

# Zinc Chemistry in BWRs, PWRs and VVERs

*Authors*

Juan de Dios Sánchez Zapata  
Albacete, Spain



A.N.T. INTERNATIONAL®

© February 2025

Advanced Nuclear Technology International  
Spinnerivägen 1, Mellersta Fabriken plan 4,  
448 50 Tollerød, Sweden

[info@antinternational.com](mailto:info@antinternational.com)

[www.antinternational.com](http://www.antinternational.com)

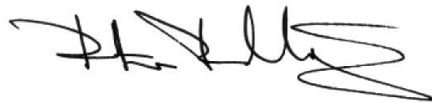


Ecolabelled printed matter, 4041 0799

## **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 report.

### **Quality-checked and authorized by:**

A handwritten signature in black ink, appearing to read 'Peter Rudling', is centered below the text 'Quality-checked and authorized by:'. The signature is fluid and cursive.

Mr Peter Rudling, Chairman of the Board of ANT International

## Contents

<b>1</b>	<b>Introduction</b>	<b>1-1</b>
<b>2</b>	<b>Background</b>	<b>2-1</b>
	2.1 BWR	2-1
	2.2 PWR	2-7
	2.3 VVER	2-11
<b>3</b>	<b>The Development of Zinc Technology for BWR/PWRs Applications</b>	<b>3-1</b>
	<b>3.1 BWR plants</b>	<b>3-1</b>
	3.1.1 Discovery of Zn Effect	3-1
	3.1.2 Plant qualification and demonstration	3-4
	3.1.3 Isotopically Depleted Zinc (DZO)	3-7
	<b>3.2 PWR plants</b>	<b>3-9</b>
<b>4</b>	<b>Effectiveness of Zinc Injection in Controlling Shutdown Dose Rates</b>	<b>4-1</b>
	<b>4.1 Background</b>	<b>4-1</b>
	<b>4.2 Mechanism of Zinc Technology</b>	<b>4-3</b>
	<b>4.3 BWR Plants</b>	<b>4-8</b>
	4.3.1 BWR under NWC	4-8
	4.3.2 BWR under HWC	4-10
	4.3.3 BWR under Noble Metals	4-15
	4.3.4 Final remarks on Zn addition in BWR	4-18
	<b>4.4 PWR Plants</b>	<b>4-19</b>
	4.4.1 Zn and the Mechanism of Radiation Build-up	4-19
	4.4.2 Plant Experience with Zinc Chemistry	4-22
	4.4.3 Zinc and Plant Commissioning and Significant Activities	4-33
<b>5</b>	<b>Effect of Zinc on Corrosion and SCC</b>	<b>5-1</b>
	<b>5.1 Background and Laboratory Research</b>	<b>5-1</b>
	<b>5.2 BWR experience</b>	<b>5-6</b>
	<b>5.3 PWR experience</b>	<b>5-7</b>
	5.3.1 Materials Compatibility with Zinc	5-7
	5.3.2 PWSCC Mitigation	5-8
<b>6</b>	<b>Effects of Zn Addition on Fuel Performance</b>	<b>6-1</b>
	<b>6.1 Background</b>	<b>6-1</b>
	<b>6.2 BWR</b>	<b>6-5</b>
	6.2.1 CRUD Spalling under Noble Metals Addition	6-8
	6.2.2 Other BWR Fuel Events	6-12
	6.2.3 Recent experiences	6-15
	<b>6.3 PWR</b>	<b>6-16</b>
	6.3.1 Influence of Zinc on Fuel Deposits	6-16
	6.3.2 Influence of Zinc on Cladding Corrosion	6-17
	6.3.3 Influence of Zinc on AOA	6-22
	6.3.4 Zinc and Silica	6-23
<b>7</b>	<b>Impact of Zn Additions on Radwaste Production</b>	<b>7-1</b>
	<b>7.1 BWRs</b>	<b>7-1</b>
	<b>7.2 PWRs</b>	<b>7-1</b>

<b>8</b>	<b>VVER experience</b>	<b>8-1</b>
<b>9</b>	<b>References</b>	<b>9-1</b>
	<b>Appendix A - High Duty Core Index</b>	<b>1</b>
	<b>List of Abbreviations</b>	<b>9-1</b>
	<b>Unit conversion</b>	<b>9-4</b>

# 1 Introduction

This report describes the use of zinc injection technology in both Boiling Water Reactor (BWR) and Pressurized Water Reactor (PWR) plants worldwide. A review of the available laboratory work applicable to VVER plants is also included. The review covers the range from basic information to current knowledge and understanding of operational behaviour. The basis of this report is the published information collected by ANT International and presented in several Special Topic Reports specific on Zinc of the LCC and ZIRAT programs, as well as annual updates on water chemistry, materials and fuel reports.

In 2010/11, for the LCC6 program, ANT International issued a report entitled “Effect of Zinc in BWR and PWR/VVER on Activity Build-up, IGSCC and Fuel Performance” [Odar et al., 2010] which covered all published knowledge about zinc chemistry in BWR and PWR plants as of 2010. Ten years later, in 2021, for the LCC16 program, ANT International published an update for PWR with the title “Zinc Chemistry in PWR Plants from Mid-1990s up to Present: Mechanism and Worldwide Field Experience” [Odar, 2021]. After 4-5 years, ANT has decided to issue the present report based on the published information so far, including the proceedings of the latest International Conference on Water Chemistry of Nuclear Reactor Systems that took place in 2023 in Antibes (France), updating the information for the three main technologies of reactors that are susceptible to apply zinc chemistry.

Zinc addition is a mature technology applied both in PWR and BWR reactors. It has been a crucial milestone in coolant chemistry for controlling and reducing radiation build-up and operational radiation exposure to personnel for most of BWR, particularly important to counteract the negative effects of the IGSCC mitigation actions on dose rate control. Likewise, for PWR reactors, zinc addition is considered paramount for many plants for the control of radiation fields in general and for the mitigation of Primary Water Stress Corrosion Cracking (PWSCC), in particular at PWR plants that used Alloy 600MA as construction material (SG tubes, Reactor Pressure Vessel (RPV) penetrations, nozzles and welds).

As a mature technology integrated in the normal practices of many nuclear plants BWR and PWR with a broad experience along the years, the number of papers describing research and operating results has reduced in the last years, while its implementation in VVER plants is still waiting to the commissioning of new reactor designs. However, it has been considered appropriate to issue this report, summarizing the most important aspects of the theoretical basis and the plant implementation experience, to provide a summarized view of the origin, fundamentals, operating experience and different aspects to take into consideration for the implementation or to forecasts when significant changes in the plant operation are foreseen, (i.e. changes in the chemical regime, cycle extension, higher fuel duty, etc.), particularly for new personnel incorporated in the recent years to the nuclear industry. This has been completed with new information publicly available that has been added to each chapter to get a view of the present situation.

Section 2 provides an introductory overview of the general characteristics, materials and chemical regimes for each type of reactor, with the aim of introducing the reader to each reactor technology in order to understand the rest of the report. Section 3 makes a historical review of the discovery, first qualifications tests and first experiences of BWR and PWR plants implementing Zn addition. Section 4 starts with a background information on the mechanism of Zn interaction with the reactor coolant and the materials oxide films and then reviews the effectiveness of Zn for radiation fields control at the two types of reactors and its different chemistry regimes. Section 5 covers the effects of Zn on materials corrosion and particularly, Stress Corrosion Cracking (SCC), and the experience of plants in mitigating it. Section 6 deals with the effects on fuel performance reviewing the fundamentals of the Zn effect on fuel CRUD and the operating experience, highlighting the fact that Zn implementation for some plants occurred in a period of increasing demand for fuel (higher cycle length, higher fuel demand, non-optimized or changes in water chemistry, etc.). Section 7 deals with the secondary aspects of radwaste treatment and solid radwaste production after Zn chemistry implementation. Finally, Section 8 summarizes the VVER testing and impact evaluation experience with update of the latest limited publicly available information. Each section of the report contains a short summary at the end, so it has not been considered necessary to repeat them in a summary section.

Personal opinions of the author are written in italic font.

Interested reader to extend the information on zinc addition and its related consequences for LWR reactors are referred to the following ANT reports references:

- ZIRAT6/IZNA1 STR on CRUD ZIRAT6/IZNA1 STR on Water Chemistry and CRUD Influence on Cladding Corrosion by Gunnar Wikmark and Brian Cox, ANT International, 2001.
- ZIRAT7/IZNA2 STR on Corrosion of Zirconium Alloys by Ronald Adamson, Brian Cox, Friedrich Garzarolli, Alfred Strasser, Gunnar Wikmark and Peter Rudling, ANT International, 2003.
- ZIRAT8/IZNA3 STR on The Effects of Zn Injection(PWRs and BWRs) and Noble Metal Chemistry (BWRs) on Fuel Performance by Brian Cox, Friedrich Garzarolli, Alfred Strasser, and Peter Rudling, ANT International, 2004.
- ZIRAT12/IZNA7 STR on Corrosion Mechanisms in Zirconium Alloys by Ronald Adamson, Friedrich Garzarolli, Brian Cox, Alfred Strasser, and Peter Rudling, ANT International, 2007.
- LCC6 STR on Effect of Zink in BWR and PWR/VVER on Activity Build-up, IGSCC and Fuel Performance, by Suat Odar, Robert Cowan and Jan Kysela, ANT International, 2010.
- LCC7 and 8 STR on Introduction to Boiling Water Reactor Chemistry Volume I and II, by Robert Cowan, Wilfried Rühle and Samson Hettiarachchi, ANT International, 2011 and 2012.
- LCC7 and 8 STR on PWR/VVER Primary Side Coolant Chemistry Volume I and II, by Rolf Riess, Suat Odar, Francis Nordmann and, Jan Kysela, ANT International, 2011 and 2012.
- LCC9 STR on Effects of Coolant Chemistry on Fuel Performance, by Peter Rudling, Ron Adamson, Alfred Strasser, Brian Cox, Friedrich Garzarolli, Suat Odar. 2013
- LCC16 STR on Zinc Chemistry in PWR Plants from Mid-1990s to Present: Mechanism and Worldwide Field Experience by Suat Odar. 2021
- LCC17 STR on Deposit Formation on Fuel Cladding in PWR Primary Systems by Jim Henshaw. 2022.

## 2 Background

This section provides some basic information on the characteristics, materials and chemistry regimes for the three types of LWR reactors that are discussed in this report. It is not intended by far to be exhaustive but, at least, is trying to present a minimum information for those less familiar with some of the specific reactor technologies that will be dealing with on the following sections, with the idea that the understanding of the issues and solutions for other technologies may be of help for managing the issues of the own ones.

### 2.1 BWR

According to the IAEA's PRIS database, in 2024 there are 41 BWR reactors in operation and 21 in "suspended operation" mostly in Japan. BWR reactors have evolved since the first leading prototypes from General Electric (GE) to the recent advanced designs. All designs share several technical features such as direct cycle, main steam is generated in the reactor vessel, on top of the core there is a steam separator and a steam dryer, control rods are introduced from the bottom of the vessel, Zircaloy-2 fuel cladding, stainless steel as the main structural material for reactor internals and piping, oxidizing environment due to radiolysis and reactor water quality mainly conditioned by the final feedwater (FW) impurities and the Reactor Water Clean Up (RWCU) system.

BWR reactors operate at 68-74 bars (6.8-7.2 MPa) and 283-288°C and the reactor vessel directly generates a steam with a quality normally well above 99.5%.

The first GE-BWR designs in the early 60's had several external recirculation loops as the first ASEA BWR in Sweden. Later, the most of GE BWR adopted two recirculation loops with internal jet-pumps. In the late 70's and 80's, in Europe, ASEA in Sweden and KWU in Germany and later, GE with Japanese Hitachi and Toshiba developed a design with internal pumps (six to ten internal pumps, depending on the reactor size) (ABWR), avoiding the problems of the recirculation piping and valves, that contribute significantly to the operational dose (Figure 2-1).

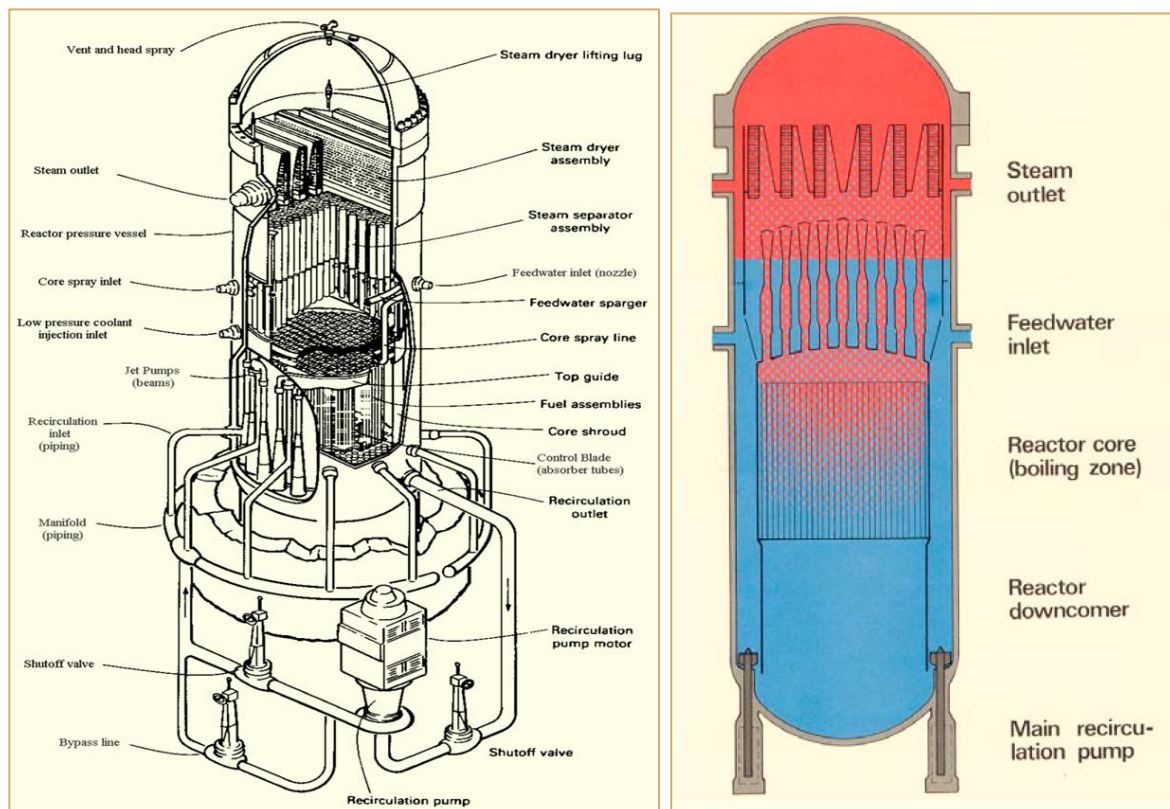


Figure 2-1: (Left) BWR Vessel arrangement for jet pump recirculation system [BWR6, 1975]. (Right) BWR with internal recirculation pumps Advanced Boiling Reactor (designed by GE, Hitachi, Toshiba).

Regarding materials, all the reactor structures in contact with water and the recirculation piping are made of austenitic stainless steels, with some internal structures made of nickel alloys (Alloy 600) as well as the material used for dissimilar welds (Alloys 82 and 182). The European designers used stabilized stainless steels, SS-321 with Ti or SS347 with Nb, whereas GE started using 304 or 304L and 316L and later 316NG (Table 2-1). Main steam and feedwater lines connected to the reactor are made of carbon steel (CS) and the steam-water cycle piping are either carbon or low alloy steels, to provide resistance to flow accelerated corrosion (FAC). Feedwater heaters are made of stainless steel and the main condenser used to be in some older BWRs of copper alloys (admiralty brass, 71% Cu, 28% Zn and 1% Sn, or Cu-Ni alloys), others had stainless steel and the new plants have titanium; many of the older BWR have replaced the copper condenser with titanium. Fuel cladding material is Zircaloy-2 with different manufacturing process and fuel bundle sheaths (channel) are made of Zircaloy-4 or other Zr alloys and the grid spacers can be either of Zircaloy or nickel alloys, depending on the fuel manufacturer.

Table 2-1: Worldwide most used austenitic stainless steel types.

Denomination	Composition	Stabilization	Carbon content
304	18Cr 10Ni	Non stabilized	0.03 – 0.08 %
304 L	18Cr 10Ni	Non stabilized	<0.03 %
316	18Cr 10Ni 2Mo	Non stabilized	0.03 – 0.08 %
316 L	18Cr 10Ni 2Mo	Non stabilized	<0.03 %
316 ELC	18Cr 10Ni 2Mo	Non stabilized	<0.02 %
321	18Cr 10Ni	Stabilized with Ti	
(German designation for 321: 1.4541)			
347	18Cr 10Ni	Stabilized with Nb	
German designation for 347: 1.4550			
ANT International, 2025			

As the reactor pressure vessel (RPV) is part of the water steam cycle, the reactor water (RW) quality is absolutely conditioned by the feedwater (FW) quality. BWR reactors are provided with a Reactor Water Clean-Up system (RWCU), that have filters and ion exchangers to purify the water, which capacity is limited to 1% of the feedwater flow (up to 2-3% in older lower power BWR). This means that non-volatile soluble impurities are concentrated, typically, 100 times in the reactor water. Figure 2-2 shows a sketch of the complete water steam cycle for a BWR with forward pumped heaters drains. The fact that the reactor vessel is part of the water-steam cycle prevents the use of any chemical additive to reduce corrosion in the secondary system such as those used in PWR or fossil fuel plants, as these additives will be decomposed by radiolysis and will generate high dose rates. Therefore, BWR operate with high purity water and, thus, an efficient condensate treatment system is mandatory to retain any impurities from the main condenser materials or in-leakage from the circulating water and the corrosion products generated by flow accelerated corrosion phenomena (FAC) in the steam and water lines. The presence of impurities in RW is strictly limited in a BWR reactor and even more in FW. Only limited amounts of additives, such as oxygen, hydrogen or zinc are used in some plants to prevent corrosive phenomena in the condensate-feedwater or Stress Corrosion Cracking (SCC) and for dose control in the reactor system. All additives are injected via FW system.

The condensate treatment system, also called condensate polishing (CPS), is crucial for the quality of FW and RW. Figure 2-2 shows the ideal configuration for this system, that is, a dual treatment with filters and deep bed ion exchangers, but the initial BWR used to have either only deep beds, which have a low filtration efficiency (85%) or filter demineralizers (powder ion exchange precoat filters) that have a limited retention of soluble impurities, such as copper or zinc from the brass condenser or circulating water impurities from condenser in-leakage, due to the small thickness of ion exchange resins in the precoat. These BWR had to operate in the first case with high inputs of iron in feedwater and in the second case with a certain copper and zinc input to the reactor water (natural Zn plants).



Iron (more precisely, iron oxide) is the most abundant impurity in the FW for most of BWR, although it has decreased significantly along the years due to the efforts in many plants of installing a dual system or improving the filter demineralizers filtration efficiency with significant modifications (Figure 2-3). Iron input plays an important role in dose rate control in BWR and its reduction has been one of the main goals in the BWR industry. Some BWR in Sweden and Japan have operated since the commissioning with very low levels of Fe ( $< 0.1\text{-}0.2 \mu\text{g}/\text{kg}$ ). For these plants the Fe/Ni ratio in RW plays a role in the dose rate control.

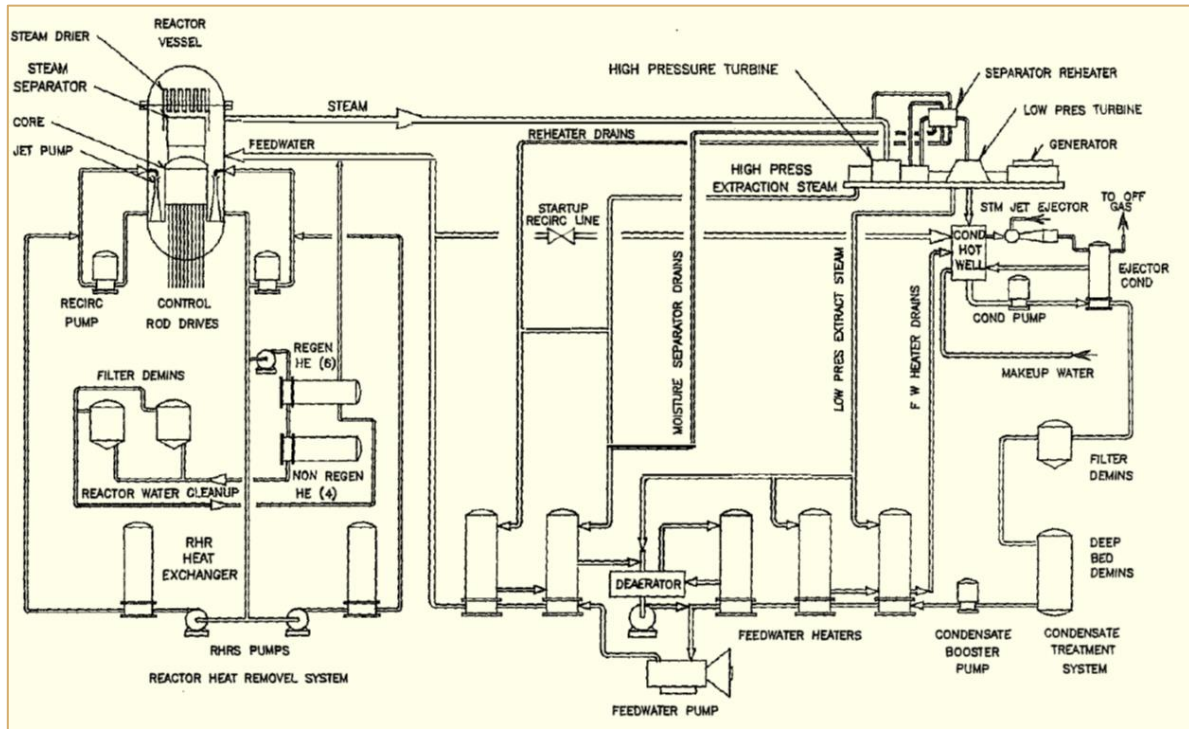


Figure 2-2: Direct cycle Boiling Water Reactor System with Forward-Pumped Heater Drain modified according to [Lin, 1996]

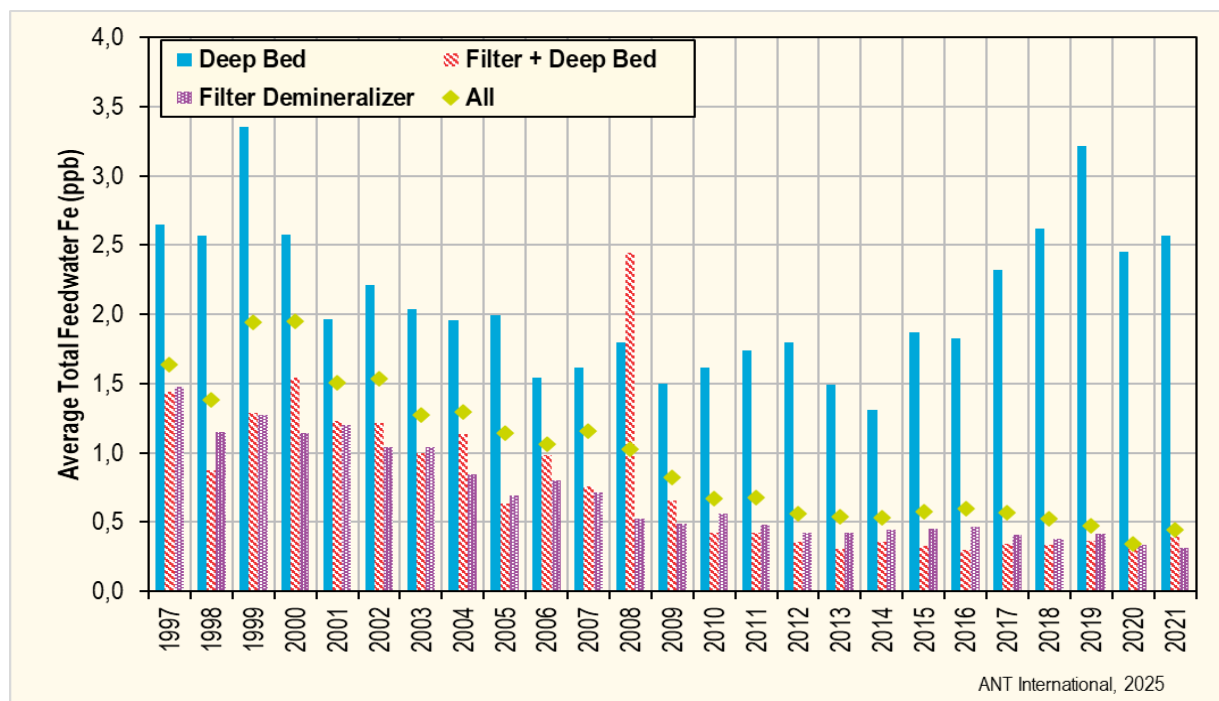


Figure 2-3: BWR Feedwater Iron from 1997 to 2021 [Lynch et al., 2023].

Another important fact for dose control in BWRs in the use of Stellite in the older plants, both in the reactor internals (control rod pins and rollers or hard surfaces in Jet-Pumps) as well as in valves trims, in the recirculation system and in all the FW system downwards the condensate treatment system. New operating BWRs have eliminated this material in a great extent, but old plants are doing a continuous effort replacing it from a large inventory of valves and other components. For most of BWRs,  $^{60}\text{Co}$  is the main activated corrosion product (CP) responsible of the components dose rate and the Occupational Radiation Exposure (ORE). Other isotopes are  $^{54}\text{Mn}$ ,  $^{58}\text{Co}$ ,  $^{51}\text{Cr}$  and  $^{59}\text{Fe}$  (and  $^{65}\text{Zn}$ , in natural Zn plants).

Additional to high dose rate, the key issue that BWR have afforded in the USA and other countries is Intergranular Stress Corrosion Cracking (IGSCC), a degradation phenomenon that affects stainless steel welds in piping and reactor internals, and nickel alloys in dissimilar metal welds. This corrosion, that affects sensitized materials in welds, crevice, etc., is promoted by impurities ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) and, mostly, by the oxidizing environment that is produced by water radiolysis in the reactor system. There are three approaches to cope with this phenomenon that are the basis for the BWR chemical programs:

- Normal Water Chemistry (NWC): Operation in the aggressive radiolytic environment (significant concentrations, 200-400  $\mu\text{g}/\text{kg}$  of  $\text{H}_2\text{O}_2$  and  $\text{O}_2$  in reactor water) is only possible in the long term for those BWR that have used stabilized materials as the Niobium stabilized 347 steels, used by the European designers in Germany and Sweden. This material allows the operation of BWRs with NWC. However, it has to be mentioned that the manufacturing of this material as well as the installation, which includes e.g. specific welding methods, and surface finishing treatments, are most important. The manufacturing and installation must be such as to avoid any residual stresses or cold work to reduce the tendency for SCC.
- Hydrogen Water Chemistry (HWC): Is the approach taken in the USA by GE and in the older plants in Sweden for IGSCC mitigation. In contrast to PWR reactors, it is not possible to cancel completely the radiolysis of water in BWRs. Hydrogen injection has been applied to suppress radiolysis, but this is only efficient for materials exposed to water before it enters the reactor core, such as the recirculation piping, the RPV bottom head and, partially, the core shroud. Once water enters the core, the boiling makes the hydrogen to partition to the steam phase produced and leave the RPV almost completely with the main steam. The injection of hydrogen via FW was applied first to provide a reducing environment to the recirculation piping at low  $\text{H}_2$  injection rates in FW (0.3-0.8 mg  $\text{H}_2/\text{kg}$ ) and, later, to the RPV bottom head and core shroud at higher injection rates (1-2 mg  $\text{H}_2/\text{kg}$ ),<sup>1</sup> sometimes called moderated HWC (mHWC). A side effect of HWC, among others, is the significant increase produced in main steam radiation, a factor 3-6 versus NWC, depending on the injection rate and the RPV geometry, as it is shown in Figure 2-4. This is produced by the conversion of  $^{16}\text{N}$  to volatile species under the reducing environment. This is a hurdle for HWC implementation in many plants and, for others, it requires costly investments in turbine building shielding. It is also affecting significantly the shutdown radiation dose, as we will see.
- Noble Metals Technology (NMCA and later OLNK): is an alternative method for achieving reducing conditions to mitigate IGSCC while minimizing most of the negative side effects of mHWC. The basis consists of applying a thin deposit (equivalent to an atom layer) of noble metal particles to the reactor components. The catalytic effect of noble metals makes the radiolytic oxidizing species ( $\text{O}_2$  and  $\text{H}_2\text{O}_2$ ) to recombine with  $\text{H}_2$ , when the molar ratio of  $\text{H}_2/(\text{O}_2 + 1/2 \text{H}_2\text{O}_2)$ , is greater than 2. This causes a drop in the material ECP at a FW hydrogen injection rate much lower than the required for achieving protective conditions on stainless steel and, at this hydrogen injection rate, the effect on main steam radiation is very small and tolerable for any plant. The point is to achieve very reducing conditions at the materials surface, without affecting the bulk mass of reactor water. This is shown schematically in Figure 2-6. The protective effects of this conditions were confirmed in a qualification program that

<sup>1</sup> The IGSCC is mitigated when the environment is sufficiently reducing. This is achieved at BWR when the Electrochemical Corrosion Potential (ECP) is  $\leq -230 \text{ mV}(\text{SHE})$ . Hydrogen injection in FW is adjusted until ECP (measured or estimated according to a radiolysis model) is below this value. ECP is a quantitative measurement of the driving force for the oxidation of a metal in an aqueous environment. It is measured in volts on the Standard Hydrogen Electrode scale (SHE), with lower values (often negative numbers) being less oxidizing.

### 3 The Development of Zinc Technology for BWR/PWRs Applications

#### 3.1 BWR plants

##### 3.1.1 Discovery of Zn Effect

The positive effect of zinc addition on radiation field control was discovered coincidentally in BWR plants in the early 1980s. It was observed that the GE designed BWR plants in the USA with stainless steel condenser tubes were experiencing very high dose rate, whereas others having brass condenser tubes have acceptable low dose rates (see Figure 3-2). In order to identify and understand the parameters and the conditions that were affecting the radiation fields in BWR plants, Electric Power Research Institute (EPRI) and GE jointly started a research study called “BWR Radiation Assessment and Control” program (BRAC<sup>4</sup>). The evaluation of the existing BWR plants radiation field data, performed within the follow-up of this program, indicated that the plants with brass condenser tubes and filter demineralizers (Powdex or precoat filters) in the condensate polishing, operating with up to 1 µg/kg zinc in their feed water and 5-20 µg/kg zinc in the reactor water had significantly lower out-of-core pipework radiation fields [Marble, 1983]. A hypothesis was raised [Marble & Wood, 1985]:

*“The zinc cations will incorporate into and modify the normal magnetite crystal defect structure so that a more protective film is formed and corrosion is significantly inhibited.”*

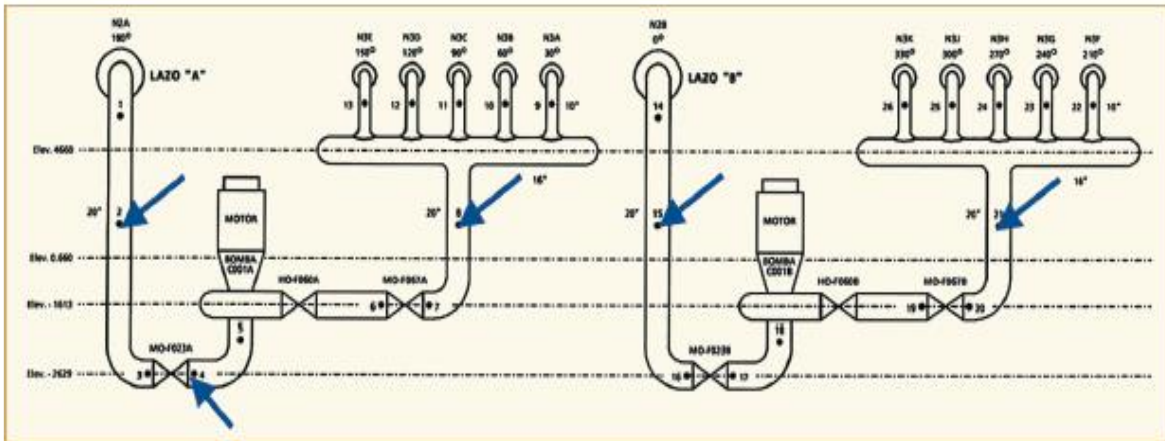


Figure 3-1: Typical BWR Radiation Assessment and Control BRAC measuring locations on recirculation loop A and B

<sup>4</sup> BRAC established a criterion for measuring the contact dose rate in the vertical section of the recirculation piping at GE-BWR plants, see [Figure 3-1]. The average of these values is usually called “BRAC dose rate”. The data base for these data for a huge number of plants continue being the basis for studies and correlations of dose rates for these fleet of plants.

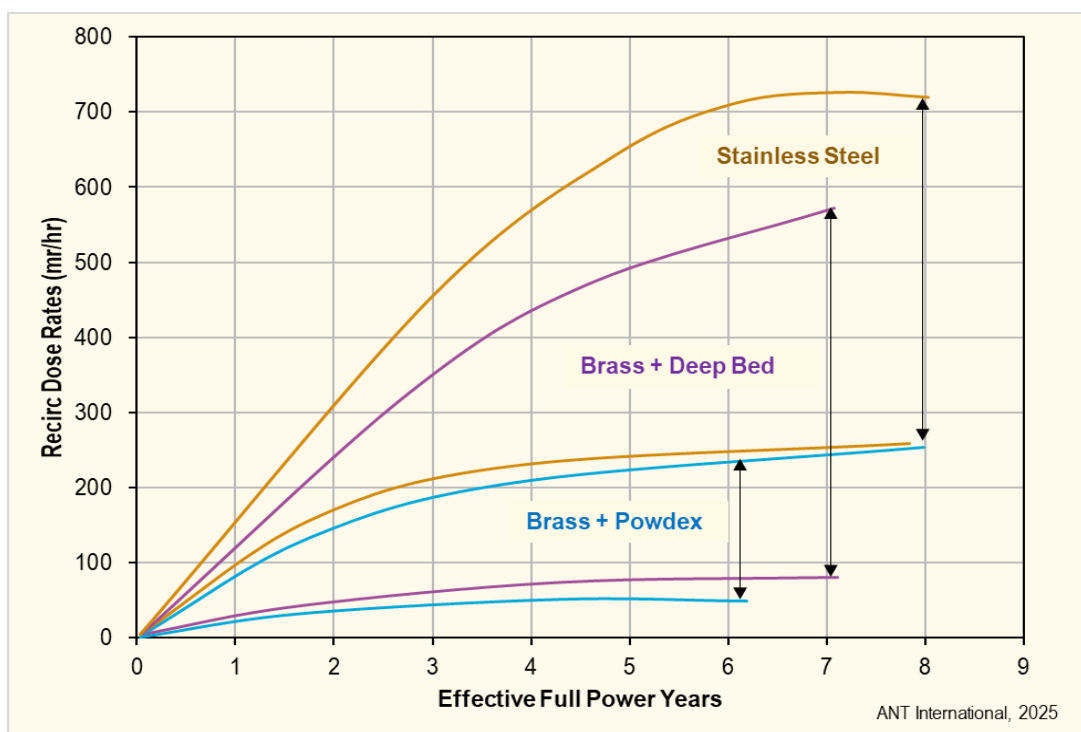


Figure 3-2: BWR radiation behaviour for generic plants when sorted by condenser metals and condensate type, modified according to [Marble & Wood, 1985].

At that time, it was identified that the source of radiation fields on out-of-core surfaces in BWRs is  $^{60}\text{Co}$ , which in mature plants usually accounts for 80 to 90% of the total dose rate. The  $^{60}\text{Co}$  originates when  $^{59}\text{Co}$ , the naturally occurring form of elemental cobalt, is activated by a  $(n,\gamma)$  reaction in the reactor core. Cobalt is a minor element in the system materials, it is a natural impurity of nickel and it is the main component (up to 60%) of a wear resistant alloy, Stellite™, that was extensively used both in wear surfaces in the reactor system (i.e. in control rods pins and rollers) and applications requiring outstanding wear resistance, such as valve trims in the recirculation system, auxiliary systems and, in general, in the condensate and feedwater system (BOP).

Based on the observations, research was sponsored by EPRI/GE to confirm and quantify the hypothesis. In a series of autoclave tests under BWR conditions (285°C at 1200 psi with 200  $\mu\text{g}/\text{kg}$  or 8 mg/kg dissolved oxygen) in SS-304 coupons it was demonstrated that, at 10  $\mu\text{g}/\text{kg}$  Zn, the oxide thickness was decreased by a factor of 5 after 1000 hours of exposure and the corrosion film was significantly changed, being uniform, instead the double layer formed in absence of Zn. The microscopic exam of the outer film was a mixed ferritic spinel structure [Niedrach & Stoddard, 1985 and 1986].

What was surprising from this study is that other ions incorporated into the film to a higher concentration than zinc, but only Zn appeared to be unique in its property to reduce the film thickness from the no addition case (Figure 3-3). The level of incorporation was  $\text{Ni} \approx \text{Co} > \text{Zn} > \text{Mn} > \text{Cu}$ . The observation of the high affinity of stainless steel oxide films for the cobalt ion is unfortunate as  $^{60}\text{Co}$ , that is always present in BWR water, will occupy those sites in proportion to its specific activity. Therefore, for the Zn to be effective it is necessary to keep a much higher concentration than cobalt in reactor water. Ni showed an even more effective effect of Co suppression but it was decided to adopt Zn as there was a large experience with “natural Zn plants” and it was considered of much lower risk.

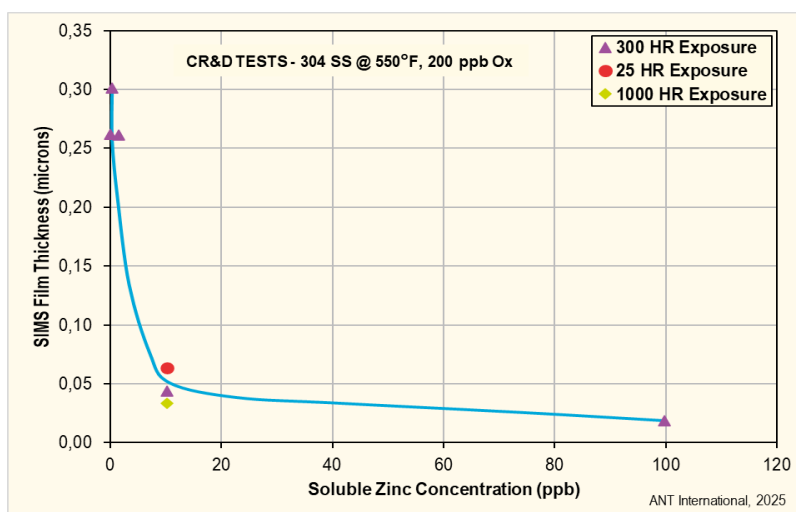


Figure 3-3: Film thickness measurements after exposure to different zinc concentrations, modified according to [Niedrach & Stoddard, 1985].

Additionally, in an active loop at Vallecitos Nuclear Center (VNC), GE demonstrated the effect of Zn addition to suppress the <sup>60</sup>Co incorporation into the oxide layer. Tests were performed first under NWC conditions, that was the common strategy for BWRs in the early 80's, and later under HWC. One of the first findings was that Zn-prefilmed coupons did not show any <sup>60</sup>Co suppression if no Zn was added to the water, therefore, a continuous addition of Zn was necessary to obtain this effect [Marble, 1986].

The results of the test in this active loop extended from 1986 to 1994, are shown in Figure 3-4. Test covered the different water chemistry approaches that were developed along these years, that is NWC, HWC and even NMCA. The results show a clear effect of Zn on suppressing the <sup>60</sup>Co build-up under NWC conditions and a more dramatic effect under HWC and NMCA. The test showed that SS-304 and SS-316 showed the same behaviour.

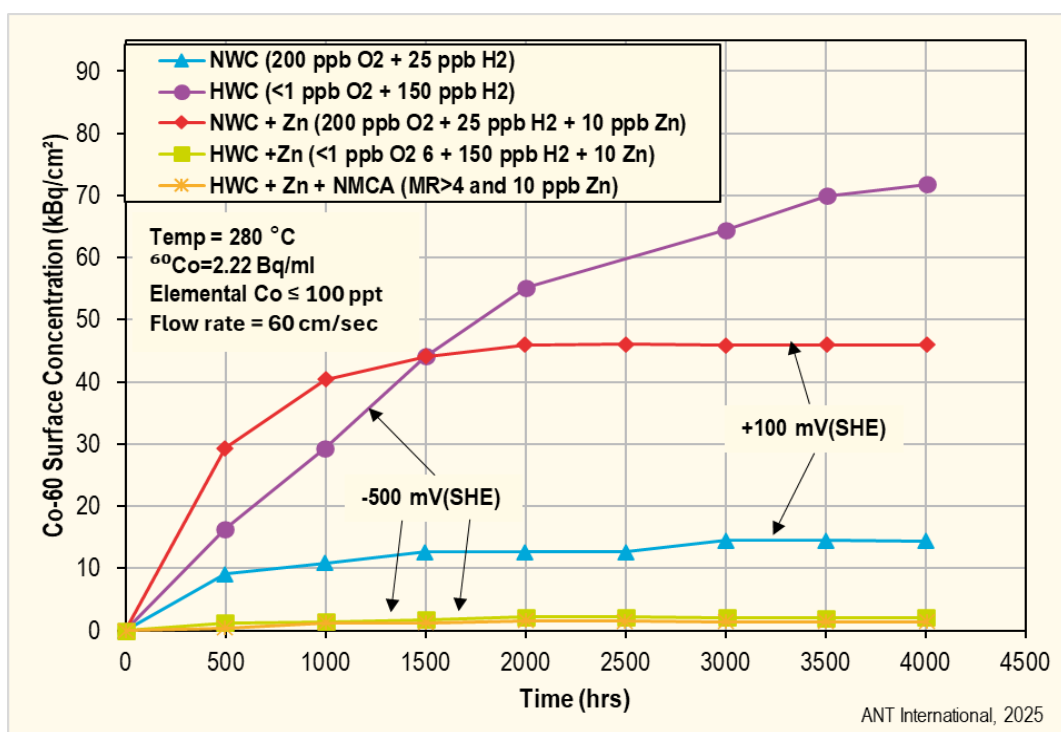


Figure 3-4: GE-VNC <sup>60</sup>Co loop results circa 1984-94, modified according to [Lin et al, 1988a and b] and, modified according to [Lin et al, 1996].

Additional information from this research, very important for the understanding of the Zn effect mechanism, was the characterization of oxide films generated under the different chemical conditions, such as composition and film thickness for 2000 hours exposure, confirming the significant reduction in thickness when Zn is in the water under oxidizing conditions (NWC), whereas, under reducing conditions (HWC) the film thickness reduction is not the key parameter for the <sup>60</sup>Co incorporation to the film as film thickness is similar with and without Zn (Table 3-1).

Table 3-1: Oxide film thickness and major chemical elements for the tests in Figure 3-4 [Lin et al, 1988a and b]

Water chemistry conditions	Film thickness, Å	Fe (%)	Cr (%)	Ni (%)	Zn (%)
NWC	4000	68	20	10	0.1
NWC + Zn	500	40	35	8	14
HWC	400	45	40	12	0.1
HWC + Zn	400	40	40	10	8
base metal	0	70	18	10	0.1

The key factor is the film composition and the crystal structure (Table 3-2). For the non-zinc case, the NWC outer surface is composed of both a spinel structure ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and a non-spinel hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). When zinc is present, a zinc ferrite phase begins to form, essentially making a ferrite by substituting into the divalent sites in the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. This substitution occupies sites favoured by <sup>60</sup>Co in the matrix. Under HWC condition, without zinc present, magnetite and some substituted spinel can form with a chrome rich layer underneath. The result is a magnetite surface layer that has more sites for <sup>60</sup>Co and, without any competition, the resulting dose rate is higher, a fact later observed in operating BWR. Under reducing HWC conditions, with 10 to 15 µg/kg zinc present in the water, the spinel on the outer surface is fully enriched with zinc and effectively excludes most <sup>60</sup>Co from incorporating into the film, resulting in greatly reduced <sup>60</sup>Co incorporation.

Table 3-2: Crystal structure in oxide films formed under NWC and HWC from [Niedrach, 1980] and [Lin et al, 1994].

Oxide layer	NWC	HWC	NWC + Zn	HWC + Zn
Outer layer				
(Large Particles)	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	MFe <sub>2</sub> O <sub>4</sub> or Fe <sub>3</sub> O <sub>4</sub>	(M <sub>n</sub> +Zn <sub>n-1</sub> )Fe <sub>2</sub> O <sub>4</sub>	(M <sub>n</sub> +Zn <sub>n-1</sub> )Fe <sub>2</sub> O <sub>4</sub>
(Intermediate particles)	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	MCr <sub>2</sub> O <sub>4</sub> and Cr <sub>2</sub> O <sub>3</sub>	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	(M <sub>n</sub> +Zn <sub>n-1</sub> )Cr <sub>2</sub> O <sub>4</sub> and Cr <sub>2</sub> O <sub>3</sub>
Inner Layer	FeCr <sub>2</sub> O <sub>4</sub> through MFe <sub>2</sub> O <sub>4</sub>	FeCr <sub>2</sub> O <sub>4</sub> through MFe <sub>2</sub> O <sub>4</sub>	FeCr <sub>2</sub> O <sub>4</sub> through MFe <sub>2</sub> O <sub>4</sub>	FeCr <sub>2</sub> O <sub>4</sub> through MFe <sub>2</sub> O <sub>4</sub>

### 3.1.2 Plant qualification and demonstration

The following steps was to determine the optimum Zn concentration to minimize the <sup>60</sup>Co incorporation. Based on new test [Marble, 1986] and the experience of “natural zinc” plants (3 to 20 µg/kg in RW), it was established a concentration around 10 µg/kg or less in case of HWC.

Next, a qualification process needed to be performed to make sure that no undesirable effects could be promoted. The main areas of concern were:

- Effect of zinc on fuel deposits that could cause an adverse effect on fuel performance,
- The effect of <sup>65</sup>Zn (produced from n →  $\gamma$  of <sup>64</sup>Zn) on radwaste activity, shut down dose rates and isotopic release during shutdowns,
- The general corrosion and IGSCC response of reactor materials with zinc in the water



## 4 Effectiveness of Zinc Injection in Controlling Shutdown Dose Rates

### 4.1 Background

Shutdown dose rates are directly related with the Occupational Radiation Exposure (ORE) that comprises the radiation dose accumulated by station staff and contractors during all the plant situation of operation, it is called sometimes as dose personnel or collective personnel dose. 80-90% of the ORE come from shut down operations. Shutdown doses are produced by the activated corrosion products of the system structural materials that are accumulated or deposited in the internal surfaces of the components of the Reactor Coolant (RC) System. The main sources of radiation are the isotopes  $^{58}\text{Co}$ , activation product of nickel and, specially,  $^{60}\text{Co}$  produced by activation of cobalt. Nickel is one of the main components of Steam Generators (SG) tubing in PWR, as well as in stainless steels. Cobalt is the main component of the Stellite (> 60%) used mainly in RPV internals as hard-face material and in hard face of valves. Due to its long half-life and its irradiating gamma emission,  $^{60}\text{Co}$  ends up in most of plants as the main source of shutdown dose rate. Other activated corrosion products that have a role for components dose rate in shutdown are shown in Table 4-1.

Initially, the corrosion products originated in the structural materials are transported by the reactor coolant and deposited in the heated areas of fuel where they are activated by the intense core particle flux. The release of these in-core activated radiocobalts to circulating reactor coolant results in radiation build-up on out-of-core areas by its incorporation into the corrosion films [Figure 4-1].

Table 4-1: Major activated corrosion products relevant for shutdown dose rates in nuclear plants.

Nuclide	Half life	Gamma energy (%ABN)	Formation reaction
Co-60	5.27 Yrs	1173 KeV (100%) 1332 KeV (100%)	$\text{Ni}^{60} (n,p) \text{Co}^{60}$ $\text{Co}^{59} (n,\gamma) \text{Co}^{60}$
Co-58	71 Days	811 keV (99%) 511 keV (30%)	$\text{Ni}^{58} (n,p) \text{Co}^{58}$
Mn-54	312 Days	834 keV (100%)	$\text{Fe}^{54} (n,p) \text{Mn}^{54}$
Fe-59	45 Days	1099 keV (56%) 1292 keV (43%)	$\text{Fe}^{58} (n,\gamma) \text{Fe}^{59}$
Cr-51	28 Days	320 keV (9.8%)	$\text{Cr}^{50} (n,\gamma) \text{Cr}^{51}$
Zn-65	244 Days	1116 keV (51%)	$\text{Zn}^{64} (n,\gamma) \text{Zn}^{65}$
Ag-110m	250 Days	657 keV (95%) 885 keV (73%)	$\text{Ag}^{109} (n,\gamma) \text{Ag}^{110m}$
Sb-124	60 Days	603 keV (98%) 1691 keV (50%)	$\text{Sb}^{123} (n,\gamma) \text{Sb}^{124}$
ANT International, 2011			

This incorporation is in two main phases: The first phase is the adsorption of the small size particulate, colloidal and soluble corrosion products (including radio-cobalts) on the porous outer oxide layers of the structural materials and its complexation (steps 1-2 in Figure 4-2). The driving mechanism for the adsorption of the colloidal and soluble species is their surface charge and the zeta potential relative to that of the outer oxide layers. As second phase, these on surface adsorbed cations can penetrate through the pores and cracks inside of the oxide layers and can incorporate there (see steps 3-5 in Figure 4-2). The affinity for this second step depends on the spinel composition due to its Site Preference Energy.

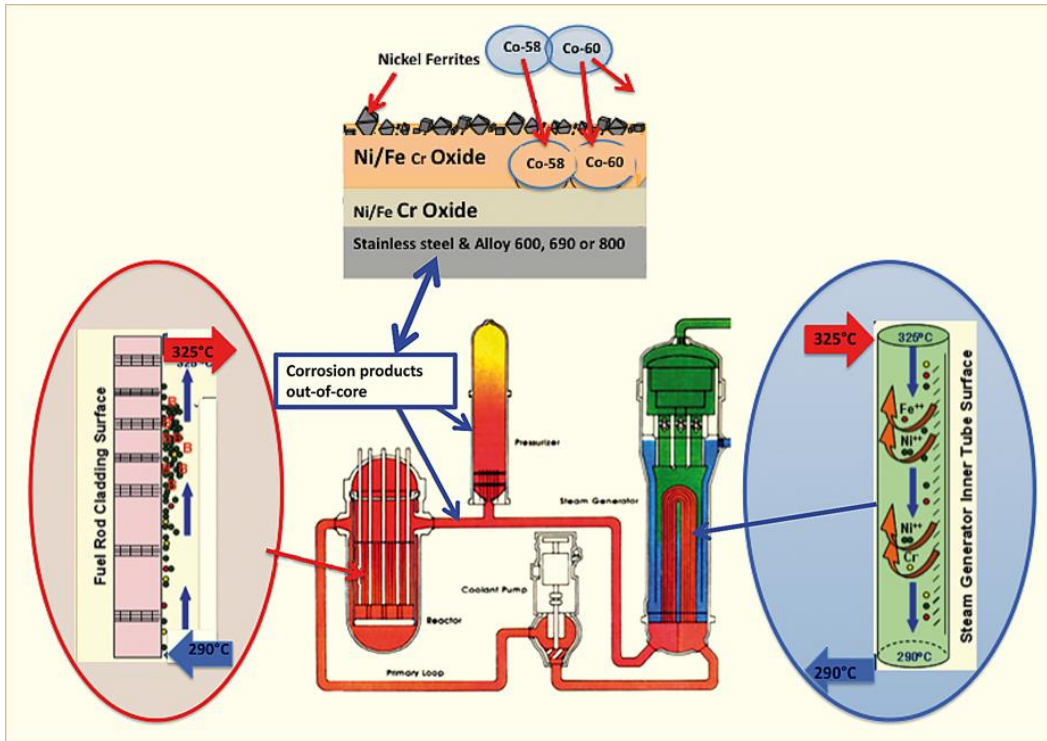


Figure 4-1: Schematic explanation of radiation build-up in PWR plants, modified according to [Odar S. 2021]

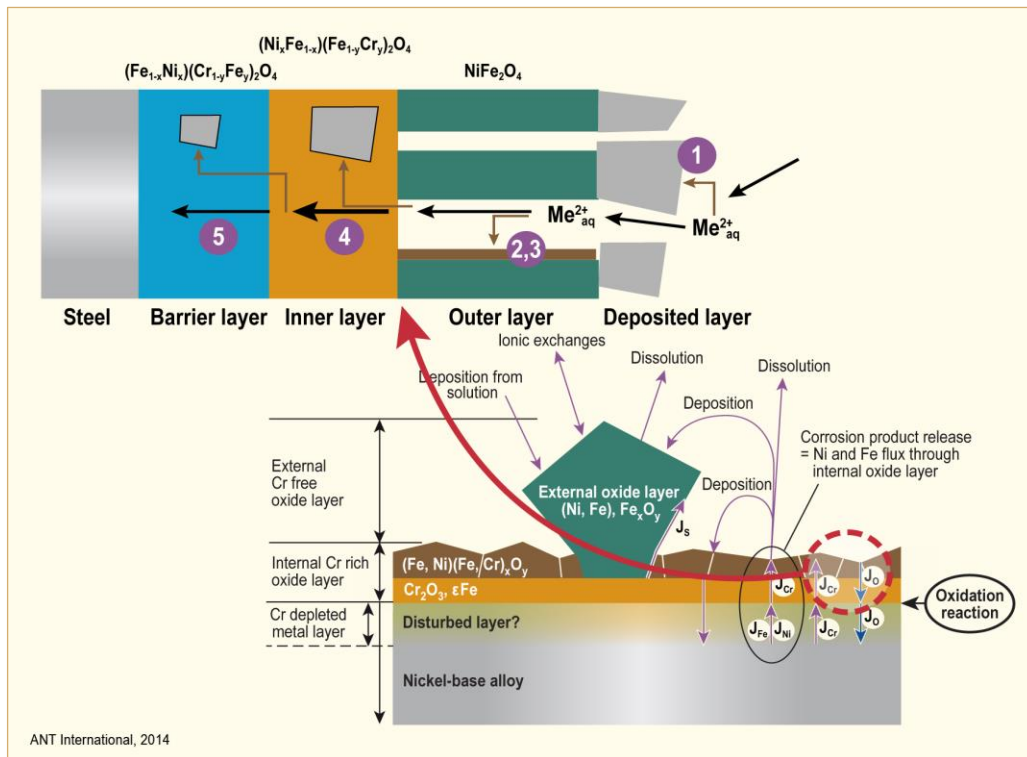


Figure 4-2: Possible steps of the reaction of interaction of a foreign cation from the coolant water with the oxide layer on structural materials. 1 – incorporation in the particulate deposited layer, 2 – adsorption and surface complexation in the porous outer layer, 3 – incorporation in the outer layer by reprecipitation, 4 – incorporation in the compact outer layer by filling interstices, 5 – incorporation in the inner layer by filling cation vacancies, modified according to [Bojinov et al., 2002] and [Combrade et al, 2005].



The major construction materials in contact with the reactor water in nuclear plants are high alloyed CrNi-Steels and Nickel based alloys. At low temperatures, these materials have a very low corrosion rates because of the formation of the passive oxide layers that protect them. The thickness of these low temperature passive layers is in the range of several nanometres and their chemical composition is chromium rich. With increasing temperature above 150 °C the general corrosion rate of these metals increase [Winkler & Lehmann, 1985] because the passive oxide layers become thicker and more porous but still protective. The composition and thickness of these protective layers depends on different factors, like the chemical composition of the base material, environmental conditions like the ECP, pH and temperature of the medium to which they are exposed. The thickness of these protective oxide layers is in the range of several hundred nanometres.

At plant power operation temperature, 285-330 °C, a dual layer is formed. The existence of duplex oxide layers is a result of different diffusion rate of the cationic substituents of the alloy or steel through the inner protective oxide layer. The inner oxide layer grows at the interface oxide and metal as the water penetrates through the pores and cracks in the oxide layer to the metal surface, where it reacts with the metal ions to build oxides. This inner oxide layer grows mainly by anion mass transport towards the oxide metal intersection although there is clearly iron and nickel cation transport in the reverse direction. The driving force for metal cation diffusion is the metal ion concentration difference between the metal surface and the coolant. Due to different diffusion coefficients of different metal ions their diffusion rates are also different. Iron and nickel have much higher diffusion rates than chromium. Therefore, the inner part of the protective oxide layer becomes chromium-rich, whereas the outer part is iron and nickel-rich. The chromium rich inner layer is practically insoluble while the outer layer in contact with the coolant experience a growth controlled by dissolution and precipitation of iron and nickel oxides from the material and from precipitation of metal cations in the coolant that, if it is saturated, can produce larger crystals in the outer layer. Other cations in the coolant, such as cobalt or zinc precipitate or are adsorbed in the outer layer and can incorporate in the compact outer layer and, eventually, can be incorporated in the inner layer by filling cation vacancies (Figure 4-2). The affinity for the incorporation depends on the oxide film composition due to its Site Preference Energy. As we will see, cobalt (and  $^{58}\text{Co}$  and  $^{60}\text{Co}$ ) has a great affinity for the incorporation to the film as well as zinc.

## 4.2 Mechanism of Zinc Technology

The inner oxide layer and the compact outer layer environment are mixed oxides with a spinel<sup>5</sup> structure, which has a general composition of  $\text{AB}_2\text{O}_4$  with A as divalent cations, and B as trivalent cations. The unit cells within the lattice are essentially cubic in structure with 32 oxygen ions forming a face centred cubic lattice (FCC) and metal ions occupying interstitial 8 tetrahedral and 16 octahedral sites as shown in Figure 4-3 and Figure 4-4.

There are two types of spinel structure, regular and inverse spinels. In regular spinel structures the divalent metal occupies the tetrahedral sites and the trivalent metal the octahedral sites. Iron chromite,  $\text{FeCr}_2\text{O}_4$ , and nickel chromite ( $\text{NiCr}_2\text{O}_4$ ) are examples for regular spinels. In inverse spinel, the divalent metal occupies half of the octahedral sites; the trivalent metal occupies the other half of the octahedral sites and all of the tetrahedral sites. For example, magnetite and nickel ferrite have inverse spinel structures.

---

<sup>5</sup> Spinel is natural mineral that has the formula  $\text{MgAl}_2\text{O}_4$  and gives name to a group of minerals with the same cubic structure.

## 5 Effect of Zinc on Corrosion and SCC

### 5.1 Background and Laboratory Research

As we have seen in previous chapters, the presence of zinc in the reactor coolant results in its incorporation into the oxide layers on different materials that stabilizes the oxide film and improves their protective behaviour. Zinc addition reduces the general corrosion [Figure 5-1] and thus, the release of corrosion products from the primary system materials. This has been confirmed by different autoclave exposure and electrochemical tests [Guo et al. 2023]. The compatibility program for zinc in BWR included general corrosion tests that were mentioned in Section 3.1.2. Regarding PWR, the general corrosion and materials compatibility will be developed in more detail in next Section 5.3.1.

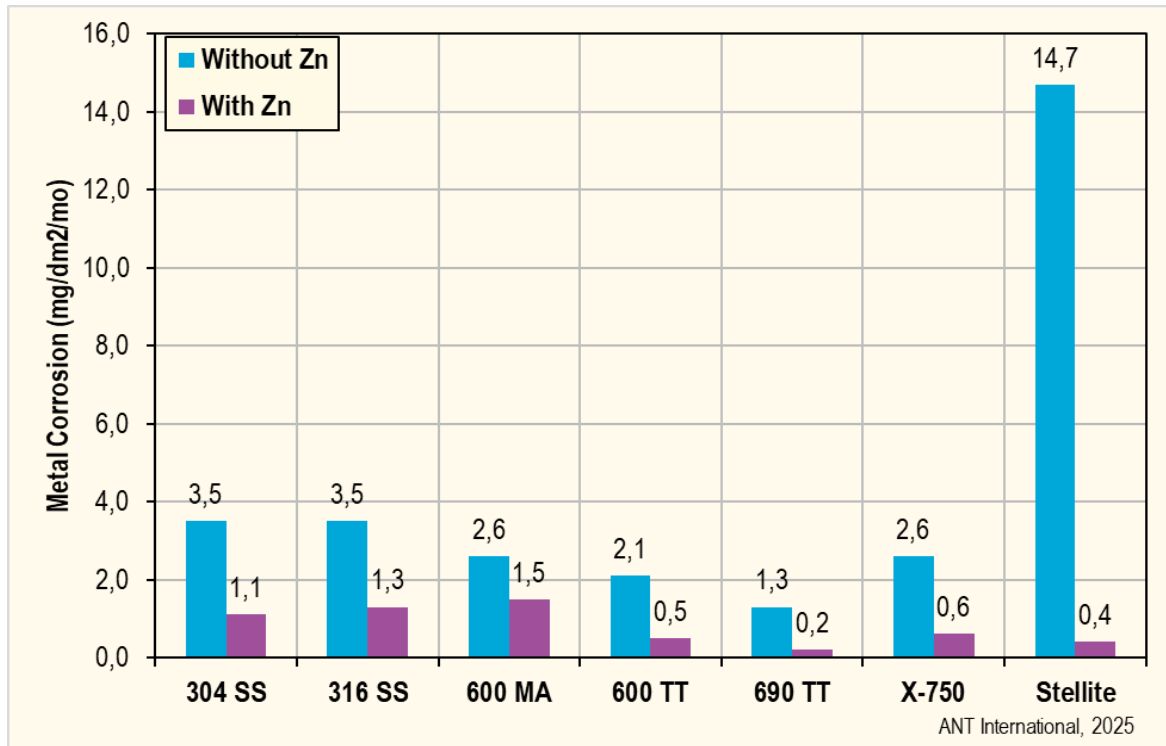


Figure 5-1: Effect of zinc addition on the general corrosion rates of PWR construction materials, (modified according to [EPRI, 1990] and [Esposito et al, 1991]).

Concerning SCC, the thin, adherent and stable layer generated by the presence of Zn is expected to benefit the SCC initiation both in SS and in Ni based alloys, in BWR and PWR. This was observed first in the qualification tests for Zn addition in BWR performed by General Electric in SS under NWC in CERTs and creviced bent beam (CBB) tests [Aldred, 1985] and under HWC using Compact Tension (CT) fracture mechanics specimens and Double Cantilevered Beam (DCB) specimens [Andresen & Diaz, 1992]. Regarding IGSCC crack propagation, materials tested were type 304 SS, Alloy 600 and Alloy 182, all sensitized at 288°C and under NWC (ECP in the +100 mV<sub>(SHE)</sub> range) and HWC conditions (ECP in the -500mV<sub>(SHE)</sub> range) with Zn additions of 5 to 10 µg/kg. Some benefits were found for NWC conditions, but for HWC it was clearly demonstrated a positive effect, as shown in Figure 5-2 with reductions in crack growth rate (CGR) of a factor 5 for 304 SS and a factor 2 for Alloy 182 and Alloy 600. In both cases, when the environment turned to be absent of Zn, the CGR rose slowly.

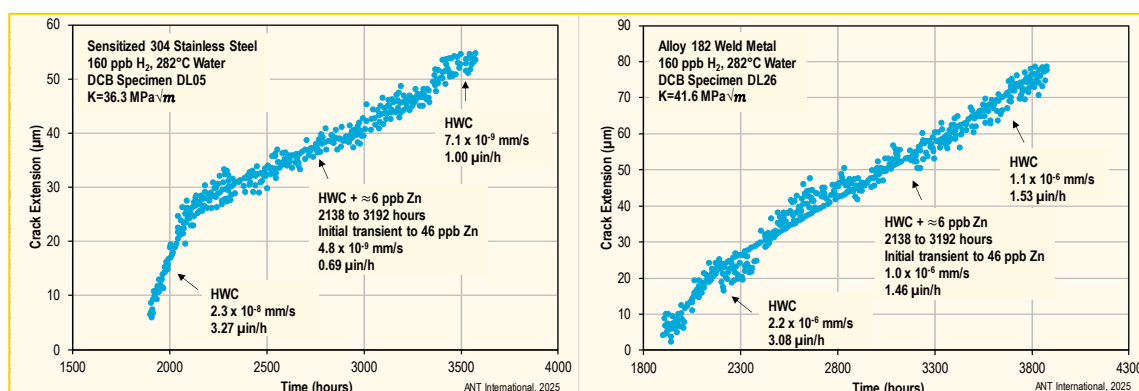


Figure 5-2: **(Left)** Crack length vs. time for sensitized Type 304 stainless steel DCB specimen showing the effect of transitions to and from 6 µg/kg Zn in 282 °C water containing 160 µg/kg H<sub>2</sub> at an ECP of -550 mV<sub>(SHE)</sub>. **(Right)** Crack vs. time for sensitized Alloy 182 DCB specimen showing the effect of transitions to and from 6 µg/kg Zn in water containing 160 µg/kg H<sub>2</sub> at an ECP of -550 mV<sub>(SHE)</sub>, modified according to [Andresen & Diaz, 1992].

Even more, in the early 90's, General Electric investigated the "Low Impact Synergistic Zinc" strategy to find a mitigation method that coupled the apparent IGSCC reduction properties of Zn with lower levels of hydrogen addition that gave less than an increase factor of 2 in main steam line operating dose rates. This strategy was formally dropped in 1994, as the results were inconclusive and the required Zn levels were not acceptable (>100 µg/kg) [Cowan & Kiss, 1993]

For PWR, the Westinghouse laboratory studies on the initiation of PWSCC in nickel base alloys under simulated PWR primary coolant conditions [Esposito et al, 1991] confirmed the positive effect of Zn. Highly stressed Reverse U-Bend (RUB) specimens of thin-walled Alloy 600MA, 600TT and 690TT SG tubes were tested under simulated BOC PWR coolant conditions with (20 and 120 µg/kg Zn) and also without zinc addition. The results of these tests indicated a significant reduction of PWSCC initiation time in the Alloy 600 heats (see Figure 5-3 for the results at 20 µg/kg Zn). Overall, reported factors of improvement in terms of PWSCC initiation time have ranged from ~ 2 (for 20 µg/kg Zn) to greater than 10 (for 120 µg/kg Zn). Based on these results, the authors concluded that to mitigate the PWSCC initiation, higher coolant zinc concentrations are needed than those used for radiation field reduction. These tests indicated also a reduction of crack depth.

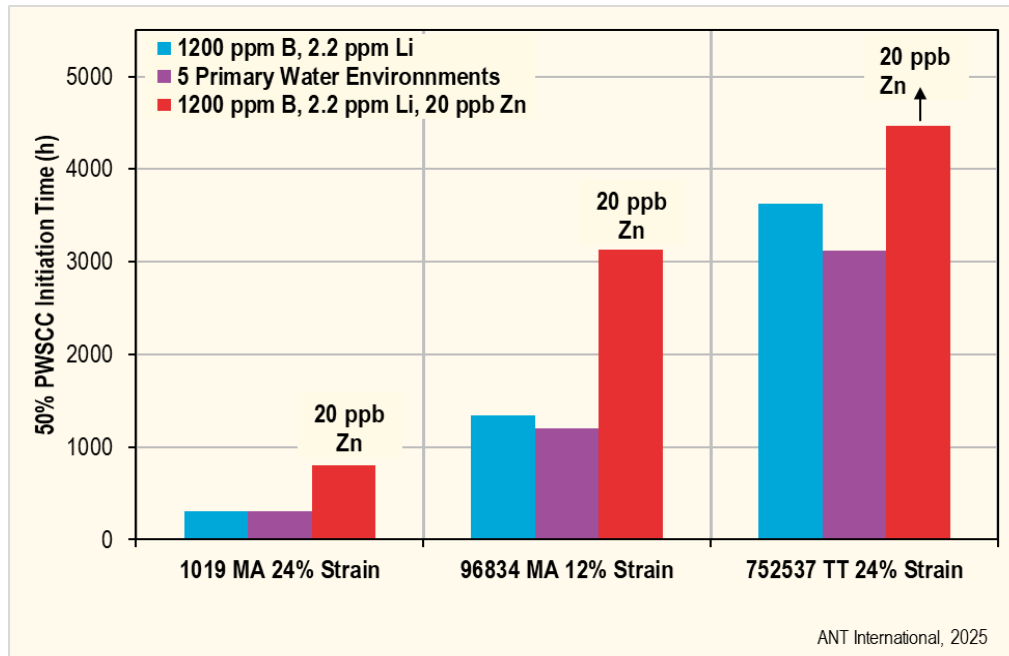


Figure 5-3: Effect of zinc on time to initiate PWSCC in Alloy 600MA (heat 1019, 96834) and Alloy 600TT (heat 752537), modified according to [Esposito et al, 1991].

In recent paper by Paul Scherrer Institute (PSI) that makes a recompilation of the research results on Zn addition [Guo et al. 2023], it is highlighted that there are no direct or quantitative studies that systematically investigate the effect of Zn concentration on the SCC initiation behaviour of Alloy 600 or other nuclear structural materials. From the review, it is expected that a sufficiently high Zn concentration in high temperature water will be able to mitigate SCC initiation due to the thinner and more protective Zn treated oxide films formed. In fact, recent results of ongoing research at PSI showed that Alloy 182 presents a higher SCC initiation resistance both, in BWR-HWC and PWR chemistries, even down to 15 µg/kg Zn [Chen, 2023] on CT specimens subject to a systematic combined slow rising-constant load test. In these experiments, they confirmed a CGR reduction at 15 µg/kg Zn and no benefit of rising the Zn concentration to 40 µg/kg Zn.

## 6 Effects of Zn Addition on Fuel Performance

### 6.1 Background

Based on more than 35 years of LWR field experience with zinc injection, no direct effect of zinc on fuel cladding corrosion has been reported. This is also not expected based on the evaluation of all in-pile data and out of pile loop tests with respect to material compatibility of zinc injection [Kawamura et al., 2003]. Injection of zinc into reactor coolant causes release of corrosion products from RCS surface oxide layers, which results in increase in coolant iron and nickel concentrations. This increased corrosion product concentration may result in an enhancement of deposits on fuel rods.

Corrosion products in the reactor system trend to deposit in layers on the hot surface of fuel cladding; this is what is traditionally called CRUD. These layers have physical structures that may vary from dense layers to porous ones. The porous layer types can vary as well and be fluffy loose deposits, dense structures with pores and cracks, relatively loose deposits with convective coolant chimneys (wicks), all of which have a different thermal conductivity. The characteristic and morphology for these layers depends on the elemental composition, the temperature and the chemical environment, oxidizing or reducing. Zn, as a specie that interacts with the oxide layers deposited on fuel cladding can have an impact on the layer composition and its mechanical properties, as well as being an additional load of species prone to deposit on surfaces. As a short summary, the possible impacts of crud are as follows:

- A local environment formation: The high voidage (during boiling) of the crud will permit it to form a local environment since enrichment in the constricted water may occur. This is described as a “hide out” mechanism: In certain circumstances, chemical species soluble in the coolant may enrich or deposit in the CRUD and will be released when the heat flux is lowered. An example of this phenomenon is the Axial Offset anomaly (AOA).
- An increase in thermal resistance due to insulation of the crud: This causes an increase in cladding surface temperature. More drastically, a steam pocket formed in the cladding oxide/crud layer will increase surface temperature much more than crud or oxide alone (steam blanketing, Figure 6-1).

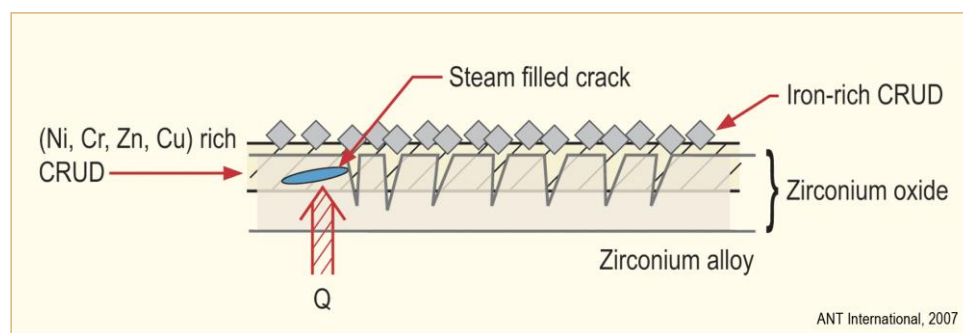


Figure 6-1: Schematics showing “steam blanketing”, steam filled cracks leading to a dramatic increase in fuel clad temperature [Rudling et al, 2012].

As an example, a small steam gap ( $\sim 15 \mu\text{m}$ ) can raise the nominal  $295^\circ\text{C}$  clad surface temperature to over  $550^\circ\text{C}$  within the typical range of LWR operation, thereby accelerating the corrosion rate (Figure 6-2).

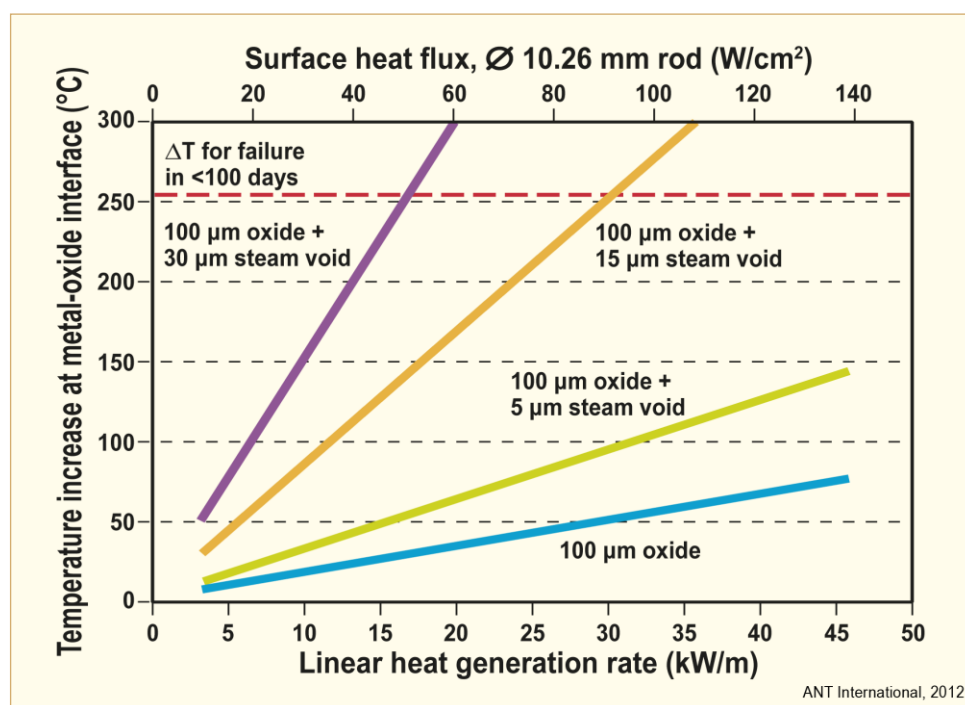


Figure 6-2: Temperature increase at cladding surface relative to LHGR and steam void (BWR conditions), after, Patterson in [Rudling & Patterson, 2009].

- The crud as a parasitic absorber of neutrons: Elements such as e.g. Fe, Ni and Cr absorb thermal neutrons to a much larger extent than Zr. More drastically, if Boron is retained.
- Crud deposits can produce a flow restriction in the fuel assembly: The increased coolant pressure drop will reduce the coolant flow and may reduce the elevation at which boiling starts. If flow is sufficiently impeded, cooling can be insufficient and leading to fuel overheating due to dry-out (BWR) or departure from nucleate boiling (DNB) (PWR).

Zinc in reactor coolant can incorporate in crud resulting in a densification of the deposits and, in the first stages of the application, Zn promotes a redissolution of Ni and Fe by its substitution in the spinel oxides deposited in the external surfaces. In general, the operation with thicker crud layers without enhanced cladding corrosion indicates that the assumed thermal properties usually are much better due to a permeable, porous deposit structure. This can be explained by the mechanism of “Wick Boiling”:

Most of crud is deposited on the heat transfer-boiling region of fuel, which indicates that boiling is the driving mechanism for deposits. According to the Tentative Boiling model, as illustrated schematically in Figure 6-3(a), once the steam bubbles grow (1), the colloidal CP particles are trapped at the steam-water interface (2). These particles then move downwards to the heated fuel rod surface (3), where they deposit as the steam bubble with high speed grows and disappears (4). The deposition is similar for nucleate and sub-cooled boiling, although faster for nucleate boiling. Once the particles come sufficiently close to each other they form agglomerates by the “van der Waals” forces. The crud deposits grow one layer after the other. As the deposit thickness increases the boiling turns into so called “Wick Boiling”, where the water with soluble species penetrates into the oxide layers through capillary pores to the Steam Chimney (see Figure 6-3(b)). There, the water evaporates and leaves the chimney, whereas the soluble species are concentrated. BWR as well as PWR fuel contain lots of such chimneys looking visually like pores in the oxide surface (5000 per mm<sup>2</sup> [Macbeth, 1971]). These steam chimney pores enhance the heat transfer from the fuel rod into coolant and thus reduce drastically the thermal resistance of the crud layer. Due to these pores, the fuel deposits are porous with less density and high voidage. The estimated density of the PWR fuel deposits is in the range of 1.2 g/cm<sup>3</sup>, [Hazelton, 1987] and the total voidage due to chimneys is approximately 10% [Macbeth, 1971].

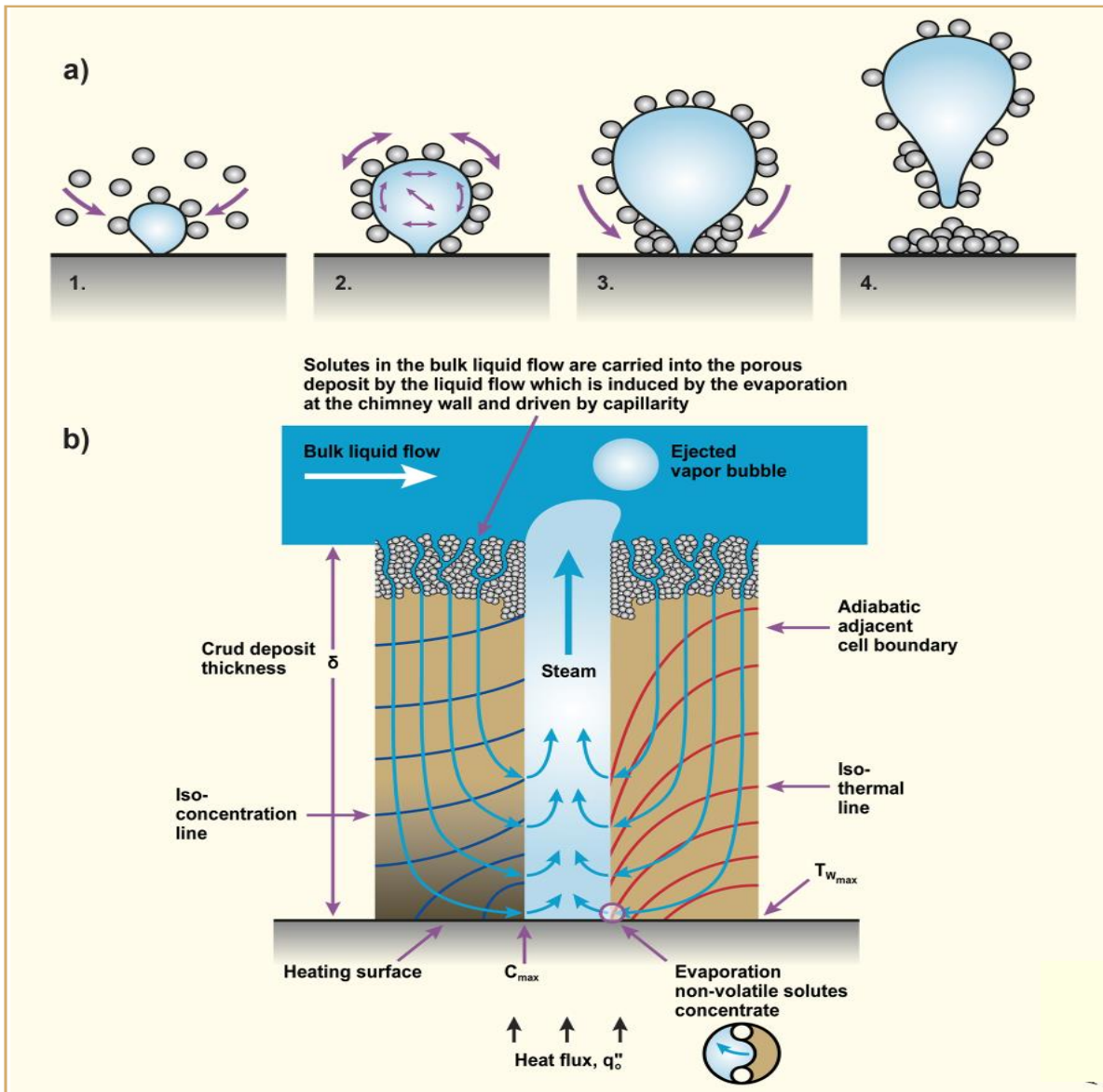


Figure 6-3: Fuel deposits: (a): Formation of deposits according to Tentative Boiling Model; (b): Principle of Wick boiling, modified according to [Iwahori et al, 1979] and [Pan et al, 1985] respectively.

Recently, in a lab experiment in Korea, crud was synthetically generated on a Zr-Nb-Sn alloy at different corrosion products concentrations and it was found a pore density between 4-19.000 per  $m^2$  depending on CP concentration. The thermally enhanced characteristics of the CRUD layer were demonstrated and quantitatively determined [Lee Y. et al. 2023], see Figure 6-4 .

## 7 Impact of Zn Additions on Radwaste Production

### 7.1 BWRs

During the initial evaluation of Zn injection in BWRs, a review of NRC records showed that 'natural zinc' plants were shipping significantly less activity of radwaste and, in particular, 4 to 5 times less  $^{60}\text{Co}$  "curies"<sup>11</sup> [Marble, 1986] than "regular" BWRs. The  $^{65}\text{Zn}$  isotope was present in the radwaste (from 6 to 30% of the activity content) but trading it for  $^{60}\text{Co}$  "curies" was concluded to be a net positive because of its shorter half life (276 days vs. 5.27 years for  $^{60}\text{Co}$ ) and because of the lower energy of  $^{65}\text{Zn}$  radiation. From a shutdown radiation point of view, even if the only effect of zinc injection was trading  $^{60}\text{Co}$  in the corrosion films for equal amounts of  $^{65}\text{Zn}$ , the effect would be reduced dose rates. Release of  $^{65}\text{Zn}$  during shutdowns was not reported as an issue at 'natural zinc' plants and radwaste from water cleanup during outages indicated nothing unusual [Marble, 1989].

Actual experience with Zn injection showed that it reduced the level of  $^{60}\text{Co}$  in the reactor water because the  $^{60}\text{Co}$  was more tightly bound to the fuel deposits. Thus, the  $^{60}\text{Co}$  activity in radiation waste associated with water treatment decreased significantly, only partially offset by an increase in  $^{65}\text{Zn}$  activity. With the introduction of DZO as the Zn source, even this source of activities was eliminated.

Any effect of Zn is also 'confounded' because of the introduction of mHWC, NMCA and OLNC soon after Zn implementation at many BWRs.

The one possible negative effect that Zn injection could have on radwaste shipments is the increased release of  $^{60}\text{Co}$  and other radioisotopes during plant shutdown, but, once more, it is "confounded" by the introduction of HWC and, with more impact, NMCA and OLNC. The increased level of clean-up flow and resins usage to achieve desired refuelling outage levels of isotopes in the cavity water should produce more retained activity (and possibly more volume) of waste. However, no quantification of this effect was found.

According to Dr. Cowan in the LCC6 report on Zn [Cowan et al. 2010], "A search of the literature and a significant number of personal enquires of those technically active in the field have revealed no additional sources of information on this subject. If Zn injection was causing any issues in the radwaste area, it would certainly have surfaced in the technical community. The author's hunch is that the use of Zn injection had a small positive impact on overall radwaste issues but the effect has been ignored"

*The author of this report fully confirms Dr. Cowan's assessment at present time of this report.*

### 7.2 PWRs

The field experience confirmed that, in spite of increased CP concentrations and radiocobalt activities in the reactor coolant that are caused by zinc addition, neither the operational performance of the CVCS demineralisers and filters nor their service life time was significantly affected by zinc injection. Although in some PWR plants with nickel base alloy SG tubes some increased replacement of mechanical filter cartridges during the first zinc addition cycle was reported, this filter usage returned during subsequent RFOs to pre-zinc injection levels. An adverse change of the resin clean-up kinetic by zinc was also not experienced, which may result in increased time needed for coolant clean-up during the critical path of the plant shutdown.

Concerning liquid waste effluents, the addition of zinc supposes a net input of water to the primary system, and it causes a comparable removal of coolant to compensate it. However, the injected zinc solution is a negligible part of the amount of coolant that must be removed for boron dilution to compensate the fuel burn-up.

---

<sup>11</sup> Curie (Ci) is a traditional unit of activity, still used regularly in the USA. 1 Ci = 37 GBq



EdF has investigated the impact of zinc at Bugey-2 plant since its implementation and have reported results after 3 and 6 cycles [Tigeras, 2010] and [Piana, 2014]. Based on these results, EdF confirmed that zinc addition at Bugey plant has not caused any significant changes even in the detailed isotopic distribution in the liquid waste effluent (Figure 7-1). They confirmed further that the level of the liquid released activities remained unchanged since zinc injection, and there have been no problems with regard to the operation of CVCS purification system in presence of zinc.

Additionally, concerning contaminants in liquid discharges, EdF has confirmed that zinc injection has not had any significant impact on the presence of zinc in the liquid effluents of their Zn plants [Philippot, 2018]

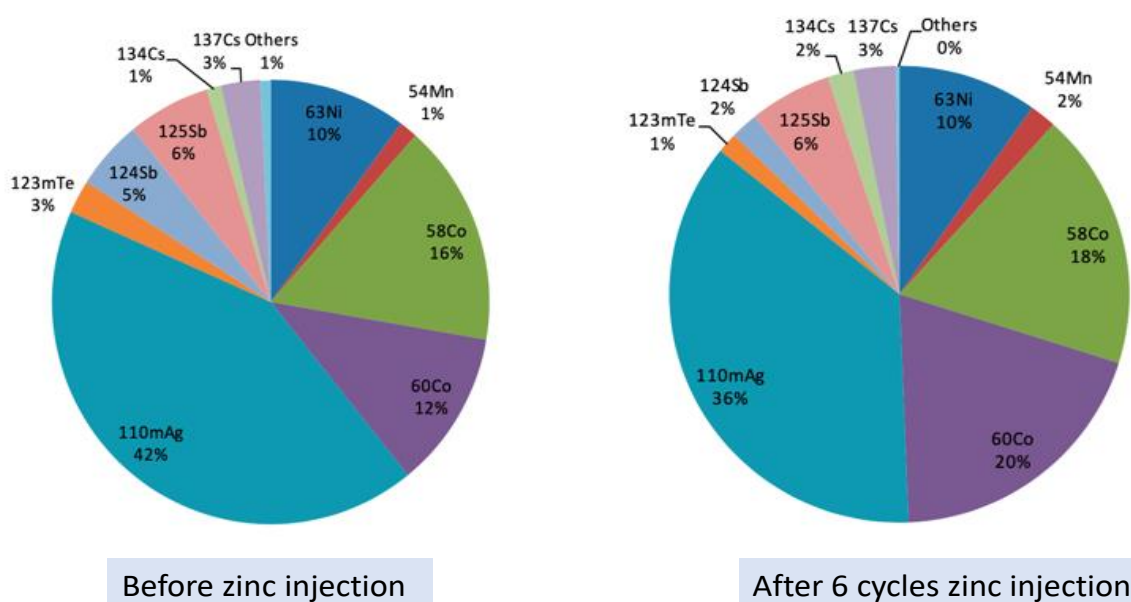


Figure 7-1: Isotopic distribution in liquid effluents at Bugey PWR before zinc injection and after 6 fuel cycles of zinc injection, modified according to [Piana, 2014]

Regarding spent resins in the CVCS, zinc causes an additional loading of cations (Zn, Fe, Ni), anions (carbon dioxide from acetate) and activated CPs ( $^{58}\text{Co}$ ,  $^{60}\text{Co}$  and  $^{65}\text{Zn}$  particularly if natural zinc is used) to the resins in the CVCS letdown demineralizers. However, field experience confirmed that, up to date, in none of the zinc addition US PWR plants demineralizers had to be replaced earlier than plants experience neither due to exhaustion nor due to unacceptable high activity or pressure drop,  $\Delta p$ , [EPRI, 2006a]. EdF also published their experience in NPC 2014 as follows [Piana, 2014]: The total amount of spent filters, spent resins and concentrates produced over different cycles with zinc injection is similar to cycles prior to injection and corresponds to the average value for EdF units. There is a low increase in several units but this is not a general trend.

Due to increased radiocobalt concentrations in the reactor coolant, there will be more radioactivity in the demineralizer resins that may result in increased cost for spent resin disposal. For the case of EdF plants, it will require a modification of the standard spectrum for the package type isotopic distribution and the need for, temporarily, perform measurements on each waste package to ensure the accuracy of the radiological characterization. This must be taken into consideration for packaging, shipping and burial.

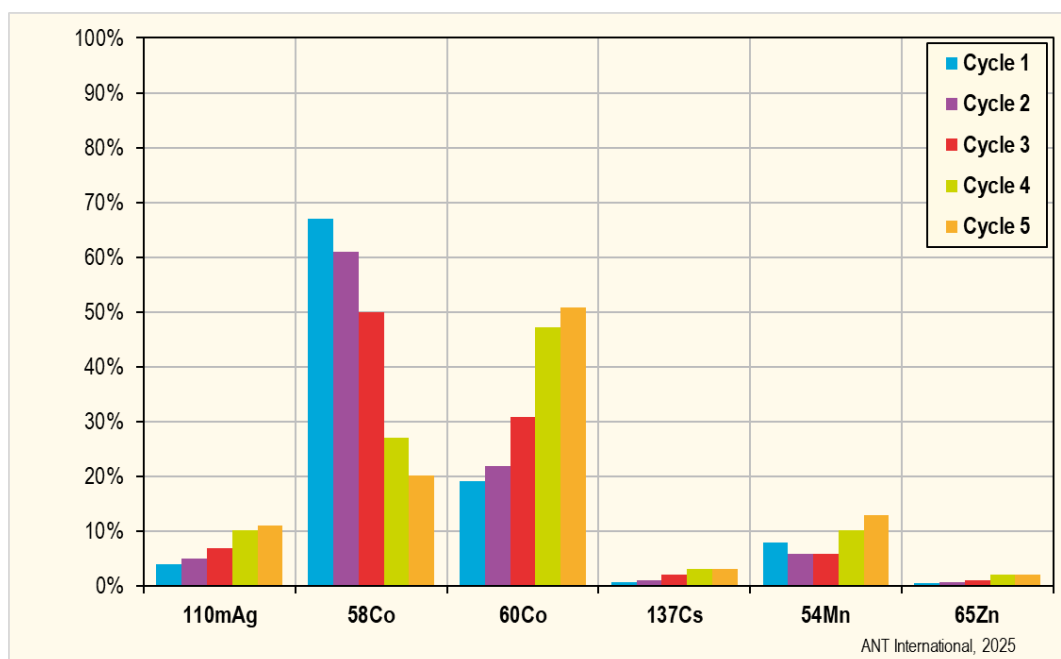


Figure 7-2: Evolution of the main radionuclides distribution in the waste packages from purification filters of the primary system during the first 5 zinc injection cycles at an EdF plant, modified according to [Philippot, 2018]

The impact of zinc addition on filter performance has been mixed and highly plant specific. The use of sub-micron (mesh size) filters, and the concentration of zinc in the reactor coolant appear to be the major influencing factors. In most cases, increased CP concentrations in the reactor coolant as a result of zinc injection have not caused an increased CVCS filter usage. Plants like Farley-2, and Diablo Canyon reported filter clogging or increase of filter usage, but this situation returned to pre-zinc levels after two cycles. In the long term, it can be expected that the filter usage even reduces due to stabilization of out-of-core surface films, which results in reduced corrosion rates and metal release rates of the materials exposed to reactor coolant.

In NPC 2010, EdF confirmed that the total amount of spent CVCS filters and spent demineralizer resins produced over three cycles with zinc injection at Bugey plant is similar to that produced during cycles before zinc injection and corresponds to the average value for EdF 900 MW units [Tigeras, 2010].

Based on the lack of available conclusive data on filter usage, it is recommended for the first two fuel cycles with zinc injection to consider several more spare filters. If necessary, the criteria for filter replacement should be modified to have maximized criteria with respect to dose rates and differential pressure to avoid frequent filter change-out.

Concerning the solidified waste generation, the increase in radioactivity after zinc addition may result in an increased number in solidified waste drums, as the increase in radioactivity may exceed the allowed maximum activity or contact dose rate. However, according to EdF, the experience at Bugey plant indicates that the total amount of nuclear waste concentrate produced over six cycles with zinc injection has not changed.

In summary, based on published field experience, there was up to date no such increase of solidified radwaste amount or drums due to zinc injection. However, this issue is highly plant specific and depends on the spent resin or solidified waste handling policy applied at individual plants such as:

- Mixing of other resin or waste sources of less radioactivity to optimize the waste volume,
- Waste/spent resin storage for decay.

Based on current PWR field experience, it is not expected that zinc addition may have any significant impact on the amount and volume of treated radwaste.

## 8 VVER experience

The radiation situation in VVER units is among the lowest in the world. This is due to good corrosion resistance of SG stainless steel tubing, to reduced cobalt content in all primary circuit materials, and to avoidance of the use of highly resistant cobalt alloys (Stellites) in valve seats. VVER reactors are operating at lower temperatures than PWR reactors, which can play a role in the transport of activity in the primary circuit.

Despite the above, it is in the interest of operators to use zinc to reduce activity transport. Western PWR and BWR reactors widely utilize zinc injection, with excellent results. The goal of operators is to maintain low levels of Operational Radiation Exposure while also extending power station life and, at the same time, resolve the situation in some VVER units where staff radiation dosage levels continue to be high.

Most of the information made public on Zn addition for VVER reactors was collected by Jan Kysela for LCC6 zinc report presented in 2011 [Cowan et al. 2010] and it was also compiled in the subsequent LCC16 ANT report, by Suat Odar [Odar, 2021]. The information given in these reports is limited to laboratory and loop testing results. So far publicly known, as of now, zinc addition has not been applied in VVER plants. Since the Kysela's report only a few new research reports on Zn in VVER plants are made public, all in predicting or modelled calculations of Zn behaviour in these reactors. The VVER TOI design is the new advanced VVER plant which is designed to enable zinc injection in its coolant chemistry program, but the leading plant, Kursk-II, is under construction in a region near the Ukraine-Russia War scenario, although its commissioning is planned for 2025, according to a draft report on "The Unified Energy System of Russia" [WNN, 2024].

For detailed information on the laboratory and experimental reactor water loop testing on Zn in VVER conditions, as well as comparisons of CP surface activities and coolant concentration of VVER reactors and western PWR we refer to the mentioned LCC6 and LCC16 zinc reports.

The conclusions and recommendations from these mentioned reports are as follows:

1. As we have seen in section 2.3, VVER reactors differ from PWR in the SG design (horizontal tubing as opposed to vertical in PWR reactors), different materials (SGs are made of 18%Cr-10%Ni, Ti stainless steel, and fuel is clad with Zr/Nb alloys) and water chemistry, which in a VVER uses an alkaline agent (KOH) and ammonia, whose decomposition results in radiolytic hydrogen.
2. VVER stations have excellent CP behaviour, which produces low primary circuit radiation fields, low Co-58 and Co-60 surface activities, low circulating nickel and cobalt concentrations in primary water and generally low dose rates and operational personnel doses.
3. Zn injection has a significant effect on the oxides formed in PWR/VVER coolant, altering both the thickness and the in-depth composition of the oxide. Zn incorporation seems to play an important role in the restructuring of the inner layer.
4. In the experimental reactor loop tests, the presence of zinc in deposition layers was found in plant tubes samples after exposition in zinc containing coolant. Zinc was detected in locations where the original deposition layers were continuously compact. It was not observed in deposition areas composed of crystallographically well-distinguishable oxide particles 0.1  $\mu\text{m}$  and larger. The ability to absorb zinc was not observed for a plant sample where initial surface layers were influenced by decontamination.
5. CPs behaviour in the loop coolant after zinc injection showed that cobalt activities were released to the coolant from surface. The same is observed for soluble forms of radioactive CPs. Activity was more released in soluble than insoluble form and this can show the mechanism of the process. Similar behaviour was observed at PWR plants where, after starting zinc injection, Ni and Fe content in the primary coolant was increased.
6. It can be concluded, in spite of the type of water chemistry used in primary coolant system – either Lithium/Hydrogen or Potassium/Ammonia - that the mechanism of zinc behaviour is the same: replacement of cobalt and iron in spinel crystals.

7. Final evaluation of the water chemistries (including zinc) tested at a reactor water loop was based on corrosion products measurements (soluble and insoluble), radioactivity measurement in the coolant and surface radioactivity measurements on SG tube model. The best results are, in the order: Hydrogen followed by Elevated Ammonia, Zinc and Standard Ammonia at the end.
8. Comparison of PWR channel head radiation fields with SG collector radiation at VVER is possible (in spite of the different geometry). Activities on Westinghouse PWR stainless steel surfaces are significantly higher than in VVERs, including VVER-1000 plant, that operate at a similar primary coolant temperature. This is particularly the case for  $^{58}\text{Co}$  and  $^{60}\text{Co}$ , which are typically one to two orders of magnitude higher on PWR surfaces activity. The dominant role played by  $^{60}\text{Co}$  in PWRs is absent in VVERs.
9. On VVER 1000 reactors, high-temperature filtration technology is used in the primary circuit. The effect of zinc could probably be reduced by replacement of cobalt that has accumulated over years of operation on these high-temperature filters. Frequent RCS decontamination used in VVERs can also reduce the effects of zinc injection.
10. The greatest positive effect for VVER can be expected on new nuclear reactors (AES-2006, VVER 1200) if zinc injection takes place from the beginning of their operation. Zinc injection could be of benefit on power plants already in operation with so-called small-series VVER 1000 reactors that are not equipped with high-temperature filters, and on NPPs of the VVER 440/V213 type

The latest published papers found on VVER and zinc confirm and extend these conclusions. In 2014, at NPC conference, the Ukrainian KIPT presented a paper on VVER-1000 primary chemistry optimization [Krasnorutskyy, 2014]. Among other options, zinc chemistry and its effects on SS corrosion and E110 Zirconium-1%Nb cladding alloy was discussed and tested. Corrosion tests on Ti stabilized stainless steel, series Ch18Ni10Ti, were carried out in VVER-1000 primary coolant ( $\text{H}_3\text{BO}_3$ : 3.108 g/dm<sup>3</sup>, KOH: 0.025g/dm<sup>3</sup> and  $\text{NH}_3$ : 3.0 mg/dm<sup>3</sup>), at 275-350°C for 3000 hours, with zinc added at 0,01 and 0,03 mg/dm<sup>3</sup> Zn. Figure 8-1 show the SS corrosion kinetics at 350°C and 16.5 MPa. Zinc addition to the primary system corrosion environment results in a weight gain on stainless steel, meaning that dissolution of oxide film is slowing down significantly or even stops on stainless steels Ch18Ni10Ti, concluding that zinc has a positive effect on the total corrosion of stainless steels and on reduction of cobalt content in oxide films.

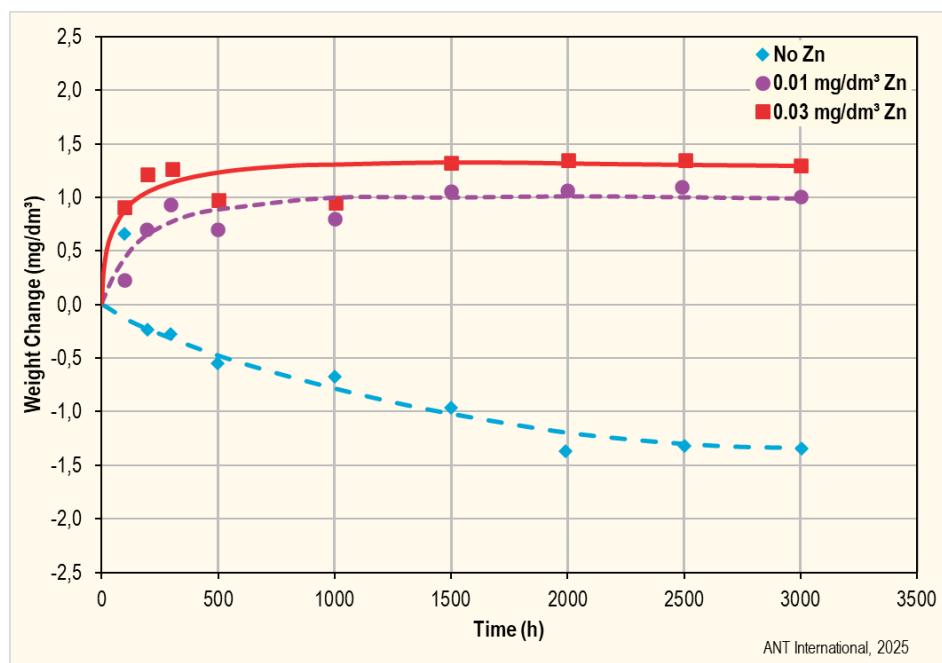


Figure 8-1: Corrosion kinetics of stainless steels Ch18Ni10Ti in WWER-1000 primary coolant model medium without Zn and with 0,01 and 0,03 mg/dm<sup>3</sup> Zn during oxidation at 350 °C, modified according to [Krasnorutskyy, 2014].

For cladding material E110 (Zr-1%Nb), similar autoclave corrosion tests at the same chemical and temperatures in typical VVER-1000 with the same Zn concentrations. The obtained results confirmed that zinc does not lead to the reduction of corrosion resistance of the zirconium in these conditions. The paper assesses that zinc in VVER primary coolant may reduce the activity of primary circuit inner surfaces due to lower amounts of corrosion products yielded into the coolant and activated in the core. As a result, the personnel dose rates will reduce and the equipment lifetime will increase. Zinc, however, may displace cobalt from oxides accumulated over a long-term operating period in high-temperature titanium filters, which will increase coolant activity. Another point is that it anticipates a less tangible effect in VVER chemistry than in PWR, as Co activity accounts for less than 50% of total activity in VVERs.

A Russian paper warns on the behaviour of Zn compounds in VVER primary systems chemistry [Kharitonova, 2018]. After analysing the different interactions of zinc with the species present in primary system, it concludes that the presence of boric acid with silicates and zinc, with the formation of borate complexes, reduce the risk of deposition of zinc silicates in the layer of deposits on the fuel rod surface, but with 20µm crud thickness, it is possible the precipitation of Zn<sub>2</sub>SiO<sub>4</sub> at 10µg/kg Zn and 1 mg/kg SiO<sub>2</sub> (maximum tolerated concentration at VVER-TOI specifications).

Another Ukrainian paper analyses the experience of Zn in PWR and estimates that the Zn addition will suppose a significative reduction of dose rate and personnel exposure in VVER-1000 [Maltseva, 2018].

Finally, at NPC 2023, NPP Dukovany, Czech Republic, showed the result of the last 12 years of monitoring the deposition of CP in its 4 VVER-440 reactors. As a result of a closed control of primary water chemistry, a decreasing trend in its already low deposition specific activity is presented, with <sup>58</sup>Co as the dominating isotope. These results show that, for some plants with this type of reactors, there is limited interest in applying Zn addition to control activity build-up.

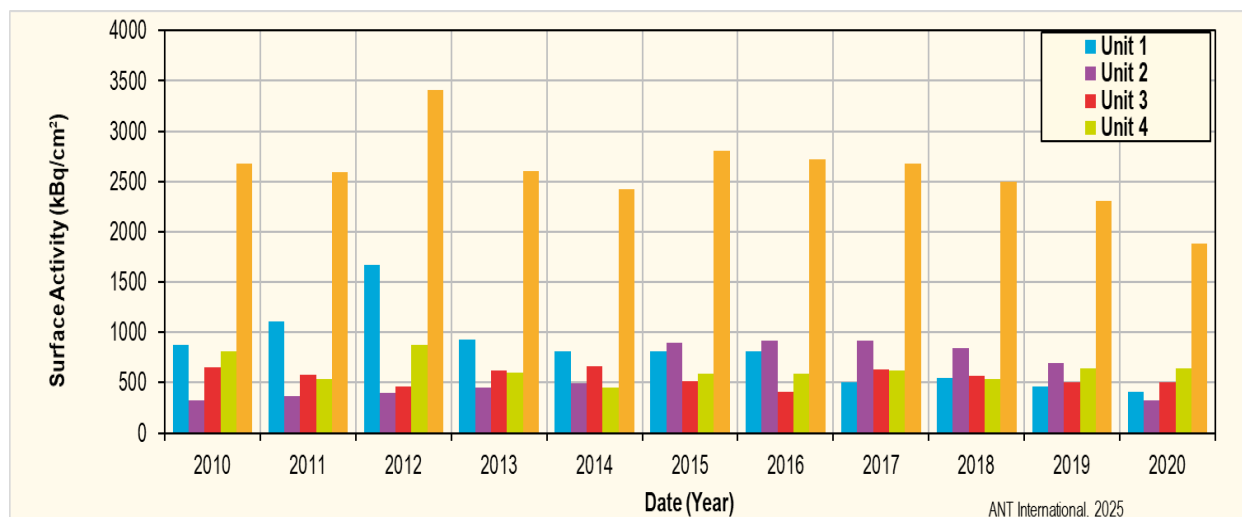


Figure 8-2: Dukovany NPP cumulated surface activity of activated corrosion products at each unit, modified according to [Kunešová & Janák, 2023]

## 9 References

- Alder H. P. and Brélaz P., *Overview of activities for the reduction of dose rates in Swiss boiling water reactors*, Water chemistry in nuclear Reactor Systems 6, BNES, London, 1992.
- Aldred P., *Materials Qualification for GEZAP/GEZIP Treatments Applied to BWR Piping and Structural Alloys*, GE Report NEDO-30962, Class I, April 1985.
- Andresen P. L., Ford P. *Life Prediction by Mechanistic Modelling and System Monitoring of Environmental Cracking on Iron and Nickel Alloys in Aqueous Systems*. Materials Science and Engineering: A 1988, 103(1), 167.
- Andresen P. L. and Diaz T. P., *Effects of Zinc Additions on the Crack Growth Rate of Sensitized Steel and Alloys 600 and 182 in 288 °C Water*, Water Chemistry of Nuclear Reactor Systems 6, Vol. 1, BNES, London, October 1992.
- Andresen P. I., Wilson J. A. and Ahluwalia K. S., *Use of primary water chemistry in PWRs to mitigate PWSCC of Ni-base alloys*, International Conference on Water Chemistry of Nuclear Reactor systems, 2006, Jeju Island, Korea, Oct. 23-26, 2006.
- Angell M. G., Allan S. J. and Airey G. P., *The effect of primary coolant zinc addition on the SCC behavior of Alloy 600 and 690*, Proceedings of ninth International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, 1999.
- Airey G. P., Allan S. J. and Angell M. G., *The effect of zinc on stress corrosion cracking of inconel Alloys*, Water Chemistry of Nuclear Reactor Systems, 7, BNES, 1996.
- Beverkog B., *The role of zinc in LWRs*, Water Chemistry Nuclear Reactor systems, San Francisco, 2004.
- Bénézech P., Palmer D. A., Wesolowski D. J. and Xiao C., *New measurements of the solubility of zinc oxide from 150 to 350 °C*, Journal of Solution Chemistry 31, p. 947-973, 2002.
- Bojinov M., Buddas T., Halin M., Helin M., Kinnunen P., Kvarnström R., Laitinen T., Mutilainen E., Mäkelä K., Reinvall A., Saario T., Sirkiä P. and Tompuri K., *Correlating Activity Incorporation with Properties of Oxide Films formed on Material Samples exposed to BWR and PWR Coolants in Finnish Nuclear Power Plants*, Proceedings of Chimie 2002, Avignon, France, SFEN, French Nuclear Energy Society, paper No.143, 2002.
- Byers W. A., Wang G., Deshon J. C., *The limits of zinc addition in high duty PWRs*, International Conference on Water Chemistry in Nuclear Reactor Systems, Berlin 2008.
- Chen K., Mackievicz A., Seifert H.P., Virtanen S., Ritter S., *Role of Zn injection on mitigating stress corrosion cracking initiation of Alloy 182 weld metal in simulated light water reactor environment*. Corrosion Science 221 (2023) 111364.
- Cheng B. et al, *Effects of Noble Metal Chemical application on fuel Performance*, Proceedings of the 2004 International meeting on LWR Fuel Performance, paper 1069, Orlando, Florida 19-22, 2004.
- Cheng B., Smith F., and Lemons J., *BWR Fuel Reliability under Challenging Water Chemistry Conditions*, paper 2149, Proceedings of Top Fuel 2009, Paris, France 6-10, 2009.
- Combrade P., Scott P.M., Foucault M., Andrieu E., Marcus P., *Oxidation of Ni base alloys in PWR water: Oxide layers and associated damage of the base metal*, 12<sup>th</sup> Inter. Conf. on Deg. of Materials in Nucl. Pow. Syst., 2005.
- Corbineau M. et al., *Taishan EPR Commissioning: Chemistry of the Primary and Secondary Water Circuits during Hot Functional Tests*, 21<sup>th</sup> International Conference on Chemistry in Nuclear Reactors Systems. EPRI, San Francisco, USA 9-14<sup>th</sup> September 2018.

- Cowan R. L., Lin C. C., Marble W. J. and Skarpelos, J. M., *Recent Developments in BWR Water Chemistry*, 2nd International Topical Meeting on Nuclear Power Plant Thermal Hydraulics and Operations, Tokyo, Japan, April 15-18, 1986.
- Cowan R. L. and Kiss E., *Optimizing BWR Water Chemistry* 6<sup>th</sup> International Symposium on environmental Degradation in Nuclear Plants, San Diego, CA, August 5, 1993.
- Cowan R. L. and Garcia S. G., *The Technical Basis for Limiting Copper In The BWR Primary Coolant*, Conference on Water Chemistry in Nuclear Power Reactors, Quebec, 2010.
- Cowan R.L., Odar, S, Kysela J. *Effect of Zinc in BWR and PWR/VVER on Activity Build-up, IGSCC and Fuel Performance*. ANT International LCC6 report. Oct 2010.
- Cowan R. L., Varela J. and Garcia S.E., *The Effect Of On-Line Noble Metal Addition On The Shut Down Dose Rates Of Boiling Water Reactors*, 15th Environmental Degradation Conference, Colorado Springs, Colorado Springs, Colorado, August 2011.
- Cowan R. L., Garcia S. E. and Goldstein J., *BWR Chemistry Impacts on Shut Down Dose Rates*, International BWR and PWR Materials Reliability Program Conference and Exhibition 2012, Washington D.C., National Harbor, Maryland, National Harbor, Maryland, July 16-19, 2012
- Davies J. H. et al, *Hot Cell Characterization of Zinc Rich Crud Layers*, Loen, Norway: Enlarged Halden Program Group Meeting, HPR-347/31, 1996.
- Deshon J., *PWR Axial Offset Anomaly (AOA) Guidelines*, Revision 1, EPRI Report 1008102, 2004.
- DeVito R. et al., *Westinghouse Experience with AP1000 Plant Hot Functional Testing Chemistry*, 21th International Conference on Chemistry in Nuclear Reactors Systems. EPRI, San Francisco, USA 9-14th September 2018.
- Drexler A. et al., *Chemistry Concept for Dose Rate Minimization Treatment of New and Decontaminated PWRs and PHWRs*, 20th NPC International Conference Brighton, United Kingdom – October 2-7, 2016.
- Engler N., Clinard M.H., Skocic M., Tompuri, K. *OL3 EPR™ experience with Hot Functional Testing Chemistry*. Paper 118. Proc. of International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023.
- EPRI Report NP-6975, *The effect of dissolved zinc on the transport of corrosion products in PWRs*, 1990.
- EPRI Report TR-101463, *Hydrogen Water Chemistry Effect on BWR Radiation Buildup*, Volumes 1 through 5, November 1995.
- EPRI Report 1009568, *Overview report zinc addition in PWR 2004*, 2004.
- EPRI Report 1003213, *PWR Axial Offset Anomaly (AOA) guidelines, Revision 1*, Palo Alto, CA, 2004a.
- EPRI Report 1008103, *Assessment of NMCA Effects on BWR Coolant Chemistry and Product Transport on Fuel Surfaces*, December 2004b.
- EPRI Report 1008102. *PWR Axial Offset Anomaly (AOA) Guidelines, Revision 1*, EPRI, Palo Alto, CA: 2004c
- EPRI Report 1011312, *Proceedings of the August 2004 EPRI PWR Primary Zinc Addition Workshop*, 2005.
- EPRI Report 1013420, *Pressurized Water Reactor Primary Water Zinc Application Guidelines*, EPRI, Palo Alto, CA, 2006.
- EPRI Report 1013425, *Evaluation of fuel cladding corrosion and corrosion product deposits from Callaway Cycle 14, Final report*, 2006a.

- EPRI. BWRVIP-190: BWR Vessel and Internals Project, *BWR Water Chemistry Guidelines—2008 Revision*. EPRI, Palo Alto, CA: 2008. Ref. 1016579.
- EPRI Materials Reliability Program: *Mitigation of Stress Corrosion Crack Growth in Nickel-Based alloys in Primary Water by Hydrogen Optimization and Zinc Addition*"; MPR-280; EPRI, Palo Alto, CA: 2010, 1021013
- EPRI Report 1025316, *Pressurized Water Reactor Primary Zinc Application Sourcebook volume 1*, Palo Alto, Calif.: Electric Power Research Institute, July 2012
- EPRI Report 3002015884. *Behavior of Zinc and Silica in the PWR Primary System: PWR Chemistry Technical Strategy Group Report*. EPRI, Palo Alto, CA: 2019.
- Esposito J. N. et al, *The Addition of Zinc to Primary Coolant for Enhanced PWSCC Resistance*, Corrosion '91, NACE, USA, 1991, and Proc. 5th Int. Symp. On Env. Degradation of Materials in Nuclear Power Systems-Water Reactors, 495-501, 1991.
- Forsberg S., Odelius H., and Granath G., *Release Rates from Stellite in Simulated Boiling Water Reactor Environments*, Water Chemistry of Nuclear Reactor Systems, San Francisco, Oct. 2004.
- Fruzzetti K. et al, *PWR water chemistry controls: A perspective on industry initiatives and trends relative to operating experience and the EPRI PWR water chemistry guidelines*, International Conference on Water Chemistry in Nuclear Reactor Systems, Quebec City, Canada, 2010.
- Garbett K., *Primary Water Chemistry*, IAEA Seminar in Karlsruhe, Germany, 2006
- Gardner J., *RCS zinc status Diablo Canyon*, EPRI PWR Primary Zinc Addition Workshop, Toronto, 2004.
- Garcia S. E. and Cowan R. L., *Zinc Addition Experience in BWRs Under Normal and Hydrogen Addition Chemistry* Japan International Conference on Water Chemistry in Nuclear Power Plants, Water Chemistry 98, Kashiwazaki, Japan, October 13-16, 1998.
- Garcia S. E. and Wood C. J., *Recent Advances in BWR Water Chemistry*, NPC'08 - International Conference on Water Chemistry of Nuclear Reactor Systems – Berlin, September 14-18, 2008.
- General Electric. *Advanced Boiling Water Reactor Plant General Description*. 2000
- General Electric-Hitachi. *ESBWR Plant General Description*. 2011
- Gold R. E., Byers W. A. and Jacko R. J., *Zinc oxide corrosion film interactions in PWR primary coolant*, International Symposium Fontevraud III, 1994.
- Gold R., *Effect of zinc addition on mitigation of PWSCC of Alloy 600*, EPRI report TR1003522 (MRP-78), 2002.
- Guillermier P. et al, *M5 cladding behavior with zinc injection: results obtained at Sequoyah-2*, International Conference on water chemistry of Nuclear Reactor Systems, Berlin, Sept. 15-18, 2008.
- Gou X., Chen K., Seifert H.P., Ritter S., *Effect of Zinc Water Chemistry on the Corrosion and Stress Corrosion Cracking Behaviour of Structural Materials in Light Water Reactors-A Review*. PPCHEM Journal 25, 2023/03.
- Harding J. H., *Modeling the effect of zinc addition on the uptake of cobalt by oxide films in PWRs*, Proceedings of the International Conference Water Chemistry of Nuclear Reactor Systems, BNES 7 in Bournemouth, 1996
- Hayakawa H. et al, *Zinc injection during hot functional test (HFT) in Tomari Unit 3* International Conference on Water Chemistry in Nuclear Reactor Systems, Quebec City, Canada, 2010.
- Hazelton R. F., *Characteristics of Fuel Crud and Its Impact on Storage, Handling, and Shipment of Spent Fuel*, Pacific Northwest Laboratory, PNL-6273, Sept. 1987.



## Appendix A - High Duty Core Index

EPRI introduced the so-called “High Duty Core Index” (HDCI) in order to aid in ranking core susceptibility to fuel crudding and AOA associated with sub-cooled boiling. The HDCI is a simple method to index the boiling duty of PWR cores and is calculated using core parameters such as fuel surface heat flux, flow rate through the core, fluid temperature in the core, fuel design, and cycle specific features such as the core power distribution, and saturation temperature for the highest duty assembly in the core [EPRI, 2004c]. The equation is given as follows:

$$\text{HDCI} = (\text{Peak Assembly Heat Flux}) * 1000 / [(\text{Assembly Flow Rate}) * (T_{\text{sat}} - \{T_x + T_{\text{out}}\})]$$

Where,

Peak Assembly Heat Flux = (core average heat flux)\*(peak assembly power),  
in BTU/hr-ft<sup>2</sup> or W/m<sup>2</sup>

Assembly Flow Rate = (system flow rate at T<sub>cold</sub>)/number of assemblies, in gph<sup>12</sup> or m<sup>3</sup>/s

T<sub>sat</sub> = Saturation temperature at system pressure, in °F or °C

T<sub>out</sub> = Vessel temperature in the hot legs (ave.) in °F or °C

T<sub>x</sub> = A temperature correction, 23 °F or 12.8 °C

1000 = Scaling factor applied to the numerator to present the index as a whole number

With this formulation, the units of HDCI are [BTU/ft<sup>2</sup>-gal-°F] or [Wh/m<sup>2</sup>-l-°C]

The calculation is very sensitive to the RPV outlet temperature ( $\Delta T = T_{\text{sat}} - T_{\text{out}}$ ) and can easily underestimate or over-estimate core boiling duties of some PWR plants. Therefore, it should be considered that the index offers only a rough relative scale of core boiling duty and the propensity of that core crud deposition on that core, defining HDCI (in British units) the following categories:

- High duty: >150
- Medium duty: 120-150
- Low duty: <120

High duty cores are normally characterized as high temperature plants with significant Sub-cooled Nucleate Boiling (SNB) occurring at lead assemblies. Such conditions can give rise to enhanced CP deposition in the core, which can lead to higher cladding corrosion. Changes to the parameters used for the HDCI calculations in different fuel cycles may result in increases in boiling duty of the core that would result in the plant changing its categories with respect to core duty. The plant chemist should be aware of the potential impact of zinc addition that is associated with the core duty. Whether a plant is high, medium or low duty PWR should be evaluated on a cycle-by-cycle basis to ensure current chemistry practices and zinc addition conditions do not adversely impact fuel corrosion and also crud deposition performance.

According to the scaling given above, the first PWR plants that injected zinc at elevated concentrations of 30-40 µg/kg, such as Farley-2&1, Diablo Canyon-1&2, are all low duty core plants; whereas the Sequoyah-1&2 units belong to the lower range of the category medium duty plants (see Figure A-1).

It is recommended to use this HDCI scaling only for plants with similar core designs. Even HDCI is the most used scaling aid for comparison the core duties of different plants, the fuel vendors are using their own core-thermodynamic calculation programs to evaluate the duty of the core. Their calculations are based on the local steaming rate of the highest duty assemblies in the core.

---

<sup>12</sup> gallon per hour

ZINC CHEMISTRY IN BWRs, PWRs AND VVERs

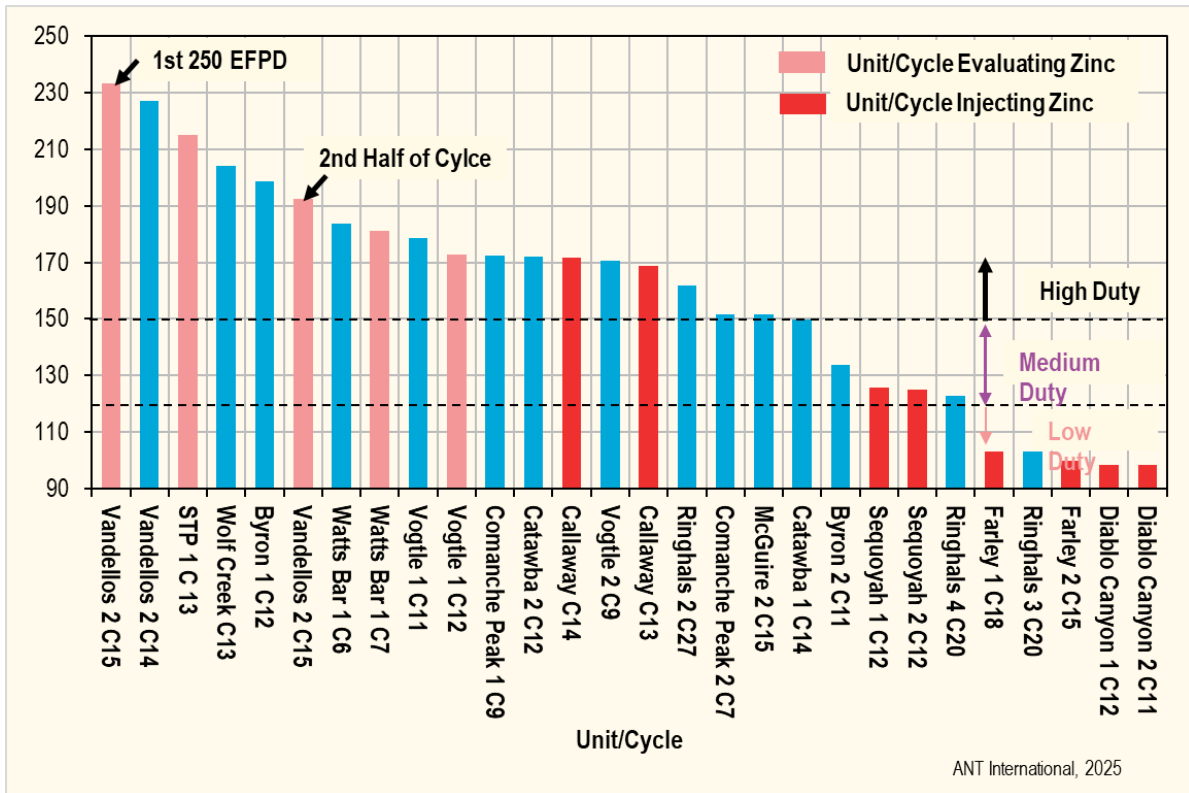


Figure A-1: HDCI comparison of various Westinghouse designed PWR plants [Deshon et al, 2004].

## List of Abbreviations

AAS/HGA	Heated Graphite Atomic Absorption Analysis
ABWR	Advance Boiling Water Reactor (Name of GE to the BWR with internal pumps)
AECL	Atomic Energy of Canada Limited
AL	Action Level (for Guidelines)
ALARA	As Low As Reasonably Achievable
ALARP	As Low As Reasonable Practicable
ANO	Arkansas Nuclear One (a PWR plant in the US)
ANT	Advance Nuclear Technology
ANTI	ANT International
AOA	Axial Offset Anomaly
APR	Advanced Pressurized Reactor (Advanced PWR, Korean design)
ARC	Alternative Repair Criteria (for SG tube cracking)
ASTM	American Society for Testing and Materials
BAST	Boric Acid Storage Tank
BNFL	British Nuclear Fuel Limited
BOC	Beginning of Cycle
BOP	Balance Of Plant (Systems out of the Nuclear Island)
BRAC	BWR Radiation Assessment and Control
BWR	Boiling Water Reactor
CBB	Crevice Bent Beam Test
CERT	Constant Extension Rate Test
CIPS	Crud Induced Power Shift
CILC	Crud Induced Localized Corrosion
CP	Corrosion Products
CPD	Cumulated Percentage of Data
CPS	Condensate Polishing System
CRDM	Control Rod Drive Mechanism
CRUD	Deposits on fuel cladding. (Chalk River Unidentified Deposits)
CS	Carbon Steel
CT	Compact Tension Test
CVCS	Chemical and Volumetric Control System
DB	Deep Bed of resins, a type of demineralizer
DBB	Double Cantilever Beam Test
DNB	Departure from Nucleate Boiling
ECP	Electrochemical Corrosion Potential
ECT	Eddy Current Test
EDS	Energy Dispersive X-Ray Spectroscopy
EDX	Energy Dispersive X-Ray Spectroscopy
EDY	Effective Degradation Years
EFPY	Effective Full Power Years
EOC	End of Cycle
EPR	European Pressurized Reactor (Advanced PWR designed by Framatome)
EPRI	Electric Power Research Institute
ESSC	Enhanced Spacer Shadow Corrosion
DZA	Depleted Zinc Acetate
DZO	Depleted Zinc Oxide
F/D	Filter Demineralizer or Powdex Filter, a type of demineralizer
FA-3	Flammanville-3 (EPR plant in France)
FAC	Flow Accelerated Corrosion
FW	Feed Water System
GDOES	Glow Discharge Optical Electronic Microscopy
HDCI	High Duty Core Index
HDFP	High Duty Fuel Plants
HFT	Hot Functional Test
HP	High Pressure
HWC	Hydrogen Water Chemistry (Hydrogen Injection in BWR)
IAEA	International Atomic Energy Agency

ICP-OES	Induced Coupled Plasma-Optical Atomic Emission
ICP-MS	Induced Coupled Plasma-Mass Spectrometry
IGSCC	Intergranular Stress Corrosion Cracking
KEPCO	Korea Electric Power Corporation
KHNP	Korea Hydro & Nuclear Power Corporation
KIPT	Ukrainian Institute of Physics and Technology
KKL	Kern Kraftwerk Leibstadt (Swiss BWR)
KKM	Kern Kraftwerk Mühleberg (Swiss BWR)
MA	Mild Annealed
MELLLA	Maximum Extended Load Line Limit Analysis Plus (Extended BWR operating flow-power conditions)
mHWC	Moderated Hydrogen Water Chemistry (1.5-2 mg H <sub>2</sub> /kg)
MRP	Materials Reliability Program (EPRI program)
NMCA	Noble Metal Chemical Addition
NOP	Normal Operating Pressure
NOT	Normal Operating Temperature
NPP	Nuclear Power Plant
NUPEC	Nuclear Power Engineering Corporation of Japan
NWC	Normal Water Chemistry
OL-3	Olkiluoto-3 (EPR Plant in Finland)
OLNC	On Line NobleChem
ORE	Occupational Radiation Exposure (collective personnel dose)
PIE	Post-Irradiation Examination
PRIS	Power Reactor and Information System, IAEA Data Base
PSI	Paul Scherrer Institute (Switzerland)
PWR	Pressurized Water Reactor
PWROG	PWR Owners Group
PWSCC	Primary Water Stress Corrosion Cracking
PZ	Pressurizer
RFO	Refueling Outage
RC	Reactor Coolant (normally used in PWR)
RCP	Reactor Coolant Pump
RCS	Reactor Coolant System or Primary System in a PWR
RFO	Refueling Outage
RHR	Residual Heat Removal System
RPV	Reactor Pressure Vessel
RSG	Replacement Steam Generator
RUB	Reverse U-Bend Test
RW	Reactor Water (normally used in BWR)
RWCU	Reactor Water Clean Up System
SCC	Stress Corrosion Cracking
SIF	Stress Intensity Factor
SG	Steam Generator
SGMP	Steam Generator Management Program (EPRI Program)
SEM	Scanning Electronic Microscopy
SHE	Standard Hydrogen Electrode
SNB	Sub-Nucleate Boiling
TEM	Transmission Electronic Microscopy
TOI	типовой оптимизированный информатизированный (Universal Optimized Digital)
TS	Tube Sheet
TSP	Tube Support Plate
TT	Thermal Treated
UT	Ultrasonic Test
VCN	Vallecitos Nuclear Center (GE research facility)
VCT	Volumetric Control Tank
VGB	Technische Vereinigung der Großkraftwerksbetreiber (The Technical Association of Large Power Plant Operators)
VTT	Technical Research Center of Finland Ltd
VVER	Водо-водяной энергетический реактор, Water -Water Energetic Reactor

WDS Wavelength-Dispersive X-ray spectroscopy  
WOG Westinghouse Owners Group  
XPS X-ray Spectroscopy

## Unit conversion

TEMPERATURE		
$^{\circ}\text{C} + 273.15 = \text{K}$	$^{\circ}\text{C} \times 1.8 + 32 = ^{\circ}\text{F}$	
T(K)	T( $^{\circ}\text{C}$ )	T( $^{\circ}\text{F}$ )
273	0	32
289	16	61
298	25	77
373	100	212
473	200	392
573	300	572
633	360	680
673	400	752
773	500	932
783	510	950
793	520	968
823	550	1022
833	560	1040
873	600	1112
878	605	1121
893	620	1148
923	650	1202
973	700	1292
1023	750	1382
1053	780	1436
1073	800	1472
1136	863	1585
1143	870	1598
1173	900	1652
1273	1000	1832
1343	1070	1958
1478	1204	2200

Radioactivity	
1 Sv	= 100 Rem
1 Ci	= $3.7 \times 10^{10}$ Bq = 37 GBq
1 Bq	= $1 \text{ s}^{-1}$

MASS	
kg	lbs
0.454	1
1	2.20

DISTANCE	
x ( $\mu\text{m}$ )	x (mils)
0.6	0.02
1	0.04
5	0.20
10	0.39
20	0.79
25	0.98
25.4	1.00
100	3.94

PRESSURE		
bar	MPa	psi
1	0.1	14
10	1	142
70	7	995
70.4	7.04	1000
100	10	1421
130	13	1847
155	15.5	2203
704	70.4	10000
1000	100	14211

STRESS INTENSITY FACTOR	
MPa $\sqrt{\text{m}}$	ksi $\sqrt{\text{inch}}$
0.91	1
1	1.10