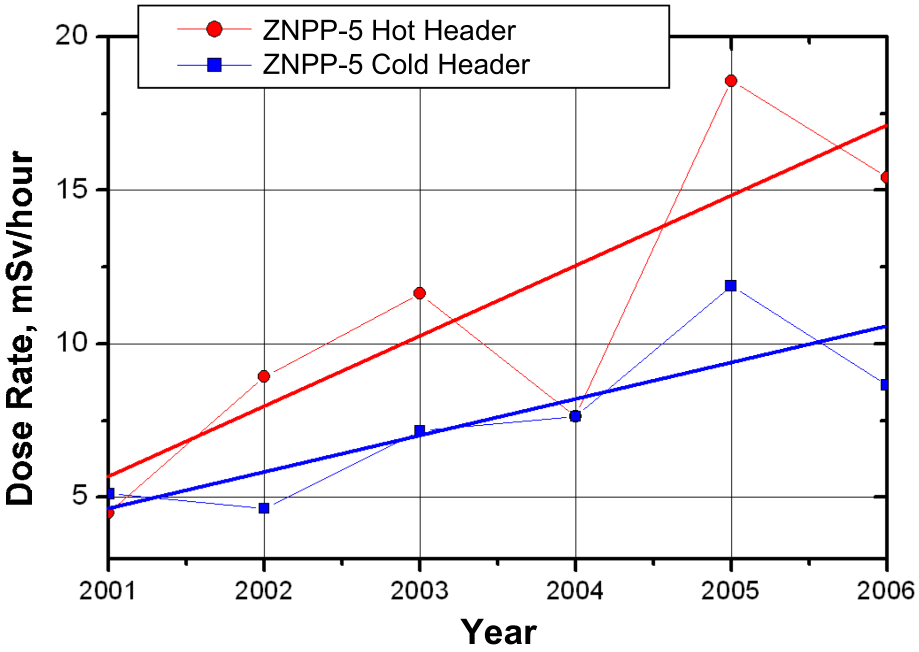


FIG. 4.12. Dose rates from the hot and cold Zaporozhe 5 headers of the YB10-40W01 steam generator.

4.4.3. NPP in the Czech Republic

Proper operational practise, efficient primary water chemistry etc., result in lower dose rates and other operational benefits. A comparison with world occupational exposure (collected in The Information System on Occupational Exposure (ISOE) information sheets) shows the long term quality of Czech operational practise. European dosimetric results for the year 2006 compared long term results from European WWER countries (Czech Republic, Slovakia, Hungary and Finland). A 3-year rolling average is instead of an annual average for better representation of the general trend in dose. The Czech Republic showed the lowest 3-year rolling average annual collective dose per reactor in 2004–2006 (and also in the total scope) with 0.17 man-Sv, followed by the Slovak Republic (0.32 man-Sv), Hungary (0.40 man-Sv) and Finland (0.82 man-Sv). Very low values of outages and total effective doses represent the outcome of good primary chemistry water regimes, well organised radiation protection structures and strict implementation of as low as reasonable achievable (ALARA) principles during working activities where there is high radiation risk. As well as the occupational exposures described, Czech NPPs report very low corrosion product levels in the primary water and on primary surfaces. Low corrosion product release and subsequently low corrosion product activities can be induced by many factors, e.g. the passivation of primary circuit during the hot tests, the usage of high temperature filtration or simply good primary chemistry control practise.

NPP Temelín was built during the years 1987–1999. During the years 2000–2002 hot tests and power activation took place in the first unit. In the middle of 2002 the first ETE-1 cycle was launched. ETE-2 unit was activated a year later. The installed output of NPP Temelín is 2×1000 MW; both units are of type WWER 1000-V320. Four units of WWER-440 of B-213 design are in operation at Dukovany NPP. Radiation fields at Dukovany NPP are amongst the lowest for WWERs (Fig. 4.13).

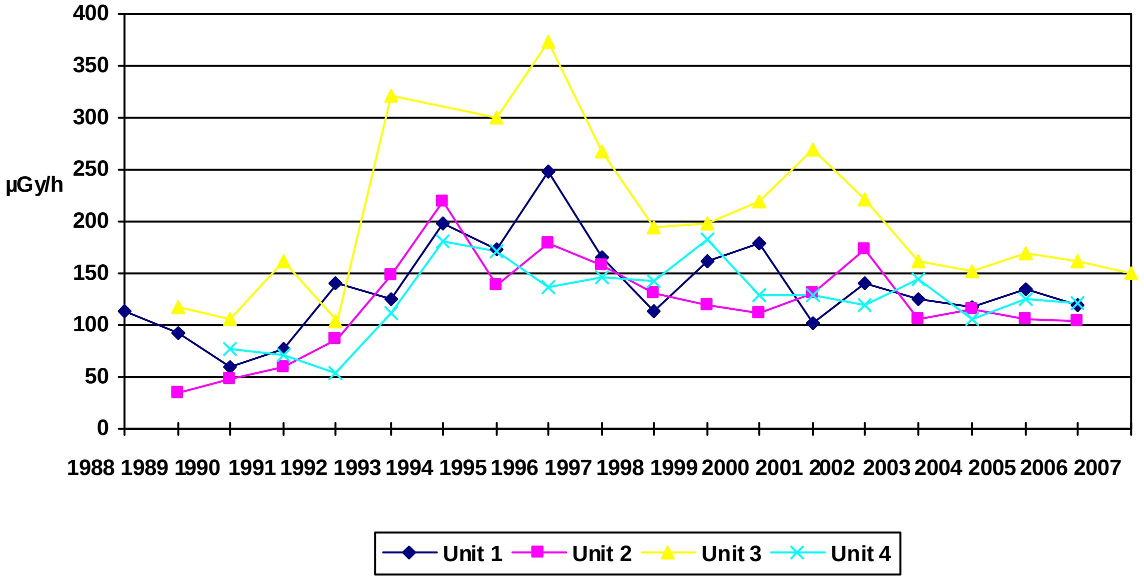


FIG. 4.13. Dukovany: average dose rates of main loops after shut-down.

Despite of the similar operation of each Dukovany unit (with the same operation team and chemistry), each unit has its own specific behaviour. Each Dukovany unit's specification properties are as follows:

- Unit 1 - the highest concentration of isotope ^{51}Cr on the surface of main loops,
- Unit 2 - the lowest concentration corrosion products in reactor cooling water and on the surface of the main loops,
- Unit 3 - the highest total concentration of corrosion products on the surface of main loops,
- Unit 4 - the highest concentration of activated corrosion products in reactor cooling water.

4.4.4. NPP in Bulgaria

In the primary coolant of the WWER-1000 reactors at NPP Kozloduy, the antimony isotopes ^{122}Sb and ^{124}Sb are observed. The plant coolant activity data for cycle 14 and 15 of unit 5 (Fig. 4.14) shows that the activities of antimony isotopes ^{122}Sb and ^{124}Sb are always higher than the activities of isotopes ^{58}Co, ^{60}Co, ^{51}Cr, ^{54}Mn and ^{59}Fe.

These data show that activated antimony ^{122}Sb and ^{124}Sb isotopes are continuously observed in the coolant. The ^{122}Sb activity during the operational period remains practically unchanged and is generally the highest in the coolant. The relatively short half-life period (2.7 days) for ^{122}Sb is the reason to believe that this isotope is continually added to the coolant and that the origin of this phenomenon is not connected with power change or with the corresponding changes of coolant chemical-physical characteristics. This ingress of ^{122}Sb in RCS is believed to be connected with a process of continuous generation of ^{122}Sb and its dissolution into the reactor coolant.

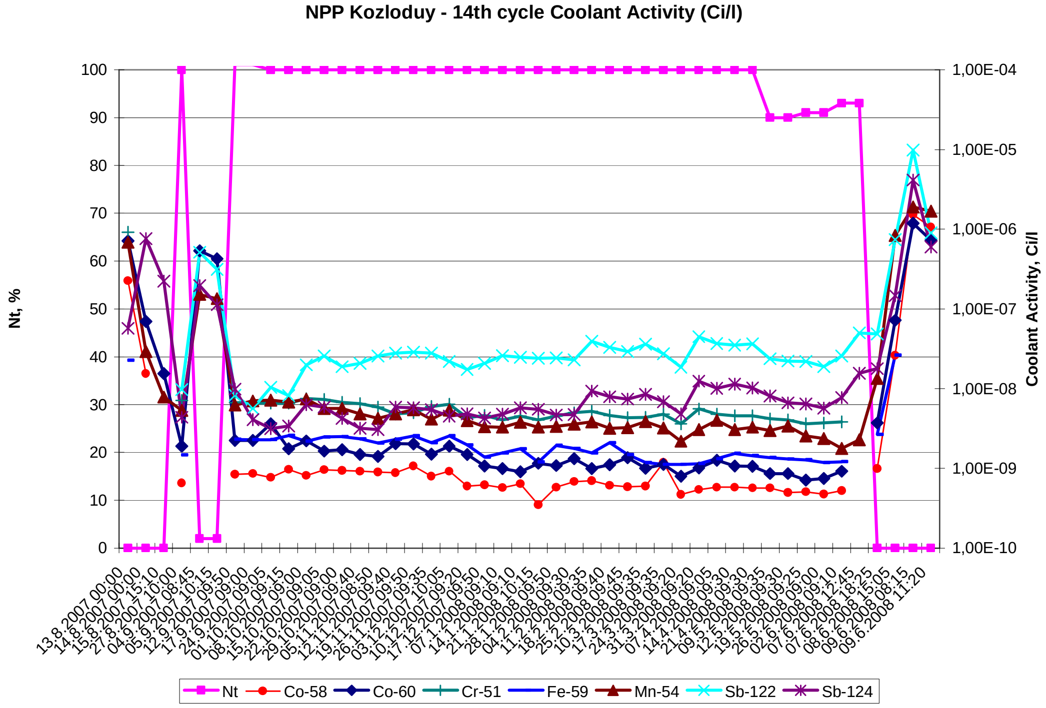


FIG. 4.14. Coolant activated corrosion products (cycle 14, unit 5) including shutdown period [11].

4.4.5. NPP in India

PHWR is a tube type reactor having 306 Zircaloy-2/Zr-Nb alloy pressure tubes. Each pressure tube is connected to the steam generator through the same number of carbon steel feeders on both sides of the horizontal core and headers. Thus, the carbon steel feeders constitute an important component of the primary coolant system in PHWRs. Subsequent to the observation of excessive wall thinning in PHWRs elsewhere, extensive wall thickness measurements were made in Indian PHWRs, which indicated thinning of feeder elbows (in certain locations) at rates which are more than the rates normally expected for carbon steel under normal flow conditions. Under static conditions and under PHWR PHTS chemistry conditions the corrosion rate of carbon steel is less than 10 µm/year. The plant measurements are between 49–156 µm/year, and the latter value far exceeds the corrosion allowance of 75 µm/year assumed during design. Efforts made to understand the phenomenon indicated that the coolant, which is under-saturated with iron when it exits the core, dissolves the magnetite film present on the feeder surfaces. The rate of dissolution is governed by complex variables such as extent of under saturation of iron, pH_a, dissolved oxygen, temperature and the hydrodynamic conditions prevailing in that location. Thus, the chemistry of the heavy water coolant and the hydrodynamic conditions decide the extent of wall thinning of feeders.

5. FUEL CORROSION AND FUEL OXIDES

5.1. Cladding

The zirconium alloy fuel rod cladding provides a barrier against the release of the radioactive fission products formed during operation. Zirconium alloy corrosion is affected by the temperature, local boiling, CC and microstructure and composition of the cladding material. The zirconium alloy corrosion reaction forms zirconium dioxide (ZrO_2) on the oxidising surface. The formation of a ZrO_2 layer causes cladding thinning and the absorption of hydrogen by the zirconium alloy embrittles the cladding. To improve fuel cycle economy, fuel burn-up is being extended through longer cycle operation and higher heat ratings. The consequent increased duty on fuel cladding has led to improved cladding materials with higher corrosion resistance to assure fuel reliability and safety in PWR operation condition.

From the Bulgarian presentation, it can be seen that the advanced fuel assemblies, containing Gd_2O_3 as a solid neutron burnable absorber show good behaviour. The Russian advanced fuel element ‘TVSA’ with a fuel cladding containing 1% Nb did not show any problem in operation at Kozloduy NPP. The plant is operating with boron versus alkali (mainly potassium) curve corresponding to an optimum pH of 7.0–7.2.

The Finnish laboratory used the control distance electrochemistry (CDE) technique to compare fuel cladding oxide thickness in various chemical environments on the fuel cladding material, E110. For the experimental condition, a lithium increase from 2–10 mg/kg gave an oxide thickness increase from about 220–300 nm while for a secondary water treatment with potassium, and a corresponding lithium concentration of 10–56 mg/kg, the oxide thickness is slightly lower, ranging from 180–260 nm, showing that potassium is to be preferred to lithium for mitigating fuel cladding oxidation on the E110 material. Fluoride concentration showed a significant effect on oxide thickness, with a sharp increase as the fluoride concentration increases but then a small decrease as the concentration approached 1 mg/kg. The maximum oxide thickness was about 300 nm.

The Romanian Laboratory experimentally studied the influence of pH on Zr cladding oxidation and hydriding, with high burn up fuel. A porous oxide is observed after the tests on samples with initial oxide films up to 4 µm thick. The oxide layer is formed by corrosion in LiOH at high pH (pH =12.3, equivalent to 70 mg/kg Li) and is an accelerated and non uniform corrosion process. There is no acceleration of Zr-4 corrosion for pH < 11.8, corresponding to 3.5 mg/kg Li. As pH increases there is an initial oxidation process and then lithium concentrates in the pores of thicker oxides which induces further oxidation and hydriding with the development of micro cracks. The presence of boron with LiOH inhibits the oxidation acceleration by lowering the pH and preventing the formation of Zr-O-Li groups due to the interfering reaction between LiOH and anion vacancies. Boron substitutes for Lithium in the oxide lattice

The complex corrosion mechanism for Zr-Nb alloys has been studied by the Russians. The rate of Zr alloy corrosion under reactor irradiation depends on heat flux through fuel cladding, CC (in addition to H_2O_2, OH^-, O^{2-} concentrations one should account for the concentrations of hydrogen, ammonia, strong alkali–LiOH, KOH, pH, etc.) and some other parameters.

A correlation between E110 alloy corrosion and the ion hydratation energy (ΔHi) in solution at various water coolant chemistries has been observed in Russian experiments. Alloy E110 shows strong corrosion resistance.

The team from the Ukraine carried out analytical and experimental research on the effect of primary water chemistry on corrosion in WWER 1000 cores.

Improvements in Ukrainian NPP include (or are under consideration):

- upgrading automatic and laboratory chemical control systems;
- establishing expert diagnostic water chemistry systems;
- improvement of supplying water chemistry systems;
- modernization of chemical and volume control system;
- implementation of hydrogen water chemistry;
- zinc addition;
- implementation of enriched boric acid;
- morpholine water chemistry of secondary circuit.

Application of EBA in Ukrainian NPPs is being considered for new fuel loads (high burn up and MOX) but not with units operated with present fuel loads. For 99% EBA this will allow a decrease in the concentration of boric acid in the primary water by a factor of 5 and substantially reduce the amount of LRW and improve the corrosion behaviour in the RCS.

The Ukrainian study included the possibility of replacing ammonia by hydrogen to gain a substantial reduction of impurities in the primary water, which would also reduce their corrosive effects on the RCS materials. This is not being done to improve the ion exchange resin behaviour as frequently claimed.

Based on the operational data with the mixed core of Westinghouse fuel assemblies and Russian standard TVSM fuel loads at the South Ukraine NPP, no corrosion problems have been seen on the Westinghouse ZIRLO^{TM} or the Russian Alloy E110 fuel claddings. No crud was observed on the surface of any of the fuel rods throughout their life in the WWER-1000 core.

It has been shown that during a 7200 hour testing period, that alloy E110 exhibits similar kinetics in corrosion environments with pH_T between 5 and 7.2. At a pH_T of 10.0 the corrosion rate is higher.

5.2. Film morphology

5.2.1. Autoclave testing

China undertook autoclave testing to improve the understanding of zirconium alloy corrosion performance under high burn-up water chemistry conditions. The corrosion tests have been carried out at 300°C, 335°C and 350°C under water chemistry condition of 3.5 mg/l Li^+ and 650 mg/l B. Weight gain data from specimens manufactured from a new Chinese zirconium-based alloy and from optimized Zr-4 alloys has been obtained. Test durations were 50, 100, 150, 200, 250, 280, 331, 401 and 500 days. A loop test was operated with heat flux specimens of fuel cladding materials to simulate the operating water chemical conditions (3.5 mg/l Li^+ and 650 mg/l B) of PWR primary circuit for duration of 400 days. The micro-structure of specimens has been analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The experiment conclusions are as follows:

- Weight gains of both optimized Zr alloys and Zr-Nb based alloys increased with duration time for high temperature, water chemistry conditions of 3.5 mg/l Li, and 650 mg/l B up to a duration of 500 days.
- The weight gains of specimens of both materials cleaned by acid pickling were similar to those of specimens cleaned by acetone.
- The oxide film of specimens of both materials was adherent and protective and black.
- The test specimens, with a heat flux 100 K/cm^2 through the samples, have seen a duration of 400 days in the high temperature and pressure experimental circuit. The resulting oxide films have been analyzed by optical microscopy and by SEM (Fig. 5.1) and were found to be thinner and better adherent.

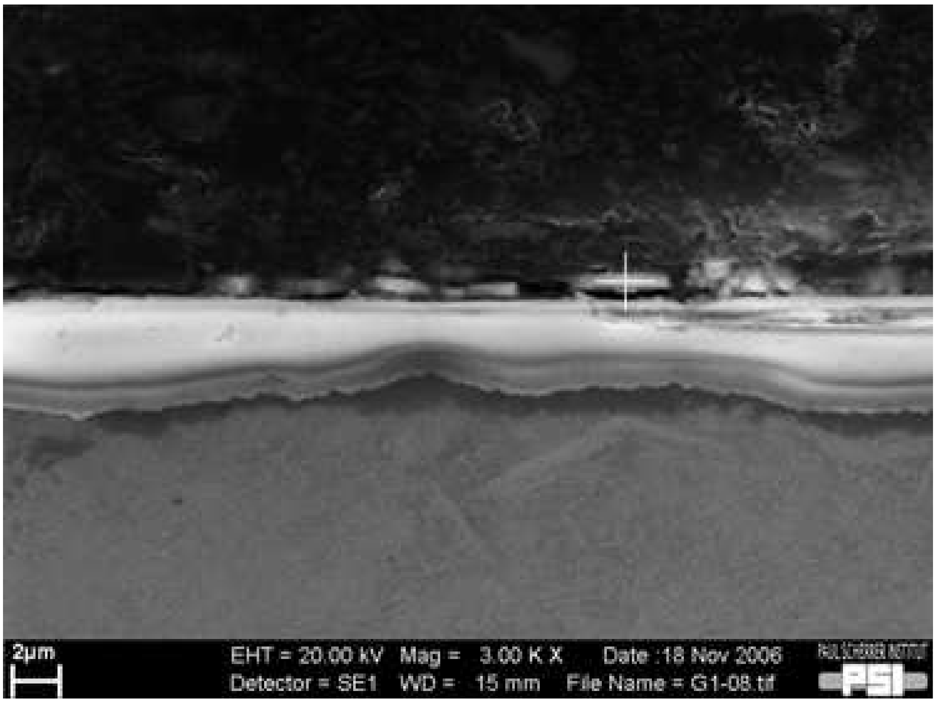


FIG. 5.1. Oxide film on Zr-Nb alloy after 400 days duration in the pile loop (SEM).

5.2.2. Oxide modelling

In order to help to understand observed features in experimental results on thin oxide films undertaken in Finland, oxide film modelling using the Mixed Conduction Model (MCM) was employed. A scheme of the reactions considered in the proposed model for the initial stages of oxidation of a fuel cladding alloy is shown in Fig. 5.2. It is based both on the evidence for the bi-layer structure of the formed oxide obtained

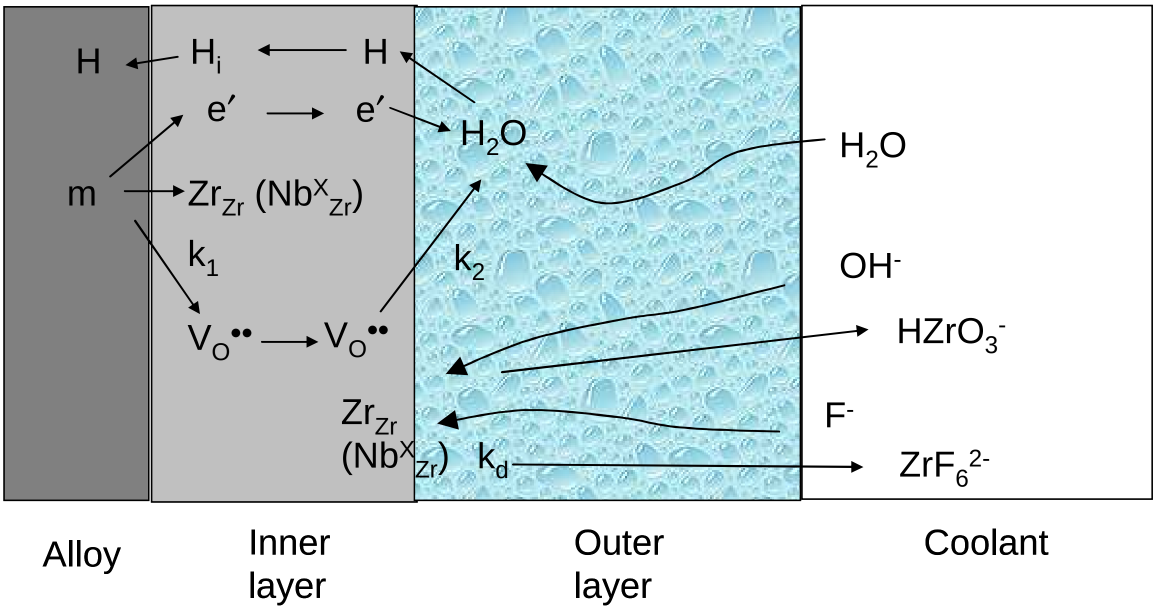


FIG. 5.2. A scheme of the proposed model for the corrosion of a fuel cladding material in a PWR/WWER coolant.

from in-situ impedance measurements in the present study and previous reports by a number of authors [19]–[25].

Oxidation of zirconium (and also of niobium and other alloying elements in the zirconium matrix [26]) proceeds at the alloy/barrier layer interface. This reaction is written in complete analogy to the Point Defect Model PDM and MCM as follows

$$m \xrightarrow{k_1} Zr_{Zr} + 4e' + 2V_O^{\bullet\bullet} \tag{5.1}$$

The oxidation reaction is considered to be irreversible since the corrosion potential of zirconium alloys in simulated PWR and WWER coolants (determined in this case by the dissolved hydrogen content) is much higher than the equilibrium potential for Zr oxidation. The effective valence state of niobium substitute ions in the Zr sub lattice of the oxide have recently been estimated by X-ray Adsorption Near Edge Spectroscopy (XANES) to be between 2 and 4 [26]. This means that Nb can be considered either as hypovalent or isovalent defect, at variance to previous discussions that consider the presence of Nb(V) as a hypervalent defect [28]. The overall impedance of the Zr alloy/oxide/coolant system can be written as:

$$Z = R_{el} + Z_b + Z_{out} \tag{5.2}$$

For the impedance of the outer layer, trials of different distributed functions demonstrated that the so-called Havriliak-Negami impedance [29] gave the best fit to the experimental data:

$$Z_{out} = \frac{R_{out}}{\left[1 + \left(j\omega R_{out} C_{out}\right)^u\right]^n} \tag{5.3}$$

where C_{out} and R_{out} are the capacitance of the outer layer and the apparent resistance of defect migration through that layer, whereas u and n are fractional exponents. The Havriliak-Negami response represents a generalisation of the constant phase element to account for asymmetric capacitive loops. It is also closely related to the Williams-Watts distribution derived from the continuous random walk model of Scher and Lax for transport in disordered and composite media, which has already been used to describe charge transport in zirconium oxides [30]. The Havriliak-Negami element has been proposed originally for polymer dispersions [31] and can be regarded according to the original authors as the impedance of a two phase mixture, which seems to be a good approximation for the outer layer of oxide.

The kinetic and transport parameters were estimated using non-linear least square fitting of the experimental spectra to the transfer function derived in the previous paragraph. Statistical weighting was used for the experimental data set and the errors of parameter estimation were multiplied by the square root of the reduced χ^2-value resulting from the fit. In spite of the relatively large number of parameters, this resulted in a sufficient number of degrees of freedom in the system in order to obtain statistically reliable values of the kinetic parameters.

A collection of the estimated parameters as a function of exposure time is presented in Fig. 5.3 for E110 in PWR coolant with different Li^+ contents, showing the dependencies of the steady-state values of k_1, D_O, ρ_d and $\rho_{out} = R_{out} / L_{out}$ on Li^+ content of the simulated coolant. Data for E110 and Zircaloy-4 in WWER coolant with different K^+ contents and E110 in WWER coolant with different fluoride contents are also given in the full paper. The following main conclusions can be drawn from the calculated parameter values:

- The calculated estimates of the thickness of the whole oxide film after 120 hours of exposure agree very well with the microscopic estimates of the total oxide thickness, indicating the validity of the proposed model for the oxide film. The thickness of the inner layer is several times smaller than that of the outer layer, which indicates that the corrosion properties of the zirconium alloys in the initial stage of oxidation are controlled by a thin layer close to the alloy/oxide interface. The thickness of the outer layer increases with the concentration of $Li^+/K^+/F^-$ in the electrolyte.
- The thickness of the whole oxide and the outer layer is larger on Zircaloy-4 when compared to E110 and in general increases with K^+ concentration. On the other hand, the thickness of the inner layer is somewhat smaller on Zircaloy-4 than on E110 and tends to decrease with increasing K^+ concentration, which points to different properties of the inner layer on the two alloys.
- The values of the $\rho_d\varepsilon$ parameter are in general also lower in the electrolytes containing higher amounts of hydroxides. Unfortunately, the present calculation procedure does not allow for the determination of the diffusion coefficient of electronic carriers as an independent parameter.
- No meaningful differences between the values of $\rho_d\varepsilon$ are found for the two alloys, which is in line with the statement that conduction in the barrier layer at the interface with the alloy is governed by generation and transport of oxygen vacancies.
- For the oxide on Zircaloy-4 at a K^+ concentration of 11 ppm and 28 ppm, both the diffusion coefficient in the barrier layer and the rate constant of Zr oxidation decrease with oxidation time. Within the frames of the proposed approach this observation can be tentatively explained by the deceleration of the dissolution rate of the oxide with time of exposure.
- The increase of the diffusion coefficients for films formed in solutions with higher alkali and/or fluoride concentrations can be correlated to the higher rate of film growth needed to compensate for an increase in dissolution rate. The decrease of the diffusion coefficient with time of exposure in the solution with 2.2 ppm Li^+ can be explained by a decrease of the available easy paths for oxygen diffusion via grain boundaries as the oxide grows.
- The values of the field strength in the barrier layer preserves rather low values (around 10 $kVcm^{-1}$), which demonstrates the viability of the low-field approximation of the transport equations used in the present model. A certain decrease of the field strength with increasing Li^+ concentration is detectable, and can be correlated to the increase of the defectiveness of the barrier layer e.g. via incorporation of Li ions in it. The field strength in the inner layer on Zircaloy-4 seems to decrease when the K^+ content is increased from 11–28 ppm, whereas something of a reverse effect is observed for the inner layer on E110. In fact, the effect of K^+ concentration on the field strength in the inner layer on E110 is on the overall small in comparison to that effect on the inner layer formed on Zircaloy-4.
- The resistivity of the outer layer, which can be regarded as an inverse of the transport rate in this layer by easy path migration, decreases with increasing alkali and fluoride content, indicating that this layer becomes more defective and thus indirectly supporting the hypothesis that the restructuring process that leads to the formation of that layer is dependent on the solution composition, i.e. water chemistry. The resistance of the outer layer R_{out} does not depend on the type of alloy.
- The diffusion coefficient of oxygen vacancies in the inner layer D_O does not change appreciably with exposure time and is reproducibly smaller for the oxide formed on E110 when compared to that on Zircaloy-4, which is in good accordance with the generally lower corrosion rate of E110, as observed experimentally. D_O in general increases with K^+ concentration, i.e. the ionic conductivity of the inner layer seems also to be a function of K^+ content in the WWER water. In line with the hypotheses

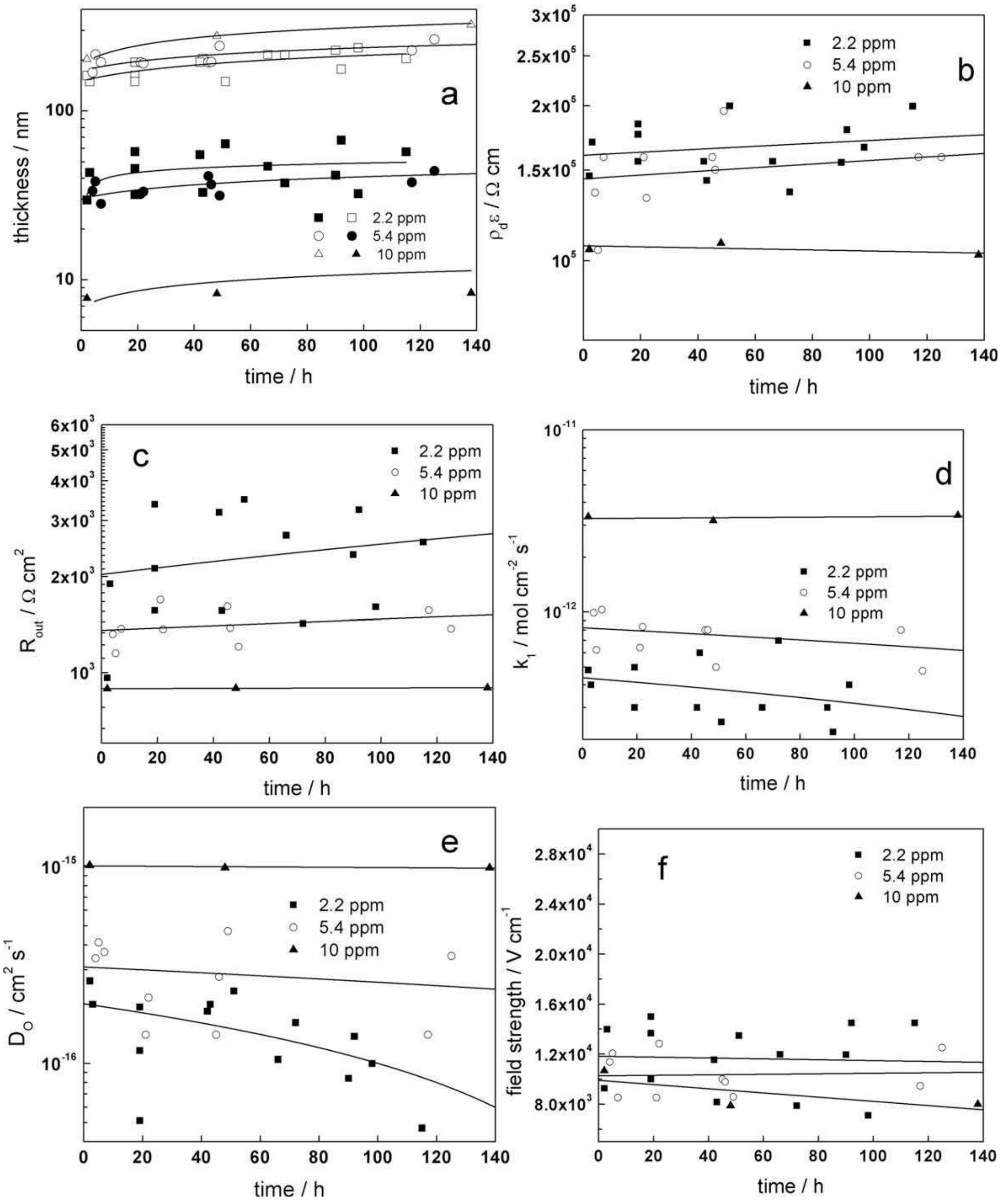


FIG. 5.3. Dependences of the (a) inner (full symbols) and outer (open symbols) layer thickness, (b) the parameter $\rho_d\varepsilon$, (c) the resistance of the outer layer R_{out}, (d) the rate constant of zirconium oxidation at the alloy/oxide interface k_1, (e) the diffusion coefficient of oxygen vacancies D_O and (f) the field strength in the inner layer on the time of exposure of alloy E110 to the simulated PWR coolants with different Li^+ content.

proposed above, if oxide transformation via dissolution is rate limiting and depends on K^+ concentration, in steady state so should be the ionic conductivity and hence the diffusion coefficient.

5.3. Chemistry

The corrosion mechanism for Zr-Nb alloys shows complex character and depends on many parameters described in detail. The oxidation rate can be expressed as:

$$V = \frac{dS}{dt} = k_T + k_\phi \qquad (5.4)$$

Where

k_T , k_φ are the thermal and neutron radiation components respectively.

Empirical studies of numerous oxidation reactions have shown that under constant oxygen pressure in the environment the temperature dependence on the oxidation rate of Zr alloys can be described by the Arrhenius equation:

$$k_T = k_o \exp [- Q/R(T+\Delta T)] \tag{5.5}$$

Where

Q is the activation energy;
R is the gas constant;
T is the absolute temperature at the coolant/cladding interface;
ΔT is the growth of cladding temperature under corrosion deposits layer.

Experimental values of Q/R are (6.5–13) × 10^3 K (Reference [32]–[34]). The following experimental facts have revealed the influence of water chemistry on Zr-alloy corrosion:

- influence of water pH (Fig. 5.4);
- influence of H_2O_2 concentration;
- decrease of corrosion film thickness in the transient stage (i.e. practically its partial dissolution) [35];
- morphology of >3–5 mm thick films (formation of grains and pores of different size but the same geometric form) [35];
- crystallization of the dissolved phase in the form of fine ZrO_2 powder in the water volume of the steam separator of RBMK reactor.

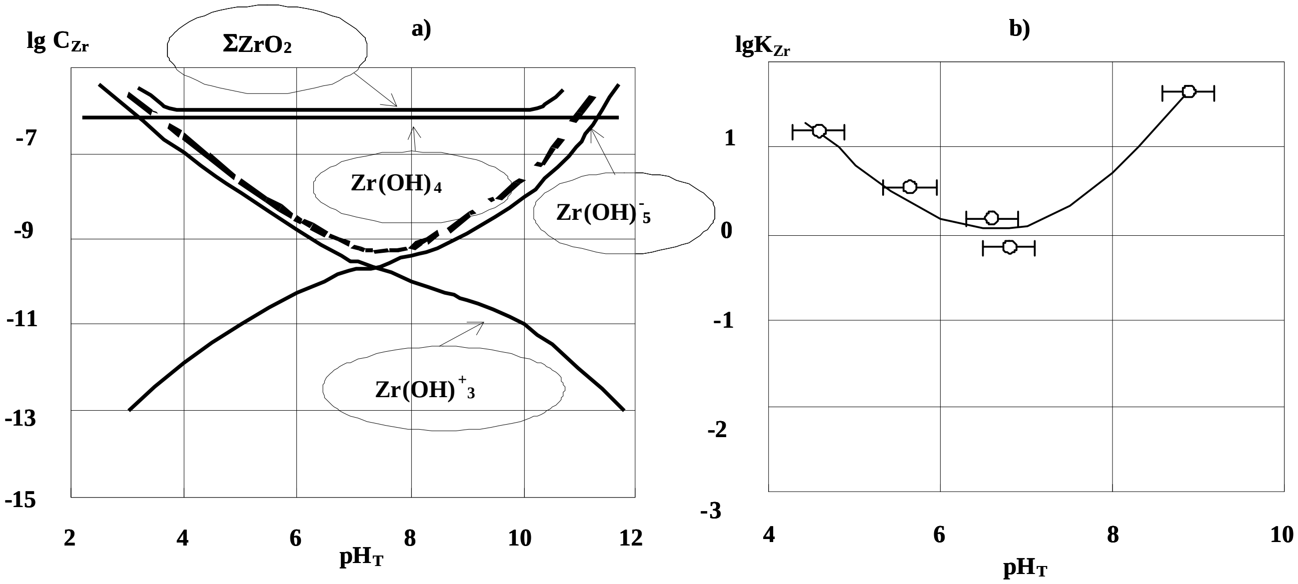


FIG. 5.4. (a) The values of calculated solubilities of zirconium corrosion products (mol/kg) in PWR conditions [35] and (b) corrosion rate (μ·y-1) versus pH_T [37].

The most studied parameters on fuel cladding corrosion, before this FUWAC project, have been the pH and alkali (lithium) concentration, particularly at the beginning of the fuel cycle and with higher values for high performance fuel and high boron content. For many years the selection of potassium (WWER) versus lithium (PWRs) has been evaluated for the influence on various components of the primary system. One participant explained that potassium might more easily induce fuel cladding corrosion. This may be explained by the higher solubility

The Pitesti (Romania) INR laboratory performed experiments at different temperature on Zy-4 samples and showed that the quantity of the adherent corrosion products was dependent on thickness and especially on the physical-chemical characteristics of the initial zirconium oxide film. Thus, in the case of compact and adherent oxides with thickness of 1–1.5 μm, formed at 310°C, only a small quantity of corrosion products was found.

From metallographic and electronic microscopy examination after testing in LiOH solution with pH=11.8, a continuous and adherent oxide with uniform aspect can be seen. Layered oxide films were formed on initial oxidized samples after 120 testing days in LiOH solution. The layered oxide structure is best evidenced in the case of initially oxidized samples with oxide films of 4 μm thickness (Fig. 5.5). The SEM micrographs indicate that the boundaries between layers are not continuous, but consist of numerous different contrast forming bands that are aligned parallel to the metal/oxide interface with this morphology, it is clear that these micro structural features are not cracks.

The corrosion process in LiOH solution with pH=11.8 did not conduct to an accelerated hydriding process, the important differences did not obtain regarding morphology and quantity of hydrides after testing.

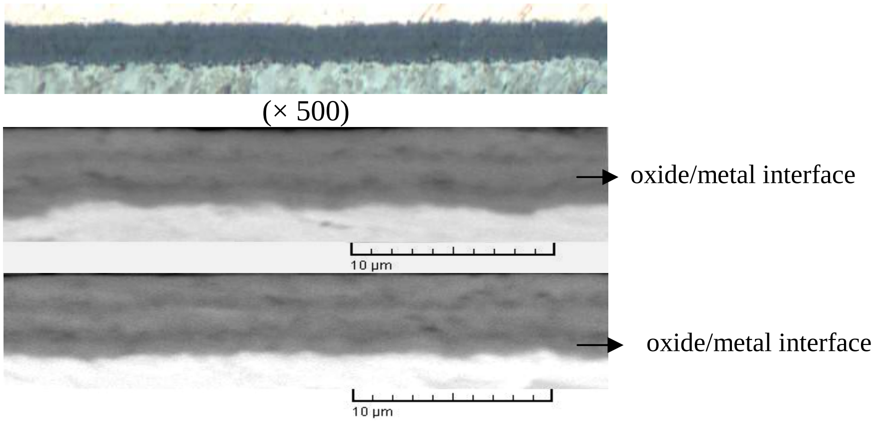


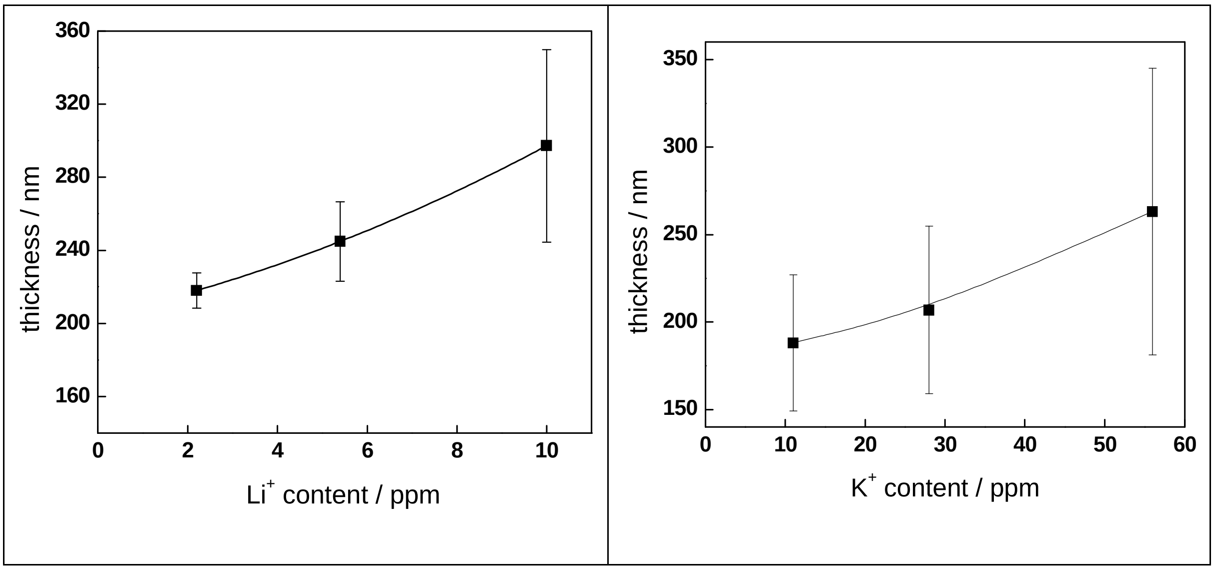
FIG. 5.5. Sections of oxide films formed on Zircaloy-4 samples (initial oxidized condition – oxide of 4 μm) tested for120 days at 310ºC (10 MPa) in LiOH solution with pH=11.8.

Conclusions from the Pitesti experiment are as follows:

- The corrosion rate and hydriding process of Zircaloy-4 alloy do not accelerate in LiOH solution, when the pH of LiOH solution is under 11.8. When the solution pH exceeds the value of 11.8–12, the oxidation rate accelerates and the hydrogen absorption fraction increases.
- Experimental results show that in presence of pH=12.3, an intensive and non-uniform corrosion process took place. The morphological analysis of the oxidized surfaces showed the non-uniform aspect and non–adherent character of whitish-grey or brown zirconium oxide, as well as the presence of cracks on surface.
- The initial oxidation condition of surface, particularly the existence on the surface of some relatively thick oxide films, influenced the subsequent oxidation process. When the pH value is increased. LiOH can concentrate in pores of the thicker oxides and local increasing lithium concentration can enhance the oxidation and hydriding process.
- In the case of the existence of some initial adherent and protective oxide films with thickness about 4 μm on a sample surface, exposure in an environment with a high pH led to a clear degradation of the corrosion behaviour by the development of pores and micro-cracks during oxide growth.
- The lithium effect is to destroy the interior barrier layer, preventing the development of the columnar structure, which ensures protection, compared to the equiaxed structure of oxide grains. After accelerated oxidation, through a pH increase, a new oxide layer is formed near the metal/oxide interface, which consists of equiaxed grains with a weak intergranular cohesion. The newly formed oxide layer is probably more hydrous and the boundaries of grains are particularly liable to dissolution. The oxides formed have a layered structure and present pores and micro-cracks.
- Examination in transverse section of oxide films formed in LiOH solution – pH=12.3 on initial oxidized samples (oxide about 4 μm) showed the presence of the pores and cracks in oxide layer, as well as the delimitating zone between the initially formed, exterior oxide layer and the new oxide layer formed by corrosion process in LiOH solution with high pH. The exterior oxide layer presented swellings and grain morphology consists from equiaxed grains with weak intergranular cohesion which detached in shape of faults.

Estimates of oxide film thickness have been obtained from scanning electron microscopic examination of sample cross sections in Finland. Figure 5.6 summarises the effect of Li^+ and K^+ content on the thicknesses of oxide films formed on E110 in simulated PWR and WWER coolant conditions for 140 h at 310°C. There is a noticeable increase in film thickness with increasing alkali concentration, the trend of this increase being supra-linear.

On the other hand the difference between alloys can be seen in Fig. 5.7. The thicknesses increases with K^+ content, this increase being more pronounced when the concentration is changed from 28–56 ppm. Another important fact is that the thickness of the oxides on the Zircaloy-4 samples are significantly higher than those on E110 electrodes, the difference between the oxides on the two alloys becoming larger for higher K^+ content in the electrolyte. It is also worth noting that the range of the oxide thickness increases with K^+ content and is much more pronounced for the oxides on Zircaloy-4.



a) b)

FIG. 5.6. Microscopic estimates of the oxide film thickness on E110 after 140 h of exposure to simulated coolant as depending on the Li^+ content (a), K^+ content (b).

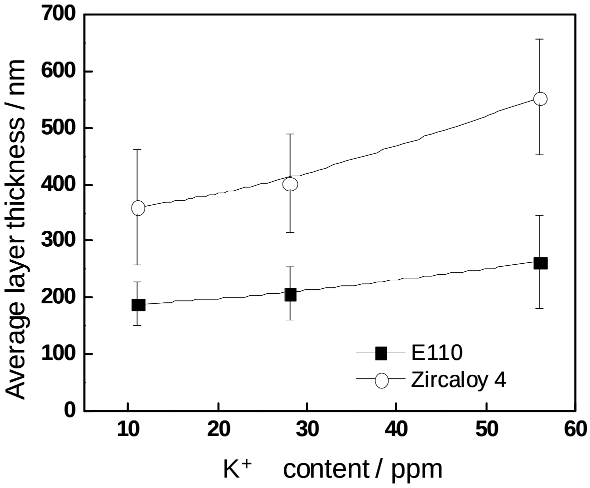


FIG. 5.7 Microscopic estimates of the oxide film thickness on E110 and Zircaloy-4 after 120 h of exposure to simulated WWER water as depending on the K^+ content.

The manufacturer of E110 fuel cladding has set a limit of 100 ppb on fluoride concentration at BOC conditions, while the peaks of fluoride concentration at Loviisa WWER plants have stayed well below this limit. In this work the effect of fluoride concentration in BOC WWER water chemistry on the oxidation of E110 fuel cladding has been studied. The goal was to see whether F^- has any effect on the oxidation above and below the concentration limits set for the fuel cladding.

The results from the oxide film thickness measurements are shown in Fig. 5.8. Summarising, the addition of 120 ppb of fluoride to the simulated WWER coolant containing 11 ppm of K^+ leads to a noticeable increase in film thickness, whereas the oxide film formed in a solution containing 1000 ppb of F^- has been found to be somewhat thinner. Increasing the fluoride content of the simulated coolant leads to an increase in the thickness of the oxide film formed for identical exposure periods, the trend does not lead to a simple relationship between film thickness and concentration. Explanations for these features were sought by conducting in-situ Electrochemical Impedance Spectroscopy (EIS) measurements during exposure of the alloy to the simulated coolant.

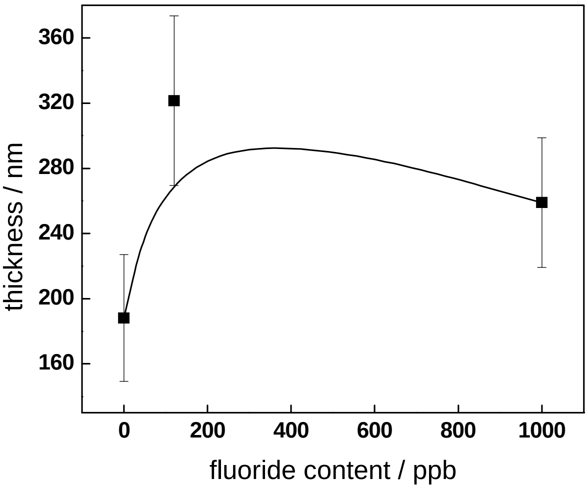


FIG. 5.8. Microscopic estimates of the oxide film thickness on E110 after 140 h of exposure to simulated coolant as depending on fluoride content.

From the impedance measurements it can be stated that $Z_{f \to 0}$ decreases with increasing F^- content in the coolant, the decrease being more pronounced at the highest concentrations of fluoride. This observation is in accordance with the increase of estimated oxide layer thickness after 120 h of exposure and demonstrates the accelerating effect of the investigated additive on the oxidation rate. A possible explanation similar to that with the elevated alkali concentrations, that the increase in fluoride concentration leads to an increase of the solubility of zirconium oxide at its interface with the electrolyte, therefore a quasi-steady state is reached at a higher respective rate of oxide growth to compensate for dissolution.

Summarising, the in-situ impedance measurements point to a notable effect of Li^+, K^+ and fluoride concentrations on the initial stages of the oxidation process of zirconium alloys in simulated PWR/WWER coolant. These measurements allow a definition of the contributions of the electric properties of two layers of oxide – a thin barrier layer and a thicker (more defective, and hence probably less protective) outer layer, as well as a solid-state transport process of point defects probably occurring in the barrier sublayer.

No impact of zinc addition has ever been seen on fuel cladding, at the zinc concentration required for dose rate mitigation.

5.4. Impurities

Extensive studies were carried out under simulated and accelerated PWHR conditions to estimate the kind of deposits that are formed over three types of Zircaloy surfaces namely Zry-2, Zr-1Nb and Zr-2.5Nb as these materials are likely to be extensively used in future reactors. They will also be residing in the core for extended periods of time because of long fuel cycle lengths. In addition this study considered their role in older plants.

The experimental domain of this investigation was:

- at T = 400°C, steam with (a) deaerated condition and (b) high DO content, in static autoclave for up to 90 days exposure;
- weight gain and SEM analysis;
- hydrogen pick up studies;

- EIS studies in high temp, pressure loop at 310°C, with controlled levels of DO in alkaline water chemistry.

The weight gain shown by conventional Zircaloy-2 under accelerated conditions either in the presence or absence of oxygen was not very different for long term or short term exposure. Zr-Nb alloys showed a substantial increase in weight gain when exposed to oxygen for periods beyond 2 months under accelerated conditions. The oxides are suspected to be formed around on a Nb depleted phase in the zirconium alloy.

The hydrogen pick up was found to be low and comparable in all of the three Zr alloys when the DO levels are high. Zr-2.5Nb alloy showed very low levels of hydrogen pick up even at extended exposure condition and irrespective of the DO levels. For Zr-1Nb and Zircaloy-2, the hydrogen pick up was higher when the DO levels were low.

This study has raised considerable interest especially in the context of using the competitor Zr-Nb alloys in place of the conventional Zircaloy-2. The following points need to be clarified:

- Reason for preferential attack on Nb depleted area.
- Correlation between ASTM G2M test results and the long term test under similar conditions with the loop tests at reactor operation conditions (for short term) are to be clearly correlated.

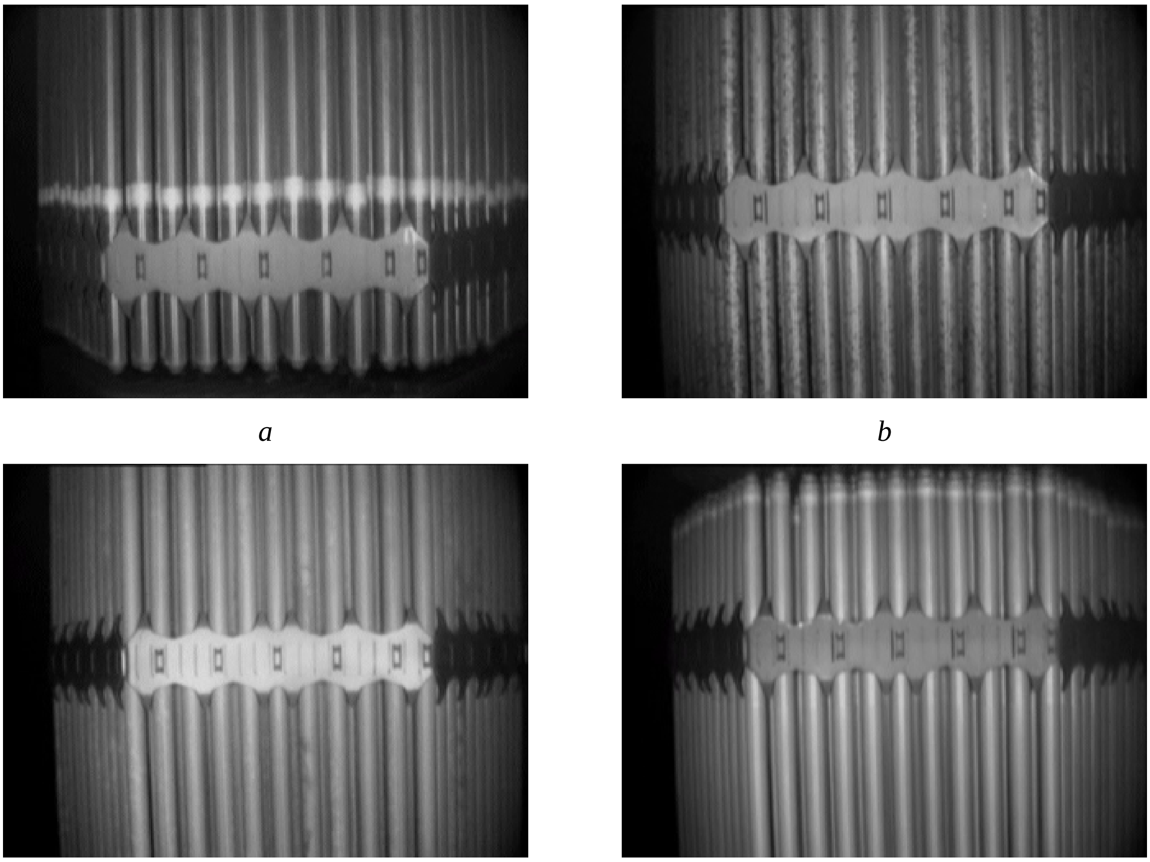
For WWERs the deposition mechanism is most likely influenced by leftovers from decontamination, whose behaviour in the active zone and role in the management mechanism is unknown. There are different mechanisms for fuel corrosion deposition, as well as different areas of the active zone between PWR and WWER; in PWRs, deposition on the fuel takes place in the upper part of the active zone, while in WWERs it is mostly in the lower portion of the active zone, on the first spacer grids.

5.5. NPP feedback

South Ukraine NPP is currently operating 6 Westinghouse-produced lead test assemblies in which the fuel rod cladding, the guide thimble tubes and the instrument tube are made of the alloy ZIRLO^{TM} [38] Westinghouse fuel has been operated for some time and has demonstrated good corrosion resistance in PWRs. A number of experiments were previously carried out in the Czech WWER reactors to determine corrosion resistance of the structural materials used in the Westinghouse fuel rods and demonstrated their satisfactory corrosion resistance. However, these materials had not been operated in Ukraine's WWER mixed cores. Therefore, an experiment objective was to monitor the effects of the WWER-1000 primary CC on the changes in corrosion resistance of the fuel-rod and fuel-assembly materials used in mixed cores.

To date, the mixed core has completed its 3rd operation cycle. The appearance of fuel assemblies and fuel rods changes in the same way for both Russian and Westinghouse types. At the beginning, after the first operation cycle, the upper part of the FA in the area of the top spacer grid developed white-and-gray spots, which are shades of the protective oxide film. After subsequent cycles the spots spread downward, gradually approaching the bottom spacer grid. At the same time, in the upper part of the FA, the area of the fuel rods covered with white-and-gray spots increased, and after the 3rd operation cycle, the top part of the fuel rods in both TVSM and Westinghouse FA became completely gray-and-white. It should be noted that the spots appear not in the maximum power deposition area or at the beginning of the fuel stack area, but specifically in the upper part of the FA.

Fig. 5.9 shows the appearance of a Westinghouse FA after 3 cycle operation at SUNPP-3. The Figure shows the bottom grid (a), second grid from the bottom (b), grid in the area of the fuel stack beginning (c), and top grid (d). In the region of the bottom grid (a) and top part of the FA (d) there are visible white bands of oxide films in the weld joints areas. The pictures were obtained from FA visual inspection during the outage of 2008 [38].



a b

c d

FIG. 5.9. Appearance of a Westinghouse FA face after three cycles of operation in the WWER-1000 reactor core: (a) bottom grid; (b) second grid from the bottom; (c) grid in the fuel stack end area; (d) top grid.

Russian FAs were inspected after their 1st, 3rd, and 4th cycles of operation on three faces adjacent to the Westinghouse fuel assemblies. There was no appreciable mutual impact of the new core structural materials on corrosion behaviour of the fuel rod cladding, FA spacer grids, and FA top and bottom nozzles of either Russian or Westinghouse fuel. No failure of the fuel rod cladding or other Westinghouse FA elements was identified.

Visual inspection of the fuel rods and the FA demonstrated absence of defects (pitting or cracks) in the area of the fuel rod weld joints, which testifies to resistance of the joints under CC-1 operation conditions.

The operation of lead test assemblies demonstrates that Westinghouse fuel can be operated in WWER-1000 mixed cores with the primary coolant parameters which meet the standard GND 95.1.06.02.001–07. Further, the established design safety limits are met. Activities in this area are ongoing.

6. CRUD

6.1. Composition, thickness, evolution

Fuel cladding made from Zr-alloy can be covered with deposits, which have precipitated from the coolant as a result of temperature changes. Precipitation of this deposit in the core must be avoided as far as possible, as it leads to fouling of the fuel, loss of heat transfer efficiency, potentially leading fuel failures, and increased radiation fields.

Crud is important because it influences fuel behaviour. Crud is very porous (a porosity of about 80%). The pore (a kind of crevice) can be enriched in B (neutron poison which induce AOA) or Li^+ (a corrosion enhancing species for Zircaloy) if boiling occurs. Moreover, the boiling of the environment inside crud may decrease its hydrogen concentration. Oxidizing species, such as H_2O_2 formed by radiolysis, may be concentrated in the crud and corrosion can be accelerated. In addition, the crud on cladding behaves as a thermal barrier and the activated crud would increase the radiation dose rate.

6.1.1. *CANDU and PHWR systems*

Magnetite behaviour is important for crud formation and its solubility depends on electrochemical potential of the solution. It depends on temperature, pH of the solution, (Fig. 6.1), and concentration of H_2 (D_2) [39].

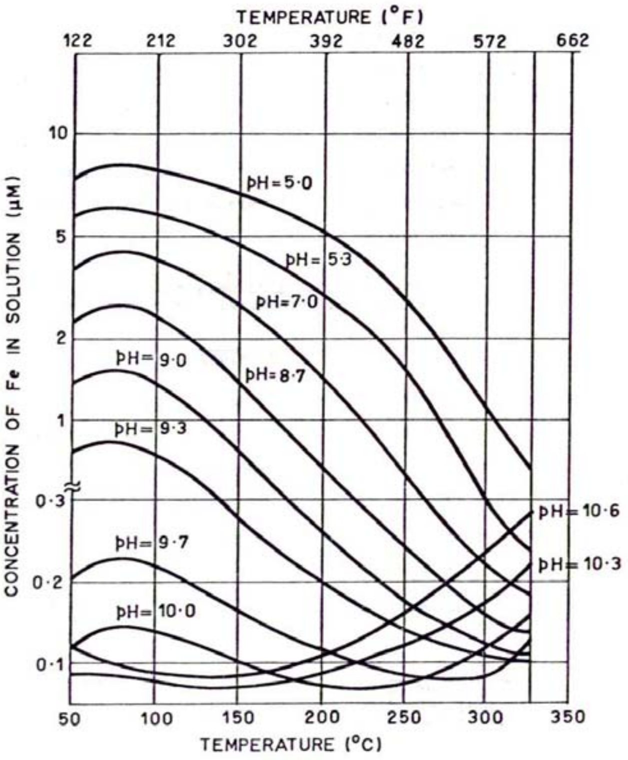


FIG. 6.1. Fe^{2+} solubility vs. temperature and pH.

Above a certain pH the solubility increases with temperature; this is the region where the HTS coolant of a PHWR type plant should be operated.

Below a certain pH the solubility decreases with temperature. This regime must be avoided in a CANDU reactor, as it can lead to deposits being formed in the core and increase the barrier to heat transfer.

The composition, thickness and evolution of crud of FA surfaces depend very much on operational conditions, such as steady state operation, water chemistry conditions, and different oxidation conditions.

Laboratory investigations for steady state operation have been done in a Romanian laboratory using corrosion deposits on the surface of Zircaloy-4 coupons extracted from autoclaves circuits assembled in a by-pass loop of a CANDU-6 Reactor at NPP Cernavoda, and Zircaloy-4 fuel rods tested in the irradiation loop of the TRIGA Reactor.

The chemistry conditions for the coupon samples were the standard conditions for the reactor, which comply with the chemical control and diagnostic parameters for steady state operation of CANDU-6 Reactor, which are summarized in Table 6.1 [40].

The corrosion testing conditions for the fuel rods in the irradiation loop of the TRIGA Reactor were:

- LiOH solution, pH = 9.5–10.5;
- oxygen concentration <50 ppb, conductivity <100 mS/cm;
- maximum temperature at fuel rod surface is 3000ºC, and pressure is 10.6MPa;
- coolant flow is 3 l/h;
- linear power is 420W/cm;
- burnup is 190 MWh/kg U.

TABLE 6.1. CHEMICAL CONTROL AND DIAGNOSTIC PARAMETERS SPECIFICATION

Parameter	Sample origin	Specification	Desired value
pH	Main system IX* outlet	10.2–10.8 N/A	10.2–10.4 IX inlet
Dissolved D_2 (ml/kg)	Main system	3–10	7
Chloride (mg/kg)	Main system IX* outlet	≤ 0.2 < IX inlet	ALARA ** ALARA
I-131 (MBq/kg)	Main system IX outlet	< 500 < IX inlet	ALARA ALARA
D_2 (%by vol.)	Storage tank cover gas	≤ 2	ALARA
O_2 (% by vol.)	Storage tank cover gas	≤ 1	ALARA
N_2 (% by vol.)	Storage tank cover gas	≤ 6	ALARA
Lithium (mg/kg)	Main system	0.4–1.1	0.5
Conductivity (μS/cm)	Main system	8–25	8–20
Fluoride (mg/kg)	Main system IX outlet	< 0.1 < IX inlet	ALARA ALARA
Suspended solids (mg/kg)	Main system gland seal	< 0.1 < 0.010	ALARA ALARA
Total organic carbon (mg/kg)	Main system	≤ 1.0	ALARA
Radionuclide gamma scan (MBq/l)	Main System IX outlet	0.1 < IX inlet	ALARA ALARA

** IX – ion exchange; ** ALARA – As Low As Reasonable Achievable*

The experimental FA is presented in Fig. 6.2.

FIG. 6.2. Experimental fuel assembly.

The characterization of crud deposits on the Zircaloy-4 coupons was performed using a gravimetric method, metallographic and electronic microscopy and gamma spectrometry analysis [41].

The deposition of crud was gravimetrically determined from the coupons of Zircaloy-4 alloy inserted in reactor outlet autoclaves (310ºC) and reactor inlet autoclaves (260ºC) during 825 exposure days. Table 6.2 presents the results for both adherent and loose crud.

TABLE 6.2. ADHERENT AND LOOSE CRUD ON ZIRCALOY-4 COUPONS AFTER 825 EXPOSURE DAYS

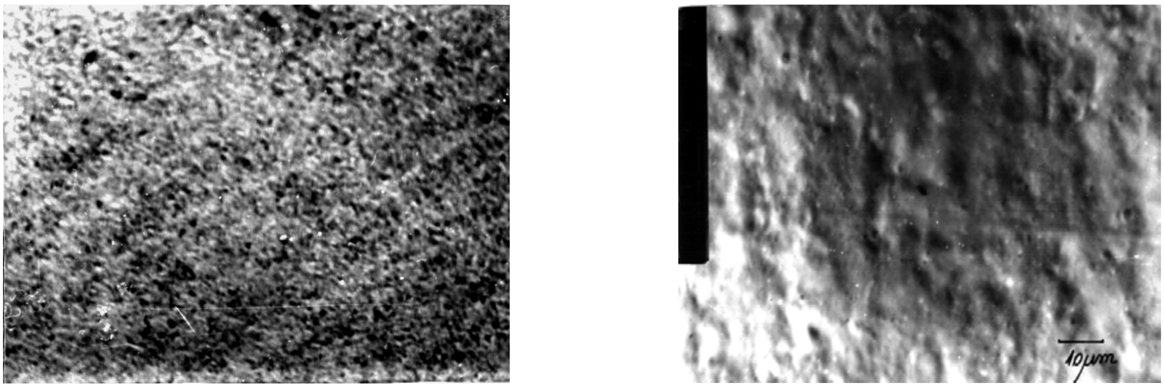
Autoclave (location)	Total crud (g/m^2)	Adherent crud (g/m^2)	Loose crud (g/m^2)
Reactor outlet (310ºC)	1.4	0.42	0.98
Reactor inlet (260ºC)	2.7	1.62	1.08

The values of crud thus obtained are in agreement with theories that explain the mechanism of generation of corrosion products in CANDU reactors with carbon steel feeders [42]–[43].

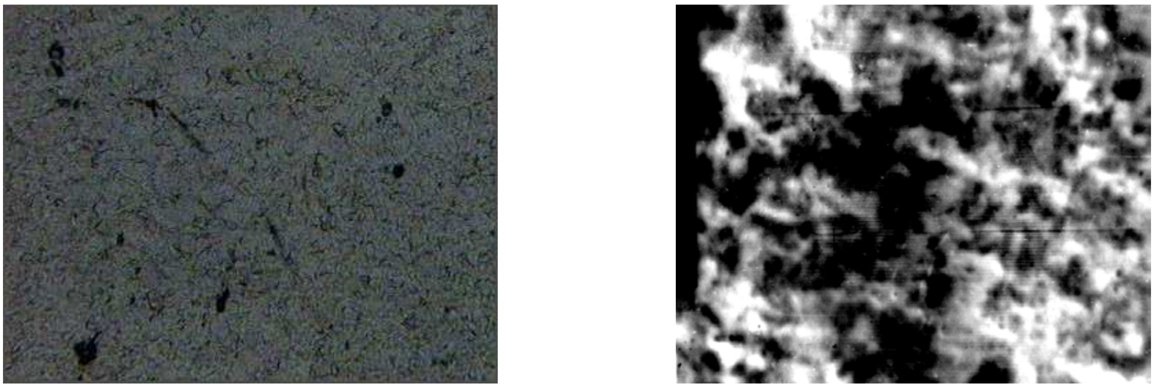
The coupons from the inlet reactor autoclaves (260ºC) have larger deposits since the coolant is probably still supersaturated in iron with respect to its solubility value and present a higher percentage (60%) of adherent crud deposited on the surface. The coupons inserted in outlet reactor autoclaves (310ºC) show smaller values of total deposits and a smaller percentage of adherent crud (30%), this difference can be attributed to the presence of particulate matter that is formed by erosion of recently precipitated crystalline crud.

The thickness of crud was measured from the metallographic samples. The thickness of the film with adherent corrosion products was about 3–5.5 µm.

Corrosion products deposits in shape of black magnetite crystallites were found on the surface of the coupons, Fig. 6.3.



a) Microscopical aspect (× 200) Morphological aspect (× 1000)



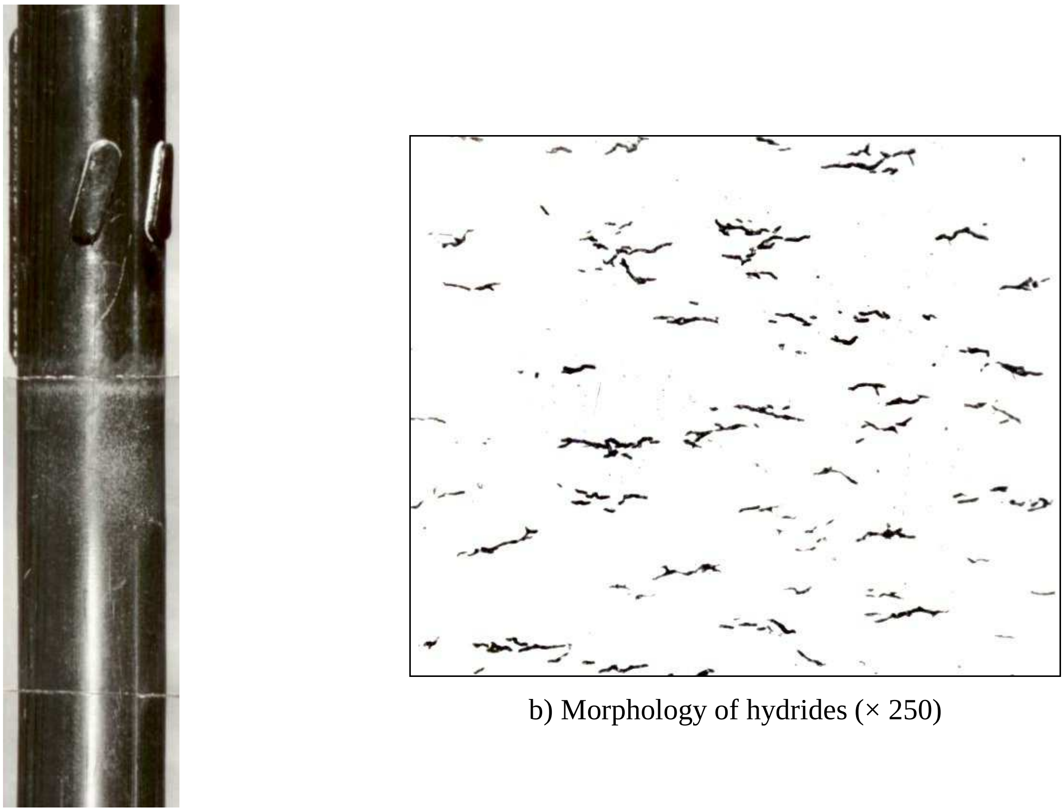
b) Microscopical aspect (× 200) Morphological aspect (× 1000)

FIG. 6.3. Deposits of the corrosion products on Zircaloy-4 coupons surface after 825 exposure days: a) reactor inlet autoclaves and b) reactor outlet autoclaves.

These deposits consisted of fine, relatively numerous and adherent magnetite crystallites on the coupons inserted in reactor inlet autoclaves and were larger and less numerous on coupons inserted in the reactor outlet autoclaves.

Radionuclides found by gamma spectrometry were generally, ^{54}Mn, ^{60}Co, ^{95}Zr, ^{95}Nb. Further radionuclides, ^{65}Zn, ^{59}Fe, ^{103}Ru, ^{124}Sb, ^{125}Sb, and ^{141}Ce were present after 568 exposure days.

Visual examination of fuel rods after 190 irradiation days showed good corrosion behaviour. Very fine, black magnetite deposits were present on the Zircaloy-4 sheath surface. Fig. 6.4 a) shows that these deposits did not influence the oxidation or hydriding of the cladding material. Metallographic examination showed the presence of a uniform zirconium oxide, having a thickness of 5–6 μm and an acceleration of hydriding did not occur. Fig. 6.4 b) shows that the morphology of hydrides was similar to that of coupons tested in identical conditions from out of reactor experiments.



b) Morphology of hydrides (× 250)

a) General aspect of the fuel rod (× 1.5)

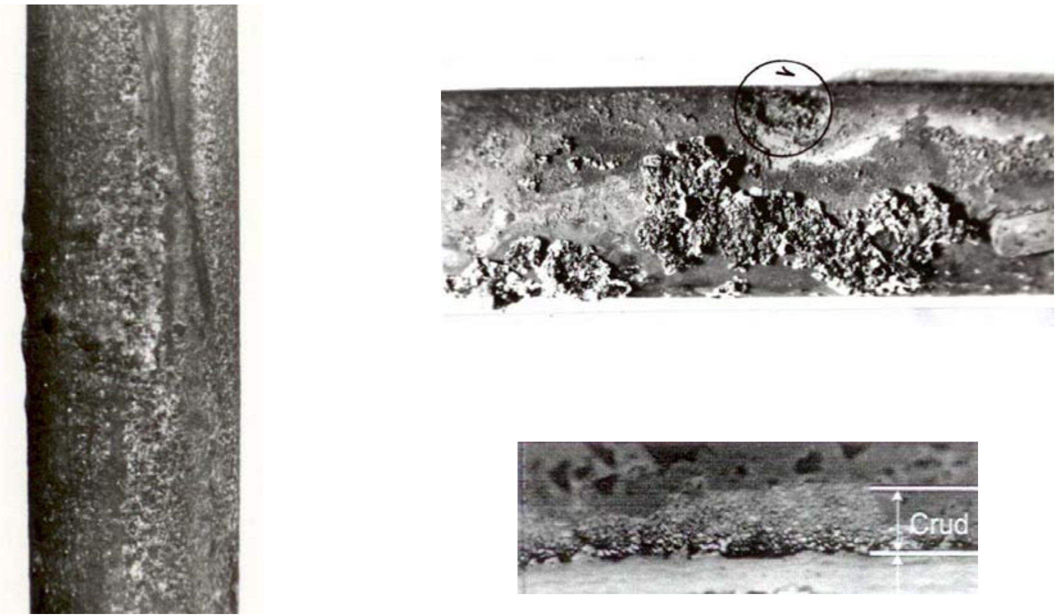
FIG. 6.4. CANDU fuel rod tested 190 days in TRIGA reactor, using irradiation capsule.

An important factor influencing the deposition process is water chemistry (pH and presence of dissolved oxygen) In this context, CANDU fuel rods were tested in the irradiation loop of the TRIGA Reactor in the following conditions:

- pH~11.7, adjusted with LiOH;
- oxygen concentration > 100 ppb;
- maximum temperature at the fuel rod surface is 330ºC and pressure of 10.6–10.7 MPa;
- the coolant flow is 1.45 – 1.5 l/s;
- the linear power is 250 W/cm;
- the burn-up is 110 MWh/kgU.

An assessment of crud and the impact of crud on corrosion were performed by sending fuel rods to the hot cell for visual examination and destructive evaluation [44].

The destructive examinations included cutting transverse cross-sections of the cladding for metallographic examination. These examinations were performed to measure the thickness of crud and to show the effect of these deposits on fuel rod material corrosion. Crud deposits on fuel rods have been observed during visual examination after 90 and 180 irradiation days (Fig. 6.5).



180 days

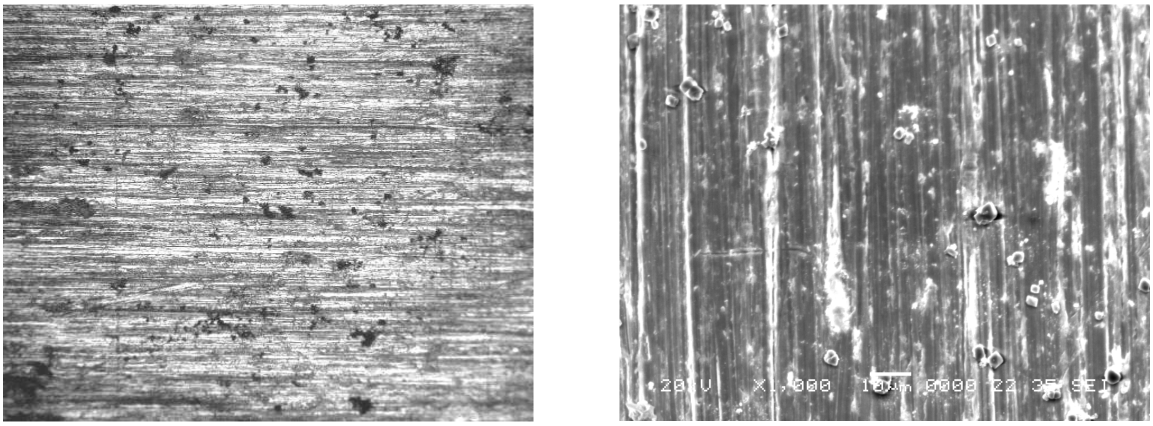
90 days

FIG. 6.5. Deposits of corrosion products on CANDU fuel rods tested in TRIGA reactor (× 3).

Non-uniform, brown-reddish and whitish-gray deposits were observed. Some of them were adherent, but others were removed relatively easily. A cracked layer of deposits was observed, the cracks being either radial or parallel with the wall sheath, a fact that led to stratified crud deposits. XRD analysis of the deposits showed the presence of the following elements: Fe, Sn, Sb, Cr, Ni, Zn, Ti, Mg, Cu, Li and Zr. The thickness of deposits varied from 60–107 μm.

Several laboratory experiments performed at different temperature on Zy-4 samples [45] showed that the quantity of the adherent corrosion products was dependent on thickness and, especially, the physical-chemical characteristics of the initial zirconium oxide films. Thus, in the case of compact and adherent oxides with thickness of 1–1.5 μm, formed at 310ºC, a small quantity of corrosion products was determined (Fig. 6.6).

Through optical and scanning electron microscopy analysis, the presence of relative fine and adherent corrosion products (orthorhombic crystals of Fe_3O_4 and hexagonal crystals of Fe_2O_3) with isolated or less

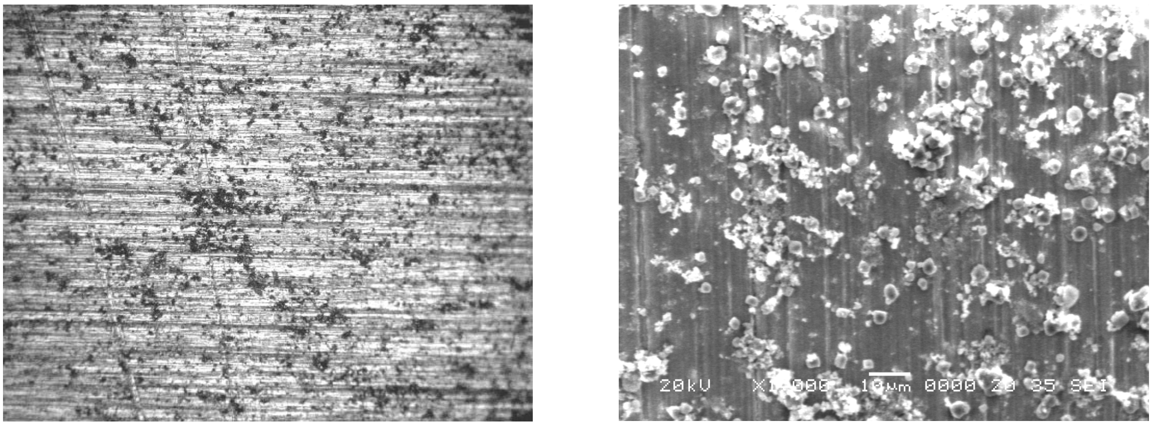


Microscopic aspect (× 200)

Morphological aspect (× 1000)

FIG. 6.6. Microscopic and morphological aspect of the adherent deposits on oxidized samples with oxide of 1–1.5 μm.

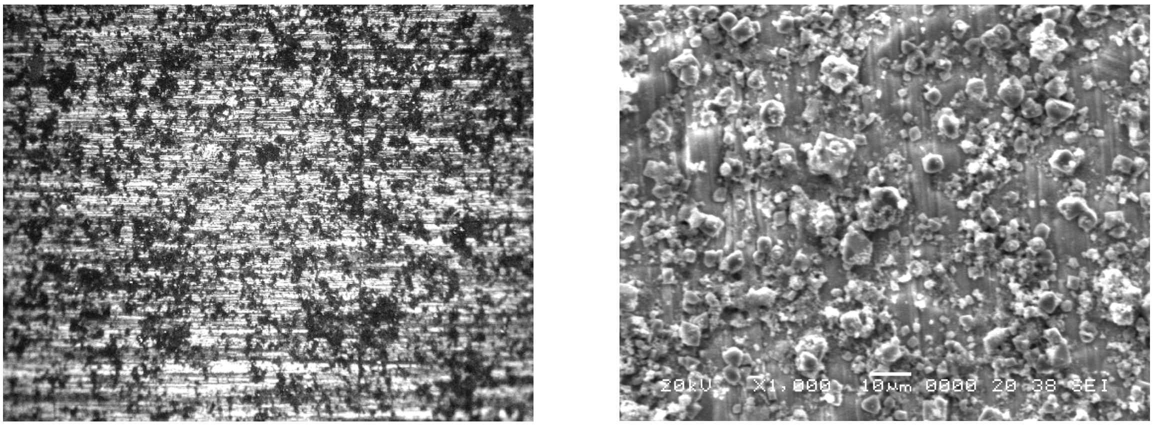
crowded aspect was shown on oxidized surfaces with zirconium oxide to about 5 µm thickness, formed at 350ºC (Fig. 6.7).



microscopic aspect (× 200) morphological aspect (× 1000)

FIG. 6.7. Microscopic and morphological aspect of the adherent deposits on oxidized samples with oxide of 4.5–5 µm.

On surfaces oxidized in steam at 400ºC with thicker oxides (8–12 µm) and with a porous character, adherent deposits of corrosion products with a dense aspect were formed and they were much more numerous (Fig. 6.8).



microscopic aspect (× 200) morphological aspect (× 1000)

FIG. 6.8. Microscopic and morphological aspect of the adherent deposits on oxidized samples with oxide thickness of 10–12 µm.

Both gravimetric analysis and microscopic analysis showed that the adherence of corrosion deposits increased with the thickness and especially with the porosity of zirconium oxide on the sample surface; a significant quantity of the corrosion deposit incorporates in pores and lateral cracks of oxides, as shown by EIS determinations.

6.1.2. PWR systems

An investigation into the effects of water chemistry on the crud deposition on the fuel cladding was done in Korea Atomic Energy Research Institute (KAERI) in order to quantify the effects of water chemistry and boiling. Test conditions are designed to simulate the real operation water chemistry of PWR as shown in Fig. 6.9 and are summarized in Table 6.3. The target temperature was set at 309˚C in the upper part of the test tube. The test pressure was maintained at 96.5 kg/cm^2 (equilibrium temperature at 307˚C) as shown in Fig. 6.10. Sub-cooled boiling is induced along the test rod where the temperature is above 307˚C.

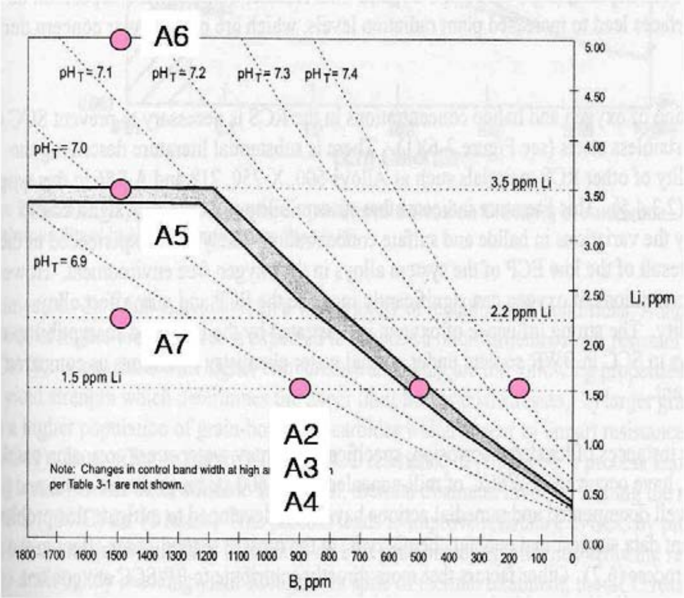


FIG. 6.9. Schematic diagram of coordinated water chemistry in PWR.

TABLE 6.3. CRUD DEPOSITION TEST CONDITIONS

Test	Material	Solution	pH (RT)	Exposure time (days)	Others
A1		1.5 ppm Li, 870 ppm B 20 ppm Ni as $Ni(NO_3)_2$ 20 ppm Fe as $Fe(NO_3)_3$	3.6	5	– Hydrogen: $21 cm^3/kg\ H_2O$ – DO < 5 ppb – $96.5\ kg/cm^2$ (307°C)
A2		1.5 ppm Li, 870 ppm B 200 ppb Ni as $Ni(NO_3)_2$ 200 ppb Fe as $Fe(NO_3)_3$	6.4	5	
A3	ZIRLO™	1.5 ppm Li, 870 ppm B 200 ppb Ni as Ni(NO3)2 200 ppb Fe as Fe(NO3)3	6.4	28	
A4	ZIRLO™	1.5 ppm Li, 870 ppm B 2.0 ppm Ni as Ni Acetate 2.0 ppm Fe as Fe Acetate	6.3	14	
A5	ZIRLO™	3.5 ppm Li, 1500 ppm B 2.0 ppm Ni as Ni Acetate 2.0 ppm Fe as Fe Acetate	6.3	14	
A6	ZIRLO™	5.0 ppm Li, 1500 ppm B 2.0 ppm Ni as Ni Acetate 2.0 ppm Fe as Fe Acetate	6.5	14	
A7	ZIRLO™	2.2 ppm Li, 1500 ppm B 2.0 ppm Ni as Ni Acetate 2.0 ppm Fe as Fe Acetate	6.2	14	

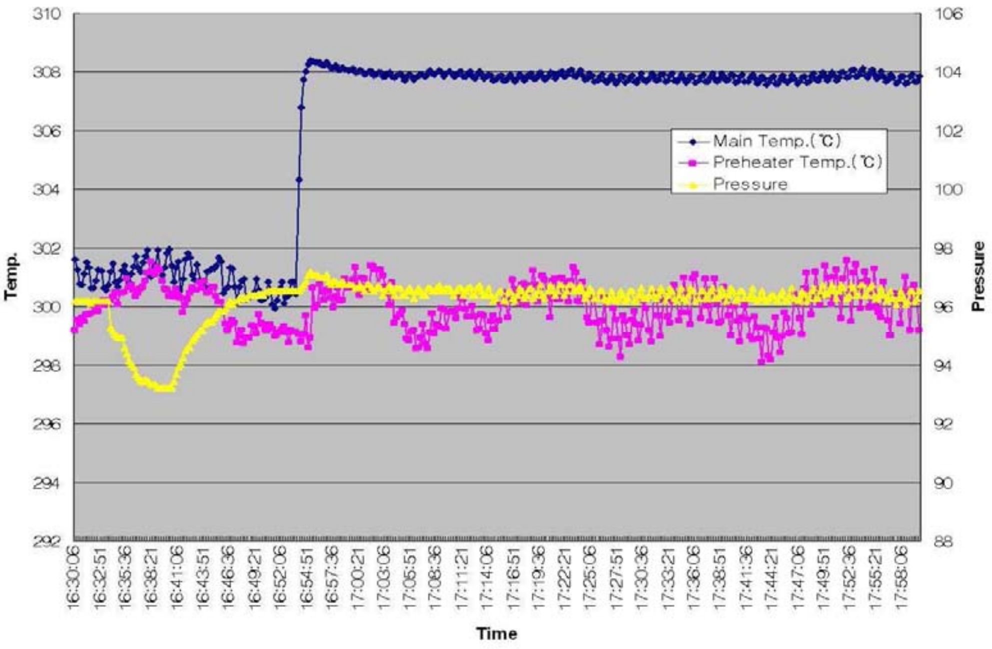


FIG. 6.10. Temperature and pressure change during the crud deposition test.

The quantity of deposited crud is different for the 3 sections of the test tube as shown in Fig. 6.11. More crud was deposited for the section with higher sub-cooled boiling.

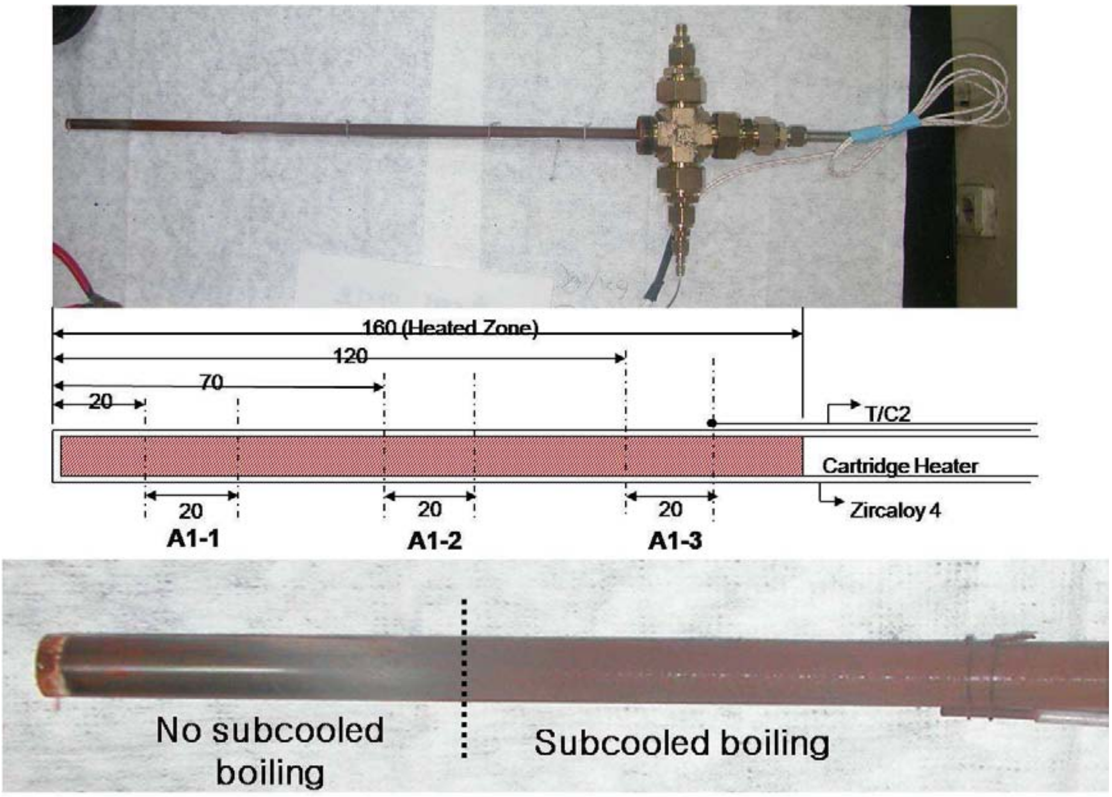
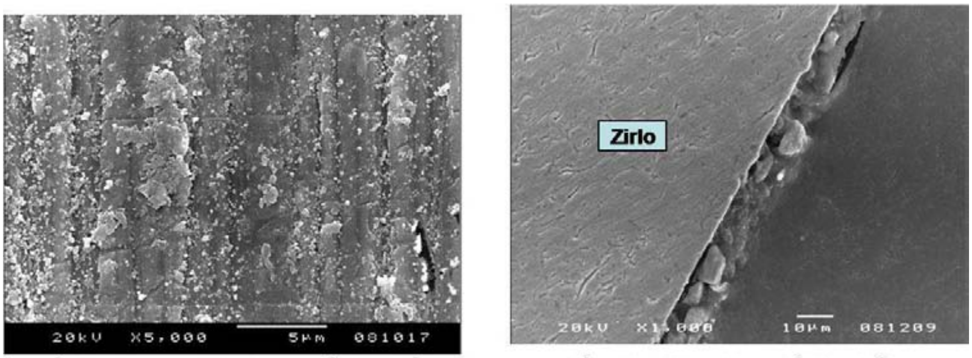
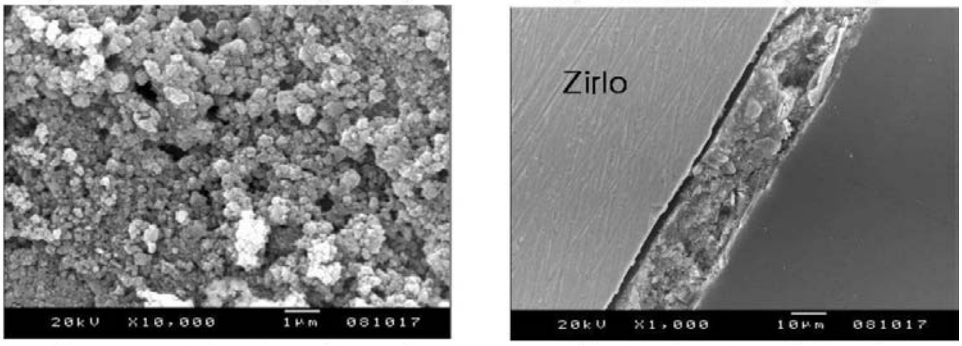


FIG. 6.11. Crud deposition variation along the test rod (comparison of non sub-cooled boiling and sub-cooled boiling).

The surface morphology of deposition for the A1 test of very high Ni, Fe concentration of 20 ppm is shown in Fig. 6.12. The deposition has a porous structure and the thickness of the deposition is about 15–20 µm.



a) External Surface (A1−1) b) Cut Surface (A1−1)



c) External Surface (A1−3) d) Cut Surface (A1−3)

FIG. 6.12. Surface with SNB of A1-3 by SEM after 5 day test.

The effect of Ni and Fe concentration on the amount of crud deposition is shown in Fig. 6.13. The effect of concentration on crud deposition is clear, comparing the two experiments in Fig. 6.13, A2 (200 ppb) and A1 (20 ppm). The amount of deposit is much larger in the test with the higher concentration of Fe and Ni concentration (A1).

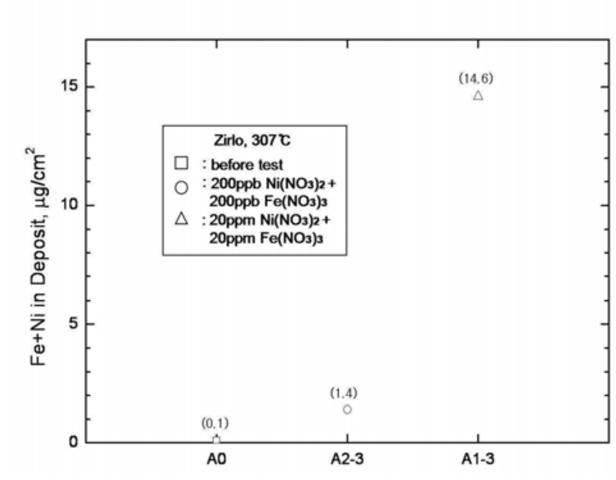


FIG. 6.13. Effect of Ni- and Fe-nitrate concentration on surface deposit in solution containing 1.5 ppm Li as LioH and 870 ppm B as H_3BO_3 (5 day test).

In Fig. 6.14, the surface morphology of 3 different sections from the A3 tests is shown. About 10 µm of deposit was formed on the surface. The surface crystal formation is not clear for the area of no sub-cooling (A3–1) in contrast to the crystallite formation seen in the area of sub-cooling (A3–2, A3–3). Sub-cooling significantly influences the crud deposition behaviour.

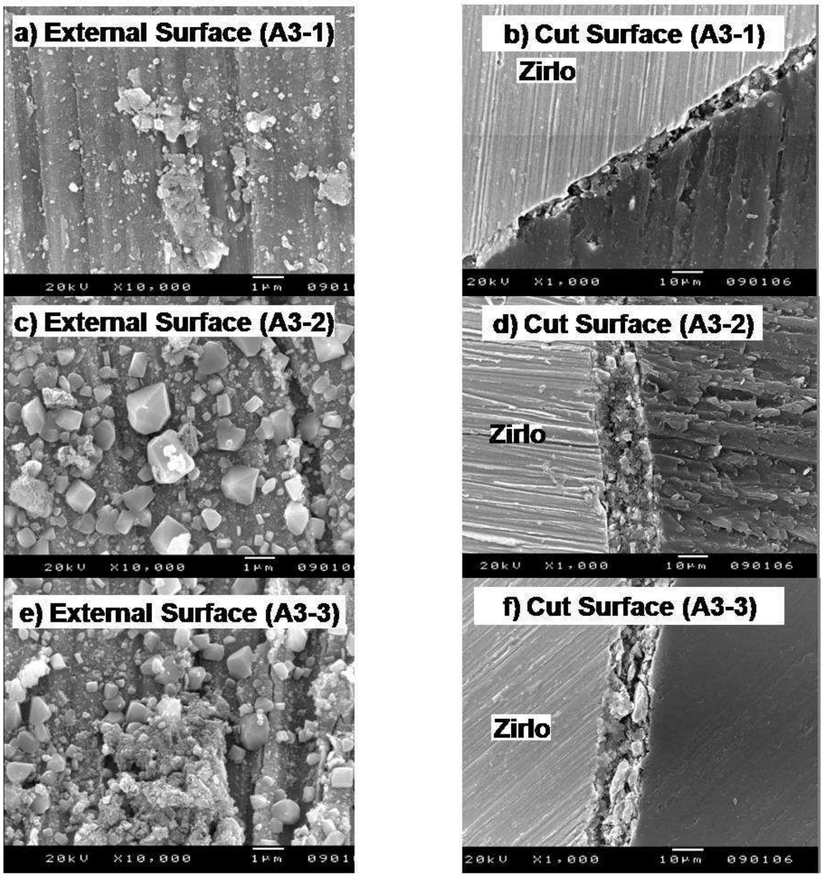


FIG. 6.14. Surface morphology of various sections of A3 by SEM after a 28 day test.

The effect of pH on crud deposition is shown in Fig. 6.15. As pH increases, the amount of deposition decreases. The amount of deposit (2.8 $\mu g/cm^2$) in the A7 test (pH: about 6.8) was more than 5 times the amount of the deposit (0.5 $\mu g/cm^2$) in test A6 (pH: about 7.2). The pH effect on deposition is similar to the results of other studies [46].

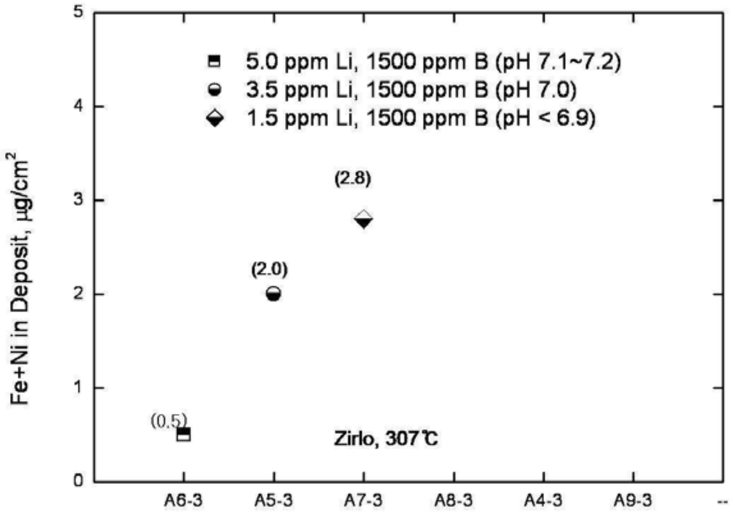


FIG. 6.15. Effect of pH variation (ICP-AES results on surface deposit for specimens after 14 day tests in solution containing 2 ppm Ni and Fe acetates).

A Japanese study considering micro-layer evaporation as the mechanism for nuclear boiling (dry out) allows a prediction of iron crud deposition on boiling surfaces of BWR fuel rods. This has been extended to apply to metallic ion deposition, affected by chemical forms of the deposits. The deposition rate decreases when the flow rate increases but increases with the pressure. The deposition rates can be applied to an evaluation of soluble and insoluble species on the fuel surface and also to determine the local pH caused by local concentration of chemical species.

The calculated deposited boron amount is one or two orders larger than the deposited corrosion product. The average residence time of 1 through 10 min results in a slight increase in boron concentration factor. It is difficult to evaluate the deposit during operation and the hide out return is unknown.

Another Japanese study was related to crud deposition on Zr-4 surface. No CIPS has been seen in Japanese units. Tests have been performed with various pH_T values (7.2, 7.3, and 7.7). The crud layer analysis respectively showed 10–25 and 35 µg/kg Ni with Ni/Fe ratio either >0.5 or <0.5. Fe and Ni may easily be enriched in the deposit which is increasing with the heat flux. During the various tests, Zr-4 corrosion resistance was maintained.

The Swedish project studied the characteristics of PWR fuel crud and possible impact on CIPS. Metallic nickel has been found in fuel crud samples. Mixed oxides are $(Cr_xNi_yFe_z)_3O_4$, Cr_8O_{21} containing Cr^{III} and Cr^{VI}, and thus oxidizing. Plant parameters have been looked at to evaluate the reason for the abnormal ^{58}Co increase and focused on shutdown (mixed oxides) and H_2O_2 injection (more iron oxide). The crud varies from plant to plant, for various materials but it is not clear if pH and H_2 have an influence.

The essential parameters required for CIPS are:

- SNB with local heat flux, fuel power, core design, fuel management;
- Boron, with Li, pH and chemistry regime;
- Crud, with corrosion rate, surface area, cycle length, crud clean up, crud characteristics.

It is considered that much of the crud is released during shutdown, explaining a critical influence of the cycle length. Boron is supposed to be in crud as bonaccordite $NiFeBO_5$. Under SNB, LiB_4O_7 may be seen and also H_3BO_3 and B_2O_3. Alloy 600 induces higher Ni content in crud than Alloy 690 and even more than Alloy 800, corresponding to the Ni content of the steam generator tubing. The pH is supposed to have a limited effect in the short term due to the prevailing Ni effect; in the long term it may affect the corrosion rate and thus the crud amount. EBA (Enriched Boric Acid, higher concentration of ^{10}B isotope) is considered of marginal influence.

Depending on the PWR power and history, the characteristics of PWR fuel crud, in terms of crud composition, thickness and evolution, could be plant-specific. In some high duty power plants with considerable SNB, the crud may be very thick (e.g. Callaway PWR with AOA problem). In low or medium duty PWRs, the reported crud thicknesses are generally thin. It has been noted that for the same PWR, fuel crud elemental composition varies with crud sampling position along the fuel bundle height, and with fuel cycle and burn-up (Fig. 6.16, Table 6.4). It is likely, yet unconfirmed, that fuel crud phase composition may also depend on crud sampling position along fuel bundle height, fuel cycle and burn-up.

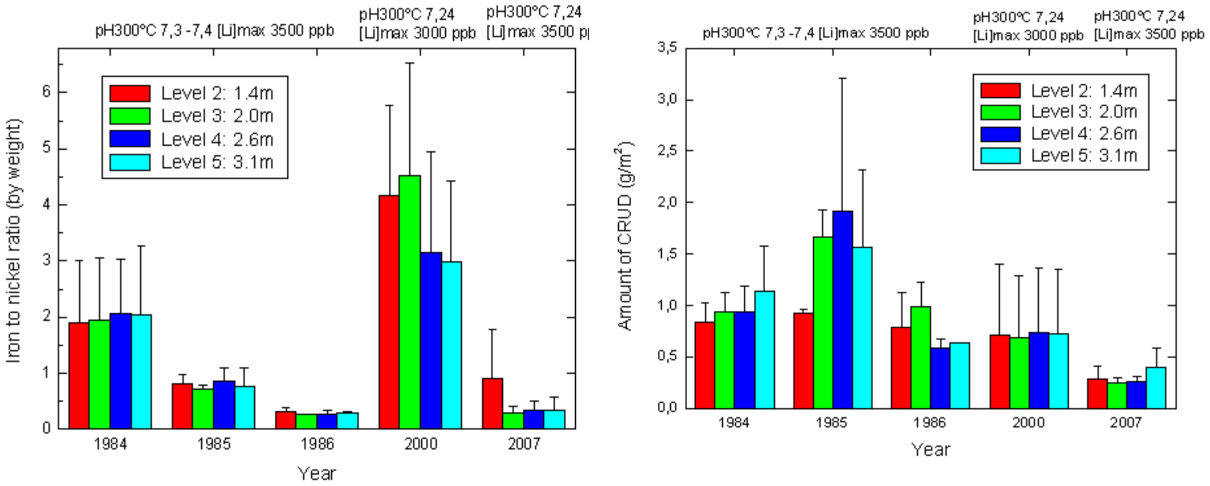


FIG. 6.16. Crud quantities and composition at different axial locations. Iron to nickel weight ratio of fuel CRUD at different axial locations for the once-burnt fuel rods (left) and amount of fuel CRUD at different axial locations for the once-burnt fuel rods (right). Only Ni, Fe, Cr, Mn, Co, Zn and Cu masses are included.

Some PWR operations, such as shutdown and H_2O_2 injection may have some impact on the composition and thickness of fuel crud. It has been confirmed that during the shutdown and H_2O_2 injection operations, some unexpected solid phases such as NiOOH are found in fuel crud samples, which is an indication that the elevated potential of reactor water could lead to a change in the stability of some solid phases. Therefore, what is seen in the fuel crud samples after shutdown is not representative of crud under normal reactor operation conditions.

TABLE 6.4. ESTIMATED PARTICLE SIZE AND ABUNDANCE OF PHASES SEEN IN FUEL CRUD

Phase	Size (nm)	Abundance	Determined with
Ni (metal)	Ø50	<5%	SAED + EDS
NiOOH	Ø10	<5%	SAED + EDS
Ni-rich oxides	Ø50	<10%	EDS
$(Cr_xNi_yFe_z)_3O_4$ (x=0.1-0.4; y=0.2-0.6; z=0.6-0.9)	Ø20	Approx 60%	SAED + EDS
Fe_3O_4	Ø100-150	<5%	SAED + EDS
FeOOH	Ø15-150	<5%	EDS
Cr_8O_{21}	Ø50	<5%	SAED + EDS

***Note**: Selected Area Electron Diffraction (SAED), Energy Dispersive Spectrometry (EDS).*

There have been few reported cases of crud induced cladding failure for PWRs. However, there has been an increased concern about the elevated dose rate due to formation of an increased amount of fuel crud on cladding surfaces. There are also an increased number of reported CIPS cases, probably due to the formation of an increased amount or unfavourable type of fuel crud. The CIPS occurrence is often associated with high duty cores and steam generator replacement. The latter is often accompanied by replacing with a nickel based alloy (such as Alloy 690) with improved corrosion resistance, but it is not uncommon for the new steam generator to have a much larger water contacting surface area, which would basically lead to the formation of a similar amount of corrosion products in the reactor water.

6.1.3. WWER systems

Three cases of corrosion product deposition on fuel surfaces in WWERs are known. These have all been in WWER-440: NPP Loviisa, Paks and older Russian units. In all cases, pressure losses in the active zone increased during the fuel cycle. The dependence of the deposition rate, inferred from the pressure loss trend, was not influenced by pH (if the influence of pH was observed, the results were not reproducible). The influence of pH on the formation of deposits does not correspond to transport activity models heretofore developed.

Up to now, observations based on post-irradiation evaluation of fuel elements have confirmed crud deposition on grids as well as on fuel. In the case of grids, the deposition takes place on both stainless-steel as well as zirconium ones. The crud on the grids has a crystalline appearance – crystals growing out of the inner surface of the grid against the surface of the fuel, thus against the direction of high coolant flow, causing increasing pressure losses. The crystals appearance confirms the possible substance transport mechanism, which is crystallization.

There are differences in the incidence of failed fuel elements as a result of crud deposition. In the case of the Paks NPP, failed elements were not observed. Corrosion layers in all NPPs are unique in their character and reflect they history of each block's chemistry (memory effect).

Pressure loss during a campaign is the only parameter that can provide information regarding deposition on fuel surfaces during operation. This cannot be determined from measurements of the concentration of iron or other corrosion products. The value of the pressure loss, however, only gives information about a certain point when corrosion layers reach a critical value. Pressure loss won't give us information about deposition that exists below this point. In the case of the Loviisa and Paks NPPs, problems with increased pressure loss were eliminated after the removal of affected fuel elements from the core.

Long term loop experiment carrying on the NRI Řež is focused on the decontamination processes and their dependences on the primary components' surface layers. It is proved that used decontamination method satisfactorily removed activated crud and additional flushing doesn't entirely destroy the oxide passivation layer. Whilst the decontamination compounds' remainders (especially carbon) are flushed off. Recontamination process could be slowed with short time layers' re-passivation.

6.2. Elimination

The elimination of crud and deposits from the primary circuit surfaces is considered to be beneficial and advisable in order to decrease:

- future occupational dose exposure during operation and maintenance periods,
- future risk of CIPS associated with corrosion product transport.

However, such an operation is time consuming, expensive, includes severe risks of corrosion and induces a large quantity of undesirable LRW. It is important to thoroughly evaluate the advantages and drawbacks of such an operation before applying it.

Chemical decontamination has been mainly considered for WWERs where crud deposition can affect coolant flow, while the CIPS and dose rate mitigation has mainly been a problem for PWRs and such decontamination of fuel assemblies is not usual, though ultrasonic cleaning has been used at some plants. Decontamination using concentrated solutions leads to relatively high surface roughness on the treated surfaces, characterized by more intensive corrosion and carryover of its products, which causes a tendency towards high radioactive contamination of the surface and high rate of subsequent reactivation. A higher carryover rate after deactivation is the root of the problems encountered at the Paks NPP and the Novovoronezh NPP, and to a smaller degree at the Loviisa NPP Unit 2, where more intensive corrosion and carryover of its products led to growth of deposits on the fuel.

The Czech laboratory of NRI performed loop tests that demonstrated the capability of decontamination for eliminating corrosion products and also tests showing the beneficial effect of surface preconditioning. It was concluded that practical methods to control crud formation are accurate primary water chemistry, a careful decontamination and a surface layer passivation. However, decontamination is only needed in the event of refurbishment of any important component that requires a drastic decrease of dose rates to allow such significant maintenance activities. The difference between WWER-440 and WWER-1000 was noted, with coolant temperature ranges for the two plant types of 269–295°C and 289–322°C respectively.

One of the purposes of decontamination is to remove the radioactive deposits which can represent a danger to plant workers. Decontamination of plant components which are intended to be returned to service should avoid any damage to materials exposed to the process. Chemical decontamination procedures using organic acids such as oxalic and citric acids performed on steam generators, which constitute most of the surface of the primary circuit, is therefore the most probable cause for increased corrosion product formation elimination.

Chemical decontamination procedure can also lead to operational problems. Precipitates of organic salts with metal cations are formed during decontamination on the steel surfaces and with the standard cleaning procedure at the end of the decontamination procedure, these are not fully eliminated. Moreover, the steam generators are open to air-saturated aqueous solutions during a certain period of time prior to subsequent operation. Consequently, amorphous corrosion products, such as hydroxides, remain on the steel surfaces. Insufficient treatment (passivation) of these surfaces and secondary deposition of existing corrosion products can create additional amounts of corrosion products, which are then redistributed throughout the entire primary circuit (Fig. 6.17).

In the Czech Republic there is operational decontamination experience from Dukovany NPP (Temelín primary circuits have never been decontaminated). During the period of 1988/2005 34s steam generators decontaminations were carried out at Dukovany NPP - the majority of them during the 1990s.

No significant problems with recontamination have been indicated for WWER reactors. This may be partly because overall personnel doses are very low, and thus a dosage increase in tens of percent is practically indistinguishable. Great differences in recontamination exist, where some power plants (Dukovany, Novovoronezh) exhibited recontamination, whist others (Loviisa, Paks) have exhibited none.

The NRI, Řež experience from the operation of WWERs and the experimental loop RVS-4, which was used for decontamination studies, showed these that the final effect of decontamination depends on the correct implementation of the different decontamination steps. For example for the AP-CITROX method requires: alkaline mode, acid mode, peroxide mode, ammonia mode, flushing after each mode and the final flush. The biggest effect on the overall result of decontamination is believed to be the flushing between alkaline and acid modes and flushing after the acid mode. Where there is insufficient flushing during decontamination, a higher content of carbon was found in the corrosion layer after exposition. The corrosion layer thickness was almost doubled.

The Hungarian investigation was carried out after the Paks incident which caused severe fuel damage in a fuel cleaning tank in the reactor pond.

They found that absorption of actinides on stainless steel surfaces was significant. Actinides are found as micron sized particles or as colloids. Cm is mainly in the form of particles (~µm size) and colloids, while Pu and U are mainly in the form of cationic species, and Cs is also found bound to these particles.

There were radioactive corrosion product deposits on in-core and out-core surfaces. No corrosion problems have been observed on Paks Unit 4 which has never been decontaminated.

A study of the circulation of particulates in the primary coolant showed that the residence time in core of particles is < 1 day for particles from the steam generator, 1–7 weeks for particles migrating with the coolant and ¼ to ½ year for particles from the fuel assemblies. These studies on particles have given a better understanding of contamination/decontamination, corrosion and transport of elements.

The Russians developed a model with different parameters (power, boron concentration, redox-potential, CC) to explain the observed rise in the in-core pressure drop and the redistribution of deposits in the core and in the primary circuit of WWER-440 NPPs. The physical-chemical basis of the model is the dependence of transport corrosion products on the temperature and pH_T of the coolant, and the correlation between rates of corrosion products (Fe) formation (after steam generator decontamination) and their removal from the circuit. The deposits along the fuel rod induce SNB and result in an acceleration of corrosion product and boron precipitation on the fuel cladding surface, and an increase of coolant radioactivity. ^{58}Co is the indicator of the acceleration of the growth of deposits.

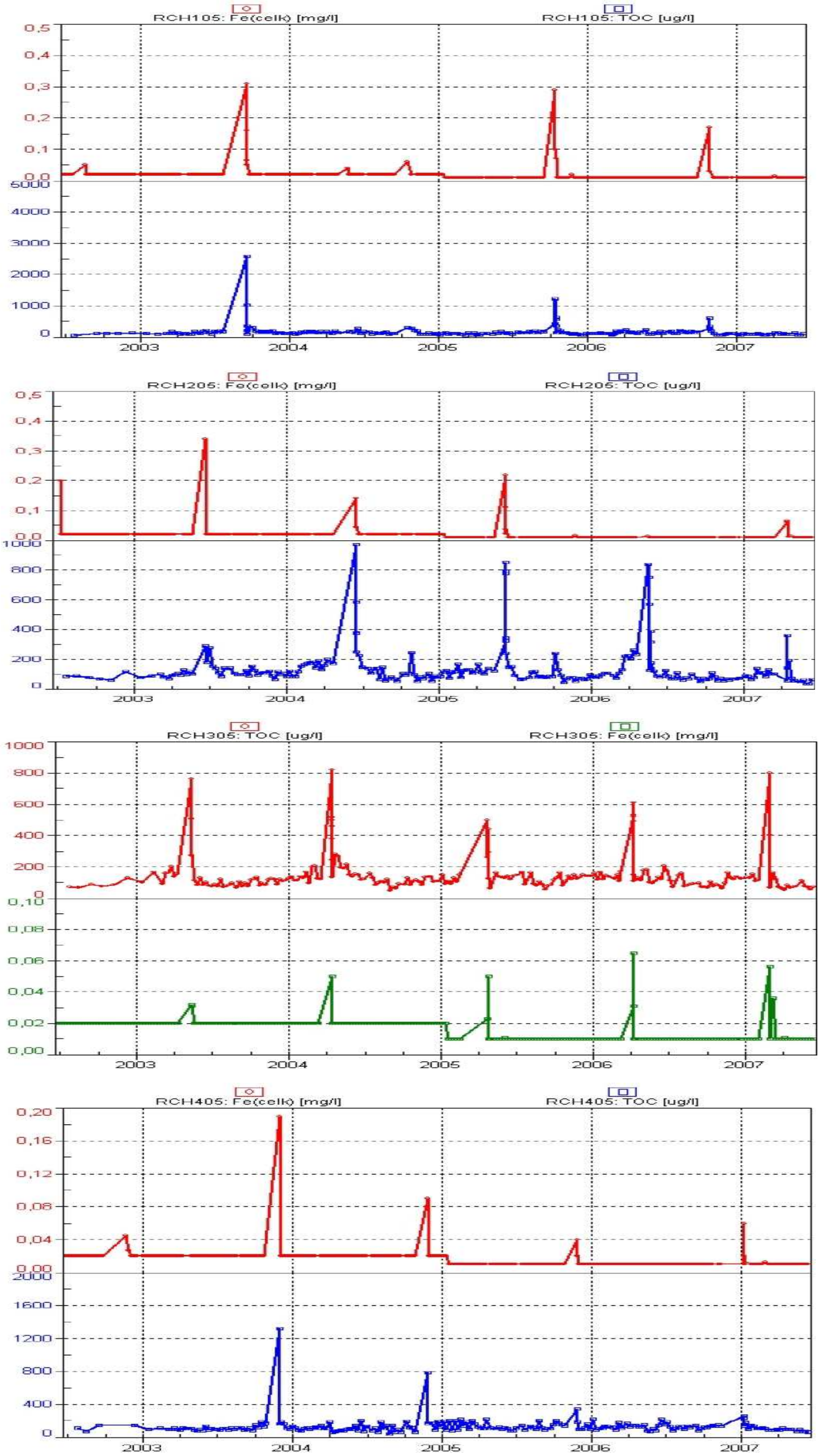


FIG. 6.17. Concentration of Fe and TOC in primary coolant of NPP Dukovany unit 1–4.

The Indian Laboratory evaluated the feasibility of a high temperature decontamination process for the removal of fuel deposits. They showed that crud deposition and formation on core internals are unavoidable, and whilst crud needs to be minimised, high temperature oxide dissolution with a single reagent such as nitrilo-triacetic acid (NTA) derivative was shown to be very effective. There is a considerable increase in the dissolution rate of Fe_3O_4 in NTA with temperature. The dissolution rate of $Ni_{0.2}Fe_{2.8}O_4$ was comparable to that of Fe_3O_4. Even the normally stable oxide Cr_2O_3 can be dissolved to an appreciable extent at high temperature (160°C). An NTA formulation containing N_2H_4 at high temperature was found to dissolve the oxide formed over SS-304 very efficiently. The addition of N_2H_4 to NTA (near neutral pH) reduces the corrosion rate of base metal. However, it also reduces the oxide dissolution rate, though within acceptable range. Zinc ferrite could be effectively dissolved. The process can be tuned for PWR fuel surfaces by implementing zinc addition. Magnesium ferrite dissolution was significantly lower than zinc ferrite, indicating its utility for passivation and in reducing flow accelerated corrosion. Bonaccordite could be effectively dissolved. High temperature chemical decontamination can be effective in mitigating CIPS.

PHWRs in India are adopting a full primary system chemical decontamination to reduce the radiation field. Decontamination is carried out with fuel in the core. Even though the focus of chemical decontamination is removal of radioactive contaminants fixed on the out-of-core surfaces, the removal of deposits from the core Zircaloy /fuel surfaces has significant effect in reducing the recontamination of the system subsequent to chemical decontamination. Some PWRs adopting an extended fuel cycle have attempted to chemically dissolve the fuel deposits that cause CIPS. Hence, an attempt was made to evaluate an improved chemical decontamination method that would be effective in removing the oxides transported from the out-of-core surfaces and deposited over the fuel and other Zircaloy surfaces.

Normally, chemical decontamination is carried out at temperatures < 100ºC. However, it has been observed that if the temperature of decontamination is increased to 140–180ºC, the effectiveness of dissolution of certain oxides such as nickel ferrite, zinc ferrite, bonaccordite and chromites, that are known to resist the dissolution in organic chelating media, can be improved significantly. Since the choice of chelants and their concentrations is limited due to various factors, high temperature dissolution is a way to solve this problem. It is well known that dissolution of steam generator sludge is carried out at high temperatures. In this context, experiments have been carried out to evaluate the effectiveness of nitrilo-tri-acetic acid in dissolving oxide deposits at 160ºC.

Fig. 6.18 clearly indicates the effect of temperature in enhancing the rate of magnetite dissolution by temperature. Fig. 6.19 shows that chromium oxides, which normally require oxidative pre-treatment, could be solubilised with a high temperature, single stage chemical decontamination

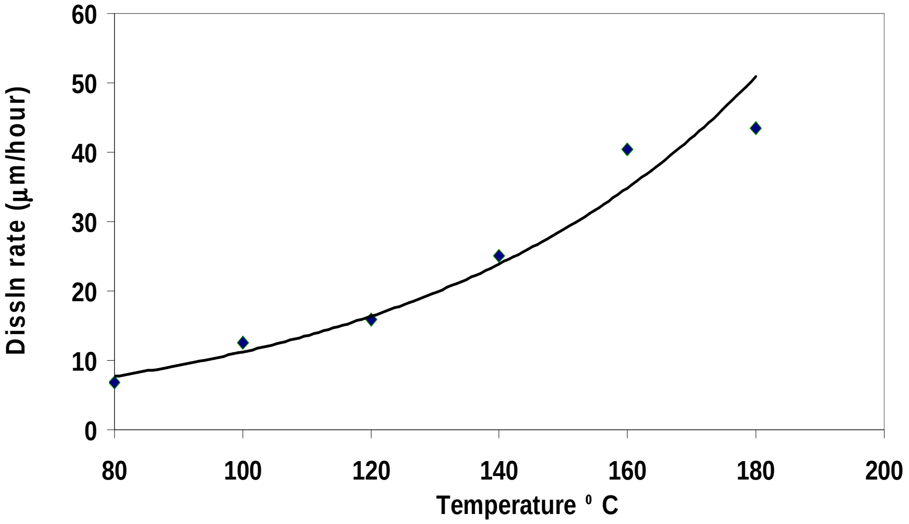


FIG. 6.18. Dissolution rate of magnetite pellets as a function of temperature.

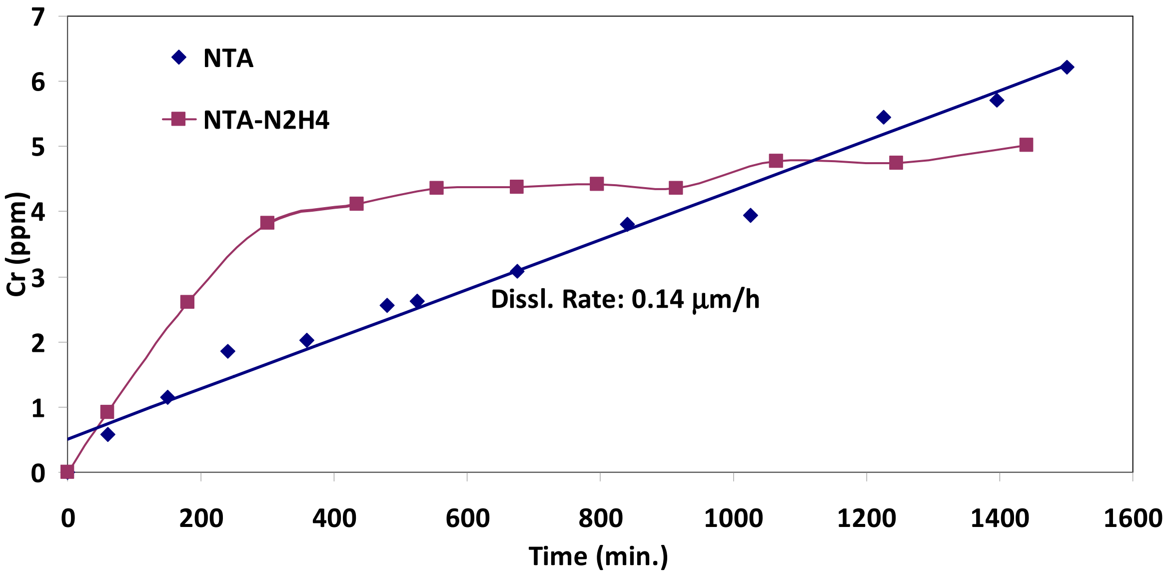


FIG. 6.19. Dissolution rate of Chromia at 160°C.

The high temperature dissolution rate of various synthetically prepared oxides is given in Fig. 6.20. It shows the potential of this process to address the CIPS problem. Periodic chemical cleaning of in-core components at the EOC will enable minimization of CIPS.

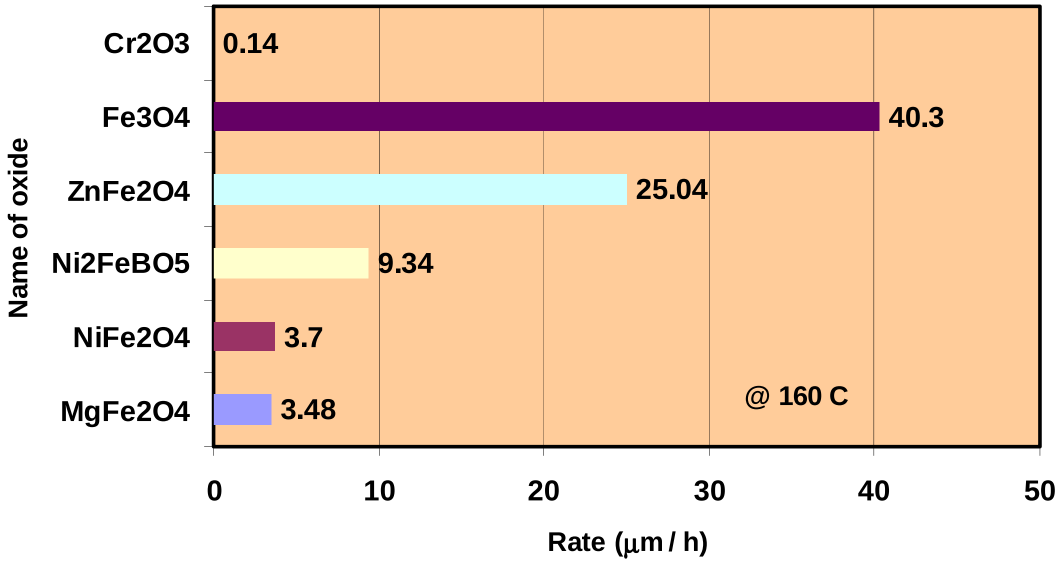


FIG. 6.20. Dissolution rates of prepared oxides.

While addressing the dissolution of oxides from core internals, it is necessary to demonstrate material compatibility of different reactor materials with the dissolution formulations at high temperature. Stainless steels and zirconium alloys are not affected by the formulation whilst carbon steel is subjected to enhanced corrosion relative to SS depending on the pH of the medium (Fig. 6.21).

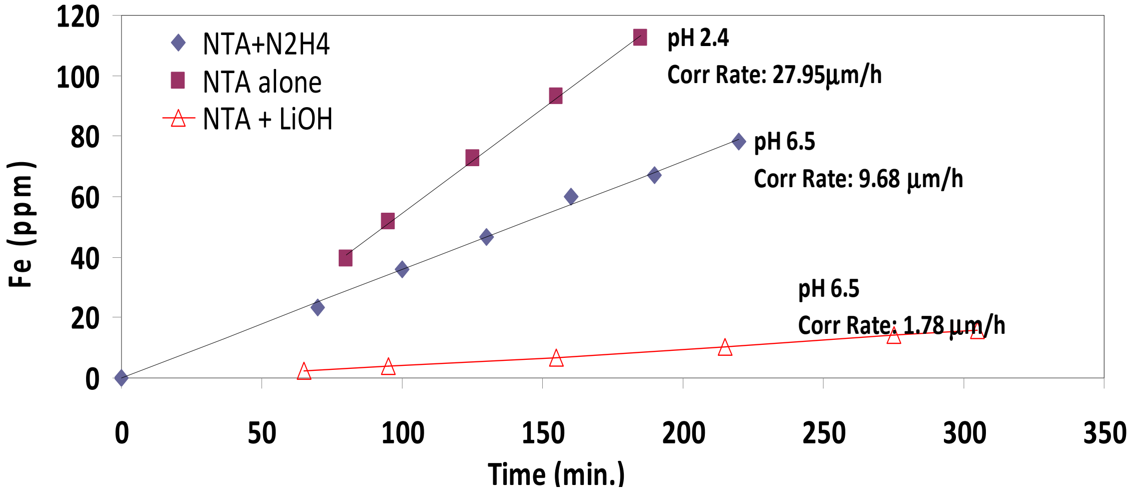


FIG. 6.21. Corrosion of carbon steel in decontamination solution.

In conclusion, the kinetics of high temperature dissolution shows that the methodology of using periodic high temperature dissolution of crud bearing Ni and B could be carried out to minimize the effect of CIPS.

6.3. Mitigation

For the latest Czech and Slovak stations commissioned (Temelín and Mochovce) a modified hot functional test (HFT) chemistry was developed in the NRI Řež in order to mitigate crud formation during operation. This procedure was designed to produce a better initial chromium rich passive layer and to prepare the commissioned unit for the proper water chemistry practise. The revised recommendations for the HFT chemistry included e.g. $pH_{300°C}$ 6.9–7.5, KOH dosing and hydrogen. The target HFT temperature was 260ºC for Mochovce and 285ºC for Temelín. Mochovce 1 was the first station commissioned using these recommendations, and it was also used at Mochovce 2 and Temelín 1 and 2. Samples indicated that duplex oxide layers up to 20 µm thick were produced, which were mainly magnetite substituted with nickel and chromium (e.g. 60–65% Fe, 18–28% Cr, 9–12% Ni, <1% Mn and 1–2% Si on a stainless steel primary circuit sample).

The operation of the Czech WWER at Temelín, after initial passivation, showed a low level of corrosion products in the primary system as well as low dose rates during the 5th and 6th fuel cycles. Thus, there is no need for any decontamination. Temelín-1 is operating with 20 mg/kg of K corresponding to a pH_T of 7.1±0.1. The passivation process used during hot tests at NPPs Temelín and Mochovce has been shown to be insufficient when this method (hot test) was used on decontaminated steam generator tubes. The surfaces of these tubes were not passivated. Decontaminations had led to changes in the surface composition in comparison to the as manufactured surface. So, there is a need to prove the preconditioning method of surface passivation for each type of material used in operation (steam generator tubes) and it cannot be presumed that following decontamination that steam generator tubes will return their surfaces to an original state.

6.4. NPP feedback

Crud samples from several Republic of Korean units (mainly from units U-b and Y-a) were investigated. The burn-up history of the samples and the sampling methods are listed in Table 6.5. Crud samplings were carried out by various methods such as tapping, smearing, and scraping of cladding surface. Some claddings were cross-sectioned to observe the microstructure variation across the thickness of the crud. The crud samples were analyzed by SEM, EDS and EPMA. Crud has not been investigated systematically in the Republic of Korea and the crud data shown are collected results from various scattered sources in Korean institutes. The crud data are usually produced as a subsidiary work of post irradiation examination of burn-up fuel performance. Some samples (B, C, D and E in.) were prepared from the crud collected in filtering system after an ultrasonic cleaning of FA in U-b unit.

The surface morphology of the fuel cladding A of unit U-b along the tube axial direction is shown in Fig. 6.22. The presence of crud on the fuel cladding is reflected in the variation of surface colour of the fuel cladding. In the upper part (above 2500 mm from rod bottom) of fuel cladding, the colour is becoming dark black compared with the white gray colour of the lower part.

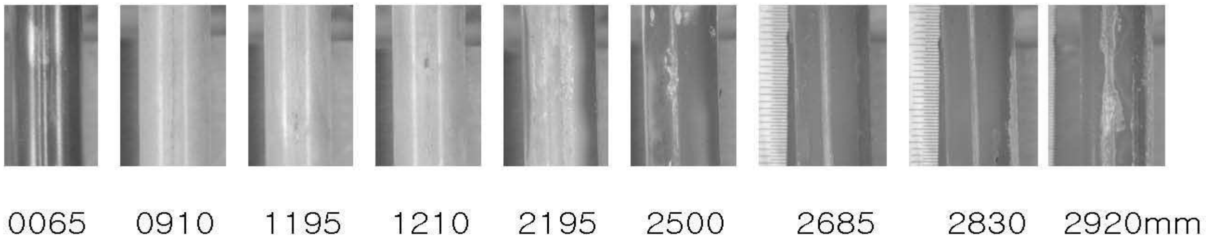
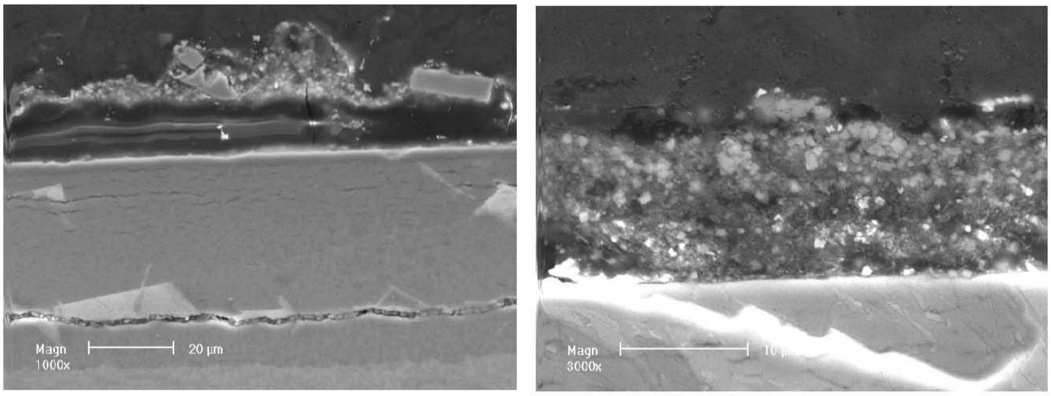


FIG. 6.22. Surface morphology of the fuel cladding A of U-b unit along the tube axial direction.

TABLE 6.5. BURN-UP HISTORY OF THE SAMPLES AND THE SAMPLING METHODS OF CRUD

Units	Fuel rods	Burnup (MWd/tU)	Cycle	Sample	Location (mm)	Fuel mat.	T_{in}	T_{avg}	SG mat.	pH	AOA
Y-a							291	310	600TT	6.9~7.4	
	A	40 531		Tapping, Cross section	400, 3000	Zr-4					No
	B	53 754		Smear paper	500, 3300	Zr-4					No
	C	52 961				Zr-4					No
	D	55 247		Tapping	410 ~3230	Zr-4					No
	E	50 111		Scraping	3000	Zr-4					No
Y-b							291	310	600TT	6.9~7.4	
Y-c							292	308	600HT MA	6.9~7.4	
U-b							285	305	600TT	6.9~7.4	
	A	50 494	8,9,10	Tapping, Cross section		Zr-4					Occurred
	B	41 996	10,11	Ultra. Clean.		Zr-4					Occurred
	C	41 996	10,11	Ultra. Clean.		Zr-4					Occurred
	D	44 994	12,13	Ultra. Clean.		ZIRLO™					No
	E	44994	12,13	Ultra. Clean.		ZIRLO™					No

The crud on the upper part of cladding A of unit U-b is shown in Fig. 6.23. Crud is usually deposited in scattered local areas below 3300 mm from bottom as shown in (a) of Fig. 6.23. At above 3300 mm as shown in (b) of Fig. 6.23 crud is usually deposited uniformly around the cladding tube surface. The crud thickness at 3300 mm is about 10–15 µm. The crud layer was mixed with large particles of sharp edge and small particles. In the lower part below 2500 mm, crud is rare and not observed easily on the fuel cladding [47].



a) At 2851mm b) above 3300mm

FIG. 6.23. Crud in the upper part of fuel of fuel cladding A of U-b unit.

The cross section of the fuel cladding A in Y-a unit at 2975 mm is shown in Fig. 6.24. Crud is deposited around the fuel cladding. The thickness of the crud is measured about 5–15 µm.

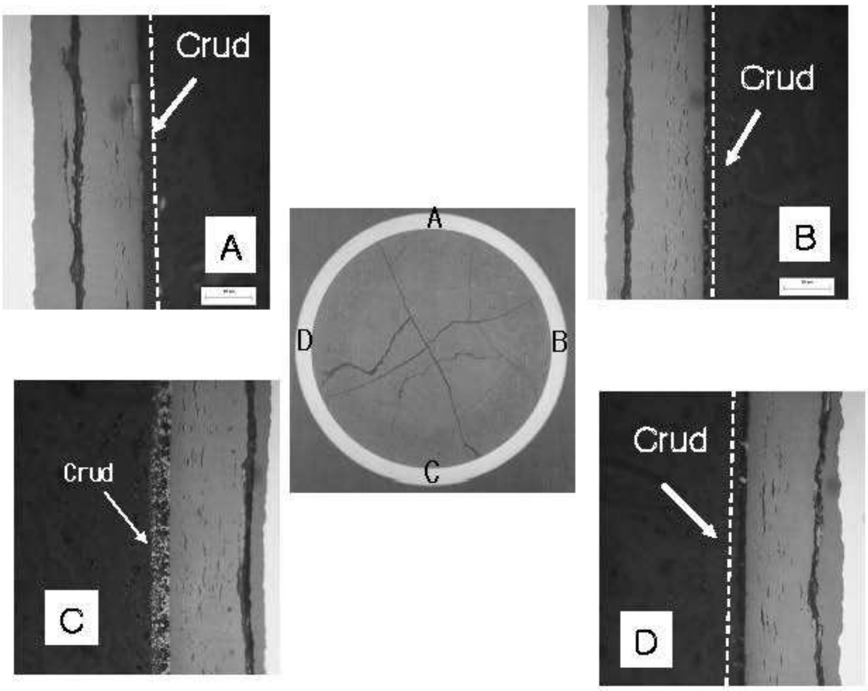
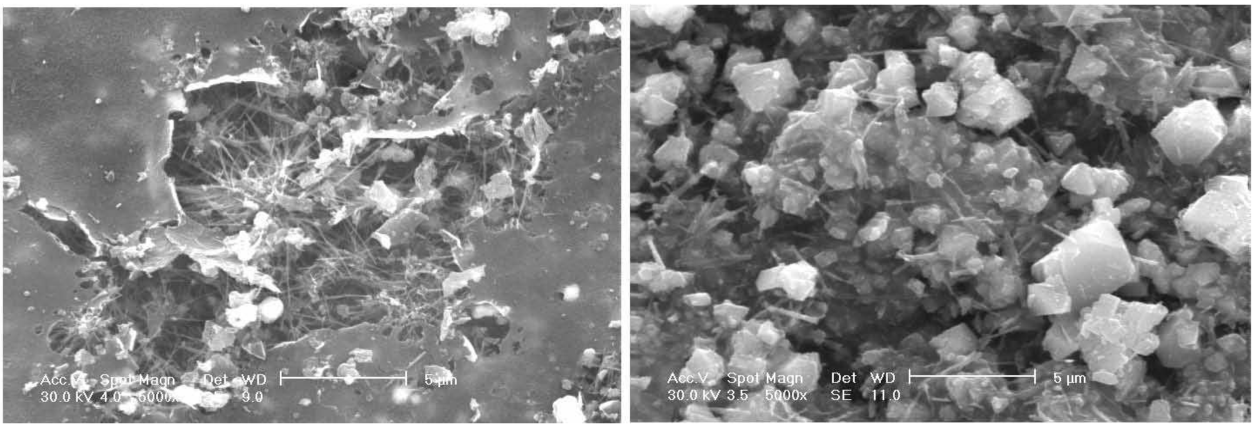


FIG. 6.24. Crud in the upper part at 2975 mm of fuel cladding A of Y-a unit.

The morphology of two cruds (from U-b and Y-b) sampled by tapping method is shown in Fig. 6.25. The morphology of the surface crystals is quite different from each other. The crud from U-b has many needle-shape crystals mixed with relatively large grains. However, the crud from Y-b has comparatively large sharp edge crystals mixed with small grain particles. The crud of Y-b also has needles. But the numbers are very few. We have no information for the phase identification, but based on other work [48] the needles seem to be NiO whiskers. Further work is needed to identify if the morphology difference between the two cruds (from U-b and Y-b) is typical.



U-b, 3200mm

Y-b, 3200mm

FIG. 6.25. Crud morphology sampled by tapping method from the cladding of two Korean units (U-b, Y-b units).

The variations of the composition of crud on fuel cladding A of the Y-a unit along the tube thickness are shown in Figs 6.26–6.27. The composition of the crud is basically Fe, Ni and O as shown in Fig. 6.26. The composition of the points identified in Fig. 6.27 is listed in the accompanying Table in that Figure. In the points (1–3) near the interface of crud and water, the Ni/Fe ratios are about 0.5. In the points (4–7) near the interface of the Zircaloy and crud, the Ni/Fe ratio is relatively large because of the Zircaloy component's interference.

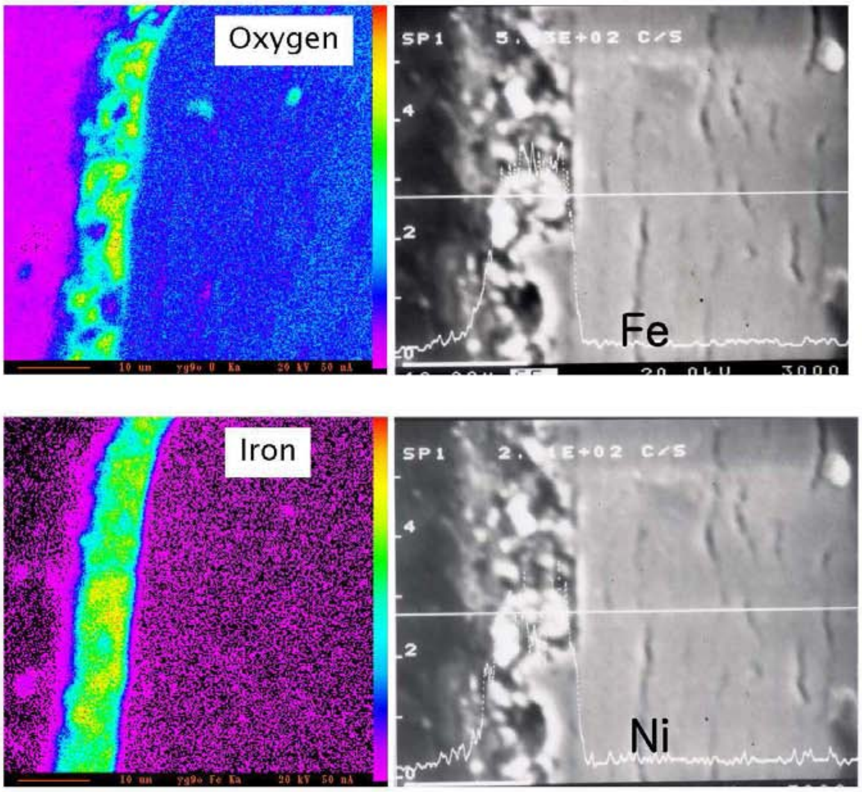
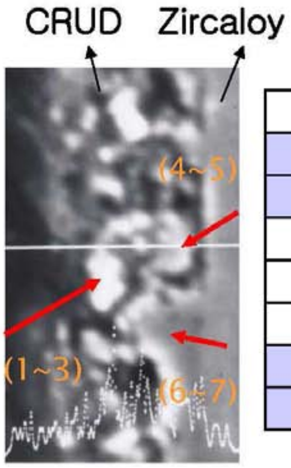


FIG. 6.26. Fe, Ni and O concentration of the crud on the fuel cladding A of Y-a unit along the tube thickness.



at%	O	Fe	Ni	Cr	Mn	Ni/Fe
#1	47.407	33.468	17.418	0.836	0.693	0.52044
#2	47.337	33.843	16.939	1.086	0.602	0.50052
#3	45.708	34.901	17.702	0.664	0.762	0.50721
#4	81.586	11.415	6.154	0.11	0.31	0.53912
#5	69.633	18.837	10.563	0.141	0.586	0.56076
#6	56.3	27.671	15.181	0.579	0.162	0.54862
#7	62.329	23.077	13.635	0.385	0.251	0.59085

FIG. 6.27. Composition of the crud on the fuel cladding A of Y-a unit at various points along the tube thickness.

The composition along the line scan direction for the fuel cladding (A of U-a) is shown in Fig. 6.28. The crud layer is divided into three layers (inner, middle and outer layer) based on the O/Fe ratio. The O/Fe ratio of the middle layer (4–11 µm) is about 1.5–2.0. The Ni/Fe ratio of the middle layer is about 0.5. It is quite reasonable to conclude that the middle layer is mainly $NiFe_2O_4$ (Ni:Fe:O=0.5:1.0:2.0). Towards the outer layer, the Ni/Fe ratio and the O/Fe ratio increase. It seems that the outer layer is composed of other oxide phases besides $NiFe_2O_4$.

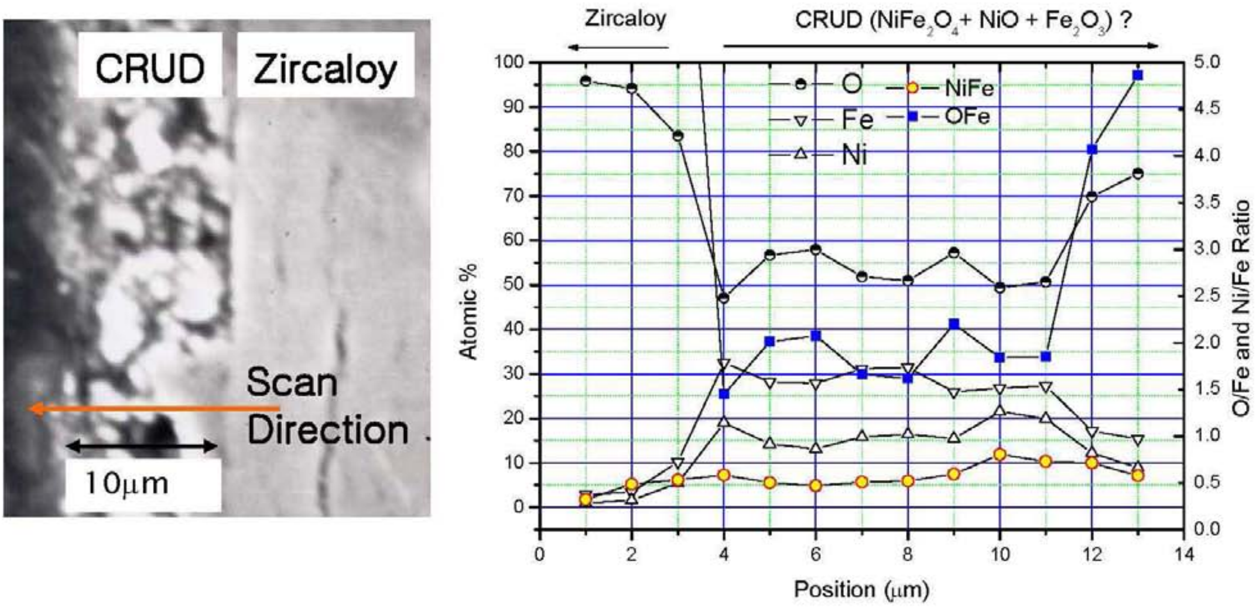


FIG. 6.28. Composition and Ni/Fe, O/Fe ratio of the crud on the fuel cladding A of Y-a unit along the tube thickness.

In Table 6.6, the composition of the out-most crud on the fuel cladding A of Y-a prepared by tapping method is shown. The Ni/Fe ratio is about 0.9. The Ni content is highest in the outermost surface which interfaces with the primary water.

TABLE 6.6. THE COMPOSITION AND NI/FE RATIO OF CRUD FROM CLADDING A, UNIT Y-A PREPARED BY TAPPING

Points	1.0	2.0	3.0	4.0	5.0	Average
Cr	2.1	1.7	2.3	2.7	1.4	2.1
Fe	50.5	52.6	50.8	48.0	54.8	51.3
Ni	47.5	45.8	46.9	49.3	43.8	46.6
Ni/Fe	0.9	0.9	0.9	1.0	0.8	0.9

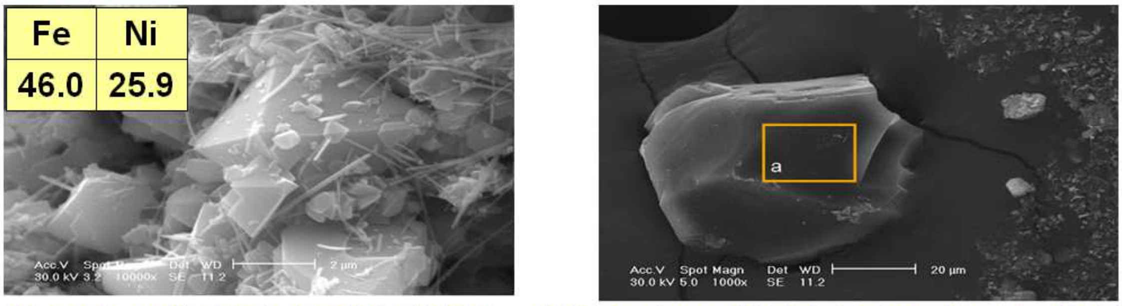
The composition of the crud of U-b units is shown in Table 6.7. The crud samples are prepared by collecting crud particles in the filtering system during ultrasonic fuel cleaning for the fuel cladding of U-b unit. The Ni/Fe ratio of the sample is about 1.2–1.4. This value is quite large compared with the Ni/Fe ratio of the Y-a crud (0.5–0.9). Considering that the ratio is the mean value of bulk collected crud particles, it is a significant difference. The high value of Ni/Fe ratio in the crud in U-b unit can be related with the AOA history of U-b unit. U-b had AOA during cycle 9–11. The B and C crud samples are from fuel burned during cycles 10–11. The D and E samples are from fuel burnt during cycles 11–12. The relatively high Ni/Fe ratio of the crud from claddings A (1.3) and B (1.4) compared to those from the D (1.2), E (1.2) and Y-a claddings may be related to the AOA history of the unit. Doncel et al (Ref. [49]) report that the nickel concentration in crud has a decisive influence on the boron deposition in crud. Nickel rich crud is associated with the onset of AOA. The high boron deposition in nickel rich crud may be due to the ease of boron hideout in the shallow crevice (or small interconnected pore) structure made by nano-size NiO needles.

TABLE 6.7. THE COMPOSITION AND NI/FE RATIO OF CRUD FROM CLADDING FROM UNIT U-B COLLECTED FROM THE FILTERING SYSTEM OF THE ULTRASONIC FUEL CLEANING APPARATUS

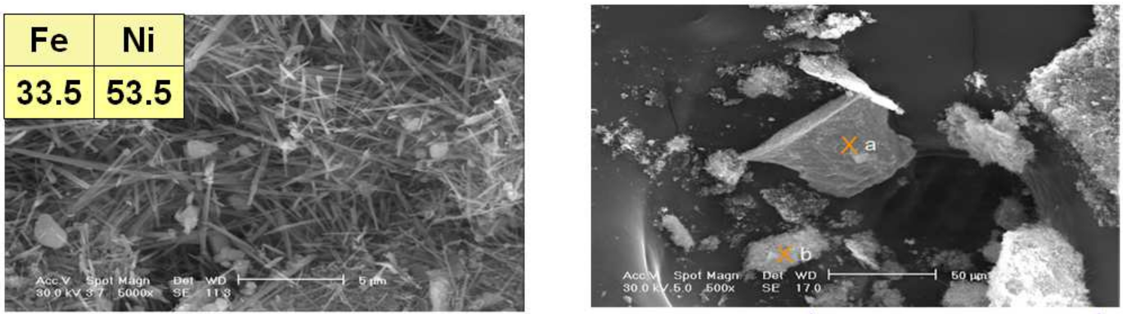
	Cr	Mn	Fe	Ni	Zr	Cu	Ni/Fe
B	7.0	2.0	26.1	33.4	28.6	4.3	1.3
C	7.5	1.7	26.5	36.1	27.3	0.9	1.4
D	7.6	3.4	30.9	36.2	22.0	0.0	1.2
E	7.7	4.0	30.4	36.1	21.9		1.2

Various phases in the crud found in Korean units are shown in Fig. 6.29. The crud from Y-a unit seems to be $NiFe_2O_4$ with Nickel Oxide (NiO) from the composition data collected. One interesting observation was that a $ZnFe_2O_4$ phase was found in the Y-a crud (though zinc was not injected in the unit). The Y-a unit has less experience of AOA. Zinc impregnation in the crud of theY-a unit may be related to the lack of AOA.

There is not enough information to identify the phases systematically in the crud in the U-b unit, because there is only crud samples collected during ultrasonic cleaning of the FA. However, Ni rich and Si rich phases were observed. The presence of these phases is understandable considering that Zircaloy has a silica content. A zirconium rich phase was also observed. This phase has been detected in Callaway and in the other units also. It is not known that the zirconium rich phase (ZrO_2) comes from detached cladding oxide or originated from the ZrO_2 particles in the coolant.



$NiFe_2O_4$ with Nickel Oxide (NiO) Silica phase(Si:64, Zr:22, Fe:10, Ni:1%)



Ni rich phase (NiO) Zr rich phase(Zr:87, Ni:3, Fe:2%)

FIG. 6.29. Various crud phases from Korean units.

As of the start-up of its commercial operation, crud scraping and other chemistry data from Ringhals-4 (R4) have also been reviewed. The amount of the deposited crud in R4 core has been low. Little or no influence of the crud presence on the fuel performance (e.g. elevated cladding surface temperature or CIPS-risk) is therefore anticipated under the present reactor operational regime. However, the nickel concentration of the fuel crud was found to be high in some cases, which would be unfavourable when heavy crud deposition occurs. After the scheduled steam generator replacement, the build-up of fuel crud should be carefully monitored. A study of the mechanisms of crud deposition behaviour and its microstructural evolution would be essential for more precise theoretical modelling of CIPS.

7. AXIAL OFFSET ANOMALY AND CRUD INDUCED POWER SHIFT

7.1. Definition

CIPS is the term generally used in this document for the axial distortion of the power shape due to crud deposition and the subsequent local accumulation of boron. The term is used to cover local power distortions as well as more global effects affecting a whole core.

This phenomenon was originally known as AOA. In a reactor the measured axial offset (AO) of the power in a core is controlled by the operator and may vary with time in the cycle. It is predicted by the core monitoring system and is defined as a percentage:

$$AO = \frac{P_{top} - P_{bottom}}{P_{top} + P_{bottom}} \times 100 \tag{7.1}$$

Where:

P_{top} is the integrated power in the top half of the core;

P_{bottom} is the integrated power in the bottom half of the core.

The Russian definition is that there is an AOA when there is a difference of at least 3% between the measured and predicted axial offsets. This definition is for the whole core and is widely used in other countries as well. These differences between measured and predicted axial offset (AO), indicating anomalous behaviour in the axial power distribution is typically illustrated with example, presented in Fig. 7.1, clearly indicating that the AOA phenomenon is associated with fuel burnup [50].

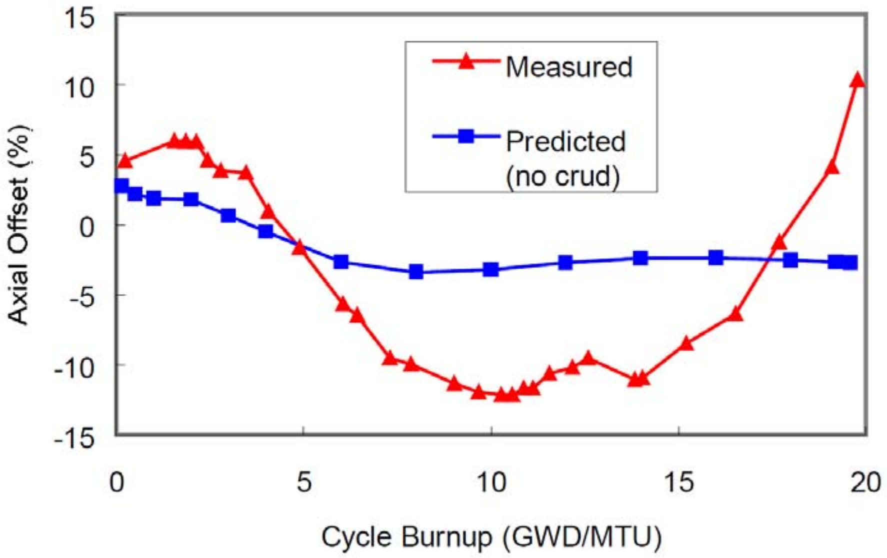


FIG. 7.1. Typical example, indicating the anomalous behaviour in the axial power distribution.

The term AOA reflects the outcome of the problem seen at a reactor, whilst CIPS refers to the ultimate cause of the power distortions. CIPS can therefore be used to indicate any level of power distortion caused by crud deposition and is readily used to describe weaker or more local phenomena than AOA. However, through custom and practice, both of the terms AOA and CIPS are widely used in the industry to refer to the same issue of CIPS.

7.2. Processes

There are 3 conditions that are believed necessary for CIPS to occur:

- SNB at fuel rod surfaces.
- Crud (corrosion products) deposition on fuel rod surfaces.
- Boron deposition on fuel rod surfaces or adsorption in the crud.

All of these are necessary, but not sufficient on their own. Fig. 7.2 shows a schematic of the overlap necessary for AOA onset [51]. There is a consensus that hideout of boron on the fuel is the ultimate, direct cause for AOA.

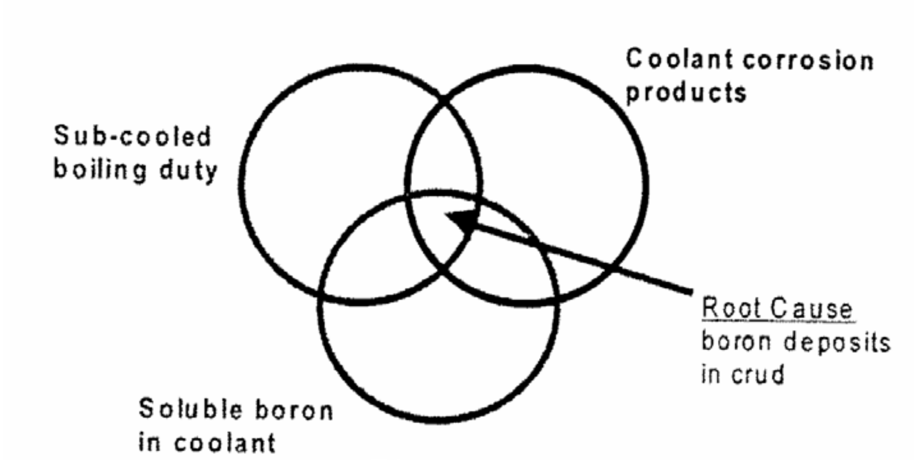


FIG. 7.2. Root cause of AOA.

Because the hidden boron is located (embedded) into the corrosion product deposits on the fuel cladding surfaces, the formation of these deposits must be evaluated as a necessary precondition of CIPS. This statement is in correspondence with the Electric Power Research Institute (EPRI) opinion that ‘the root cause of axial offset anomaly is corrosion product deposition in the upper spans of fuel assemblies.’

Usually corrosion product deposition on the heat transfer surfaces is connected with a high enough concentration of corrosion products in the coolant, but there exists Korean plant data which show that deposition can also include effects due to cladding material corrosion.

United States PWR practice shows that higher duty cores are always attended with increased boiling on the feed fuel assemblies, and that fuel cladding deposits tend to accumulate to the greatest extent in the higher SNB regions of the core.

The boiling in the core causes a change in the type, thickness and composition of deposits, a change from a standard nickel ferrite based crud, to one that is dominated by nickel oxide formation [52]. According to Bulgarian opinion, this change in the deposit composition, the nickel oxide formation, is the reason why the SNB has a significant impact on the chemical environment of the PWR fuel cladding [53]. This effect is not a direct boiling consequence, but it is a result of a localised stripping out of dissolved hydrogen at cladding surfaces and the favouring of local water radiolysis. As a result of this water radiolysis process, the local oxidants, hydrogen peroxide (H_2O_2) together with some radiolytical radicals are produced.

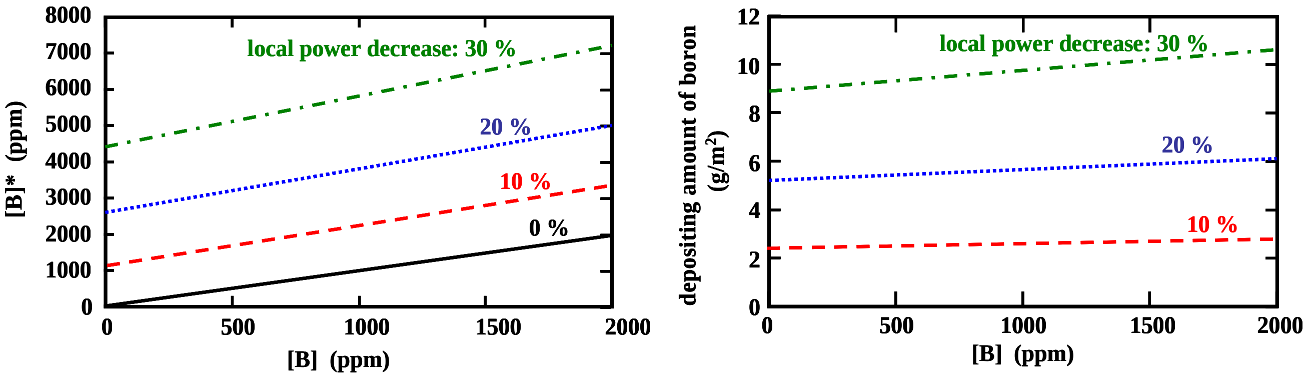
It is clear that the cladding environment is changed as a result of the synergic impact of the boiling and water radiolysis processes on the PWR fuel cladding surface.

Corrosion processes in primary circuit and corrosion product transport depend directly on coolant water chemistry and out-of-core constructional materials, while SNB depends on the core duty and the consequential change of cladding chemical environment is determined by the local degree of water radiolysis at cladding surfaces. The cladding corrosion damage under these conditions depends mainly on the cladding material properties and cannot be influenced by the coolant water chemistry characteristics.

As a result of chemical analyses of corrosion product deposits taken from the upper regions of once-burnt fuel assemblies from Cycle 9 at Callaway PWR where a significant amount of AOA had been seen, a large amount of Ni_2FeBO_5 (bonaccordite) was observed. This compound had not previously been reported as a component of fuel crud and it was suggested that formation of bonaccordite increased boron retention on fuel rods to result in CIPS [54].

Further analysis has been undertaken to quantify the effect of bonaccordite and its effect on CIPS and how it might be formed on fuel rods. It was reported that the AOA reached -14% during Cycle 9 at Callaway, which meant that the local power of the fuel rods decreased to less than 84% of the design value due to local deposition of boron.

The relationship between an increase in boron concentration in the water and the original boron concentration in the water to achieve constant local power shifts is shown in Fig. 7.3 (a). The relationship between the deposition amount of boron on the fuel rods and the local power shift is shown in Fig. 7.3 (b). About 4 g/m^2 of boron deposition is required for a 10% local power decrease, while the measured boron on the upper regions of fuel rods after Cycle 9 in the Callaway PWR (estimated from the literature data: 2 g/m^2) was almost as same as the estimated result [54]. The calculations were made from the following data: deposited flake thickness is 100 μm, flake density is 1 g/cm^3, bonaccordite fraction is 50 %. A small discrepancy between the measured and estimated values can arise from the presence of boron on the rod surface in another form.



a) Boron concentration increase for CIPS

b) Depositing amount of boron for CIPS

FIG. 7.3. Required boron concentrations to achieve CIPS.

The deposition mechanism of boron on fuel rods under sub-cooled boiling conditions can be considered as an analogy of the soluble metallic ion deposition on BWR fuel rods. Under BWR conditions, bubbles grow until their release from the heated surface due to buoyancy. The maximum diameter of such bubbles is a function of the local flow velocity. Unstable deposits on BWR fuel surfaces, such as NiO and CoO, react with stable Fe_2O_3 and then change to stable $NiOFe_2O_3$ and $CoOFe_2O_3$. It is considered that the major species in the PWR primary cooling water, boron and lithium, deposit as $Li_2B_4O_7$ on fuel surface due to sub-cooled boiling (Fig.7.4). However, $Li_2B_4O_7$ is unstable and readily released into the water and does not accumulate on the fuel surface, but some will react with NiO and $NiOFe_2O_3$ to become the rather more stable Ni_2FeBO_5, which does accumulate on the fuel surface to cause CIPS.

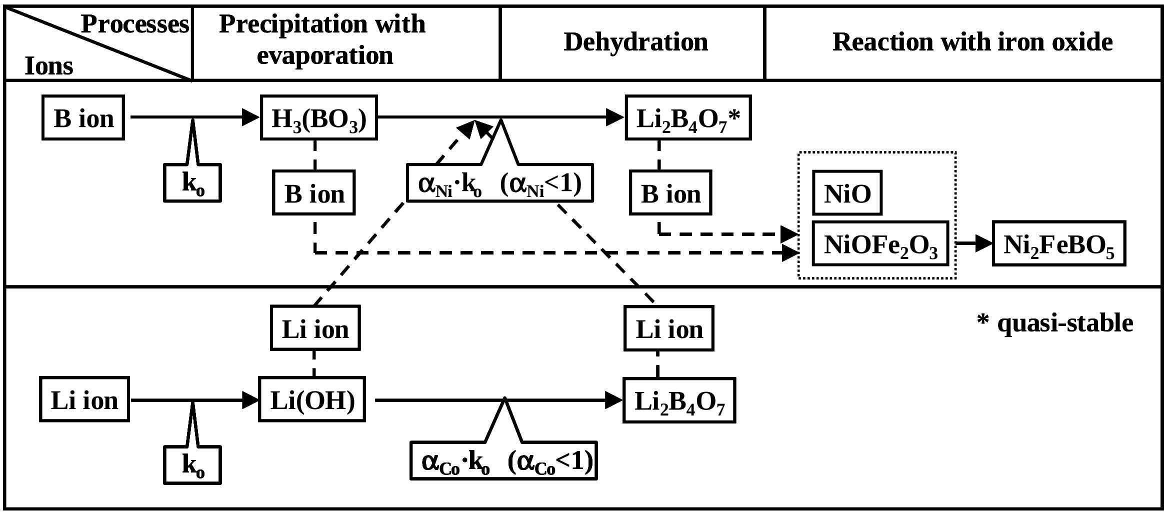


FIG. 7.4. Scheme of chemical change of deposited nickel and boron.

Deposited amounts of boron on the fuel surface are calculated by the model and shown in Fig. 7.5 [55]. The total amount of deposited boron under plant operation is determined mainly by quasi-stable $Li_2B_4O_7$, while the deposition quantities of Ni_2FeBO_5 are much affected by the amount of NiO and $NiOFe_2O_3$ deposited on the fuel.

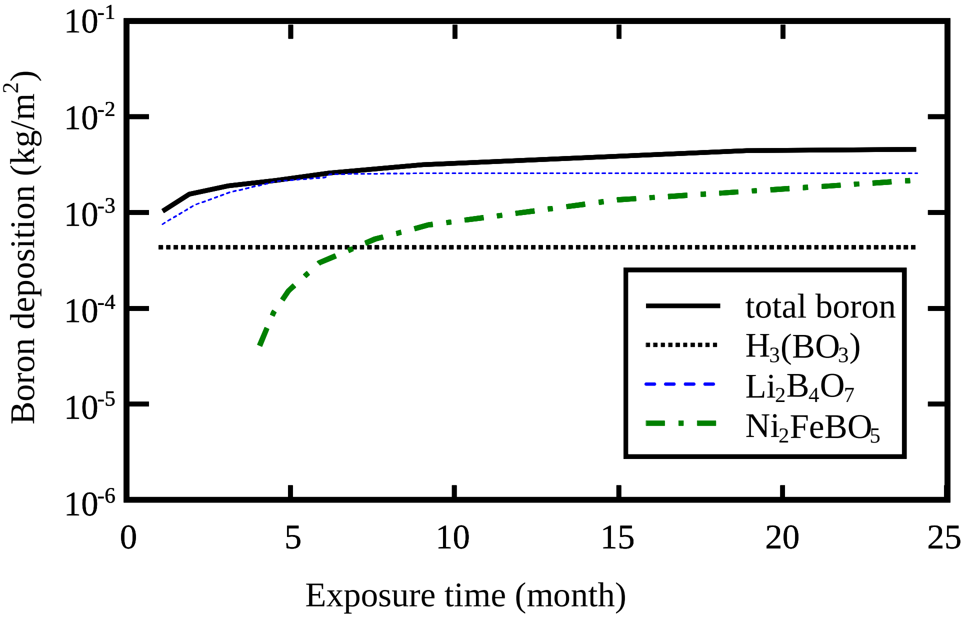


FIG. 7.5. Boron on the fuel surface.

Transient concentrations of boron in the reactor water and deposited amounts on the fuel surface can be calculated and are shown in Fig. 7.6 [55]. The total amount of boron depositing on the fuel surface is not too small to influence hide-out return, and deposited $Li_2B_4O_7$ is released too rapidly from the fuel surface to determine the deposition amount under plant operation.

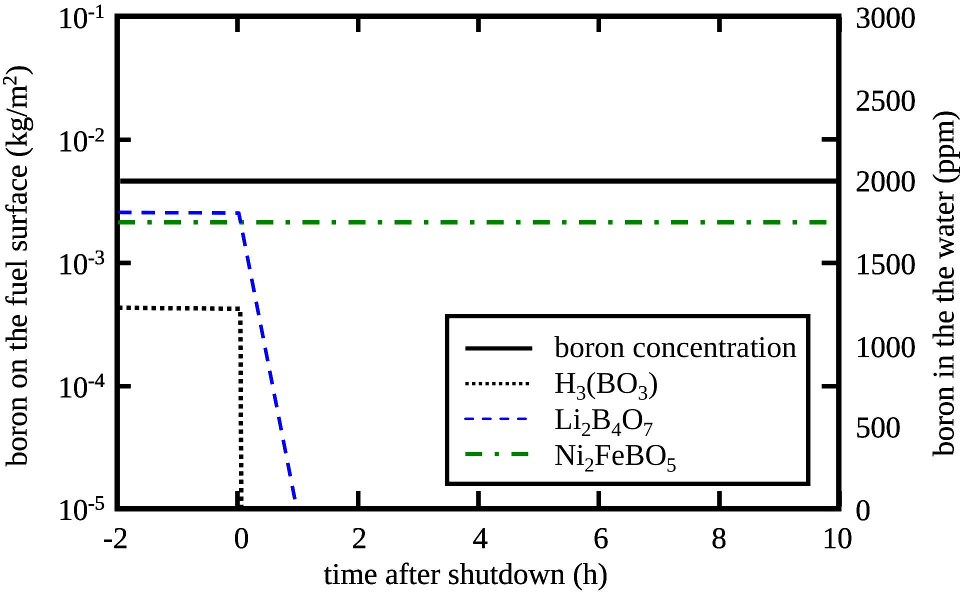


FIG. 7.6. Transient of Boron concentration and deposition after plant shutdown.

Very unstable boron deposits ($Li_2B_4O_7$) and quasi-stable deposits (Ni_2OFeBO_5) increase with exposure time. The total deposited amount of unstable species is much larger than that of quasi-stable ones, and reactor reactivity may be determined by the unstable deposits. After plant shutdown, unstable species release very quickly and disappear, whilst quasi-stable species still remain on the fuel surface where they can be detected. Therefore, the measured deposits might differ from the active deposit during operation.

7.3. Chemistry and materials

The effects of major chemical parameters on boron deposition are listed as follows, Table 7.1.

TABLE 7.1. CHEMICAL PARAMETERS ON BORON DEPOSITION

Chemical parameters	Effect
Boron	Boron concentration, C_B, has direct effects on boron deposition.
Lithium	Lithium enhances chemical reaction on the fuel surface to produce $Li_2B_4O_7$. The contribution of [Li] on boron deposition is modelled as the conversion factor from unstable boron to quasi-stable $Li_2B_4O_7$.
pH	Decreasing pH enhances boron deposition on fuel due to the lower dissolution rate.
Ni	Ni enhances boron deposition in three ways: 1) Thick NiO and $NiOFe_2O_3$ deposits result in thermal insulation effects and increasing the potential for sub-cooled boiling on the fuel surface. 2) Thick NiO and $NiOFe_2O_3$ deposits provide hidden sites for soluble boron and quasi stable $Li_2B_4O_7$ deposits and enhance their deposition. 3) Nickel enhances the chemical reaction of the fuel surface to produce $NiOFe_2O_3$. The contribution of [Ni] on boron deposition is modelled as the conversion factor from quasi-stable $Li_2B_4O_7$ to stable $NiOFe_2O_3$.
Oxygen	Under sub-cooled boiling conditions the concentrations of oxygen and OH radicals might increase and then they enhance chemical reactions of NiO, $Li_2B_4O_7$ and $NiOFe_2O_3$ formation. The oxidation reactions are not involved in the models described in this document.

Chemistry is the most important opportunity for CIPS mitigation in the short term for a defined NPP in operation. However, each plant may have its own optimal chemistry programme depending on its characteristics.

Several chemistry parameters that may have an impact on CIPS have been identified from the various contributions of the project and are classified by decreasing order of potential importance.

7.3.1. pH selection with Ni solubility

As previously discussed, CIPS is clearly associated with the presence of nickel in crud, which is favourable for boron precipitation in nickel ferrite (spinels) $Ni_x(Cr,Fe)_{3-x}O_4$. It has been demonstrated that pH and other physico-chemical environment conditions (redox potential, concentration of corrosion products temperature) have a strong influence on crud composition (nickel proportion). This is why the study of pH influence on CIPS is of utmost importance for CIPS.

7.3.2. Use of boric acid enriched with ^{10}B (EBA)

The use of EBA reduces the total boron in the coolant and therefore will reduce the risk of crud formation. However, it is not so clear if the use of EBA is proportionally beneficial to EBA enrichment since the cause of CIPS is due to ^{10}B influence in crud. If boron deposition is not a precipitation driven phenomenon, the amount of ^{10}B in the crud might remain at the same order of magnitude with enriched boron or natural boron, given that core control needs the same amount of ^{10}B in solution.

7.3.3. K vs. Li for pH regime

According to the Bulgarian study, potassium being more soluble than lithium, there is less risk of crud deposition with potassium in WWER coolant and thus less risk of CIPS. However, some studies have shown that potassium may more easily induce corrosion on some of the RCS materials than Li. Consequently, there is no clear advantage for one or the other alkaline reagents for the control of pH in the primary coolant.

7.3.4. Importance of H_2 concentration

High H_2 in old plant can cause transient high crud. There is a trend to selecting hydrogen concentrations at low values (about 10 ml/kg) in Japanese NPPs and higher values (near 50 ml/kg) in US NPPs, but the objective is more the protection of Alloy 600 from PWSCC than CIPS or dose rate mitigation. Consequently, the participants did not consider that hydrogen concentration should be of high priority in FUWAC studies. This question has nevertheless been raised due to the easier possibility of regulating the concentration at a low value through ammonia addition than with direct hydrogen injection (which requires a minimum pressure) while a high hydrogen concentration with ammonia addition would impact the ion exchange resin behaviour,

7.3.5. Silica and other compounds (Al, Ca, Mg) effect

Plant data from France does not show any significant effect of silica, although this could have been an important parameter due to the low solubility of zeolite, rich in silica and aluminium or similar compounds, including silicates.

7.3.6. Zinc injection

Zinc is added to the primary coolant mainly for mitigation of dose rate and in some cases for PWSCC of Alloy 600. There has been no clear evidence of an impact of zinc on CIPS in this project, though evidence from the Republic of Korea suggested that there may be some benefit. This parameter is not believed to be important as zinc merely replaces cobalt in crud but does not decrease crud thickness. Zinc addition remains an extremely high priority for dose rate minimization.

Zinc is currently being added to PWR units in an increasing number of countries, including USA, Spain, Germany, Japan, Brazil, Switzerland and France. Between 2009 and 2012, it is expected to be added to units in the Republic of Korea, South Africa and China as well as further units in the original countries. Moreover, the zinc injection is expected to be injected from the 1st cycle of operation in the new reactors (AP1000, EPR). The main objective is for dose rate mitigation, but also to protect against PWSCC of Alloy 600 in a very limited number of units.

It is nevertheless suggested that zinc addition be considered where there is steam generator replacement or fuel core management modification.

The occurrence of enhanced cladding corrosion at Farley after zinc had been added to one unit is not attributed to this addition, since the other unit, without zinc, experienced the same phenomenon. The cause is believed to be more likely due to the power increase of the units.

In BWR, the crud in units adding Zn is more tenacious, but it is considered that Zn is not an issue for such crud, since the thickness is lower and has a uniform distribution of Zn (<8% weight basis). No $ZnSiO_3$ or zinc ferrite has been seen in scraping analyses. Zinc only precipitates with an initial crud thickness > 50 µm. EDF have modified the silica limit from 1–1.5 mg/kg. This modification is to allow optimization of zinc injection at the beginning of a cycle, without needing to wait to reach the silica limit.

Further work is needed before a final decision on the possibility of zinc addition at Ukrainian NPPs can be taken. This includes a comparison of the RCS structural materials in WWER and PWR units where the zinc addition technology is currently used, the influence of zinc addition on the activity accumulated in high temperature filters during their operation in WWER-1000 reactors and finally the estimation of equipment changes and the dose levels required.

7.3.7. Structural materials

The influence of structural materials on CIPS is particularly important for PWR where Steam Generator tubing, representing the largest surface of the primary coolant, differs from plant to plant. In the early times, a few PWR had steam generators with austenitic stainless steel tubes with 18%Cr – 10%Ni. Later, most western PWRs used Alloy 600 with high nickel content, as shown in Table 7.2.

Due to the Alloy 600 sensitivity to SCC in pure water, the German units quickly switched to the Alloy 800, with a much lower Ni content, and since the 1990’s most of the PWRs put in operation used Alloy 690, with an intermediate Ni content. Many plants which have replaced their steam generators have chosen Alloy 690 for the new steam generator. WWER plants have always used a low Ni content stainless steel stabilized with Ti.

TABLE 6.2. COMPOSITION OF THE MOST FREQUENT ALLOYS USED FOR STEAM GENERATOR TUBING (%)

Type (Usual name)	C	Ni	Cr	Fe	Co
Typical austenitic stainless steels used in many primary system components					
(AISI) 304L	≤ 0.03	8–12	18–20	Balance	
(AISI) 316L	≤ 0.03	10–14	16–1 8	Balance	
Alloy 18–10 Ti (WWER steam generator tubing)	≤ 0.08	10–11.5	17–19	Balance	< 0.05
Nickel base alloy used for steam generator tubing and some other components					
Alloy Inconel 600	≤ 0.05	> 72	14–17	6–10	< 0.1
Alloy Inconel 690	≤ 0.05	> 58	27–31	7–11	< 0.035
Alloy Incoloy 800	≤ 0.10	30–35	19–23	Balance	< 0.5

The composition of the other materials present in the primary coolant are of lower importance since their surface in contact of the primary coolant is much lower and they all have lower Ni concentrations, typically about 10%.

It is obvious that the nickel content of the structural materials may have a direct influence on CIPS since nickel is directly involved in the crud composition and morphology partially formed from corrosion products circulating in the primary coolant. Consequently, this aspect of material influence particularly through the surface state and release rate of corrosion products is covered in Section 3. There is a significant correlation with the nickel content of the steam generators, but it is noted that Alloy 690 plants have experienced CIPS and according to French experience operating units with various steam generator tubing materials, there is no difference in CIPS results on units with Alloy 600 or 690. The Korean units with 690 steam generator tubing do not have CIPS but the experience feedback here is insufficient to draw any conclusion.

7.4. Fuel management

There are several parameters that may have a significant impact on CIPS. These include the following Sections 7.4.1–7.4.4.

7.4.1. Fuel options (cycle length and enrichment)

This has the most important consequence on Boron concentration at the beginning of the fuel cycle to cope with neutronic needs. The answers to this question is either to use other neutronic absorbers or to use EBA (see above chemistry influence).

7.4.2. Temperature

Several participants confirmed that temperature is a key parameter in CIPS clearly explained by its strong influence on boiling, corrosion product and other compounds solubility. The trend towards higher powers for fuel means increased temperatures and several associated risks (corrosion, CIPS, etc.), that must be clearly evaluated with new a NPP or when upgrading older ones.

7.4.3. Operating options and specificities

Independent of the fuel cycle length, the number and type of transients or load follow is another potential influencing parameter for CIPS occurrence, because there is solubility modification during such transients, associated with temperature and heat flux. The example of French NPP, where nuclear energy represent about 80% of electricity generation is an excellent example for evaluating these parameters. For the moment, no specific impact has been observed

7.4.4. Core design – SNB

In relation with previous fuel options, core design, may influence CIPS, through the selection of control rod and subsequently boron concentration and neutronic flux in various parts of the fuel length. SNB is another key parameter that has been considered for CIPS appearance and core design can help to reduce power peaking.

7.5. NPP feedback

During the entire observation period, Ukrainian WWERs did not record any axial offset caused by corrosion products deposit on the surface of fuel rods. Taking into account global trends towards higher fuel burnup and increased cycle length, axial offset may be expected to appear at Ukraine's NPPs as well.

The occurrence of AOA in Korean NPPs is shown in Table 7.3 [56]. Korean plants have experienced AOA several times up to February, 2006. In a reactor at the Kori site, significant AOA occurred during cycle 9. Ulchin reactors also have experienced several occurrences of AOA recently. Power was reduced by 1.17% due to AOA during cycle 11 in U-b unit.

TABLE 6.3. AOA STATUS OF KOREAN POWER PLANTS (UNTIL FEB. 2006) [56]

Unit	AOA cycle	AOA (%)	Current cycle	Ref
Kori site (K)	9	-7.50%	15	16 cycle: AOA
Younggwang site (Y)	9	-3.50%	14	
Ulchin site A (U-a)	9, 10, 13	-5.1% (10)	13	
Ulchin site B (U-b)	9, 10, 11	-4.9% (10)	12	11 cycle – 1.17% Power reduction

The influence of a very porous deposit, equivalent to a crevice where chemical species may concentrate, has been seen. Boron and lithium enrichment have been found in these deposits. The Ni/Fe ratio is 0.5 on fuel cladding in the Younggwang units at various points, whilst at Ulchin B where CIPS has occurred, the ratio is 0.8–1.0 on cladding samples from tapping and 1.2–1.4 from ultrasonic cleaning and filtering. In this unit, nickel needles and pure boron have been noted. The crud (thickness: ~10 μm) is located in the upper part of fuel rod. Pure boron is considered as a candidate phase that induces AOA. The Ni/Fe ratio is higher in the crud on units with AOA than on units without AOA. The Koreans also initiated a crud simulation study. A pH_T increase (6.9–7.2) reduces the crud deposition.

Axial Offset difference (designed AO value minus the measured AO value) from cycle 9–15 in a Kori unit is shown in Fig. 7.7 [56]. The AO difference increases rapidly during cycle 9 when the burn up reached 12000 MWD/MTU. Following a power transient (100%–30%–100%) the AO difference varied from -1% to -8% within about a month. It seems that AOA is a dynamic process during a power transient. Crud or boron can be deposited to induce significant AOA within a month when some condition is met in the reactor. Careful consideration is required for the AOA evaluation in reactor.

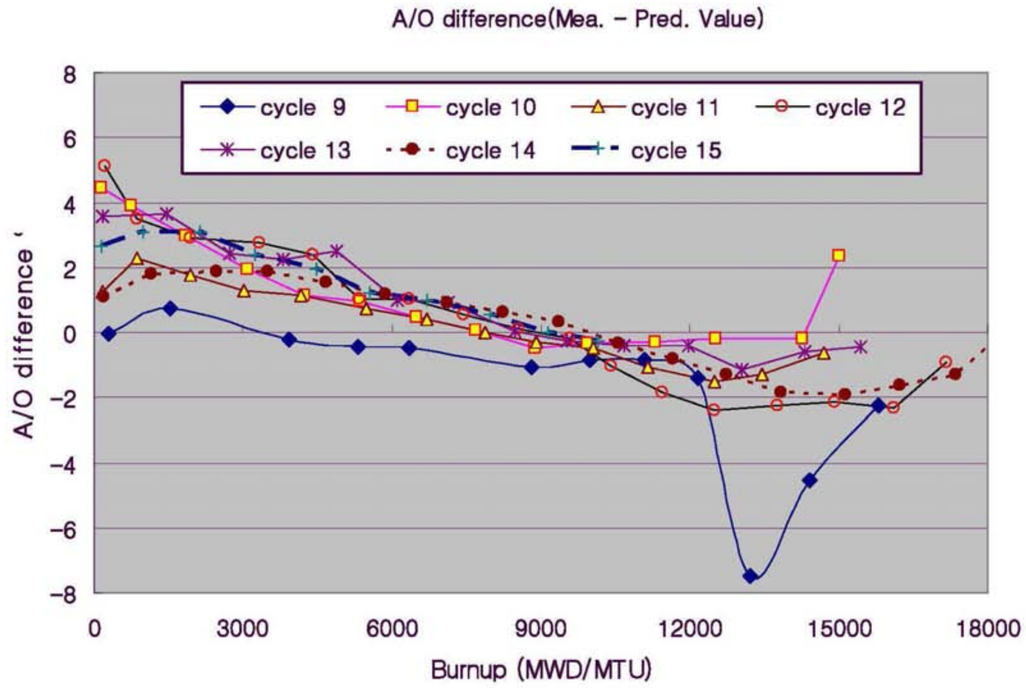


FIG. 7.7. AO difference (designed, measured AO values) for cycles 9–15 in a Kori unit.

The large number of French NPPs allowed an interesting analysis of various potential influencing parameters on CIPS occurrence. No whole core effects of CIPS have been seen in France, but there are a number of localized events, each affecting small numbers of assemblies to some extent.

The French utility, EDF, tries to minimize corrosion product transport from out-of-core to in-core regions by selecting the most appropriate chemistry, which is currently based on Ni ferrite solubility rather than that of magnetite. This is the reason why the target pH_T is increasing. However, whilst Li is allowed up to 3.5 mg/kg in American and Spanish units with ZIRLO^{TM} or M5^{TM} fuel claddings, such a concentration is not yet allowed in all French units. With M5^{TM} and ZIRLO^{TM} cladding, the upper limit is also 3.5 mg/kg but remains at 2.2 mg/kg for plants with Zircaloy cladding, except in Cattenom 2 which is used as a lead test plant for this change.

Since 1988, 29 cycles have been affected by local power deformations, with one case after Steam Generator Replacement. There has been an increase of cases in recent years (2006–2007). None of these localised cases have lead to any operational constraints [57].

The French feedback indicates that the risk of CIPS is correlated with the length of cycle and boron concentration. Between 2004 and 2007, 10 cycles have been affected by CIPS with a length higher than 430 full power days and a boron concentration higher than 1300 mg/kg at the beginning of the cycle.

The most significant local axial anomaly detected in France is illustrated in Fig. 7.8 which shows predictions (calculated with 2 different codes) and the measured values. Figures 7.9–7.10 show the anomaly evolution, growing and shrinking, during the cycle.

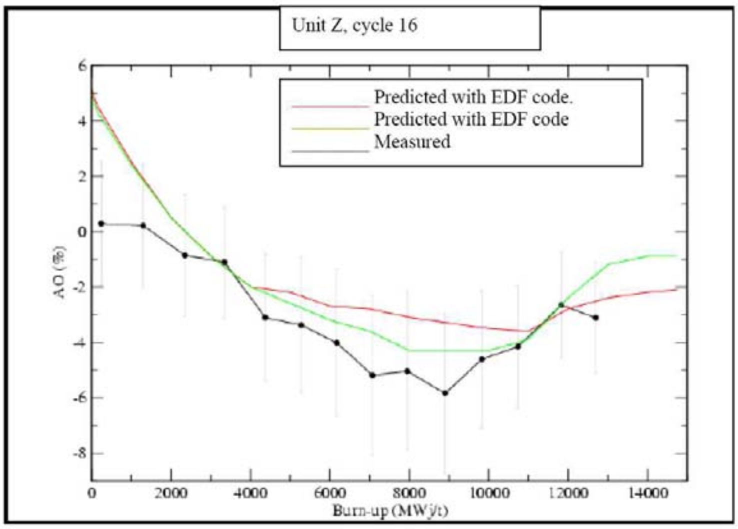


FIG. 7.8. AO difference (predicted and measured) in a French unit.

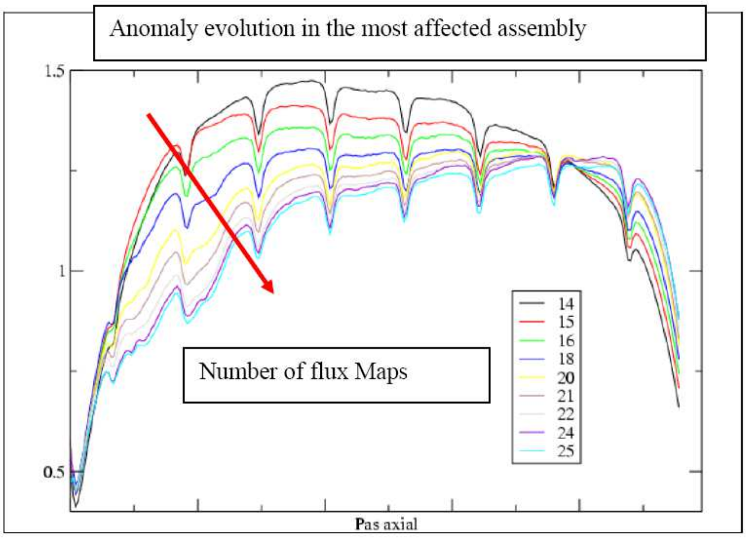


FIG. 7.9. Anomaly evolution in a French unit: flux map representation.

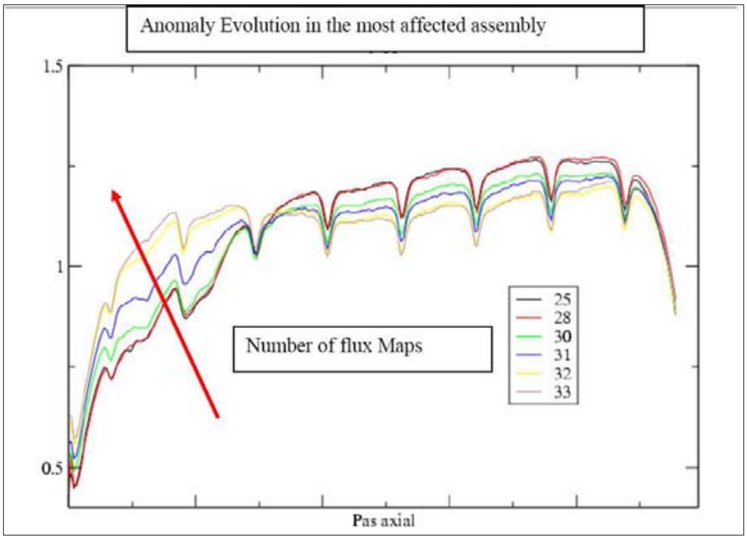


FIG. 7.10. Anomaly disappearance in a French unit: flux map representation.

The international feedback shows that a key chemistry indicator of CIPS is lithium return during power transients. Lithium is not systematically monitored during transient periods. For this reason, the data concerning this indicator is very limited. It should be noted that in some cases, lithium peaks coming from the resins have been observed in the primary coolant. Before concluding the possible presence of CIPS, following the detection of a lithium peak, it is important to verify the resin condition. In one of the units affected by CIPS in France, the lithium concentration has been monitored and lithium hideout has been observed (Fig. 7.11).

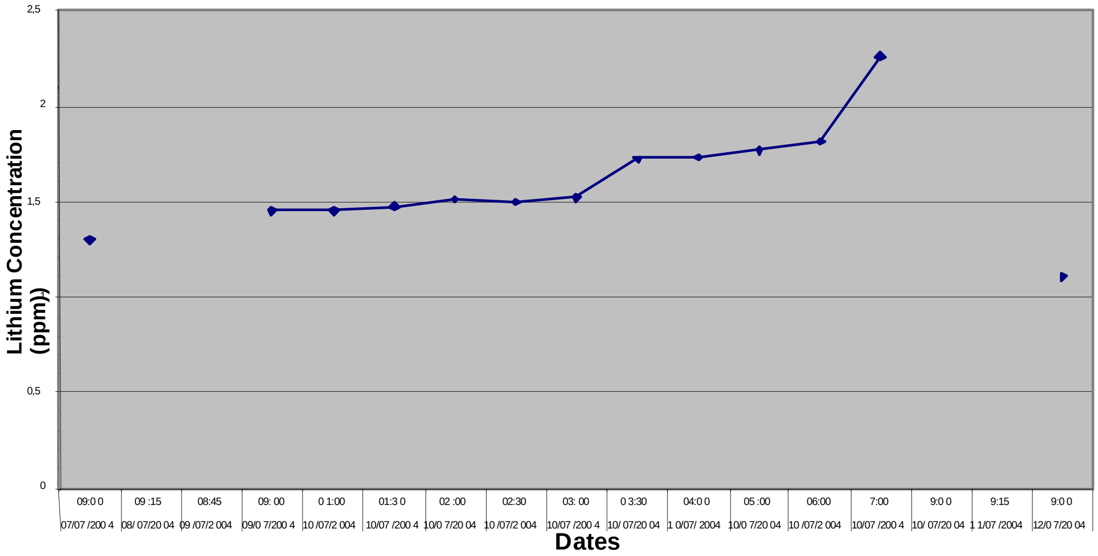


FIG. 7.11. Lithium behaviour during a power transient in a French unit affected by CIPS.

French feedback shows that the corrosion product evolution during the cycles affected by CIPS is very similar to that from units without CIPS during the first part of the cycle. When the anomaly starts to disappear, the corrosion product activity begins to increase progressively due to the crud dissolution. Cycles affected by CIPS are characterized by corrosion product activities during operation at the end of the cycle higher than these from units without CIPS. For instance, the ^{58}Co activity at the end of the cycle 15 of unit Z was 60 MBq/t, while at the end of the cycle 16 (affected by CIPS) was 800 MBq/t.

According to French experience, the peak activity during the shutdown after a cycle with CIPS does not systematically increase, Fig. 7.12.

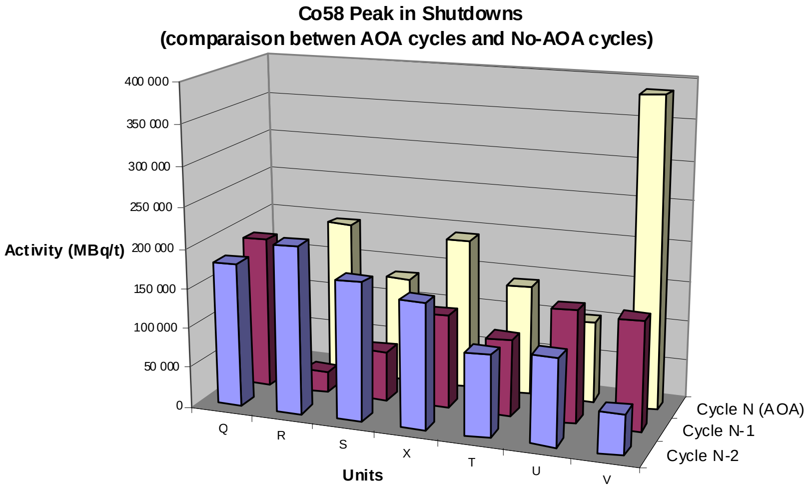


FIG. 7.12. ^{58}Co peak in shutdowns.

The evolution of the activity in the CVCS-filters and the ΔP should be monitored carefully during cycles affected by CIPS. The French feedback shows that the activity increase of the filters is in accordance with the corrosion product activity increase in the primary coolant following the disappearance of the anomaly. This, therefore, suggests that the corrosion products coming from the crud are in insoluble form.

French experience shows that the dose rate does not systematically increase after a cycle affected by CIPS. In some cases the dose rates decreases or stays constant, Fig. 7.13.

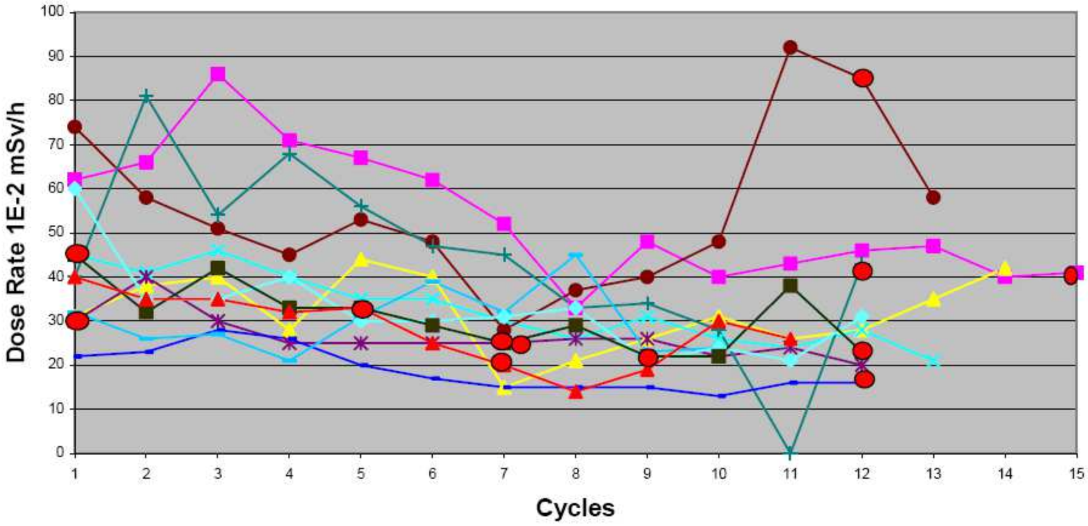


FIG. 7.13. Dose rate evolutions in units affected by CIPS at French PWR units.

The Canadian investigation showed that no CIPS has been seen in plants where the steam generator tubes had previously been passivated, highlighting the benefit of such a treatment to minimise corrosion product release from the steam generators and thus less risk of crud formation and CIPS.

A pH increase seems to be beneficial for corrosion product and dose rate limitation, but it does not appear to prevent the occurrence of CIPS, which has appeared in some US units despite a pH and lithium increase. A similar observation has been made at Cattenom 2 in France where, in spite of modified chemistry, a local power deformation has been detected.

Increasing lithium concentration might be beneficial for limiting corrosion product transport and for dose rate, but there remains concern for fuel cladding uncertainties and for the possibility of deposition of B-Li compounds.

German units operate at a pH_T of 7.4 which is more easily achieved with the presence of EBA and 12 months fuel cycles.

Affected assemblies in French units are in their 2nd cycle. This is a difference with international experience (mainly in the USA), where assemblies affected by CIPS (or full AOA) are generally those in their 1st cycle. This difference can be explained be the different core design and fuel management.

Some participants thought that the number of coolant loops in a plant might be significant, as 4-loop plants had seen more evidence of the phenomena; this is not confirmed by the experience of the French units where 900 MW units (3 loop plants) are also affected in an increasing number of cases.

The influence of hydrogen has also been investigated in the French units and did not show any impact on CIPS occurrence within the specified range of 25–50 ml/kg (though no unit actually operated above 44 ml/kg). According to Japanese results reported by the French representative, a lower hydrogen value is believed to be favourable for lowering the fuel crud thickness and the PWSCC of Alloy 600. A low hydrogen limit favours the presence of NiO instead of Ni which will increase the total nickel solubility. The American approach is to prefer an increase of hydrogen to mitigate PWSCC of Alloy 600. However, there are many uncertainties with levels of hydrogen above 50 ml/ kg, and it seems advisable to be cautious before increasing hydrogen above the current limit.

The CIPS evaluation in the French fleet allowed the conclusion that chemistry parameters (lithium upper value, pH_T, zinc) within the applied range, are not the main cause of the phenomenon which is more related to steam generator replacement and increased cycle length. In the presence of CIPS, high values of nickel, iron or cobalt have not been seen in the primary coolant. Theoretically, an increase of pH_T, and lithium should be beneficial for corrosion product transport, but they seem not to be sufficient to suppress the onset of CIPS.

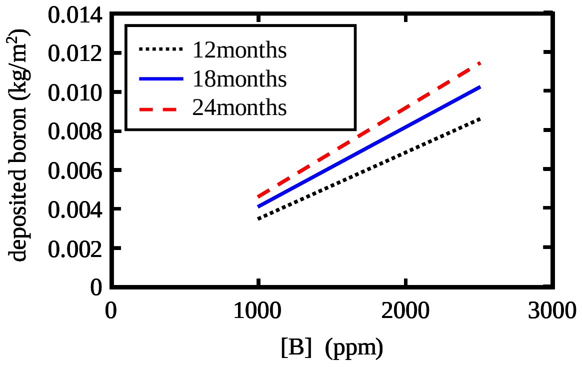
7.6. Mitigation

The High Duty Core Index (HDCI) of most Korean PWR is above 150. Most Korean NPPs can be classified as ‘High Duty Plant’ according to the HDCI scale. It was recognized by the Korean power utilities that countermeasures to CIPS are necessary for safe and efficient operation of NPPs. Korea Nuclear Fuel Co. Ltd (KNF) developed ultrasonic crud removal technology recently and have started operation in Korean plants.

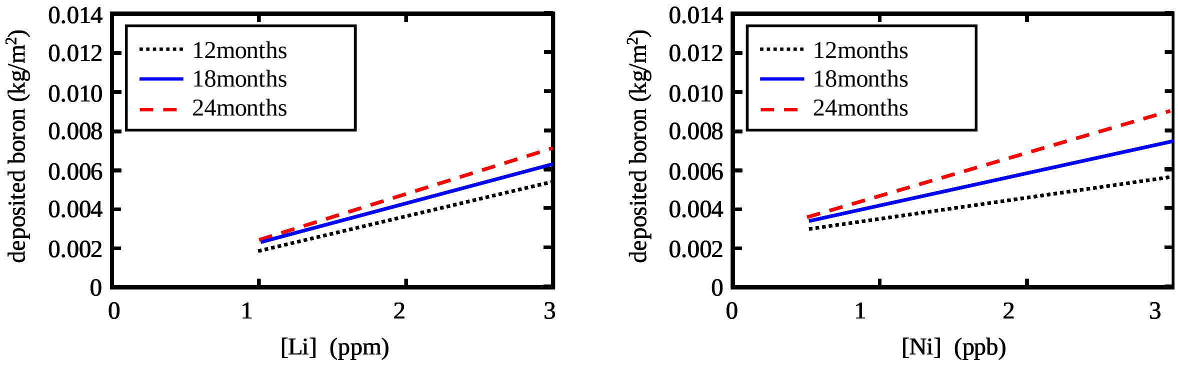
The Bulgarian WWER-1000 plant at Kozloduy has implemented several improvements:

- implementation of Russian fuel assemblies TVSA which have as fuel cladding material E-110 alloy (Zr1%Nb) with sufficient corrosion resistance in the presence of SNB;
- use of burnable absorber (gadolinium) integrated in the uranium-gadolinium (U-Gd_2O_3) fuel (fuel rods with 5.0% Gd_2O_3);
- development and implementation of water chemistry primary circuit guidelines, with pH_{300} = 7.0–7.2.

These conditions have avoided the occurrences of AOA with TVSA assemblies with 4.4% ^{235}U fuel. The effects of boron, lithium and nickel on boron deposition can be evaluated by a Japanese model and the chemistry can then be optimised. The mitigation effects of nickel concentration on boron deposition were calculated as shown in Fig. 7.14 [55]. Decreases in [B] and [Li] reduce boron deposition on fuel surface and reduce the CIPS risk, while a decrease in [Ni] also reduces boron deposition on fuel surface through several processes to reduce CIPS risk. An increase in pH results in increased boron solubility from fuel deposits to reduce CIPS risk.



a) Boron concentration



b) Lithium concentration

c) Nickel concentration

FIG. 7.14. Effects of chemical factors on boron deposition on fuel surface.

Zinc addition is mainly aimed at decreasing dose rates and in some cases PWSCC of units with Alloy 600. However, its potential positive or negative impact on CIPS has been carefully considered. If the zinc injection is carried out according to the specifications, the zinc is considered as a possible action to mitigate the CIPS risk:

- Zinc injection contributes to reduce the source term and consequently the crud should be reduced after some cycles of injection.
- The visual inspections show that in presence of zinc the crud is relatively uniform from top to bottom of the rods. Without zinc, the crud deposition is higher at the top of rods where the power is more significant and the sub-nucleate boiling may occur.

Primary coolant pH is a main parameter to control the corrosion product release from the out-of-core materials ant the crud deposition on the fuel rods. An elevated pH is recommended to reduce the release of corrosion products and the transfer of crud during the cycle. However, an increase of pH needs a higher lithium concentration which may favour $LiBO_2$ precipitation in the core and consequently on AOA development.

The recent investigations show that the negative impact of lithium concentration is limited. The results of modelling calculations (Nexia Model) predict lithium borate precipitation when the crud thickness is higher than 25–30 µm. The solubility behaviour of magnetite and nickel ferrites has been also studied as a function of temperature and lithium and boron concentrations [4]. For lithium concentrations higher than 3.5 mg/kg and boron concentration between 800–1000 mg/kg, the coefficient of solubility for the nickel ferrite (oxide composition more representative of PWR) is positive and the risk of corrosion product precipitation is lower than in conditions with a lithium concentration lower than 3.5 mg/kg.

These results are in agreement with the Studsvik observations on laboratory loops. The presence of $LiBO_2$ has only been identified in deep crud.

According to these results, the increase of lithium concentration in the primary coolant may have different impacts depending on the unit characteristics:

- For units with a low inventory of corrosion products and without an AOA history: a lithium concentration increase can be considered as a preventive way to limit the risk of crud deposition thanks to the pH rise.
- For units with a high inventory of corrosion products: a lithium concentration increase can produce precipitation of borates in the crud and develop flux anomalies.

EDF is also working on shutdown guidelines for the units affected by AOA in order to limit the risk of crud deposition after a cycle affected by AOA. Some aspects are being analyzed:

- pH reduction at the end of cycle can contribute to maintain the crud on the assemblies and avoid a positive deviation at the end of the cycle, but this practice may have a negative impact on dose rates.
- Chemistry during shutdown to favour the crud dissolution: pH, $[H_2]$, H_2O_2 injection.
- Filter practices to improve the retention of particulate coming from the crud.

8. CONCLUSIONS

The thirteen teams participating in the CRP have studied many aspects of water chemistry technology. Information has been gathered for all types of power producing, water cooled reactors, and the main areas where there are concerns or opportunities for improvements have been studied. This chapter draws together the issues studied and provides an overview of the outcomes of the research work undertaken.

8.1. Overview of the types of CC in operation for different plant types

8.1.1. WWER and PWR

WWER power plants use potassium instead of lithium hydroxide, as used in PWR, to balance the acidity in the coolant, with two main advantages:

- cost limitation by avoiding the use of enriched ^{7}Li;

- higher solubility of potassium as compared to lithium, with lower risk of precipitation and axial offset anomalies.

But there is one constraint with potassium, the necessity to monitor total potassium plus lithium for pH control, since ^{7}Li is produced from neutron activation of ^{10}B. In addition, as sodium is present as an impurity with potassium it is also monitored.

Western standards for the primary CC of PWR-type reactors allow that water chemistry conditions can be controlled by the addition of H_3BO_3, LiOH, H_2, N_2H_4 and H_2O_2, as necessary. These standards are continually being improved depending on plant power, materials used and the accumulation of data on the mechanisms of corrosion, mass transfer and radioactivity levels. The latest recommendations utilise ‘coordinated’ water chemistry, with the pH_T value varying throughout a reactor cycle.

The experience of improving Western PWR primary chemistry, for example where ten years of zinc microinjections at the Biblis NPP have resulted in reductions in primary-circuit equipment activity by 10–15% a year, demonstrates that equipment dose rates and radioactive waste can be decreased by appropriate water chemistry. One WWER operator considers that it may be possible to improve primary CC along the following lines:

- replacement of ammonia injection with gaseous hydrogen injection;
- zinc injection;
- application of boric acid enriched with ^{10}B isotope.

8.1.2. RBMK and BWR

RBMK and BWR have common water chemistry, with no alkaline reagent addition and operate with the pH_{25} of the coolant close to neutral (6.5–8.0).

The content of corrosion products and impurities in the feed and reactor water of RBMK are considered to be among the most important parameters affecting sedimentation on fuel elements and activity accumulation. Adherence of the feed and reactor water quality to the standard indicators is controlled through regular analysis of water samples.

In BWR systems the primary water chemistry is determined by:

- soluble/insoluble impurities in the feedwater;
- species (O_2, H_2 and H_2O_2) generated by the radiolysis of water in the reactor core;
- deposition and release of soluble/insoluble species on fuel;
- and removal of reactor water impurities through the clean-up system.

The challenge faced by the BWR industry is to balance these processes to maintain water chemistry within operating guidelines to optimize the performance of the plant. Typically, BWR primary water is largely oxidizing due to the presence of O_2 and H_2O_2 in the reactor water. The oxidizing nature of the water increases the ECP of internal metal surfaces in a positive direction that in turn makes materials susceptible to intergranular SCC.

Currently, most BWRs employ hydrogen injection into feedwater, HWC, to mitigate intergranular SCC of reactor internals by suppressing radiolytically generated oxidants. In addition, a majority of the US BWRs and a few others internationally now employ NobleChem^{TM} in combination with low HWC that improves the effectiveness of recombination of H_2 and oxidants to achieve low ECPs. The advantages of ONLC in BWR units for mitigating Crack Growth Rate of SCC on different materials are:

- a combination of DZO addition and NobleChem^{TM} is more effective in dose rate reductions;
- noble metal or On-line NobleChem^{TM} lowers ECP and crack growth rates;
- On-line NobleChem^{TM} releases activation corrosion products from surfaces resulting in lower dose rates;
- there is no impact on fuel performance.

With OLNC, Fe_2O_3 is transformed into Fe_3O_4. ONLC has been applied on 6 units and could be considered for WWER instead of switching from ammonia to hydrogen.

8.1.3. CANDU and PHWR

In the PHTS of CANDU reactors, heavy water is used as coolant and moderator. The aggressiveness of PHTS water is reduced by controlling dissolved oxygen content, pH, impurities, radioactive crud and fission products.

The operating objective is to maintain the concentration of dissolved oxygen < 10 μg/kg of D_2O. Production of oxygen is suppressed by the addition of extra deuterium to the coolant. A high concentration of dissolved deuterium should be avoided to minimize any potential for dissolved deuterium to accelerate the formation of zirconium hydrides in any inadvertently overstressed regions of the pressure tubes. There is a critical CDC required to suppress oxygen formation. Dissolved deuterium specification is 3–10 ml/kg.

The pH value in accordance with AECL specification is $10.2 < pH_a < 10.8$. (pH_a is the reading on a pH meter calibrated in light water buffers. At 25^oC; $pH_a=pH+0.463$).

The pH_a of the PHTS coolant is controlled by the concentration of LiOD by using a Li^+/OD^- form ion exchange resin. There is a narrow band of pH_a values: $10.2<pHa<10.4$, within which the PHTS operates optimally. At Cernavoda NPP Unit # 1, a major issue for PHTS chemistry control is to reduce the pH_a value from 10.2–10.8 to the optimum range: 10.2–10.4.

8.2. Corrosion of primary circuit materials

Primary circuit materials undergo general corrosion in high temperature, deoxygenated, neutral or mildly alkaline solutions to form thin oxide films. Corrosion products are formed by the release of metal-oxide ions, colloids and particles, they are typically comprised of iron and nickel oxides with small amounts of manganese, chromium, and traces of cobalt. The source of nickel in PWR primary circuits is mainly the Ni-based alloy steam generator tubing, which generally represents about 75% of wetted surface area (in WWER steam generator tubing the material is stainless steel as are other reactor construction materials – piping, vessel). The corrosion process in such alloys is non-uniform. A significant impact on the rate and mechanism of oxidation is exerted by the chemical composition of the environments and availability of oxidizing components.

Corrosion processes lead both to formation of an adhesive (tightly adherent to the surface) oxide layer and to dissolution of some of the oxide layer and base material into the circulating coolant flow. Experimentally it is found that less than half of the maximum possible total thickness of oxides is expected to transfer from a surface to the corrosion environment. Although the corrosion rate generally reduces with time relative to an initial level, there always is a tendency towards a constant oxide layer formation rate. Ultimately there is an equilibrium rate of corrosion product transfer to the coolant water which is equal to the removal by the coolant cleanup system and deposition on the fuel. The rate of corrosion in corrosion resistant steels is a function of temperature, oxidation-reduction conditions, and hydrogen factor (pH_T).

The corrosion rate of corrosion resistant alloys depends on the surface finish which affects surface micro roughness and changes surface properties. This effect has been seen for steam generator tube samples in these studies. Mechanical treatment or polishing increases the size of surface micro roughness and leads to sub-surface damage. This increases the rate of diffusion on the grain boundaries causing increased corrosion rate and oxide layer formation. A surface treatment that produces a smoother finish, such as electrolytic polishing, does not produce sub-surface damage and ensures formation of a thin and uniform chromium-enriched layer. This encourages a low corrosion rate and the formation of thin oxide films.

Experiment results at Nuclear Research Institute Řež (Czech Republic) examined elevated hydrogen levels, which were produced either by higher ammonia or direct hydrogen dosing. Elevated hydrogen inhibits corrosion product content and in consequence also mitigates Crud layers and leads to lower dose rates. The lowest surface activities were measured for ‘Elevated Ammonia Water Chemistry’. Further, zinc dosing had a detectable, positive impact on activity spikes during shut-downs.

Zinc injection significantly reduces the rate of corrosion processes in the primary circuit.

Proper operational practice, efficient primary water chemistry and other good practices result in lower dose rates and other operational benefits. Very low values of outage and total effective doses represent the outcome of good primary chemistry water regime, well organised radiation protection structures and strict implementation of ALARA principles during the working activities related to high radiation risk.

8.3. Corrosion of fuel materials

The corrosion of zirconium based alloys will produce zirconium dioxide (ZrO_2) as the main product. The formation of a ZrO_2 layer on fuel cladding alloys by water based oxidation also causes wall thinning and the absorption of hydrogen into the zirconium alloy which has the potential to embrittle the cladding.

Russian advanced fuel, TVSA, with a fuel cladding alloy containing 1%Nb, did not show any problem in operation at Kozloduy NPP. Finnish experimental work, comparing Russian alloy E110 (a 1%Nb alloy) in either lithium or potassium based solutions showed potassium as preferable to lithium for mitigating fuel cladding oxidation. Also, the Ukrainian study shows the strong corrosion resistance of alloy E110.

Fluoride concentration in the coolant was shown to exhibit a significant effect on oxide thickness, with a sharp increase as the fluoride concentration increases but then a small decrease as the concentration approached 1 mg/kg.

In Korean studies it has been noted that fuel cladding corrosion decreases as hydrogen increases, related to the absence of hydrogen peroxide in the coolant.

Based on operational data with the mixed core of Westinghouse fuel assemblies and Russian standard TVSM fuel loads in the South Ukraine NPP, no corrosion problems have been seen on either the Westinghouse ZIRLO^{TM} or the Russian Alloy E110 fuel claddings. No crud was observed on the surface of any of the fuel rods throughout their life in the WWER-1000 core. The operation of lead test assemblies demonstrates that Westinghouse fuel can be operated successfully in WWER-1000 mixed cores with the primary coolant parameters that meet the Chemistry Guidelines. Further, the established design safety limits are met

Finnish mathematical model of cladding corrosion calculated the thickness of an inner layer as several times smaller than that of an outer layer, which indicates that the corrosion properties of the zirconium alloys in the initial stage of oxidation are controlled by a thin layer close to the alloy/oxide interface. The thickness of the outer layer was shown to increase with the concentration of $Li^+/K^+/F^-$ ions in the electrolyte and the effect of potassium concentration on the field strength in the inner layer on E110 was smaller than on the inner layer formed on Zircaloy-4. The thickness of the whole oxide and the outer layer is larger on Zircaloy-4 than Alloy E110 and in general increases with potassium concentration. On the other hand, the thickness of the inner layer is somewhat smaller on Zircaloy-4 than on E110 and tends to decrease with increasing potassium concentration, which reflects the different properties of the inner layer on the two alloys.

No impact of zinc addition at the concentration required for dose rate mitigation (5–15 µg/kg) or for corrosion of reactor materials (15–40 µg/kg) has ever been seen on fuel cladding. This parameter has been listed as having a potential influence on cladding corrosion, but no evidence of negative impact of zinc on fuel cladding is reported.

8.4. Crud deposition

Fuel rods can become covered with deposits of corrosion products, which have precipitated from the coolant during operation. Precipitation of this crud deposit in the core must be avoided as far as possible, as it can lead to fouling of the fuel, loss of heat transfer efficiency, fuel failures, increased radiation fields and neutronic disturbances in the core.

Crud is important because it can affect fuel behaviour. Crud is very porous, with porosity typically around 80%. If localized boiling occurs, this porosity can be enriched in boron, a neutron poison which can induce AOA, or lithium which can enhance the corrosion of zirconium alloys. Moreover, boiling inside crud porosity may decrease the local hydrogen concentration. Oxidizing species, such as H_2O_2 formed by radiolysis, may be concentrated in the crud and corrosion can be accelerated. In addition, the crud on cladding behaves as a thermal barrier and the activated crud released back to the coolant would increase radiation dose rate around the circuit.

The composition, thickness and evolution of crud of FA surfaces depend very much on operational conditions, such as steady state operation, water chemistry conditions or different oxidation conditions. The deposits along the fuel rod may induce SNB and result in an acceleration of corrosion products and boron precipitation on the fuel cladding surface and an increase of coolant radioactivity. ^{58}Co in the coolant was found to be an indicator of the acceleration of the growth of deposits.

A lot of laboratory experiments performed at different temperature on Zy-4 samples, used in PHWR systems, showed that the quantity of the adherent corrosion products was dependent of thickness and especially physical-chemical characteristics of the initial zirconium oxide films. Thus, in the case of compact and adherent oxides with thickness of 1–1.5 μm (formed at 310°C) a small quantity of corrosion products was deposited. On surfaces oxidised in steam (at 400°C with 8–12 μm thick and porous character) thicker, adherent deposits of corrosion products were formed. Both gravimetric analysis and microscopic analyses showed that the adherence of corrosion deposits increased with the thickness and especially with the porosity of zirconium oxides; a significant quantity of the corrosion deposits incorporate in pores and lateral cracks of oxides.

The quantity of deposited crud depends on boiling conditions: in Korean PWRs more crud was deposited for the section of the higher sub-cooled boiling within the test conditions, so the sub-cooling significantly influenced the crud deposition behaviour. There was no evidence of crystalline crud formation where there was no sub-cooling in contrast to the crystal growth seen in where sub-cooled boiling had occurred.

The amount of crud deposition is much larger in experimental tests with higher concentrations of iron and nickel in the test solution. The deposit has a porous structure and the thickness is about 15–20 μm in the test case when the nickel and iron concentrations were both 20 mg/kg.

In PWRs it was found that as pH increases, the amount of deposition decreases. The amount of deposit in one study was 2.8 μg/cm^2 at pH 6.9 and more than 5 times the amount of the deposit (0.5 μg/cm^2) seen at pH = 7.2.

At higher values of pH, a Japanese study also considered crud deposition on a Zr-4 surface as a function of pH value. Tests were performed with various pH_T values in the range of 7.2–7.7. The crud layer analysis showed increasing nickel (ranging from 10–35 μg/kg) with Ni/Fe ratio either >0.5 or <0.5. Iron and nickel are enriched in the deposit with increasing heat flux.

The Swedish project studied the characteristics of PWR fuel crud and its possible impact on AOA/CIPS. Metallic nickel and mixed oxides (Cr_8O_{21}, $(Cr_xNi_yFe_z)_3O_4$) have been found in fuel crud samples taken from the surfaces of real fuel. The structure and composition of crud varies from plant to plant and for various materials but it is not clear if pH and H_2 have an influence. It was noted that the increase in steam generator surface area following the upgrading a unit with new steam generators with Alloy 690 rather than Alloy 600 tubing was also an influencing parameter.

Operational experience from Korean plants showed that the structure of the crud could be divided into three layers (inner, middle and outer layer) based on the O/Fe ratio. The O/Fe ratio of the middle layer (4–11μm) is about 1.5–2.0. The Ni/Fe ratio of the middle layer is about 0.5. It is quite reasonable to conclude that the middle layer is mainly $NiFe_2O_4$ (Ni:Fe:O = 0.5:1.0:2.0). In the outer layer, the Ni/Fe ratio and the O/Fe ratio increase. It seems that the outer layer is composed of other oxide phases as well as $NiFe_2O_4$. Ni content is highest in the outermost surface which is interface with primary water. The high value of Ni/Fe ratio in the crud can be related to the CIPS history of given units.

The crud scraping data and other chemistry data of R4 since the start-up of its commercial operation have been also reviewed. The amount of the deposited crud in R4 core has been low. Little or no influence of the crud presence to the fuel performance is therefore anticipated under the present reactor operational regime. However, the nickel concentration of the fuel crud was found to be high in some cases, which would be unfavourable if heavy crud deposition occurs.

There have been few reported cases of crud induced cladding failure for PWRs. However, there is increasing concern about the elevated dose rate due to formation of an increased amount of crud on fuel cladding surfaces. There are also an increasing number of reported CIPS cases, probably due to the formation of an increased amount or an unfavourable type of fuel crud. CIPS occurrence is often associated with high duty cores and steam generator replacement. The latter is often accompanied by replacing the steam generator tubing with a nickel based alloy (such as Alloy 690) with improved corrosion resistance, but it is not uncommon that new steam generators often have a much larger water contacting surface area, which would lead to the formation of a similar amount of corrosion products in reactor water as from the original steam generator.

8.5. Decontamination

One possibility for the elimination of crud is decontamination. However, such an operation is time consuming, expensive, includes additional risk of corrosion and induces a large quantity of undesirable LRW. It is important to thoroughly evaluate the advantages and drawbacks of such an operation before applying it. There was a strong view that decontamination is a maintenance action that should be avoided as much as possible.

Decontamination using concentrated solutions leads to relatively high surface roughness characterized by more intensive corrosion and carryover of its products, which in turn can cause renewed, higher contamination during subsequent operation A higher carryover rate after decontamination is the root cause of the problems encountered at several WWER plants (Paks, Novovoronezh, Loviisa, etc.) where more intensive corrosion and carryover of its products led to growth of deposits on the fuel. Amorphous corrosion products, such as hydroxides, remain on steel surfaces. Insufficient treatment (passivation) of these surfaces and secondary deposition of existing corrosion products can create additional amounts of corrosion products, which are then redistributed through the entire primary circuit.

The Czech NRI performed loop tests that demonstrated the capability of decontamination to eliminate corrosion products and also tests showing the beneficial effect of surface preconditioning. It was concluded that the practical methods to control crud formation are accurate control of primary water chemistry, careful decontamination and a surface layer passivation. However, decontamination is only needed in the event of the refurbishment of any important component that requires a drastic decrease of dose rates to allow such maintenance activities.

The Indian laboratory evaluated the feasibility of a high temperature decontamination process for the removal of fuel deposits. They showed that crud deposition and formation on core internals are unavoidable and whilst crud needs to be minimised, high temperature oxide dissolution with single reagent such as NTA was shown to be very effective.

8.6. Passivation

The Canadian investigation showed that no CIPS has been seen in plants where the steam generator tubes had previously been passivated, highlighting the benefit of such a treatment for less corrosion product release from the steam generators and thus less risk of crud formation and CIPS.

The operation of the Czech WWER at Temelín, after initial passivation, showed a low level of corrosion products in the primary system as well as low dose rates during the subsequent fuel cycles.

The passivation process used successfully during hot tests at NPPs Temelín and Mochovce has been shown insufficient when it was used on decontaminated steam generator tubes. The surfaces of these tubes were not passivated by the treatment. Decontamination had changed the surface composition in comparison to an as-manufactured surface. There is, therefore, a need to prove the preconditioning method of surface passivation for each type of material used in operation and it cannot be presumed, that steam generator tube decontamination will return their surfaces to the original condition.

8.7. AOA and CIPS

8.7.1. Definition and causes

CIPS is the term generally used in this document for the axial distortion of the power shape due to crud deposition and the subsequent local accumulation of boron. The term is used to cover local power distortions as well as more global effects affecting a whole core.

This phenomenon was originally known as AOA. In a reactor the measured Axial Offset (AO) of the power in a core is controlled by the operator and may vary with time in the cycle. It is predicted by the core monitoring system and is defined as a percentage:

$$AO = \frac{P_{top} - P_{bottom}}{P_{top} + P_{bottom}} \times 100$$

Where:

P_{top} = integrated power in the top half of the core.
P_{bottom} = integrated power in the bottom half of the core.

The Russian definition is that there is an AOA when there is a difference of at least 3% between the measured and predicted axial offsets. This definition is for the whole core and is widely used in other countries as well.

The term AOA reflects the outcome of the problem seen at a reactor, whilst CIPS refers to the ultimate cause of the power distortions. CIPS can therefore be used to indicate any level of power distortion caused by crud deposition and is readily used to describe weaker or more local phenomena than AOA. However, through custom and practice, both of the terms AOA and CIPS are widely used in the industry to refer to the same issue of CIPS.

There are 3 conditions that are believed necessary for CIPS to occur:

- SNB at fuel rod surfaces.
- crud (corrosion products) deposition on fuel rod surfaces.
- boron deposition on fuel rod surfaces or adsorption in the crud.

There is a consensus that hideout of boron on the fuel is the ultimate, direct cause for CIPS and that the root cause is corrosion product deposition in the upper spans of fuel assemblies.

As a result of chemical analyses of corrosion product deposits taken from the upper regions of high axial offset anomaly once-burnt fuel assemblies after Cycle 9 in the Callaway PWR, large amount of Ni_2FeBO_5 (bonaccordite), which had not previously been reported as a component of fuel crud, were observed and it was suggested that formation of bonaccordite increased boron retention on fuel rods to result in AOA.

Deposition mechanism of boron on fuel rods under sub-cooled boiling conditions was considered as an analogy of soluble metallic ion deposition on BWR fuel rods. Under BWR conditions, bubbles grow until their release from heated surface due to buoyancy. Their maximum diameter was as a function of flow velocity.

Korean operational experience shows that AOA is associated with a high Ni/Fe ratio in the crud. The influence of a very porous deposit, equivalent to a crevice, where chemical species may concentrate, has been seen. Boron and lithium enrichment have been found in such deposits.

From reported CIPS cases in the USA and the Republic of Korea, it is evident that high duty crud formed in high duty PWR may have very different crud thicknesses. In the USA the thickest crud layer is about 140 µm whilst in the Republic of Korea it is only about 20 µm. There are also cases where crud thicknesses are around 40 µm but the PWR had no experience of even slight CIPS. Therefore, crud thickness alone is not a able to trigger a CIPS occurrence. From several laboratory studies, Chen (Sweden) has proposed that it is the crud density which initiates a CIPS occurrence. The reason is that a dense crud layer, which does not need to be very thick, can effectively increase boron precipitation through a hide-out mechanism. In other words, if a crud layer is very porous then CIPS would not occur.

The existing understanding from plant observations and laboratory simulation studies suggest the following mitigation approaches:

- To choose better steam generator materials, which would form little or porous fuel crud layer.
- To modify water chemistry, to one which is unfavourable to the formation of a dense crud layer.
- To reduce SNB by improved fuel management.
- To remove corrosion products in primary water and on fuel cladding surfaces as much as possible, through e.g. fuel cleaning.

8.7.2. Chemistry parameters

The effects of major chemical parameters on boron deposition are listed as follows Table 8.1.

TABLE 8.1. CHEMICAL PARAMETERS ON BORON DEPOSITION

Chemical parameters	Effect
Boron	Boron concentration, C_B, has direct effects on boron deposition.
Lithium	Lithium enhances chemical reaction on the fuel surface to produce $Li_2B_4O_7$. The contribution of [Li] on boron deposition is modelled as the conversion factor from unstable boron to quasi-stable $Li_2B_4O_7$.
pH	Decreasing pH enhances boron deposition on fuel due to the lower dissolution rate.
Ni	Ni enhances boron deposition in three ways: 1) Thick NiO and $NiOFe_2O_3$ deposits result in thermal insulation effects and increasing the potential for sub-cooled boiling on the fuel surface. 2) Thick NiO and $NiOFe_2O_3$ deposits provide hidden sites for soluble boron and quasi stable $Li_2B_4O_7$ deposits and enhance their deposition. 3) Nickel enhances the chemical reaction of the fuel surface to produce $NiOFe_2O_3$. The contribution of [Ni] on boron deposition is modelled as the conversion factor from quasi-stable $Li_2B_4O_7$ to stable $NiOFe_2O_3$.
Oxygen	Under sub-cooled boiling conditions the concentrations of oxygen and OH radicals might increase and then enhance chemical reactions of NiO, $Li_2B_4O_7$ and $NiOFe_2O_3$ formation. The oxidation reactions are not involved in the models described in this document.

8.7.3. Chemistry control

Chemistry control is the most important method for CIPS mitigation in the short term for a defined NPP in operation. Several parameters that may have an impact on CIPS have been identified during the various contributions to the project and are listed in decreasing order of potential importance:

– pH selection with Ni solubility. CIPS is clearly associated with the presence of nickel in crud, which is favourable for boron precipitation in nickel ferrite (spinels) $Ni_x(Cr,Fe)_{3-x}O_4$. It has been demonstrated that pH and other physico-chemical environmental conditions (redox potential, concentration of corrosion products temperature) have a strong influence on crud composition (nickel proportion).

– Use of enriched ^{10}B. The risk of crud formation is dependent on the total boron concentration, and this concentration can be lowered throughout a cycle through the use of boric acid enriched with the neutron absorbing isotope, ^{10}B (EBA). However, whilst the influence of total boron on solubility and risk of deposition has been shown, it is not so clear if the benefit from the use of EBA is proportional to the EBA enrichment, as the cause of CIPS is due to ^{10}B deposition in the crud. If the boron deposition in the crud is not driven by a precipitation process, the amount of ^{10}B in the crud might be similar with either EBA or natural boric acid, as core control is dependent on the concentration of ^{10}B alone.

– Potassium vs. lithium for pH regime. According to the Bulgarian study, as potassium is more soluble than lithium, there is less risk of crud deposition with potassium in WWER and thus less risk of CIPS. However, some studies have shown that potassium may more easily induce corrosion on RCS materials than Li. Consequently, there is no clear advantage of one or the other alkaline reagent for pH control in the primary coolant.

– Importance of hydrogen concentration. High H_2 in old plant has the potential to cause transient high crud, but is not considered to be of significance. There is the possibility of controlling the concentration through ammonia addition rather than with direct hydrogen injection (which requires a minimum pressure) though a high hydrogen concentration achieved with ammonia addition would impact the ion exchange resin behaviour.

– Silica and other compounds (Al) effect. Plant data from France does not show any significant effect of silica, although this could have been an important parameter due to the low solubility of zeolite, rich in silica and aluminium or similar compounds, including silicates.

– Zinc injection. Zinc is currently being added to PWR units in an increasing number of countries, including USA, Spain, Germany, Japan, Brazil, Switzerland and France. Between 2009 and 2012, it is expected to be added to units in the Republic of Korea, South Africa and China as well as further units in the original countries. Moreover, the zinc injection is expected to be injected from the 1st cycle of operation in the new reactors (AP1000, EPR). Zinc addition remains an extremely high priority for dose rate minimization, but also to protect against PWSCC of Alloy 600 in a very limited number of units.

There has been no clear demonstration of an impact of zinc on CIPS in this project, though there is some evidence that there may be a benefit. It is nevertheless suggested that zinc addition be considered where there is steam generator replacement or fuel core management modification.

The occurrence of enhanced cladding corrosion at Farley after zinc had been added to one unit is not attributed to this addition, since the other unit, without zinc, experienced the same phenomenon. The cause is believed to be more likely due to the power increase of the units.

In BWR, the crud in units adding zinc is more tenacious, but it is considered that zinc is not an issue for such crud. Zinc addition shows a good feedback, without any negative impact on fuel oxide, on fuel failure or on CIPS.

8.7.4. *Outstanding chemistry issues*

One open issue is the behaviour of M5™ fuel cladding with Zn > 15 µg/kg.

Further work is needed before a final decision on the possibility of zinc addition at the WWER-1000 reactors in the Ukraine can be taken. This includes a comparison of the RCS structural materials in WWER and PWR units where the zinc addition technology is currently used, the influence of zinc addition on the activity accumulated in high temperature filters during their operation in WWER-1000 reactors and finally the estimation of equipment changes and the dose levels required.

8.7.5. *Materials*

The material influence on CIPS is particularly important for PWR where the Steam Generator tubing, representing the largest surface of the primary coolant, may differ from plant to plant. It is clear that the nickel content of these materials may have a direct influence on CIPS, since nickel is directly involved in the crud composition and morphology formed from corrosion products circulating in the primary coolant. There are large differences in the nickel content of the various alloys used for Steam Generator tubing (>72% for Alloy 600, >58% for Alloy 690, 30–35% for Alloy 800 and 10–11.5% for 18–10 Ti stainless steel in WWER steam generators).

Several studies have shown that crud deposition associated with the risk of CIPS is related to the presence of crud with high nickel content. Therefore it would be expected that steam generator tubing material made from Alloy 600 should be one of the causative parameters of CIPS. However, CIPS has also occurred in units with Alloy 690 steam generators. The absence of CIPS in German units may thus be only partly related to the still lower nickel content in Alloy 800. Finally, the steam generator tubing with the lowest content (10% in WWER) is likely to provide a lower risk but the Hungarian representative believed that these units are not immune.

Results of operational experience of CIPS in EDF units with various steam generator tubing materials, show no difference in CIPS results between units with Alloy 600 or 690. The Korean units with 690 steam generator tubing do not have CIPS but the experience feedback is insufficient to draw any conclusion. Overall it can be concluded that the plants with the higher nickel content steam generators are more prone to CIPS, but there still seems to be risk associated with lower nickel materials.

8.7.6. Operational matters

There are several operational parameters affecting the fuel that may have a significant impact on CIPS. These include:

- Fuel options: cycle length and fuel enrichment have the most important direct consequence on boron concentration at the beginning of the fuel cycle to cope with neutronic needs. Mitigation would be to use other neutronic absorbers or to use EBA.
- Temperature is a key parameter for CIPS, with its effect on the solubility of corrosion products and other compounds. The trend towards higher power in power plants can mean increased temperatures and associated risks that must be clearly evaluated with new NPP or when upgrading older ones.

Independent of the fuel cycle length, the number and type of transients experienced or load follow operation are potential influencing parameters for CIPS occurrence as there is solubility variation during such transients, associated with temperature and heat flux. The operational experience of French NPPs, where load follow is practiced, has not shown any specific impact.

Details of the core design may also influence CIPS through the selection of control rod operation, boron concentration and neutronic flux in various parts of the fuel length. Sub Nucleate Boiling is another key parameter that has been considered for CIPS appearance but may not be the most important.

The operational experience from WWER power plants showed no incidence of any axial offset caused by corrosion products deposit on the surface of fuel rods. There is a trend towards higher fuel burnup and increased cycle length in WWERs and CIPS remains a concern for the future.

The international feedback shows that the key chemistry indicator of AOA is lithium return during power transients; however, lithium is not systematically monitored during transient periods. For this reason, the data concerning this indicator is very limited and it should be taken into account that in some cases, lithium peaks coming from the resins have been observed in the primary coolant. Therefore, before concluding that CIPS is present following the detection of a lithium peak, it is important to verify the resins conditions.

Cycles affected by AOA are characterized by corrosion product activities during operation at the end of cycle which are higher than these from units without CIPS. For example, in one French unit the ^{58}Co activity at the end of the cycle 15 was 60 MBq/t while at the end of cycle 16 (affected by CIPS) it was 800 MBq/t.

8.7.7. pH_T control during operation

Primary coolant pH is a major parameter for the control of corrosion product releases from the out-of-core materials and crud deposition on the fuel rods. An elevated pH is recommended to reduce the release of corrosion products and the transfer of crud during the cycle. However, an increase of the pH needs a higher lithium concentration which may favour the $LiBO_2$ precipitation on the core and consequently on AOA development.

EDF tries to minimize corrosion product transport from out-of-core to in-core regions by selecting the most appropriate chemistry, which is currently based on nickel ferrite solubility rather than magnetite. This is the reason that the target pH_T is increasing. However, whilst lithium is allowed up to 3.5 mg/kg in American and Spanish units with ZIRLO^{TM} or M5^{TM} fuel cladding, such a concentration is not yet allowed in all French units. Increasing lithium concentration might be beneficial for limiting corrosion product transport and for dose rate control but there remains concern for fuel cladding oxidation and for the likelihood of deposition of B-Li compounds.

German units operate at a pH_T of 7.4 which is more easily achieved through the use of EBA and 12 months fuel cycles.

The CIPS evaluation in the French fleet showed that chemistry parameters (lithium upper value, pH_T, Zn) within the allowed range were not the main cause of the phenomenon which was more related to steam generator replacement and increased cycle length. In the presence of CIPS, high values of nickel, iron or cobalt have not been noted in the primary coolant. Theoretically, an increase of pH_T, and lithium should be beneficial for corrosion product transport but they are not sufficient to avoid CIPS.

Further work shows that the negative impact of lithium concentration is limited. The results of modelling calculations (Nexia Model) predict lithium borate precipitation when the crud thickness is higher than 25–30 μm. For lithium concentrations higher than 3.5 mg/kg and boron concentration between 1000 mg/kg and 800 mg/kg, the coefficient of solubility for the nickel ferrite (oxide composition more representative of PWR) is positive and the risk of corrosion product precipitation is lower than in conditions with a lithium concentration below 3.5 mg/kg.

These results are in agreement with the Studsvik's observations in laboratory test loops. The presence of $LiBO_2$ has only been identified in deep crud. According to these results, the increase of lithium concentration in the primary coolant may have different impacts depending on the unit characteristics. For the units with a low inventory of corrosion products and without a history of CIPS the lithium concentration increase can be considered as a preventive way to limit the risk of crud deposition thanks to the pH rise. Conversely for units with a high inventory of corrosion products a lithium concentration increase can produce the precipitation of borates in the crud and develop flux anomalies.

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ABBREVIATIONS

AECL	Atomic Energy of Canada Limited
ALARA	As low as reasonable achievable
BOC	Beginning of cycle
BWR	Boiling water reactor
CANDU	Canada deuterium uranium
CC	Coolant chemistry
CD	Cold-drawn
CDC	Deuterium concentration
CDE	Control distance electrochemistry
CILC	Crud induced localized corrosion
CIPS	Crud induced power shift
CRP	Coordinated Research Project
CS	Carbon steel
DAWAC	DAta processing technologies and diagnostics for WAter Chemistry and corrosion control in Nuclear Power Plants
DEHA	Diethylenhydrazineamine
DZA	Depleted zinc acetate
DZO	Depleted zinc oxide
EBA	Enriched boric acid
ECP	Electrochemical corrosion potential
ECP	Electrochemical corrosion potential
EDF	Electricité De France
EIS	Electrochemical impedance spectroscopy
EPRI	Electric Power Research Institute
FA	Fuel assembly
FAC	Flow accelerated corrosion
HDCI	High duty core index
HDCI	High duty core index
IAEA	International Atomic Energy Agency
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
IGA/SCC	Intergranular attack/stress corrosion cracking
ISOE	The Information System on Occupational Exposure
KAERI	Korea Atomic Energy Research Institute
KNF	Korea Nuclear Fuel Co. Ltd
LRW	Liquid radioactive waste
MA	Milled annealed
MCM	Mixed conduction model
MHWC	Moderate hydrogen water chemistry

MOX	Mixed oxide fuel
MSLR	Main steam line radiation
NPP	Nuclear power plant
NTA	Nitrilo-triacetic acid
ONLC	On line noble chemistry
OWC	Optimum water chemistry
PDM	Point defect model
PHTS	Primary heat transport system
PHWR	Pressurized heavy water reactor
PWR	Pressurized water reactor
PWR	Pressurized water reactor
PWSCC	Primary water stress-corrosion cracking
R&D	Research and design
R4	Ringhals-4
RBMK	Reaktor bolshoy moschnosti kanalniy
RCM	Research coordination meeting
RCM	Research Coordination Meeting
RCS	Reactor coolant system
SCC	Stress-corrosion cracking
SEM	Scanning electron microscopy
SEM/EDS	Scanning electron microscope with energy-dispersive x-ray spectroscopy
SHE	Standard hydrogen electrode
SNB	Sub-nucleate boiling
TECDOC	Technical document
TEM	Transmission electron microscopy
TRU	Transuranic
TT	Thermally treated
TVSA	Russian fuel assembly
TVSM	Russian fuel assembly
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
WCS	Water cleanup system
WWER	Water-water energetic reactor
XANES	X-ray adsorption near edge spectroscopy

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ANNEX I

1st RCM report:

Notes on the 1st RCM of the FUWAC CRP, held at Vienna, 4th–6th July 2006.

The meeting was attended by representatives of 12 of the 13 Water Chemistry teams who have Agreements or Contracts to participate in FUWAC, two further representatives from teams interested in joining FUWAC attended as observers.

1. TUESDAY 4TH JULY

The first day started with a welcome to the participants from Mr Killeen, the Scientific Secretary and a presentation describing the methodologies used by the IAEA to promote nuclear power. In particular he gave details of the work programme B2, Power Reactor Fuel Engineering.

Mr Killeen then gave a second presentation covering the background to the CRP, describing the work carried out in the four previous Water Chemistry CRPs. He discussed the results of the consultancies that had been held prior to the start of the FUWAC project, to determine the main objectives of the programme, which include monitoring, maintaining and optimising the water chemistry regime in the primary circuit of water-cooled power reactors, taking into account high burnup operation, mixed cores and plant aging.

The main research objectives to support the programme objectives are to understand the causal mechanisms for the following issues:

- deposit composition and thickness on the fuel;
- AOA/CIPS and power limitation (both AOA and CIPS are used for the same crud related phenomenon in NPPs. For simplicity and consistency, throughout these notes AOA is used as the acronym);
- fuel oxide growth and thickness;
- corrosion related fuel failure;
- CILC;
- radioactivity build-up in RCS.

The consultants suggested that specific research topics to achieve these targets could include work to determine:

- The influence of the reactor design on the studied issues: various operating water reactor designs will be looked at (PWR, WWER, BWR, RBMK, CANDU and other PHWR) where participants are able provide data from these types of reactors;
- The influence of cladding, spacer grid, steam generator and reactor pressure vessel materials will be considered, taking into account current burnups and cycle lengths;
- The influence of other input data, including reactor age, fuel tramp contamination, fuel duties, neutron flux profile, sub-cooled boiling, radiochemistry results linked to activity release and build-up, fuel cleaning and RCS decontamination;
- The influence of operating parameters having an impact on the studied issues, including burnup and enrichment, cycle length, load follow, transients and fuel element cycle number;
- The effects of important chemical parameters which may affect the fuel, including type and concentration of boron and alkaline reagent, pH, hydrogen, oxygen and some others;
- The role of chemical additives and other advanced water chemistry regimes on fuel (deposits and corrosion);
- The role of important operational events, e.g. shutdown and trip processes, on fuel (deposits and corrosion) and dose accumulation.

In the course of the CRP performance all participants will exchange information and experience in monitoring, maintaining and optimising water chemistry regimes in primary circuits of water cooled power reactors. They will study remedies for the minimization of corrosion and crud deposition by chemistry optimization for high burnup, mixed cores, plant aging. At the end of the CRP it is expected that all participants will have an improved understanding of the causes and mechanisms of fuel corrosion and crud deposition on fuel, and be able to better control the composition and mode of formation of crud, particularly at high burnups and also for advanced water chemistry regimes (noble metals or zinc addition, etc) and in ‘old’ units.

A final report, either as a TECDOC or as a TRS, will be published.

Mr Killeen (IAEA) concluded by outlining the meeting programme and agenda.

The participants then each gave a presentation describing their particular concerns and the research proposals submitted to the coordinated project.

Mr Dobrievski (Bulgaria) noted that he had three main concerns; AOA which was the result of SNB; the increase of corrosion rate of primary circuit materials; and crud deposition. He stated that these issues are all related to SNB aligned to higher boron concentrations for advanced cycles. His aim was to develop different chemistry conditions for different parts of the cycle to minimise AOA and corrosion. He described the differences between WWER and PWR type plant, noting the potassium hydroxide additive for pH control, and the Austenitic (08Cr18N10T) composition of WWER boilers. The main object of his investigations is the determination of high temperature coolant pH_T values by varying concentration of both boric acid and applied alkalizing reagent (KOH) at different coolant temperatures in different parts of primary circuit.

He described the conditions for AOA in PWR plant and explained why there was concern with the potential for a similar phenomenon in WWER, in particular through the presence of lithium in the later part of an extended (18 month) cycle arising from boron in the coolant, even though potassium is used for pH control rather than lithium as in a PWR. His work programme for the first year of the CRP will focus on a review of AOA in PWR plant and preparation for a study of hideout and hideout return processes in primary circuits of operating WWER-1000. Plant data from Kozloduy NPP will be collected.

Mr Lister (Canada) felt that there were many unresolved issues with fuel crud and wanted to go back to basics. He questioned whether crud deposition was controlled by surface processes or by transport of depositing species in the coolant. Kinetic models can assume that the water is saturated with relevant species, e.g. Fe has a solubility limit of around 2.45ppb, which varies with temperature, and so static tests can be misleading. He proposed to determine ‘release’ rates: a) in-reactor, crud scrapes etc; b) out-of-reactor coupon tests; and c) loop tests. He discussed experimental problems, including noting that reactor circulation is too rapid to allow thermodynamic equilibrium and that release from steam generators occurs under heat flux conditions. He stated his belief that kinetic effects are important. He was intending to study a simulated primary coolant system in an autoclave, seeking to improve modelling, determine the effect of zinc additions and why some plants are more prone to crud deposits than others.

Mr Zhang (China) showed pictures of the autoclaves where he was carrying out oxidation tests in a loop containing high lithium concentrations. The tests are on a new Zircaloy-4 with heat flux and at lithium concentrations up to 10mg/l. The intention is to study SCC sensitivity as a function of lithium concentration. This report gave rise to considerable discussion on the appropriate levels of lithium to use in autoclave tests, and this was followed up later in the meeting.

Mr Splichal (Czech Republic) described the differences between PWR and WWER water chemistry and noted that he was looking to find an OWC to respond to challenges from radiation fields, material integrity and fuel integrity. Currently the 440 WWERs operate at around pH of 7.2 and the WWER 1000s at 7.1, using potassium rather than lithium for pH control and ammonia rather than hydrogen for oxidation potential control. He showed that radiation doses were lower at Temelín NPP, where Hot Functional Testing Passivation had been carried out, than at Mochovce NPP, He concluded by noting that there were no significant oxidation problems in WWER Primary Water, and that passivation during Hot Functional Testing was successful and useful. He proposed to summarise experience and provide plant data from Temelín and Dukovany, to evaluate decontamination processes out-of-pile, and to investigate the effect of crud on fuel oxides.

Mr Kinnunen (Finland) was interested to study high lithium and potassium concentrations with various zirconium alloys, including M5^{TM}, Zr/Nb and Zr-4. He would investigate the initial oxidation of fuel using a matrix of alloys and water compositions in autoclave testing.

Mr Nordmann (France) described the French nuclear programme, with its 58 NPPs. He noted that there was no indication of a water chemistry indicator for the onset of AOA/CIPS. He was interested to determine if it would be possible to predict AOA risk by evaluating chemistry and radiochemistry, and was interested in the effect of B/Li on AOA, both before and after onset. He proposed to provide operational information from the French reactors.

Mr Schunk (Hungary) described the PAKS incident, where very significant fuel damage occurred accidentally during a cleaning operation to remove deposit from assemblies due to be reloaded in the reactor. Large quantities of crud had been deposited on the assembly grids following a decontamination process carried out on the reactor. His objectives were to characterise particulates in the primary water, the corrosion state of fuel assemblies, transport of deposit and hot particles.

Mr Narasimhan (India) was not present at the meeting, but his presentation was given by Mr Lister. The interest in India was for studies on flow accelerated corrosion and metal ion passivation techniques for Water Chemistry Management. It is proposed to use a high temperature loop to study flow assisted corrosion and the effect of various additives. Subsequent work would develop deposits and study their formation and dissolution and to undertake appropriate modelling.

At the end of the day, Mr Nordmann, chairing the session, summarised the discussions following the presentations, noting the following topics as highlights:

- Data from operating plant and from plant investigations would be made available.
- Lab test data will be available for comparison.
- More data for key parameters will inform the choice between potassium and lithium.
- Optimization of pH from the concentrations of K or Li.
- Optimise operational exposure.
- CANDU fuel deposition and flow assisted corrosion .

2. WEDNESDAY 5TH JULY

Mr Uchida (Japan) described the purpose of his study; to review experiences with experiments of crud deposition on BWR fuels, developments of models related to crud deposition and their extension to metallic ion behaviours; to review experiences with evaluation of corrosive conditions in BWR primary coolant and at the fuel surface and to introduce future subjects for application of the models for evaluating corrosion behaviors of fuel cladding materials. He provided a detailed model of iron deposition as a function of flow and pressure and described crud scraping experiments which showed a deposit profile along a fuel rod, and noted that he was trying to measure Fe deposition in situ, to avoid problems with loss of deposit on cooldown. He described modelling of nickel, cobalt and iron oxides and a radiolysis model for BWR coolant. He provided his work programme, commencing with an attempt to understand the crud deposition mechanism by considering boiling conditions, heat transport properties of deposits and their composition, as well as estimating local pH dissolution of alkaline species from the deposits

Ms Pirvan (Romania) discussed the effects of water chemistry on Zircaloy-4 alloy cladding of advanced CANDU fuel. She provided a review of work previously carried out on corrosion product deposits, giving information from coupon testing in autoclaves on the bypass loops at Cernovoda NPP, a CANDU-6 PHWR, and in a TRIGA research Reactor. Abnormal chemistries were tested in the Research Reactor tests, showing a range of damage to the cladding material. Her forward work programme included experimental studies allow understanding of problems during operation at high burn-ups and for longer residence time; crud build-up on fuel cladding and the effect on oxidation and hydriding process; water radiolysis and acceleration of Zircaloy-4 alloy oxidation rate and hydriding process; water chemistry changes and thermal gradient increase effects on localized clad corrosion; SCC parameters in presence of an iodine increased volume.

Mr Kritski (Russian Federation) described how deposition of crud on the spacer grids of WWER-440 had caused flow resistance problems. He also noted that immediately after decontamination of the circuit there had been an increase in corrosion rate and deposition. The phenomenon of ‘pressure drop’ which takes place in the core of WWER-440 reactors was considered. A model was developed to explain the increase in pressure drop in-core and the redistribution of deposit in the core and primary circuit. The physical-chemical basis of the model is the dependence on temperature of the transport of corrosion products, pH_T value of coolant, and the correlation between rates of corrosion product (Fe) formation (after steam generator decontamination) and their removal from the circuit. His contribution to the project in the first instance will be to provide operational details from the Power Plants and continue to develop the model.

Mr Chen (Sweden) noted the difficulties inherent in simulating AOA out-of-pile. There is no irradiation; it is difficult to reproduce the correct boiling conditions, crud oxide composition and to avoid dissolving them. Excellent experimental control is required. He described some of the equipment available in Sweden and proposed a programme for the FUWAC CRP that included an exchange of knowledge of the characteristics of PWR and BWR cruds; crud data analysis using statistical correlation methods; pre-crudding techniques; autoclave techniques; analytical techniques and ideas and hypotheses.

Mr Zuyok (Ukraine) described the work carried out in his institute on advanced fuel concepts. Of particular interest to the CRP was the work on a Zr1%Nb alloy manufactured in the Ukraine. Out-of-pile testing had shown good behaviour compared with standard E-110 alloy tubing. Operational data for water chemistry at operating reactors would be studied. Further autoclave testing at WWER-1000 operational conditions (parameters such as temperature, water pressure and WWER-1000 coolant composition) would be undertaken, along with simulated deviations from steady-state conditions. Monitoring will collect data on CC, generalize the results, and make suggestions for CC improvements which could decrease the rate of zirconium alloy corrosion.

Mr Hettiarachchi (United States) discussed the challenges facing BWR water chemistry, including intergranular SCC, operator dose and fuel performance. He noted ‘good’ (Zn, H, Rh, Pt) and ‘bad’ (Cl, S, O, peroxides) additives in BWR coolant for intergranular SCC control and gave a brief history of problems in BWR plant, and how water chemistry has been improved, so that conductivity is now below 0.1 mS/cm. He showed the GE optimum feedwater chemistry guidelines and discussed how NobleChem^{TM} was effective in lowering ECP, lowering crack growth rates and drywell dose rates.

Discussion Sessions

Following the participant’s presentations, discussion sessions were held to allow a sharing of concerns and ideas, and to attempt to optimize the sharing of effort in the CRP to maximize the benefit for all the participants.

The first discussion session was chaired by Mr Uchida and considered the topic of Crud transportation and composition. The discussion focused on the nature of the crud, and what were the characteristics of cruds that were capable of inducing CIPS/AOA in NPPs. It was noted that soluble species may not be seen in post irradiation examination and there are crud releases (bursts) on shutdown in both BWR and PWR plant due to chemistry changes. It was also noted that RBMK plant have similar cruds and that WWER plants tend to have more magnetite and less nickel in the crud than PWRs. Mr Schunk noted that a study in Hungary showed that the oxide layer on WWER fuel was changed by the decontamination process and was very similar to PWR crud, but that no AOA had yet been observed.

Consideration was given to the composition of the steam generators and it was noted that WWER plant had 18/10 steel Steam generators, and there was therefore less nickel in the coolant. It was also noted that WWER used potassium rather than lithium for pH control and that differing solubilities might affect crud compositions. The correlation between AOA and steam generator tube material was recognized, with plants with steam generators manufactured from alloys 690 and 800 less likely to give rise to AOA. Mr Beverskog stated that Westinghouse believed that nickel enrichment in the crud was necessary for AOA, and that perhaps bonaccordite or a crud with a high specific surface area was necessary e.g. needles.

Mr Kritsky noted that power plant operated at an oxygen potential that was close to the $Ni/NiO/Ni_xFe_{(3-x)}O_4$ phase boundaries, and that perhaps AOA plants were operating in the more oxidizing conditions. Mr Chen noted that many species have been found on filters including iron, iron/chromium/nickel iron/chromium oxides and also needle like NiO after peroxide injection. Silicates had also been found. Mr Uchida wanted to know if the chemical form of the cruds can change when on the fuel surface and exposed to a temperature flux. He noted that radiotracer measurements can demonstrate x3000 concentration of species in a crud oxide. Mr Chen noted that hideout return can be very slow and believed that crud density was important. Mr Lister noted that nickel could be relevant due to absorption on a large surface area; Mr Beverskog considered that physisorption was important, but Mr Chen disagreed because the boron fraction by monolayer physisorption should be tiny and was interested in the lithium concentration in crud spinels. This was usually experimentally difficult to determine by SEM/EDS, as lithium is not seen by X-ray fluorescence techniques. Mr Chen referred to the most recent paper to be presented to Water Chemistry Conference in the Republic of Korea that lithium tetraborate crystals were seen to precipitate in the crud, Mr Beverskog stated that the boron and lithium peaks are not in relation to each other for precipitation of a borate compound as the difference is a factor of 200 in AOA plants during shut-down.

The discussion then focused on experimental techniques to determine the boron and lithium in crud, and Mr Chen noted that a very high concentration of B was needed for reliable detection by SEM/EDS. The detection of small concentrations of B and Li can be readily made by inductively coupled plasma mass spectrometry (ICP-MS). Mr Nordmann asked what the differences were between WWER and PWR cruds. Mr Splitchal described his loop tests, and said that he was studying modifications from normal chemistry, but that the cruds were mainly Cr and Fe rich, with some rare, small areas with high nickel content. He was not able to identify boron or potassium deposits. Neutron absorption might help, but was an expensive test method.

At the end of the session the participants gave a list of their main concerns:

Participant	Main Issue of concern for the CRP
Mr Hettarachchi	OWC can improve plant performance in BWR.
Mr Beverskog	AOA – the morphology of the crud.
Mr Chen	Plant data from AOA plant – AOA is rare.
Mr Kritsky	Influence of operating parameters and chemical parameters for AOA. New WWER NPPs will experience boiling conditions.
Mr Pirvan	The effect of water chemistry on fuel oxidation in CANDU. Hydriding with varying water chemistry and increasing local temperature. Zinc deposition.
Mr Uchida	Modelling as a bridge between the plant and laboratory.
Mr Schunk	Experience based monitoring and control of particulate transport.
Mr Nordmann	What is the optimum lithium level for i) corrosion, ii) dose rate and iii) AOA. For mitigating these three issues, is potassium better than lithium?
Mr Kinunnen	Oxidation of different cladding materials for potassium and lithium additions.
Mr Splichal	Correlation of water chemistry parameters in WWER to deposition on surfaces. Thickness and composition of corrosion products, their deposition and dissolution. Radioactivity buildup and to compare NPP and laboratory data.
Mr Zhang	Fuel corrosion under boiling conditions. The effect of steam generator materials in new NPPs as they go to 18 month cycles. Increase of lithium concentration and the corrosion of stainless steels.
Mr Lister	Identify and quantify the transport, quantities and composition of corrosion products and the effect of heat flux.
Mr Dobrievski	Factors leading to high local boron concentration in crud, concern with extended cycles and hideout caused by transient and shutdown needs to be understood.
Mr Zuyok	Optimum boron and pH chemistry to control fuel crud. Need chemistry recommendations.

Mr Lister chaired the final discussion session of the day, which focused on issues concerning experimental techniques and problems in relating such experiments with plant data. The challenge was seen to be how to make representative crud out of reactor. The participants exchanged information on the differences between the various reactor systems and the crud types seen, noting high concentrations of magnetite particulate in BWR due to the oxidizing conditions, whereas the conditions were less stable in WWER, in CANDU the issue of mass transfer due to fluid shear stress was highlighted. The crud bursts in PWR on shutdown and the levels of particulate and soluble species at startup and during transients were described. Mr Nordmann offered to provide additional detail of Co^{58} release during crud burst.

Mr Chen described his autoclave facilities and said that he was able to simulate PWR crud, in particular the chimney structure and with a ratio of Ni/Fe ratio of around 1.5. A threshold thickness of crud of 20 μm was noted as necessary for an AOA type of crud. It was noted that Calloway had had the most extensive experience with AOA and they would be asked to provide detailed information to assist experimental simulation of their crud.

The effects of zinc additions were discussed and it was noted that there were concerns that zinc injection early in cycle could enhance the probability of AOA.

3. THURSDAY 6TH JULY

Mr Nordmann described an IAEA programme to develop water chemistry guidelines for WWER plant. This would include both primary and secondary coolant circuits and the intention was to hold a series of consultant meetings, with a final Technical Meeting at the end of 2007 to finalize the document. It was noted that advanced fuel cycles for WWER would allow boiling duty.

Mr Killeen described the IAEA Technical Cooperation Programme which was being carried out in Romania. The main objective of the proposed work is to obtain data which can be used by the NPP operators to evaluate ways to avoid crud deposition on fuel after decontamination.

To reach this objective the following activities will be performed:

- To summarize experiences with radiation build-up crud deposition, primary water chemistry and decontamination.
- To evaluate Loviisa and Paks data and experiences.
- To propose analyses and experimental programme set-up.
- To realise experimental programme and its evaluation.
- To formulate recommendation and strategy for water chemistry and decontamination in future.

The effect of decontamination and passivation on crud deposition on primary circuit surfaces will be investigated under steam generator operation parameters with steam generator tube model equipment. The investigations on the effect of tube decontamination and passivation process on crud deposition on fuel surface will be performed on reactor water loop 4 (RVS 4) of reactor LVR 15. The experimental programme consists of short term examinations involving decontamination, if need be passivation and long-term examinations under primary water chemistry parameters. Decontamination experiments will be carried out with pre-oxidized steam generator tube.

Following these presentations the participants prepared a matrix showing the various concerns and how the various proposals would address the identified problems. The following Tables AI.1–AI.7 reflect the outcome of these discussions.

TABLE AI.1. ACTIONS

Country/Org.	Action
France	*to provide Belleville data for AOA correlations*
IAEA	*to circulate meeting notes*
All	*to respond to draft meeting notes with corrections*
IAEA	*to coordinate any new collaborations*
France	*to seek Callaway information*

TABLE AI.2. POSSIBLE COORDINATION ACTIVITIES

Someone to provide Sweden with characteristic AOA crud data
Collaborations – samples tested elsewhere?
Collaborations – data reviewed elsewhere?
Quality assurance – comparative studies
No crud on CANDU fuel
Autoclave intercomparison
Range of parameters to study (e.g. Li concentration)

TABLE AI.3. RECOMMENDED LITHIUM AND BORON CONCENTRATIONS FOR TESTING.

Clad corrosion tests	CRP Recommended values to allow for intercomparison of studies			
		ppm		
Li effect	2.2	3.5	7	
Boron		1100		10–16 g/kg (acid)

TABLE AI.4. EXPERIMENTAL PROGRAMMES

Country	Experimental programmes
Bulgaria	Causes of boron deposition in crud. Extended cycles need reactor system approach. Hideout return from transient and shutdown.
Canada	Identify and quantify transport, amounts and composition of corrosion products. Heat flux effects, materials effects.
China	Fuel corrosion in boiling, effect of steam generator in new NPP and 18 month cycles, increased Li. Corrosion of stainless.
Czech	Correlation of different modifications to WWER water chemistry parameters to deposit on surfaces includes Zn. Thickness, composition, deposition and dissolution of corrosion products.
Finland	Oxidation of different claddings, K or Li as alkali.
France	Optimization of Li for corrosion, dose rate and AOA if Li inadequate, is K a better reagent for PWR.
Hungary	Plant experience, monitoring and control. Particle transport.
India	(FAC Decontamination).
Japan	Modelling as a bridge between plant and lab.
Romania	Water chemistry on fuel oxidation and hydriding in CANDU. Zinc deposition.
Russia	Influence of operating and chemistry parameters, new NPP will expect boiling.
Sweden	Real AOA is rare, Plant data from AOA plant.
(Sweden)	AOA and crud morphology.
Ukraine	Optimise B and pH for fuel corrosion. Water chemistry recommendations.
USA	OWC can improve plant performance – BWR.

TABLE AI.5. MAJOR CONCERNS

AOA	PWR – some?
Potential for AOA	Higher duty fuel in WWER, PWR
Need to discover bounds	Longer cycles in WWER
	PWR – those plants so far immune
	BWR
	Old steam generators with varied histories
	Crud composition
	Operating conditions
	Operation transients
	Zinc
Clad corrosion	New claddings
	Li limits
Crud induced flow resistance	WWER issue
Dose reduction	RBMK; BWR

TABLE AI.6. EXPECTED OUTCOMES

Water chemistry guidelines	Type specific?
Bounds to avoid AOA crud	
Avoid AOA	
Corrective action	
Optimization of additives	Data to show separate effects?
Corrosion data	Li or K limits, clad specific?
Corrosion data	Heat flux, boiling.
KOH or LiOH	Is it possible to change alkaline additive between reactor types.
Bounds to avoid heavy crud	
Share best practice	
Identify generic and type specific issues	

TABLE AI.7. MATRIX OF CONCERNS AND MEANS FOR ADDRESSING THEM – (A) AUTOCLAVE, (TR) TEST REACTOR DATA, (PD) PLANT DATA, (M) MODELLING, (I) INVESTIGATION

Issues		How addressed
PWR	KOH/LiOH?	Finland (A)
	AOA initiation	France (PD)
	Crud composition	Sweden (PD); Canada (A)
	Transport of crud	Canada(A,M) (India) France (PD)
	Steam generator materials	Canada; IAEA
	SCC steam generator materials	China (A)
	Clad oxidation	China (A); Finland (A); Romania (A)
	Higher power/cycle length	Finland (I); Bulgaria (I); France (PD)
	Li concentration	France (PD) Finland (A)
WWER	KOH/LiOH	Finland (A) Bulgaria (PD)
	Clad deposits following decontamination	Czech (TR); Hungary (PD), Russia (PD)
	Higher power/cycle length	Russia (PD) Bulgaria (I); Ukraine (I); Hungary (PD)
	Clad oxidation	Ukraine (A, PD); Russia (PD, M)
	Evaluation water chemistry and radioactivity	Czech (PD, TR) Bulgaria (PD, I)
BWR	Clad oxidation	Japan (A)
	Crud deposition	Japan (M)
	Crud composition	Sweden (PD); Japan (PD)
	Dose control	USA (PD) Japan (PD); Sweden (PD)
	SCC	USA (A, PD), Japan (A)
PHWR	FAC	Canada (M); (India(A)(PD))
	Clad oxidation	Romania (A)
	CANFLEX issues	Romania (A)
	Crud deposit analysis	Romania (A, TR)
	Initiation of clad SCC	Romania (I)
RBMK	Activity build-up	Russia (PD, M)
	Clad oxidation	Russia (PD, M)
AOA	Definition	France (I); Bulgaria (I)

TABLE AI.7. MATRIX OF CONCERNS AND MEANS FOR ADDRESSING THEM – (A) AUTOCLAVE, (TR) TEST REACTOR DATA, (PD) PLANT DATA, (M) MODELLING, (I) INVESTIGATION (CONT.)

Issues		How addressed
AOA	Threshold boron content of AOA crud	Sweden (I)
	Crud composition	Sweden (I)
	Crud morphology	Sweden (I)
	Operational experience	France (PD)
	Steam generator materials	France (PD)
	Sub-cooled boiling/heat flux	Sweden (I); Hungary (PD)
	Hideout/hideout return	Bulgaria (PD,I)
	Chemistry or radiochemistry indicator?	France (I)
	Zinc effect	France (I,PD)
Zinc data	Effect on AOA potential	Canada (I)
Plant data	Comparison with lab data	Czech (TR) France (PD,I) Sweden (I)
	AOA causal conditions?	Bulgaria (TR); All (I)
	Fuel corrosion	Russia (PD)
	Decontamination	Russia (PD); Hungary (PD) (India (PD))
Fuel crud	Density	Sweden (I); Canada (M)
	Morphology	Sweden (I); Canada (M)
	Composition	Romania (A);
	Deposition	Russia (M); Japan (PD)
	Dissolution	Japan (PD)
Suspended crud	Deposition	Canada (M)
	Dissolution	Sweden (I)
	Particulate	Hungary (PD)
	Transport	Canada (M)
	Composition	Hungary (PD)

ANNEX II

2nd RCM report:

Notes on the 2nd RCM of the FUWAC CRP, held at Chennai, India, 11th–14th December 2007.

Each participant gave a report summarising their work. Many participants considered that the knowledge of crud composition and deposition mechanism was one of the most important issues for FUWAC. From the various presentations made during the technical sessions, and the discussions of the last session, the following areas of interest were defined.

1. AOA/CIPS

1.1. The influence of structural materials

The influence of materials, particularly steam generator tubing is of interest since there is a large surface area and release of corrosion products from the steam generator tubing. Consequently, steam generator tubing material should therefore be selected appropriately either during initial manufacture or for steam generator replacement, which is a common event for aging plant.

Several studies have shown that crud deposition associated with the risk of boron compound deposition and CIPS are related to the presence of crud with high nickel content. It was seen that steam generator tubing material with Alloy 600 (the highest Ni percentage) is associated with CIPS, but this can also occur when the steam generator tubing material is of Alloy 690 (lower Ni proportion). The absence of CIPS in German units may thus be only partly related to the lower Ni content in Alloy 800. Finally, the steam generator tubing with the lowest Ni content (10% in WWER) is likely a positive point. It was concluded that Ni, either as Ni metal or Ni oxide, is one important cause of CIPS

1.2. The influence of water chemistry

The influence of water chemistry is the most important means of CIPS mitigation in the short term for a defined NPP in operation. Several parameters that may have an impact on CIPS have been identified during the presentation and then classified by decreasing order of potential importance:

- pH selection with Ni solubility: CIPS is clearly associated with the presence of nickel in crud, which is favourable for boron precipitation in nickel ferrite (spinels) $Ni_x(Cr,Fe)_{3-x}O_4$. It has been demonstrated that pH and other physico-chemical environment (redox potential, concentration of corrosion products temperature) conditions have a strong influence on crud composition (nickel proportion). This is why the study of pH influence on CIPS is of utmost importance for CIPS.
- Use of Enriched ^{10}B (EBA): The effect of EBA is uncertain, if crud formation is not dependent on total boron concentration, then the effect of the higher concentration of ^{10}B will balance the lower total boron concentration and not affect the risk of CIPS.
- K vs. Li for pH regime: Potassium being more soluble than lithium, there are less risk of crud deposition with K in WWER and thus less risk of CIPS. But some studies have shown that K may more easily induce corrosion on RCS materials than Li. Consequently, there is no clear advantage of one or the other alkaline reagent for the pH in the primary coolant.
- Importance of H_2 concentration: High H_2 in old plant could cause transient high crud. There is a trend in selecting hydrogen concentration at low values (10 ml/kg) in Japanese NPP and higher values (near 50) in US NPP but the objective is more Alloy 600 PWSCC than CIPS or dose rate mitigation. Consequently, the participants did not consider that hydrogen concentration should be of high priority in FUWAC studies. This question has nevertheless been raised due to the easier possibility of regulating the concentration at low value trough ammonia addition than with direct hydrogen injection (which requires a minimum pressure) while a high hydrogen concentration with ammonia addition would impact the ion exchange resin behaviour.
- Silica and other compounds (Al) effect: Plant data from France does not show any significant effect of silica, although this could have been an important parameter due to the low solubility of zeolite, rich in silica and aluminium or similar compounds, including silicates. Silica has also been noted in

crud composition. After discussion, it has been decided that this would not be a proprietary chemical parameter to further investigate

- Zinc injection: this is added mainly for dose rate and in some cases for PWSCC of Alloy 600 mitigation. There has been no clear evidence of a potential impact of zinc on CIPS and this parameter has been placed at the last position for CIPS, but keeps an extremely high priority for dose rate minimisation.

1.3. Design and operation; fuel cycle options

There are several other parameters that have been identified during the meeting and that may have a significant impact on CIPS. These include:

- Fuel options (cycle length and enrichment) – boron concentration of BOC is important.
- Temperature. Several participants confirmed that temperature is a key parameter in CIPS with a strong influence on corrosion product and other compounds solubility. The trend in choosing higher powers in NPP means increased temperatures with associated risks, (corrosion, CIPS, etc) that must be clearly evaluated with new NPP or when upgrading older ones.
- Operating conditions and options: Independent of the fuel cycle length, the number and type of transients or load follow is another potential influencing parameter in CIPS occurrence Solubility modifications occur during such transients, associated with temperature and heat flux. The example of French NPP, where nuclear energy represent about 80% of electricity generation is an excellent example for evaluating these parameters. For the moment, no specific impact has been observed.
- Core design – sub-nucleate Boiling (SNB): This is not seen as a key parameter at this time.

2. DECONTAMINATION

This is a way to eliminate crud and deposits in the primary coolant for decreasing future occupational exposure from dose rates and future risk of CIPS associated with corrosion product transport. However, such an operation is time consuming, expensive, includes several risks of corrosion and induces a large quantity of undesirable LRW. It is important to fully evaluate the advantages and drawbacks of such an operation before applying it.

This has been mainly a WWER issue, while the CIPS and dose rates mitigation has mainly been a problem for PWRs. Thus, a clarification on this decontamination, its purpose and how to decide to apply it or not is of great importance in the FUWAC project.

3. FUEL CLADDING CORROSION

Several important presentations of this second FUWAC meeting dealt with fuel cladding corrosion which is a crucial issue regarding safe operation of NPP The following parameters have been evaluated.

- Cladding Material: There are many studies on the behaviour of various fuel cladding: Zr-2, Zr-4 as well as new materials such as ZIRLO^{TM}, M5^{TM} and E110. In addition to material corrosion, the oxide growth, with a direct impact on CIPS as well is being studied.
- Core characteristics: As for CIPS, several parameters may influence fuel cladding corrosion. These are burn up, temperature, heat flux, SNB.
- Chemistry:
  - pH selection with Ni solubility: The most studied parameters on fuel cladding corrosion, before this FUWAC project, have been the pH and alkali (lithium) concentration, particularly at the beginning of the fuel cycle and with always higher values with high performances fuel and high boron content.
  - K versus Li: For many years the selection of Potassium (WWER) versus Lithium (PWRs) has been evaluated for the influence on various components of the primary system. One participant explained that K might more easily induce fuel cladding corrosion. This may be explained by the higher solubility.
  - Radiolysis, Hydrogen: This phenomenon is easily controlled in operating NPP but may nevertheless affect fuel cladding corrosion in relation with the redox potential of the water near

the material surface. Hydrogen stripping at SNB may also be evaluated in relation with hydriding and redox potential.

  - BWR; NWC, HWC, Noble Metal: The type of chemistry applied in BWR is evaluated with a limited effort. Noble Metal Chemical Addition is the most studied chemistry allowing the decrease of hydrogen addition.
  - Zinc, noble metal: no impact of zinc addition has ever been seen on fuel cladding, at the zinc concentration required for dose rate mitigation. This parameter has been listed as one that might have a potential influence, but not with a high priority.

4. DOSE RATE MITIGATION

The material selection (importance of nickel), its release and activation into ^{58}Co, presence of cobalt and its activation into ^{58}Co, presence of antimony in pump sealing, of silver in various components is not covered by the FUWAC project. Chemistry is deeply evaluated for its impact on dose rate, being also related to corrosion product transport and CIPS phenomenon.

- K versus Li and pH: The main interest of the study for the FUWAC project is related to the alkali selection for reaching the optimum pH for minimizing the presence of activated corrosion products. No specific laboratory or plant data have yet been presented in the FUWAC project but this may be kept in mind for the alkali selection, in addition to other contingencies (material corrosion, CIPS) discussed during the meeting as noted earlier.
- New fuel and fuel cycle options with, in some cases, higher boron concentration at BOC can affect dose rates.
- Zinc addition. Noble metal: There is an increasing number of PWR adding or considering the addition of zinc for dose rate mitigation. There has been a clear demonstration of the benefit in many cases (though not in all) of zinc addition which is evaluated in the frame of the FUWAC project for PWRs. Such an addition as not been evaluated for WWERs but there is no reason not to consider it as a potential improvement, although no specific need for such an addition appears at this time. Similarly, noble metal addition is studied for BWR.

5. FUTURE WORK

The participants considered the future work programme and agreed to a matrix of projects and targets for the next period. Each described the main outcome that they hoped to see from FUWAC and for the majority it was clear that their projects had been well planned at the outset of the CRP and were proceeding to plan.

ANNEX III

3rd RCM report:

Notes on the 3rd RCM of the FUWAC CRP, held at Turku, Finland, 15th–18th September 2009.

This third meeting was the last one where all the contributors to the project made presentation of their results. After introductory presentations reminding the participants what where the objectives of the projects, the main results obtained and what was still expected, 15 presentations from various countries were made and provided the opportunity for interesting discussion on the projects results, issues and conclusions.

After these presentations, further discussion took place, evaluating whether or not participants and the Agency expectations on the project had been fulfilled as well as considering specific technical issues.

Finally, the structure of the final report with the detailed content of each chapter was been prepared followed by the list of volunteers to contribute to these chapters. This is in the appendix to this Annex.

1. CORROSION PRODUCTS

The loop tests carried out by the Canadian team did not show any relation between the steam generator tubes heat treatment and the grain size, but the steam generator material gave different results with smaller (10 µm) and harder grain sizes for Alloy 600 (high Ni content) compared with Alloy 690 or 800 (15–35 µm). The corrosion product transport has been evaluated in the loop and will continue with longer duration to get more representative results.

2. CRUD COMPOSITION AND IMPACT OF CIPS

The Japanese representative presented a study considering micro-layer evaporation as the mechanism for nuclear boiling (dry out). It allows a prediction of iron crud deposition on boiling surfaces of BWR fuel rods and it was extended to apply to metallic ion deposition, affected by chemical forms of the deposits. The deposition rate decreases when the flow rate increases but increases with the pressure. The deposition rates can be applied to an evaluation of soluble and insoluble species on the fuel surface and also to determine the local pH caused by local concentration of chemical species.

The calculated deposited boron amount is one or two orders larger than the deposited corrosion product. The average residence time of 1 through 10 min result in a slight increase in boron concentration factor. It is difficult to evaluate the deposit during operation and the hide out return is unknown.

The Swedish project studied the characteristics of PWR fuel crud and possible impact on CIPS. Metallic nickel has been found in fuel crud samples. Mixed oxides include $(Cr_xNi_yFe_z)_3O_4$, and Cr_8O_{21} containing Cr^{III} and Cr^{VI}, which are thus oxidizing. Plant parameters have been looked at to evaluate the reason for the abnormal ^{58}Co increase and focused on shutdown (mixed oxides) and H_2O_2 injection (more iron oxide). The crud varies from plant to plant, for various materials but it is not clear if pH or H_2 have an influence. It was noted that the increase in steam generator surface area when upgrading a unit during steam generator replacement and switching form Alloy 600–690 tubing had an influence.

The essential parameters for CIPS are:

- SNB (Sub Nucleate Boiling) with local heat flux, fuel power, core design, fuel management;
- boron, with Li and pH, EBA (enriched boric acid) and chemistry regime;
- crud, with corrosion rate, surface area, cycle length, crud clean up, crud characteristics.

It is considered that much of the crud is released during shutdown, explaining a critical influence of the cycle length. Boron is supposed to be in crud as bonaccordite $NiFeBO_5$. Under SNB, LiB_4O_7 may be seen and also

H_3BO_3 and B_2O_3. Alloy 600 induces higher Ni content in crud than Alloy 690 and even more than Alloy 800, corresponding to the Ni content of the steam generator tubing. The pH is supposed to have a limited effect on the short term due to the prevailing Ni effect; in the long term it may affect the corrosion rate and thus the crud amount. EBA (Enriched Boric Acid, higher concentration of B10 isotope) is considered of marginal influence.

A second Japanese study was related to crud deposition on Zr-4 surface. No CIPS has been seen in Japanese units. Tests have been performed with various pH_T values (7.2, 7.3 and 7.7). The crud layer analysis respectively showed 10–25 and 35 µg/kg Ni with Ni/Fe ratio either >0.5 or <0.5. Fe and Ni may easily be enriched in the deposit which is increasing with the heat flux. During the various tests, Zr-4 corrosion resistance was maintained.

3. FUEL INVESTIGATIONS

From the Bulgarian presentation, it can be seen that the advanced fuel assemblies, containing Gd_2O_3 as a solid neutron burnable absorber show good behavior. The Russian advanced fuel element ‘TVSA’ with a fuel cladding containing 1%Nb did not show any problem in operation at Kozloduy NPP. The plant is operating with Boron versus Alkali (mainly K) curve corresponding to an optimum pH of 7.0–7.2. The diagram also includes various zones with limited duration which decreases when difference from actual and target pH value increases.

Temelín WWER in Czech Republic will also use the TVSA fuel.

The Finnish laboratory used the CDE technique to compare fuel cladding oxides thickness in various chemical environments on the fuel cladding material, E110. For a Li increase from 2–10 mg/kg, oxide thickness increases from about 220–300 nm while for a primary water treatment with potassium, and a corresponding Li concentration of 10–56 mg/kg, the oxide thickness is slightly lower 180–260 nm, showing that potassium is to be preferred to lithium for mitigating fuel cladding oxidation on the new E110 material. Fluoride showed a significant effect on oxide thickness, with a sharp increase as the fluoride concentration increases but then a small decrease as the concentration approached 1 mg/kg. The maximum oxide thickness was about 300 nm.

In Korean studies it has been noted that fuel cladding corrosion decreases as hydrogen increases, related to the absence of hydrogen peroxide.

The Romanian Laboratory experimentally studied the influence of pH on Zr cladding oxidation and hydriding, with high burn up fuel. A porous oxide is observed after the tests on samples with initial oxide films up to 4 µm thick. The oxide layer is formed by corrosion in LiOH at high pH (pH =12.3, equivalent to 70 mg/kg Li) and is an accelerated and non uniform corrosion process. There is no acceleration of Zr-4 corrosion for pH <11.8, corresponding to 3.5 mg/kg Li). As pH increases there is an initial oxidation process and then lithium concentrates in the pores of thicker oxides which induces further oxidation and hydriding with the development of micro cracks. The presence of boron with LiOH inhibits the oxidation acceleration by lowering the pH and preventing the formation of Zr-O-Li groups due to the interfering reaction between LiOH and anion vacancies. Boron substitutes for Lithium in the oxide lattice

The complex corrosion mechanism for Zr-Nb alloys has been studied by the Russians. The rate of Zr alloy corrosion under reactor irradiation depends on heat flux through fuel cladding, CC (in addition to H_2O_2, OH^-, O^{2-} concentrations one should account for the concentrations of hydrogen, ammonia, strong alkali - LiOH, KOH, pH, etc.) and some other parameters.

A correlation between E110 alloy corrosion and the ion hydration energy (ΔHi) in solution at various water coolant chemistries has been observed in Russian experiments. Alloy E110 shows strong corrosion resistance.

The team from the Ukraine carried out analytical and experimental research on the effect of primary water chemistry on corrosion in WWER 1000 cores.

Improvements in Ukrainian NPP include:

- upgrading automatic and laboratory chemical control systems;

- establishing expert diagnostic water chemistry systems;
- improvement of supplying water chemistry systems;
- modernization of chemical and volume control system;
- implementation of hydrogen water chemistry;
- zinc addition;
- implementation of enriched boric acid;
- morpholine water chemistry of secondary circuit.

Application of EBA in Ukrainian NPPs is being considered for new fuel loads (high burn up and MOX) but not with units operated with present fuel loads. For 99% EBA this will allow a decrease in the concentration of boric acid in the primary water by a factor of 5 and substantially reduce the amount of LRW and improve the corrosion behaviour in the RCS.

The Ukrainian study included the possibility of replacing ammonia by hydrogen to gain a substantial reduction of impurities in the primary water, which would also reduce their corrosive effects on the RCS materials. This is not being done to improve the ion exchange resin behaviour as frequently claimed.

Based on the operational data with the mixed core of Westinghouse fuel assemblies and Russian standard TVSM fuel loads at the South Ukraine NPP, no corrosion problems have been seen on the Westinghouse ZIRLO^{TM} or the Russian Alloy E110 fuel claddings. No crud was observed on the surface of any of the fuel rods throughout their life in the WWER-1000 core.

It has been shown during a 7200 hour testing period that alloy E110 exhibits similar kinetics in corrosion environments with pH_T between 5 and 7.2. At a pH_T of 10.0 the corrosion rate is higher.

According to the experiments in the Ukraine, at 350°C the corrosion rate of stainless steels increases with increasing pH values. However, the observed increase is not significant.

4. DECONTAMINATION – PASSIVATION

The operation of the Czech WWER at Temelín, after initial passivation, showed a low level of corrosion products in the primary system as well as low dose rates during the 5th and 6th fuel cycles. There is thus no need for any decontamination. Temelín-1 is operating with 20 mg/kg of K corresponding to a pH_T of 7.1 +/- 0.1.

The Czech laboratory of NRI performed loop tests that demonstrated the capability of decontamination for eliminating corrosion products and also tests showing the beneficial effect of surface preconditioning. It was concluded that practical methods to control crud formation are accurate primary water chemistry, a careful decontamination and a surface layer passivation. However, decontamination is only needed in the event of refurbishment of any important component that requires a drastic decrease of dose rates to allow such significant maintenance activities.

The difference between WWER-440 and WWER-1000 was noted, with coolant temperature ranges for the two plant types of 269–295°C and 289–322°C respectively.

The Hungarian investigation was carried out after the Paks incident which caused severe fuel damage in a fuel cleaning tank in the reactor pond. The absorption of actinides on stainless steel surfaces was found to be significant. Actinides are found as micron sized particles or as colloids. Cm is mainly in the form of particles (~µm size) and colloids, while Pu and U are mainly in the form of cationic species, and Cs is also found bound to these particles.

There is deposition of radioactive corrosion products on in-core and out-core surfaces. No corrosion problem has been observed on Paks Unit 4 which has not been decontaminated.

A study of the circulation of particulates in the primary coolant showed that the residence time of particles is less then one day for particles from the steam generator, 1–7 weeks for particles migrating with the coolant and ¼ to ½ year for particles from the fuel assemblies. These studies on particles have given a better understanding of contamination/decontamination, corrosion and transport of elements.

The Indian Laboratory evaluated the feasibility of a high temperature decontamination process for the removal of fuel deposits. They showed that crud deposition and formation on core internals are unavoidable, and whilst crud needs to be minimised, high temperature oxide dissolution with single reagent such as NTA was shown to be very effective. There is a considerable increase in the dissolution rate of Fe_3O_4 in NTA with temperature. The dissolution rate of $Ni_{0.2}Fe_{2.8}O_4$ was comparable to that of Fe_3O_4. Even the normally stable oxide Cr_2O_3 can be dissolved to an appreciable extent at high temperature (160°C). An NTA formulation containing N_2H_4 at high temperature was found to dissolve oxide formed over SS-304 very efficiently. The addition of N_2H_4 to NTA (near neutral pH) reduces the corrosion rate of base metal. However, it also reduces the oxide dissolution rate, though within acceptable range. Zinc ferrite could be effectively dissolved. The process can be tuned for PWR fuel surfaces by implementing Zinc addition. Magnesium ferrite dissolution was significantly lower than zinc ferrite, indicating its utility for passivation and in reducing flow accelerated corrosion. Bonaccordite could be effectively dissolved. High temperature DCD can be effective in mitigating CIPS.

The Russians developed a model with different parameters (power, B, redox potential, chemistry) to explain the observed pressure drop rise in-core and the redistribution of deposits in the core and in the primary circuit of WWER-440 NPPs. The physical-chemical basis of the model is the dependence of transport corrosion products on temperature, pH_T of the coolant, and the correlation between rates of corrosion products (Fe) formation (after steam generator decontamination) and their removal from the circuit. The deposits along the fuel rod induces SNB and results in an acceleration of corrosion products and boron precipitation on the fuel cladding surface, and an increase of coolant radioactivity. Co-58 is the indicator of the acceleration of the growth of deposits.

5. CHEMICAL ADDITIVES

According to the French representative, zinc is currently being added to PWR units in an increasing number of countries, including USA, Spain, Germany, Japan, Brazil, Switzerland and France. Between 2009 and 2012, it is expected to be added to units in the Republic of Korea, South Africa and China as well as further units in the original countries. The main objective is for dose rate mitigation, but also to protect against PWSCC of Alloy 600 in a very limited number of units.

The important occurrence of CIPS at Farley after zinc had been added is not attributed to this addition, since the other unit, without zinc, experienced the same CIPS phenomenon. The cause is believed to be more likely due to the power increase of the units. In BWR, the crud in units adding Zn is more tenacious, but it is considered that Zn is not an issue for such crud, since the thickness is lower and has a uniform distribution of Zn (<8% weight basis). No $ZnSiO_3$ or Zn ferrite has been seen in scraping analyses. Zn only precipitates with an initial crud thickness >50 µm. Consequently, EDF now have a silica limit of 1.5 mg/kg since no problem has been identified in the presence of this impurity and it is difficult to eliminate.

Zinc addition shows a good feedback, without any negative impact on fuel oxide, on fuel failure or on CIPS which may even be a smaller concern in the presence of Zn. The remaining questions are the behaviour of M5^{TM} fuel cladding with Zn >15 µg/kg. Should there be an increase in Zn content in SNB region, it will continue to be benign.

Zn addition to the primary coolant is beneficial for dose rates and PWSCC and may also help to alleviate CIPS. It is suggested that zinc addition be considered where there is steam generator replacement or fuel core management modification.

Further work is needed before a final decision on the possibility of zinc addition at Ukrainian NPPs can be taken. This includes a comparison of the RCS structural materials in WWER and PWR units where the zinc addition technology is currently used, the influence of zinc addition on the activity accumulated in high temperature filters during their operation in WWER-1000 reactors and finally the estimation of equipment changes and the dose levels required.

The American representative explained the advantages of ONLC in BWR units for mitigating Crack Growth Rate of SCC on different materials. The conclusion is that,

- Combination of DZO and NobleChem^{TM} is more effective in dose rate reductions;
- noble metal addition lowers ECP and crack growth rates;
- on-line NobleChem^{TM} lowers ECP and crack growth rates;

- on-line NobleChem^{TM} releases activation corrosion products from surfaces resulting in lower dose rates;
- there is no impact on fuel performance.

With OLNC, Fe_2O_3 is transformed into Fe_3O_4. ONLC is applied on 2 Swiss units and 4 US units. It could be considered for WWER instead of switching from ammonia to hydrogen.

6. NPP FEEDBACK ON CIPS

The Canadian investigation showed that no CIPS has been seen in plants where the steam generator tubes had previously been passivated, highlighting the benefit of such a treatment for less corrosion product release from the steam generators and thus less risk of crud formation and CIPS

The large number of French NPPs allowed an interesting analysis of various potential influencing parameters on CIPS occurrence. No whole core effects of CIPS have been seen in France, but there are a number of localised events, each affecting small numbers of assemblies to some extent.

EDF tries to minimize corrosion product transport from out-of-core to in-core regions by selecting the most appropriate chemistry, which is currently based on Ni ferrite solubility rather than magnetite. This is the reason that their target pH_T is increasing. However, whilst Li is allowed up to 3.5 mg/kg in American and Spanish units with ZIRLO^{TM} or M5^{TM}, such a concentration is not yet allowed in all French units. With ZIRLO^{TM} cladding, the upper limit is 3.5 mg/kg but remains at 2.2 mg/kg for Zircaloy cladding, except in Cattenom 2 which is used as a lead test plant for this change.

If a pH increase seems to be beneficial for corrosion products and dose rate limitation, it does not appear to prevent the occurrence of CIPS which appeared in some US units despite the pH and Li increase. The same observation has been made at Cattenom 2.

German units operate at a pH_T of 7.4 which is more easily achieved with the presence of EBA (Enriched Boric Acid) and 12 months fuel cycles.

It appears that the affected assemblies are generally those in a second cycle, though the USA, some 1st cycle assemblies have also been affected.

Some participants thought that the number of coolant loops in a plant might be significant, as 4-loop plants had seen more evidence of the phenomena; this is not confirmed by the experience of the French units where 900 MW units (3 loop plants) are also affected in an increasing number of cases.

Increasing Li concentration might be beneficial for corrosion products transport limitation and for dose rates as well but there is concern for fuel cladding uncertainties and for the likelihood of deposition of B-Li compounds.

The influence of hydrogen has also been investigated in the French units and did not show any impact on CIPS occurrence within the specified range of 25–50 ml/kg (though no unit actually operated above 44 ml/kg). According to Japanese results reported by the French representative, a lower H_2 value is believed to be favourable for lowering the fuel crud thickness and the PWSCC of Alloy 600. A low H_2 favours the presence of NiO instead of Ni which will increase the total nickel solubility. The American approach is to prefer an increase of H_2, trying to mitigate PWSCC of Alloy 600. However, there are many uncertainties with levels of hydrogen above 50 ml/ kg, and it seems advisable to be cautious before increasing H_2 above the current limit.

The CIPS evaluation in the French fleet allowed the conclusion that chemistry parameters (Li upper value, pH_T, Zn) within the applied range are not the main cause of the phenomenon which is more related to the core design and fuel management. In the presence of CIPS, high values of Ni, Fe or Co have not been noted in the primary coolant. Theoretically, an increase of pH_T, and Li should be beneficial for corrosion products transport but not for CIPS.

Korean NPPs have also experienced CIPS on several occasions and crud analyses have been performed to understand the phenomenon (see Table 7.2).

The influence of a very porous deposit, equivalent to a crevice where chemical species may concentrate, has been seen. B and Li enrichment have been found in these deposits. The Ni/Fe ratio is 0.5 on fuel cladding in the Younggwang units at various points, whilst at Ulchin B where CIPS has occurred, the ratio is 0.8–1.0 on cladding samples from tapping and 1.2–1.4 from ultrasonic cleaning and filtering. In this unit, Ni needles and pure B have been noted. The crud (thickness: ~10 µm) is located in the upper part of fuel rod. Pure B is considered as a candidate phase that induces AOA. The Ni/Fe ratio is higher in the crud on units with AOA than on units without AOA.

The Koreans also initiated a CRUD simulation study. A pH_T increase (6.9–7.2) reduces the crud deposition.

7. DISCUSSION

The information from the EDF units with various steam generator tubing materials shows that there is no difference in CIPS results on units with steam generators made from Alloy 600 or Alloy 690, although these materials have different Ni contents. The variability of Ni is a known parameter on crud deposits which have caused CIPS. The Korean units with 690 steam generator tubing do not have CIPS but the experience feedback is insufficient to draw any conclusion.

When EDF units switched from 12–16 months fuel cycles, no CIPS was observed. In the absence of stretch out, the increasing probability of CIPS is explained by the absence of corrosion product elimination and higher boron concentration.

It was suggested by the Canadian representative that a parametric study of Ni/Fe ratio and the relation to the corrosion products and crud composition should be carried out.

A discussion took place for defining what may be considered as a CIPS/Axial Offset Anomaly. The Russian representative considers that AOA means a difference of at least 3% between the measured and theoretical flux. The French member claimed that very few assemblies in EDF units have such a deviation.

The Hungarian member confirmed that decontamination is a maintenance action that should be avoided as much as possible.

8. PROPOSITION AND COMMENTS ON THE FUWAC PROJECT

Every participant was asked to give his point of view on how the FUWAC project had met their expectation and if their goals had been achieved.

IAEA (John Killeen) highlighted issues to be captured, including the need or not to perform decontamination, crud, Zn injection, dose rates, crud control, PWSCC, WWER cruds, primary water chemistry which is supposed to protect from everything, oxidation in CANDU. The Agency officer asked participants to write to IAEA if there were any questions, concerns or input.

Bulgaria (Ivan Dobrevski) claimed that FUWAC was a real success. He said that Kozloduy has few problems and will increase the fuel enrichment to allow 18–24 months fuel cycles. This change needs to be fully investigated, including consideration of new cladding materials, new neutron absorbers and other issues.

Canada (Derek Lister) estimated the meeting as excellent. He had learned a lot and noted that whilst the out-of-core chemistry had been fully discussed, the in-core chemistry and its influence on corrosion products could be more deeply evaluated.

Czech Republic (Katerina Vonkova) found the project interesting and fulfilling her expectation. She now has a closer view on operating units and was happy to get data on corrosion and NPP problems as well as corrosion tests results from other laboratories.

Finland (Timo Saario and Petri Kinnunen) considered that the root causes of CIPS are still unknown. They said that SNB can be unavoidable, it may occur and the only remedy is to keep corrosion products at a low level. OL3 (new EPR) will have an optimised passivation, carried out before the unit raises power for the first time, for this purpose. He also would like to discuss the start up and shutdown chemistry and processes. Finally zinc addition may be considered. They confirmed the importance of mitigating the presence of corrosion products. They noted that the final report will be read by other people than laboratory experts, referring for example to the Safety Authority. Thus, any recommendations must be carefully evaluated.

France (Arancha Tigeras) said that the project was compete and interesting. She has seen many parameters, composition and distribution of crud, influence of Ni, Li, etc. as well as the relationship with operating conditions.

Hungary (János Schunk) considered that the FUWAC project fulfilled his expectations. He concluded that he still would like to find the right decontamination process if this appears necessary and said that there is no real CIPS in WWER, probably due to the hydraulic conditions of the plants.

India (S. V. Narasimhan) got an insight on CIPS related to corrosion transport. The investigation on decontamination may be used for CIPS mitigation and heconsidered that operating parameters should be looked at in order to overcome CIPS.

Japan (Shunsuke Uchida) enjoyed the discussions, having examined corrosion products and CIPS issue that may happen in Japan. He claimed that he learned a lot but still needed to study in Japan, to evaluate potential countermeasures, including H_2 content in addition to its optimization for PWSCC.

Republic of Korea (Wan Young Maeng) found that the project fulfilled his expectations. He listed the good points : meeting other experts, obtaining many technological information related to all the systems and not only on chemistry.

Romania (Iona Pirvan) appreciated the correlation between corrosion products and chemistry. She particularly noted the various structures of materials, hydriding of cladding and influence of initial oxidation on corrosion product behaviour that is important for water chemistry.

Russian Federation (Vladimir Kritsky) found the results interesting and complete. He focused on CIPS, fuel oxide growth, and thickness and considered that no relation has been seen with fuel failure, corrosion products and their release. He also noted the decontamination and radioactivity build up issues.

Sweden (Jiaxin Chen) found that the project fulfilled his expectations. He had been interested in exchanging information with other experts allowing him to learn a lot.

Ukraine (Mykhaylo Tretyakov) agreed with the French and Finnish opinion. He said FUWAC fulfilled his expectation and will be useful for the future of WWER units.

USA (Sam Hettiarachchi) found important the lessons learned on water chemistry, corrosion transport and CIPS. He would like to know if B-Li are the primary reason for CIPS and how to predict CIPS from water chemistry.

The technical chairman (Francis Nordmann) deeply appreciated the interesting results and active participation of the members to respond to the project expectation. He will be happy to contribute in the final report preparation and its success to conclude the FUWAC project.

APPENDIX TO ANNEX III

TABLE AIII.1. STRUCTURE/TABLE OF CONTENT OF THE FINAL FUWAC REPORT

Chapter	Sub-chapter	Comment	Contributor
1 Chemistry	Description, PWR, WWER	What is done in various NPP (practices chemicals, additives Zn, etc.).	JS, VK, ID, KV, AT
	Description, BWR, RBMK	What is done in various NPP (practices chemicals, additives Zn, NMCA, etc.).	VK, SH, SU
	Description, PHWR/CANDU	What is done in various NPP (practices chemicals, additives).	SVN, IP, DL
2 Corrosion products (CP)	Formation, deposition	Influencing parameters ((pH, Li, K, B, H_2, T), materials, burn up, FAC).	JC, SH, SVN, IP, KV, AT, DL
	Steam generator tubing	Release rate, material influence, surface state.	JS, VK, JC, KV, DL
	Dose rate concern	Relation with dose rate and mitigation.	VK, SH, KV, AT
	NPP feedback	Influence of all above parameters.	AT, KV
4 CRUD	Composition, thickness, evolution	Influencing parameters, deposition and release mechanism, lab tests and models.	WM, JC, SH, SU, DL
		Relation with fuel oxides and CP.	VK
	Elimination	Decontamination, fuel cleaning (when why, etc), dose rates before major maintenance, other reasons.	JS, SVN, KV
	Mitigation	Steam generator passivation (before start up, other cases) Zinc injection.	WM, SH, SU, KV, AT, DL, PK
	Consequences	Corrosion failure, CIPS, dose rates.	VK, WM, JC, IP, SU, AT
	NPP feedback	Influence of all above parameters.	WM, AT
3 Fuel corrosion and fuel oxides	Cladding	Various types of cladding.	VK
	Film Morphology	Influencing parameters, lab tests and models on formation, elimination.	VK, IP, DL
	Chemistry	Influencing chemical parameters (pH, Li/K, T), lab tests and models.	VK, IP, AT, DL, PK, KV
	Impurities	Influence of impurities (lab tests).	VK, SVN, PK
	NPP feedback	Influence of all above parameters.	VK, AT

TABLE AIII.1. STRUCTURE/TABLE OF CONTENT OF THE FINAL FUWAC REPORT (cont.)

Chapter	Sub-chapter	Comment	Contributor
5 CIPS (AOA)	Definition	Definition, root causes and consequences	ID, SU, AT, DL
	Chemistry	Influencing parameters, (pH, Li/K, H2, lab tests and models	WM, JC, ID, DL, SU
	Impurities	Influencing parameters, lab tests and models	WM, JC, DL, SU
	Materials	Lab tests and models (Ni in steam generator tubes)	WM, DL
	CRUD influence	Composition and structure, lab tests and models	WM, JC, SU, VK, DL
	Fuel management	Burn-up, cycle length, Power, T, plant aging	WM, AT
	NPP feedback	Occurrence, influence of all above parameters	WM, AT
	Mitigation	Remedies	WM, JC, ID, AT
6 Contributions	Each country	Summary of main contributions during all project	All
7 Conclusion	Above chapters	How to avoid CIPS, to mitigate it, compatibility and compromise with dosimetry, fuel behaviour	
	Future work	What is missing?	

Note: The participants agreed to structure the final report according to the order noted in the table.

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ISSN 1011–4289