

ZINC CHEMISTRY IN PWR PLANTS FROM MID-1990S UP TO PRESENT:  
MECHANISM AND WORLDWIDE FIELD EXPERIENCE

# Zinc Chemistry in PWR Plants from Mid-1990s up to Present: Mechanism and Worldwide Field Experience

*Author*

Suat Odar  
Erlangen, Germany



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Advanced Nuclear Technology International  
Spinnerivägen 1, Mellerta Fabriken plan4, SE-448 50 Tollerød,  
Sweden

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

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

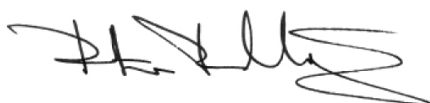


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A handwritten signature in black ink, appearing to read 'P. Rudling', with a stylized flourish at the end.

Mr Peter Rudling, President of ANT International

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# 1 Introduction

In 2010/11 a report, with the title “Effect of Zinc in BWR and PWR/VVER on Activity Build-up, IGSCC and Fuel Performance” was issued for LCC6, which covered all published knowledge about zinc chemistry in BWR and PWR plants as of 2010. Since that time, within 10 years lot of new knowledge and field experience was published especially by PWR industry, which contributed to understand much better the zinc chemistry mechanism. Therefore, ANT decided to issue an updated report on zinc chemistry in PWR plants for LCC 16 program. The basis of this report is the published information including the proceedings of the latest International Conference on Water Chemistry of Nuclear Reactor Systems that took place in 2018 (NPC 2018). The proceedings of NPC 2020 could not be considered because it was cancelled due to Corona pandemic. In this updated report, the personal opinions and interpretations of the author are written in *italic* letters.

Zinc addition into the reactor coolant in PWR plants is now one of the most important considerations regarding coolant chemistry. The main objectives of zinc injection are: a) the control of radiation fields and b) 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). This strategy of the zinc addition into reactor coolant started in the 1990s in PWR plants. The field experience of about 30 years confirmed that Zinc chemistry is the most powerful tool for radiation field control in PWR plants.

This updated report reviews, as of 2020, the laboratory and field results of zinc injection technology in PWR plants worldwide. The review covers the range from basic information to current knowledge and understanding of operational behaviour. This information on PWR plants given in this report is also applicable for VVER plants. So far publicly known, as of presence, zinc addition was not applied in VVER plants. The VVER TOI design is the only VVER plant, which is designed to consider zinc injection in its coolant chemistry [Susakin, et al, 2012]. This plant is, as of 2019] still under construction. However, lots of preparatory investigations such as laboratory tests also were performed in the past. The results of these investigations might be also useful for the PWR units. Therefore, a review of the available laboratory work results applicable to VVER plants is also included in this report. Accordingly, content of this report is very useful for both PWR and VVER plants to establish their own plant specific coolant chemistry strategies. ANT is also convinced that the information given in this report will highly support the Authorities in performing their regulatory work.

The content of this report can be summarized as follows:

The basis for the “how and why” the plants started to inject zinc and their motivation for this strategy is explained briefly in Chapter 2.

The beneficial effect of zinc addition on radiation field reduction was first discovered in BWR plants in the early 1980s. This finding was followed by detailed qualification work to confirm structural material and fuel compatibility of zinc addition for BWR plants including the conduction of plant demonstration tests. Based on good results of zinc addition gained in BWR plants, many PWR plants started to think also to inject zinc in their reactor coolant to control the radiation fields and the PWR plants with Alloy 600MA also as remedy to mitigate PWSCC. For this purpose, detailed investigations were performed to qualify the zinc addition for PWR units in particular, to confirm its effectiveness for dose rate reduction, its compatibility with PWR construction materials and with fuel performance. The results of these extensive investigations and the field experience gained worldwide by applying the zinc injection at PWR units are summarized in Chapter 3, which starts with Section 3.1 with the information how oxide films on the out-of-core surfaces of Reactor Coolant System (RCS) is formed and how the radiation fields are built-up in the PWR units in Section 3.2. The purpose of giving this information is to provide better understanding of the mechanism how zinc addition works, which is explained in

Section 3.3. The investigations performed to qualify the zinc addition for PWR units confirmed that zinc injection has some beneficial influence on RCS and on fuel.

These were explained in Section 3.4; Coolant chemistry in Section 3.4.1; Out-of-core dose rates in Section 3.4.2; RCS material compatibility in Section 3.4.3; Influence on PWSCC in Section 3.5; Fuel performance in Section 3.6; and finally Influence on Chemical and Volume Control System (CVCS) in Section 3.7.

The worldwide experience gained in the field by applying zinc addition is summarized in Section 3.8. The information included in this Section is important and valuable not only for those PWR utilities that intend to introduce zinc addition in their units, but also for the plants that already apply zinc addition to optimize their zinc addition program. This information includes: Solubility aspects of zinc compounds in Section 3.8.1; Implementation of zinc injection concept in Section 3.8.2; Sampling and monitoring concept of zinc injection in Section 3.8.3; Zinc surveillance programs for fuel performance and dose rate reduction in Section 3.8.4; Control of zinc addition criteria in different plant operation modes in Section 3.8.5. Finally, the results of zinc addition in US and European PWR units are compared in Section 3.9.

Based on public information, zinc addition is as of 2020, still not yet applied in VVER plants. However, lots of preparatory investigations such as laboratory tests were performed. The results of these investigations might be also useful for the VVER plants, which intend to introduce zinc injection in the future and also for PWR units. They are explained in Chapter 4.

There is a common concern that zinc injection might have negative impact on plant radwaste production due to release of radiocobalt into reactor coolant by zinc injection and also due to production of  $^{65}\text{Zn}$ , particularly if natural zinc is used. The confirmation that zinc addition doesn't have any negative effect on radwaste production is explained by the results of field experience gained in zinc PWR plants in Chapter 5.

Finally, Chapter 6 summarizes the information related to zinc injection in PWR plants and gives valuable recommendations regarding implementation of zinc addition.

## 2 Background Information

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 BWR plants with stainless steel condenser tubes were experiencing very high dose rate, whereas others having brass condenser tubes have acceptable low dose rates (see Figure 2-1). 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). The evaluation of the existing BWR plant radiation field data, performed within the follow-up of this program, indicated that the plants with brass condenser tubes operating with 5-15 µg/kg zinc in their feed water had significantly lower out-of-core pipework radiation fields [Marble, 1983]. The laboratory investigations on the composition of the plant fuel deposits and corrosion films on corrosion coupons confirmed that zinc was incorporated into these oxide films [Marble & Wood, 1985]. Following this discovery with “natural zinc plants”, GE initiated a comprehensive laboratory work to evaluate the corrosion behaviour of the main structural materials used in GE designed BWR plants. This qualification work confirmed not only the compatibility of the materials but zinc was also improving the protective features of the passive oxide layers on reactor system surfaces; hence, mitigating the Intergranular Stress Corrosion Cracking of the stainless steels by delaying crack initiation [Aldred, 1985]. After this comprehensive qualification testing, zinc addition was introduced for radiation field control first in US BWR plants.

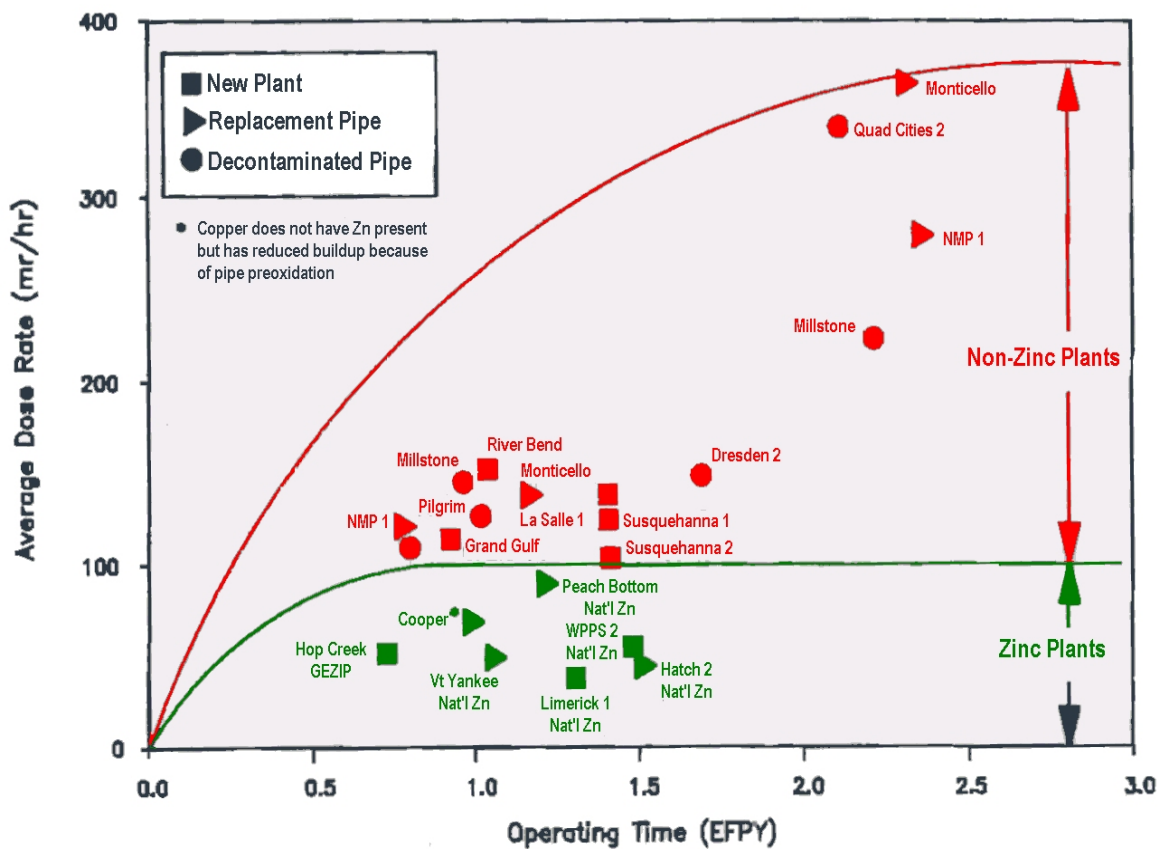


Figure 2-1: Radiation field build-up on GE designed BWR recirculation system piping, [Lin et al 1980].

Zinc injection into reactor coolant of PWR plants both in the USA and Germany is based on the experience gained in BWR plants. Encouraged from the good results of the zinc addition in BWR plants, in the end of 1980s PWR industry realized that zinc could similarly inhibit  $^{60}\text{Co}$  formation and incorporation into the oxide films on out-of-core surfaces and thus reduces the radiation fields in the PWR plants. Before implementing the zinc addition in the PWR plants, plant qualification programs were also necessary to confirm not only the positive effect of the zinc addition but in particular, its compatibility with the fuel and structural materials under PWR coolant operating conditions. The main and most important qualification work in this area is performed in the period of late 1980s and in the 1990s in two locations, in the USA and in Germany.

For US PWR plants, laboratory tests were initiated by EPRI in the late 1980s at Atomic Energy of Canada Limited (AECL) (located in Canada) to investigate the effect of zinc on Corrosion Product (CP) transport in the reactor coolant of PWR plants [Lister & Godin, 1990]. The results of this work showed that zinc addition reduces the  $^{60}\text{Co}$  pick-up into oxide films of both Alloy 600 and stainless steel, and that it produces thinner oxide films than those produced without zinc exposure. Based on the results achieved it was predicted that zinc addition of about 10-40  $\mu\text{g/kg}$  to the reactor coolant would reduce the radiation fields in the PWR plants.

Almost at the same time Westinghouse started with their laboratory testing to investigate the effect of zinc addition on PWSCC of Alloy 600MA, a material that is widely used for SG tubing and for numerous penetrations in RPV head in the Westinghouse designed PWR plants and, which is extremely sensitive against PWSCC. The results of their work, which is later sponsored by Westinghouse Owner Group (WOG) published in open literature, confirmed that zinc can mitigate significantly the PWSCC of Alloy 600MA. In addition, they showed also that overall corrosion and material release rates for Alloys 600, 690 and 750 as well as for stainless steels 304 and 316 were reduced (see Section 3.43 and 3.5) [Esposito et al, 1991] and [Gold et al, 1994].

After having these positive results, it was jointly decided by EPRI and WOG to perform a plant demonstration program at Farley-2 in 1994. In parallel, tests would be carried out in Halden test reactor, which were cosponsored by Siemens, to investigate the effect of zinc injection on fuel performance under PWR coolant operating conditions.

In Germany, similar effort was performed to reduce the radiation fields in the older PWR plants. Due to the use of stellites as hard facing material in the RCS particularly in the RPV inlets, (see Figure 2-2) and also in several PWR units due to the use of fuel assemblies, which had  $^{60}\text{Co}$  contaminated Inconel spacer grids, the radiation fields were relatively high in those older PWR units. In order to avoid such radiation field evolution, cobalt replacement program was introduced in the design of new plants. The new PWR units (Pre-Convoy plants: Philippsburg-2, Brokdorf, and Convoy plants: Emsland, Isar-2 and Neckarwestheim-2) that are cobalt free have very low radiation fields (see Figure 2-3). This remedy of replacing cobalt materials in conjunction with partial or full system decontamination to reduce the existing radiocobalt inventory was not realistic for old PWR plants due to high cost and expected difficult issues associated with radwaste disposal. The Occupational Radiation Exposure (ORE) at these old PWR plants, accumulated by station staff and contractors during normal operation, maintenance, inspection and refuelling was in the range of 3-5 man-Sv per year in the 1980s (see Figure 2-3), of which about 90% was caused by  $^{60}\text{Co}$ .

A lot of effort was applied to reduce the ORE in these old PWR units by implementing better shielding, improved maintenance planning and equipment, etc. Consequently, although ORE at these units fell steadily it stabilized at about 1-2 man-Sv per year in the beginning of 1990s and there was no indication for further reduction [Stellwag et al, 2006]. Therefore, it was jointly decided by PWR utilities and Siemens to initiate a program to evaluate the feasibility of zinc injection for radiation field reduction as alternative remedy to cobalt replacement.

This independent research program, “Basic research into activity build-up in Light Water Reactor (LWR) plants” to qualify zinc injection for PWR units was sponsored by VGB (The Technical Association of Large Power Plant Operators) in the period of 1994 to 1996, [Stellwag & Staudt, 1995]. The main objective of this program was to confirm the compatibility of the zinc addition with fuel performance and PWR operation and the effectiveness of the method for reduction of the radiation fields. The program was managed by Siemens and was performed in two phases. Phase 1 included the work performed by Siemens, VTT, University of New Brunswick and Halden Research Reactor, which covered loop tests, oxide morphology studies, coolant specification studies, and fuel compatibility tests.

On the basis of these tests for the phase 2 work, it was decided to perform three plant demonstration tests at Biblis-B (1996), followed by Biblis-A (1998) and Obrigheim (1998). Based on the good results obtained at these lead PWR plants for zinc addition, the VGB “PWR Chemistry” and “Radiation Protection” committees gave a general recommendation for zinc addition at all Siemens designed PWR units that have a significant stellite hard facing alloy inventories.

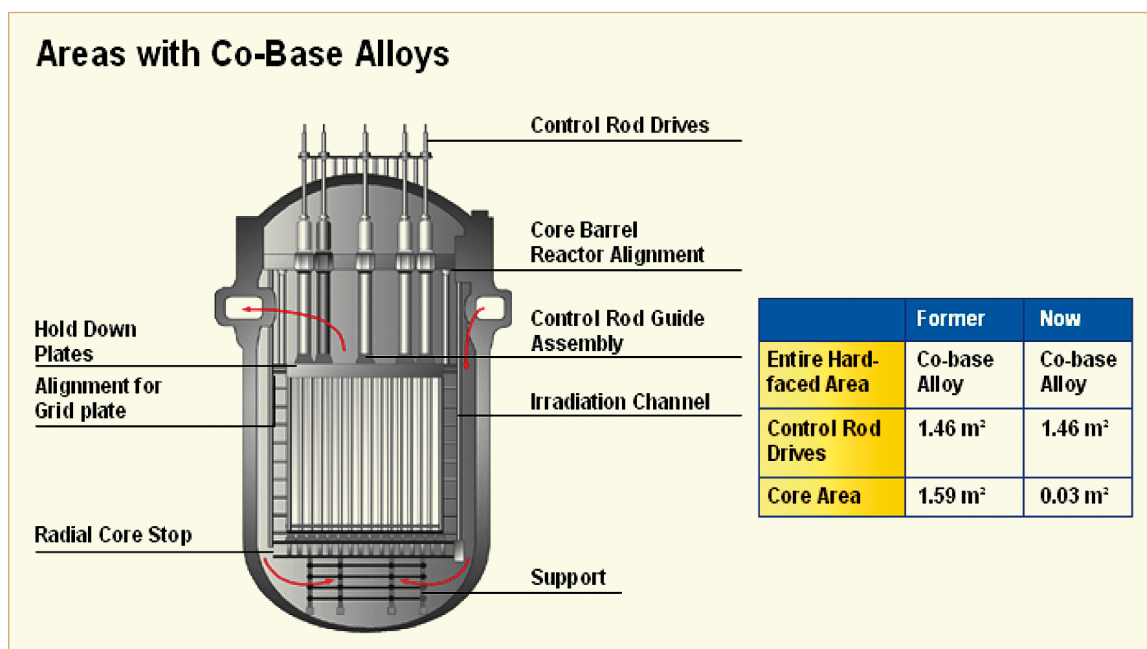


Figure 2-2: RPV internals with stellites in old Siemens designed PWRs and the reduction of stellite areas by their replacement in new PWRs, [Stellwag and Schneider, 2009].

Based on the results of qualification testing and plant demonstrations performed in USA and Germany, considerable body of valuable data gained on the long-term benefits of zinc injection in PWR plants. Many other plants worldwide had benefit from these work results and had followed the leadplants to add zinc in their plants. At the present, about 100 PWR units worldwide using zinc injection. The majority of the PWR units are injecting zinc for radiation field reduction, several with the main objective as remedy to mitigate PWSCC of Alloy 600MA.

In the following chapters information is collected that is related to zinc addition in PWR plants, which is gained by laboratory testing as well as at field experience from zinc addition plants. This information can be used by plants that intend to introduce zinc addition, as well as it is useful for the plants that already add zinc to assist them in optimizing their zinc addition strategy.

## 3 Zinc Chemistry in PWR Plants

As in Chapter 2 already explained, in US the main interest for zinc injection was to mitigate PWSCC of Alloy 600 Meal Annealed (MA), a material that is used for SG tubing material and widely in many penetrations of the Reactor Coolant System (RCS). In contrast to the US, PWSCC was not an issue for PWR plants in Germany due to the use of Alloy 800NG as SG tubing material and avoidance of the use of Alloy 600MA in the RCS. The main interest for the German PWR utilities was radiation field reduction in their old PWR plants, which had rather high dose rates due to the use of cobalt containing hard facing-materials (stellites) in the RPV internals.

In the following sections the characteristics of the oxide layers on the out-of-core structural materials and radiation build-up will be explained, in order to understand the mechanism of zinc chemistry better, how it mitigates the PWSCC of sensitive nickel-based alloys like Alloy 600 and how it can reduce the dose rates.

### 3.1 Oxide Layers on RCS Structural Materials

#### 3.1.1 RCS Design and Structural Materials

The reactor coolant system operates at a pressure of 150 bar (15.5 MPa) and in a temperature range of 280 to 330°C, depending on the core duty design. Whereas the operating temperature range of the older PWR with low core duty was between 280 and 320°C, the new ones with high duty cores are operating in the range of 290 to 330°C. The RCS pressure boundary consists of the Reactor Pressure Vessel (RPV), the recirculation loop-piping, pressurizer, Steam Generators (SG) tubing, and pumps. The pipework of each loop is normally sub-divided into a hot leg (RPV to SG), a crossover or intermediate leg (SG to Reactor Coolant Pump (RCP)) and a cold leg (RCP to RPV). A pressurizer is connected to the hot leg of one of the loops via a surge line. There are two heat transfer surfaces within the system that consist of the fuel cladding transferring nuclear fission heat to the reactor coolant (approximately 25% of the RCS surface) and the SG tubing transferring heat to the secondary system (about 70% of the total RCS surface). The surface area of the residual components and loop pipe work is about 5%. This PWR plant surface area relation is similar to other pressurized reactor types (VVER and CANDU plants), as shown in Table 3-1. All influence of the oxide layers of the structural materials on the behaviour and performance of the RCS is coming from these two main surface areas and the plant performance is demanded by the interaction between these two surfaces, as it will be described later.

The RCS structural materials were selected based on the Plant operating experience and available information gained with the pioneer PWR plants in the early 1960s or 1970s. An identification of all materials used in the RCS of the various NSSS vendors is not possible; therefore, in this chapter the materials selected and applied worldwide for the main components of the PWR RCS will be described, which are together with their chemical composition summarized in Figure 3-1. From all these materials listed in this figure, the steam generator tubing materials and the fuel cladding materials are the most important ones having the highest surface areas and thus influencing the RCS performance and the coolant chemistry. In addition, two further materials, stellites and Inconel 718, are also listed, which are used mainly in Reactor Pressure Vessel (RPV) with very small surface areas, because these materials had in the past (in several older PWR plants still) significant influence on radiation field build-up.

Table 3-1: Surface areas of structural materials in PWR, VVER and CANDU plants

Reactor Type	Components	Material	Relative Surface Area
PWR	Steam Generator	Alloy 600, Alloy 690 and Alloy 800	70–75%
	Fuel Cladding	Zry-4, Zirlo, M5	20–25%
	Loop pipe work, Pressure Vessel, Pressurizer, Main Coolant Pump	Stainless Steels	~5%
CANDU (PHWR)	Steam Generator	Monel 400*, Alloy 600 or Alloy 800	~77%
	Fuel Cladding	Zircaloy 4	~13%
	Loop pipe work, Pressure Vessel, Pressurizer, Main Coolant Pump	Carbon Steel	~10%
VVER 440/1000	Steam Generator	Stainless Steel	~77%/~72%
	Fuel Cladding	Zirconium 1% Niobium	~20%/~21%
	Loop pipe work, Pressure Vessel, Pressurizer, Main Coolant Pump	Stainless Steel	~3%/~7%
* Monel 400 is used only in oldest CANDU plants			

These structural materials were considered to perform for the life of the reactor, but for a variety of reasons their integrity was impaired and they had to be replaced or repaired. The major reason for such actions was corrosion behaviour of the selected materials, mainly Primary Water Stress Corrosion Cracking (PWSCC) in nickel base Alloys (Alloy 600 MA and its weld materials), and Irradiation Assisted Stress Corrosion Cracking (IASCC) in several stainless steels. One consequence out of such material behaviour is to replace the component, which is a costly and time-consuming process.

All these structural materials in bare form are instable in high temperature water against corrosion. However, this corrosion attack slows down significantly very soon, because protective oxide layers are build-up on the materials, which protect them. The chemical composition and the stability of these oxide layers depend on the chemical composition of the materials on which they are built and demands highly the corrosion performance and the radiation field build-up in RCS. In the following sub-chapters, the characteristics of the oxide layers and their behaviour will be explained.

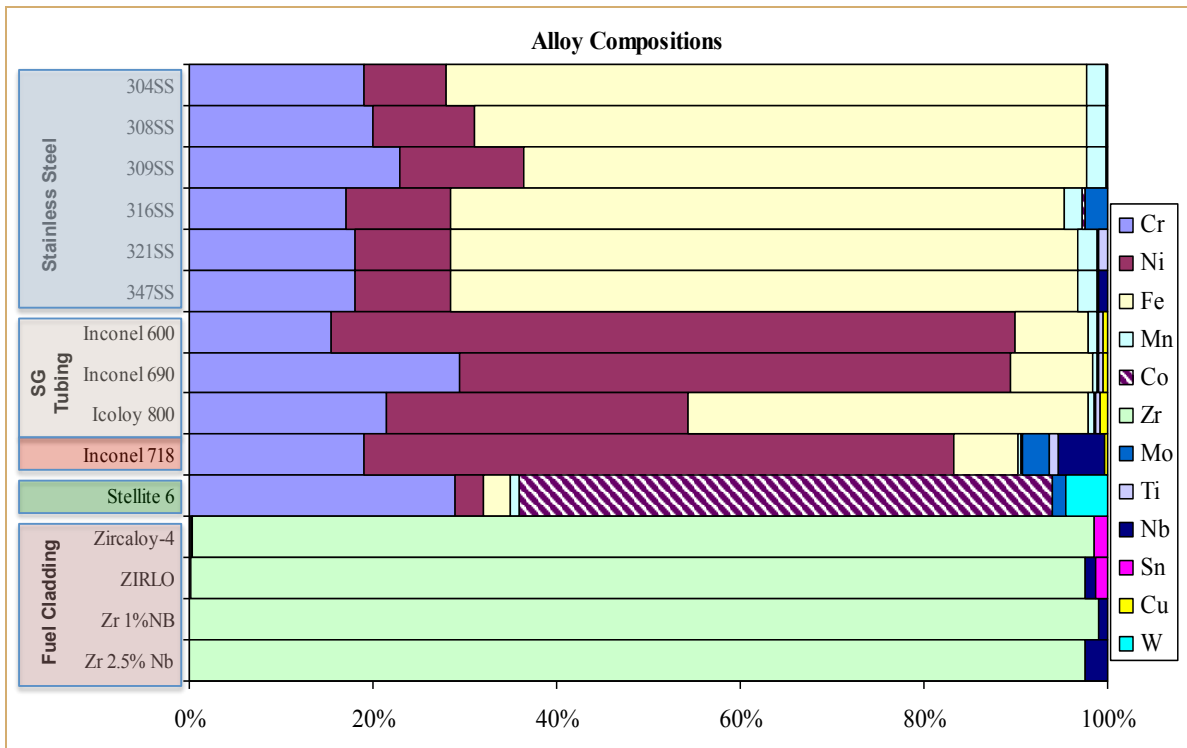


Figure 3-1: Structural materials used worldwide for the PWR RCS main components, [Garbett, 2006]

## 3.1.2 Oxide Layers on Structural Materials

### 3.1.2.1 Incore Oxide Layers

In the core region, a film consisting principally of the zirconium dioxide ( $ZrO_2$ ) is formed from the zirconium alloy on the fuel assembly cladding, guide tubes and fuel grids. In addition to  $ZrO_2$  Corrosion Products (CP) called CRUD, deposits (nickel ferrites, metallic nickel and nickel oxides) are also found on fuel rods, which are precipitated from dissolved cations transported by coolant (see below). Even, the fuel assemblies have a large surface area of about 25% of the total RCS surfaces, the  $ZrO_2$  oxide layers have influence mainly on fuel cladding corrosion performance; and, almost no influence on RCS corrosion and radiation performance. Only, the activated fuel CRUD deposits together with the out-of-core oxide layers have significant influence on radiation build-up (see Chapter 3.1.2.2 and Chapter 3.2).

### 3.1.2.2 Out-of-Core Oxide Layers

At ambient temperatures all selected construction materials for RCS have 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 ( $> 30\%$  Cr and usually free of nickel), either  $Cr_2O_3$  or a mixture of  $Cr_2O_3$  and hydrated chromium hydroxide [Kaesche, 1990], [Brüesch et al, 1984] and [Sato & Okamoto, 1981]. With increasing temperature above  $150\text{ }^\circ\text{C}$  the general corrosion rate of these metals increases slightly [Winkler & Lehmann, 1985] because the passive oxide layers become thicker and more porous but they are still very protective. The composition and thickness of these protective layers depend 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 build at higher temperatures is in the range of several hundred nanometres.



Under PWR operational conditions oxide layers build-up on the structural materials (stainless steels, nickel- and/or iron-based alloys) that protects the materials against corrosion. These oxide layers are consisting of duplex oxide layers, an inner oxide layer and overlying outer oxide layer [Lister, 1987] which is illustrated in detail in Figure 3-2, [Combrade et al, 2005] and [Bojinov et al, 2002]. Actually, the inner oxide layer consists of two sub-layers: “Internal” or “barrier” layer with chemical composition of  $\text{Cr}_2\text{O}_3$ ; and a chromium rich “intermediate” layer of mixed spinel oxides so called chromites. The “external layer” or former so-called “outer-oxide layer” has the chemical composition of spinel-type nickel ferrites and this layer is on stainless steels almost chromium free ( $<5\%$  Cr) and on nickel-based alloys completely chromium free.

The  $\text{Cr}_2\text{O}_3$  “internal” or “barrier” layer, which is built on the steels and/or alloys surfaces having  $\geq 10\%$  chromium, has extremely thin thickness of few nm. The  $\text{Cr}_2\text{O}_3$  internal layer is formed very rapidly on the bare surface and its thickness increases with the Cr content of the alloy. It is believed that this  $\text{Cr}_2\text{O}_3$  internal layer is actually the real protective passive layer. Therefore, for achieving adequate coolant CRUD control, actually this “barrier” layer needs to be improved; so that it prevents or slows-down the nickel and/or iron metal ion transport from base metal to outer oxide layers, where they are released to coolant by dissolution under the PWR/VVER operating coolant reducing conditions.

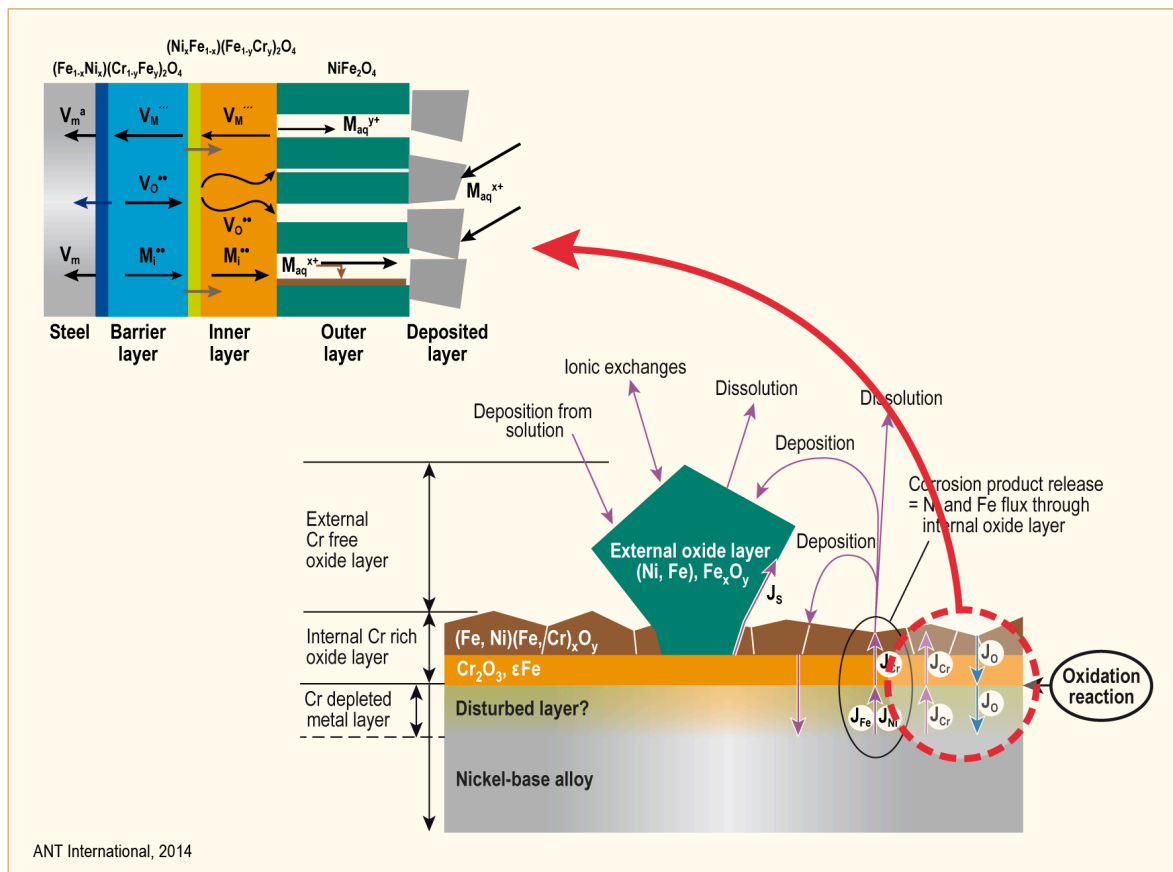


Figure 3-2: Schematic illustration of oxide film growth by ion transportation through the oxide layers, after [Combrade et al, 2005] and [Bojinov et al, 2002]

The existence of duplex oxide layers is a result of different diffusion rates of the cationic substituents of the alloy or steel through the inner protective oxide layer. As shown in Figure 3-2, the inner oxide layer (or intermediate layer) grows at the metal/oxide interface as the water penetrates through the crystal defects such as pores and cracks in the oxide layer to the metal surface, where it reacts with the metal ions to build oxides.

## 4 VVER Plants

The information given in this section is written by Jan Kysela for LCC6 zinc report in 2010. The information given in this report consist in only laboratory and loop testing results. So far publicly known, as of presence, zinc addition was not applied in VVER plants. The VVER TOI design is the only VVER plant, which is designed to consider zinc injection in its coolant chemistry program [Susakin, et al, 2012]. This plant is, as of 2019] still under construction. Since in the time period of 2010 up to present, no published new information is available for the zinc application activities in VVER industry, this section cannot be updated.

### 4.1 Introduction

VVER reactors operate in Eastern Europe, some Asian countries and the Russian Federation differ from PWR in their primary circuit technology. This is given by SG design (horizontal tubing as opposed to vertical in PWR reactors), different materials (SGs are made of stainless steel 18 % cr-10 % Ni, Ti, 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.

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.

The first part of this Section deals with the corrosion behaviour of stainless steels in the presence of zinc in coolant. Zinc also has a beneficial effect on transport activities in the primary circuit by replacing cobalt in the oxide layer coating equipment.

The second part of this Section assesses the results of an experimental programme at NRI Rez (Czech Republic) whose goal was to compare water chemistries with ammonia, hydrogen, and zinc injection. It discusses the results of crud behaviour in the coolant and active crud deposition on surfaces.

### 4.2 Impact of Zinc on Material Compatibility and Oxide Properties Related to VVER Plants

The utilization of zinc injection must be preceded by an analysis of possible effects on circuit materials and chemistries. We focused on data regarding the influence of zinc on corrosion behaviour of the primary material of the VVER circuit, stainless steel.

This section summarizes some studies of the influence of zinc on the corrosion resistance of stainless steel and its behaviour in oxide layers.

The oxidation of AISI 316L(NG) stainless steel in simulated PWR coolant with or without addition of 1ppm Zn at 280 °C for up to 96 h has been characterized in situ by Electrochemical Impedance

Spectroscopy (EIS), both at the corrosion potential and under anodic polarization up to 0.5 V vs. the Reversible Hydrogen Electrode (RHE) [Betova et al, 2009].

Additional tests were performed in simulated PWR coolant with the addition of 0.01M  $\text{Na}_2\text{B}_4\text{O}_7$  to exclude the effect of pH excursions probably due to Zn hydrolysis reactions. The thickness and in-depth composition of the oxide films formed at open circuit and at 0.5 V vs. RHE in the investigated electrolytes have been estimated from XPS depth profiles. The kinetic and transport parameters characterizing the oxide layer growth have been estimated using a calculation procedure based on the mixed conduction model for oxide films. Successful simulations of both the EIS and XPS data have been obtained. The estimated parameters are discussed in terms of the effect of Zn on the oxide layers on stainless steel in PWR conditions.

The ultimate goal of this work was to develop a deterministic model for activity incorporation in coolant circuits of LWRs and to increase the theoretical understanding of the oxide film build-up and breakdown, controlling the localized corrosion phenomena of structural materials in such reactors.

The predictions of the MCM (mixed-conduction model for oxide films) are for the first time fitted to both in situ EIS and ex situ XPS data for oxides on AISI 316L(NG) formed in simulated PWR water at 280 °C with or without Zn addition.

The electrolyte was simulated PWR coolant (1200 ppm B as  $\text{H}_3\text{BO}_3$ , 2.2 ppm Li as LiOH) with or without the addition of 1 ppm Zn as  $\text{Zn}(\text{NO}_3)_2$  and/or 0.01M  $\text{Na}_2\text{B}_4\text{O}_7$  which was added to buffer the electrolyte and prevent any pH excursions due to hydrolysis reactions of soluble Zn.

Figure 4-1 presents the XPS depth profiles for the films formed in this type of solution at open circuit with and without Zn injection.

In the presence of tetraborate, the thicknesses of the films in both Zn-free and Zn-containing electrolytes are more than two times larger than those formed in solutions that did not contain tetraborate. This effect could be related to the decrease of the solubility of Fe with increasing pH. Such an explanation is corroborated by the fact that outer layers (i.e. layers that are formed by dissolution-precipitation mechanism) are observed in both Zn-free and Zn-containing electrolytes and their thickness is larger than that of the inner layer.

A notable effect of Zn injection is that the Ni content of the inner layer formed as a result seems to be larger than that of Cr, which is opposite to the inner layer formed in the absence of Zn. Thus, Zn incorporation seems to play an important role in the restructuring of the inner layer also in tetraborate-containing PWR water.

Profiles of the atomic concentration of oxygen, as well as Ni, Cr, Fe and Zn contents normalized to the total metallic content of the film are presented on Figure 4-1.

The experimental and calculation results obtained by [Betova et al, 2009] have clearly indicated the significant effect of Zn injection in simulated high-temperature PWR water on the initial stages of the growth and restructuring of the oxide film on AISI 316L(NG). In unbuffered PWR water, a drastic decrease of the thickness of the oxide is observed after Zn injection. This is demonstrated to be due to both the change in the pH of the electrolyte as a reset of Zn hydrolysis reactions and the Zn adsorption on/incorporation in the oxide film, which leads to significant decrease of the rates of ion transport in the inner layer and the interfacial reactions at the inner layer/electrolyte interface. On the other hand, the effect of Zn on film growth and restructuring in buffered PWR water is much less dramatic, but still significant. This effect is demonstrated to be due to Zn incorporation in the inner layer.

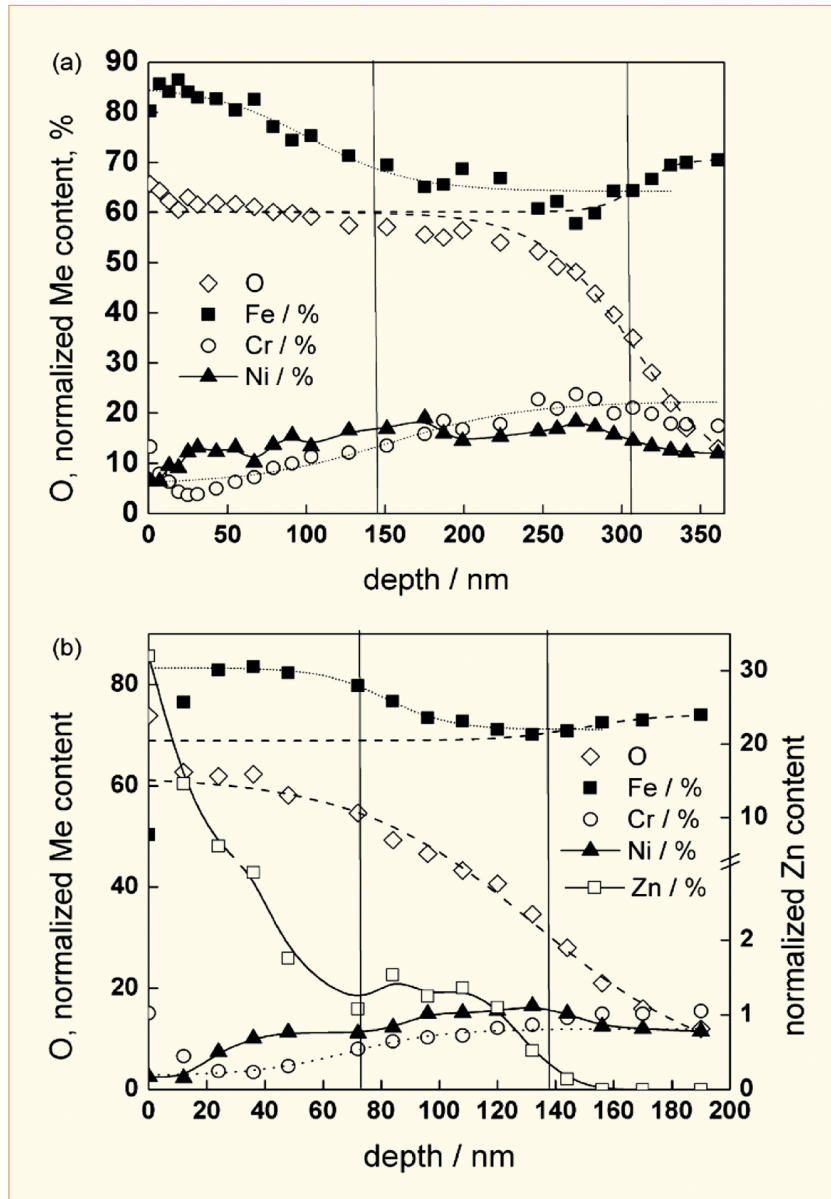


Figure 4-1: XPS depth profiles of the oxides formed on AISI 316L(NG) in simulated PWR water+0.01M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> without (a) and with 1 ppm Zn (b) at 280 °C at open circuit.

Summarizing, Zn injection has a significant effect on the oxides formed for 72 h in both unbuffered and buffered PWR water, altering both the thickness and the in-depth composition of the oxide and its electrical and electrochemical properties as reflected by the impedance spectroscopic results.

Several studies have been carried out by [Laitinen, et al, 1998], to evaluate the effects of different blocking agents to reduce the incorporation of radioactive species into oxide films growing in typical PWR environments. The results have shown that dissolved zinc in the range of 10 to 40 ppb reduces the pickup of Co-60 by a factor of 8 to 10. The aim of the current work was to clarify the long-term beneficial effects of zinc addition as well as to find out the possible changes in activity pickup behaviour when the zinc addition is interrupted.

The oxides formed on stainless steel samples exposed to simulated primary PWR coolant during three subsequent zinc injection periods were thin and dense, and the oxide thicknesses remained almost constant (see Figure 4-2). After the zinc dosing periods, the oxide films were found to be enriched with Cr when compared with the base metal composition, and incorporation of Zn was clearly detected (see Figure 4-3).

Incorporation of Co-60 into the oxide films was found to be low during the zinc injection periods. The elemental depth profiles in the oxide films were found to remain unchanged during the subsequent injection of Zn.

The activity incorporation into the stainless-steel oxides started to increase as soon as zinc dosing to the coolant was stopped (Figure 4-2). However, the Co-60 concentration was lowest on the samples, which were first oxidized in Zn containing primary coolant. This could indicate that zinc in the oxide continued to block the adsorption sites for Co-60 incorporation even though Zn concentration in the coolant was lower than 1 ppb. After the zinc injection period the thicknesses of all oxide films increased, which partly explains also the increase in total activity incorporation.

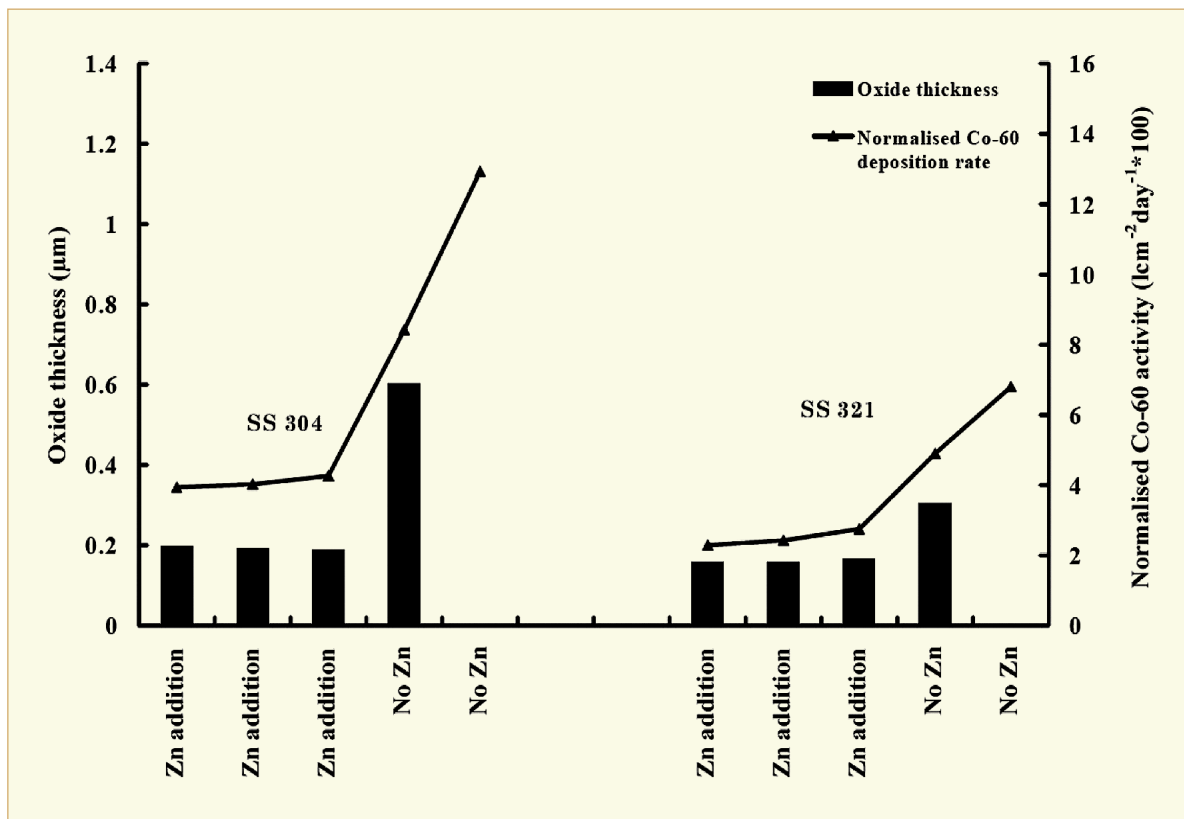


Figure 4-2: Oxide thicknesses and normalised Co-60 pickup rates in the new SS samples during exposures to different test phases [Laitinen et al, 1998].

## 5 Zinc Influence on Radwaste Production in PWR Plants

Zinc injection at PWR units results in significant increase of radiocobalt and CP concentrations in the reactor coolant. Therefore, zinc addition has potential to affect adversely the liquid and/or solid radwaste production in the zinc addition PWR plants. However, no problems or difficulties have been reported neither by US nor by European PWR units with the performance of CVCS demineralizers, handling or storage of resins, or performance of other waste treatment systems that could be attributed to zinc addition. Potential areas of waste generation, where zinc addition might have impact are the following:

- Liquid waste effluents.
- Spent resins and filters in the CVCS.
- Handling and storage of treated radwaste.

In the following, possible impact of zinc addition in these areas is discussed.

### 5.1 Liquid Waste Effluents

Since the addition of zinc constitutes a net put of water into reactor coolant, there is a comparable removal of coolant to compensate for the added zinc solution. However, the amount of zinc solution added is negligible to be considered compared to the amount of coolant that has to be removed for boron dilution to compensate the fuel burn-up.

The amount of coolant removed for dilution needs to be considered with respect to influence of zinc on liquid waste effluents. If plant has Boron Recycling System (BRS), this dilution coolant is directed to BRS where it is recycled. In this case, zinc addition doesn't impact the liquid waste effluent of the plant.

If the plant has no BRS, the dilution coolant is usually discharged via a waste hold-up tank. In such cases, an impact of zinc addition on liquid waste effluent may occur depending of the zinc injection rate. For example, for the zinc injection demonstration program at Farley-2 during fuel cycle 10, an increase in liquid waste effluent of about 20% was reported, [EPRI, 2003]. During that time the zinc injection rate was relatively high with 15-20 gph (57-75 l/h). If injection rates were much lower, the additional waste processing load for discharges due to zinc injection would be much less, as confirmed by field experience. For example, Callaway plant, that had injection rate of about 0.016 gph (1 ml/min), has reported that the additional liquid waste effluent processing due to zinc injection at their plant was not discernible.

EdF has compared the analyses of the liquid waste effluents before and after starting the zinc injection at Bugey-2 and 4 (see Figure 5-1). Based on the results of their surveillance, they have confirmed that the increase in radiocobalt concentrations in the reactor coolant during power operation and plant shutdown does not necessarily cause an increase in the plant liquid waste effluents if the correct and efficient operation of the plant purification systems is ensured, [Tigeras et al, 2008a].

EdF continued to investigate the influence of zinc injection on liquid waste effluent at Bugey plant, and published the results in NPC 2010, Quebec City and NPC 2014, Sapporo, which are shown in Figure 5-2, [Tigeras, 2010] and Figure 5-3, [Piana, 2014], respectively.

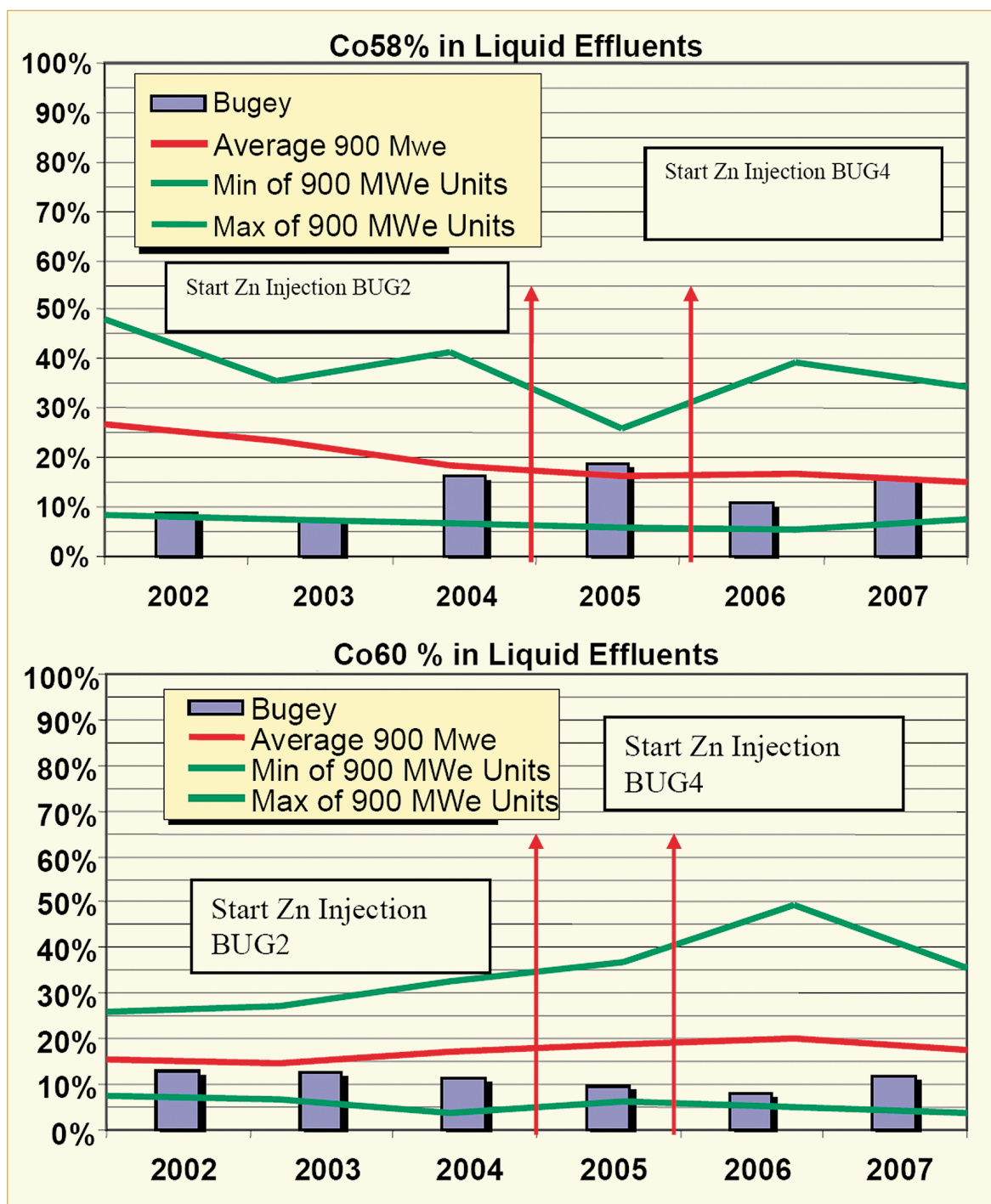


Figure 5-1:  $^{58}\text{Co}$  and  $^{60}\text{Co}$  contribution to liquid waste effluent at EdF Bugey plant [Tigeras et al, 2008a].

Based on these results, EdF confirmed that neither three cycles nor six cycles of zinc addition at Bugey plant caused any significant changes even in the detailed isotopic distribution in the liquid waste effluent. 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.

Based on this field experience, it can be concluded that the liquid waste effluent releases remain manageable with the addition of zinc into reactor coolant. It should further be mentioned that other plant operation events such as shutdown, plant trip, fuel defects, etc could impact the reactor coolant activity and pollution that exceed the effect of zinc injection by several orders of magnitude.



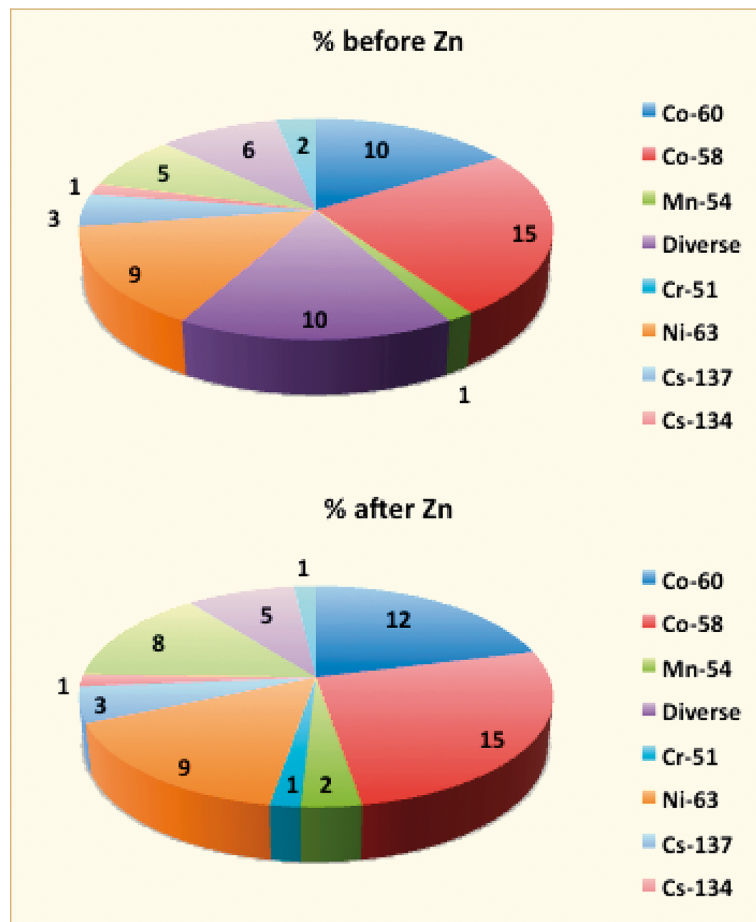


Figure 5-2: Isotopic nuclide distribution in the liquid waste effluents at Bugey plant before and after three cycles of zinc addition [Tigeras et al, 2010].

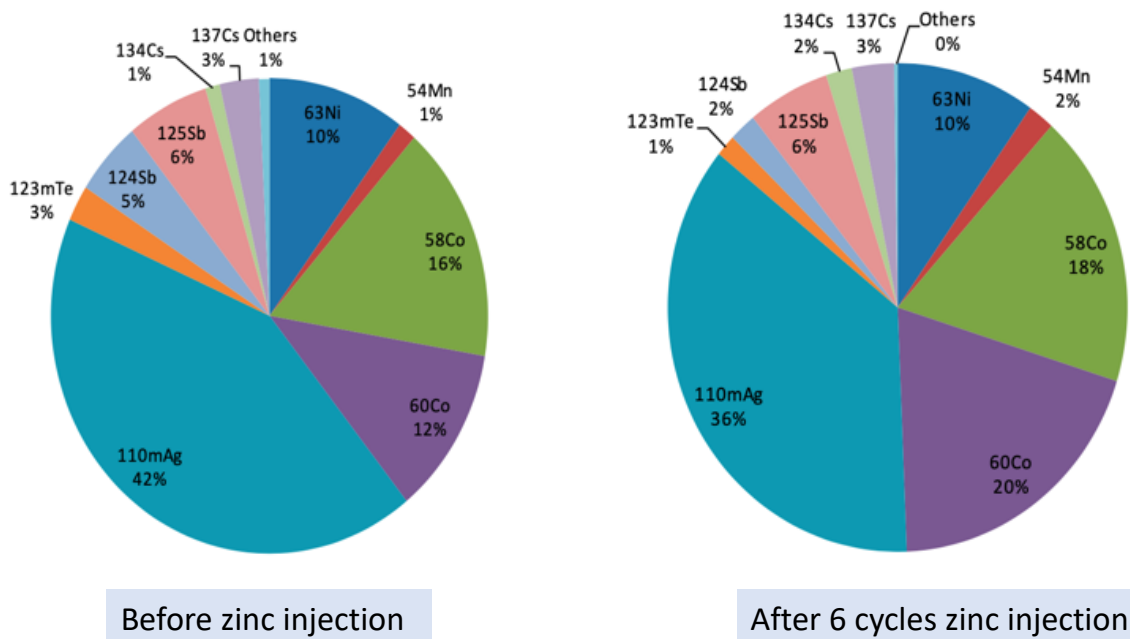


Figure 5-3: Isotopic distribution in liquid effluents at Bugey PWR before zinc injection and after 6 fuel cycles of zinc injection, [Piana, 2014]



## 5.2 Spent Resins and Filters in CVCS

Zinc injection adds to the inventory of cations (in particular iron and nickel), anions (carbon dioxide from zinc acetate), and radioactive isotopes ( $^{58}\text{Co}$ ,  $^{60}\text{Co}$  and  $^{65}\text{Zn}$  particularly if natural zinc is used) to be removed by demineralizers in the CVCS letdown line. Coolant CP concentrations can be increased by factor 2-3,  $^{58}\text{Co}$  and  $^{60}\text{Co}$  activities by factor 10, in US PWR units an increase in  $^{58}\text{Co}$  even up to 30 was experienced, [EPRI, 1999]. All these causes additional loading of the demineralizer resins. However, field experience confirmed that, up to date in none of the zinc addition 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. If natural zinc is used, this additional cost will even be more due to additional radioactivity associated with  $^{65}\text{Zn}$ . This increased amount of activity in the spent resins must be considered in their packaging, shipping, and burial.

In Siemens designed zinc addition PWR plants, there is no reported information regarding abnormal dose rate increase in CVCS demineralizers after zinc addition, or any negative effect of zinc on operating performance of mechanical filters downstream of demineralizers.

## 5.3 Spent Filter Cartridges in CVCS

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. In few cases, increased filter replacements were reported in some PWR units with zinc addition, such as Farley-2 which reported repeated filter clogging in one cycle in 1999, and Diablo Canyon-1 which estimated in the first zinc cycle that the filter usage had doubled. However, the usage of CVCS filters returned to pre-zinc levels in later fuel cycles. Another example is the Beaver Valley-1 unit that has reported an increase in CVCS filter usage since commencing zinc injection. Figure 5-4 shows the increased filter usage during the fuel cycles 15 to 17 comparing filter replacements to zinc concentration and radiocobalt concentration levels. This filter is a 6 micron filter located downstream of the CVCS demineralizers. Prior to zinc injection, the plant had little experience with filter replacement, but during fuel cycle 16 through to 17 several filter replacements were necessary.

It should be noticed that although an increase in usage of CVCS filters may occur in the first few fuel cycles with zinc injection, this trend usually returns to previous filter usage during pre-zinc injection in the subsequent fuel 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.

## 6 Executive Summary and Recommendations

### 6.1 PWR Plants

#### 6.1.1 Summary

In this Section, the summary of Chapter 3 of this report is given. It comprises the most relevant information:

Zinc is injected in PWR plants for twenty-six years with the objective to reduce the dose rates and/or to mitigate PWSCC of Alloy 600MA. Whereas zinc is injected at target concentrations of about 5 µg/kg for reduction of dose rates, the selected target concentration are in the range of 15–40 µg/kg for mitigation of PWSCC. In both cases, zinc injected into reactor coolant incorporates into oxide films on the RCS surfaces and improves their protective behaviour. This improvement of oxide films leads to reduction of radiation fields and can inhibit the occurrence of PWSCC of Alloy 600MA. The mechanism how the zinc injection works and influences positively the dose rate evolution, material compatibility of structural materials, PWSCC mitigation of alloy 600MA and fuel performance can be summarized as follows:

#### **Dose rate reduction:**

The worldwide most accepted model that explains how zinc injection into reactor coolant can fulfil the above mentioned objectives is the “Site Preference Energy” model. According to this model, zinc has high incorporation affinity for the tetrahedral sites of the spinel oxide structure. Its site preference energy is the highest among all other cations that are relevant for the PWR reactor coolant. Hence, zinc can displace these cations that occupy tetrahedral spinel sites, such as iron, nickel from the oxide films. Whereas zinc has the highest site preference energy for tetrahedral sites, chromium has the highest site preference energy for the octahedral sites. Therefore, zinc is incorporated preferentially into inner oxide layers, which mainly consists of chromites, and builds very stable oxide films that improve the protective behaviour of the passive layers. This effect of the zinc addition results in reduced metal release and corrosion rates of the RCS structural materials, which leads to formation of thinner oxide layers due to reduction of source term. In addition, once the tetrahedral sites are occupied by zinc, this incorporated zinc inhibits the further incorporation of fresh radiocobalt into oxide layers, because its site preference energy for tetrahedral sites is higher than that of cobalt. These two behaviours of zinc, displacement of radiocobalt from the oxide layers and inhibition of fresh radiocobalt into oxide layers, are the mechanisms how zinc addition results in reduction of radiation fields.

The field experience confirmed that the effect of zinc addition on out-of-core dose rate reduction is plant specific and depends on different parameters, such as age of the plant, structural materials used (in particular, the SG tubing material), composition and morphology of the oxide films on the RCS surfaces and the way how the plants operate (base load or load follow operations). In some plants, in particular in PWR units that have nickel base alloy SG tubes, high decrease of radiation fields in the range of 20-30% was observed after zinc injection during the first several fuel cycles with zinc injection, which declined later during subsequent cycles. In the case of PWR units with iron base alloy SG tubes, such high dose rate reduction was not observed at the beginning of zinc injection. The dose rate reduction experienced was usually in the range of about 10-12% per year. In some cases, even the radiation field reduction was observed after several cycles of zinc injection. This is because the standard dose rate monitoring equipments used in the plants have usually an accuracy of  $\pm 25\%$ . These differences in dose rate reduction observed in different PWR plants can be explained as follows:

The radiation fields in PWR plants are mainly built-up by radiocobalts, i.e.,  $^{58}\text{Co}$  and  $^{60}\text{Co}$ , which incorporate into oxide layers on the RCS out-of-core surfaces. The main source of  $^{58}\text{Co}$  is the  $^{58}\text{Ni}$  in the nickel content (depending on used material: 32-72%) of the SG tubing material with huge surfaces that is about 70-75% of the total RCS surfaces. The main source of  $^{60}\text{Co}$  is the  $^{59}\text{Co}$  in the cobalt content (~60%) of the stellites used as hard facing in RCS (mainly as RPV internals with insignificant surface area of several  $\text{m}^2$ ). Both radiocobalt isotopes,  $^{58}\text{Co}$  and  $^{60}\text{Co}$ , are produced in the radiation field of the core by nuclear reactions  $^{58}\text{Ni}(\text{n},\text{p})^{58}\text{Co}$ , and  $^{59}\text{Co}(\text{n},\gamma)^{60}\text{Co}$ , respectively. Whereas,  $^{58}\text{Co}$  has a relatively short life time ( $t_{1/2}$ : 70.8 d),  $^{60}\text{Co}$  is a long-life radioisotope with  $t_{1/2}$ : 5.27 years. Therefore, on the long term,  $^{60}\text{Co}$  dominates the radiation fields in PWR plants, in particular if stellites are used in RCS, although more  $^{58}\text{Co}$  is produced in the radiation field of the core. This influence of  $^{60}\text{Co}$  on radiation fields is more pronounced in PWR plants with iron base alloy SG tubes, where less amount of  $^{58}\text{Co}$  is produced. For example, in old Siemens designed PWR units where stellites are used in core internals, 90-95% of the radiation fields are due to  $^{60}\text{Co}$ . Especially in old PWR units, this  $^{60}\text{Co}$  is incorporated in the lower part of the inner oxide layers since years, where old  $^{58}\text{Co}$  no more exists due to its short lifetime. To these lowest parts of the inner oxide layers, zinc has difficult or slow access by diffusion and therefore, cannot displace  $^{60}\text{Co}$  there, at least within a time of several fuel cycles of zinc injection. However, zinc that is incorporated into upper part of the inner oxide layers inhibits the further incorporation of fresh radiocobalt. Hence, without replenishment by fresh radiocobalt, the radiation fields decrease by natural decay of already incorporated  $^{60}\text{Co}$ , which is about 10-12% per year. This is what is experienced at all older Siemens designed PWR units with iron base Alloy 800NG SG tubes and also in some old PWRs with nickel base Alloy 600 SG tubes. If dose rates decrease by zinc injection according to natural decay of  $^{60}\text{Co}$ , then zinc addition has solely inhibition effect as mechanism. If radiation field reduction is in excess of that, what is caused by natural decay of  $^{60}\text{Co}$ , then zinc injection has also displacement effect in addition to inhibition effect as mechanism. This was experienced particularly at US PWR units that have nickel base Alloy 600 SG tubes. In the case of alloy 600 SG tubes that have high nickel content as  $^{58}\text{Co}$  source, much more  $^{58}\text{Co}$  is produced by core radiation. This may result in more incorporated  $^{58}\text{Co}$  in the upper part of the inner oxide layers than in PWR units with iron base alloy SG tubes, which are then displaced by zinc after introducing the zinc injection. This radiocobalt displacement in addition to natural decay leads to higher dose rate reductions at the beginning of zinc injection as observed in US PWR plants.

Based on field data, the following additional conclusive summary with respect to effect of zinc injection on dose rate reduction can be given:

- Low zinc concentration, as low as 5  $\mu\text{g}/\text{kg}$ , have been shown to reduce dose rates by about 30-40% with ~ 300 ppbxmonth zinc exposure corresponding to 4-5 zinc cycles. This reduction is in the same range as that experienced at PWR plants with similar zinc exposure at higher zinc concentrations, as high as 20-40  $\mu\text{g}/\text{kg}$ , but in shorter times.
- For the long term, the dose rate reduction achieved by adding depleted zinc is very similar in PWR plants, which have nickel base Alloy 600/690 SG tubing material to that experienced in plants with iron base Alloy 800NG SG tubes.
- For equivalent zinc exposures (expressed in terms of the compound unit ppbxmonth), the radiation field reduction is about 10-20% more at plants using depleted zinc than at those using natural zinc. This is attributed to the effect of  $^{65}\text{Zn}$  at the plants using natural zinc.  $^{65}\text{Zn}$  is formed by  $(\text{n},\gamma)$  reaction from the natural zinc isotope  $^{64}\text{Zn}$  and it is a hard  $\gamma$ -emitter with energy of 1.116 MeV and has a half lifetime of 244 days. There are only five US PWR units (Farley-1 & 2, Diablo Canyon-1 & 2 and Beaver Valley-1) that are injecting natural zinc at high coolant concentrations of 15-40  $\mu\text{g}/\text{kg}$  in order to mitigate PWSCC, and have selected natural zinc solely for economic reasons. After years of operation with high natural zinc concentration in the primary coolant,  $^{65}\text{Zn}$  activity could begin to contribute significantly to the total coolant activity because of the considerable reduction of radiocobalt activity.

- The effect of zinc injection on dose rate reduction is influenced by the way in which the PWR plants are operated. The field experience confirmed that “Load Follow Operation”, “Mid-Cycle Shutdowns” and/or “Plant Trip” affect the positive influence of zinc addition on dose rate reduction. Such operational events with coolant temperature decrease result in release of incorporated zinc from oxide films to reactor coolant due to retrograde solubility behaviour of zinc oxide. This usually influences adversely the dose rate reduction.
- The best and most adequate method to verify the effect of zinc injection on dose rate reduction is the  $\gamma$ -activity measurements of RCS ex-core surfaces. This method is recommended to understand the evolution of dose rate in the plants.
- If the zinc addition is applied at the beginning of the plant service life, excellent protective oxide films with zinc incorporation can be formed on the RCS out-of-core surfaces that inhibit the incorporation of radiocobalt, which results in extremely low radiation fields in the future. This is confirmed by field experience gained at Angra-2 plant in Brazil, at Tomari Unit 3 in Japan and in Atucha Unit 2 in Argentina.
- Zinc addition is also recommended to use as passivation step after full system chemical decontamination (FSD) to mitigate the recontamination rates. This was successfully demonstrated at NPP Grafenrheinfeld after FSD.

### **Material compatibility:**

The improvement of oxide films by zinc injection on the surfaces of RCS structural materials results in reduced metal release and corrosion rates. This observation is valid for all structural materials used in PWR plants including the fuel cladding materials. The reduction of source term of CPs leads to reduced fuel deposits and thus to reduced radiation fields.

### **PWSCC mitigation:**

Based on the laboratory testing data and the field data, due to the improvement of oxide films on the nickel base Alloy 600MA surfaces, zinc injection can be used as remedy against PWSCC of Alloy 600MA or Alloy 600TT, as explained in the following.

Almost all laboratory tests confirm the beneficial effect of zinc on PWSCC initiation. This is easy to understand, because the large surface area of the non-pre-cracked coupons provides easy access to zinc ions for incorporation into spinel oxide films. Zinc incorporation enhances the stability of spinel oxide films thus increases PWSCC resistance of the nickel base alloys. This results in delay or inhibition of the PWSCC initiation. In the case of zinc effects on the PWSCC CGRs, the laboratory tests results are not so consistent as they are for initiation and, indeed they are rather contradictory. The conclusions of the various research teams range from partial or total inhibition of CGRs to no effect at all. This is because the situation is different and more complicated in case of inhibiting crack propagation.

In order to have a beneficial effect on PWSCC propagation, zinc must be able to penetrate into the crack, reach the crack tip, and incorporate into oxide layers in that location. It should be considered that zinc has strong incorporation affinity for mainly tetrahedral sites of the spinel structures. If on the crack tip surface no spinel oxide film is formed, zinc should not have any effect on CGR even if it reaches the crack tip. In addition, zinc needs to reach the crack tip faster than the crack propagates or otherwise the crack tip would run away faster than zinc can migrate to the crack tip. In other words, for fast growing long cracks, zinc may have little chance to reach the crack tip on time before the crack continues to propagate. It can also be postulated that in long cracks, zinc could be fully consumed by the more mature oxide films formed on the crack fracture surfaces on the way before it reaches the crack tip.

A review of laboratory tests results indicates that the tests that failed to show a beneficial zinc effect on PWSCC CGR were mainly those from thick-walled nickel base alloy specimens such as archived CRDM nozzles or when testing under extreme high stress intensities. It is possible that such long and fast propagating PWSCC occurs in thick-walled nickel base alloys under high stress intensities, like CRDM nozzles, Butt Welds, etc, that would explain some of the observed laboratory tests results. However, according to some experts, there should be no such evidence for this. On the other hand, the tests with thin-walled SG tube samples under realistic lower stress levels could show a beneficial effect of zinc on PWSCC CGR. In such tests, the presence of chromium spinel type oxides and zinc at the crack tip was also observed and reported. Maybe again, it is possible that, in thin-walled nickel base alloys under realistic stress intensities, shallow and slowly growing cracks occur. Under such conditions, it could be expected that zinc has the ability to penetrate into the crack tip and can inhibit the PWSCC CGR by incorporation into oxide films on the crack tip surface.

At field, beneficial effect of zinc addition to reduce the PWSCC initiation is definitely observed. Hence, the use of zinc injection at the PWR plants can be warranted for this purpose alone since there are no obvious disadvantages for other systems and components. However, the effectiveness of zinc on PWSCC propagation is not so clear. Field results indicate that zinc addition has a moderate slowing effect on the growth of PWSCC cracks in SG tubes. This effect of zinc addition on CGR in SG tubes can possibly be explained by the rather shallow and slow growing cracks in thin-walled SG tubes, where zinc can more easily have impact on PWSCC propagation. The experience gained at Diablo Canyon units and also at other units regarding the effect of zinc on PWSCC in SG tubes is encouraging because the rate of PWSCC growth at these plants was decreasing, instead of increasing as would be expected in the absence of zinc injection. In the case of deeper and fast-growing cracks, the PWSCC CGR response to zinc injection might not be so good due to a relatively slow migration velocity of the zinc in the crack towards crack tip that may be too slow for deep and fast growing PWSCC cracks, as discussed above. Maybe this is the reason, why positive effect of zinc addition could not always be seen in thick-walled nickel base alloys like Butt welds or CRDM nozzles. At the present, not enough field inspection data exist to evaluate the effectiveness of the zinc injection on PWSCC CGR in thick-walled nickel base alloys such as CRDM nozzles and butt welds.

The field experience gained with zinc injection with respect to PWSCC mitigation is encouraging and, in the absence of any known significant detrimental effects other than  $^{65}\text{Zn}$  production from natural zinc, can warrant the use of zinc for the PWR plants that have used Alloy 600MA or Alloy 600TT and its compatible weld metals in their RCS.

### **Fuel performance:**

Zinc injection results in release of CPs into reactor coolant. This increase in the coolant concentration is actually the main concern of the fuel vendors with respect to zinc injection, in particular for plants with high duty core. However, based on over 16 years of PWR field experience with zinc injection, no direct affects of zinc on fuel cladding corrosion have been reported, and is not expected based on the evaluation of all in-pile data and recent out-of-pile loop tests with respect to material compatibility of zinc injection. In addition, the laboratory studies have shown that dissolved zinc in PWR simulated coolant has no effect on zirconium alloys, either positive or negative, because zinc only effects the corrosion of alloys containing chromium and the benefit is proportional to the chromium content of the alloy. Fuel cladding zirconium alloys contain less than 1% chromium. The only possible mechanism for deleterious effects of zinc injection on fuel cladding corrosion could be the modification of the fuel deposits or change of the local fuel deposit chemistry by zinc injection that could cause enhanced cladding corrosion. This is because increase in CP concentration of reactor coolant can result in more and dense crud deposits on fuel rods. This type of fuel deposit may cause a decrease in heat flux, which results in an increase in the clad surface temperature and the corrosion rate of the cladding material.

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