

LCC5 ANNUAL REPORT

LCC5 Annual Report

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Acronyms and expressions

Unit conversion

1 Introduction

The overall objective of the *LWR Chemistry and Component integrity* (LCC5) program is to enable the LCC5 Member to:

- Gain increased understanding of reactor water chemistry related to a successful plant operation and a continued integrity of Reactor Coolant System (RCS) materials while keeping radiation exposure low.
- Gain increased understanding of secondary side water chemistry related to an improved Steam Generator (SG) performance and avoiding Flow Accelerated Corrosion (FAC) in secondary side systems for a reliable plant operation.
- Assist in the training and education of a new generation of chemistry and materials experts.
- Establish a new independent meeting point for experts to enable free and critical discussions and experience exchange.

The objective is met through critical review and evaluation of the most recent data related to reactor water chemistry, identification of the most important new information, and discussion of its significance in relation to water chemistry now and in the future.

The evaluations are based on the large amount of non-proprietary data presented at technical meetings and published in the literature.

The 2009 technical meetings covered include:

- CQCNF-2009 conference at Hyderabad, India, February 18-20, 2009.
- IAEA13th International Topical Meeting on Research Reactor Fuel Management (RRFM), Vienna, Austria, 22 -25 March 2009.
- Reduction of Dose Rate in PWRs Workshop, Würzburg, Germany, April 6-9, 2009.
- Jahrestagung Kerntechnik, Dresden, Germany, May 12-14, 2009.
- NEI Dry Storage, FL, May 11-14.
- US Utility Conference, USA, summer 2009.
- SMIRT20, ESPOO, Finland, August 9-14, 2009.
- 14th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Virginia Beach, Virginia, USA, August 23 - 27, 2009.
- Top Fuel, Paris, September 6-11, 2009.
- The 8th International Conference on VVER Fuel, September 26 to October 3, 2009, Bulgaria.
- VGB Chemistry in Power Plants Conference, Dresden, Germany, October 28-29, 2009.
- International Symposium on Water Chemistry and Corrosion in Nuclear Power Plants in Asia 2009, Nagoya, Japan, October 28 – 30, 2009.
- Matériaux pour les tubes de GV REP et leur résistance à la CSC », Journée SFEN ST 2, Paris, 25. November 2008.

The extensive, continuous flow of journal publications is being monitored by 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 of Vendors (if published)
- International Atomic Energy Agency (IAEA) Documents

The open literature information is collected throughout the last couple of years and the most relevant data is selected for the Annual Report (AR). The large collective experience gained by the Report authors in past and current projects is an important factor in making the evaluation, hence ensuring that the presented compiled information is put in perspective, and that the most important information is emphasized. The authors of the report are Dr. Rolf Riess, Dr. Suat Odar, Dr. Jan Kysela, Dr. Peter Ford, Dr. Peter Scott and, Dr. Pierre Combrade.

The topics covered in the LCC5 AR, are as follows:

- Primary side reactor water experience in Boiling Water Reactor (BWR), Pressurized Water Reactor (PWR) and Voda Voda Energo Reactor (VVER) reactors.
- Secondary side reactor water experience in PWR and VVER reactors.
- Material degradation management.

Regarding the first two items some requirements were introduced which should make the preparation of Annual Reports easier in the future. These requirements were:

- Preparation of a standard “Content” list.
- Formulation of a document describing the background of the captioned subjects.

In accordance with these requirements, this AR describes recent advances in PWR Primary and Secondary Water Chemistry, BWR Reactor Water and VVER Water Chemistry Management with examples of plant experiences for plants in the U.S., and Europe. Historically, the objective of a water chemistry control strategy has been to optimize the chemistry between the often conflicting requirements of controlling materials degradation, avoiding fuel performance issues and minimizing radiation fields. This objective remains today in the U.S. and in Europe as well, but the emphasis on each of the three constraints has changed over time. For example, the early emphasis in PWRs and VVER was to minimize build-up of radiation fields in out-of-core areas. Within the limits imposed by fuel CRUD concerns, they were driven by the large amount of radiation exposures received in special maintenance and repair work.

As improved cladding materials were introduced, the fuel cladding concern decreased, but subsequent increases in fuel cycle duration maintained the constraint. The move in the past ten years to greater fuel duty increased sub-cooled nucleate boiling, which brought about the phenomenon in U.S.-PWRs of localized flux depression as a result of build-up of boron-containing CRUD. More recently, materials degradation concerns have received higher priority, following problems with Primary Water Stress Corrosion Cracking (PWSCC) in Alloy 600 penetrations in primary systems. In European PWR (in particular the German NPPs) the AOA problem did not show up because of the more Fe-rich coolant CRUD.

In PWR and VVER Secondary Side Chemistry the greatest emphasis is the materials integrity in particular of the SG tubing material. The SG tubes are endangered by Corrosion Products (CPs) coming from the steam water cycle and from impurities and oxygen as well.

In BWRs, control of stress corrosion cracking has been the prime objective for the past 25 years, with mitigation of the resultant radiation field increase as a secondary objective. Improvements in water purity reduced the incidence of fuel failures in the late 1980s and 1990s, but margins were reduced as fuel duty increased. Between 1999 and 2004 a significant number of fuel failures in four U.S. plants resulted in tighter Electric Power Research Institute (EPRI) limits on water chemistry to minimize CRUD build-up. Although these new limits were successful in avoiding any further failures in the past four years, chemistry specifications continue to tighten in response to fuel duty increases.

In European BWRs the GE built units can be integrated into the U.S. experience, whereas the Scandinavian and German plants have a trend to practice a chemistry that needs a sound support by the material selection and processing.

Over the past several years the U.S. nuclear industry has established a number of initiatives with the goal of mitigating materials degradation through a proactive approach to existing and potential new corrosion problems, improving fuel integrity with the goal of zero fuel failures by 2010 [Tompkins 2008] and enhancing radiation protection over the next decade. Water chemistry plays a key role in achieving each of these goals.

Due to the political situation in Europe regarding Nuclear Energy, the centre of R&D work is located in France. The responsible French organizations are permanently investigating how to improve PWR primary side chemistry, e.g. by identification of the optimum pH. Metal release of the RCS materials is one of the key issues.

- Reference should be made to previous *LCC Annual Reports* in this series (LCC1, 2005, LCC2, 2006 and LCC3, 2007, LCC4, 2008) and *LCC Special Topic Reports* (LCC-2 Special Topic Report on CRUD 2006, LCC-3 Special Topic Report on Consequences of Power Up-rating 2007, and the Special Topic Report on Materials Degradation for more detailed information. This review identifies the most relevant of more recent publications. Since the Berlin Water Chemistry Conference is covered in LCC4 Annual Report, the focus here is to evaluate all recent information.

The work reported herein will be presented in two Seminars: One in Hilton Head Island, SC, USA on February 4-5, 2010 and one in Bilbao, Spain on March 10-12, 2010.

The Term of LCC5 started on April 1, 2009 and ends on March 31, 2010.

2 PWR primary side coolant chemistry (Rolf Riess)

2.1 Background

Currently, there are 70 PWRs operating in the United States, 49 designed by Westinghouse (W), 14 by Combustion Engineering (CE) and 7 by Babcock and Wilcox (B&W). There are several differences between the designs, most notably B&W units having once-through SGs whereas the W and CE units have re-circulating U-tube SGs. In contrast to secondary chemistry issues, these design differences have little effect on primary chemistry strategies, so in this review little distinction is drawn between the designs.

In Western Europe there are currently 90 PWRs in operation. The principle design of these stations is from W. They were built by W itself or by the two former licensees which were Framatome and Siemens. Differences in design and operational experience between the U.S. and the European stations will be explained in various sections of this AR or a detailed evaluation is recommended.

In the very early days of PWR operation, heavy Chalk River Unidentified Deposits (CRUD) build-up on fuel cladding surfaces was caused by the transport of CPs from the SGs into the reactor core, as for example in the first cycle of the Obrigheim NPP. As a result, activated CPs caused high radiation fields on out-of-core surfaces (Figure 2-1), fuel performance was compromised and even coolant flow issues were observed in some plants.

In any case the CPs are a challenging factor when it comes to mitigation methods in the areas of concern.

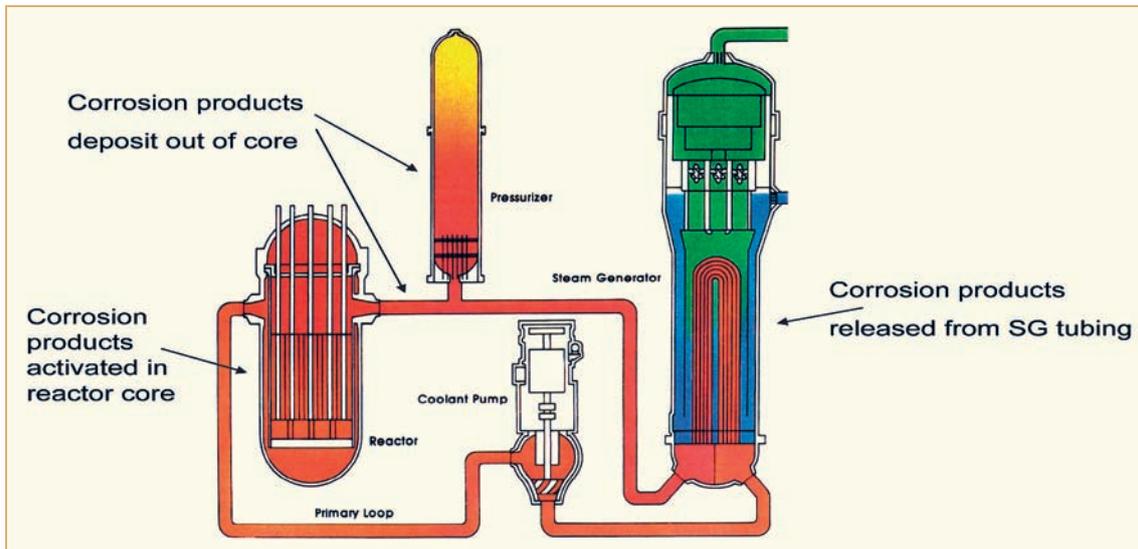


Figure 2-1: Transport and activation of CPs in PWR primary systems, [Wood 2008].

These problems were initially mitigated by imposing a hydrogen overpressure on the primary system, to reduce the electrochemical corrosion potential, and raising the primary chemistry pH. Materials degradation in primary systems was then not a major concern, with most of the emphasis focused on secondary side corrosion issues in the SGs. Commercial PWR power plants use a steadily decreasing concentration of boric acid as a chemical shim throughout the fuel cycle, which results in the use of lithium hydroxide to control pH. Some 30 years ago, the concept of “coordinated boron and lithium” was developed, whereby the concentration of LiOH was gradually reduced in line with the boric acid reduction to maintain a constant pH. Furthermore, it was determined that heavy fuel CRUD build-up was avoided if a constant pH of at least 6.9 was maintained. This was possible with 12 month fuel cycles, but fuel cladding corrosion concerns limited the maximum LiOH concentration to 2.2 ppm. As a result, plants often started the fuel cycle with pH below 6.9, which resulted in radiation fields remaining relatively high. Although research and plant demonstrations showed that the 2.2 ppm limit was excessively conservative, the move to higher Li concentrations has been slow. However, detailed fuel examinations from a recent plant demonstration in the U.S. (that will be discussed later) have indicated that Li can be raised to as high as 6ppm. In parallel optimizations of the fuel cladding material allow the operation at enhanced pH-values.

About 25 years ago, PWSCC of Alloy 600 SG tubes were observed in a few plants, leading to studies on mitigating this effect. Following successful demonstration of zinc injection in BWRs, initial field tests at European and U.S. PWRs revealed, that radiation fields were reduced, and laboratory studies in U.S. indicating that PWSCC was reduced, these facts were eventually confirmed. As a result, zinc injection is being implemented at an increasing rate, although concerns about fuel performance at high duty plants have not been completely resolved. Most recently, especially in the U.S. plants, build-up of boron-containing CRUD in areas of sub-cooled nucleate boiling leading to localized flux depression (AOA) has encouraged the use of higher Li concentrations to minimize CP transport. However, in particular in German PWRs these problems were not experienced because of more iron-rich CRUD. Concerns about the potential adverse effects of zinc deposited in high-CRUD regions has resulted in several highly-rated plants applying in-situ Ultrasonic Fuel Cleaning (UFC) before implementing zinc injection.

The identification of PWSCC in reactor vessel penetrations in the last 15-20 years has encouraged the use of zinc injection, but has also focused attention on the effects of dissolved hydrogen, for which the recommended range has remained in 25-50ml/kg for 30 years. It now appears that raising hydrogen will reduce PWSCC propagation rates, while lowering it may delay initiation of PWSCC. The interactions of materials, radiation fields and fuels in PWR primary chemistry and optimization issues covered in the Water Chemistry Guidelines, are depicted in (Figure 2-2).

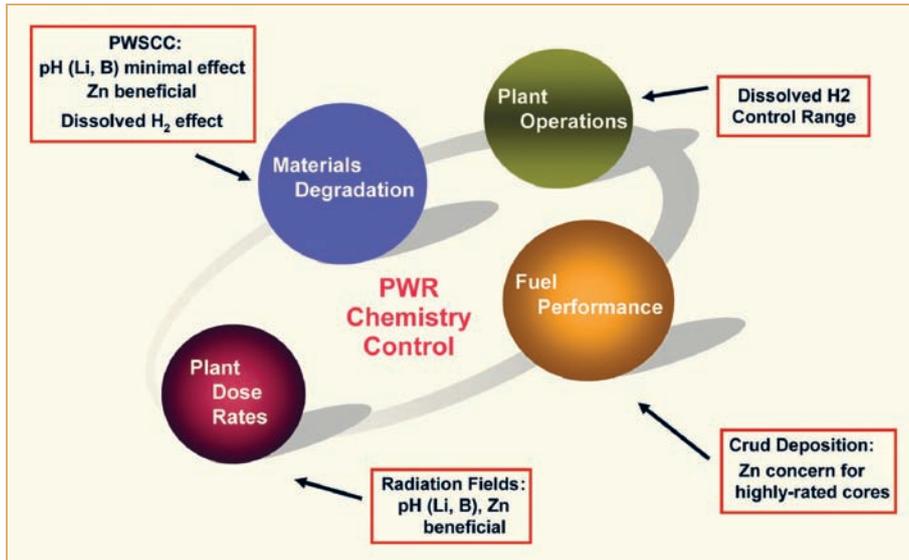


Figure 2-2: PWR primary chemistry optimization, [Fruzzeti & Perkins 2008].

The evolution of water chemistry control in PWR primary systems in USA over the last 30 years is shown in (Figure 2-3) whereas in Europe the “modified” chemistry prevails, which consists of a constant Li- concentration of max 2.2 ppm at Beginning of Cycle (BOC) till reaching a pH300 °C of 7.4, which is kept till End Of Cycle (EOC).

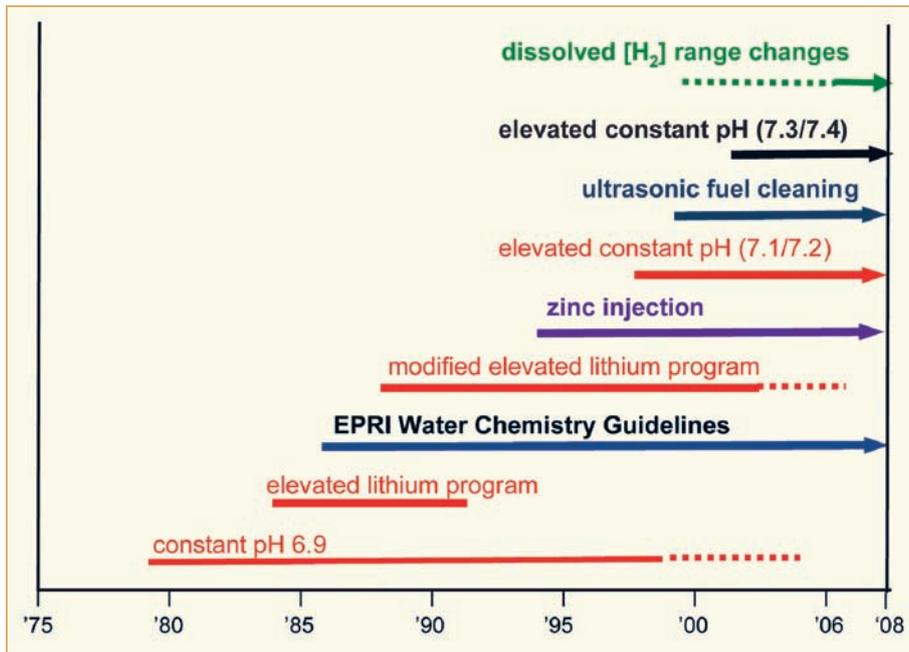


Figure 2-3: PWR primary chemistry changes at US plants, [Wood 2008].

The concerns of the early years of operation are summarized in (Figure 2-4).

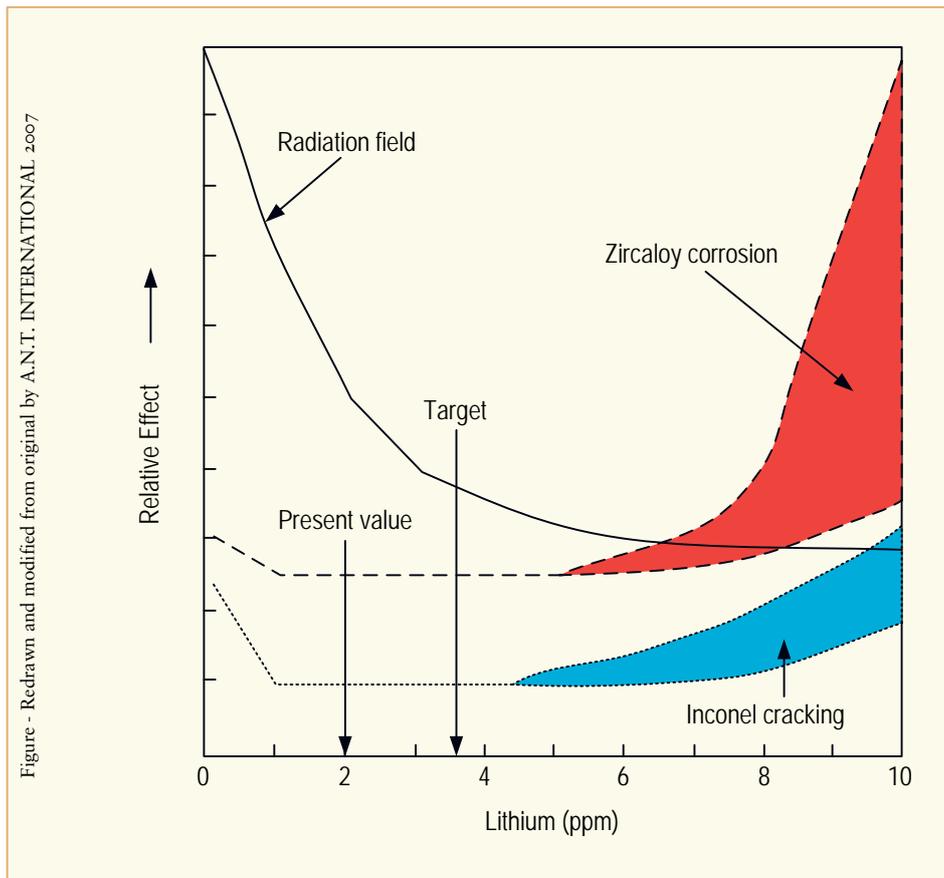


Figure 2-4: PWR primary coolant chemistry effect of Li-concentration (schematic), [Riess & Millet 1994].

The three main factors -pH control, Zinc injection and dissolved hydrogen control- that have dominated PWR primary chemistry strategies in the past, continue to do so today, [Fruzzeti & Perkins 2008]. Each of these factors is considered from the viewpoint of materials degradation, radiation field control and fuel performance concerns.

In recent years PWR primary chemistry has become complicated by demands of longer fuel cycles, causing e.g. higher initial Boron concentration. In addition, increased sub-cooled boiling and material- as well as fuel- concerns required further optimization of the coolant chemistry.

The key problem, caused by the above mentioned demands, is the existence of a CRUD inventory, which creates problems due to (1) its volume/mass of material and (2) the complex chemical composition of the participating elements. From the fuel element perspective the resulting main area of concern is AOA or CRUD Induced Power Shift (CIPS) especially in the U.S. plants with its use of nickel based alloys as SG tubing material. From a plant operational view the material integrity and the radiation exposure situation may obtain highest attention. In all cases to be discussed in this AR, CPs are involved in the basic mechanism. Since one of the objectives of this report is to describe how to mitigate the CRUD-related problems, the attempt is made to identify the countermeasures, which are appropriate to improve the operational situation. As it will be mentioned several times in this AR, the barrier oxide layer (the oxide layer adjacent to the base metal) is most important for the passivation of the inner surface of the reactor system. Furthermore, it is evident, that chromium spinels enhance the protective properties of the barrier oxide. Details on CRUD formations and CRUD properties may be taken from the LCC2 STR "CRUD in PWR/VVER and BWR Primary Circuits".

There is a consensus worldwide that an operational success depends on three key factors, which are: Design, material, and chemistry. If one of these factors would fail, operational problems will result.

With respect to the design of the PWRs (and the VVER) the majority of the plants are built on the basis of the Westinghouse design concept. The exceptions are the PWRs built by Combustion Engineering and Babcock & Wilcox. The CE units are different by using SGs that have about twice the size of the heat transfer surface of W SGs and that of its licensees. The B&W design differs by using Once-Through Steam Generators (OTSG) with a surface area comparable to CE SGs. In VVER units the SGs used are of the horizontal type. Despite the differences in design there is a common understanding that it has no consequences for the selection of the plant chemistry.

However, the chosen material has a great influence on details of the chemistry to be applied. The greatest evidence for such an influence is the material used for SG tubing. This can be either Nickel based Alloys, like Alloy 600 MA¹/TT² and Alloy 690 TT or Alloy 800 NG³ in some European and Canadian stations, but especially in Germany. Details of the differences between the two types of materials are mentioned in Section 2.2.1.

Early operating experience both in the U.S. and Europe confirm that insufficient control of pH and redox potential leads to enhanced CRUD formation and its negative consequences like fuel CRUD deposits, fuel cladding corrosion, and Axial Offset Anomaly.

2.2 Areas of concern

2.2.1 Material degradation

Material degradation was covered in two sections of the LCC4 AR by Chris Wood and Rolf Riess. Therefore it is recommended to pick up this information in the referenced paper.

In these documents it is recognized that the principles of primary side chemistry are not depending on the plant design but there is an influence by the materials used. The greatest difference between US-plants and in particular German PWR is related to primary water stress corrosion cracking. In the U.S. the preferred materials are of the 304 or 316 type in combination with nickel based alloys as SG tubing material. The German concept however, is to use stabilized materials corresponding to American Society for Testing and Materials (ASTM) 347 material. From a technical point of view it can be stated, that the stabilized austenitic materials are less susceptible to PWSCC compared to the materials used in the U.S. The greatest difference between the U.S. and Germany regarding material selection is the use of SG tubing material. In the U.S. nickel based alloys are preferred, which are susceptible for PWSCC. With Alloy 800 NG this problem can be excluded because the material is immune against PWSCC.

Although Alloy 800 NG has some advantages compared to the Inconel Alloys (600 MA) regarding primary side chemistry, the majority of new plants and also in replacement SGs, Alloy 690 TT is selected. It seems that secondary side corrosion problems are over-ruling the primary side arguments. There is even a rumour that Alloy 800 NG is no longer available. In order to clarify those details there may be a good starting point for a detailed evaluation by the paper presented by [Scott et al 2008].

¹ Milled Annealed

² Thermal Treated

³ Nuclear Grade

Another important issue, which should be investigated, is the source for Co60, which is i.e. the use of Stellite in the primary system. The replacement activity worldwide has been reviewed by [Steltzlen et al 2008] his findings for alternatives were (in French):

- Deloro 40 et 50 ou Colmonoy 4 et 5 (base Nickel – utilisés dans la robinetterie aux USA et au Canada).
- Norem 02 (base Fer – mis au point par EPRI).
- Everit 50 (base Fer – Siemens).
- Delchrome 910 (base Fer – utilisé dans la robinetterie aux USA et au Canada).
- Cenium Z 20 (base Fer – Technicatome, Siemens).
- Fox Antinit DUR 300 (base Fer – Siemens).
- Nitronic (base Fer).

2.2.2 Fuel performance

With progressive up-rating of fuel duty, the margin to tolerate CRUD has been reduced and additional care has to be taken in specifying the water chemistry to avoid undesirable fuel performance issues. Details of this subject are described in LCC4 AR by Chris Wood and Rolf Riess.

(Figure 2-5) shows the root causes of PWR fuel failures since 2000. In contrast to the BWR situation, very few failures in recent years have been attributed to CRUD/corrosion.

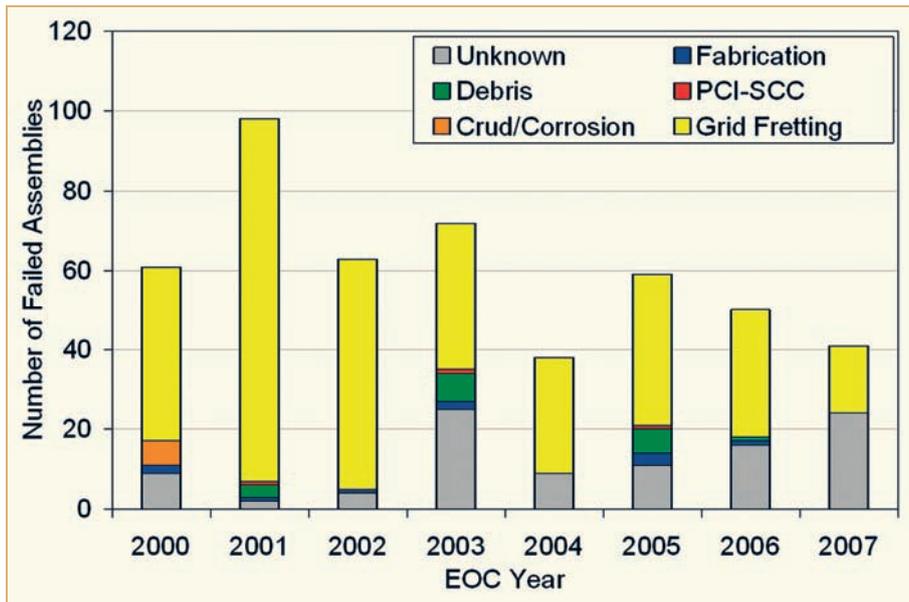


Figure 2-5: U.S. PWR fuel failures by mechanism, [Wood 2008].

A phenomenon called Axial Offset (AO) has caused concern over the past 10 years. AO is a measure of the relative power produced in the upper and lower parts of the core and is normally expressed as a percent, with a positive percent indicating that more power is produced in the upper part of the core. AOA occurs when boron concentrates in CP deposits (CRUD) on the upper spans of fuel assemblies undergoing sub-cooled nucleate boiling, causing a reduction in neutron flux. AOA has affected at least 20 PWRs in USA, as well as several in other countries. An example of the decrease in AO is shown in (Figure 2-6).

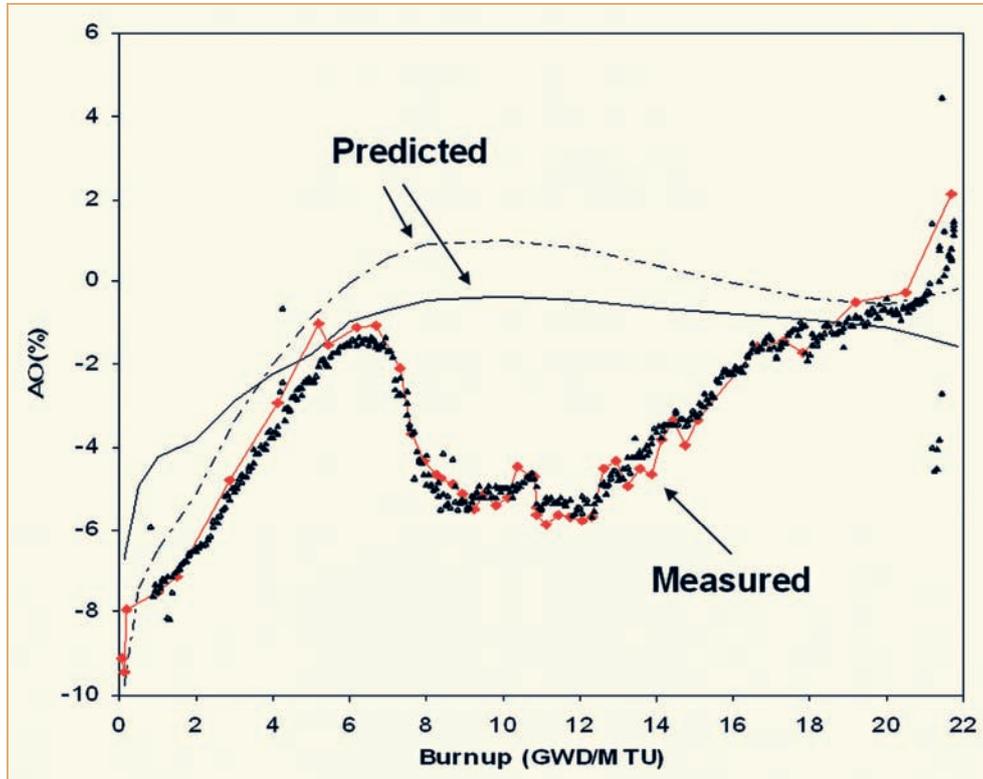


Figure 2-6: Axial offset during a fuel cycle at Callaway PWR, [Wood 2008].

Clearly, fuel CRUD is involved in the AO phenomenon, and water chemistry effects must be considered in controlling AO. Besides their axial asymmetry, the composition of fuel deposits in boiling cores is different from non-boiling fuel. Instead of the iron-rich nickel ferrites that deposit on lower duty PWR fuel, deposits on cores with high boiling duty tend to be rich in nickel, with sizeable fractions of NiO. Other unexpected compounds have been found in significant quantity in deposits on boiling cores, notably *m*-ZrO₂ and Ni-Fe oxyborates. The nickel-rich deposits on boiling cores tend to be removed much less effectively by conventional chemistry shutdown evolutions than the nickel-ferrite deposits on non-boiling cores. Alternative methods are therefore required for cleaning CP deposits from reload fuel from high-duty cores: One of these techniques, UFC, is described by [Wood 2008].

The common understanding in the U.S. and in Europe regarding fuel cladding performance is identical with respect to two items related to water chemistry: The first one is enhanced corrosion due to CRUD deposits. The second is in areas of nucleate boiling where the concentration of coolant additives in such CRUD deposits is causing AOA. The operational experience varies from country to country. The highest number of AOA observations is in the U.S. whereas in France some slight indications were observed. However, the German experience is that there is no evidence for AOA. The different experiences may be explained by the following parameters: The U.S. plants are operating with longer fuel cycles and the consequence that the CRUD accumulation is enhanced. Moreover the CRUD composition is characterized by a lack of iron.

The French experience should be similar as the U.S. but the operating time for one cycle is shorter than in the U.S. As already mentioned before, the German experience is that no CRUD induced corrosion nor AOA has been experienced, although these plants have the highest High Duty Core Index (HDCI) values.

An important difference exists between plants with Alloy 600 or 690 SG tubing and those (such as German-designed plants) with Alloy 800 tubing. The latter have a much lower proportion of nickel in fuel CRUD, and have not experienced the AO phenomenon, [Riess & Lundgren 2006].

2.2.3 Radiation field control

CPs released from out-of-core materials (primarily SG tubing) deposit on the fuel and become activated, are released back into the coolant and may be deposited on out of core surfaces. Both soluble and insoluble species may be involved, with the latter tending to deposit in stagnate areas (“CRUD traps”). As discussed below, chemistry changes to control radiation fields have contributed to the decreasing trend in radiation exposures at U.S. plants, (Figure 2-7).

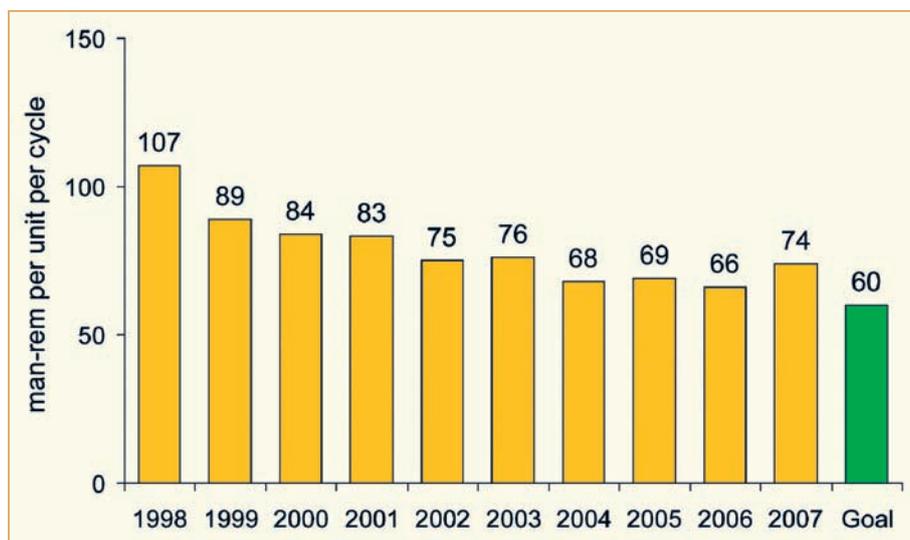


Figure 2-7: Median collective exposures at U.S. PWRs, [Wood 2008].

Note that the green bar on the right in (Figure 2-7) represents the 2010 goal, set by the U.S. Institute of Nuclear Power Operations.

The key mechanism of activity build-up is undisputed between the U.S. and Europe. However, the pre-conditions are different: The CPs are playing an important role in the whole mechanism. All plants (e.g. in France and in the U.S.) which are equipped with nickel-base SG tubing material are suffering from higher metal release rates compared to the Siemens-KWU designed plants. These higher metal release rates are generating a higher CRUD inventory and this CRUD is suffering from a lack of iron in the system, which would allow the formation of CRUD closer to Ni-ferrite or magnetite. Such compounds show regular solubility behaviour at the temperature of interest.

In addition to the chemistry items discussed below, it must be stressed that other factors are important to the goal of reducing radiation fields. In particular, the success of the later German-designed plants in eliminating cobalt sources, and thereby achieving very low radiation fields, demonstrates the benefits of cobalt source reduction. With many plants replacing SGs, a correlation between recontamination rates and surface finish of the new SG tubing has been noted by [Hussey et al 2008].

In this section only information has been evaluated which was generated after the Berlin Water Chemistry Conference in September 2008. One eminent case is a World Association of Nuclear Operators (WANO) Workshop in Würzburg. In this Workshop, two organizing groups presented their objectives and responsibilities. These organisations are WANO Paris and VGB in Germany. This was created by the following circumstances: Some time ago AREVA requested VGB to support an R&D project in the area of radiation field control.

Inside VGB, a special technical committee is responsible for approving the budget of such projects. However, this committee did not approve the above mentioned project and asked the utilities to collect information on Radiation Field Control in a worldwide survey. VGB on behalf of the German utilities contacted WANO and they agreed to organize a workshop in Würzburg. The first technical presentation in this workshop was by [Stellwag & Schneider 2009], entitled: “Dose Rate Situation in PWRs”. The content of their presentation has been:

- Dose rate survey for European PWRs.
- Milestones of dose rate reduction at Siemens PWRs.
- Source term reduction assessment for further options.
- Outline of the R&D project “Dose rate reduction”.

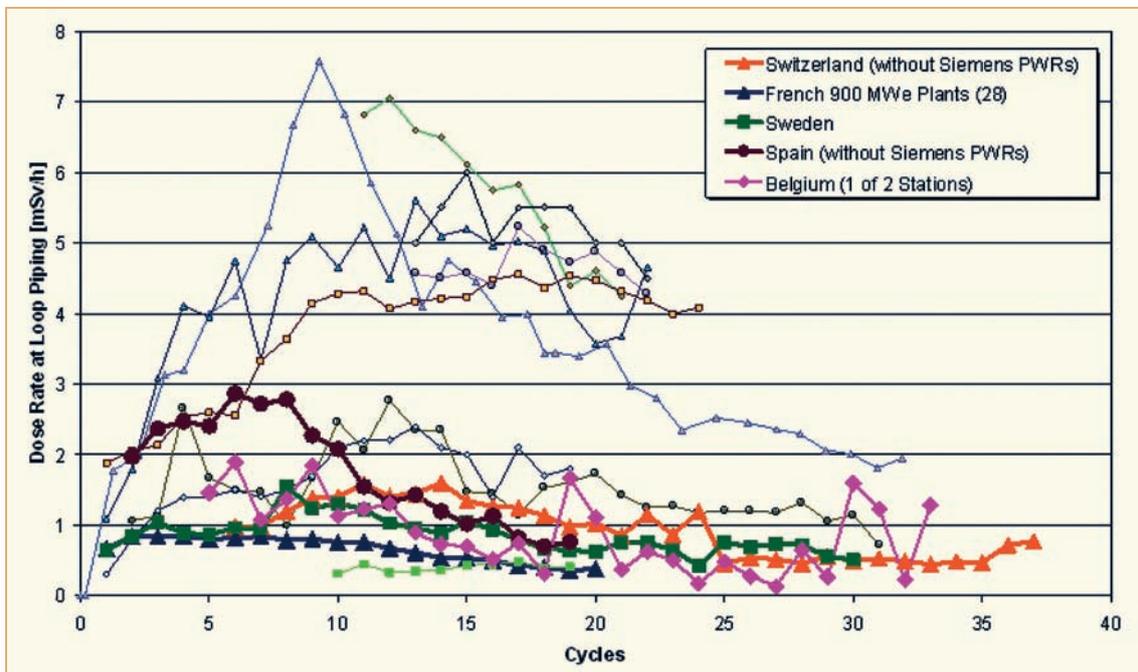


Figure 2-8: Loop dose rate averages of older-generation PWRs in Europe. (Fine data points and lines: Data of individual Siemens plants in D, CH, NL and Es), [Stellwag & Schneider 2009].

This overview, (Figure 2-8) on loop dose rate averages of older-generation PWRs in Europe is followed by (Figure 2-9) showing the data of more recent PWRs.

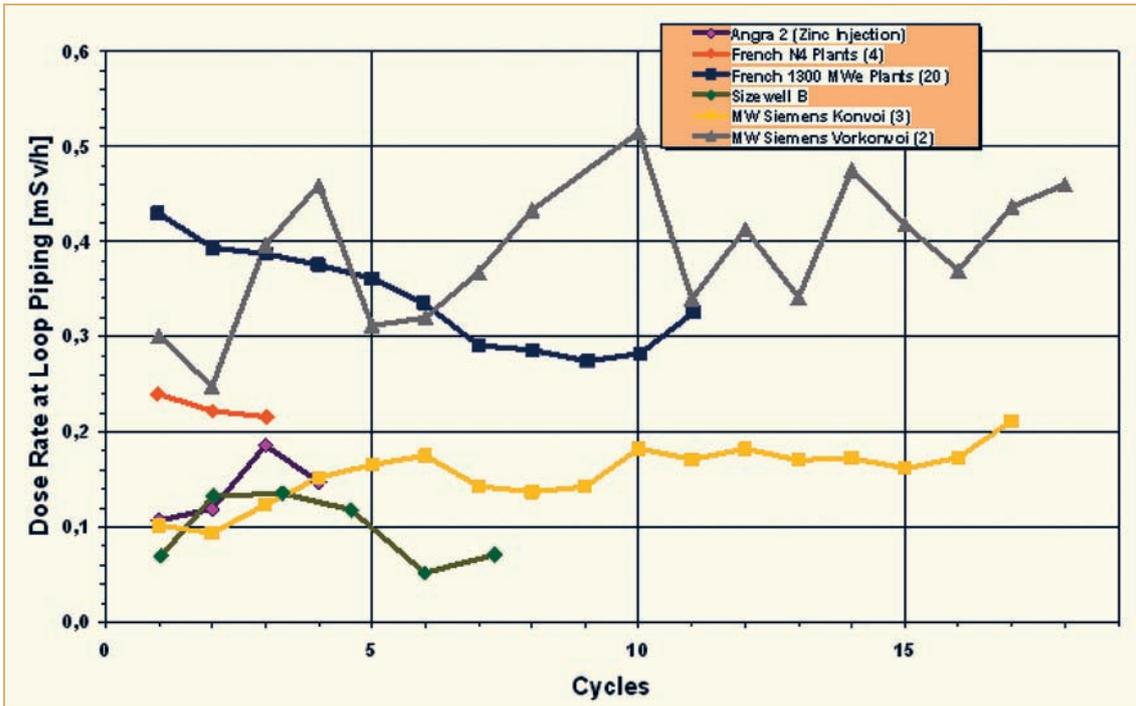


Figure 2-9: Loop dose rate averages of more recent PWR plant generations in Europe, [Stellwag & Schneider 2009].

In order to explain the situation of Siemens PWRs with (Figure 2-8) and (Figure 2-9) as background the authors described the chronology of the Source Term Reduction Measures in Siemens PWRs as shown in (Figure 2-10).

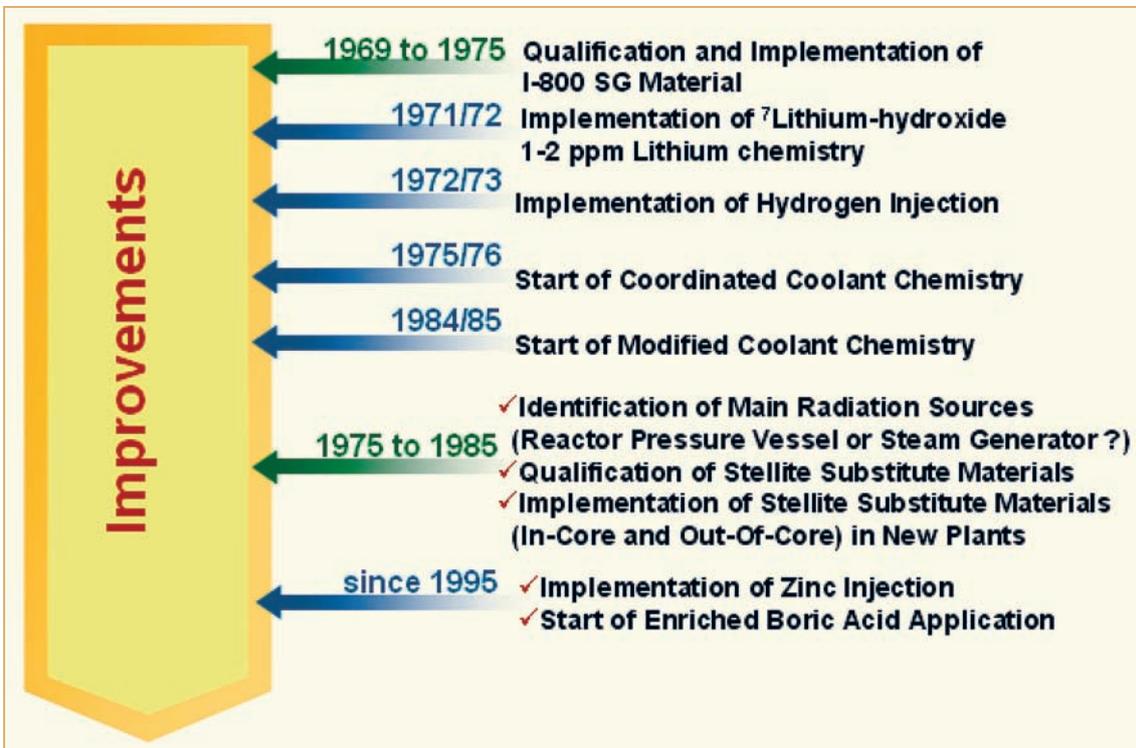


Figure 2-10: Source term reduction measures for Siemens PWRs, [Stellwag & Schneider 2009].

In this list of reduction measures there seems to be one action to be specifically important: It is the Stellite substitution in new plants, which were under construction from 1975 to 1985. Typical locations for Stellite substitutes are shown in (Figure 2-11).

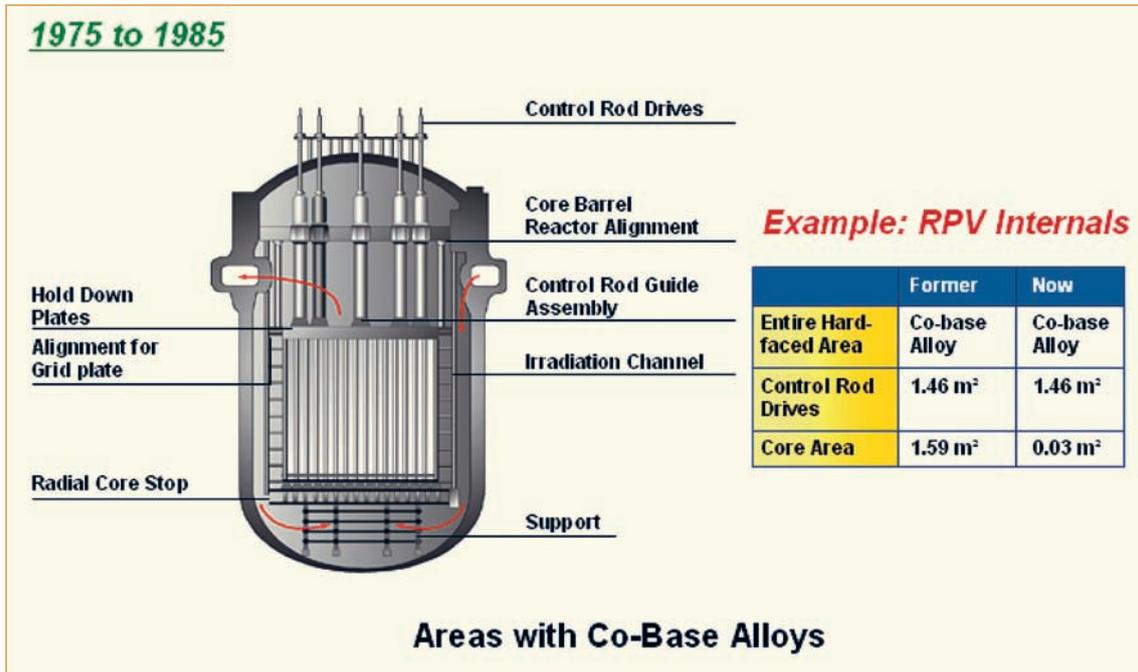


Figure 2-11: Stellite substitutes for new plants, [Stellwag & Schneider 2009].

In addition to this Stellite replacement program the author discussed some chemistry issues by showing the dose rate as a function of the cycle number with the intent to demonstrate that modified chemistry will give better data than plant operation with coordinated chemistry. An item to modified B/Li-chemistry in Siemens PWRs is the use of Enriched Boric Acid (EBA). The enrichment of B-10 is around 30%. With this type of chemistry, which is practiced in Siemens PWRs, it is possible to reach a pH (300 °C) of 7.4 earlier than in plants operating with natural boric acid. Based on plants data it is impossible to demonstrate that the plants with EBA have lower radiation field values than the other plants. The operating experience is illustrated in (Figure 2-12).

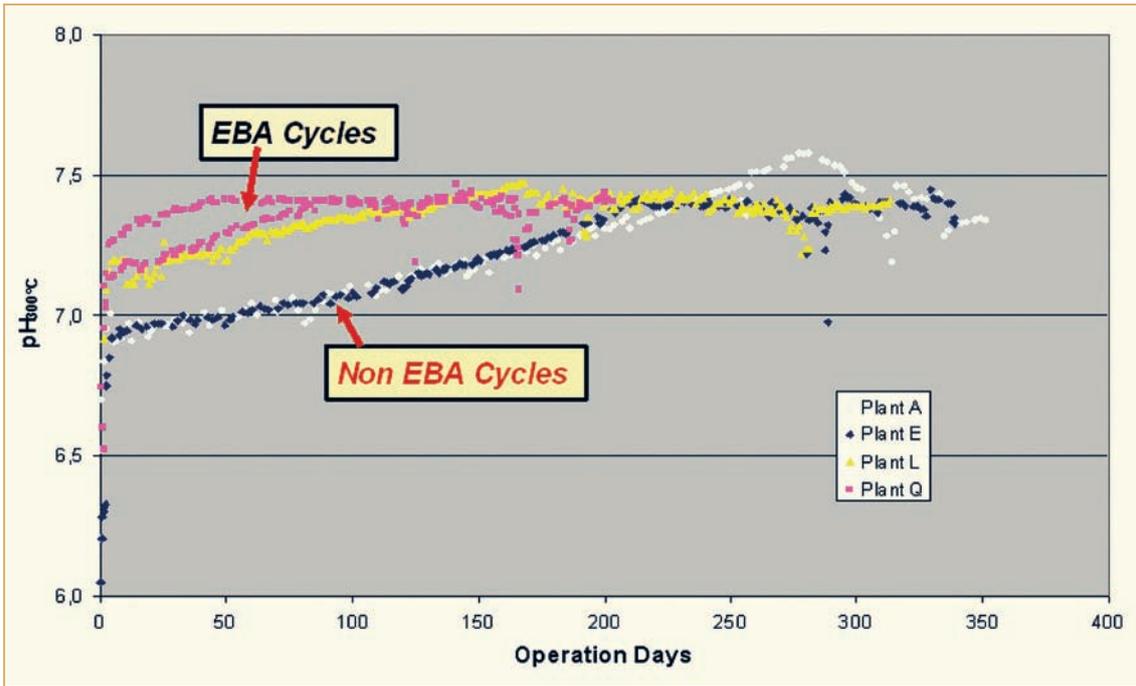


Figure 2-12: Enriched boric acid chemistry data, [Stellweg & Schneider 2009].

Furthermore, Stellweg and Schneider presented data on zinc injection showing the beneficial effect of Zinc. In (Figure 2-13) the authors summarized the coolant chemistry of Siemens PWRs in 2008.

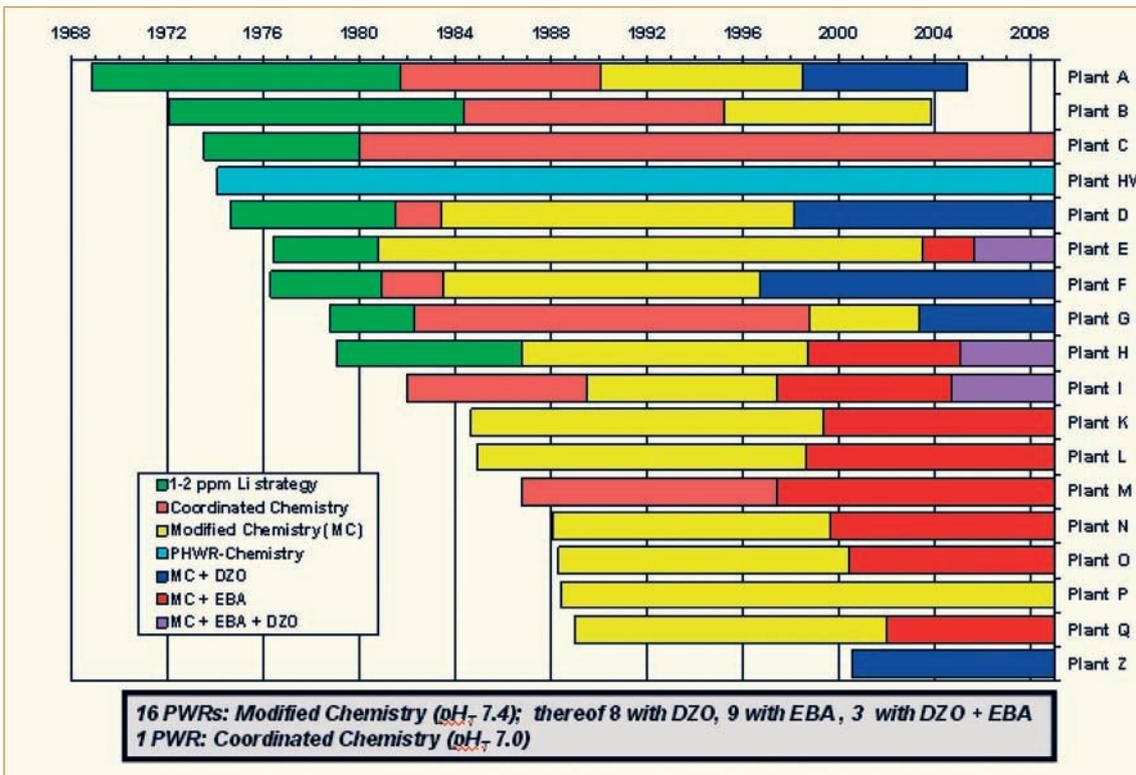


Figure 2-13: Coolant chemistry of Siemens PWRs in 2008, [Stellweg & Schneider 2009].

The resume of Stellwag and Schneider for Siemens PWRs was the following (whereby they made reference to the status of 2005/2006 only): At the end of their summary they recognized that loop dose rate averages in other European countries are $<1 \text{ mSv/h}^4$ and they stated that these values were achieved with other method than Zinc injection. So the conclusion was that the practices, which resulted in such low dose rates, have to be evaluated and they went back to the basics by showing the schematic of the contamination processes in the reactor systems.

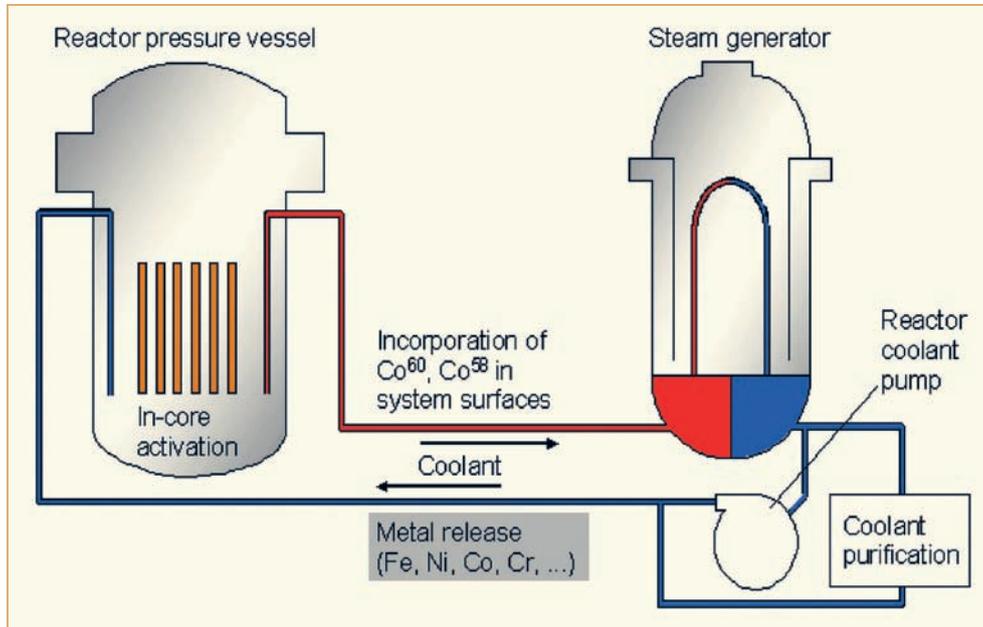


Figure 2-14: Contamination processes in reactor systems, [Stellwag & Schneider 2009].

The measures identified at many plants of other vendors, and not applied in Siemens PWRs, were summarized as follows:

- Optimized cycle chemistry, e.g. elevated Li/pH operation.
- Optimization of start-up and shutdown.
- Improvement of particle filtration efficiency, e.g. by mechanical filters with low porosity, use of macro-porous ion exchange resins.
- Other plant specific options and measures implemented, e.g. antimony removal, Stellite replacement, etc.

After identification of such additional measures they made an attempt to estimate for Siemens PWRs the dose rate reduction effectiveness of the following measures:

- Zinc injection with and without full system decontamination.
- Elevated Li/pH operation.
- Optimized shutdown operation.
- Improvement of particle filtration efficiency.

⁴ Milli-Sievert (mSv)

The results of their evaluation regarding these four issues are:

- Zinc injection:
 - Without Full System Decontamination (FSD) the reduction effect is around 50% of the initial level. This can be achieved within a time span of 5 years.
 - The expected loop dose rate level after FSD of an older generation Siemens PWR dose rate levels of <math>< 0.5\text{ mSv/h}</math> can be achieved (Angra 2 is the reference case). See (Figure 2-15).

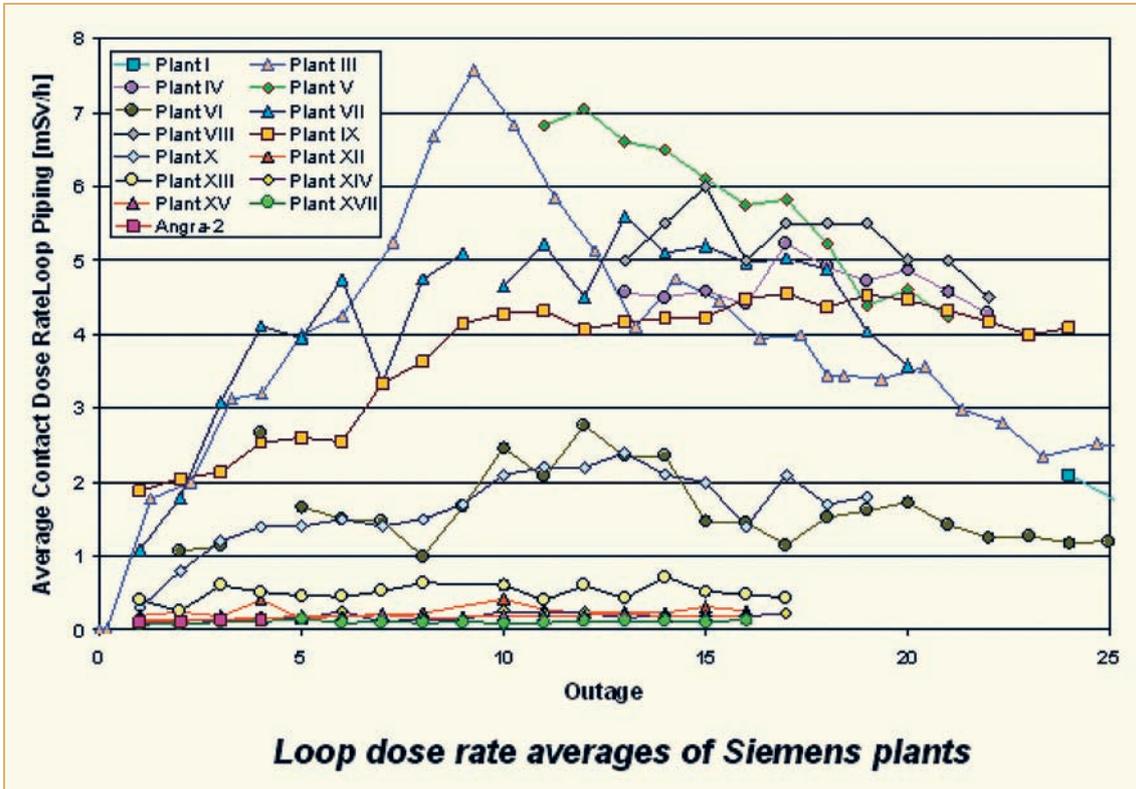


Figure 2-15: FSD plus zinc injection: reference Angra 2, [Stellwag & Schneider 2009].

Regarding an optimization of the shutdown procedures they showed the loop dose rates before and after cold shutdown. The dose rate effect of the shutdown procedure is plant specific and difficult to quantify. Some data are summarized in (Figure 2-16).

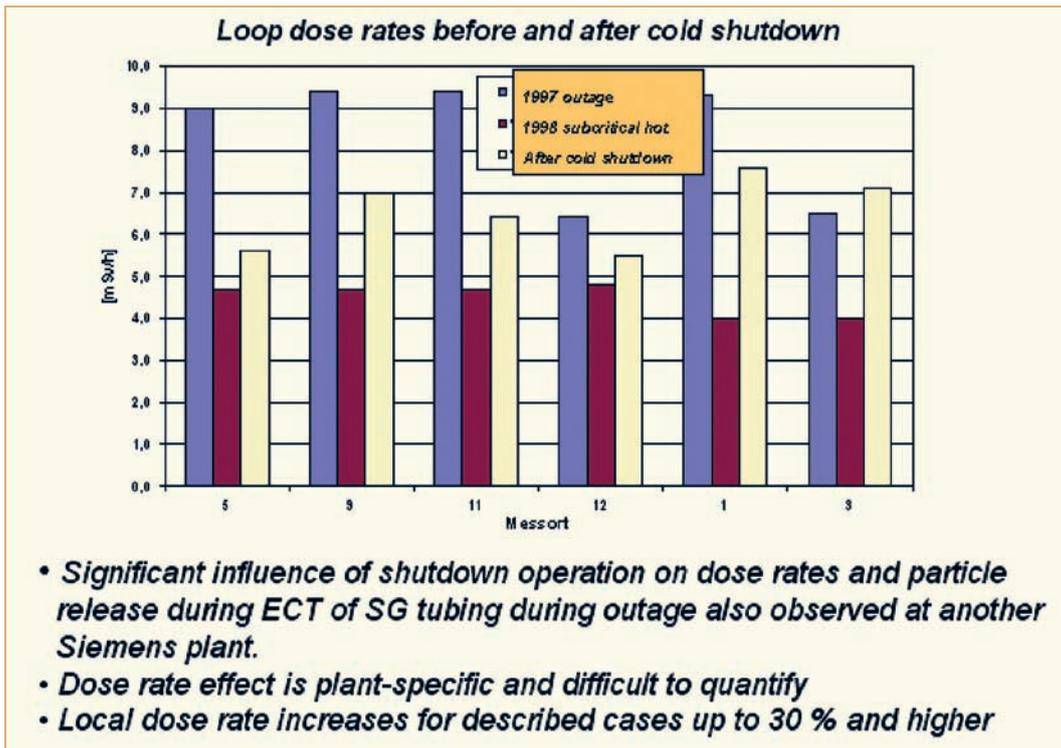


Figure 2-16: Optimized shutdown procedures, [Stellwag & Schneider 2009].

Regarding the effect of mechanical filters and macro-porous resins Stellwag and Schneider postulated a positive effect of these two measures and they summarized it.

Decrease of porosity of mechanical filters / resin traps:

- Realized, e.g. at:
 - PWR Stade in 1994 (porosity changed from 10 to 2 μm).
 - PWR Borssele (porosity changed from 3 to 0.3 μm).
- Additional measures implemented at the plants As Low As Reasonably Achievable ((ALARA) principle).
- Measures were very effective according to the operators.
- Zinc not added at both plants.

Macroporous resins:

- Positive influence reported.
- No operating experience at Siemens plants.
- Might be an alternative to modification of mechanical filters.

After the collection of data in other plants regarding the best practices, Stellwag and Schneider identified the discussed items as an area, where further improvements can be made in Siemens PWRs. In the same sense they formulated the VGB project entitled “Dose Rate Reduction at PWRs”. Thereby they decided a phase 1 entitled “Identification of best Practices” and a phase 2 “Implementation of Tool Box at Demo Plants”.

In addition to the WANO Seminar on Radiation Control there are 2 presentations in 2009 dealing with Zinc injection but can also be discussed under Radiation Control. The first is by Stellwag et al. entitled “Survey of Zinc Injection Experience at Siemens PWRs: Differences and Common Characteristics”. This paper was presented in Nagoya on Oct. 28/29, 2009. The second paper which is identical to the before mentioned presentation is by [Rich et al 2009] and was presented at the same time in Dresden. After a short introduction and a description of the mechanism of activity build-up Stellwag et al. are describing in great detail the Siemens plant experience with Zinc injection. There are 8 plants injecting Zinc and they are operating with the modified B/Li chemistry. Three of them are using enriched boric acid with a B-10 concentration in the range of 30 %. The operating periods of these plants are between 4 and 13 years.

The Co-60, Co-58 and Fe concentrations of plants VII and VIII are plotted in (Figure 2-17) to (Figure 2-25).

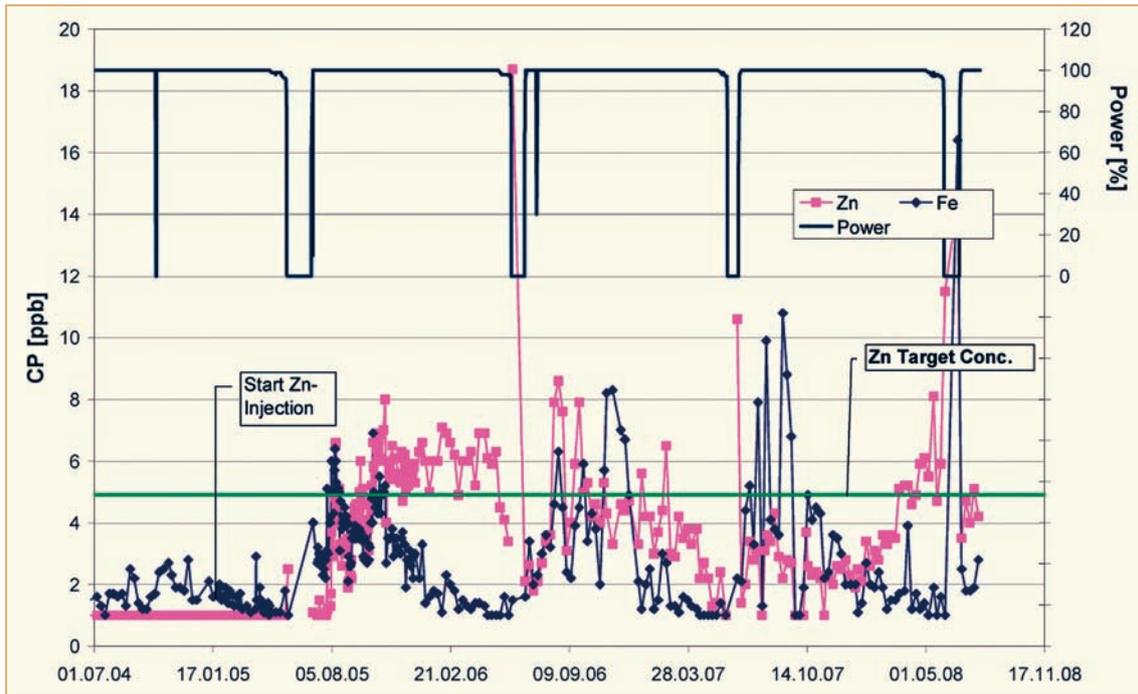


Figure 2-17: Coolant Zn and Fe concentrations of plant VII, [Stellwag et al 2009].

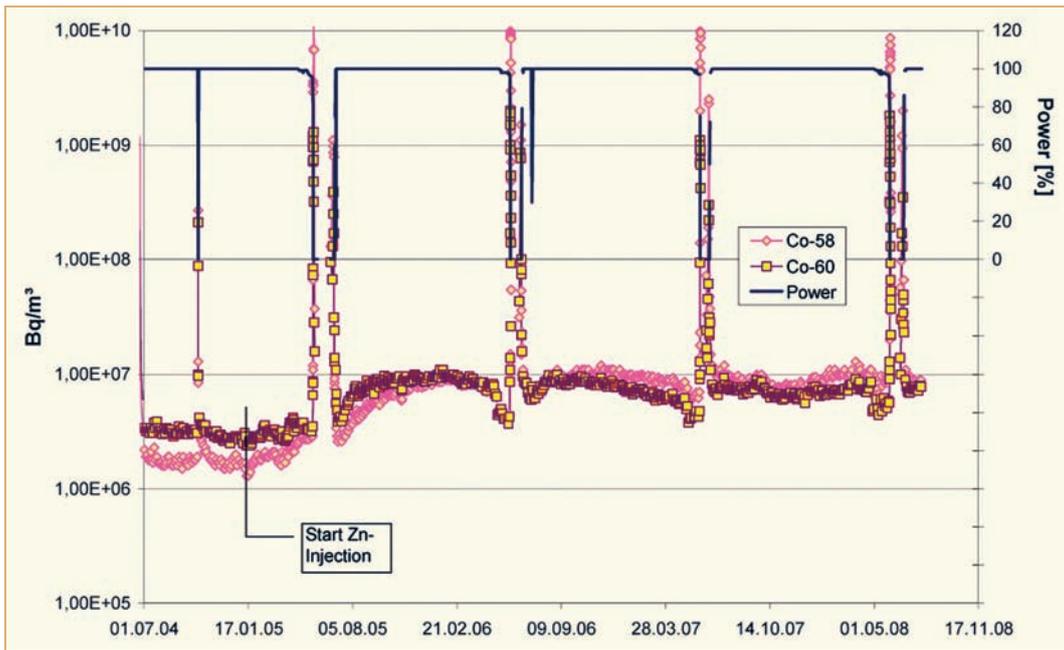


Figure 2-18: Coolant Co-58 and Co-60 concentrations of plant VII, [Stellwag et al 2009].

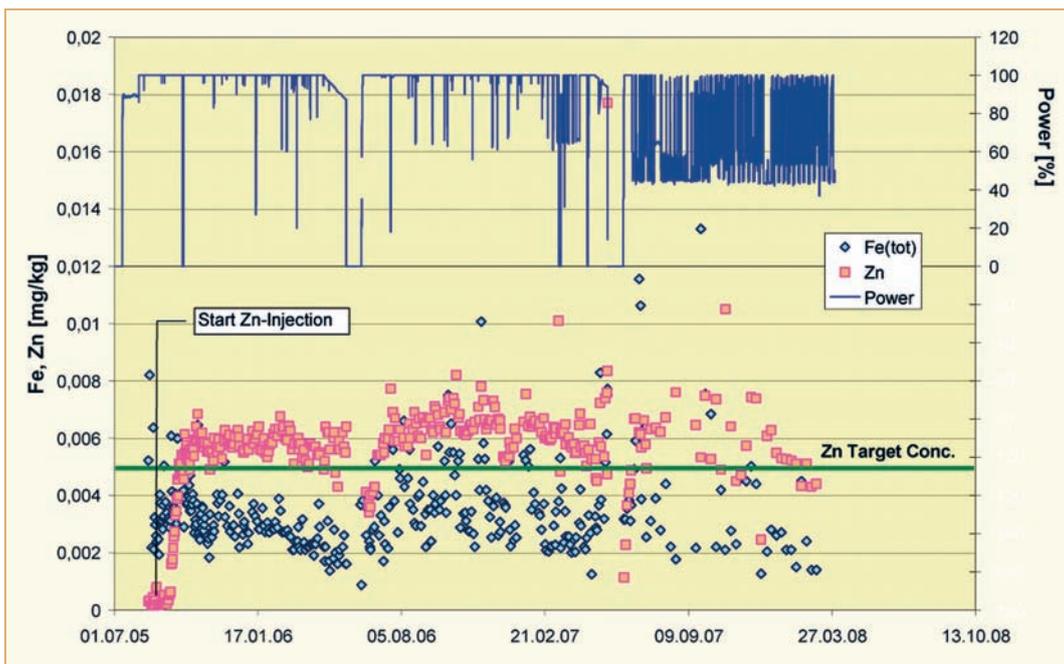


Figure 2-19: Coolant Zn and CP concentrations of plant VIII, [Stellwag et al 2009].

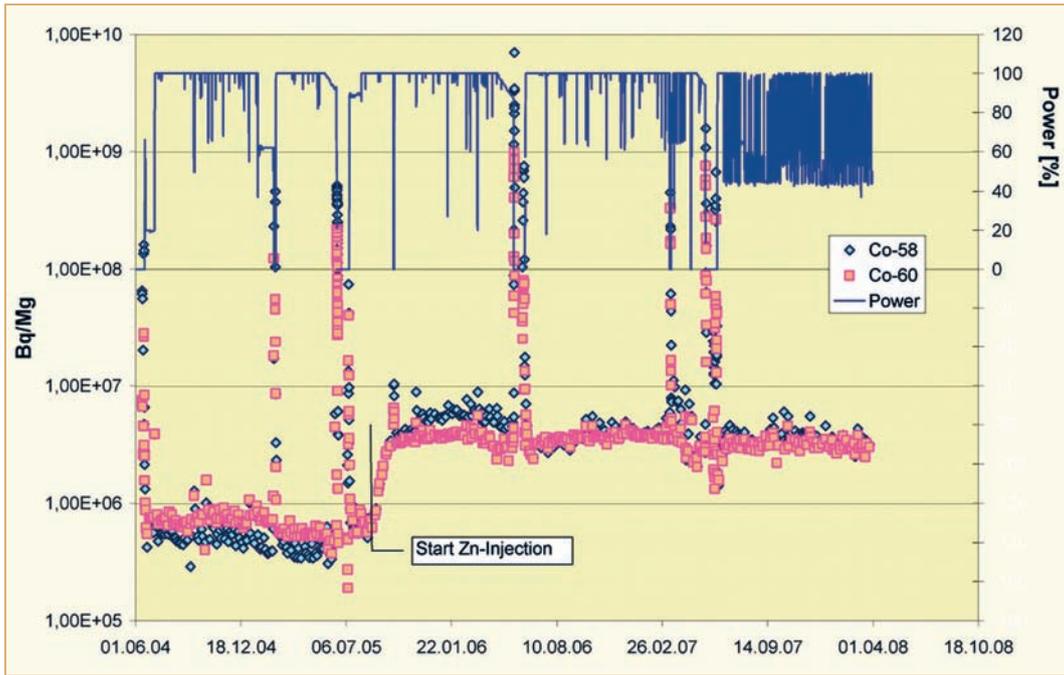


Figure 2-20: Coolant Co-58 and Co-60 concentrations of plant VIII, [Stellwag et al 2009].

Plant operators are also reporting an increase in Co-60 and Co-58 during shutdown as shown in (Figure 2-21).

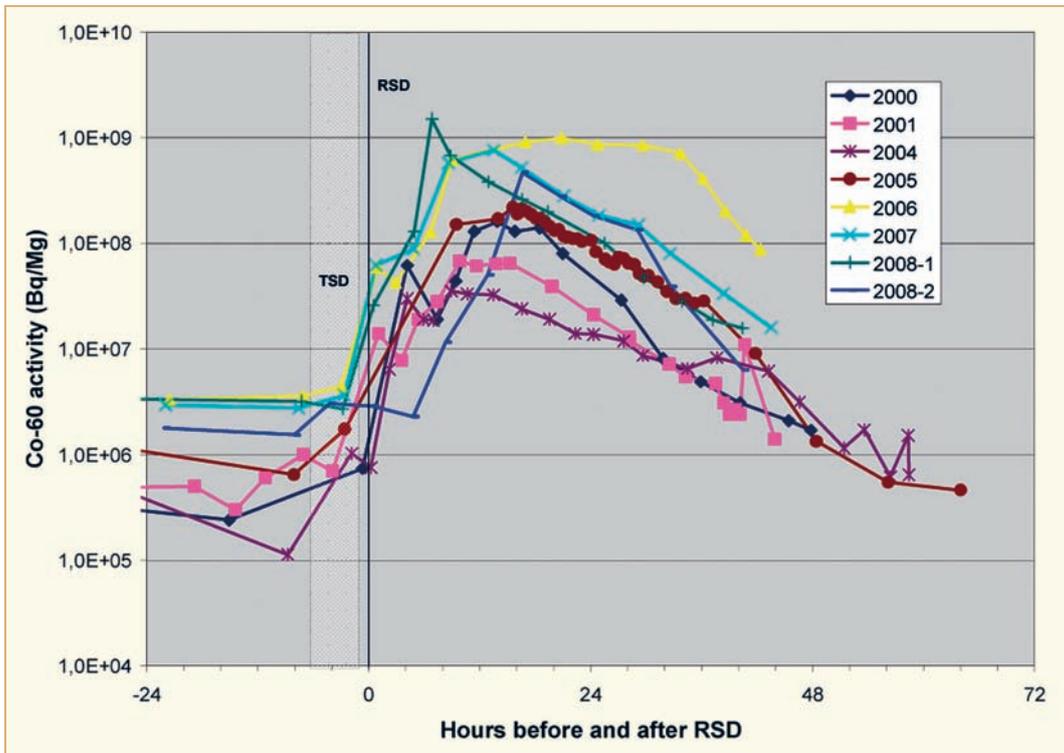


Figure 2-21: Co-60 activity of reactor coolant during shutdown of Plant VIII to refuelling outages between 2000 and 2008. Zinc injection was started after the outage in 2005. TSD: Turbine shutdown; RSD: Reactor shutdown, [Stellwag et al 2009].

The chemistry data of all 8 Siemens plants are summarized in (Table 2-1).

Table 2-1: Change of coolant chemistry parameters due to zinc injection, [Stellwag et al 2009].

Plant	Co-60 before Zn dosing (Bq/ml)	Co-60 increase factor	Co-58 before Zn dosing (Bq/ml)	Co-58 increase factor	Fe content before Zn dosing (ppb)	Fe increase factor	Co-60 increase factor during shutdown op.
I	5	1	0.2	5	2	3	10
II	0.3 – 1	5 – 10	0.1 – 0.2	2	1.5	2	n. d.
III	1	5	2	10	1	3	1
IV	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.	n. a.
V	1 – 2	5 – 10	0.2 – 0.4	5 – 10	n. d.	-	10 ¹⁾
VI	2 – 3	5	0.4 – 1	5	2	2	2
VII	3	3	2	5	1 – 2	3	2
VIII	0.5 – 1	6	0.6	10	2	1	10

¹⁾ Other parameters were also changed.

The loop dose rate changes are plotted in (Figure 2-22). Due to these data the authors concluded the following:

- Zinc injection results in a decrease in dose rates at main loop piping by 50 percent. This level is reached after 7-10 years.
- Change of Co-60 and Co-58 activities of coolant can not be used as an indicator for the dose rate reduction effect of the method. For instance, Co-60 and Co-58 activities increased by a factor of 5-10 at Plant V. However, loop dose rates remained unchanged at the plant until now.
- The rate of decrease in loop dose rates is lower than estimated from Co-60 decay (see the Co-60 decay curve).
- Plants I, III, VI and VII show a steady decrease in dose rates already in the first few outages after zinc injection start. At plants II, V and VIII, the influence of the method on loop dose rates has been rather small in this time period.

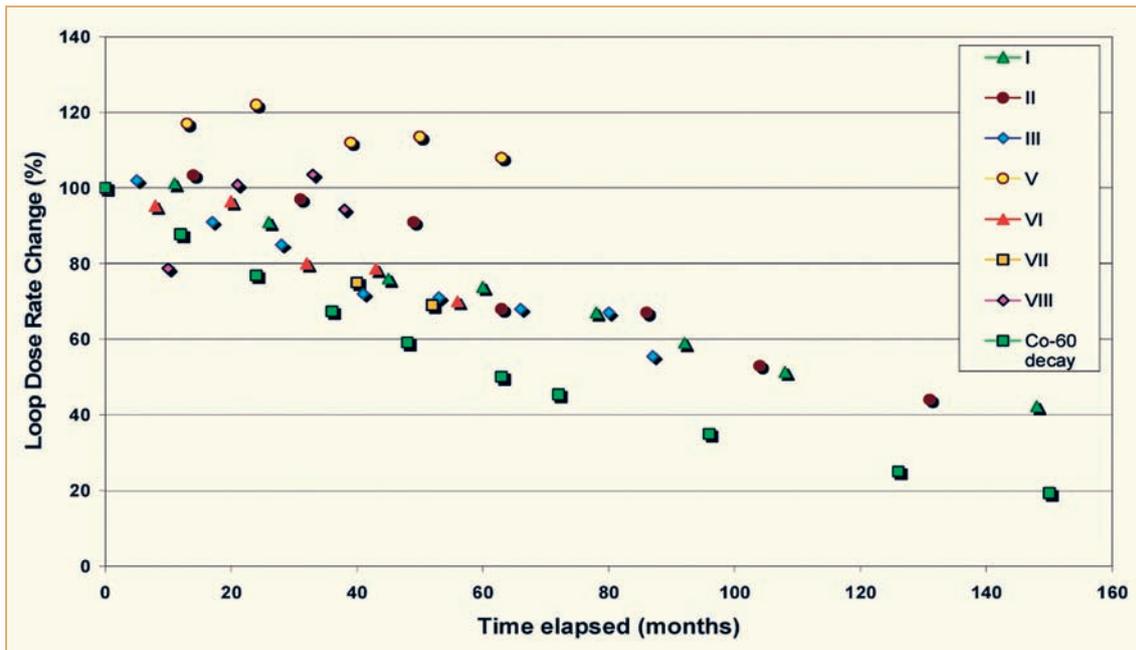


Figure 2-22: Dose rates at main loop piping plotted as a function of operation time with Zinc injection. Data are normalized to the average loop dose rate measured in the outage before implementation of the method, [Stellwag et al 2009].

In summary the authors concluded that Zinc injection leads to an increase of Co-58 and Co-60 in the reactor coolant. The dose reduction at main loop piping is in the range of 50 %. This level is reached after 7 – 10 years. Co-60 is dominating the dose rates in older Siemens plants and the Co-60 ions can not be displaced by Zinc. The rate of decrease is therefore limited by the decay of Co-60. Negative side effects due to Zinc injection are not reported. Zinc addition to a new plant resulted in very low dose rates which is about 4 times lower than in plants without Zinc injection.

A unique radiation control problem arose at the Lingao NPP in outage 5 of unit 1 (L 105), as presented by [Yang 2009]. At this time it was found that the bearing of a primary pump was damaged and about 2 kg of Co⁵⁹ were lost into the primary system. The consequence out of such an event is the formation of Co⁶⁰ in high quantity (see Table 2-2). Due to this high Co⁶⁰ level radiation protection becomes a challenging problem. In L106 and L107 the concentration of Co⁶⁰ in the primary system is about 5 to 10 times higher than in former outage. The measures taken to reduce the source term were:

- To increase the purification rate by a factor of 2.
- To improve the reactor cavity and spent fuel pit cooling by enhancing the cleanup capacity.
- Decontamination of reactor cavity and spent fuel pit cooling and treatment tank.
- Replacing the mechanical pre-filters from 6 µm to 0.45 µm.
- Flushing of hot particles in all accessible primary pipes.
- Oxygenation and purification during the shutdown operation.

Table 2-2: Co⁶⁰ peaks during a pump stop and oxygenation for the first 7 outages, [Yang 2009].

	Co-60 MBq/m ³						
	L101 (21 h)	L102 (16 h)	L103 (9 h)	L104 (14 h)	L105 (17 h)	L106 (11 h)	L107 (25 h)
Oxy. peaks	1500	591	505	646	450	3366	3386
Stop pumps	247	126	193	176	110	1649	450

Beside the Co⁶⁰ problem the Lingao plant experienced some radiation field control problem because the radiation at the chemical and volume control system had very high values from outage no. 4 onwards. The radionuclide being the problem is Ag-110m. Up to now there is no clear picture about the source of this Ag-110m.

2.3 Mitigation tools

The scheduled sections on pH control and H₂-addition will not be handled in detail because:

- Lithium, Boron, and pH Effects has new information only in conjunction with “Radiation Control”.
- H₂-Control: There are no new data. This means, the LCC4 documents are representing the actual status.
- However, Radiation Control is the key subject in this AR.

Early work showed that lithium increased Zircaloy oxidation rates, although the adverse effects were reduced in the presence of boric acid. As a result, a limit of 2.2 ppm lithium was generally imposed to reduce Zircaloy corrosion, although excessive CRUD formation at low pHs was likely to be more detrimental to the cladding than higher lithium concentrations, especially as the resistance to corrosion of Zircaloy improved. This was confirmed by one of the few failures in recent years, which were uniquely attributed to CRUD build-up. In this example, a move to a longer fuel cycle necessitated increasing the boron concentration at start of cycle; however the 2.2 ppm lithium limit was retained, resulting in the pH being well below 6.9 for the initial period of the cycle. This in turn caused heavy CRUD formation, to which subsequent fuel failures were attributed.

The move in the past ten years to greater fuel duty, with operation of fuel at higher temperatures (with localized sub-cooled nucleate boiling) have caused CRUD-related problems to reappear, particularly the localized flux depression as a result of build-up of boron-containing CRUD, which are discussed above. This in turn has renewed interest in elevated pH/lithium to minimize CP transport, the use of enriched boric acid and the more immediate mitigation that can be obtained from fuel cleaning.

[Fruzzeti & Perkins 2008] have recently reviewed the data on elevated pH, which provides a number of benefits including decreased general corrosion (and thus reduced CP transport to the core) and improved solubility characteristics to limit both the concentration of soluble CPs in the bulk and the deposition of CPs on the core due to precipitation as a function of the temperature increase through the core. They point out that general corrosion of carbon steel, Stainless Steels (SSs) and Alloy 600 at temperatures corresponding to primary coolant condition is at a minimum at pH values from 7.4 to 8.4 at 300 °C).

CPs are transported, dissolved or deposited by the coolant based on solubility differences. The solubility of nickel and iron depend on pH, temperature and redox potential, all of which vary with location around the non-isothermal system. A key result from the initial correlation of nickel ferrite solubility by William Lindsay in the 1980s was that the temperature coefficient at 300 °C (572 °F) for solubility of iron (assuming constant concentration of lithium, boron and hydrogen) was predicted to change sign (from retrograde solubility to “normal” temperature dependence) at a $\text{pH}_{300\text{ }^\circ\text{C}}$ of about 7.4. This key result forms the basis of all the pH regimes currently in use, even though the fuel CRUD formed in high duty plants is nickel-rich and contains both metallic nickel and nickel oxide. For higher duty plants in particular, recent strategies in pH optimization support optimizing the pH based on nickel solubility because the solubility of both nickel and nickel oxide is significantly lower than the solubility of iron or nickel ferrites in most conditions. (Figure 2-23) shows that as the pH_T is increased, the solubility of nickel decreases at the core inlet temperature, which limits the nickel concentration entering the core and reduce the available inventory for CRUD deposition on the fuel.

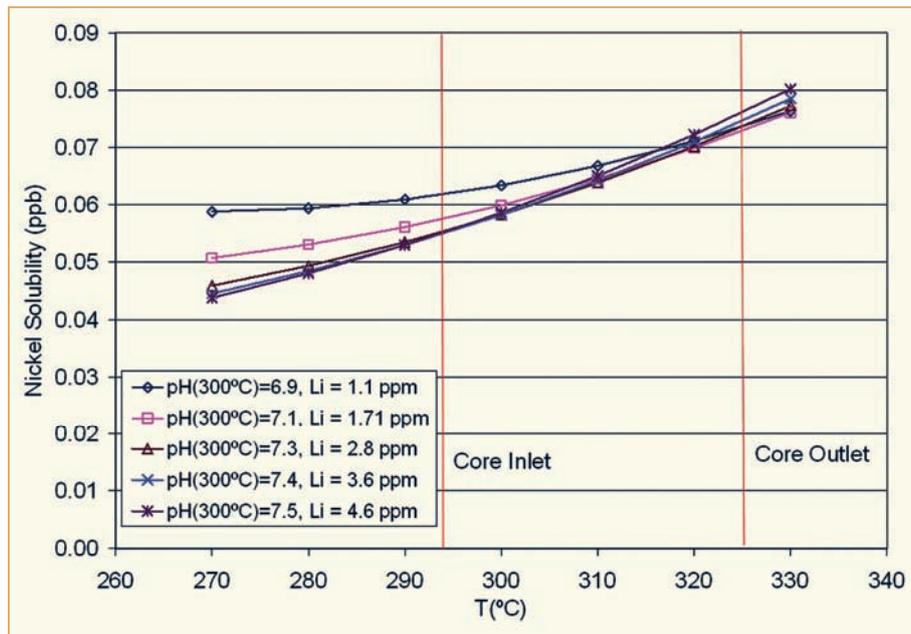


Figure 2-23: Variations in nickel solubility from core inlet to outlet as a function of pH_T at 300 °C, (boron = 600 ppm, $\text{H}_2 = 35 \text{ cc/kg}$), [Wood 2008].

Initially, coordination of lithium hydroxide with boron to maintain a constant at-temperature pH of 6.9 was recommended based on the minimum solubility of magnetite. Even though the prime constituent of the CRUD turned out to be nickel ferrite, which would require a higher pH for minimum solubility, raising the pH to 6.9 was a move in the right direction. This coordinated chemistry remained the standard for many years. However, extending the duration of the fuel cycle from the then-typical 12 months to 18 months, or even longer, meant that the boron concentration at the start of the fuel cycle had to be raised from 1200 ppm to 1800 ppm or even more. This in turn required lithium concentrations of greater than 2.2 ppm if the minimum pH was to be maintained at 6.9. Unfortunately, a limit of 2.2 ppm was imposed to avoid excessive fuel cladding corrosion (despite the fact that excessive CRUD formation at low pHs was likely to be more detrimental to the cladding than higher lithium concentrations). As a result the modified lithium regime was introduced in the United States, whereby a maximum lithium of 2.2 ppm was maintained until the boron concentration declined till a pH of 6.9 was reached, with this pH maintained till the end of the cycle.

3 BWR coolant chemistry (Rolf Riess)

This section of the Annual Report is comprised by the contribution of several authors to LCC4. The lead contribution is from Chris Wood, describing the U.S. situation, whereas the two other authors (Wilfried Rühle and Klas Lundgren) represent the European point of view. Through this editorial effort, it becomes evident where we have a consensus between U.S. and European plants but also the differences become obvious. Based on such discrepancies future detailed studies should be performed.

3.1 Background

There are currently 35 BWRs operating in the United States designed by GE. In Europe the operating 18 plants are designed by:

- GE (Spain 2 and Switzerland 2).
- ASEA-ATOM (Sweden 6 and Finland 2).
- Siemens/KWU (Germany 6).

Chemistry issues and areas of concern are similar for all these plants. However, different design and materials concepts may require different chemistry conditions. In particular, the still operating BWRs in Germany were designed 1969 and in 1972 and were named “Type Series 69” or “Product Line 69” and “Type Series 72” or “Product Line 72”, see (Table 3-1). They have a unique position regarding the materials and chemistry concept.

Table 3-1: Product lines and station output for Siemens BWRs.

Station	Abbreviation	Product line	MWe	First commissioning
KKP1	KKP 1	69	926	1979
Isar-1	KKI 1	69	912	1977
Brunsbüttel	KKB	69	806	1976
Krümmel	KKK	69	1402	1983
Gundremmingen-B	KRB-II-B	72	1344	1984
Gundremmingen-C	KRB-II-C	72	1344	1984

The type series 69, four units, and the series 72, two units are all equipped with internal recirculation pumps and so they do not need external recirculation loops. This design is nowadays standard in modern BWRs.

At two of the six units, the heater drains are cascaded to the condenser and the units were constructed without Feed Water (FW) tanks, while the drains in the other units are forward pumped and they have FW tanks. The older series use precoat filters for reactor water purification and for condensate polishing. The series 72 units use precoat filters for the reactor water clean-up systems and deep bed filters for condensate polishing. Caused by the plant design the cascaded plants can treat the whole condensate flow, while the forward pumped plants can only clean about 70% of the condensate of the FW.

Regarding the Water Chemistry in German plants, the material concept of the reactor part allows to operate with Normal Water Chemistry (NWC) as described below.

From GE's perspective nuclear power plant water chemistry has evolved through many changes over the years, largely in response to emerging technical issues associated with degradation of structural materials, nuclear fuel performance and reliability concerns, and control of radiation fields in primary systems. As in the case of PWRs, BWR water chemistry has to be optimized between these sometimes conflicting requirements, and specifications have changed in response to the relative emphasis placed on each of these issues, (Figure 3-1). Operating parameters also influence the optimization process, for example life extension (to 60 years) in the United States has focused attention on the importance of controlling degradation of reactor and circuit materials. Core up-rating through increased fuel duty and longer fuel cycles has reduced margins for tolerating CPs (CRUD) on BWR fuel pin surfaces. At the same time, regulatory limits on worker radiation exposure are tending to be tightened worldwide, putting pressure on the operators to reduce radiation dose rates. Fortunately, advances in water chemistry have enabled plant operators to respond successfully to these technical challenges, and overall performance has steadily improved in recent years.

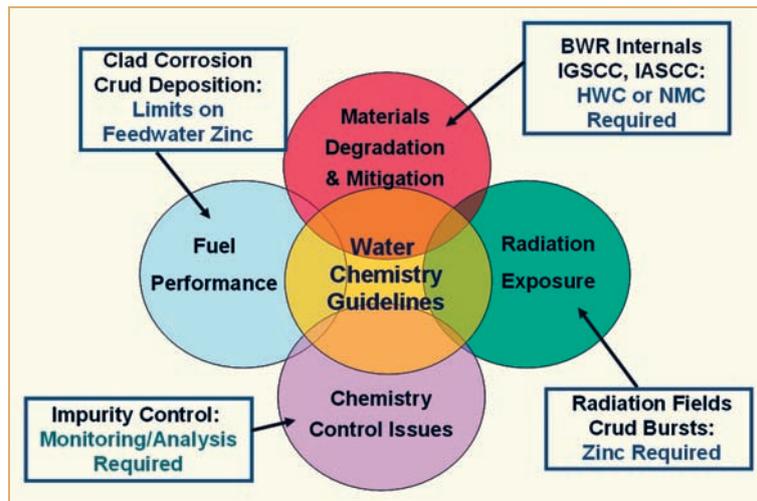


Figure 3-1: BWR chemistry interactions, [Wood 2008].

Plant-specific considerations sometimes influence or indeed limit the options for controlling water chemistry, so we see different chemistry specifications at different plants. This is especially true internationally, and significant differences in chemistry strategies between countries are noted. Design features are an important reason for these different chemistry regimes, to which must be added the effects of different operational strategies in recent years. For example, a key issue facing BWRs in the USA concerns intergranular stress corrosion cracking of reactor internals, resulting in the implementation of hydrogen water chemistry, with or without Noble Metal Chemical Addition (NMCA), to ensure that extended plant lifetimes are achieved. German plants use different materials as mentioned before, and do not have the same level of concern. Some Swedish and Japanese plants have replaced reactor internals to minimize potential problems. Secondly, BWRs in USA undoubtedly have greater cobalt sources than plants in most other countries, despite strong efforts to replace cobalt sources. This resulted in higher out-of-core radiation fields, leading all US plants to implement zinc injection to control fields, whereas only a small number of plants of other designs use zinc. Thirdly, the move to longer fuel cycles and increased fuel duty at US plants, while having major economic benefits, has led to new constraints on chemistry specifications in order to avoid fuel performance issues.

(Figure 3-2) depicts the changing chemistry strategies over the past 30 years, showing the focus on improving water quality in the early 1980s, the move to reducing chemistry to control IGSCC, which in turn resulted in increased radiation fields, subsequently controlled by zinc injection.

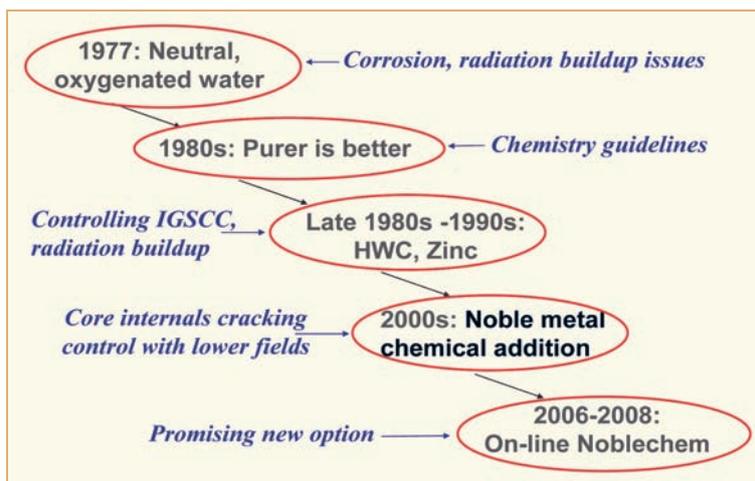


Figure 3-2: Evolution of BWR chemistry options from 1977 to 2008, [Wood 2008].

As mentioned above, concerns about core internals cracking led to the need to increase hydrogen injection rates, which in turn resulted in the introduction of NMCA to reduce operating radiation fields from N-16. (Figure 3-3) shows the rate of implementation of HWC, zinc and noble metals (NMCA), and on-line noble metal addition (OLNC). The basis, rationale and implications of these developments are discussed in greater detail in subsequent sections.

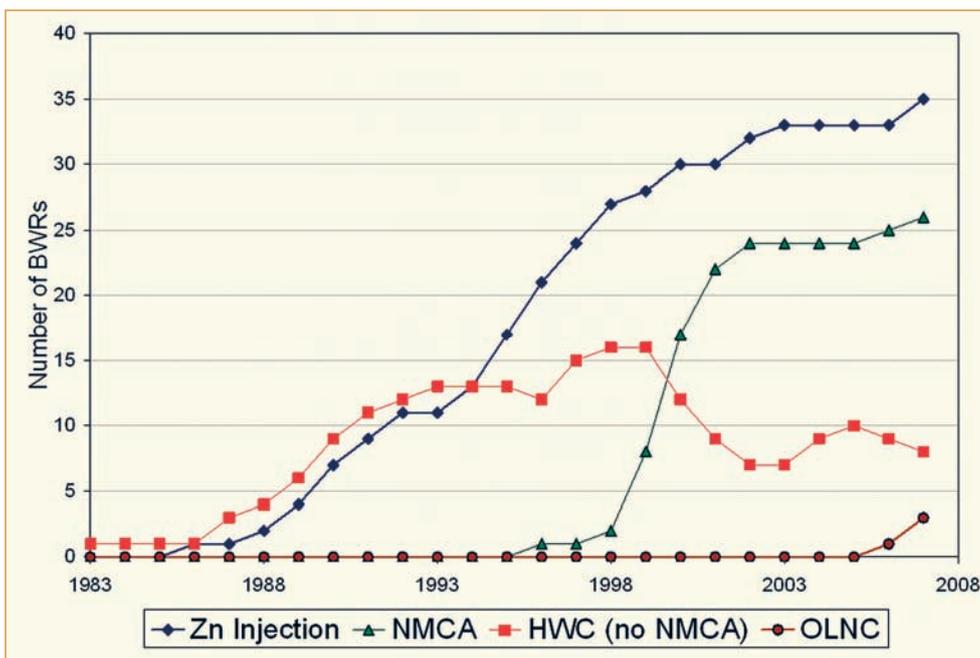


Figure 3-3: Implementation of zinc injection, hydrogen water chemistry, noble metals chemical addition and on-line noble metal at U.S. BWRs, [Wood 2008].

The US industry started developing water chemistry guidelines 25-30 years ago. The early editions of these guidelines presented impurity specifications and required actions if limits were exceeded. When advanced water chemistries were developed and qualified, the guidelines evolved into providing a menu of options, within an envelope of specifications, which should not be exceeded. Guidance is now provided on how to select the optimum plant-specific water chemistry strategy.

4 VVER Primary side coolant chemistry (Jan Kysela)

4.1.1 Historical developments

The first VVER type pressurized water reactor was a 100 MW reactor in Rheinsberg, East Germany. It was the first model of Russian pressurized water reactor that was to test primary circuit coolant technologies. This reactor had zirconium fuel cladding, and used ammonia water chemistry without KOH and without boric acid. Here water chemistry with ammonia injection without direct hydrogen injection was first tested. SS was used for both piping and SG pipes. After the technology was tested, 200 MW reactors were built and commissioned at the Novovoronezh NPP, which then served as a foundation for the development of standardized 440 and 1000 blocks.

VVERs are a type of pressurized water reactor that are in operation in Russia, Ukraine, Hungary, Slovakia, Czech Republic, Bulgaria, Armenia, Finland and China. Two major types are in operation or under construction, the 6-loop designs rated at 440 MWe (1375 MWth) and the later 4-loop designs rated at 1000 MWe (3000 MWth).

Thirty-six VVER-440 MWe units have been built, of which eight have shut down, and eleven further units were cancelled or still await completion. There are two basic VVER-440 designs. These are the first generation VVER-440s, which includes the initial V-179 design, the V-230 design and the V-270 design with enhanced seismic features. The second generation VVER-440 is standard V-213 design with a full accident confinement system.

Twenty-seven VVER-1000 MWe units have been completed and nine further units are still under construction. There are plans to build additional units in Russia and in other countries. There are a number of VVER-1000 variants, the initial prototype V-187 design, the V-302 and V-338 designs and standard V-320 design. The new export V-392, V-428, V-466, V-412 variants have enhanced safety features, but are otherwise similar to the V320 design. All the VVER-1000 units have a full containment building, [IAEA 2007].

4.1.2 Primary system

4.1.2.1 VVER Primary circuit design characteristics

The following sections summarise the design characteristics of the primary circuits of the main types of VVER reactors, the characteristics of the fuel, the purification and auxiliary circuits associated with the primary circuits and the primary circuit safety systems. Schematic layouts of the primary and auxiliary circuits in VVER-440, V213 units are shown in (Figure 4-1) and corresponding layout for VVER-1000, V320 units is shown in (Figure 4-2), [IAEA 2007].

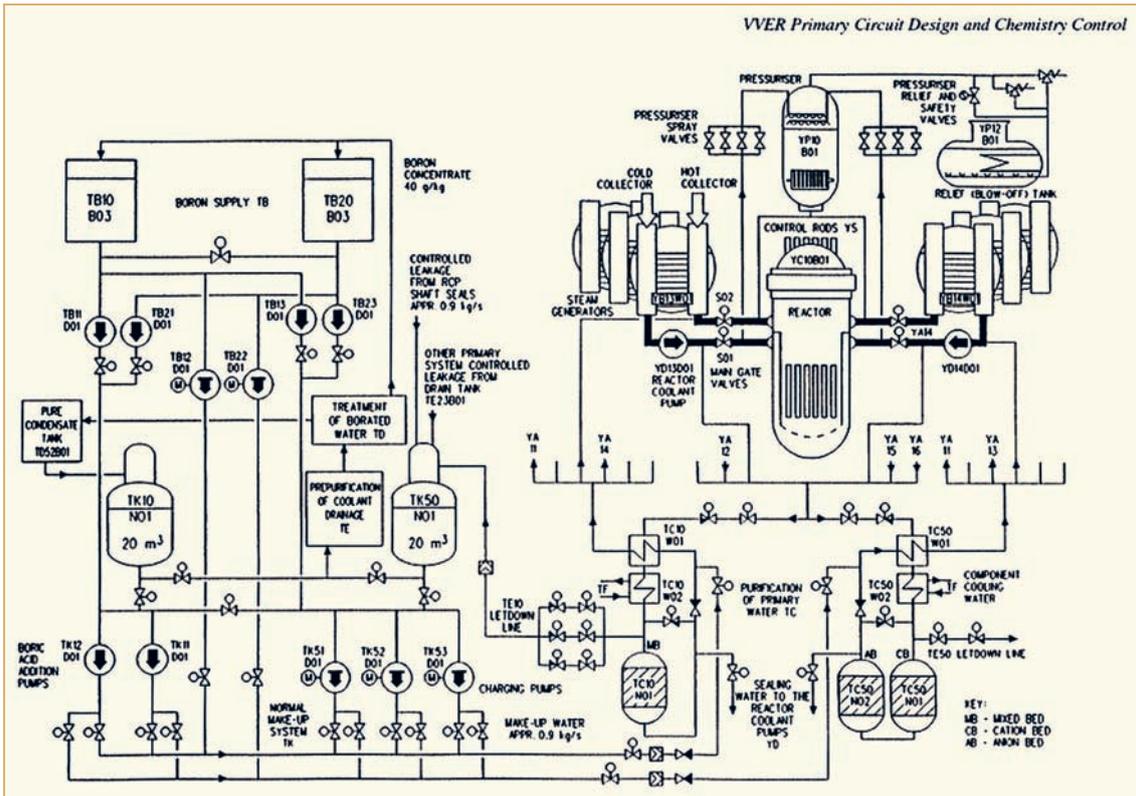


Figure 4-1: Schematic flow diagram of the primary circuit and the coolant purification, letdown and make-up systems at VVER-440 V213.

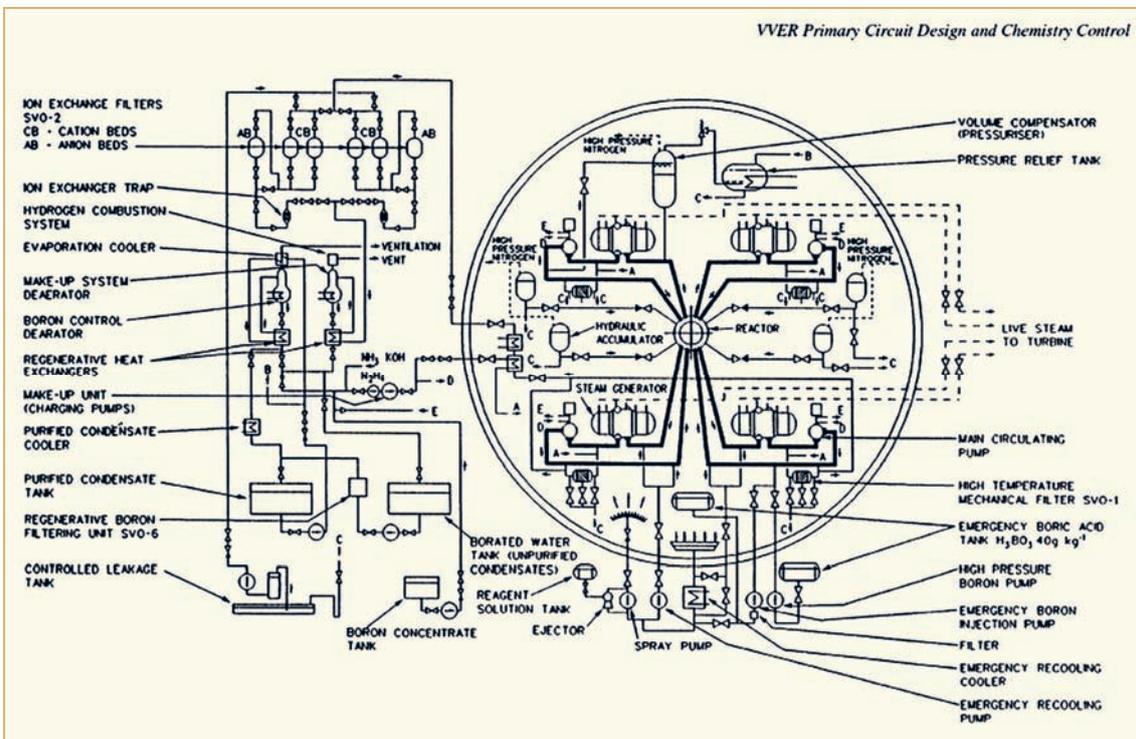


Figure 4-2: Schematic flow diagram of the primary and auxiliary circuits at the VVER-1000 V320.

VVER-440 designs

The primary circuits of the VVER-440, V-179, V-230 and V-213 designs have a RPV and six loops, each consisting of a hot leg, a horizontal SG, and a cold leg in which is mounted a Main Circulating Pump (MCP). Two isolation gate valves are fitted to the hot and cold legs of each loop, one between the RPV and SG and one between the RPV and RCP. These enable individual loops to be drained for inspection and repair, whilst circulation is maintained in the other loops. There is no separate residual heat removal system and decay heat is removed via the SGs. A pressurizer (compensator tank) is connected to the cold leg of one of the loops and a spray line to the cold leg of the same loop. Typical operating conditions are T_{hot} 297 °C, T_{cold} 267 °C, 12.3 MPa. The compositions of the most important steels are given in (Table 4-1) and cobalt impurity levels and surface areas are given in (Table 4-2). All primary circuit surfaces in contact with the primary coolant are either made from SS (main loop pipework, main coolant pumps, SG tubing, SG tube headers (collectors), gate valves and auxiliary systems pipework), from low alloy steel (reactor pressure vessel) or carbon steel (pressurizer, type-22K carbon steel) weld clad with SS. SS components, pipework including SG tubing and the pressurizer clad are normally made from the Russian-type titanium stabilised SS 08Cr18Ni10Ti, (08X18H10T equivalent to AISI⁶ (ANSI⁷) 321). The reactor pressure vessels are made from low alloy steel (15Cr2MFA; Loviisa 12Cr2MFA), weld clad internally with two SS layers.

Table 4-1: Composition of important alloys in contact with the primary coolant in VVER primary circuits.

Alloy	Composition (percent by weight)								
	C	Si	Ni	Cr	Fe	Mn	Co	Others	Zr
07Cr25Ni13	≤0.09	≤1.2	11/14.5	22/26.5	bal.	0.8/2.0	≤0.05	-	-
08Cr18Ni10Ti (a)	≤0.08	≤0.8	9/11	17/19	bal.	≤1.5	≤0.05	Ti≥5C-0.6	-
08Cr19Ni10Mn2Nb	≤0.10	≤1	8.5/11	17.5/20.5	bal.	1.3/2.5	≤0.05	Nb=0.7/1.2	-
04Cr20Ni10Nb (b)	0.03	0.6	10	18	bal.	1.7	≤0.05	Nb=0.7	-
Zircaloy-4 (c)	≤0.027	≤0.012	≤0.007	0.07/0.13	0.18/0.24	≤0.005	0.002	Sn=1.2-1.7 Fe+Cr=0.28/0.37	bal.
ZIRconium Low Oxidation (ZIRLO)	0.005/0.022	-	0.03-0.08	0.03/0.08	0.07/0.14	-	-	Sn=0.9-1.5 Nb=0.5/2	bal.
Zirc.1% niobium	≤0.05	≤0.05	≤0.025	-	≤0.07	≤0.002	≤0.007	Nb=0.8/1.2, O≤0.1	bal.
Zirc.2.5% niobium (b)	≤0.027	≤0.012	≤0.007	≤0.02	≤0.15	≤0.005	≤0.007	Nb=2.4/2.8, O=0.09/0.13	bal.

(a) Early VVER-440, V-230 units (excluding Bohunice 1 and 2) used 12Cr18Ni12Ti SS; Loviisa used 08Cr18Ni12Ti for loop pipework.
(b) Russian data quote 04Cr20Ni10Mn2Nb (0.04%C, 20%Cr, 10%Ni, 2%Mn, 0.5%Nb).
(c) ASTM standard Zr-1%Nb is Russian type Zr-1%Nb.
(d) VVER-1000 primary circuit weld metal – 04Cr19Ni11Mo3.

⁶ American Iron and Steel Institute

⁷ American National Standards Institute

5 PWR and VVER secondary side chemistry (Suat Odar)

5.1 Introduction to secondary side chemistry

This section of the Annual Report describes the secondary side water chemistry applied in PWR and VVER plants. It covers the range from basic information to current knowledge. In the following a brief introduction to the content of this section is given:

The objective of secondary side water chemistry control is to minimize corrosion damage and performance losses for all secondary system components and thereby to maximize the reliability and economic performance of the secondary system. To achieve this objective, the water chemistry has to be compatible with all parts of the secondary system including SGs (SGs), turbines, condensers, FW heaters, Moisture Separator Reheaters (MSRs), and finally piping. Special emphasis has to be put on SGs, because they are one of the key components of the PWR and VVER plants. Their degradation or performance loss greatly affects the overall plant performance. Most of the SG degradation problems are related to corrosion caused by inappropriate material and design selection or poor secondary side chemistry. For achieving a better understanding of the importance of water chemistry, the field experience regarding SG degradation problems are briefly explained in Section 5.2.

The main causes for the SG corrosion problems are the concentrated impurities beneath the deposits on the tube sheet or in the Tubes to Tube Support Plates (TSP) crevices. The mechanism of impurity concentration in the SGs is described in Section 5.3. The most crucial SG degradation problems were experienced from the early 1970s until the end of 1990s. During this period of almost 30 years of PWR operation a lot of modifications and/or improvements of water chemistry and/or SG materials and design were performed to counteract these SG degradation problems. The world wide PWR secondary side water chemistry modifications and their historical evolution is described in Section 5.4. The improvements in SG design and materials are discussed in Section 5.5. In addition to these, this section also includes description of the design and the variety of materials typically used in secondary systems.

Based on thirty years of PWR operating field experience gained with counteracting the SG degradation problems, common sense exists now worldwide, how to control the chemistry conditions to mitigate SG degradation problems; but this is unfortunately not always properly applied. Secondary side water chemistry selected to protect SGs is usually also satisfactory for entire secondary side components. The key control parameters of adequate secondary side water chemistry are described in Section 5.6. Section 5.7 describes the recent different water chemistry strategies applied worldwide to fulfill the water chemistry objectives.

Adequate secondary water chemistry application relies on water chemistry monitoring results. The concept of water chemistry sampling to control the specified chemistry goals is described in Section 5.8. Section 5.9 explains how the selected water chemistry control programs are applied in different plant operating modes, like in power operations, start-up or shutdown operations. Finally, Section 5.10 concludes the information given in the previous sections and contains recommendations for a good secondary side water chemistry practice.

5.2 Background information

The secondary side of the early PWRs, which were designed and build in the 1960s and 1970s, was based on the industrial experience gained with fossil fired conventional power plants:

As structural materials, plain carbon steels were used for the pipe work and for the components overall on the secondary side. Because of the high thermal conductivity of copper, copper bearing materials were selected for the tubes of the FW heat exchangers, MSR, and Condensers. Ferritic SS was selected for the turbine blades. After a short use of austenitic SS (18% Cr – 10% Ni) in few PWR plants, Alloy 600 meal annealed (I 600 MA), a nickel based alloy, was used as SG tubing material. In Russian designed VVER plants, austenitic SS is still used for SG tubes. In PWR Recirculating Steam Generators (RSG), carbon steel drilled hole TSP were used to support the SG tubes against vibration (see Section 5). These types of TSPs were experienced to be very sensitive against impurity concentrations and denting corrosion, as described later. For impurity control, Condensate Demineralizer System (CDS) was designed especially for the PWRs with seawater cooling and also for the PWRs with OTSG, which do not have SG blow-down capability. The water chemistry selection was again based on the well-experienced fossil power plant chemistry; i.e., “Phosphate Chemistry” (PO₄ Chemistry) was used for the RSGs and “All Volatile Treatment” (AVT Chemistry) was applied for the entire secondary side. For OTSGs, AVT chemistry was the respective SG chemistry. FW pH values, sufficiently high to adequately control the FAC of the carbon steels could not be applied, because copper bearing materials was used almost for all secondary side heat exchanger tubes. This resulted in high FW iron concentrations and accordingly high CP deposits in the SGs. So called “combined chemistry”, which is also successfully applied to control the FAC in fossil power plant industry, using ammonia together with oxygen injection, could not be selected, due to corrosion sensibility of SG tubing material Alloy 600 under oxidizing conditions. This type of secondary side plant concept (selected design and structural materials) does not allow the selection of adequate water chemistry in order to avoid high FW iron transportation (CP transport) into SGs. This poor CP control in the secondary side was together with a sensitive SG tubing material and inadequate design of the SG tube support construction the main root cause of the SG degradation problems, as it is described in the following.

Since the early 1970s, lot of SG corrosion problems was experienced in the nuclear industry. (Figure 5-1) shows the causes of SG tube degradation since 1973 up to 2006, [EPRI 2006]. In the period of early 1970s until mid 1990s, the majority of the tubes were repaired by plugging or sleeving due to corrosion problems, see (Figure 5-2). These SG problems often forced the plants to perform unscheduled or extended outages for preventive and/or corrective maintenance measures. In addition many SG replacements were necessary, which were costly in terms of repair work, personnel radiation exposure and loss of power [EPRI 2000] and [EPRI 2006]. Especially in US, where the majority of problems were reported on the secondary side of SG tubes, the industry made a lot of efforts to improve the design and materials of the SGs and the secondary side water chemistry to minimize the SG degradation problems during the period of 1970s to end of 1990s (see Sections 5.3). Although tremendous progress has been made in controlling the SG degradation problems, minimizing its impact on plant operation will remain a continuing challenge worldwide.

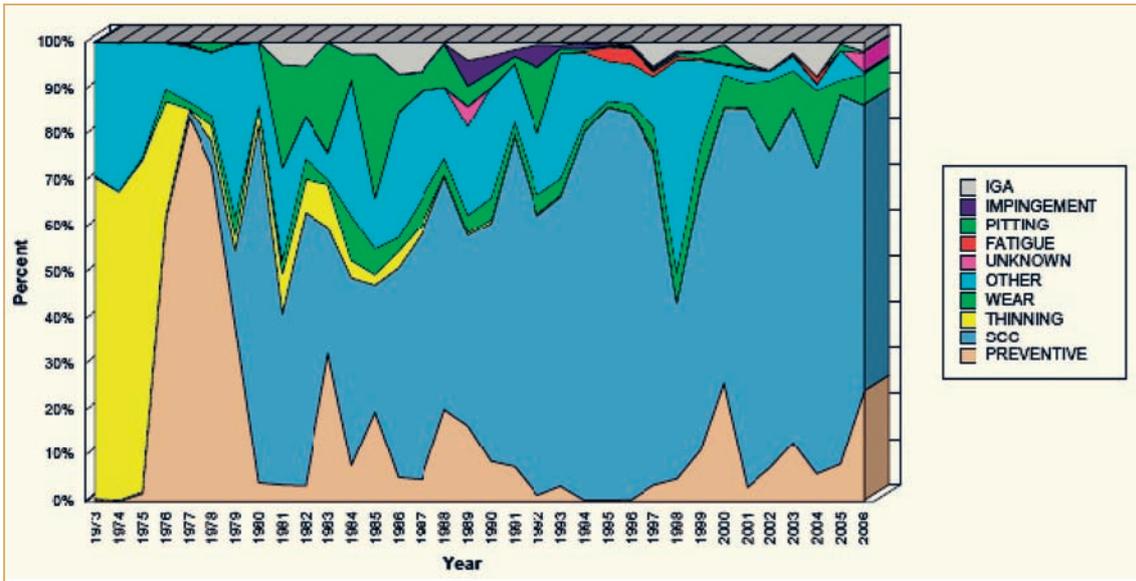


Figure 5-1: Worldwide causes of SG tube degradation, [EPRI 2006].

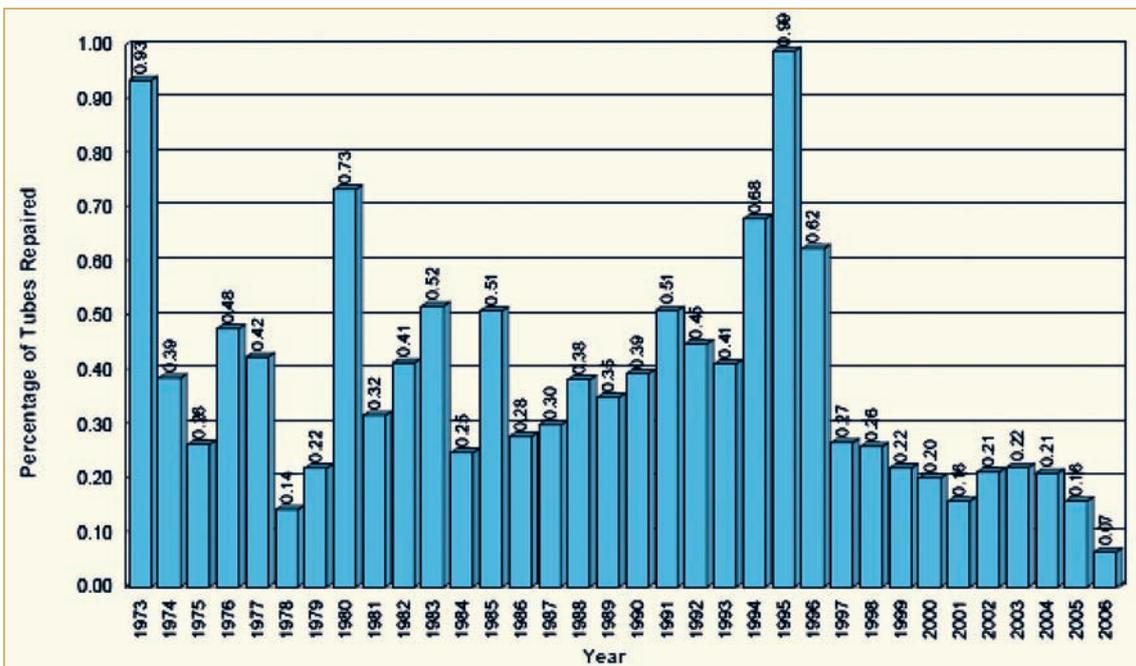


Figure 5-2: Worldwide percentage of SG tubes plugged, [EPRI 2006].

In the following sections the SG degradation problems will be described in detail.

6 Materials degradation

6.1 Introduction (Peter Ford)

6.1.1 Background

Materials degradation issues, such as crevice corrosion, pitting, flow-accelerated corrosion and environmentally assisted cracking, have presented the water-cooled reactor industry economic and/or safety concerns for decades. These problems have been exacerbated by the fact that many of these degradation modes were not considered as part of the design basis. Thus, many of these incidents have been “unexpected” and, as a result, have been addressed *reactively* by the industry via the logical sequence of:

- Evaluation of plant experience, backed up by laboratory tests, in order to determine the “root cause” of a specific degradation mode.
- Quantification of the effect of the various system parameters (e.g. environmental, metallurgical and, where applicable, mechanical conditions) on the extent of degradation.
- Definition of the appropriate mitigation actions.

Such an approach to managing material degradation, although logical, has not always been completely effective, primarily due to three factors.

First, the frequency of occurrence of the various degradation modes, and especially environmentally assisted cracking, is not governed solely by the primary actions of environment, material and stress conditions but also by secondary interactions between these conditions. Thus, mitigation actions based, for example, only on a change in environmental condition (such as lowering the oxidizing condition to counteract IGSCC of SSs in BWRs) may be completely negated if the metallurgical/strain condition is altered due to excessive surface cold work during manufacture. Therefore, unless these secondary effects are recognized and quantified, unexpected degradation can occur in a supposedly “mitigated” system.

Second, the sensitivity of degradation to the interacting primary and secondary system conditions can be high, and unless these sensitivities are known, then the experimental data may exhibit extreme dispersion over and above that associated with stochastic processes that govern some degradation modes (for example, pitting and crack initiation). Such a scatter in data creates a challenge when attempting to define operating conditions and control parameters for specific plant components.

Finally, there is a drive internationally for water-cooled reactors to operate at increased power output and for extended fuel cycles and design lives. Such business driven decisions can have a deleterious effect on time-based degradation modes due, for example, to increased coolant flow rates and irradiation damage, and unless these effects are adequately quantified, there will likely be increases in “unexpected failures”.

These issues are being addressed by various utility (e.g. EPRI) and regulatory (e.g. US Nuclear Regulatory Commission (NRC), Nuclear and Industrial Safety Agency (NISA)) organizations via the development of *proactive* life management approaches for materials degradation issues. In other words, there is a drive to predict future degradation events well before the time the degradation either is observed or presents a structural integrity problem. Such a predictive capability, therefore, would allow an effective method of prioritizing and utilizing resources to evolve effective mitigation actions and minimize the occurrence of “unexpected” events.

The ANT-International strategy in covering these complex events and assessing their effect on the capability to predict the various degradation modes is to issue two types of report:

- **Special Topical Reports (STR)** on broader issues that emphasize the interactions between the various degradation modes.

As an example an STR was issued in early 2007, “Environmentally Assisted Degradation of Structural Materials in Water Cooled Reactors” that covered degradation by various modes (e.g. general corrosion, microbiologically-influenced corrosion, pitting, cracking) in both BWRs and PWRs, and the approaches that are being taken to develop proactive life management capabilities for these degradation modes. The objective of this report was to give to engineers and scientists an *introduction* to this broad topic, with emphasis not only on the empirical observations from plant and laboratory experience, but also on the current understanding of the mechanisms of the various degradation modes.

A further STR was issued in early 2008, “Environmentally-Assisted Degradation of Carbon and Low Alloy steels in Water-Cooled Reactors”. This is a topic that has received a large amount of attention over the past 30 years, ranging from degradation modes such as general corrosion, flow-accelerated corrosion, boric acid corrosion, pitting, microbiologically-influenced corrosion, to environmentally assisted cracking. Some degradation modes, (e.g. flow-accelerated corrosion and boric acid corrosion) have received attention in recent years because of dramatic failures in operating plant. However, others (e.g. environmentally-assisted cracking), have been addressed over many years because of either earlier failures (e.g. SCC of steam turbine discs/wheels), or codification issues that would arise should degradation occur (e.g. SCC/corrosion fatigue) in the reactor pressure vessel.

- Inputs to the **Annual Report**, which cover advances that have been made in the previous two years in more detailed areas.

State of the art updates have been given in the LCC2, LCC3 and LCC4 Annual Reports covering the specific areas of:

- Stress corrosion cracking of irradiated SSs in BWRs.
- Stress corrosion cracking of nickel-base alloys in PWR primary environments.
- Degradation of SG tubing in PWR secondary environments.
- The effect of cold work on stress corrosion cracking of structural materials in BWRs and PWRs.
- The role of environment on fracture resistance.
- The effect of dissolved hydrogen concentration on stress corrosion cracking of nickel base alloys in PWR primary systems.
- Prediction Capabilities for SCC of Nickel- base Alloys in PWR Primary Systems.

6.1.2 LCC5 Objectives

The objectives in LCC5 are to:

- Prepare an STR on the topic, “Environmentally Assisted Degradation of SS in Light Water Reactor (LWR)s”. Like the previous two STRs, this report covers a subject that has received a large amount of attention over the last 30 years and keeps re-emerging due to unanticipated factors. Such factors include cracking in systems where mitigation actions have already been introduced but whose effectiveness has been compromised by secondary, uncontrolled, factors such as surface cold work, or irradiation.
- Prepare two sections for inclusion in the Annual Report on the topics:
 - Pitting and stress corrosion of austenitic SSs due to pollutants in water-cooled reactor environments with particular emphasis on practical and potential cases such as canopy seal cracking, atmospheric pitting/cracking and corrosion under insulation.
 - Intergranular stress corrosion cracking and irradiation assisted stress corrosion cracking of cold worked/irradiated austenitic SSs in de-oxygenated PWR-type coolants with particular emphasis on baffle-former bolt cracking in irradiated internals

These last two topics are the subject of this report. These phenomena are addressed for the austenitic SSs and associated weld metals commonly used in both BWRs and PWRs and whose composition specifications are listed in (Table 6-1). Compositions of cast SSs are shown in (Table 6-2).

Table 6-1: ASTM compositional specifications for wrought austenitic SSs and their associated weld metals commonly used in PWRs (wt%).

Wt%	C max	Mn max	Si max	Cr	Ni	P max	S max	Mo	N	Cu max	Other	Fe
ASTM Spec												
304	0.08	2.0	1.0	18-20	8.0-10.5	0.045	0.03					Bal
304L	0.03	2.0	1.0	18-20	8-12	0.045	0.03					Bal
304 NG	0.02	2.0	0.75	18-20	8-11	0.03	0.005	0.5	0.06-0.10	0.5	(1)	Bal
ER 308	0.08	1.0-2.5	0.3-0.65	19.5-22	9-11	0.03	0.03	0.75		0.75		Bal
ER 308L	0.03	1.0-2.5	0.3-0.65	19.5-22	9-11	0.03	0.03	0.75		0.75		Bal
ER 309	0.12	1.0-2.5	0.3-0.65	23-25	12-14	0.03	0.03	0.75		0.75	0.06-0.10 N	Bal
ER 309L	0.03	1.0-2.5	0.3-0.65	23-25	12-14	0.03	0.03	0.75		0.75	0.06-0.10 N	Bal
316	0.08	2.0	1.0	16-18	10-14	0.045	0.03	2-3				Bal
ER 316	0.08	1.0-2.5	0.3-0.65	18-20	11-14	0.03	0.03	2-3		0.75		Bal
316L	0.03	2.0	1.00	16-18	10-14	0.045	0.03	2-3				Bal
ER 316L	0.03	1.0-2.5	0.3-0.65	18-20	11-14	0.03	0.03	2-3		0.75		Bal
316NG	0.02	2.0	0.75	16-18	11-14	0.03	0.005	2-3	0.060-0.10		(1)	Bal
321	0.08	2.0	1.0	17-19	9-12	0.03	0.03				Ti>5XC	Bal
347	0.08	2.0	1.0	17-19	9-12	0.045	0.03				Nb +Ta>10XC	Bal
347 NG	0.03	2.0	1.0	17-19	9-12	0.035	0.02				0.2 Co, Nb >10XC	Bal

Notes 1: Co : 0.25%max.; Ta+Nb : 0.05%max. : B:0.001max.; Al: 0.04%max.; V:0.1%max.; Bi+Sn+As+Pb+Sb+Se: 0.02%max.

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