

# LCC-2 Annual Report

*Authors*

Rolf Riess,  
NPC Neunkirchen, Germany

F. Peter Ford  
19, Nott Road, Rexford, NY 12148, USA

Klas Lundgren,  
ALARA Engineering AB, Skultuna, Sweden

Stig Sandklef  
Advanced Nuclear Technology International Europe AB,  
Skultuna, Sweden

December 2006

Advanced Nuclear Technology International  
Krongjutarvägen 2C, SE-730 50 SKULTUNA  
Sweden

[info@antinternational.com](mailto:info@antinternational.com)  
[www.antinternational.com](http://www.antinternational.com)



## DISCLAIMER

The information presented in this report has been compiled and analysed by Advanced Nuclear Technology International Europe AB (ANT International) and its subcontractors. ANT International has exercised due diligence in this work, but does not warrant the accuracy or completeness of the information. ANT International does not assume any responsibility for any consequences as a result of the use of the information for any party, except a warranty for reasonable technical skill, which is limited to the amount paid for this assignment by each *LCC* program member.

## ACRONYMS AND EXPLANATIONS

AOA	Axial Offset Anomaly
ATEM	Analytical Transmission Electron Microscopy
BOC	Beginning Of Cycle
BRAC	<i>BWR</i> Radiation Assessment and Control
BWR	Boiling Water Reactor
CE	Combustion Engineering
CIPS	Crud Induced Power Shift
CRDM	Control Rod Drive Mechanism
CRUD	Chalk River Unidentified Deposits
CT	Compact Tension (specimen for stress corrosion crack propagation tests)
CVCS	Chemistry and Volume Control System
dpa	Displacements per atom
DCB	Double Cantilever Beam (specimen for stress corrosion crack propagation tests)
DZO	Depleted Zinc Oxide
EAC	Environmentally Assisted Cracking
EBA	Enriched Boric Acid
ECP	Electrochemical Corrosion Potential
ECCS	Emergency Core Cooling System
EDY	Effective Degradation Years
EPFY	Effective Full Power Years
EPR	Electrochemical Potentiokinetic Repassivation parameter (measure of grain boundary chromium depletion in stainless steels)
FAC	Flow Accelerated Corrosion
FIV	Flow-Induced Vibration
FRP	Fuel Reliability Program
HAZ	Heat Affected Zone
HFT	Hot Functional Test
HWC	Hydrogen Water Chemistry
IAEA	International Atomic Energy Agency
IASCC	Irradiation Assisted Stress Corrosion Cracking
IGSCC	Intergranular Stress Corrosion Cracking
IPC	Insulating Protective Coating
KWU	KraftWerkUnion
LCC	<i>LWR</i> Coolant Chemistry (Program)
LHGR	Linear Heat Generation Rate

LPSCC	Low Potential Stress Corrosion Cracking
LRA	License Renewal Application
LTCP	Low Temperature Crack Propagation
LTMA	Low Temperature Mill Anneal
LWR	Light Water Reactor
MA	Mill Annealed
MIC	Microbiologically-Influenced Corrosion
MSLR	Main Steam Line Radiation
NDE	Non Destructive Evaluation
NM	Noble Metal
NMC	Noble Metal Chemical
NMCA	Noble Metal Chemical Addition
NPP	Nuclear Power Plant
NRC	Nuclear Regulatory Commission
NWC	Normal Water Chemistry
OTSG	Once Through Steam Generator
RCS	Reactor Coolant System
RSG	Recirculating Steam Generator
RIS	Radiation Induced Segregation
PLR	Primary Loop Recirculation
PMDA	Proactive Materials Degradation Assessment
PMDM	Proactive Materials Degradation Management
PVC	Polyvinyl Chloride (tape)
PWR	Pressurized Water Reactor
PWSCC	Primary Water Stress Corrosion Cracking
RCP	Reactor Coolant Pumps
RHR	Reactor Heat Removal system
RPV	Reactor Pressure Vessel
RW	Reactor Water
RWCU	Reactor Water Clean-Up
SCC	Stress Corrosion Cracking
SGR	Steam Generator Replacement
SHE	Standard Hydrogen Electrode
SICC	Strain Induced Corrosion Cracking
SNB	Subcooled Nucleate Boiling
TGSCC	Transgranular Stress Corrosion Cracking
TLAA	Time Limiting Aging Analysis
TMI	Three Mile Island

TT	Thermally Treated
TTT	Temperature-Time-Transformation
TR	Technical Requirements
VCT	Volume Control Tank
VGB	See <a href="http://www.vgb.org">www.vgb.org</a>
VVER	Russian version of the <i>PWR</i> (“Voda Voda Energo Reactor”)
ZIRLO	Zirconium Low Oxidation

**UNIT CONVERSION**

<b>TEMPERATURE</b>		
$^{\circ}\text{C} + 273,15 = \text{K}$		
$^{\circ}\text{C} * 1,8 + 32 = ^{\circ}\text{F}$		
<b>T(K)</b>	<b>T (°C)</b>	<b>T(°F)</b>
273	<b>0</b>	32
289	16	61
298	25	77
373	<b>100</b>	212
473	<b>200</b>	392
573	<b>300</b>	572
633	360	680
673	<b>400</b>	752
773	<b>500</b>	932
783	510	950
793	520	968
823	550	1022
833	560	1040
873	<b>600</b>	1112
878	605	1121
893	620	1148
923	650	1202
973	<b>700</b>	1292
1023	750	1382
1053	780	1436
1073	<b>800</b>	1472
1136	863	1585
1143	870	1598
1173	<b>900</b>	1652
1273	<b>1000</b>	1832
1343	1070	1958
1478	1204	<b>2200</b>

<b>MASS</b>	
<b>kg</b>	<b>lbs</b>
0,454	<b>1</b>
<b>1</b>	2,20

<b>CONVERSION OF DIMENSIONS</b>	
1 Sv	= 100 Rem
1 Ci	= $3.7 \times 10^{10}$ Bq = 37 GBq
1 Bq	= $1 \text{ s}^{-1}$

<b>DISTANCE</b>	
<b>x (μm)</b>	<b>x (mils)</b>
0,6	0,02
<b>1</b>	0,04
5	0,20
<b>10</b>	0,39
20	0,79
25	0,98
25,4	<b>1,00</b>
<b>100</b>	3,94

<b>PRESSURE</b>		
<b>bar</b>	<b>MPa</b>	<b>psi</b>
<b>1</b>	0,1	14
10	<b>1</b>	142
70	7	995
70,4	7,04	<b>1000</b>
<b>100</b>	10	1421
130	13	1847
155	15,5	2203
704	70,4	<b>10000</b>
<b>1000</b>	100	14211

<b>STRESS INTENSITY FACTOR</b>	
<b>MPa√m</b>	<b>ksi√inch</b>
0,91	<b>1</b>
<b>1</b>	1,10

## CONTENTS

<b>ACRONYMS AND EXPLANATIONS</b>	<b>III</b>
<b>UNIT CONVERSION</b>	<b>VI</b>
<b>1 INTRODUCTION (STIG SANDKLEF)</b>	<b>1-1</b>
<b>2 COOLANT QUALITY AND CONTROL ISSUES</b>	<b>2-1</b>
2.1 PWR AND VVER WATER CHEMISTRY (ROLF RIESS)	2-1
2.1.1 Background	2-1
2.1.1.1 Definition of Terms in Guidelines	2-5
2.1.1.2 Status of Guidelines as of 2005	2-7
2.1.1.3 Start-up and Shutdown	2-14
2.1.1.4 Coolant Quality Issues	2-14
2.2 NEW RESULTS	2-15
2.2.1 Specifications and chemistry programs	2-15
2.2.1.1 USA	2-15
2.2.1.2 German Specification	2-21
2.2.1.3 France	2-24
2.2.1.4 Russia	2-26
2.2.1.5 Czech and Slovakian Republics	2-26
2.2.2 WANO Performance Indicators	2-29
2.2.2.1 Fuel Reliability Indicator	2-30
2.2.2.2 Chemistry Performance Indicator	2-30
2.2.3 Laboratory Quality Management	2-32
2.3 BWR WATER CHEMISTRY (KLAS LUNDGREN)	2-34
2.3.1 Water chemistry specifications	2-36
2.3.2 <i>HWC – NMCA – OLNC – HHC</i>	2-42
2.3.3 Cleanup systems	2-56
2.4 KEY RESULTS IN 2005 / 2006	2-65
2.5 SUMMARY	2-65
2.5.1 <i>BWRs</i>	2-65
<b>3 STRUCTURAL MATERIALS DEGRADATION (PETER FORD)</b>	<b>3-1</b>
3.1 INTRODUCTION	3-1
3.2 UPDATE ON UNDERSTANDING OF SPECIFIC MATERIALS DEGRADATION MODES	3-3
3.2.1 Proactive Materials Degradation Assessment ( <i>PMDA</i> ).	3-7
3.2.1.1 PWR Reactor Coolant System (RCS) under Full Power Operation Conditions	3-15
3.2.1.2 BWR Reactor Coolant System (RCS) under Full Power Operation Conditions.	3-17
3.2.1.3 Non-Steady State Operating Conditions in PWRs and BWRs	3-18
3.2.1.4 Generic (Non Component-Specific) Materials Degradation Concerns for PWRs and BWRs	3-19
3.2.1.4.1 Damage Assessment	3-19
3.2.1.4.2 Fracture Assessment	3-20
3.2.2 Life Prediction for Components Susceptible to Environmentally-Assisted Cracking.	3-21
3.2.2.1 Life Prediction for Irradiated Stainless Steel Components in BWRs.	3-31
3.2.2.1.1 The Hypothesized Crack Propagation Model	3-31
3.2.2.1.2 Qualification of the Slip Oxidation Mechanism for <i>IGSCC</i> of Unirradiated Stainless Steel	3-36
3.2.2.1.3 Effects of Irradiation on <i>IGSCC</i> of Stainless Steels	3-47
3.2.2.1.4 Effect of Irradiation on System Parameters	3-49
3.2.2.1.5 Prediction Methodology for <i>IASCC</i> of Core Components	3-55
3.2.2.1.6 Summary of Life Prediction Capabilities for Stainless Steels in <i>BWRs</i>	3-59
3.2.2.2 Life Prediction for <i>SCC</i> of Nickel-base Alloys in Primary Side Components in PWRs.	3-60
3.2.2.2.1 Service Experience	3-61

3.2.2.2.2	Controlling System Parameters for Stress Corrosion Cracking of Nickel-base Alloys in the <i>PWR</i> Primary System.	3-68
3.2.2.2.3	Mechanistic Understanding of <i>PWSCC</i> of Nickel Base Alloys.	3-80
3.2.2.2.4	Life Assessment for <i>PWR</i> Primary System Components.	3-83
<b>4</b>	<b>DOSE RATE BUILD-UP AND CONTROL</b>	<b>4-1</b>
4.1	PWRS (ROLF RIESS)	4-1
4.1.1	Background	4-2
4.1.1.1	Additional Issues contributing to Activity Build-up	4-8
4.1.1.1.1	Tube Manufacturing and Surface Pre-treatment	4-8
4.1.1.1.2	Fuel Elements Spacer Grids	4-9
4.1.1.1.3	Oxygen Control during Steady State Conditions	4-9
4.1.1.1.4	Enriched Boric Acid	4-9
4.1.1.1.5	Axial Offset Anomaly ( <i>AOA</i> )	4-9
4.1.1.2	Trends in various Countries	4-10
4.1.1.2.1	Germany	4-10
4.1.1.2.2	United Kingdom	4-11
4.1.1.2.3	Eastern Europe	4-13
4.1.1.2.4	France	4-14
4.1.1.2.5	Japan	4-15
4.1.1.2.6	USA	4-15
4.1.2	New Results	4-17
4.1.2.1	Overview on Occupational Radiation Exposure in PWRs	4-17
4.1.2.1.1	Sweden (Ringhals)	4-17
4.1.2.1.2	United Kingdom	4-26
4.1.2.1.3	Eastern Europe	4-28
4.1.2.1.4	France	4-28
4.1.2.1.5	Japan	4-32
4.1.2.1.6	USA	4-33
4.1.3	Key Results in 2005/2006	4-33
4.2	BOILING WATER REACTOR (KLAS LUNDGREN)	4-34
4.2.1	Radiation exposures	4-34
4.2.2	Radiation field control	4-36
4.2.3	Decontamination methods	4-46
4.2.4	Control of iodine activity during shutdown	4-53
4.2.5	<i>BWRs</i> (Klas Lundgren)	4-59
<b>5</b>	<b>EFFECT OF WATER CHEMISTRY</b>	<b>5-1</b>
5.1	PWR/VVERWATER CHEMISTRY (ROLF RIESS)	5-1
5.1.1	Introduction	5-1
5.1.1.1	Concerns regarding Fuel Elements	5-2
5.1.1.2	Higher pH Primary Water Chemistry; Lithium/B-Strategy	5-2
5.1.1.3	PWR Zinc Injection	5-7
5.1.1.4	PWR Fuel Crud and AOA (or CIPS)	5-11
5.1.2	Evaluation of the Data	5-16
5.1.3	New Results	5-18
5.1.3.1	Current Concerns regarding Fuel Elements	5-18
5.1.3.2	Advances in High pH Primary Water Chemistry	5-19
5.1.3.3	An Update on PWR Zinc Injection	5-34
5.1.3.4	Actual PWR Fuel Crud Data and AOA	5-38
5.1.3.5	Hydrogen Control in PWR Primary Coolant	5-46
5.1.4	Key Results in 2005/2006	5-52
5.1.5	Conclusions and Recommendations	5-53
5.2	BWR WATER CHEMISTRY	5-55
5.2.1	Introduction (Alfred Strasser)	5-55



5.2.1.1	Hydrogen Water Chemistry and Noble Metal Chemistry (Alfred Strasser)	5-57
5.2.1.2	Zinc Injection (Rolf Riess)	5-58
5.2.2	New results (Rolf Riess)	5-59
5.2.2.1	Normal Water Chemistry (NWC)	5-59
5.2.2.2	Zinc Addition	5-68
5.2.2.3	Radiation Field Build-up	5-72
5.2.3	Key Results in 2005/2006	5-74
<b>6</b>	<b>CURRENT ISSUES AND MATERIAL DEVELOPMENT</b>	<b>6-1</b>
<b>7</b>	<b>REFERENCES</b>	<b>7-1</b>

## 1 INTRODUCTION (STIG SANDKLEF)

The largest threats to safe, reliable and cost effective operation of nuclear plants have historically been related to various types of corrosion and materials problems. Even today these problems are the most costly issues experienced by operators of nuclear plants. Well known examples are the stress corrosion cracking of stainless steel piping in *BWRs* and corrosion damage to steam generators in *PWRs*. Especially, when corrosion cracking has affected pressure retaining components or core support structures safety concerns are important.

However, recent technical advances in Water Chemistry have been helping to improve the situation as for example with the Zinc Injection in *PWRs*. The benefits of *PWR* Zinc Injection have been demonstrated for example in reducing primary water stress corrosion cracking, degradation of Alloy 600 steam generator tubes, and in controlling radiation fields. The evaluation of currently available data indicates that *PWSCC* initiation will be minimised and *PWSCC* crack growth rate may be reduced in thicker cross section components depending on other factors, such as stress intensity. This means more work is needed regarding the benefit of Zinc in mitigating crack growth rates.

Fuel performance is always a concern with changes in water chemistry such as Zinc injection. The impact appears to be minimal for the majority of plants based on current experience. But insufficient data exist for plants with the highest fuel duties to allow application without post exposure fuel inspection. The operational experience in less highly rated cores suggests that there should be no fuel concern for coolant Zinc levels up to 40 ppb. However, there have been no data available until recently for higher duty cores, where significant sub-cooled nucleate boiling occurs on the fuel clad surface. Sub-cooled nucleate boiling can substantially enhance the deposition of corrosion products on the surface of the fuel cladding.

In *BWRs* the attention during last year has focussed on the online application of noble metals and first results are published. However, one key issue is unresolved which is the possibility of an adverse effect of *NMCA* on fuel. This concern has led to impose strict limits on the amount of noble metal that can end up on the fuel. And in addition, the guidance on the injection of Zinc was released. Recent plant data indicate also that the control of feed water iron ingress has positive effects, e.g. introduces the amount of crud in the fuel and it increases the efficiency of Zinc in reducing radiation fields.

Beside the option to discuss the technical issues at the *LCC* Seminars it should be emphasised, that the skill and competence of the people responsible for Water Chemistry and materials in the utilities is of great importance for successful operation. As with practically all other categories of skilled people in the nuclear industry there is now an ongoing shift of generation where new specialists are recruited with good education but not always with access to history and past experience in their fields of responsibility.

This led ANT International to launch the *LCC* program as one way of assisting nuclear utilities in meeting these challenges in a most effective way and we are pleased to have received support from our customers to continue with the program. The overall objective of the *LCC* program is to enable nuclear utilities to:

- Gain increased understanding of reactor water chemistry related to successful plant operation and a continued integrity of *RCS* materials while keeping radiation exposures low.
- Assist in the training and education of a new generation of chemistry and materials experts at nuclear utilities.
- Establish a new independent (free from big organisations and vendors) meeting point for utility experts to enable free and critical discussions and experience exchange.

The objective is met through critical review and evaluation of recent data, identification of important new information and discussion of its significance in relation to water chemistry and put in perspective to how today's situation has evolved.

The first Annual Report (*LCC-1 AR*) in the *LCC* series is a broad and extensive report which covers basically all aspects of reactor primary water chemistry and the interactions between the materials and the chemical environment in the primary circuit, including the fuel.

A considerable effort is made in that report to review the materials selected for various tasks in the systems, the historical development and different degradation modes which have influenced the selection of materials used today and in new reactors.

The first *LCC-1 AR* is thus an important platform for educational and training purposes and forms a platform on which ANT International can build further reports.

The present Annual Report (*LCC-2 AR*) has the same structure as *LCC-1 AR* but is consequently more focused on recent developments and information. The sections on material are more oriented towards mechanisms for degradation and less towards the historical perspective which was well covered in *LCC-1 AR*.

The Report on Degradation of Structural Materials in Light Water Reactors Report is a separate but associated product to the *LCC* Program. It acts as a primer for more detailed discussions of the various degradation modes which will be presented in the annual *LCC* reports and proceedings.

At the first *LCC* seminars in early 2006 it was agreed with the customers to write a Special Topical Report on *CRUD*. The parts of this AR which deal with *CRUD* are consequently less detailed.

The two *LCC-2* reports are based on large amounts of non-propriety data presented at technical meetings and published in the literature and value added through the expertise of the writers.

This report covers the following:

- Symposium on Water Chemistry and Corrosion of Nuclear Power Plants in Asia 2005, Oct. 11-13 in Kyungju, Korea
- *VGB* Conference “Chemie im Kraftwerk”, Bad Neuenahr, Germany, Oct. 11 and 12, 2006
- KTG Conference, Dresden, Germany, March 2-3, 2006
- Annual Meeting on Nuclear Technology 2006, Aachen, Germany, May 16-18, 2006
- Contribution of Materials Investigations to Improve the Safety and Performance of *LWRs*, Fontevraud 6, France, September 18-22, 2006
- 15th Pacific Basin Nuclear Conference, Sydney, Australia, October 15-20, 2006
- International Conference on Water Chemistry of Nuclear Reactor Systems, Jeju Island, Korea, October 23-26, 2006
- Top Fuel Conference, Salamanca, Spain, October 22 to 26, 2006

Journal publications are being monitored through several literature searches of worldwide publications and the important papers are summarised and critically evaluated. This includes the following journals:

- Nuclear Engineering and Design
- Kerntechnik
- Power Plant Chemistry
- Water Chemistry Guidelines (if and when published)
- *IAEA* documents

The large collective experience gained by the reviewers and authors of this report in past and current projects is an important factor in making the evaluation, ensuring that the compiled information is put in perspective and that the most important information is emphasized.

The report is structured in the following sections:

- Introduction
- Coolant Quality and Control Issues
- Materials issues for the Primary Circuit
- Primary Circuit Corrosion
- Dose Rate Build-up and Control
- Fuel/Water Chemistry Interaction
- Current Issues and Material Developments

Each section will be presented by the respective author in a one day seminar.

## 2 COOLANT QUALITY AND CONTROL ISSUES

Corrosion control, radiation field build-up, and some fuel cladding problems are dependent upon the chemical parameters of the coolant. As nuclear industry has developed, the knowledge of controlling these issues has also progressed. As examples, activity transport is controlled in *PWRs* by operating the coolant under higher pH-values and by injecting Zinc. Oxidizing conditions that promote stress corrosion cracking in *BWRs* are being counteracted by hydrogen dosing and noble metal injection.

Nevertheless, the above mentioned issues continue to occur. In addition, economic pressures are leading to more rigorous operating conditions in power reactors. Fuel burn-ups are to be increased, higher efficiencies are to be achieved by running at higher temperatures, plant lifetimes are to be extended, and an increasing number of reactor systems are load following. Constraints such as these impose greater demands on the system and compel the reactor chemists to acquire more information to keep corrosion under control.

### 2.1 *PWR AND VVER WATER CHEMISTRY (ROLF RIESS)*

#### 2.1.1 **Background**

In order to achieve the above mentioned goals, the task of *PWR* water chemistry can be divided into the following main points:

- Metal release rates of the structural materials should be minimal.
- The occurrence of localized forms of corrosion should be counteracted.
- The transport and deposition of corrosion products must be influenced in such a manner, that contamination of the primary coolant system is kept low.
- The deposition of corrosion products on heat transfer surfaces, particularly on fuel assemblies, should be prevented as far as possible.
- Radiolytic formation of oxygen should be suppressed.

In certain instances, situations may be encountered where chemistry conditions that are optimum for achieving one goal can lead to a decreased level of achievement relative to other goals. As a result of such considerations the water chemistry specifications must define parameters to achieve a balance among the five goals, recognizing that highest priority is designed to materials and fuel integrity goals. Although the other goals are in the second line of priority, like radiation build-up, they can not be ignored.

The water chemistry conditions are also requiring the proper selection of the materials which are in contact with the primary coolant, (see section 3 for more details.) They are:

- Austenitic stainless steels of components and piping of the primary system
- Zirconium alloys for the fuel cladding and structural components in the fuel assemblies
- Incoloy 800, Inconel 600 *MA*<sup>1</sup> or *TT*<sup>2</sup>; Inconel 690 *TT*<sup>2</sup> for steam generator tubes. Stainless steel tubing is used in *VVER* SGs.
- High alloy materials (ferritic stainless steels) of low surface area for internals of the primary system.

The status of the water chemistry conditions when to be applied to these materials had to fulfil the above mentioned chemistry requirements. Thus the primary coolant of *PWRs*, which contains boric acid (900 – 1800 ppm B at Beginning Of Cycle, *BOC*) as a neutron absorber is chemically conditioned by the addition of isotopically pure Lithium (Lithium-7) hydroxide (2 – 5 ppm Li at *BOC*) as a non-volatile alcalizing agent and by the addition of hydrogen.

As described by Riess in Section 2 of the *LCC-1* Annual Report, Lundgren et al., 2005, during all variations of the *PWR* primary coolant specifications, occurring in the last decades, a permanent conflict existed between increasing the pH, e.g. due to radiation field consideration or prevention of crud accumulation and the fear of Zircaloy corrosion caused by the Lithium concentration mechanisms (see Figure 2-1 as example for the conflict situation). The impact of crud on reactor performance and the impact of pH on Inconel cracking are discussed in details in the *LCC-2* Special Topic Report, Riess & Lundgren, 2006 and in the Structural Material Degradation Report by Ford, 2006.

---

<sup>1</sup> Mill Annealed

<sup>2</sup> Thermally Treated

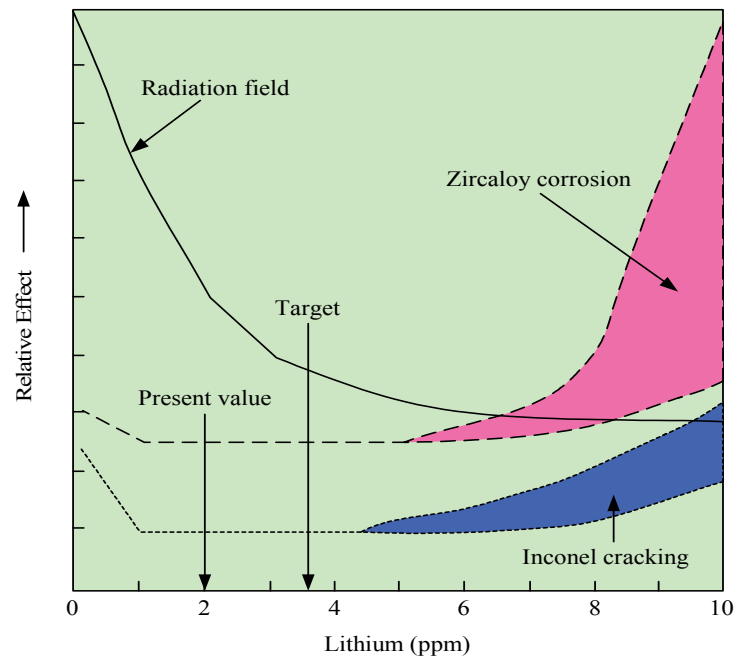


Figure 2-1: *PWR Primary Coolant Chemistry Effect of Lithium Concentration; Status in 1994 (Schematic Diagram), modified figure according to Riess & Millet, 1994.*

The permanent desire to increase the Lithium-concentration to be applied to the primary coolant requires higher target concentrations as already reported by Riess & Millet, 1994. Such modifications however, implied the risk of Zircaloy corrosion and Inconel cracking. This assumption was especially based on the operating experience in Ringhals (See below). Despite these perceived risks, the **modified and elevated Lithium/Boron chemistries** were recommended and applied specifically in many US *PWRs*. But still the radiation field problems and Axial Offset Anomaly, *AOA*, in plants with high duty cores stimulated to go to even higher Li-concentrations.

The valid Lithium specification on one side and the Lithium/Boron concentration modes on the other hand need some more country specific discussion. For example, the sequence of chemistry changes in the US is shown in Figure 2-2, by Turnage, 2004.



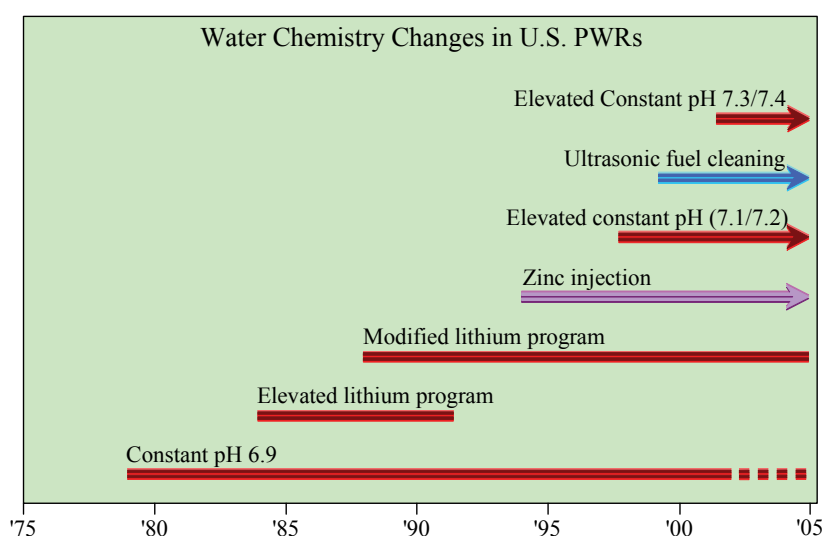


Figure 2-2: Water Chemistry Changes in U.S. *PWRs*, modified figure according to Turnage, 2004.

Regarding the application of all the LI/B-chemistries as shown in Figure 2-2 for US *PWRs* there are some differences when applied in the various countries. Such variations depend also on the dates of their application. For example, in the early 1970s worldwide the Lithium concentration was operated somewhere between upper and lower specified values. The first step to the coordinated chemistry was made in the late 70s/early 80s in order to reduce crud deposition on fuel rods and to minimize radiation fields. The selected  $\text{pH}_T$  was 6.9, which was also consistent with the  $\text{pH}_T$  for iron solubility minimum under *PWR* primary side conditions.

In the mid 1980s, many *PWRs* introduced the modified chemistry based on operational experience (see above), because at this time high and constant Lithium- as a pH strategy- produced better results than the coordinated chemistry, as far as crud deposition and radiation fields are concerned.

The German *PWRs* are still operating today with this type of chemistry and therefore the specification, given by AREVA GmbH and VGB respectively, have an upper Lithium limit of 2.2 ppm for “normal” cycle length. Only in very specific cases, utilities can apply Lithium values higher than 2.2 with the consent of the fuel manufacturer. In case of extended fuel cycles the exact definition of “modified” chemistry has to be respected.

Despite the fact that nearly all Siemens *PWRs* are operating with a modified chemistry, there are some additional improvements to be mentioned.

According to Staudt et al., 2002 the materials and coolant chemistry of Siemens designed *PWRs* have been modified in order to improve the dose rate situation. Such improvements were for instance the implementation of a Co replacement program, introduced in the latest plants (pre-convoi and convoy plants) starting operation between 1985 and 1989. This program is very successful in reducing radiation fields. Additional improvements introduced in the late 90s in several plants is Zinc Injection and the use of enriched B-10. The actual status of the primary coolant chemistry in Siemens designed *PWRs* is shown later in this section.

In the second half of the 1980s in Ringhals an elevated Lithium strategy with an initial concentration of 3.5 ppm was tested. However, this project was stopped due to concerns for corrosion of Inconel 600 steam generator tubing and Zircaloy-4 cladding corrosion. Despite this kind of “Warning”, several US *PWRs* increased the cycle length and thereby the Boron concentration at *BOC* had to be enhanced to values of  $\approx 1.500$  ppm Boron. The motivation for this step is described in the introduction of this section. According to the general understanding the  $\text{pH}_T$  of 6.9 can only be maintained when higher Lithium concentrations are allowed. This became operational practice by starting the cycle operation with 3.5 ppm Lithium. If this level of Li is kept constant till reaching a desired  $\text{pH}_T$  and the plant was following this  $\text{pH}_T$  in a constant manner, it was called “elevated” Li/B-control.

#### 2.1.1.1 Definition of Terms in Guidelines

The above mentioned modes/regimes of operation are described in various “Guidelines”, as for example:

- In the US the EPRI *PWR* Primary Water Chemistry Guidelines which are issued every 4 years and which have their fifth revision dated 2003. It is a Proprietary document.
- In France the “Specifications Chimique des Centrales RET” which are updated on a non regular basis.
- In Germany the “Richtlinie ‘R 401J’” which is the successor of an earlier guideline – *VGB – R 401 J*, released in 1988.
- In Russia: See publications as discussed later in this section.

The purpose of guidelines is to describe the **Quality Requirements** of the reactor coolant. However, it has to be distinguished between various operational modes (see Table 2-1). As far as the available Guidelines provided information to this or other issues, they were discussed in more detail by Riess in Section 2 of the *LCC-1* Annual Report, Lundgren et al., 2005.

Table 2-1: Operational Status Modes

	<b>EPRI</b>	<b>VGB</b>	<b>EdF</b>
Cold shut-down	<250°F	<120°C	<120°C
Start-up	>250 °F But not critical	>120°C But not critical	>120°C But not critical
Power operation	Reactor critical	Reactor critical	Reactor critical

As can be seen from Table 2-1, the various Guidelines concur with respect to the mode of operation, which means that the criteria are identical.

In addition, the frequently used terminologies in the Guidelines were also summarised by Riess in Section 2 of the *LCC-1* Annual Report, Lundgren et al., 2005 as for example:

### ***Typical Values***

Typical values are values, which can be achieved during undisturbed steady-state plant operation. They are plant specific. Slight deviations from the typical value will have no consequences regarding system integrity (e.g. *VGB*).

### ***Limit Values***

Limit values are values that must be respected by the plant operators under any circumstances. Deviations include the possibility of materials corrosion and the consequences thereof. Immediate corrective measures are required.

### ***Control Values***

Control values are those parameters, which determine the entire situation of water chemistry regarding an optimum plant operation and thereby ensuring the absence of corrosion in the systems. They are selected because of their decisive importance and their exact measurability with state of the art analytical methods. For control parameters Action Levels are defined.

### ***Diagnostic Values***

Diagnostic values are values which supplement the entire picture of the applied water chemistry. Because diagnostic values are connected directly or indirectly with control values, they will enable to identify the root cause of deviations considerably.

### ***Action Levels***

Action levels are values which are defined for remedial actions to be taken when parameters are confirmed to be outside the control or diagnostic values. In such cases efforts should be made to bring the values within the appropriate limit within a certain time window. Such time limits can be taken from Table 2-2.

### ***Tolerable Range***

The tolerable range is the range above the typical values and below action level 1. Deviations from the typical values up to action level 1 are of no risk for the Reactor Coolant System, RCS, materials. However, such deviations should initiate a root cause analysis and appropriate countermeasures.

Table 2-2: Overview on Definitions and Time Windows for Power-Operation

	Abbreviations	Definitions/ Consequences EPRI	Definitions/ Consequences VGB	Definitions/ Consequences EdF
Typical value (Normal-betriebswert)		No specification	Values resulting from undisturbed operation	Values resulting from undisturbed operation
Action Level 1	AL 1	7 days before power reduction	28 days before power reduction	7 days before power reduction
Action Level 2	AL 2	24 hrs before power reduction	14 days operation before 30% power reduction	24 hrs before power reduction
Action Level 3	AL 3	Immediate shut-down with temp. <250°F	12 hrs before shut-down	Immediate shut-down

#### *2.1.1.2 Status of Guidelines as of 2005*

Fruzzetti et al., 2004 reviewed the actual EPRI Chemistry Guideline for the *PWR* Primary Side and emphasised the desirability to go to a constant elevated  $\text{pH}_T$ , which may be at 7.1 and 7.3. The expected effect is a better control of crud generation especially at *BOC* and thereby the possibility to avoid *AOA*<sup>3</sup> as well as high radiation field. The EPRI Guidelines are updated every 4 years with the latest issue released in 2003. This revision 5 of 2003 consists of two volumes which handle “steady state operation” in Volume 1 and “start-up and shut-down chemistry.” In Volume 2

Fruzzetti et al., 2004 are describing the significant changes in the Guidelines since Revision 4 in their Review of the EPRI Guidelines Volume 1, as follows:

**The first point** they are mentioning is, that recent data and a revised statistical evaluation of test data were discussed regarding their impact on primary water stress corrosion cracking. This evaluation indicates that the use of higher Lithium levels, required for elevated  $\text{pH}_T$  regimes, results in little or no penalty in the characteristic time to *PWSCC*, see Figure 2-1. Beside the test data the operation experience shows e.g. in French, Swedish and US plants, that the  $\text{pH}_T$  has little influence on *PWSCC*. Another point is the discussion (by Fruzzetti) with respect to the effect of hydrogen on *PWSCC* which was revised on the basis of recent information. These data show that hydrogen concentration associated with a higher crack growth rate varies as a function of temperature.

---

<sup>3</sup> See LCC-2 Special Topic Report, Riess & Lundgren, 2006 for more details

**The second point** they are mentioning is that in Revision 5 of the Guideline an extended discussion was included on the benefits of constant high pH regimes with regard to crud, fuel deposit and radiation dose rate. This discussion is especially relevant to plants with high duty cores where risks of fuel deposits and the consequences thereof are a concern.

**The third item** in this Review is related to the use of Zinc in *PWR* plants. One aspect is the mitigation of *PWSCC* by Zinc and the conclusion that Zinc can stop the initiation of *PWSCC* but not the crack growth, Hickling 2004. The second issue related to Zinc is the reduction of the shut-down dose rates. This chapter was updated in Revision 5 in order to reflect the continuous encouraging results from US and German plants

Some US plants, however, are reluctant for the time being to introduce Zinc because they are waiting for results from units with high duty cores, e.g. in Germany.

**The fourth major item** included in Revision 5 of the EPRI Guidelines is the influence of Primary Water Chemistry on corrosion of fuel cladding and on core performance. It emphasises the importance of crud on corrosion of fuel cladding and the influence of crud on axial offset anomaly (*AOA*). According to Fruzzetti, the new EPRI Guidelines contain also a high duty core index (*HDCI*) which is calculated from the average heat flux of the peak fuel assembly, the cooling flow, and the coolant exit temperature of the plant.

Updates were also made on the effect of high silica coolant levels on fuel performance, indicating that with silica levels of up to 3 ppm no adverse effect could be observed.

**The fifth point** is a discussion on test results regarding low temperature crack propagation in thick parts made from nickel-base-alloys like Alloy X750, 82, 52 and 690, and how this cracking is affected by hydrogen levels in low temperature water.

In Section 3 of Revision 5 of the EPRI *PWR* Water Chemistry Guideline a quantitative chemistry guidance description is provided. It emphasises again the desirability of using a constant elevated  $pH_T$  between 7.1 and 7.3 for all plants. The guidance also reflects the two major concerns regarding high  $pH_T$  regimes, which are: (1) the effect of higher Lithium on *PWSCC* and (2) the effect of higher Lithium on fuel cladding corrosion. It was also agreed to raise the level from 2.2 to 3.5 ppm at which a fuel vendor review is being appropriate.

In the “Reactor Coolant System Power Operation Diagnostic Parameters”, Zinc was added as a parameter. This should be understood as a recommendation to all *PWRs* to inject Zn for dose reduction benefits.

Fruzzetti et al are listing numerous other changes in the Guidelines which are described in additional sections or appendices. These include:

- Section 4: Methodology for plant specific optimization
- Appendix A: Calculation of  $pH_T$  and Data Evaluation methodology
- Appendix B: Chemistry control of supporting Systems

- Appendix C: Status of Enriched Boric Acid (*EBA*) Application
- Appendix D: *AOA* and Ultrasonic Fuel Cleaning
- Appendix E: Oxygen and Hydrogen Behaviour in *PWR* Primary Circuits
- Appendix F: Sampling Considerations for Monitoring *RCS* Corrosion Products
- Appendix G: Reactor Coolant Radio-nuclides
- Appendix H: Definition of High Duty Core
- Guidance with respect to oxygen control in pressurizers. This guidance was expanded to cover control of oxygen during shutdowns and start-ups.

Volume 2 of Revision 5 of the EPRI Guidelines is covering start-up and shutdown chemistry. Shutdown chemistry gets its importance from the trend to shorten the refuelling outage. Chemistry can contribute considerably to minimize the time from breaker trip to reactor vessel head lift. Three other important issues are plant degassing procedures, forced oxidation results, and pressurizer oxygen control.

In an analogous way, the start-up chemistry should try to achieve power ascension in a minimum of time and meeting corrosion product transport goals that might impact core performance in the new cycle.

According to Fruzzetti et al., 2004, the significant changes made to Volume 2 of Revision 5 are as follows:

- Descriptions of the morphology and properties of the newly discovered fuel crud constituents Bonaccordite and Zirconium oxide were added to the technical basis for start-up and shutdown.
- Methods for monitoring and controlling hydrogen and oxygen in the pressurizer during shutdown and start-up.
- A discussion regarding the use of acidic reducing conditions during mid-cycle outages.
- Plant experience that showed strong benefits from using the maximum practical *RCS* cleanup flow during shutdown.
- Discussion on the needs and methods to maintain oxidizing conditions in the reactor water through flood-up for minimizing activity release during that operation.
- Oxygen control strategy in pressurizer
- Description regarding use or non-use of reactor coolant pumps during shutdown, including when adding hydrogen peroxide.
- Discussion regarding the benefits of using higher cross linked resins.

According to Fruzzetti et al., 2004 the start-up and shutdown Tables in Section 3 and 4 of the EPRI Guidelines constitute the quantitative chemistry guidance in Volume 2.

The changes made in these Tables reflect the experience gained since the last Revision, including the topics noted above. It is also recommended by the authors, that the nuclear industry must develop methods about Low Temperature Crack Propagation (*LTCP*) in Nickel-base alloys which depend on temperature and stress intensities. The interested reader of *LTCP* is referred to the Structural Material Degradation Report by Ford, 2006.

In summary, the significant modification of Volume 2 was identified by the Fruzzetti et al., 2004 as:

- Significant enhancement to fundamental knowledge to the morphology and properties of fuel crud and its effect on shut-down chemistry strategy.
- Many changes to the start-up and shutdown tables were incorporated, substantially enhancing the quantitative chemistry guidance.
- Reflect lessons learned from experience since previous revision
- Discussion of Low Temperature Crack Propagation (*LTCP*) in Nickel base alloys
- Enhanced discussion of methods for monitoring and controlling hydrogen and oxygen in the pressurizer during shutdowns and start-ups.

Since Revision 5, Volume 1 and 2 are proprietary documents, it is difficult to make a final judgement on the various items mentioned in Fruzzetti's review.

In comparison to the EPRI *PWR* Chemistry Guidelines, **the DRAFT German Guidelines, to be issued by VGB**, are considerably less voluminous. The official valid Guideline (Richtlinie "R 401 J" DWR) is a successor of a document named *VGB R 401 J*, issued in 1988. The entire Guideline was revised with the intent to address only the parameters, which have shown to be important for plant operation. This resulted among others in a stronger separation in control and diagnostic parameters.

The term "normal operating value" was still kept in the new Guideline, whereas terms like "Richtwert" and "Grenzwert" were replaced by the international term Action Level. This implies that the revised *VGB* Guideline includes also experiences from other countries like the US and France.

In the Preamble of this DRAFT Guideline it is emphasised that this document is the joint basis for the operation of all *PWR* plants in the *VGB* domain. It shall be the basis where Operation Manual and Chemistry Handbooks are in use. The task of these Handbooks (operational and chemistry) is to apply the Guideline to plant specific situations.

In the interim the Draft *VGB* Guidelines have been approved and published in 2006. They are discussed in Section 2.2.1.2.

The **French Chemistry Guidelines** are published by Stutzmann, 1997, and they were discussed recently by Bretelle et al., 2004 and Nordmann, 2005. Their discussion is concentrating on the strategy of primary coolant pH, which can be characterized as the search for the best pH. EDF always tried to keep the balance between radiation build-up and *AOA* on one side (pH too low) and the risk of *PWSCC* and Zircaloy corrosion on the other side (pH too high).

The following description belongs to the status of French Chemistry Specifications as of 2005.

This basic French attitude towards Specifications can be demonstrated by looking to the pH evolution in EDF *PWRs*. The slight variations were introduced always in accordance with some re-definitions of the chemistry goals, see Table 2-3.

Table 2-3: pH Evolution in EDF *PWR* units

Year / period	pH – Li	Goal
1977	0.2<Li<2.2	1
1978 – 80	pH >6.9 0.6<Li<2.2	2
1980 – 97	pH 7.0 0.6<Li<2.2	3
Since 1997	pH 7.2- 0.4<Li<2.2	4

**Goal:**

1. pH<sub>300°C</sub> sufficient to warrant the generalized corrosion (minimization of metal release) and to limit the fuel cladding corrosion
2. Dose rate consideration – to avoid fuel deposits
3. Decreasing Boron-Lithium coordination with Lithium constant at the end of the cycle to avoid low pH at the end of cycle and easier operation conditions
4. According to *IAEA* recommendation, code calculations, and past experience with pH of 7.0 compared to 7.2 (the international experience), EDF decided to select the pH<sub>300°C</sub> of 7.2 instead of pH<sub>300°C</sub> of 7.0 as the target pH.

Further details of the French Water Chemistry Guidelines are discussed by Riess in Section 2 in the *LCC-1* Annual Report, Lundgren et al., 2005.

Finally, it should be mentioned that Staudt et al., 2002, found a very high degree of agreement between the French and the German specifications.



The **Russian Primary Water Chemistry Specifications** were presented by Yurmanov in 2004 & 2005. His papers highlighted actual problems and recent improvements in primary water chemistry in *VVER* plants.

These improvements are aimed at:

- Enhancing fuel reliability
- Improving primary systems and its component integrity
- Eliminating cracking and corrosion failures
- Reducing radiation field and personal radiation exposures
- Minimizing radioactive effluents and waste

In contrast to Western *PWRs* Ammonia or hydrazine injection is used in *VVERs* as a source of hydrogen in primary coolant. Under reactor irradiation conditions thermal radiolysis of ammonia and hydrazine is forming hydrogen and nitrogen. Significant primary coolant ammonia concentrations of 10 – 20 ppm result, however, in additional radioactive waste formation and reduced the efficiency of ion exchangers due to absorption by ammonia. Based on the experience of Western *PWRs* the technology of hydrogen injection has been developed at 2 *VVER* 1000 plants in Russia and Ukraine. In addition an alternate source of hydrogen electrolyzers with a solid electrolyte membrane was developed.

Another characteristic of *VVER* plants is the use of Potassium hydroxide which is injected to the coolant for neutralization of boric acid. This kind of injection has from Yurmanov's view some advantages compared to Lithium hydroxide. These are:

- Low cost
- Absence of reagent isotopic separation
- No Zircaloy corrosion increase up to 0.7 mmole of KOH
- Absence of abnormal borated crud accumulation in the upper part of the fuel assemblies, and thus no axial offset anomaly effect.

Based on the before mentioned features and improvements, the revised Guidelines for Primary System Water Chemistry in *VVER* 1000 Plants were issued in 2001. The development of the Guidelines can be seen from Table 2-4.

Table 2-4: VVER-1000 Primary Water Chemistry Norms

Parameter	1982	1988	1992	2001
Chloride, ppm	<0.1	<0.1	<0.1	<0.1
Oxygen, ppm	<0.1	<0.005	<0.005	<0.005
Hydrogen, ppm	2.7-5.4	2.7-5.4	2.7-5.4	2.2-4.5
Alkaline, mmole	0.05-0.35	0.05-0.45	0.05-0.5	0.02-0.5
Cond.at 25°C	5.7-10.2	5.7-10.2	5.7-10.2	5.8-10.3
Ammonia, ppm	<5	<5	<5	<3
Iron, ppm	<0.2	<0.2	-	-
Copper, ppm	-	<0.02	<0.02	<0.02
Nitrate, ppm	-	-	-	<0.2
Fluoride, ppm	<0.1	<0.1	<0.1	<0.1
Mineral oils, ppm	-	-	<0.05	<0.05

In order to show the complexity of the VVER-chemistry, the individual history of Potassium, Lithium, Sodium and Ammonia during one cycle is shown in Figure 2-3.

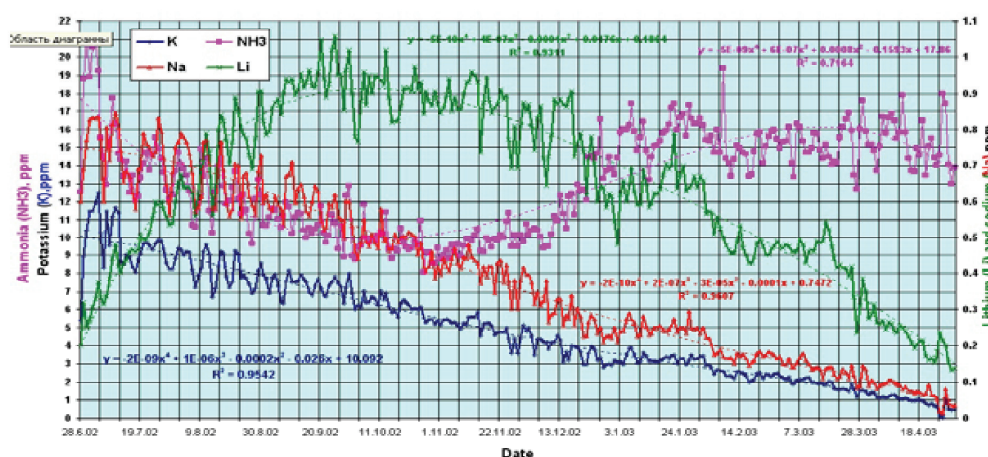


Figure 2-3: Primary Coolant Ammonia, Calcium, Sodium and Lithium during a Fuel Cycle, Yurmanov, 2004 & 2005.

The entire information from VVER plants shows, that the principle mode of operation is similar to that of Western PWRs. It is basically a coordinated chemistry with a  $\text{pH}_T$  of 7.1 to 7.2

The other area of a possible improvement is the direct hydrogen gas injection. This step also had the beneficial effect on reducing the production of radioactive waste, because the Ammonia loading of the resins could be minimized.

Even more oriented on specifications of Western *PWRs* are the *VVER* specifications for Czech and Slovakian Plants. They contain beside “Typical Values” also “Action Levels”. Regarding the impurity levels (Chloride, Sulphate, and Fluoride) they are more stringent than the Russian specifications. In case of oxygen and the pH-strategy, the values are consistent with the Russian values as well.

#### 2.1.1.3 *Start-up and Shutdown*

Some comments to start-up and shutdown have already been made in the previous Section. In addition, operational details are described by Riess in Section 2 of the *LCC 1 AR*, Lundgren et al., 2005.

#### 2.1.1.4 *Coolant Quality Issues*

Comments regarding the coolant quality issues shall be restricted to a specific area. Whereas the chemical analysis procedures are well established, the sampling of the *RCS* coolant may give rise to some concerns. When taking samples from the primary loop, the coolant undergoes significant changes during this procedure from: (1) alkaline reducing conditions to (2) acid reducing and finally (3) to acid oxidizing conditions. Moreover, the sampling flow rate is considerably lower than the system flow rate. The impact of these chemistry changes and flow characteristics is the following:

- The well soluble additives, e.g. Boron and Lithium will not be influenced by the sampling technology.
- The corrosion products, however, are subject to changes in their chemical composition. An example is Nickel- ferrite which may decompose to metallic nickel and magnetite under acid reducing conditions. In addition, due to the lower flow rate, some deposition of crud in the sampling system may occur. In summary, the corrosion product measurement is not reliable regarding the real amount and the real chemical composition.
  - The above mentioned problem may be resolved by using
    - a continuous flow at high velocities,
    - a capillary sampling system such as that used in Sizewell B (Cubitt et al., 2004) or such as that will be used in Neckarwestheim or,
    - a high temperature sampling system as described by Westinghouse (Byers & Deshon, 2004). In this case the temperature at the particular collection point was 230°C. The filters were 0.2 or 0.45 micron silver membranes held in a custom housing. The sample stream exiting the silver filter was cooled and then filtered through a cation membrane to collect dissolved metal.

- Regarding the gases in the *RCS* coolant, the sampling point at the hot leg of the *RCS* will provide information only on  $H_2$  because any oxygen that may enter the system via the high pressure injection line is recombined in the core. Better information on oxygen ingress can only be obtained via a sampling line downstream of the High Pressure, HP, injection pumps. Another issue related to the gases in the coolant is the Electrochemical Corrosion Potential, *ECP*. Nothing is known if the hydrogen will be stripped out into the gas phase during nucleate boiling in the core and thereby changing the *ECP*. Similar measurements as in *BWRs* should be considered for the *PWR* cores. In parallel, the modelling of the radiolysis processes in *PWR* with high duty cores should be encouraged.
- Sulphate impurities from resin fines may be introduced by the *CVCS*. The measurement in the *RCS* loop may give too low numbers because sulphate may hide out on the fuel.
- Organics is another impurity that may enter the *RCS*. However, it will be decomposed radiolytically ending as a hydrocarbon or as elemental carbon. This can be verified e.g. by a  $CH_4$  measurement in the gas phase of the Volume Control Tank, *VCT*.

In summary, a sampling line downstream of the HP injection pumps will enhance the insight into the real situation of the *RCS* compared to the loop sampling line alone.

## 2.2 NEW RESULTS

The new information is related to the following topics:

- Specifications and chemistry programs
- WANO performance Indicators
- Chemistry Quality Management in lab ISO 17025

### 2.2.1 Specifications and chemistry programs

The release of new specifications is in any case a long term project which means that there are not too many new developments. Therefore the specification section has been expanded in order to describe specific chemistry programs set up at individual utilities.

#### 2.2.1.1 USA

In a recent presentation by Fruzzetti & Wood, 2006, there was no report or no progress in releasing a new *PWR* Primary Side Specification. The authors only mentioned the changes made in *PWR* Primary Side from a historical perspective. This picture is shown in Figure 2-4.

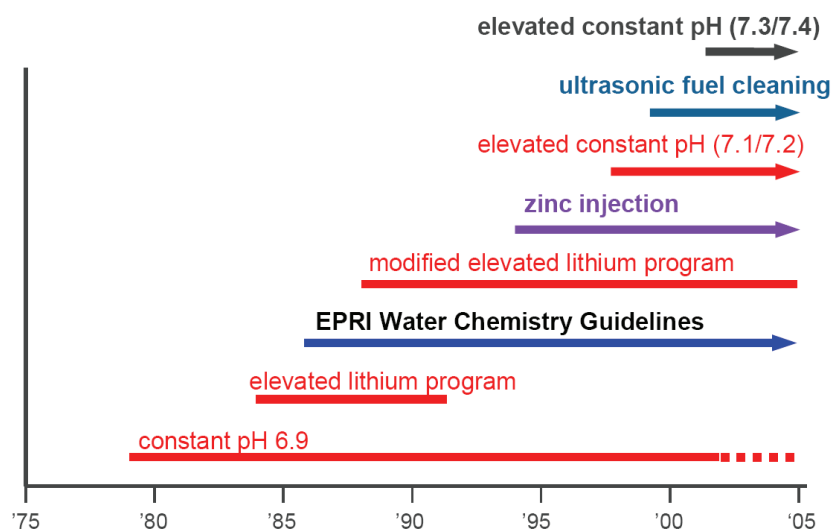


Figure 2-4: Historical Trends in *PWR* Primary Chemistry, Fruzzetti & Wood, 2006.

This information is essentially not new. However, Fruzzetti & Wood, 2006 emphasize on the effect of Zinc on Pressurized Water Stress Corrosion Cracking, *PWSCC*, and on dose rate reduction. In respect to these issues Fruzzetti mentioned in Paper 5.1 of the Korean Water Chemistry Conference (2006) two projects that may provide benefits to the industry:

5. Bench marking shutdown chemistry control recommendations in EPRI's *PWR* Primary Water chemistry Guidelines; and
6. an evaluation of steam generator non-destructive examination data to determine the effects of Zinc on *PWSCC*.

Regarding item 1. the shutdown chemistry control recommendations were reviewed on the basis of data from Byron 1 and 2, Braidwood 1 and 2, McGuire 1 and 2, Catabwa 1 and 2, and Oconee 1 to 3. The results from the review provided conclusions relative to:

- Lithium reduction prior to shutdown
- Rapid boration
- Acid reducing conditions
- Purification flow rate
- Peroxide addition
- Temperature reduction
- Reactor coolant pump operation

The results from this review will be assessed by the primary water chemistry guidelines committee for potential inclusion into revision 6 of those guidelines.

Regarding the evaluation of steam generator Non Destructive Examination, *NDE*, data to determine the effects of Zinc on *PWSCC*, plants were selected with dented tube support plate intersections and explosively expanded areas near the top of the tube sheet. The Zinc addition experience at units with both pre- and post-Zinc steam generator *PWSCC* data were used. The plants involved are Beaver Valley-1, Diablo Canyon 1 and 2, Sequoyah-2, North Anna and others if appropriate. According to Fruzzetti, the rate of *PWSCC* “initiation” in SG tubes was evaluated. The Weibull statistical methods have been widely applied to analyse and predict SG tube degradation. In these studies, initiation of *PWSCC* is defined as crack growth to a size detectable by the Eddy Current test methods.

Only 8 units are known to have experience with axial *PWSCC* at dented tube support plate intersections. Based on the individual plant results the smallest benefit of Zinc injection was seen with Sequoyah-2 (post shut peening, 5 ppb target Zinc). Based on the Weibull analysis the addition of Zinc is projected to extend the time it will take for the percentage of tubes with *PWSCC* failures to increase from 1% to 10 %, by a factor of 1.9 years as shown in Figure 2-5. For Beaver Valley-1 the results (no shut peening, 35 ppb target Zinc) indicate that the corresponding time extension factor was 9.6. as shown in Figure 2-6.

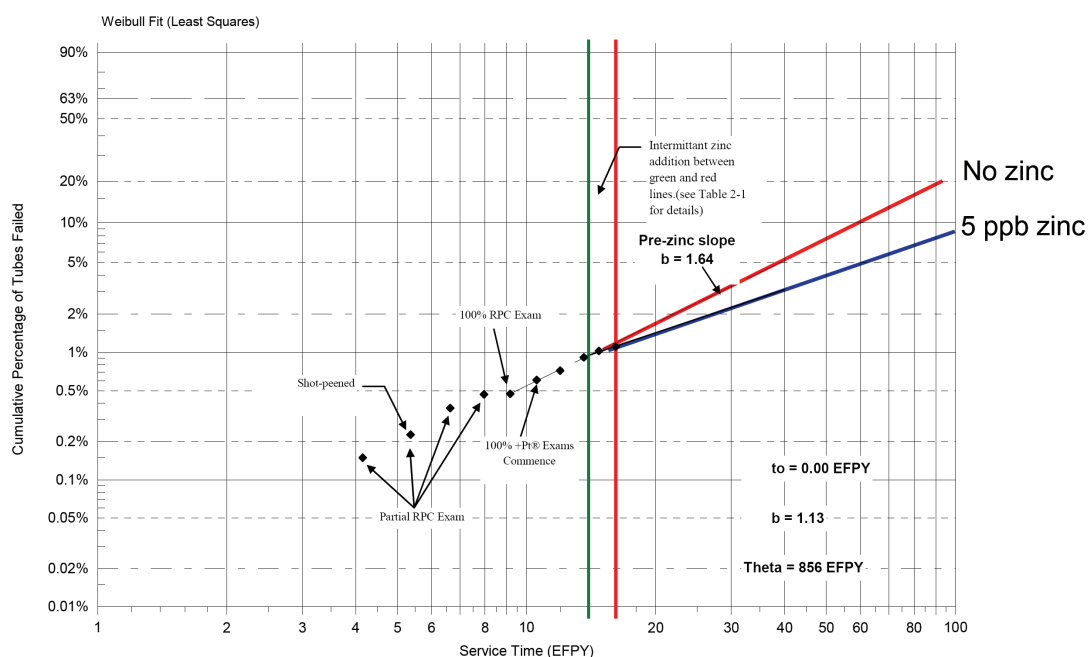


Figure 2-5: Example of Smallest Benefit Observed: Sequoyah Unit 2- Post Shot Peening, 5 ppb Target Zinc – It would take 1.9 longer time to go from 1% to 10% Tubes Affected by Tube Sheet *PWSCC* with zinc injection, Fruzzetti, 2006.

### 3 STRUCTURAL MATERIALS DEGRADATION (PETER FORD)

#### 3.1 INTRODUCTION

In the *LCC-1* Annual Report the degradation of structural materials in the reactor coolant system (*RCS*) in boiling water reactors (*BWR*) and pressurized water reactors (*PWR*) was discussed by Strasser, Riess and Lundgren, (Strasser, 2005), (Riess, 2005) and (Lundgren, 2005).

Strasser covered the reasoning behind the selection of the original materials of construction. Attention was focused on the major structural (e.g. piping, pressure vessel, reactor internals) and mechanical (e.g. pumps, valves) components, especially those that have required repair or replacement due to water chemistry and corrosion issues.

He reviewed the significant degradation modes in these *RCS* components and the various stress, material and environmental conditions that exacerbated the degradation. For instance, for the case of stress corrosion cracking, discussion centered on the interactive effects of;

- *Oxidizing species* in the reactor coolant, and the coolant temperature
- *Stress and/or strain* in the material, which could arise out of: the applied loads, the residual stress due to welding, fabrication and cold working associated with forming or surface preparation.
- *Microstructures* that promoted crack initiation and propagation. An obvious example of this is the grain boundary precipitate composition and morphology that can give rise to intergranular corrosion and cracking.
- *Reactor service time*

Particular emphasis was placed on the changes in alloy composition that were required to mitigate the damage. Attention was given to:

- Stress corrosion cracking (*SCC*) of austenitic stainless steels piping in *BWRs*, and, irradiation-assisted *SCC* of stainless steel reactor internals, (*IASCC*). Topics discussed included, for example, the use of stabilized stainless steels that minimize the creation of a grain boundary that is “sensitive” to intergranular attack and crack initiation. Conversely the relatively recent observation of the adverse role of silicon segregation to the grain boundaries during irradiation was pointed out.

- Stress corrosion cracking of nickel-base alloys in primary side components in *PWRs*, (*PWSCC*), such as Alloy 600 steam generator tubing and Alloy 600 reactor vessel and pressurizer safe-ends /nozzles, plus the associated Alloy 182/82 weldments. Discussion also included the rationale for the choice of alternative alloys (e.g. Alloy 800NG) and replacement alloys (e.g. Alloys 690/152/52) with different heat treatments (“mill-annealed” vs, “thermal treatment”), which produced more resistant grain boundary microstructures.

Riess expanded on these degradation modes by including stress corrosion cracking of steam generator tubing in the *PWR* secondary side, and both he and Lundgren emphasized the various water chemistry-based mitigation actions for *PWRs* and *BWRs* respectively. These specific actions included, for example:

For mitigation of *PWSCC* of Alloy 600/18/82 in *PWRs*

- *Zinc injection*, which (based on laboratory and preliminary service experience) seems to significantly delay crack initiation.
- *Temperature reduction*, which can be extremely effective for both crack initiation and propagation, given the high activation enthalpies for both processes.
- *Control of dissolved hydrogen* at the upper end of the specified value of 50 cc/kg H<sub>2</sub>O. This is a viable approach, since the cracking susceptibility is confined to a narrow potential range centered on the Ni/NiO equilibrium potential and, therefore, relatively small changes in corrosion potential can mitigate the problem of *PWSCC*

For mitigation of *SCC* and *LASCC* of stainless steels in *BWRs*;

- *Control of non-OH<sup>-</sup> anionic impurities*, especially chloride and sulfate, since these promote acidity at the crack tip in oxidizing environments and, thereby, accelerate the crack propagation rate.
- *Reduction in corrosion potential* at the crack mouth, since this decreases the driving force for non-OH<sup>-</sup> anionic impurity concentration at the crack tip. This reduction of the corrosion potential may be accomplished via hydrogen injection to the coolant (i.e. “hydrogen water chemistry”) with further addition of noble metals (i.e. Noblechem<sup>TM</sup>) for protection of reactor internals,. This latter development catalyses the dissolved oxygen/hydrogen recombination without the undesirable side effects of increased levels of <sup>16</sup>N in the balance of plant.



- *Application of insulating protective coatings (IPC)*, such as zirconium oxide. Such coatings deposited by, for example, air plasma spraying have a high electronic/ionic conductivity and thereby insulate the underlying stainless steel from the coolant. An added effect is that such coatings, even if cracked also prevent or restrict liquid transport to the underlying exposed stainless steel surface. Both of these properties effectively decrease the corrosion potential of the stainless steel, without the addition of stoichiometric amounts of hydrogen to the coolant. Thus this method has potential application to *BWR* reactor components such as the top guide or upper head assemblies, where hydrogen water chemistry or Noblechem<sup>TM</sup> effectiveness is restricted due to the partitioning of hydrogen to the steam phase.
- Lundgren also reviewed a further *IPC* approach involving the deposition of titanium oxide onto irradiated components. As well as exhibiting *IPC* benefits discussed above, this coating exhibits the further advantage that the corrosion potential of the coated stainless steel is further lowered due to the anodic current created by photo-excitation associated with ultraviolet irradiation impacting onto the n-type TiO<sub>2</sub> oxide coating.

All three authors concluded that as far as structural materials degradation was concerned the three major current corrosion issues were;

- *PWSCC* of nickel-base alloys and their weldments on the *PWR* primary side.
- *SCC* of steam generator tubing on the secondary side of *PWRs*.
- *SCC* of reactor internals in *BWRs*

### 3.2 *UPDATE ON UNDERSTANDING OF SPECIFIC MATERIALS DEGRADATION MODES*

A report was published in 2006 that had the primary objective of providing ANT-International members an introduction to the subject of environmentally-assisted degradation of structural materials in water-cooled nuclear reactors (Ford, 2006). The report was aimed primarily at engineers and scientists who were new to this technology so as to give them a basis for the more detailed discussions of specific subjects in the ANT-International Annual Reports.

Management of degradation requires an understanding of the complex interactions between the various material, environmental and, sometimes, stress conditions. These conditions will change with the reactor design/system and the reactor operating mode (Figure 3-1a), thereby giving rise to a wide range of, in many cases, interrelated degradation modes.

## 4 DOSE RATE BUILD-UP AND CONTROL

### 4.1 *PWRs (ROLF RIESS)*

The long term trends in occupational radiation exposure per plant and year are shown in Figure 4-1 for pressurized water reactors in various countries. It is given as courtesy by AREVA GmbH and it is an update of Figures shown by Riess & Marchl, 2000. This Figure confirms that the Nuclear Industry has been successful in reducing radiation exposures of *PWRs* within the past decades. For the 4 countries shown, the average value for occupational radiation exposure approaches 1 – 1.5 Man-Sv per plant and year. These values, however, are still above the goal for the *EPR* in Flamanville-3, e.g. <0.35 Man-Sv per year, according to Berger et al., 2006. As Hunsicker, 2006, reports, also WANO has set a goal of 0.65 Sv which is below the US industries average of 0.84 Sv. In this section the options shall be identified which may allow to achieve this goal.

In order to discuss the data of Figure 4-1 it has to be recognized, that in the 1980s the highest values for occupational exposure has been in the US. In a similar range the older Siemens plants were suffering from occupational exposures in the range of 5-6 Man-Sv per year. About half of this value did exist in the older Japanese *PWRs*, which started at about 3 Man-Sv per year in the early 80s. The best performance in the early 80s was shown by the French units. Within the last 2 ½ decades the French units improved, however, only by factor of about 2, whereas the plants in other countries had greater improvement factors.

Remarkable is the success of the Siemens pre-convoy and convoy units. In their 2 decades of operation they had an occupational exposure of <0.5 Man-Sv per year. In the same range as the Siemens pre-convoy and convoy units Sizewell B can be found, which is not shown in Figure 4-1 and which shall be explained later.

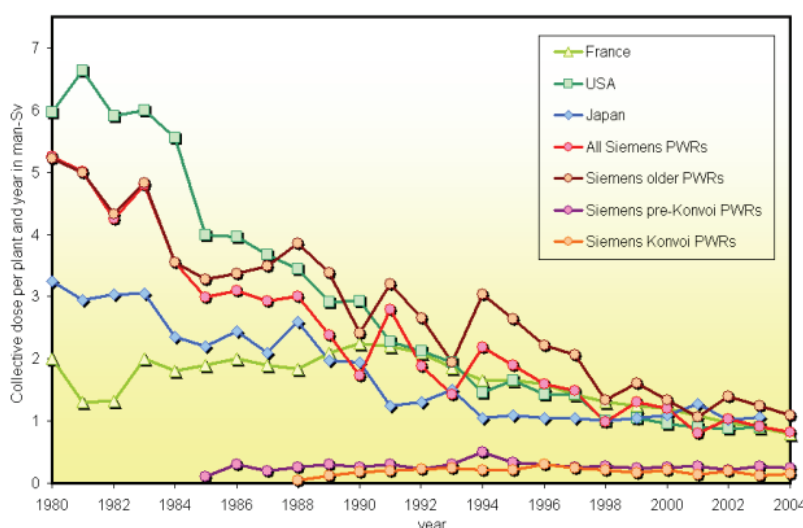


Figure 4-1: Occupational Exposure in *PWRs*: Courtesy of AREVA; Status of the Data, 2005.

#### 4.1.1 Background

The primary source of *PWR* radiation fields in older plants is Cobalt 60, formed by a (n  $\gamma$ )-reaction from Cobalt-59 (elemental Cobalt). Cobalt-58 is formed by the Ni-58 (n-p)-reaction with fast neutrons and it is the second most important contributor to out-of-core radiation fields in older *PWRs*. However, in newer plants, where the major sources of Cobalt are removed, e.g. where the Cobalt-60 problem is minimized, the Cobalt-58 becomes the most important issue. In order to minimize the contribution of these radio-nuclides to out-of-core radiation fields, the sources of elemental cobalt and Nickel have to be identified and it has to be discussed how their contribution to radiation exposure can be controlled. The major source for elemental Cobalt (and thereby Cobalt-60) is the corrosion and wear of Cobalt base alloys (e.g. Stellites) and the Cobalt impurities in *RCS* structural materials (e.g. SG tubing). The major source for Nickel is the Steam Generator Tubing material. The radiation field build-up has then to distinguish between 3 major steps:

- Corrosion product release to the coolant, mainly from out-of-core surfaces
- To some extent: Deposition of this material on the fuel element surface and activation
- Re-dissolution of the activated products and re-deposition on out-of-core surfaces.

Each of these steps strongly depends on the primary coolant chemistry and on the chemical and physical properties of the elements cobalt and nickel under *RCS* conditions. Additionally, the first step also depends on the material properties, especially the SG tubing.

However, the description of the Co- and Ni- (and thereby Co-60 and Co-58) behaviour in the *RCS* is complicated because of a variety of facts, like:

- The primary system is a non-isothermal system and the solubility and transport properties depend on the local chemistry conditions (Boron, Lithium and thereby the pH)
- Corrosion products in the coolant can be transported in three different forms:
  - as solid particles like metal or metal oxides
  - as colloids, e.g. in the form of hydroxyl complexes
  - as metal ions
- Corrosion products are metal oxides, e.g. Chromium forms under the reducing *RCS* conditions very stable Cr(III)-compounds with extremely low solubility.

- Deposits on the fuel surface can consist of non stoichiometric nickel ferrites to be formulated as  $\text{Ni}_x \text{Fe}_{3-x} \text{O}_4$ . In these nickel-ferrites the nickel can be replaced partially by cobalt in order to form complexes like  $\text{Co}_y \text{Ni}_x \text{Fe}_{3-x-y} \text{O}_4$ . Two facts can be derived from this situation:
  - Chromium is not participating in the solution transport of the activity under normal operation.
  - The contamination mechanism depends mainly on the solubility behaviour of nickel-ferrites.
- In addition to nickel-ferrites, elemental nickel or NiO is found if not enough iron is present in order to form the ferrites.
- Regarding the chemical composition of the SG inner surface layer: It consists out of multiple layers depending on the underlying model.
- Since the chromium spinels, the chromites are the most stable mixed oxides. They are the matrix to accumulate divalent radio nuclides like Co-58 and Co-60.

The overall process, e.g. the accumulation of the activity on the out-of-core surfaces is a complex matter of chemical and physical mechanisms interacting with each other. The various mechanisms and underline models shall be described later in this review.

However, the conclusion is, that the coolant pH should be between 6.9 and 7.4 at 300 °C in order to get a minimum in the radiation field build-up. This is also reflected in the primary coolant specifications which are set for 25 °C and as they are described in detail in Chapter 2 of this Annual Report.

In the following, each of the important factors shall be discussed in more detail including and emphasizing the plant experience gained in this field. As part of this discussion there will be a cross-check of available information with possible and desirable objectives for an operating utility. Such objectives may be the following as described by Berger et al., 2006, for the *EPR* in Flamanville-3:

- The occupational radiation exposure shall not exceed 0.35 Man-Sv/year averaged out over a 10 year phase. Such value is oriented at the best performing *PWRs* which are Sizewell B and the Siemens pre-convoy and convoy units. For *PWRs* WANO has set a value of 0.65 Sv per plant and year.
- The required annual outage time should be in the range of 2 weeks. ( 16 day shutdown for refuelling and maintenance, 11 day shutdown for refuelling only)
- The availability target is >91 % for an 18 month cycle.

## 5 EFFECT OF WATER CHEMISTRY

### 5.1 *PWR/VVER WATER CHEMISTRY (ROLF RIESS)*

#### 5.1.1 Introduction

The Primary Coolant serves as a moderator and is the medium for transporting heat from the core to the steam generators. Hence, it must not endanger plant operation by the corrosion of materials and consequences thereof. The task of water chemistry can be divided into the following main points.

1. Metal release rates of the structural materials should be minimal.
2. The occurrence of localized forms of corrosion should be counteracted.
3. The transport and deposition of corrosion products must be influenced in such a manner, that contamination of the primary coolant system is kept low.
4. The deposition of corrosion products on heat transfer surfaces, particularly on fuel assemblies, should be prevented as far as possible.
5. Radiolytic formation of oxygen should be suppressed.

The materials which are in contact with the primary coolant are:

- a) Austenitic stainless steels of components and piping of the primary system.
- b) Zirconium alloys for cladding of fuel assemblies.
- c) Incoloy 800, Inconel 690 *TT* or, Inconel 600 *MA* or *TT* for steam generator tubes. Stainless steel tubing is used in *VVER* SGs.
- d) High alloy materials (ferritic stainless steels) of low surface area for internals of the primary system.

The water chemistry conditions applied to these materials must fulfil the above mentioned requirements. Thus the primary coolant of *PWRs*, which contains boric acid (900-1800 ppm B at *BOC*) as a neutron absorber, is chemically conditioned by the addition of isotopically pure lithium ( $\text{Li-7}$ ) hydroxide (2-5 ppm Li at *BOC*) as a non volatile pH-control agent and of hydrogen.

Recently, an increasing number of *PWRs* is adding Zinc (5-40 ppb) in order to (1) reduce plant activation by reducing the metal release and by replacing Cobalt isotopes in the oxide layer and (2) minimize the initiation of stress corrosion cracking of Inconel 600 material.

In *VVER* plants  $\text{NH}_3$  is added, which decays to  $\text{H}_2$  by radiolysis. Instead of  $\text{LiOH}$ ,  $\text{KOH}$  is added, so that the pH-control is accomplished by  $\text{K} + \text{Li} + \text{Na}$  ( $\text{Li-7}$  is formed by the  $\text{B-10}$  ( $\text{n}, \alpha$ )  $\text{Li-7}$  reaction) and  $\text{NH}_3$ . None of the *VVER* plants is adding Zinc like the *PWRs*.

#### 5.1.1.1 Concerns regarding Fuel Elements

From today's perspective it is most important to evaluate the factors, which are of greatest concern for the fuel element corrosion and what are the driving forces (problems) for Water Chemistry in the last 10-to 15 years.

These driving forces are moves to improve Plant Availability and Fuel Economics which can be characterized by:

- Changing to 18 and 24 month cycle
- Core up-rating
- Higher enrichment fuel, increased burn-up
- Low leakage cores combined with increased sub-cooled nucleate boiling

These moves - based on operational experience – caused concerns over coolant additives and impurities because the fuel elements in the operating plants (specially in the US) experienced heavy crud deposition at positions where sub-cooled boiling created two negative effects, namely (1) accelerated corrosion effects and (2) Axial Offset Anomaly (AOA).

The corrective actions believed to be effective, are:

- Higher pH Primary Water Chemistry
- Zinc Addition

For the pH strategy it is believed to avoid in any case  $\text{pH}_T$ -values of  $< 6.9$  by increasing the LiOH concentration above a long time valid value of 2-2.2 ppm Li. However, such Lithium increase may be a risk regarding the corrosion resistance of the Zirconium Alloys.

Specifically one environmental factor may be emphasized which is the corrosion product deposition on fuel surfaces, which can lead to increased cladding temperatures and increased corrosion rates. Such deposits have been identified as non-stoichiometric Ni-ferrites ( $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ ), Ni oxide or metallic Nickel. Such crud deposition is occurring specifically at positions with sub-cooled boiling and may cause accelerated corrosion defects locally and axial power shift by boron precipitation (AOA).

Zinc addition may also lead to a more degrading crud at positions with high steaming rates. Thus, surveillance programs after introduction of Zinc are highly recommended, especially for PWRs with high duty cores. On the other hand, Zinc reduces the corrosion product release from system surfaces.

#### 5.1.1.2 Higher pH Primary Water Chemistry; Lithium/B-Strategy

Historically, the solubility of magnetite was the basis for fixing a  $\text{pH}_T$  at 6.9 as an optimum. In addition, isotopically pure Lithium-7-hydroxide became the most suitable pH control agent to be used in the PWR Primary Coolant.

However, later on it was recognized, that the contribution of Nickel is much more important to the primary side corrosion product inventory than the iron. Further on it was found, that Nickel ferrite is a major constituent. Consequently the solubility behaviour of Nickel ferrite was investigated and it was found, that a pH of 7.4 should be the solubility minimum. However, a pH of 7.4 could not be adjusted at *BOC* since 2 or 2.2 ppm Lithium was at the upper specified limit in order to prevent Lithium induced corrosion of the fuel element cladding. As a consequence, the first two thirds of a cycle the 2 ppm were kept constant till reaching the pH of 7.4 and then Lithium/Boron ratio was adjusted to stay at 7.4 till the end of the cycle.

In order to explain the Li/B-ratio changes, it is convenient to use the information shown in Figure 5-1 for the US case by Turnage, 2004.

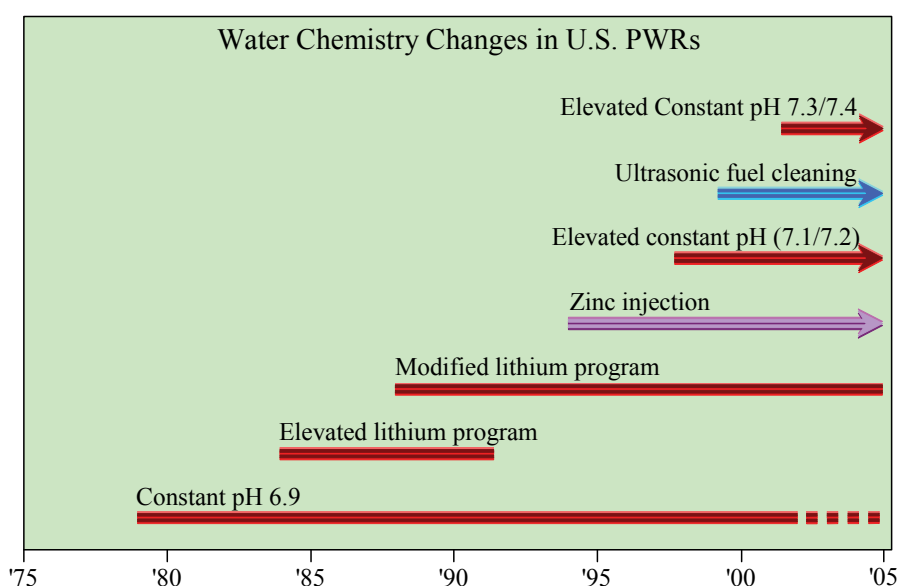


Figure 5-1: Water Chemistry Changes in U.S. *PWRs*, Turnage, 2004.

Regarding the application of all the Li/B-chemistries in operating *PWRs* there are major differences applied in the various regions and countries. Such variations depend also on the dates of the application. In the early 1970s worldwide the Lithium concentration was operated between upper and lower specified values. The first step to the coordinated chemistry was made in the late 70s/early 80s in order to reduce crud deposition on fuel rods and to minimize radiation fields. The selected  $\text{pH}_T$  was 6.9, which was also consistent with the  $\text{pH}_T$  for iron solubility minimum under *PWR* primary side conditions.

In the mid 1980s, many *PWRs* introduced the modified chemistry based on operational experience (see above), because at this time high and constant Lithium as a pH strategy produced better result than the coordinated chemistry, as far as crud deposition and radiation fields are concerned.

## 6 CURRENT ISSUES AND MATERIAL DEVELOPMENT

Environmentally-assisted degradation of structural materials in water-cooled reactors has been a constant issue for several decades and was discussed in both the *LCC-1* Annual Report and the current report. The modes of degradation have ranged from flow accelerated corrosion, to boric acid corrosion, to various forms of localized damage associated with, for example, crevice corrosion and stress corrosion cracking.

The current degradation issues of prime concern for structural components are:

- Stress corrosion cracking of *PWR* steam generator tubing in both the primary and secondary systems.
- Stress corrosion cracking of reactor internals
- *PWSCC* of Nickel base Alloys and weld metals
- Irradiation assisted stress corrosion cracking of stainless steel reactor internals in *BWRs*
- Fuel Cladding Integrity

These are all long running issues with the delay in their resolution being associated with the quantification of the complex material, environment and stress interactions that govern the kinetics of degradation.

The resolution of these particular issues is advancing, however, with defensible mitigation actions being deployed in the reactor fleet. These include water chemistry modifications, such as the adoption of noble metal additions in *BWRs* and zinc additions in the *PWR* primary side. Alloy modifications include the adoption of L-grade and stabilized stainless steels in *BWRs*, and of Alloy 690 with more cracking-resistant heat treatments in *PWRs*. These remedial actions all have a sound basis in terms of laboratory observations and, in some cases, service experience. The confidence in their application is increased in those situations where the empirical knowledge base is backed up with a quantitative understanding of the mechanism of cracking; this is epitomized, for instance, by the case of stress corrosion cracking of austenitic alloys in *BWRs*

There is an underlying issue about the extent to which these remedies are beneficial under all potential operating conditions. These concerns have been highlighted with the (re)discovery of the deleterious effect of cold work on the various cracking modes, and the fact that many of these water-cooled reactors may, in the future, be operated at increased power levels for times beyond their original licensing basis. Under these extended and uprated conditions, further changes in the system may counter the beneficial effects of current mitigation actions. An example of this is the increased amount of radiation-induced segregation of silicon to grain boundaries in stainless steels, and the fact that this may severely diminish the effectiveness of hydrogen water chemistry for stainless steel core internals in *BWR*.



This concern about future, unexpected, degradation problems is being addressed by the regulator and the utilities in the United States. The objective is to adopt a proactive management approach to material degradation issues, which allows an extended time to develop mitigation actions before the degradation presents a significant economic or safety issue. Such a proactive management approach requires an assessment of future behavior of the prime reactor components. This assessment, conducted by the *NRC* and *EPRI* in separate studies, was completed in 2006 and was summarized in Section 3. Such an assessment led to the identification of degradation modes in specific reactor components that require further knowledge in order to prevent a deleterious impact on reactor operations in the future.

Fuel reliability is a permanent area of concern because fuel has been subject to design and duty changes. In addition, water chemistry was modified significantly in the last decade. Especially the use of *NMCA* together with zinc injection seems to increase the corrosion induced fuel failures in *BWR* plants. This change of water chemistry conditions puts a pressure on the utilities to further decrease the total inflow of corrosion products to the primary circuit.

Radiation field control is an area, where the *PWR* industry has been successful in the last decade by achieving in average an exposure rate of ~1 manSv per plant and year. However, activated corrosion products (especially Co-58 and Co-60) play an important role during shutdown. In many cases they are released in concentrations, which require a time consuming cleanup process. Nowadays, where short outage periods are of top interest, the issue of minimum crud inventories gains a high priority.

Occupational exposures in *BWRs* have also been significantly reduced during the last 20 years, with recent average exposure rates of 1 – 2 manSv per plant and year. Key factors have been Co reduction, improved condensate cleanup, development of efficient decontamination methods and the introduction of Zn injection, especially in plants using *HWC* or *NMCA*. Further efforts to reduce Co sources are foreseen, as well as optimisation of the feedwater chemistry with respect to e.g. iron and copper.

The subject of corrosion product generation and transport is also of vital interest in *PWR* plants for the fuel cladding integrity as well as for the phenomenon of *AOA* (Axial Offset Anomaly) or crud induced power shift (*CIPS*). With a small inventory of corrosion products both radiation field build-up during shutdown and the *AOA* problem could be controlled properly.

In the nutshell, the key area to mitigate these problems is the control of the crud source term. This leads to the question about our knowledge of this issue:

It is understood that there are oxide layers at the interface between water environment and metallic materials, playing a decisive role in the interaction between them. Water chemistry control is the control of the interfacial oxide layers from the water side. Nevertheless, the roles of both, the material and the water chemistry, in forming protective oxide layers, are not well understood, being sometimes phenomenological, qualitative, and even neglected. Deeper understanding is needed on formations, structures, properties, surface reactions, etc. of the interfacial oxide films. Up to now, we only know beside an “optimized water chemistry”, that a properly performed hot functional test (*HFT*) as one option for passivating the ID of the SG-tubing and the addition of Zinc may have a beneficial effect.

Local chemistry inside cracks or crevices is sometimes largely different from bulk chemistry, but is very difficult to measure directly. Usually it is evaluated by simulation or model experiments. More information on crack chemistry is needed for the quantitative evaluation of crud propagation or some other local corrosion.

In situ monitoring techniques for example *ECP* monitoring or pH are very important but rather difficult especially in core. They are expected to work in combination with the proper sampling technology as key technology for preventive and predictive measures of plant aging and also to deepen the understanding of the phenomena of interest.

Finally it should be mentioned, that Water Chemistry Guidelines should be an instrument describing the water quality requirements necessary to achieve reliable operational results. Whether such Guidelines mainly shall be based on long term operational experience (like the 2006 specifications in Germany) or on more short term test results, remains open.

## 7 REFERENCES

Airey, G.P, “*The Stress Corrosion Cracking (SCC) Performance of Inconel Alloy 600 in Pure and Primary Water Environments*”, Proceedings of First International Symposium on Environmental Degradation in Nuclear Power Systems – Water Reactors, Myrtle Beach, August 22-25, 1983. Eds. J. Roberts, W. Berry, National Association of Corrosion Engineers, p 462-476, 1983.

Alexandrescu, B. Chopra, O., Cullen, W.H. and Shack, W.J “*Crack Growth Rates in PWR Environment of nickel base Alloy Welds From Davis-Besse and V.C. Summer Power Plants*” Proceedings of the International Symposium Fontevraud VI, SFEN, Paris September 18-22, pp.311-322, 2006.

Amzallag C. et al., “*Analysis of the Cracking Behaviour of Alloy 600 Reactor Head Penetrations; Part II Derivation of a Crack Growth Model and Analysis of Crack Growth Rate Field data*”, PVP Volume 324, Fatigue and Fracture Vol.2, ASME 1996.

Amzallag C.A., Boursier J.M. Pagès C. and Gimond C., “*Stress corrosion life assessment of 182 and 82 welds used in PWR components*”, Proceedings of Tenth International Conference on Environmental Degradation in Nuclear Power Systems–Water Reactors, Lake Tahoe, Eds. F.P. Ford, G. Was, National Association of Corrosion Engineers, August 5-9 2001.

Andresen P.L, “*Effect of Material and Environmental Variables on Stress Corrosion Crack Initiation in Slow Strain Rate Tests on Type 304 Stainless Steel*”, Symp. On Environmental Sensitive Fracture; Evaluation and Comparison of Test Methods” April 1982. Published in ASTM STP821, pp. 271-287, 1984.

Andresen P.L. and Ford F.P, “*Life Prediction by Mechanistic Modelling and System Monitoring of Environmental Cracking of Fe and Ni Alloys in Aqueous Systems*”, Materials Science and Engineering, A103, p.167-183, 1988.

Andresen P.L, Ford F.P, Murphy S.M and Perks J.M., “*State of Knowledge of Radiation Effects on EAC in LWR Core Materials*”, Proceedings of Fourth International Symposium on Environmental Degradation in Nuclear Power Systems – Water Reactors. Jekyll Island, August 6-10, 1989. Eds. D. Cubicciotti, E. Simonen. Published by National Association of Corrosion Engineers. ISBN 1-877914-04-5, pp.1.83-1.121. 1989.

Andresen P.L “*Effects of Specific Anionic Impurities on Environmental Cracking of Austenitic Materials in 288 Water*” in “Proceedings of Fifth International Symposium on Environmental Degradation in Nuclear Power Systems – Water Reactors. Monterey August 25-29, Eds. D. Cubicciotti, E. Simonen. Published, by American Nuclear Society. ISBN 0-89448-173-8, pp.209-218. 1991.

Andresen P.L., “*Effects of Zinc Additions on the Crack Growth Rate of Sensitized Stainless Steel and Alloys 600 and 182 in 288 Water*”, Paper 72, Water Chemistry of Nuclear Reactor Systems 6, BNES London 1992.

Andresen P.L, “*Application of Noble Metal Technology for Mitigation of Stress Corrosion Cracking in BWRs*”, Proc. Seventh International Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, NACE, p.563-578., 1995.

Andresen P.L and Ford F.P, “*Modeling and Prediction of Irradiation Assisted Cracking*”, Proceedings of Seventh International Symposium on Environmental Degradation in Nuclear Power Systems – Water Reactors. Breckenridge, August 7-10, 1995. Eds. R. Gold, A. McIlree. Published by National Association of Corrosion Engineers. ISBN 0-877914-95-9, pp.893-908. 1995.

Andresen P.L and Angeliu T.M “*Effects of Zinc Additions on the Stress Corrosion Crack Growth Rate of Sensitized Stainless Steel, Alloy 600 and Alloy 182 Weld Metal in 288 Water*”, Paper 409, Corrosion-95 NACE, Orlando, March 1995.

Andresen P.L., “*Conceptual Similarities and Common Predictive Approaches for SCC in High Temperature Water Systems*”, Paper No. 258, Corrosion '96, NACE, Houston, p. 258/1, 1996.

Andresen, P.L, Ford F.P, Higgins J.P, Suzuki I., Koyama,M., Akiyama,M. Okubo,Y., MishimaY, Hattori,S., H. Anzai H, Chujo H, and Kanazawa Y, “*Life Prediction Of Boiling Water Reactor Internals*”, Proc., ICONE-4 Conference, ASME, 1996.

Andresen,P.L. and Angeliu,T.M “*Evaluation of the Role of Hydrogen in SCC in Hot Water*”, Paper # 195, Corrosion '97, NACE, Houston, p. 195/1.1997.

Andresen P.L, Emigh P.E and Young L.M., “*Mechanistic and Kinetic Role of Yield Strength / Cold Work / Martensite, H<sub>2</sub>, Temperature, and Composition on SCC of Stainless Steels*”, Proc. Int. Symp. on Mechanisms of Material Degradation in Non-Destructive Evaluation in Light Water Reactors, Osaka, Japan, May published by Inst. of Nuclear Safety System, Japan,. pp. 215-239, 2002.

Andresen P.L, Diaz. T.P. and Hettiarachchi,S, “*Effect on Stress Corrosion Cracking of Electrocatalysis and Its Distribution Within Cracks*”, Proc. of 11th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, ANS, 2003.

Andresen P.L, Emigh P.W, Morra M.M and Horn R.M, “*Effects of Yield Strength, Corrosion Potential, Stress Intensity Factor, Silicon and Grain Boundary Character on the SCC of Stainless Steels*”, Proc. of 11th Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, ANS,. pp. 816-831. 2003.

Andresen P.L. and Morra M.M., “*Effects of Si on SCC of Irradiated and Unirradiated Stainless Steel and Ni Alloys*”, Paper 05591, Corrosion/05, NACE, Houston, 2005.

Andresen Peter L. et al, “*Online Noblechem Mitigation of SCC*”, 12<sup>th</sup> Int. Conf. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Snowbird, Utah, USA, August 14 -18, 2005.

Andresen P. L. et al., “*Use of Primary Water Chemistry in PWRs to mitigate PWSCC on Ni-base Alloys*”, International Conference on Water Chemistry of Nuclear Reactor Systems, Jeju Island, Korea, October 2006.

Androva K. et al., “*Primary Water Chemistry, Radiation Situation and Fuel Experience at Temelin VVER 1000 NPP*”, International Conference on Water Chemistry of Nuclear Reactor Systems, Jeju Island, Korea, October 2006.

Asano, K., Fukuya, K., Nagata, K. and Kodama, M., “*Changes in Grain Boundary Composition Induced by Neutron Irradiation on Austenitic Stainless Steels*”, Proceedings of Fifth International Symposium on Environmental Degradation in Nuclear Power Systems–Water Reactors, Monterey, Eds. D. Cubicciotti, E. Simonen, American Nuclear Society, August 25-29, pp. 838-846. 1991.

Bamford W. and Hall J. “*A Review of Alloy 600 Cracking in Operating Nuclear Plants: Historical Experience and Future Trends*” in “Proceedings of Eleventh International Conference on Environmental Degradation in Nuclear Power Systems–Water Reactors, Skamania Lodge, Eds. G. Was, L. Nelson, American Nuclear Society, August 5-9, pp. 1071-1081, 2003.

Bandy R. and van Rooyen D., “*Tests with Inconel 600 to Obtain Quantitative Stress Corrosion Cracking Data for Evaluating Service Performance; BNL-NUREG-31814*”, U.S. Nuclear Regulatory Commission, Washington, 1983.

Bardet F. et al., “*Chemical Degassing on EdF Units – Feedback, Experience and Method*”, International Conference on Water Chemistry of Nuclear Reactor Systems, Jeju Island, Korea, October 2006.

Barton M. et al., “*Corrosion Product Measurements at the Sizewell-B PWR*”, International Conference of Water Chemistry in Nuclear Reactor Systems, Bournemouth, 2000.

Bates J.C. et al., “*Corrosion Product Monitoring during the 7<sup>th</sup> Refuelling Outage at Sizewell-B*”, International Conference on Water Chemistry of Nuclear Reactor Systems, Jeju Island, Korea, October 2006.

Bengtsson B., “*Recommendation concerning an increased Lithium concentration in the reactor water for Ringhals PWRs*”, Ringhals Document 1890560/3.0, 2006.

Bennet P. et al., “*Demonstration of the PWR Axial Offset Anomaly in IFA-665 A*”, Halden Report HWR 808, 2005.