

# Historical Evolution of Coolant Chemistry for PWR and VVER Plants: 1960 to Present; Including Basis of the Guidelines

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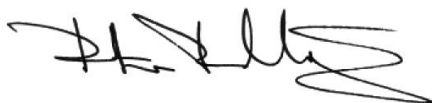


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A handwritten signature in black ink, appearing to read 'P. Rudling', with a stylized flourish at the end.

Mr Peter Rudling, President of ANT International

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# 1 Introduction

This report describes the historical development of the water chemistry in primary side of the PWR and VVER plants since 1960s up to present. Starting with the first research PWR plants in 1950s in USA without applying any water chemistry addition of neither alkaline reagent nor hydrogen, lot of fuel performance degradations were experienced in 1950s and 1960s; such as, heavy fuel deposits, flow restrictions across the core, reactivity losses and high radiation fields. Even the first AOA (Axial Offset Anomaly) indications were experienced in a PWR with low core duty operating without applying water chemistry treatment.

Due to all these degradations experienced at field, intensive root cause analysis and research work were performed to mitigate and counteract these degradations; and for this purpose, PWR industry started to inject chemicals in reactor coolant system. These investigations revealed also the influence of the structural materials, especially the steam generator tubes, on the experienced degradation phenomena. Based on the field experience and the results of the investigations with respect to plant corrosion and radiation performance in the primary circuit, the water chemistry for primary circuit had to be modified and improved stepwise to counteract these performance degradations. In this report, the root cause of the experienced degradations is discussed and the water chemistry mitigation steps are explained. This explanation includes also how the concentration of the coolant chemistry additives, e.g. dissolved hydrogen and lithium hydroxide and also the strategy of their application was changed with time. Especially, the improvements of the coolant chemistry by Utilities was stringently necessary after 1990s due to economic reasons in the light of the trend towards extended fuel cycles, higher core duty, increasing stringent dose rate control, decreasing the refuelling outage duration, and reducing operating cost.

These improvements were reflected also in continuous modifications of the coolant chemistry guidelines. However, these modifications in international coolant chemistry guidelines (e.g. EPRI, EdF, VGB, MHI and VVER coolant chemistry guidelines), were somehow not exactly the same based on the used structural materials, and the field experience gained with the plants. In this report, existing guidelines (especially EPRI, EdF and VGB guidelines) are described in comparison with each other. The similarities and differences in these guidelines and the reasons for these differences are explained. Finally, recommendations are given with respect to application of the coolant chemistry strategies with a specific focus on the optimum lithium and hydrogen concentration during the fuel cycle based on the core duty design of the plants, the fuel cycle length and the structural materials used in the reactor coolant system. In addition, the advantages and inconveniences of KOH versus LiOH for PWRs and VVERs are also discussed.

In this report it is intended to provide a detailed background description of the PWR/VVER Primary Side Coolant Chemistry for more understanding of the coolant chemistry strategies and the chemistry guidelines. Furthermore, it should provide a strong support to the utilities for establishing a responsive plant specific chemistry program. It may also help the Manufacturers and Regulators at having a detailed approach of primary water chemistry and corresponding issues.

This Report for Coolant Chemistry consists of following chapters:

Chapter 1: Introduction

In this chapter the structure of the report is described.

Chapter 2: *Worldwide historical PWR field experience*

This chapter describes the field experience regarding the plant performance problems initiated by inadequate coolant chemistry, which were the reason for improvement and modification of the water chemistry strategies.

Chapter 3: *Localized corrosion experienced in PWR reactor coolant systems*

In this chapter the mechanism of the localized type of corrosion worldwide experienced in PWR primary side is explained and the influence of coolant chemistry on corrosion

mechanism is discussed. In addition, fuel cladding corrosion and its influencing parameters are also discussed in detail

Chapter 4: *Water chemistry strategies for problem solution*

The main root cause of the experienced degradations in reactor coolant system is the coolant corrosion products (so called CRUD) and fuel deposits. In order to better understand the selected water chemistry strategies to counterattack these degradations, in this chapter the influence of structural materials on the chemical composition of the CRUD and fuel deposits is described. Coolant CRUD and fuel deposits, and especially their chemical composition, are influencing highly the fuel and plant radiation performance and fuel cladding corrosion. Therefore, the behavior of the CRUD and its influence on these degradations is described in detail. The selection of water chemistry strategies addresses to the mitigation of these problems.

Chapter 5: *Historical development of coolant chemistry*

This chapter describes the development of the water chemistry parameters and strategies based on the problems experienced at the field. Finally, VVER Coolant Chemistry that uses potassium hydroxide and Ammonia instead of lithium hydroxide and hydrogen gas respectively is described in comparison with PWR Coolant Chemistry.

Chapter 6: *Current PWR coolant chemistry guidelines*

In this chapter international water chemistry guidelines, like EPRI, EdF, VGB, are described and compared with each other; similarities and differences are explained; the reasons for differences are given.

Chapter 7: *Worldwide new aspects/strategies for coolant chemistry*

This chapter summarizes the recent discussions since 2000s regarding the modification of the established coolant chemistry for mitigation of Axial Offset Anomaly (AOA) and Primary Water Stress Corrosion Cracking (PWSCC).

Chapter 8: *ANT recommendations for PWR plants*

Finally, this chapter concludes the information given in the report with the recommended coolant chemistry strategy for the PWR plants based on their selected structural materials and core duty.

Chapter 9: *References*

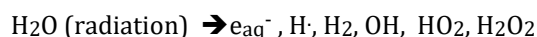
Summarizes the references used for writing this report.

## 2 Worldwide Historical PWR Field Experience

### 2.1 Objective of the Coolant Chemistry

In nuclear power plants the energy for production of electricity is produced in reactor core by fission of Uranium-235 and plutonium-239 (produced from Uranium-238) isotopes. To fission these isotopes thermal neutrons are needed, which are produced from fast neutrons by moderation with water. In case of Pressurized water Reactors (PWR) and also in VVER plants (Voda Voda Energo Reactor: Acronym for the Russian type of PWR), the energy produced in reactor core is transferred to steam generators for steam production by circulating water, called Coolant. The circulating coolant is exposed to radiation in the core area and has contact with the structural materials of the Reactor Cooling System (RCS) at high operating temperatures (300 – 330°C), which results in following phenomena:

- 1) **Water radiolysis:** Under radiation exposure water decomposes in the reactor core producing radiolysis products according to the reaction



Some of these radiolysis products (OH, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>) are oxidants and cause corrosion of structural materials.

- 2) **Corrosion of structural materials:** At high temperatures of about 300 – 330°C the structural materials selected for RCS are not stable in the water. They dissolve and release metal ions as schematically illustrated in Figure 2-1. This dissolution (corrosion) of metals is called anodic reaction. For the continuation of the corrosion, the electrons released from the metal have to be removed by cathodic reactions, either by hydrogen ion or oxygen (see Figure 2-1). If the cathodic reactions are stopped, the corrosion will also be stopped. This means to avoid the corrosion of the structural materials acidic conditions and oxygen should be avoided in RCS under operating conditions! Otherwise, based on field experience gained since 1950s, the formation of fuel corrosion product deposits, caused by corrosion of structural materials, results most likely in enhanced fuel cladding corrosion, high radiation fields and even formation of Axial Offset Anomaly (AOA), as will be explained in the following Chapters 2.2 to 2.4.

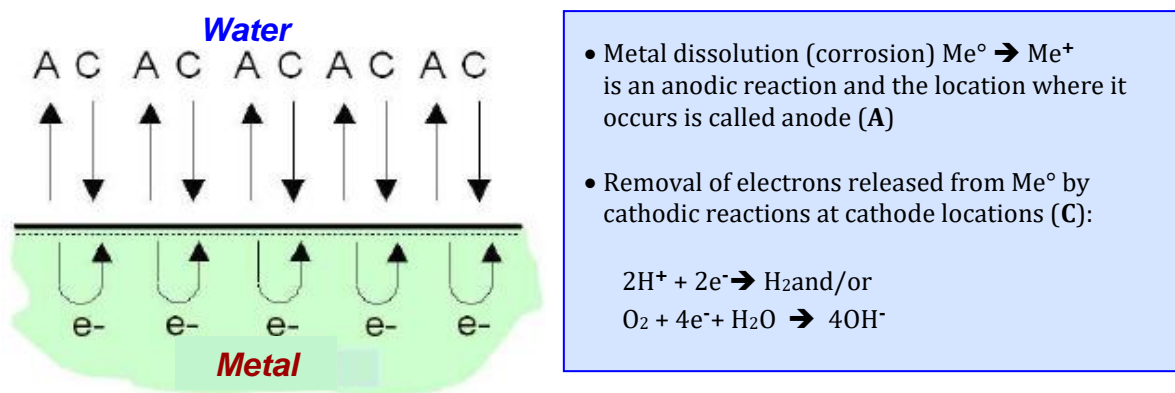


Figure 2-1: Schematic illustration of general corrosion mechanism.

Therefore, the main objective of the coolant chemistry is to counteract and minimize the water radiolysis and corrosion of the structural materials. For this purpose, slightly alkaline coolant chemistry under reducing condition is applied in RCS of the PWR and VVER plants. To minimize the water radiolysis and thus to establish reducing conditions, hydrogen gas is added to the reactor coolant (for details see Chapter 5.2) whereas, in VVER plants ammonia is added, which produces hydrogen gas by nuclear reaction in the reactor core (see Chapter 5.3). The alkaline condition is achieved by injection of lithium hydroxide (see Chapter 5.4). In VVER plants potassium hydroxide is used for this purpose (see Chapter 5.5).

This PWR coolant chemistry as applied presently is developed and established stepwise based on the field experience since 1950s to mitigate the experienced problems. Especially, due to steady increase of core duty in PWR industry demanded by economic reasons, made and still makes the modification of the coolant chemistry necessary. In the following chapters the problems experienced at field, which are induced by inadequate coolant chemistry, will be explained for better understanding the background of the coolant chemistry.

## 2.2 Fuel Deposition

The earliest research PWR plants in USA were designed to operate with pure water without applying any water chemistry. They even have not used boric acid as “chemical shim” for the control of reactor reactivity. The reactor reactivity was controlled by control rods. The early investigations of irradiated water systems in those so-called rodded reactors and in-pile loop tests under simulated PWR coolant conditions recognized that irradiated surfaces tend to accumulate corrosion product deposits. Subsequent PWR operation confirmed this observation of corrosion product deposition on fuel assemblies. Especially the acidic conditions enhance the metal release and corrosion rate of the RCS materials, which results in an increased deposition in the core. Core crud deposits are of tremendous significance for PWR operation; because, their consequences are in general

- Increased coolant flow friction resulting in pressure drop across the reactor core,
- Increased temperature of fuel assembly surfaces due to thermal isolation effect of deposits, which may result in increased concentration of coolant additives or impurities that leads to enhanced fuel cladding corrosion and/or in loss of core reactivity.

Some examples that were experienced in 1960s at the field and the influence of coolant pH on this phenomenon are given in the following, in order to demonstrate the importance of the coolant pH control for reliable PWR operation:

The characteristic increase in pressure drop caused by increased coolant flow friction during an irradiation in-pile loop test with 1500 mg/kg boric acid is shown in Figure 2-2, [Picone, 1963]. Significant decrease of pressure drops caused by addition of a base (LiOH) is important to understand why PWR coolant with boric acid for chemical shim needs to be alkalized.

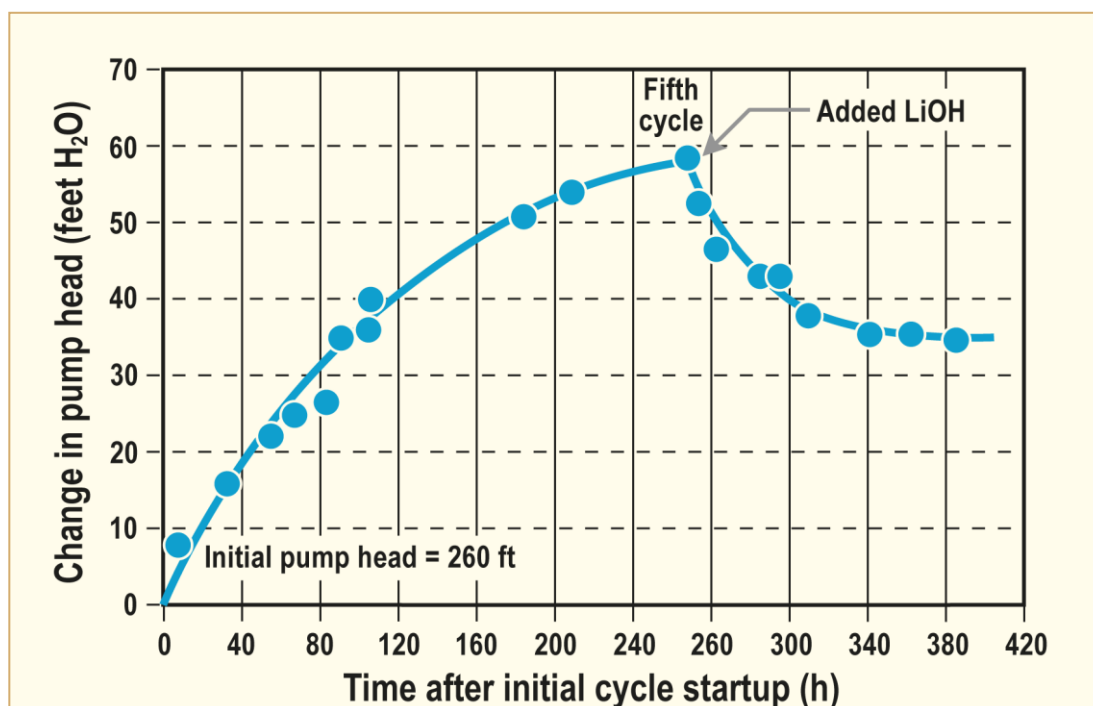


Figure 2-2: Effect of crud deposits and LiOH addition on pressure drop in core, after [Picone, 1963].

Another example of increased coolant friction ( $\Delta p$  increase across the core) and consequently of decreased flow rate in a rodged core is the observation done at Carolina-Virginia Tube Reactor (see Figure 2-3), [Sandberg, 1967]. The investigations by detailed measurements indicated that the pressure drop was localized in the fuel tubes, rather than in the external piping.

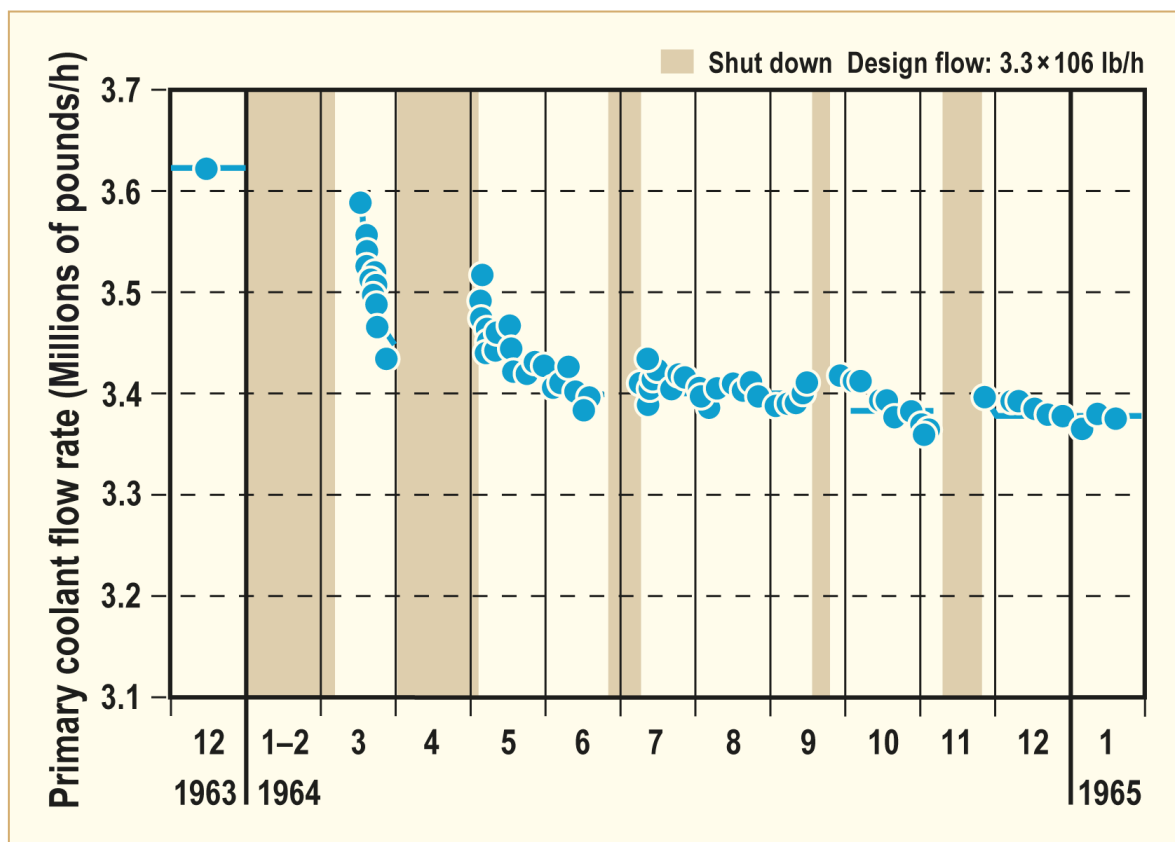


Figure 2-3: Carolina-Virginia tube reactor: Total primary coolant flow rate vs. time, after [Sandberg, 1967].

Bettis Atomic Power Laboratory of Westinghouse has summarized the experience regarding coolant core friction effects in research nuclear power reactors gained in early 1960s in their internal report [BAPL, 1964]. They have reported that the coolant friction was increasing every time as coolant pH was lowered. Decreases in friction upon addition of base were quite rapid. According to their information, it is necessary to operate the PWR cores with adding alkalizing agents such as LiOH, KOH and or ammonia, in order to prevent excessive pressure drop in the core. For example, in case of Shipping port PWR Core II they have selected to apply an ammonia concentration of 40 to 50 mg/kg in the coolant.

During the demonstration program regarding the feasibility of using boric acid as chemical shim for reactivity control (see Chapter 5.1), the effect of coolant alkalinity (pH) on the core reactivity of PWR plants was one of the first unexpected experiences. It was observed that there was loss of core reactivity with decreasing coolant pH. As the coolant pH was increased, there was regain of this reactivity. Figure 2-4 shows for a particular pH test, the change of core reactivity, measured as coolant temperature, with coolant pH at Saxton PWR plant with no boron in the coolant, [Weisman & Bartnoff, 1965]. During this test, pH was decreased by lithium removal caused by putting the CVCS (Chemical and Volume Control System) cation exchange resin filter into service over a period of about 12 hours. During this period with low pH in the coolant, a loss of reactivity (coolant temperature decrease) was observed, with the maximum effect achieved in about 24 hours after termination of lithium removal. The increase of reactivity (coolant temperature increase) following subsequent lithium addition was quicker.

### 3 Localized Corrosion Experienced in PWR Reactor Coolant Systems

As already mentioned in Chapter 2.1, the bare structural materials are not stable in high temperature water; they corrode and release metal ions till these metal ions build protective oxide layers on the metal surfaces, which slow-down and stop the corrosion. The location, where metal dissolution takes place is called anodic locations (A). The released free electrons are removed by  $H^+$ -ions or by  $O_2$  at the cathodic locations (C), according to the reactions.

- 1)  $2H^+ + 2e^- \rightarrow H_2$  and/or
- 2)  $O_2 + 4e^- + H_2O \rightarrow 4OH^-$

If the anodic locations (A) and the cathodic locations (C) are homogeneously distributed on the metal surfaces, this type of corrosion is called uniform or general corrosion (see Figure 3-1a). If the anodic and cathodic locations are not homogeneously distributed but rather huge cathodic surfaces stay in equilibrium with the small anodic surface, in this case due to electro neutrality principle the current density at anodic location will be much higher than at cathodic locations (see Figure 3-1b). This results in fast speed metal dissolution at anode causing localized corrosion. In case of localized corrosion, the corrosion damage occurs over relatively small areas but, potentially, may occur at high penetration rates. The result in such cases may be localized leakage or a decrease in structural integrity.

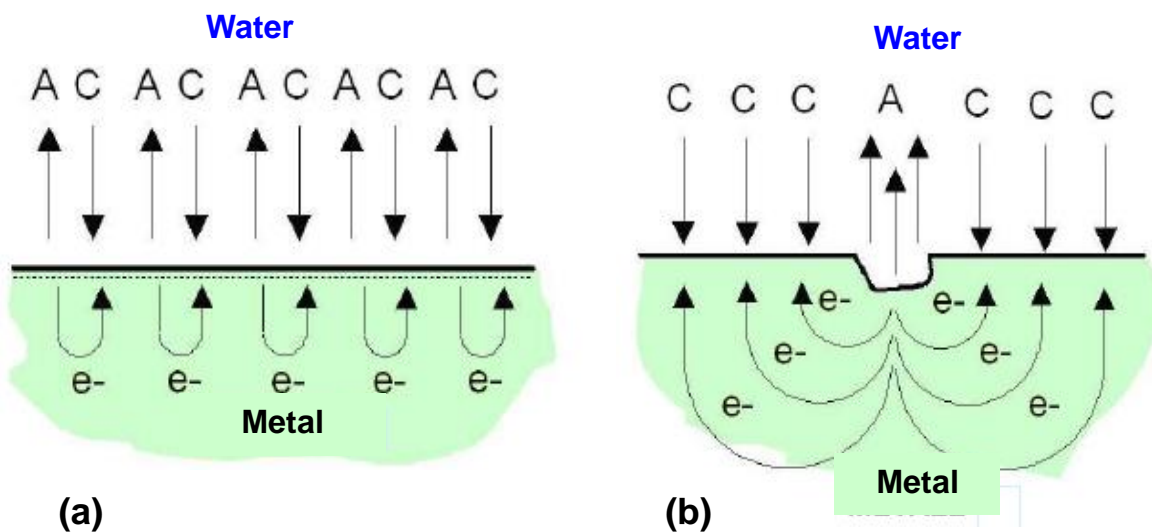


Figure 3-1: Schematic illustration of uniform/general (a) and localized (b) corrosion.

In the following sub-chapters, the mechanism of several localized corrosion types that mostly experienced in PWR RCS will be explained.

#### 3.1 Pitting

Pit initiation on RCS structural alloys that have a very protective oxide layers, such as stainless steels and nickel-base alloys is associated with specific localized material and environment conditions that lead to the locally breakdown of the surface protective oxide layer. Oxide breakdown and pit initiation is often associated with the presence of halide anions (e.g. chlorides). Based on the field experience, chlorides are in most cases the initiator of the pitting corrosion. The source of chlorides in RCS is mostly the use of inappropriate consumables on the material surfaces, which are used sometimes during annual outages for maintenance activities. The mechanism of the pitting corrosion caused by concentrated chlorides can be explained as follows (see Figure 3-2):

Chlorides can react with protective oxide layers building soluble metal chlorides, which results in local destruction of the protective layer, so that unprotective metal starts to dissolve (corrode). For this anodic dissolution of the metal, a cathodic reaction (i.e. oxidation by  $H^+$ - ions or  $O_2$  in water) is necessary to remove the released electrons from the metal surface. The released metal cations diffuse from the surface into pit cavity bulk water due to concentration difference between the bulk water and at the surface; and build there metal hydroxyl-oxides ( $Me(OH)Ox$ ). This results in increase of  $H^+$  ions in the pit cavity (pH decrease). For electrochemical neutralization of these hydrogen ions more chloride ions from bulk water outside of the pit (or from chloride polluted material surfaces) are transported into the pit cavity. This produces hydrochloric acid, which accelerates the metal dissolution. Subsequent repetition of these reactions results in pitting. Due to this autocatalytic production of hydrochloric acid in the pits, pitting rate may get very fast.

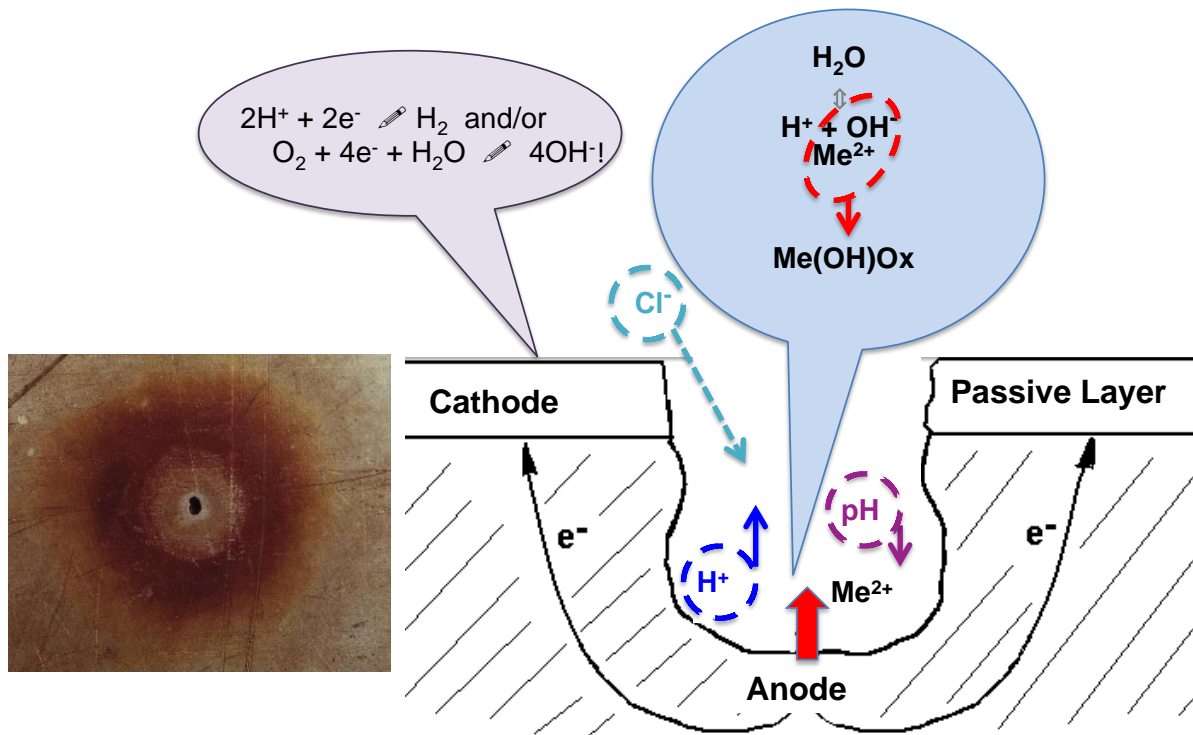


Figure 3-2: Schematic illustration of pitting corrosion mechanism.

Pitting corrosion occurs more seldom than the Primary Water Stress Corrosion Cracking in reactor coolant system; this is because RCS is usually protected against chloride pollution.

## 3.2 Stress Corrosion Cracking (SCC)

Two types of SCC were and are experienced historically and also presently in the Reactor Coolant System (RCS) of the PWR plants. The one is the classical SCC caused by impurities explained in Chapter 3.2.1; the other one is so called Primary Water Stress Corrosion Cracking (PWSCC), which is experienced only in PWR plants having nickel-based alloys (Alloy 600 and its weld materials Alloy 82 and Alloy 182) used in their RCS, like for steam generator tubes or RCS penetrations (e.g. reactor pressure vessel head). The second one doesn't need impurities for its initiation and is caused only by the weakness of the nickel-based alloy (see Chapter 3.2.2). In the following sub-chapters these two kinds of SCC are explained.

### 3.2.1 SCC Caused by Impurities

This type of SCC occurs, if in addition to local destroyed oxide layer on material surface, as described in Chapter 3.1, continues tensile stresses exist on material, which cause breaking of the healed protective

oxide layers. This cyclic healing and breaking of the passive oxide layers usually result in stress corrosion cracking (SCC), as illustrated in Figure 3-3. In case of stainless steels, cracking of material is straight through the grains, therefore called Trans-Granular Stress Corrosion Cracking (TGSCC), whereas, in nickel base alloys usually cracking is along the grain boundary and therefore it is called Inter-Granular Stress Corrosion Cracking (IGSCC).

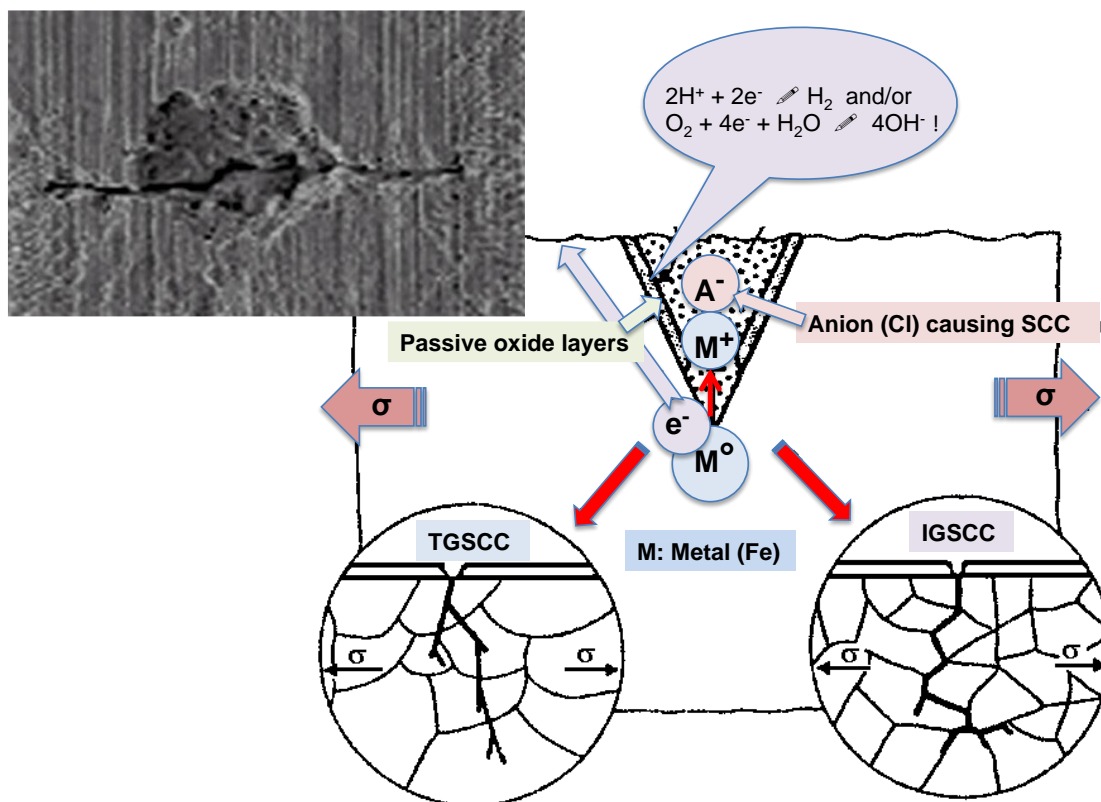


Figure 3-3: Schematic illustration of stress corrosion cracking.

SCC is influenced by chloride and oxygen concentration as shown in Figure 3-4 for stainless steels, [Gordon, 1980]. The results given in this figure indicate that the higher the chloride concentration the less is the oxygen concentration that can be tolerated to avoid SCC. This was interpreted in the past as "ppm Cl x ppm O<sub>2</sub> = 1" rule!

The temperature together with chloride concentration influences stress corrosion cracking also. The higher the temperature the lower is the chloride concentration that causes stress corrosion cracking. However, there exist a threshold temperature for causing SCC, which is in the range of 60-70°C depending on different test results (see Figure 3-5), [Ford et al., 2010].

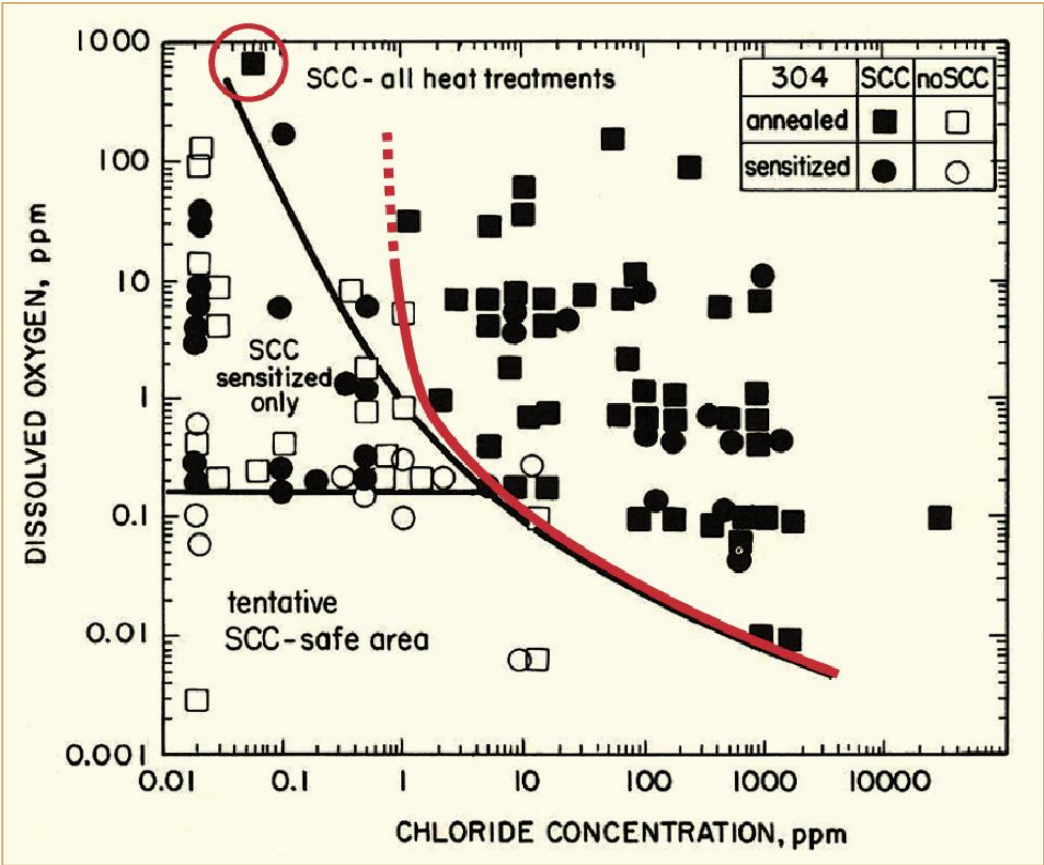


Figure 3-4: Worldwide laboratory test data confirming the influence of chloride and oxygen concentration on stress corrosion cracking for stainless steels, [Gordon, 1980].

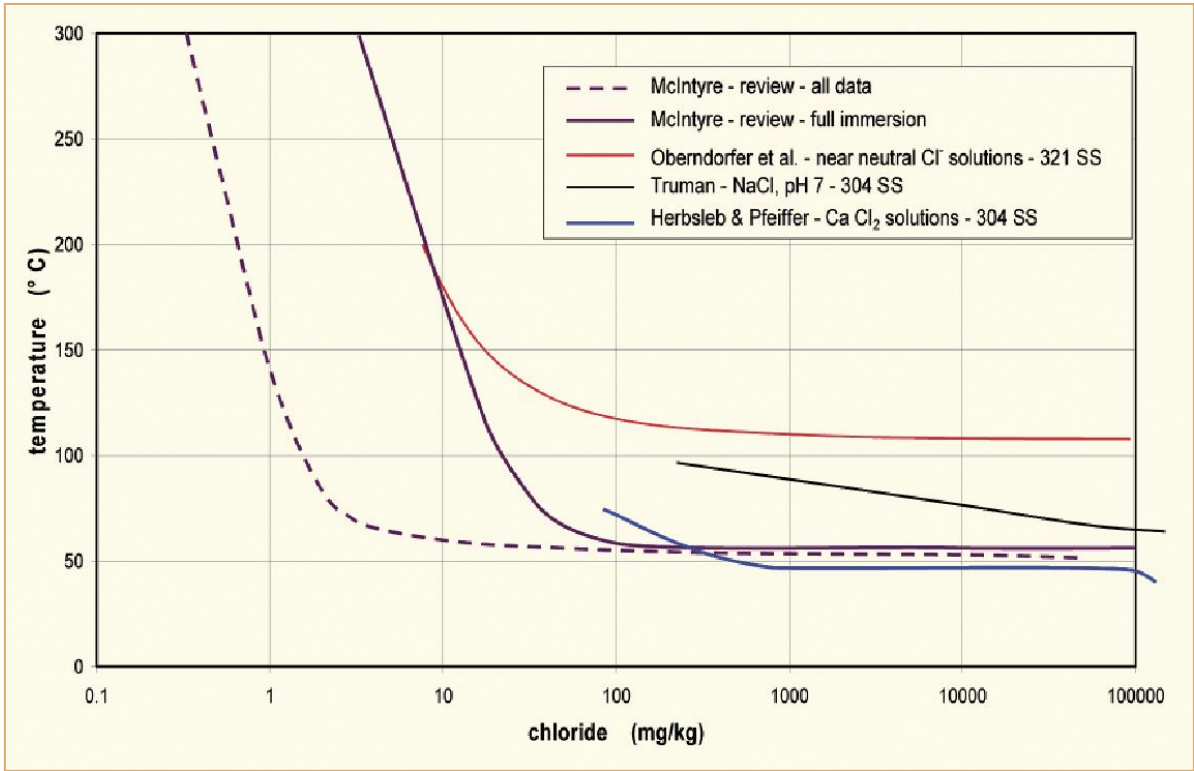


Figure 3-5: Influence of temperature on stress corrosion cracking as a function of chloride concentration, [Truman, 1977] and [Ford et al., 2010].

Figure 3-6 summarizes the crack growth rate in stainless steels at different redox-potentials as a function of chloride and sulphate concentrations, [Andresen, 2010].

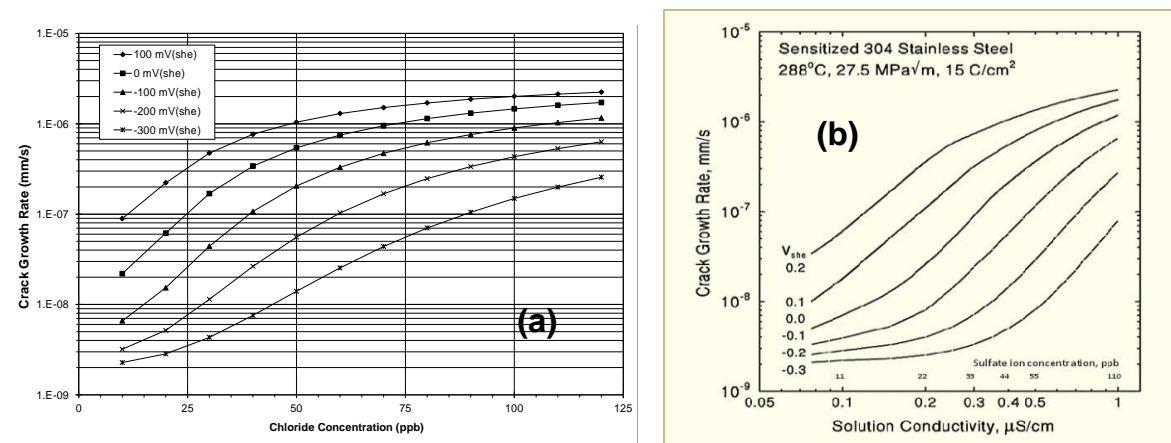


Figure 3-6: Crack growth rate of stress corrosion cracking in stainless steels as a function of chloride (a) and sulphate (b) concentration, [Andresen, 2010].

This in Figure 3-3 described SCC mechanism is the only mechanism for the SCC in stainless steels. The stress corrosion cracking experienced in nickel base Alloy 600 has different mechanism caused by nickel dissolution in the grain boundaries, as mentioned in the following Chapter 3.2.2.

### 3.2.2 Primary Water Stress Corrosion Cracking (PWSCC)

The stress corrosion cracking experienced in nickel base Alloy 600 and its weld materials Alloys 82 and 182 has different mechanism caused by nickel dissolution in the grain boundaries. This also Primary Water Stress Corrosion Cracking (PWSCC) called SCC is mainly due to corrosion sensitivity of the Alloy 600 caused by chromium depletion in presence of stresses, which are the dominant causative factor. Coriou had found that, this material is not stable even in pure water at high temperatures, [Coriou et al., 1959]. The results of his work that shows the sensitivity of alloys to SCC as a function of their nickel content, are summarized in Figure 3-7. According to these results stainless steels can suffer on SCC only in chloride containing environment whereas Alloy 600 can crack even in pure water at high temperatures. Alloys 800 and 690TT are immune against PWSCC under PWR operating conditions. In order to understand the mechanism of PWSCC, one should have more information on protective oxide layers build on the nickel-based alloys; therefore, the mechanism of PWSCC will be explained, in more detail in Chapter 7.2, after discussing the passive oxide layers in Chapter 4.2.

Nickel base Alloy 600 is not only as SG tubing material used but also in lot of RCS penetrations in Westinghouse, Combustion Engineering and Babcock Wilcox designed PWRs, as shown for Westinghouse designed PWR as an example in Figure 3-8.

## 4 Water Chemistry Strategies for Problem Solution

The design and structural materials selected for reactor coolant system and especially the core duty design influencing significantly the selection of the coolant chemistry. Based on almost 60 years of field experience, the corrosion behavior of the structural materials, not only their general corrosion but also localized corrosion forced since decades the modification of coolant chemistry to mitigate the experienced problems (see Chapter 2). The majority of the experienced problems regarding the plant performance were caused by corrosion products that are released from structural materials and transported by coolant to core building there fuel deposits. In the following sub-chapters, the influence of selected design, structural materials and coolant corrosion products on primary side plant performance will be explained.

### 4.1 Design and Material Selection in Reactor Coolant System

#### 4.1.1 Design of Reactor Coolant System

Worldwide there exist three different design type of Nuclear Power Plants (NPP) operating under pressurized water in their Reactor Cooling System. Those are Pressurized Water reactors (PWR), Russian designed VVER plants (Voda Voda Energo Reactor) and CANDU plants (CANadian Deuterium Uranium type of Reactor). Due to different type of design, structural materials and operating conditions (based on core duty design), the applied coolant chemistries are also different in these NPPs. For better understanding the difference in coolant chemistries a brief description of the RCS design and structural materials in these reactors will be given in the Chapter 4.1.1.1 to Chapter 4.1.1.3. In subsequent chapters (Chapter 4.1.2 and Chapter 4.2) the influence of structural materials and the behavior of the corrosion products in PWR RCS respectively will be discussed in more detail.

##### 4.1.1.1 Design of PWR Reactor Coolant System

A typical PWR reactor coolant system arrangement is schematically shown in Figure 4-1.

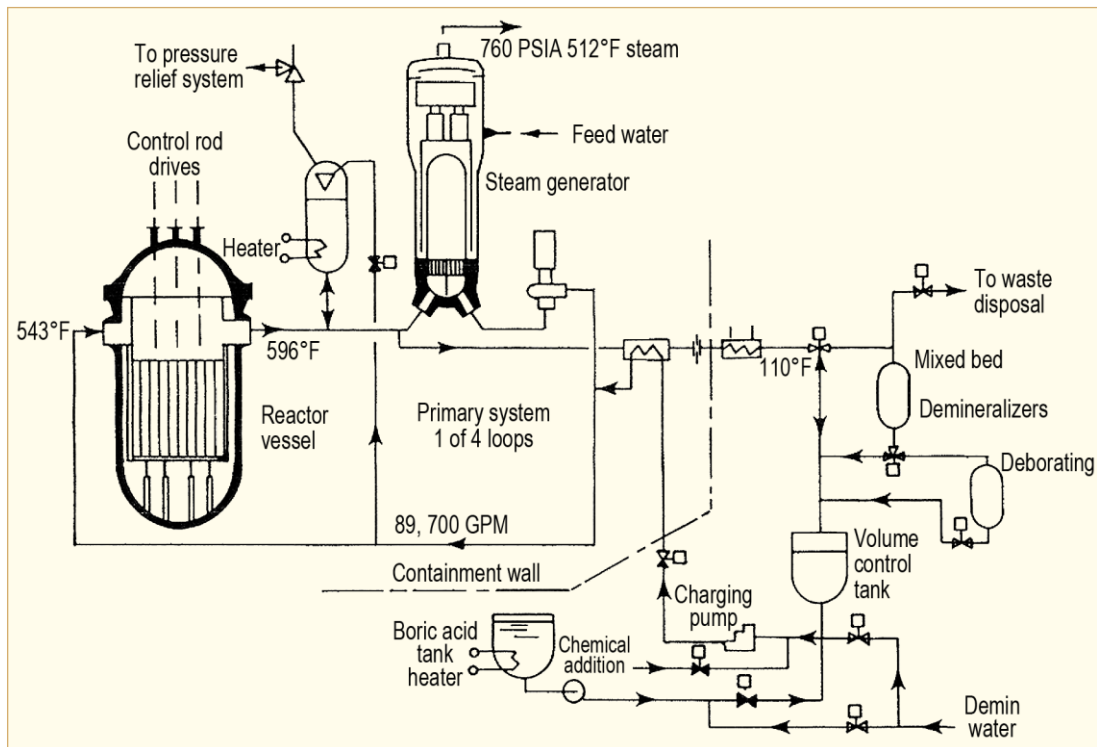


Figure 4-1: Schematic illustration of a PWR reactor coolant system, [Cohen, 1969].

The reactor coolant system operates at a pressure of about 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 Reactor Coolant Pumps (RCP). The pipe work 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). The Pressurizer is connected to the hot leg of one of the loops via a surge line. There are heat transfer surfaces within the system that consist of the fuel cladding surfaces transferring heat to the reactor coolant (approximately 20-25% of the total RCS surface) and the SG tubing transferring heat to the secondary system (about 70-75% of the total RCS surface). The surface area of the residual components and loop pipe work is about 5%. This surface area relation in PWR plants is similar to other reactor types, as shown in Table 4-1. All influence of the structural materials is coming from these two main surface areas and the plant performance is demanded by the interaction between these two largest surfaces, as it is described in Chapter 4.2.

Table 4-1: 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			

#### 4.1.1.2 Design of VVER Reactor Coolant System

VVER plants are a type of PWR that are in operation in Russia, Ukraine, Hungary, Slovakia, Czech Republic, Bulgaria, Armenia, Finland and China; they are also built recently in several other countries (e.g. Turkey). According to [Kysela, 2010], the first VVER type pressurized water reactor was a 100 MW reactor in Rheinsberg, East Germany. It was the first model of Russian pressurized water reactor that was to test primary circuit coolant technologies. This reactor had zirconium fuel cladding, and used ammonia water chemistry without KOH and without boric acid. Here water chemistry with ammonia injection without direct hydrogen injection was first tested. Stainless steel was used for both loop piping and SG tubes. After the technology was tested, 200 MW reactors were built and commissioned at the Novovoronezh NPP, which then served as a foundation for the development of standardized 440 and 1000 blocks.

Two major types are in operation or under construction, the 6-loop designs rated at 440 MWe (1375 MWth) and the later 4-loop designs rated at 1000 MWe (3000 MWth). Both designs are basically very similar with the main design difference of the number of steam generators: VVER 440 has six steam generators and VVER 1000 has four steam generators, all in horizontal position. The design concept of these VVER plants is given schematically in Figure 4-2.

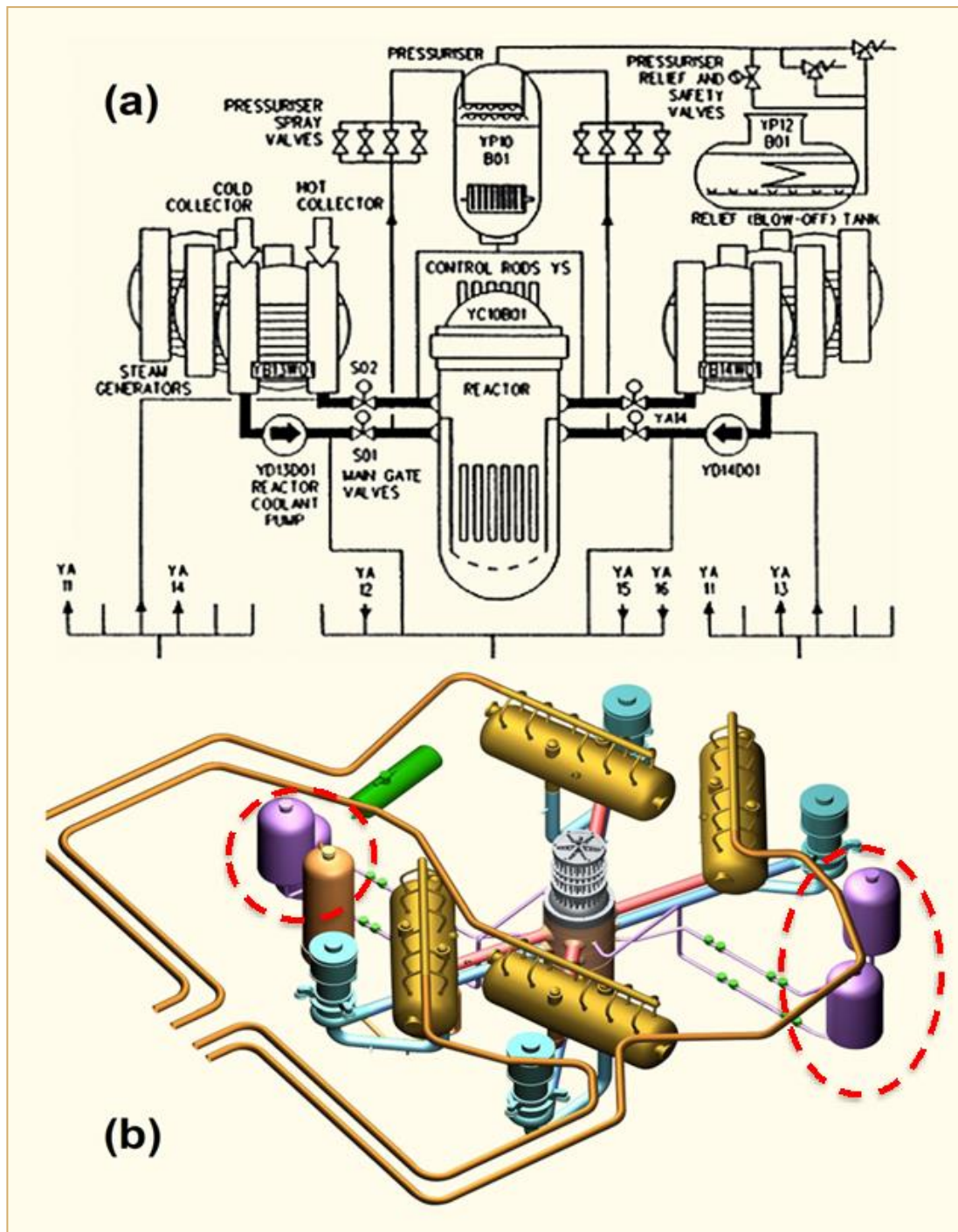


Figure 4-2: Schematic illustration of VVER RCS design (a): VVER 440; (b): VVER 1000, [IAEA, 2007].

Operating temperatures of both VVER design plants are rather lower than the of PWR plants:

VVER 440: Cold-leg temperature: 267°C; hot-leg temperature: 297°C

VVER 1000: Cold-leg temperature 290°C; hot-leg temperature: 322°C

Besides the horizontal steam generators, the main design deferens to PWR RCS is the use of 100% full-flow mechanical filters in each loop of VVER 1000 that operate at operating temperature (see Figure 4-2b in red circled). These filters are designed to remove the coolant corrosion products during the power operation. However, the field experience confirmed their poor efficiency [Dobrovol'ska & Arkhylenko, 2007] and [Martykan, 2010] due to the fact that the majority of the coolant corrosion

products are in colloidal form (see Chapter 4.2) and therefore, cannot be removed by mechanical filters adequately. In addition, due to incomplete regeneration by backwashing [Martykan, 2010], these filters created radiation field problems in many VVER plants. Probably, due to all these negative experiences the High Temperature Filtration (HTF) is no more considered in the design of the new VVER 1200 plants, which confirms the less confidence of the Russian VVER designer to the HTF performance

Both VVER design plants are using boric acid as chemical shim to control core reactivity, similar to PWR plants. However, they use different concept for coolant chemistry: For alkalization of the boric acid potassium hydroxide is added, which is supported by lithium that is produced from  $^{10}\text{B}$  of boric acid by nuclear reaction in the core. In addition, ammonia is added to produce hydrogen by radiolysis in the core that is needed to suppress the water radiolysis and to establish reducing conditions.

#### 4.1.1.3 Design of CANDU Reactor Coolant System

In contrast to PWR and VVER plants, which have design similarities, CANDU plants have completely different design and structural material concept. First of all, CANDU plants are designed to operate with natural uranium fuel and they use heavy water as coolant and moderator. Due to use of extremely expensive heavy water the structural design limits the amount of heavy water by reducing the design volume of Heat Transfer System that corresponds to reactor coolant system of PWRs, to minimum as possible. Therefore, CANDU plants don't have reactor pressure vessel but their core is designed as pressure tubes that is called Calandria. The schematic design of the CANDU plants is shown in Figure 4-3 [Guoping Ma et al., 2012].

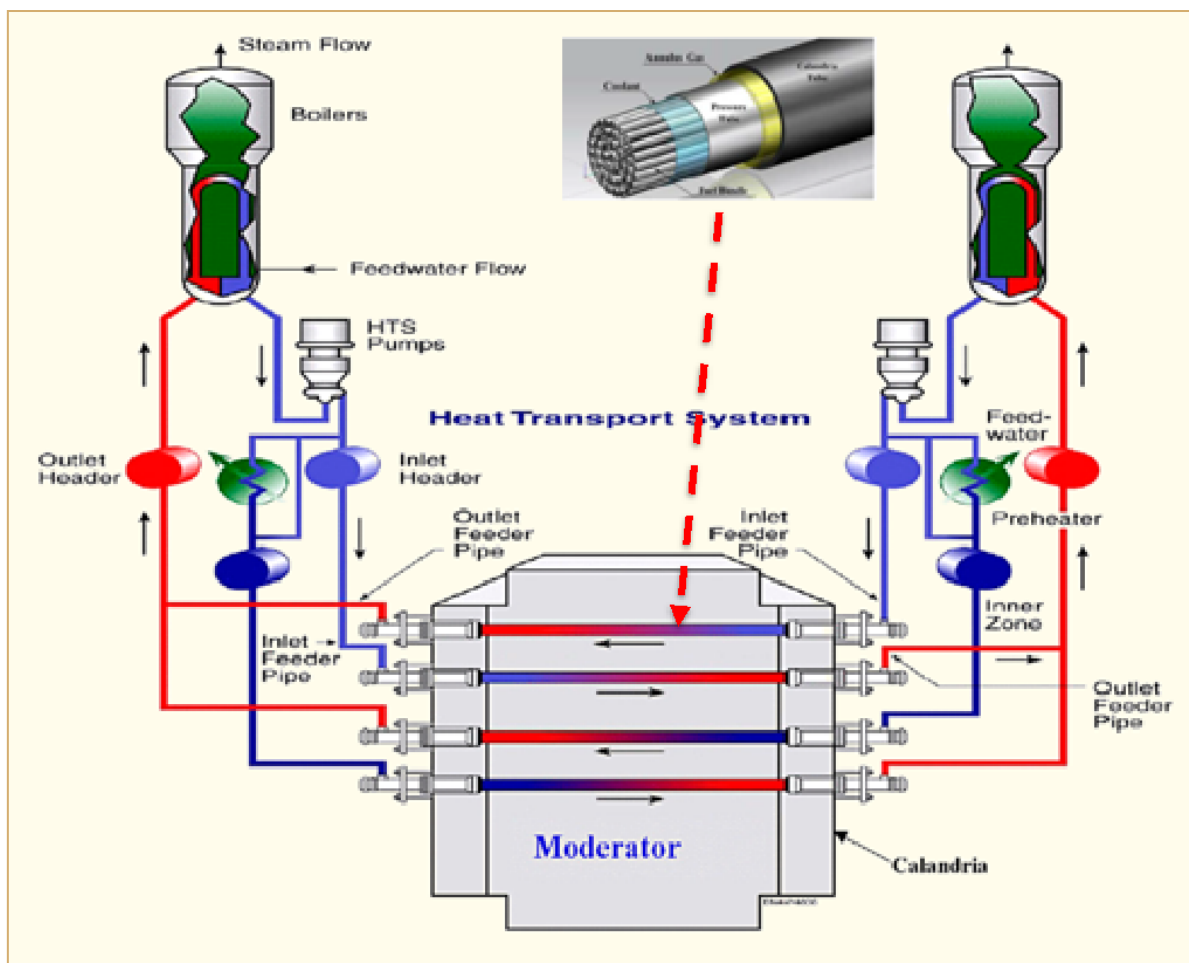


Figure 4-3: Schematic design of CANDU plants, [Guoping Ma et al., 2012].

CANDU plants are designed to perform the refuelling continuously during the power operation. Accordingly, they don't need to use boric acid as chemical shim to control excess core reactivity in contrast to PWR and VVER plants.

## 4.1.2 Material Selection in PWR Reactor Coolant System

The RCS structural materials were selected based on the Plant operating experience at the time of construction starting with the information available 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 discussed, which are together with their chemical composition summarized in Figure 4-4. 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.

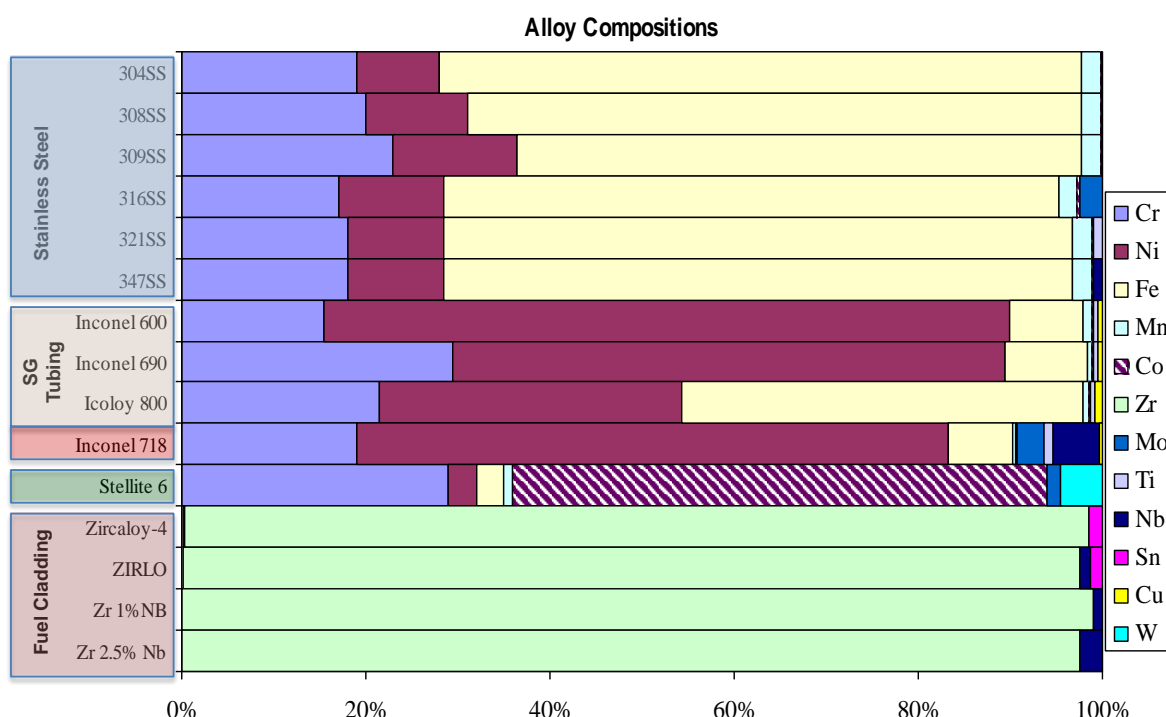


Figure 4-4: Structural materials used worldwide for the PWR RCS main components, [Garbett, 2006].

These structural materials were considered to have good performance 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. In the following sub-chapters these structural materials and their behavior will be explained in three main PWR RCS components.

### 4.1.2.1 Steam Generators

The Table 4-2 summarizes the steam generator tubing materials used worldwide in PWR, CANDU and VVER plants. These materials can be separated in two different groups based on their chemical alloyed elements and composition:

- **Nickel base Alloys:** Alloy 600 (as MA or TT) and Alloy 690 TT: These materials are used in (Alloy 600 in older; Alloy 690TT in new) PWR plants designed by Westinghouse and/or their Licensees (Framatome, Mitsubishi); and by Combustion Engineering and Babcock Wilcox. Furthermore, also in some older CANDU plants (Pickering B units and Bruce A&B Units).
- **Iron base Alloys:**
  - Alloy 800 NG: Used in PWR plants designed by Siemens-KWU and in new CANDU plants (Point Lepreau and Gentilly Unit 2; and in several CANDUs in Indian)
  - Alloy 18-10 Ti (Russian stainless steel): Used in VVER plants

Table 4-2: Chemical composition of steam generator tubing materials used worldwide in PWR, CANDU and VVER plants, [Odar, 2014].

SG tube material	Ni [%]	Cr [%]	Fe [%]	Ni/Fe ratio
<b>Inconel 600</b>	> 72	14 - 17	6 - 10	7 - 12
<b>Inconel 690 TT</b>	> 58	27 - 31	7 - 11	8 - 5
<b>Incoloy 800 NG</b>	30 - 35	19 - 23	42 - 51	0.6 – 0.8
<b>Alloy 18-10 Ti</b>	10 – 11.5	17 - 19	69.5 - 73	0.13 – 0.16

After using in 1950s stainless steels as steam generator tubing material in the first oldest research PWR plants, nickel base Alloy 600MA was introduced by US navy as steam generator tubing material for their nuclear sub-marines. The reason was the excellent resistance of this material against chloride induced pitting and stress corrosion cracking (SCC), whereas the stainless steels have high sensitivity against chloride induced SCC, as explained already in Chapter 3.2 (see Figure 3-7). However, later it was found in laboratory and confirmed also by field experience that Alloy 600MA is under PWR operating conditions, i.e. at high temperatures, even in pure water not stable and suffers on Primary Water Stress Corrosion Cracking (PWSCC). Mechanism of this PWSCC and possible mitigation methods will be explained in Chapter 4.2.1 and Chapter 7.2, respectively. Because of this, starting in 1980s, almost all steam generators, with this tubing material had to be replaced. Except Siemens-KWU, worldwide all other SG vendors have introduced in first step Alloy 600TT, later Alloy 690TT with much higher SCC resistance as SG tube replacement material. In case of Siemens-KWU replacement SGs, Alloy 800NG (NG: nuclear grade) was selected; those are the replacement SGs for Obrigheim in 1983 (as the only Siemens-KWU designed PWR with original SGs tubed with Alloy 600MA), later for Almaraz Unit 1&2, Asco Unit 1&2 in Spain and Doel Unit 3 in Belgian. Presently, for the new PWR plants, worldwide Alloy 690TT as SG tubing material is used.

In addition, Alloy 600 was used not only for steam generator tubing but also for many penetrations in the RCS in Westinghouse and its Licensees and/or other US plant vendors (CE and B&W) designed PWR plants, as described in Chapter 3.2 (see Figure 3-8). Therefore, use of this material in RCS caused lot of pressure vessel head and nozzle connection degradations (see Figure 3-9 and Figure 3-10). All these components had to be repaired or replaced, which was time-consumed and costly. In Siemens-KWU designed PWR plants these penetrations are designed with stainless steel materials; accordingly, these plants did not experience such degradation problems.

Siemens-KWU decided to introduce Alloy 800NG as steam generator tubing material after the publication of the PWSCC sensitivity of the Alloy 600MA by Coriou (see Figure 3-7) [Coriou et al., 1959]. All steam generators have Alloy 800NG tubing material in Siemens-KWU designed PWR plants after Obrigheim, which had replaced the steam generators in 1983 with Alloy 800NG tubing material.

Steam generator tubing material with the highest surface area is not only decisive due to its corrosion behavior in RCS but also for its influence on fuel performance and radiation build-up in RCS. For this the nickel content of the material is essential; especially the Ni/Fe ratio values given in Table 4-2 are extremely important, as it will be explained in Chapter 4.2.

## 5 Historical Development of Coolant Chemistry

The first research PWR plants started to operate with pure water without any chemical additives, even without the boric acid for reactor reactivity control. In those so-called rodged reactors, the reactivity was controlled by control rods. Due to the high expense of huge number of control rods for homogeneous power distribution, PWR industry decided to introduce boric acid as soluble neutron poison in the coolant. However, it was soon recognized that hydrogen gas addition to avoid water radiolysis and alkalization of coolant was also needed to avoid problems induced by fuel deposits (see Chapter 2). So, starting with beginning of 1960s Coolant Chemistry was introduced and step-wise developed and optimized with respect to coolant pH/T control based on field experience and observed problems due to improvements in core duty design. Finally, in mid of 1990s zinc injection and Enriched Boric acid (EBA) was introduced. In the subsequent sub-chapters this almost 60 years of PWR coolant chemistry development will be discussed. In addition, coolant chemistry applied in VVER plants is also discussed in this chapter. The information given is also basis for the present PWR Coolant Chemistry Guidelines.

### 5.1 Boric Acid for Chemical Shim

The core reactivity of the light water-moderated PWR plants varies as the operating temperature increases. Since PWR cores have overall negative temperature coefficient, temperature decrease results in reactivity gain, whereas the temperature increase causes reactivity decrease. In addition, burn-up of the fuel and the accumulation of nuclear poisons, xenon and samarium that are generated during fission, cause also a reactivity decrease. Therefore, to achieve full power operation at high temperatures with useful cycle time, the PWR core must contain controlled excess reactivity. In the earliest PWR plants, this excess of core reactivity was controlled by control rods containing high cross-section materials for absorption of thermal neutrons. In these so-called rodged cores, the control rods that were initially fully inserted in the core were withdrawn as required for reactor operation.

Later it was found that the use of variable amount of a nuclear poison dissolved in the reactor coolant was a more attractive alternative solution for two main reasons:

- First, it permits a substantial reduction in the number of control rods that results in considerable cost saving,
- Second, it provides a better power distribution in the core.

The two main control functions that can most conveniently be provided by nuclear poisons dissolved in the coolant are control of the cold-to-hot reactivity change and control of the reactivity required to compensate for fuel burnup. For this purpose, the concentration of the poison in the coolant is slowly reduced by poison removal system. The use of dissolved nuclear poison to perform these two functions in combination is called “Chemical Shim”. Because of advantages of chemical shim compared to “rod-only” control, all Light Water PWR plants with enriched fuel cores are designed with chemical shim concept.

For establishing the chemical shim concept, detailed investigations were performed in the 1950s by Argonne National Laboratory [Breden & Abers, 1953], [Breden et al., 1955] and Westinghouse in connection with the design of the Shippingport Atomic Power Reactor [Shapiro et al., 1953]. These investigations consisted of establishing criteria for employing poisons, evaluation of potential poison materials, and preliminary testing of candidate poisons under proposed application conditions of PWR operations. For the selection of coolant poison, there are two necessary properties of chemical compounds that need to be considered for chemical shim of a PWR plant [Cohen, 1969]:

- The solubility and the absorption cross-section for thermal neutrons must be suitable to provide the design absorption characteristics in the coolant.
- The selected compound must be chemically and physically stable over the whole range of PWR application conditions.

The first of these conditions can be met by a number of elements (see Table 5-1). However, the second condition is decisive; because only boron as boric acid was found to have the required chemical and physical stability over the full range of PWR operating conditions. All other candidate materials given in

Table 5-1 can only be stabilized in acidic solutions that are detrimental for the RCS and core material compatibility.

Table 5-1: Chemical poison cross sections of several elements that could be selected for chemical shim, [Cohen, 1969].

Elements	Absorption cross sections for thermal neutrons [ $\sigma_0$ ]	Reference concentration [Molality]
B	755	0.32
Cd	2450	0.0985
Gd	46000	0.00525
Sm	5600	0.043
Eu	4300	0.056

Before introducing the use of boric acid for chemical shim in PWR plants, detailed investigations program was performed by Westinghouse at the beginning of 1960s [Byrnes et al., 1961]. The content of these investigations was the physical-chemical properties of boric acid solutions with and without alkali additions including the demonstration of its satisfactory performance in operating PWR plants. Some of their results important for PWR plant operation are summarized in the following:

The water solubility of boric acid in the temperature range of 0-160°C is given in Figure 5-1. This curve of Figure 5-1 is calculated by using the solubility data that are given in (Table 6.4) in [Cohen, 1969]. For the design of the Boric Acid Storage Tanks, it should be considered that the solubility of boric acid is about 7000-8000 mg/kg B at ambient temperatures. If boric acid at higher concentrations needs to be stored, storage tank and the also the injection lines design must consider a heating system, to prevent any precipitations.

Boric acid is a weak acid, which gets weaker with increasing temperature due to polymerization reactions. For the qualification work, Westinghouse investigated the pH values of boric acid solutions under PWR coolant operating conditions. The pH values of boric acid solutions at 1500 mg/kg concentration with and without alkaline addition are given in Figure 5-2 as a function of temperature. As it can be seen, the pH of pure water is also decreasing when temperature increases. Even though boric acid gets less acidic, it is still acidic at coolant operating temperatures of 290-330°C (554-626°F) compared to pure water. Therefore, there is a need to alkalize the boric acid for chemical shim in order to avoid the problems that are explained in the Chapter 2.

Both ammonia and strong bases (Potassium-hydroxide or Lithium-hydroxide) are alkalizing the boric acid solutions above the pH value of pure water at PWR coolant operating temperatures; however, the alkalization by strong bases is more important than the solutions with ammonia, which is a very weak base at high temperature. For PWR operation LiOH is selected as alkalization agent; the reason of its selection together with the alkalisation of boric acid containing coolant is explained in Chapter 5.4.

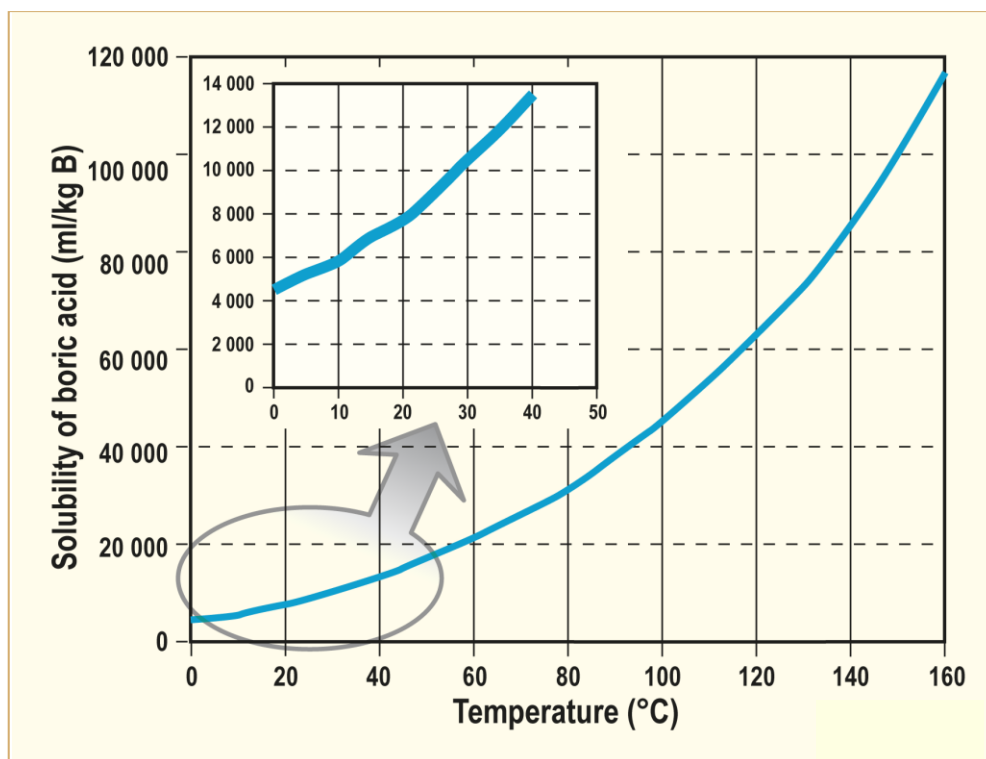


Figure 5-1: Solubility of boric acid in water as a function of temperature, after [Cohen, 1969].

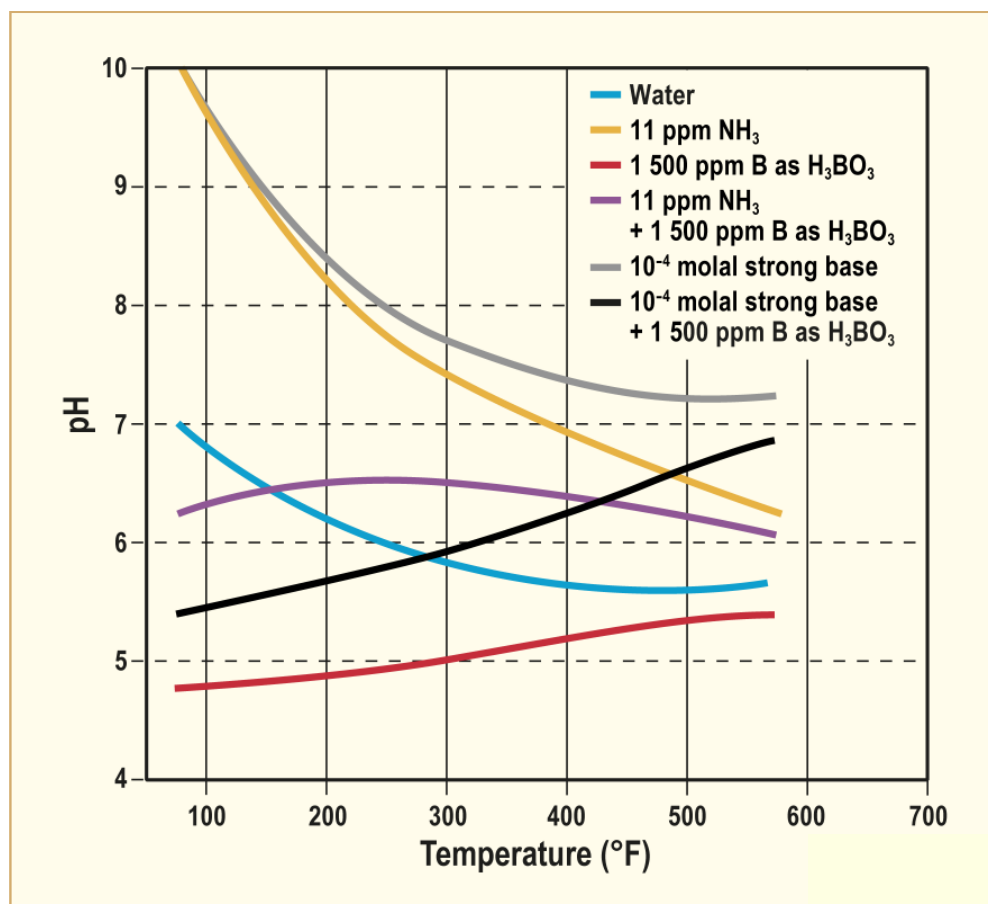


Figure 5-2: Effect of temperature on pH of chemical shim solution, after [Cohen, 1969].

## 5.2 Dissolved Hydrogen

### 5.2.1 Control of Water Radiolysis

In the radiation field of the reactor core, certain amount of the coolant is decomposed by radiolysis, producing primarily the following radicals and molecular radiolysis products:



Extend of the coolant radiolysis, the rate of the reactions between these radiolysis products, and therefore their yields depend on the temperature and the composition of the coolant (Boric acid and dissolved hydrogen or impurity concentrations for example). To understand and explain these complex phenomena the modelling of coolant radiolysis needs to consider enormous number of different chemical equations. Description of these radiolysis modelling is outside of the scope of this report; therefore, the interested readers should refer to corresponding literature (some examples are: [Buxton & Elliot, 1991]; [Christensen, 2006]; [Henshaw et al., 1998], [Henshaw et al., 2002]; [Elliot & Stuart, 2004] and [Elliot, 2010].

The oxidizing conditions, which can possibly be generated by the radiolysis products (OH, HO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> red coloured in the above equation) due to incomplete suppression of the radiolysis, may exacerbate the zirconium alloy fuel cladding performance by corrosion and hydriding, provoke PWSCC of Alloy 600MA/TT and increase the activity transport in the RCS. Therefore, it is indispensable to control the water radiolysis as explained in the following:

For suppressing the radiolysis, hydrogen gas is added to the reactor coolant in PWR plants worldwide. The mechanism how hydrogen addition can suppress the water radiolysis is shown in simplified form in Figure 5-3 [Odar, 1980]. As it can be seen, addition of hydrogen gas suppresses the water radiolysis; whereas the presence of oxygen or other oxidizing agents like H<sub>2</sub>O<sub>2</sub> enhances the radiolytic decomposition of the coolant. According to the recommendation of almost all Water Chemistry Guidelines (e.g. EPRI Guidelines), most of the PWR plants are adding hydrogen gas in the concentration range of 25 to 50 cc/kg (STP) in their reactor coolant. Some other PWR plants (e.g. in the past till 2007, Siemens designed PWRs) are applying Dissolved Hydrogen (DH) concentration of 2-4mg/kg in the coolant according to VGB Water Chemistry Guidelines [VGB Document, 1998]. This DH concentration range in mg/kg is almost the same range as recommended in cc/kg. (2-4mg/kg = 22.4-44.8 cc/kg; with the conversion factors of: 1 mg/kg = 11.2 cc/kg or 1 cc/kg = 0.09 mg/kg). The dissolved hydrogen specification defined in VGB Guidelines was changed later to 1.5 – 4 mg/kg [VGB Document, 2007].

This Guideline recommendation range for DH concentration exists since the 1960s. The lower value of 25 cc/kg was selected with the aim to suppress the coolant radiolysis that produces deleterious oxidizing species based on measurements performed at ambient temperatures in the past (see Chapter 5.2.2). The upper value was specified as 50 cc/kg in order to avoid possible hydriding of the fuel cladding material, zirconium alloys. Because at that time there was a concern that added hydrogen in higher concentrations could cause enhanced Zircaloy hydriding. However, this requirement based on the experience with fuel cladding material Zircaloy-2 that contains nickel alloyed in its composition, which reacts catalytically for hydrogen adsorption in Zircaloy-2cladding. This has no more relevance for the fuel cladding materials used presently, such as Zircaloy-4, Zirlo and M5, which are nickel free, as explained in Chapters 3.3.3.4 and 3.3.3.5.

In the following the basis of this Guideline recommendation with respect to reactor coolant DH concentration is given based on “Historical Data” (Chapter 5.2.2), “In-pile loop measurements and radiolysis model calculations” (Chapter 5.2.3) and “Plant dataMeasurements” (Chapter 5.2.4).

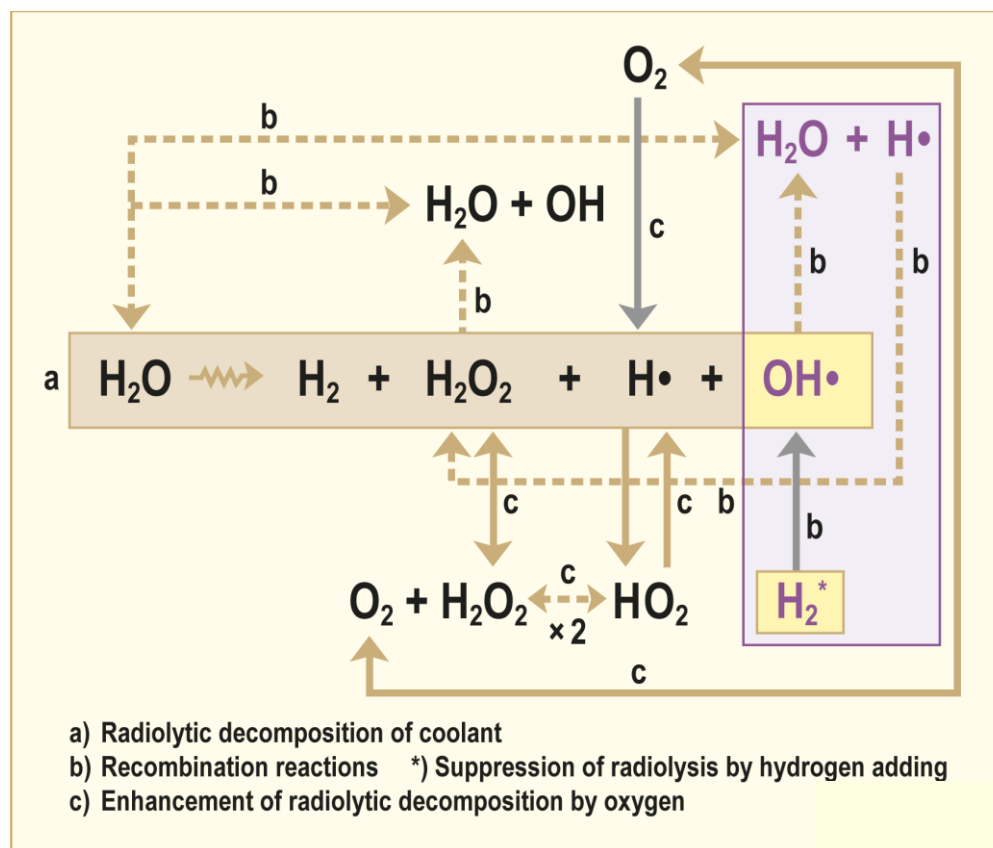


Figure 5-3: Simplified picture that describes the water radiolysis and the mechanism of hydrogen and oxygen influence on radiolysis, after [Odar, 1980].

## 5.2.2 Historical Data

The DH concentration range that is recommended by almost all Water Chemistry Guidelines and specifications is a historical value and is based on experiments carried out at low temperatures and on calculations based on such experiments [Hart et al., 1955] and [Mackintosh et al., 1967]. The modelling studies were carried out before the temperature dependence of the radiation chemical reactions had been measured. Their experimental results gained at low temperatures showed that the hydrogen concentration required to suppress the radiolysis, so called Critical Hydrogen Concentration (CHC), was ~14 cc/kg (STP) for boric acid solution of 1500 mg/kg B, [Cohen, 1969].

Another historical example that served as basis for the selection of lower DH concentration in PWR Primary Water Chemistry Guidelines is the calculations made by Fletcher and published by Solomon (see Figure 5-4), [Solomon, 1978]. These in literature so-called Fletcher curves indicate that dissolved oxygen concentration becomes undetectable at a DH concentration of ~10 cc/kg (STP), while the HO<sub>2</sub> concentration reaches its lowest value at ~20-30 cc/kg (STP) of DH concentration. Based on these old studies performed at low temperatures, the general accepted minimum DH concentration to suppress water radiolysis was about 10-15 cc/kg (STP), a value that has been used to make the Guideline recommendation of 25-50 cc/kg (STP), where the lower value of the Guidelines considers some margin.

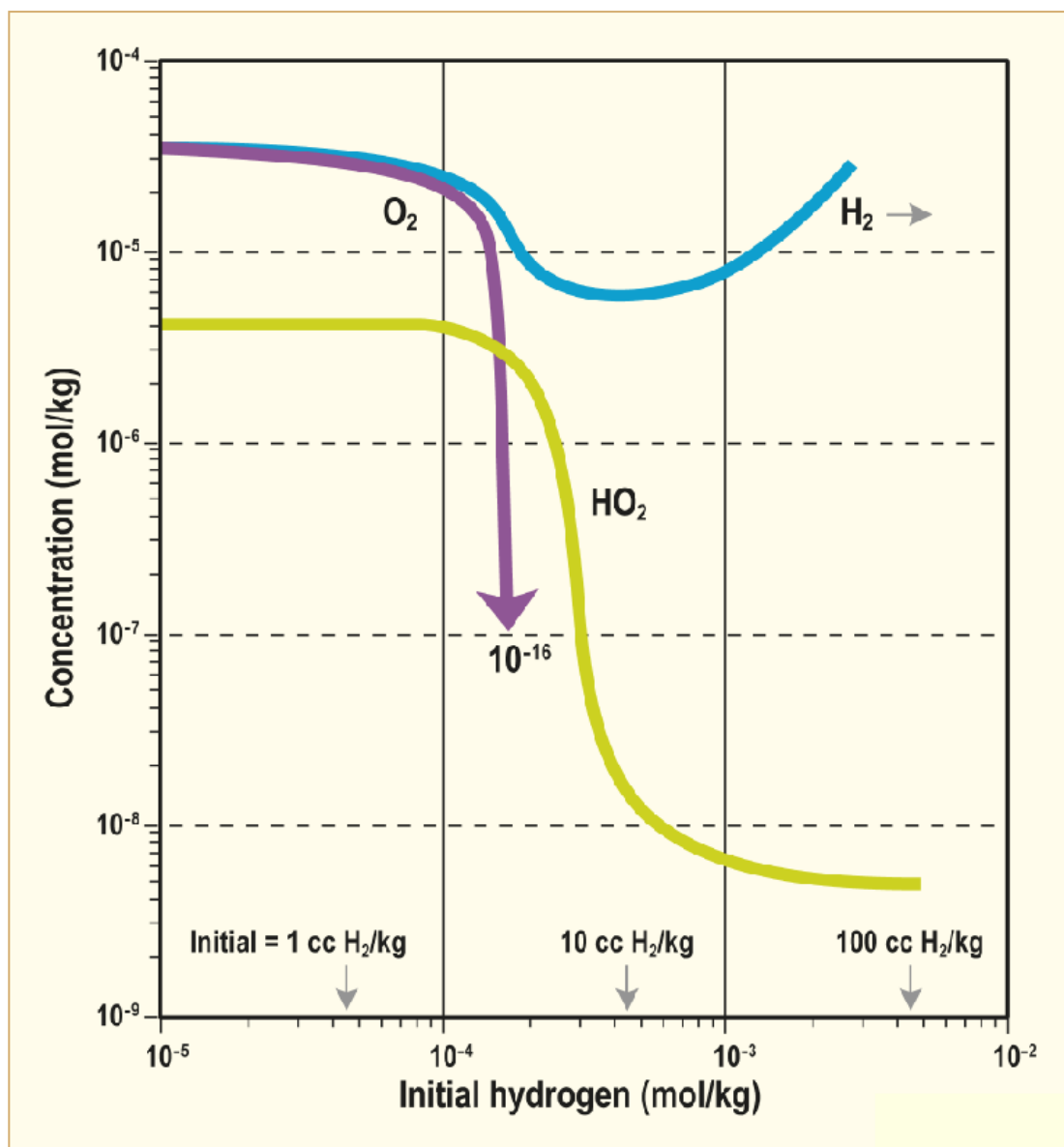


Figure 5-4: Steady state concentration of  $O_2$  and  $HO_2$  under irradiation conditions as a function of initial DH concentration, after [Solomon, 1978].

### 5.2.3 In-pile Loop Measurements and Radiolysis Model Calculations

Later it has been recognized that the chemical reactions between the radiolysis products that control the water radiolysis have activation energies of different magnitude. Consequently, the rate of radiolytic reactions and accordingly the yield of radiolytic products changes with temperature. The radiolysis modelling calculations indicate the general decrease in radiolytic products with increasing temperature (see Figure 5-5) [Jenks, 1965]. This is because, with increasing temperatures, the rate of recombination reactions increases more rapidly than the rate of decomposition reactions [Hisamune et al., 1998]. The temperature dependence of the reaction rate of the fundamental recombination reaction



is shown in Figure 5-6 as an example [Elliot & Stuart, 2004]. As a consequence, a lower Critical Hydrogen Concentration (CHC) is sufficient to suppress the radiolysis at higher temperatures like PWR operating

temperatures, as indicated by Studsvik radiolysis model calculations (see Figure 5-7) [Takiguchi et al., 2001], [Sekiguchi & Takiguchi, 1999], [Hisamune et al., 1998] and [Meguro, 2008]. Figure 5-7 shows that the influence of boric acid on CHC is insignificant at temperatures above 150°C.

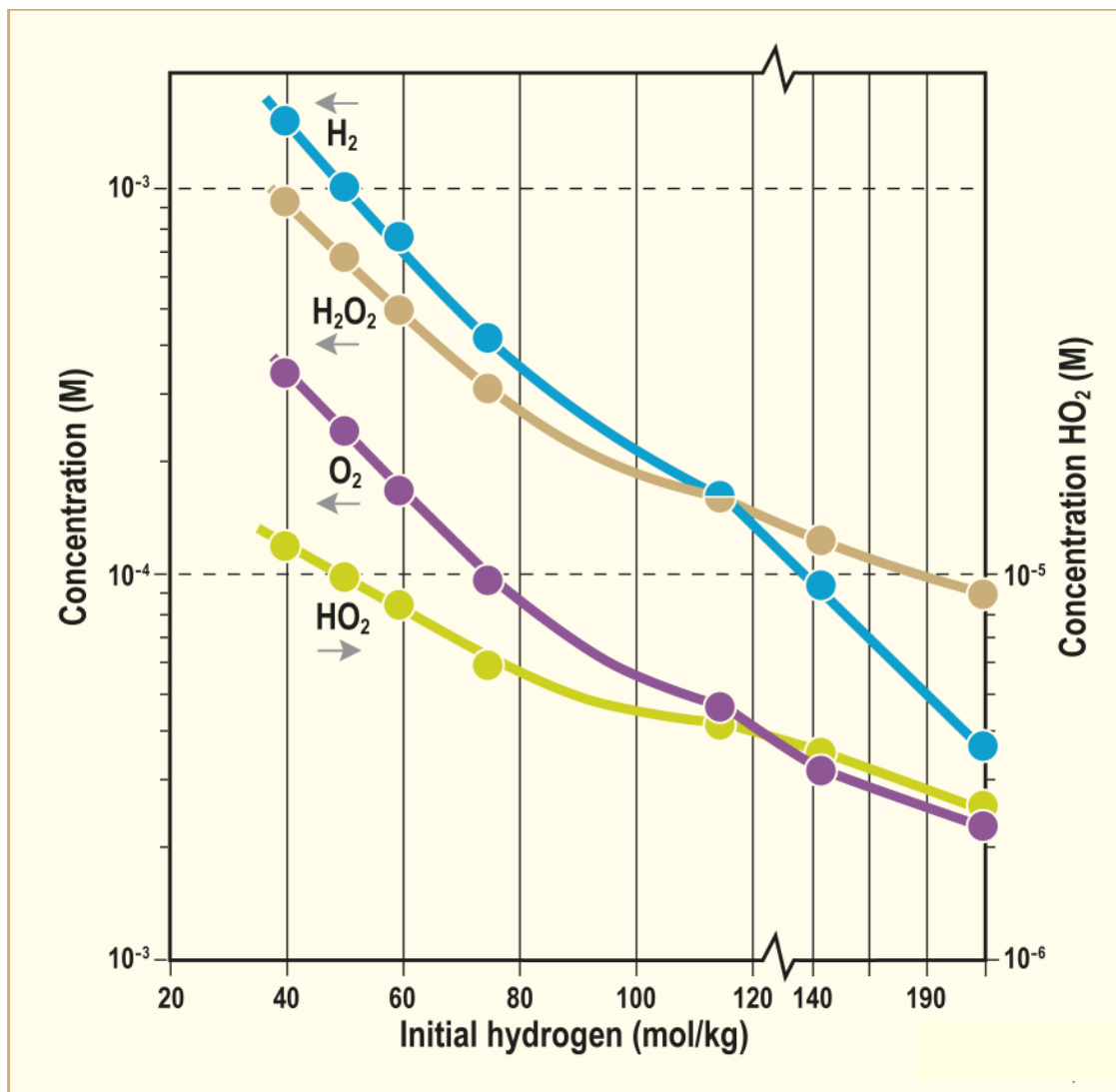


Figure 5-5: Calculated concentrations of radiolytic products in HFIR core at 100W/cc as a function of temperature, after [Jenks, 1965].

## 6 Current PWR Coolant Chemistry Guidelines

### 6.1 Introduction

All PWR Coolant Chemistry Guidelines define parameters for adequately applying water chemistry control program to achieve following goals:

- Suppression of water radiolysis resulting in formation of oxygen and other oxidizing agents; in order to prevent material degradation;
- Adequate alkalization of the coolant in order to minimize the metal corrosion and release rates and thus to reduce the fuel deposits to prevent the increased fuel cladding corrosion and out-of-core radiation fields;
- Proper impurity control to prevent localized corrosion of the structural materials.

Worldwide to achieve these goals in PWR plants coolant that contains boric acid (depending on core duty and length of the cycle 900 -1800 mg/kg at the BOC) is chemically conditioned by adding isotopically pure Lithium-hydroxide (>99%  $^7\text{Li}$ ) (depending on core duty, 2–6 mg/kg Li at BOC) as a non-volatile alkalizing agent and by the addition of hydrogen. Since mid of 1990s, the injection of Zn has been qualified as a tool to mitigate activity build-up and to delay crack initiation and reduce the crack propagation in nickel base Alloy 600 used in RCS. Accordingly, all so-called classical or standard coolant chemistry guidelines specify the water chemistry parameters in three groups as “impurity concentrations”, “Lithium concentration” and “hydrogen concentration”. In recent times a separate guideline for zinc addition is also introduced with fuel vendors approval for PWR plants that add zinc in the reactor coolant.

In certain cases, it may happen that water chemistry conditions that optimize the achievement of one goal may degrade the achievement level of the other goal. A good example for this is the lithium concentration at the BOC: Whereas, a mitigation of out-of-core radiation high BOC lithium concentrations requires, especially for longer cycles in PWRs with high duty cores; this high lithium concentration increases the risk of fuel cladding corrosion, if core has high duty design! In such cases, the water chemistry guidelines must define the parameters to achieve a balance among these goals under consideration of the core duty design, recognizing that highest priority is to be designed to materials and fuel integrity goals. Although the other goals are in the second line of priority, like radiation build-up, they cannot be ignored and became with the time of growing attention. However, fortunately the development and introduction of more corrosion resistant fuel cladding materials, like Zirlo and M5, made to solve this contradiction more easily.

Operating modes of the PWR plants are as follows:

- Power operation: At operating temperature with reactor critical;
- Start-up operation: At temperatures usually above 120°C till operating temperatures
- Shutdown operation: Temperature decrease from operating temperatures down to below 120°C to cold shutdown.

In addition, the water chemistry parameters are specified in different categories, more or less with similar definitions in different guidelines. In the following the definitions used in VGB Guidelines is selected as an example:

#### Typical Values:

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

### **Limit Values:**

Limit values are values that must be respected by the plant operators under any circumstances. Deviations include the possibility of materials corrosion and the consequences thereof. Immediate corrective measures are required. They are used only for start-up operation!

### **Control Values:**

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

### **Diagnostic Values:**

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

### **Action Levels:**

Action levels are values, which are defined for remedial actions to be taken when parameters are confirmed to be outside the control values. In such cases, efforts should be made to bring the values within the appropriate limit within a certain time window. (Allowed time window is defined differently in individual Guidelines. Therefore, this will be explained later for individual guidelines).

Depending on the selected materials and different plant designs of different vendors different water chemistry guidelines are used worldwide to control the chemistry in PWR plants. Each of these guidelines considers the years of field experience gained in their PWR plants. The most popular and used water chemistry guidelines are the following:

- **EPRI guidelines** [Fruzzetti et al., 2004]:  
For the PWRs designed by Westinghouse, B&W, and Combustion Engineering in North America, Europe and Asia.
- **VGB guidelines** [Neder et al., 2006 and 2008]:  
For the PWRs designed by Siemens-KWU in Germany, Holland, Switzerland, Spain, Argentina and Brazil
- **EdF specifications** [Staudt et al., 2002]:  
For the PWRs designed by EdF and AREVA (former and also presently again Framatome) in France, Republic of South Africa, Korea and China
- **VVERguidelines** (see Chapter 5.5.1):  
For the plants of Russian design in Russia, Ukraine, Czech Republic, Hungary, Bulgaria, and India.

The water chemistry control requirements are based on field experience gained by the Vendor-Utility organizations. Accordingly, these differences in the Guidelines are the result of different plant system designs and different materials used. Even all these guidelines have identical requirements for water chemistry control and similar structure with respect to corrective actions, like Action levels (EPRI and VGB Guidelines) or specified operating Zones (EdF Guidelines for B-Li, VVER Guidelines for Boron-Alkali coordination), they have some differences in their specification. Another difference explaining why French documents contain zones is that these documents are specifications, prepared by EdF Head Office Chemists and directly applied by the EdF plant staff. This is because, in case of EdF PWR plants, all PWRs belong to one utility and the core duties are similar and well established by EdF. In case of VVER Guidelines, they were established with the consultation of EdF! In case of EPRI or VGB guidelines these are documents prepared for PWR plants of different utilities, where the plants have usually different core duty designs. Therefore, the Utilities must prepare their own plant specific documents for water chemistry control program under considering the core duty design of their plants.

In the following sub-chapters, the background of the water chemistry parameters and the most used guidelines in comparison with each other will be explained and discussed.

## 6.2 Background of the Guidelines

The background of the water chemistry parameters, Dissolved Hydrogen (DH), Lithium concentration, is already explained in the Chapters 5.2 and 5.4, respectively. Here in the following sub- chapters, a summary will be given:

### 6.2.1 Dissolved Hydrogen Guideline Values

Worldwide, in all coolant chemistry guidelines, the coolant DH concentration is specified with 25 to 50 cc/kg, which corresponds to 2.2 to 4.5 mg/kg due to conversion factor of 1 mg/kg = 11.2 cc/kg. The coolant DH concentration range of 25 to 50 cc/kg was selected and defined by Westinghouse in 1960s. The selection of the lower value as 25 cc/kg is based on the room temperature measurements for water radiolysis and calculations made by Fletcher using these measurement results (see Figure 6-1).

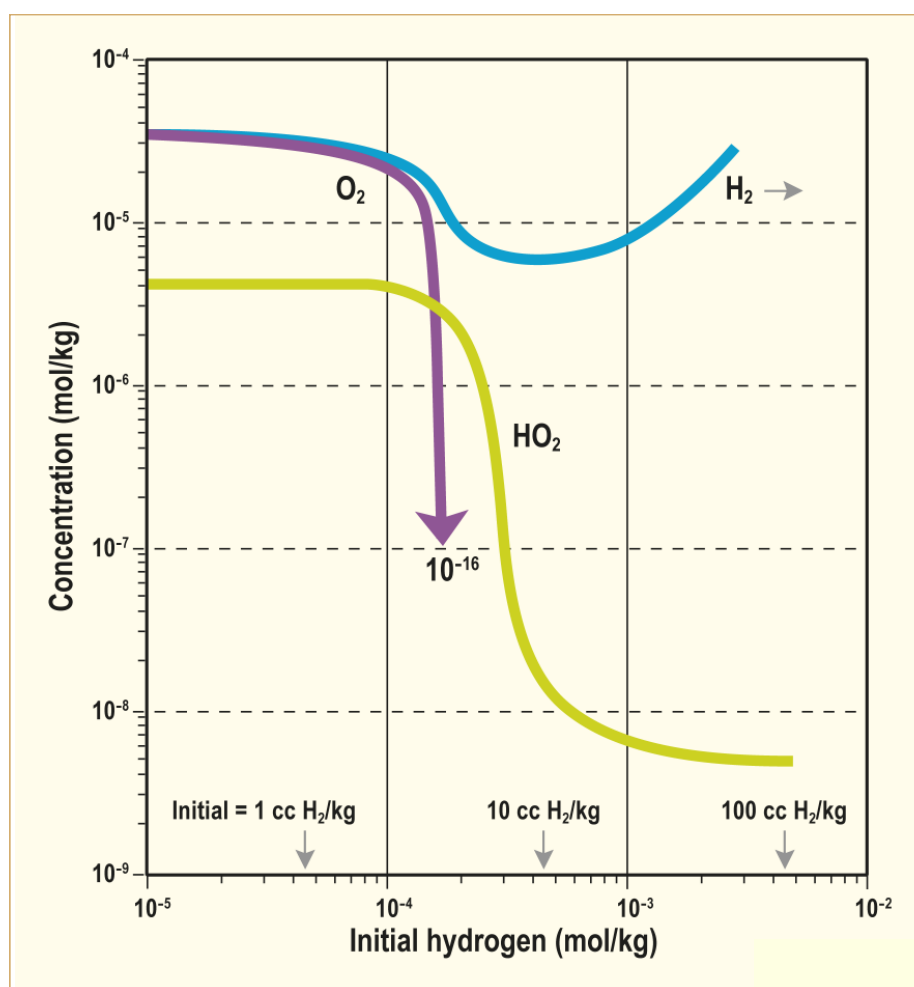


Figure 6-1: Steady state concentration of  $O_2$  and  $HO_2$  under irradiation conditions as a function of initial DH concentration, after [Solomon, 1978].

The upper value of 50 cc/kg was selected arbitrary to avoid the possibility of hydride build-up in the fuel cladding, based on the experience with Zircaloy-2 that contains nickel in its alloy (see Figure 6-2). It is now well known that only atomic hydrogen (i.e. corrosion hydrogen) is building hydrides in zirconium alloys and the molecular gas hydrogen does not contribute to hydride building, so far nickel is not involved. Accordingly, this upper value of the DH concentration specified in the guidelines is no more relevant for Zircaloy-4 and especially for the new fuel cladding materials, Zirlo and M5. However, there exists no attempt to change this upper DH concentration because of following reasons:

- In majority of the PWR plants hydrogen is added to the reactor coolant through Volume Control Tank (VCT) in Chemical and Volume Control System (CVCS). This VCT has also the function to provide the necessary pre-pressure of 2-3 bars for the HP-Charging pumps. This is done by hydrogen gas in the gas-phase of the VCT, which results in 2-4 mg/kg of DH concentration.
- Finally, no one wants to change something, which works well since decades without any problems.

However, recently in PWR industry there are some attempts to decrease the existing lower value or increase the upper value, which will be explained in Chapter 7.2.1.

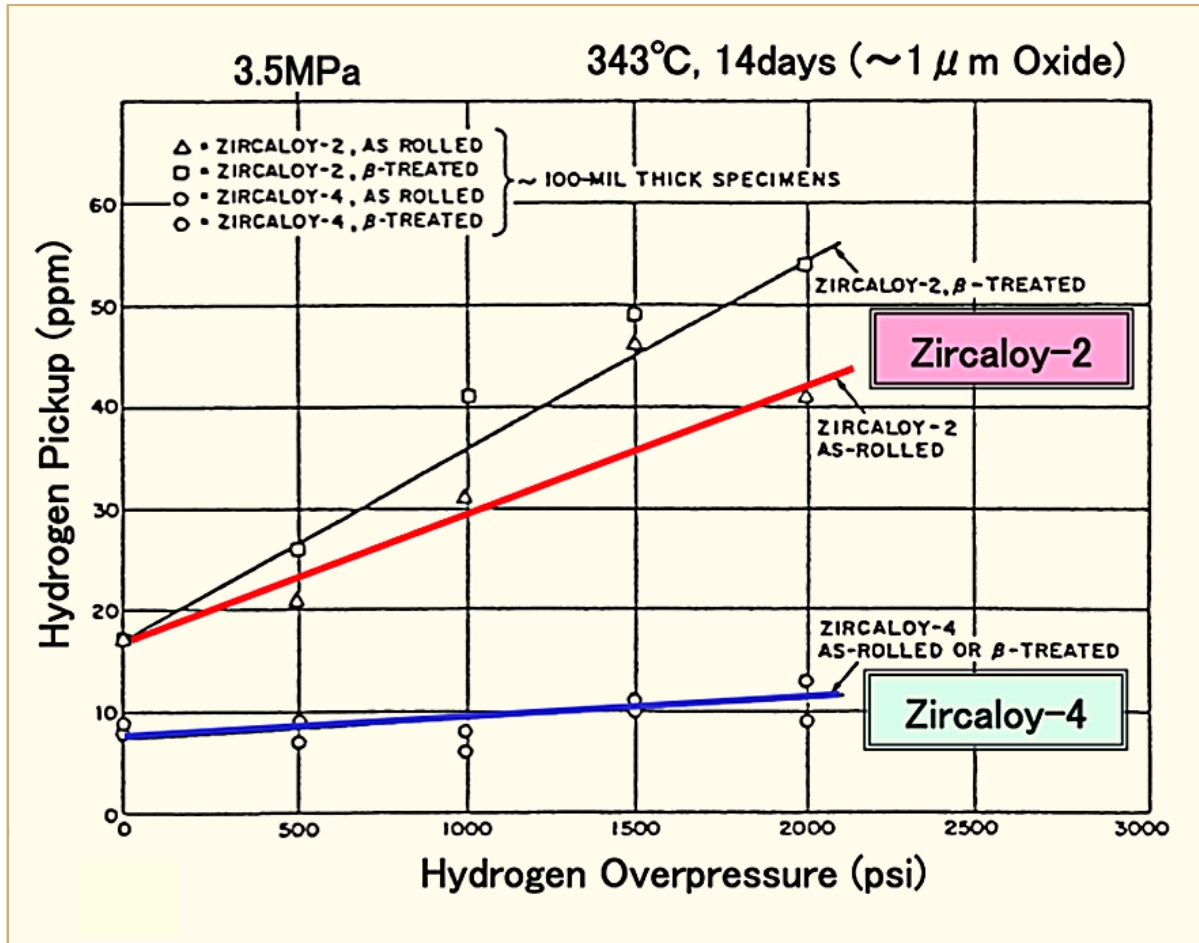


Figure 6-2: Comparison of HPUF in Zircaloy-2 and Zircaloy-4, [Hillner, 1964].

In case of VGB Guidelines, DH concentration was originally selected as 2 to 4 mg/kg. This DH concentration range was specified by PWR plant manufacturer Siemens-KWU as Westinghouse licensee for NPP Obrigheim for the second fuel cycle; based on the bad experience gained in the first cycle without hydrogen and lithium addition. Later on, these values were accepted by VGB and used for years in the VGB Guidelines. However, in the last and still present VGB Guidelines, the lower value was decreased to 1.5 mg/kg based on the Japanese field experience for the lower radiation fields caused by  $^{58}\text{Co}$ , which is explained in Chapter 5.2.5 and Chapter 7.2.1.

## 6.2.2 Lithium/pH<sub>T</sub> Guideline Values

Originally, coolant lithium concentration was specified by Westinghouse as 0.7 to 2.1 m/kg in 1960s, without specifying the pH<sub>T</sub> values. The lower lithium concentration value is based on the boric acid qualification program for its use as chemical shim, which is performed by Westinghouse in 1960s. In this qualification testing, they have used, among others, lithium hydroxide with  $10^{-4}$  molar

concentration, which corresponds to 0.7 mg/kg Li (see Figure 6-3). Factor 3 higher value of 2.1 mg/kg Li was arbitrarily selected as upper value by Westinghouse fuel people in order to avoid the risk of fuel cladding corrosion.

Based on this, Siemens-KWU, as licensee of Westinghouse specified for NPP Obrigheim the coolant lithium concentration as 1–2 mg/kg Li for the second fuel cycle of Obrigheim, due to extremely unfavourable results of the first cycle without alkalization of the coolant; again, without specifying the pH<sub>T</sub> value! That is how so-called “1-2 ppm Lithium” chemistry regime was introduced in Siemens designed PWR plants and accepted by VGB-Guidelines.

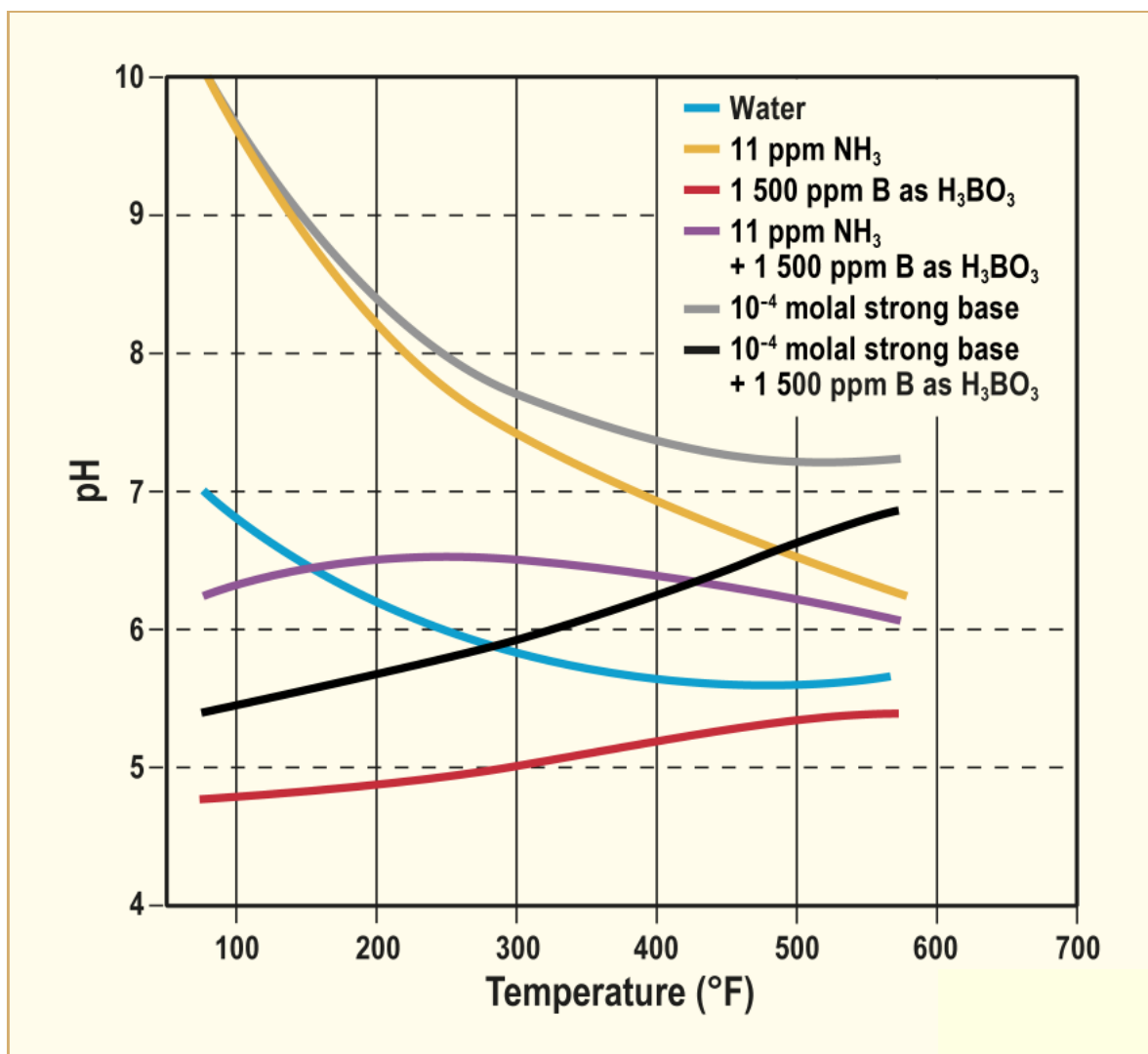


Figure 6-3: Effect of temperature on pH of chemical shim solution, after [Cohen, 1969].

Further investigations of Westinghouse with respect to dose rate reduction revealed that, minimizing the crud transport into core area by optimizing the pH<sub>T</sub> value is the essential issue for radiation field reduction. With the assumption that black oxide layers on the RCS surfaces consists of magnetite, Westinghouse recommended based on the results of magnetite solubility tests to operate at pH<sub>300</sub> of 6.9 (see Figure 6-4). At this pH<sub>T</sub> value magnetite has solubility minimum where also temperature coefficient of solubility changes its sign (with temperature increase the solubility decreases at <300°C and at >300°C the solubility increases). This is how the coordinated chemistry at pH<sub>T</sub> 6.9 was introduced in 1970s. Later on, in 1980s, the laboratory corrosion root cause investigations on pulled SG tubes with Alloy 600MA revealed that, actually the oxide layers consist of nickel ferrites and not of magnetite, which has its solubility minimum at pH<sub>300</sub> of 7.4 with temperature coefficient of solubility change at this

pH<sub>T</sub> (see Figure 6-5). Based on this discovery, Westinghouse recommended to operate at pH<sub>300</sub> of 7.4. However, to achieve this pH<sub>T</sub>, it was necessary to select BOC lithium concentrations far above the value (2.1 mg/kg) limited by the fuel vendors. Based on this, compromises were done by introducing several coolant chemistry regimes, such as Elevated Lithium Chemistry or Modified Coolant Chemistry.

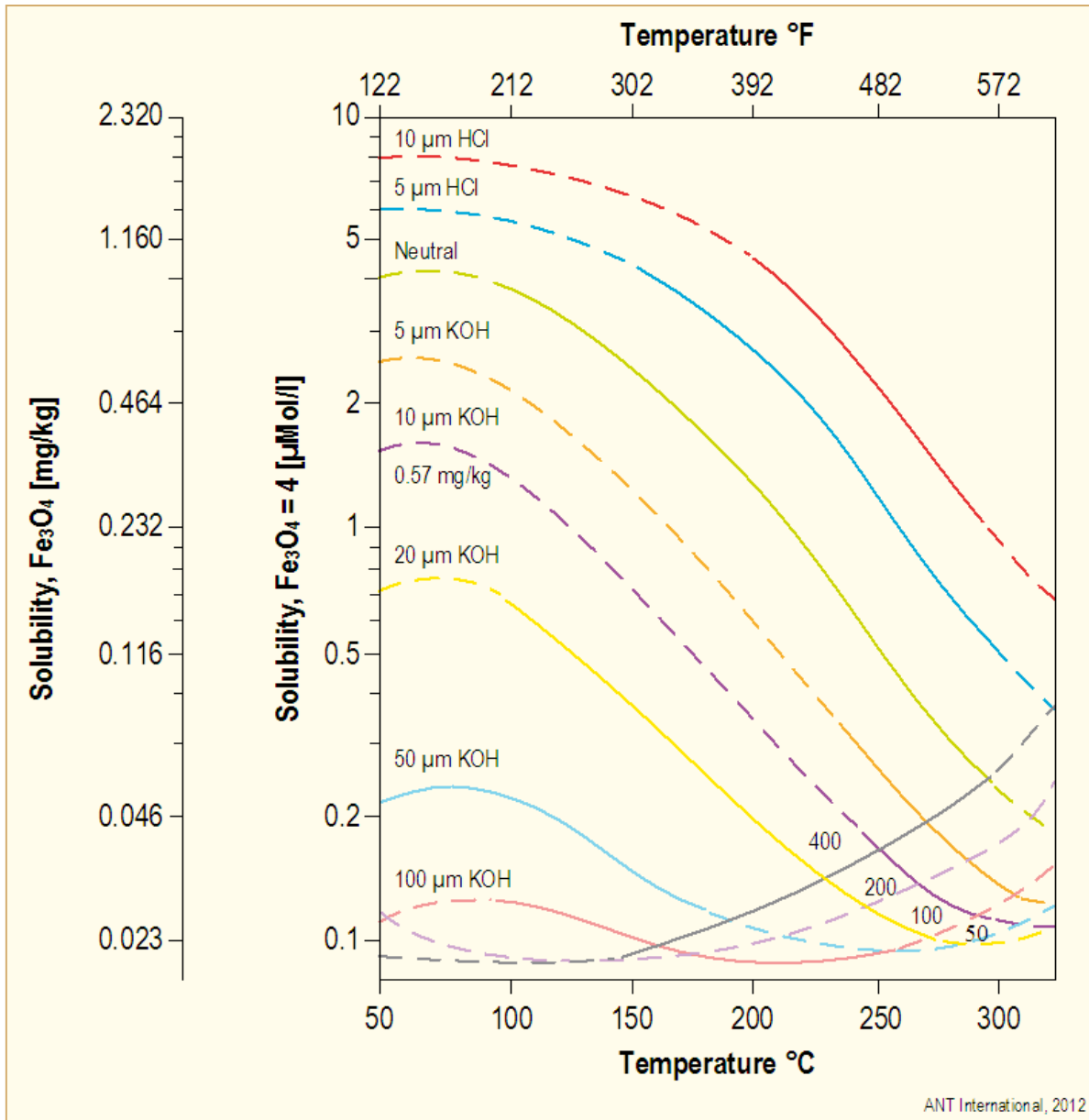


Figure 6-4: Magnetite solubility as a function of alkalinity and temperature, after [Sweeton & Baes, 1970].

Siemens-KWU as plant and fuel vendor, together with VGB has introduced Coordinated Coolant Chemistry for Siemens designed PWR plants in beginning of 1980s. The Modified chemistry started to be applied in mid of 1980s in several German PWR plants. Based on better radiation field results in these plants, other Siemens designed PWRs started one after the another to convert the coolant chemistry from Coordinated to Modified one.

In 1990s PWR industry was forced to increase the core duty for longer fuel cycles due to economic reasons in order to be competitive against fossil fired power plants. This required, especially for PWR plants with nickel base SG tubing due to AOA experience, to operate at elevated constant pH<sub>T</sub> values as long as possible with much higher BOC lithium concentrations. After developing new fuel cladding materials with higher corrosion resistance, like Zirlo and M5, fuel vendors started to allow higher BOC

## 7 Worldwide New Aspects/Strategies for Coolant Chemistry

Since several years worldwide in PWR industry, except VGB DWR industry, there exist investigations and attempts to modify the coolant chemistry programs with respect to control of lithium and dissolved hydrogen. The reason for modifying the lithium control is to counteract the AOA problem, whereas the work for modification of dissolved hydrogen control is initiated with the aim to mitigate the PWSCC in nickel base Alloy 600 and its weld materials. The status of these investigations is explained in the following sub-chapters.

### 7.1 Axial Off-set Anomaly (AOA)

AOA is recently the most discussed and concerned subject within the PWR industry for the PWR plants with nickel base SG tubing material. It has influenced the modification of the coolant chemistry with respect to lithium control extremely. The definition of the AOA was explained in Chapter 2.5. In the following chapter its root cause is explained:

#### 7.1.1 Hypothesis for AOA Root Cause Mechanism

AOA is a power shift in the core caused by boron adsorption within the fuel deposits (see also Chapter 2.5). As of today, AOA phenomena was experienced only in PWR plants with nickel base SG tubing material (mainly with Alloy 600MA/TT but also in small extent with Alloy 690TT). It was never observed in PWR plants with iron base SG tubing material (Alloy 800) or in VVER plants with stainless steel SG tubing material. This indicates that excess nickel in the fuel deposits has some influence on AOA occurrence! Field experience confirms that the severity of the AOA is influenced not only by the thickness of the fuel deposits but also by the duty of the core design. The higher the core duty and the thicker the fuel deposits, the more is the AOA extend (see Figure 7-1).

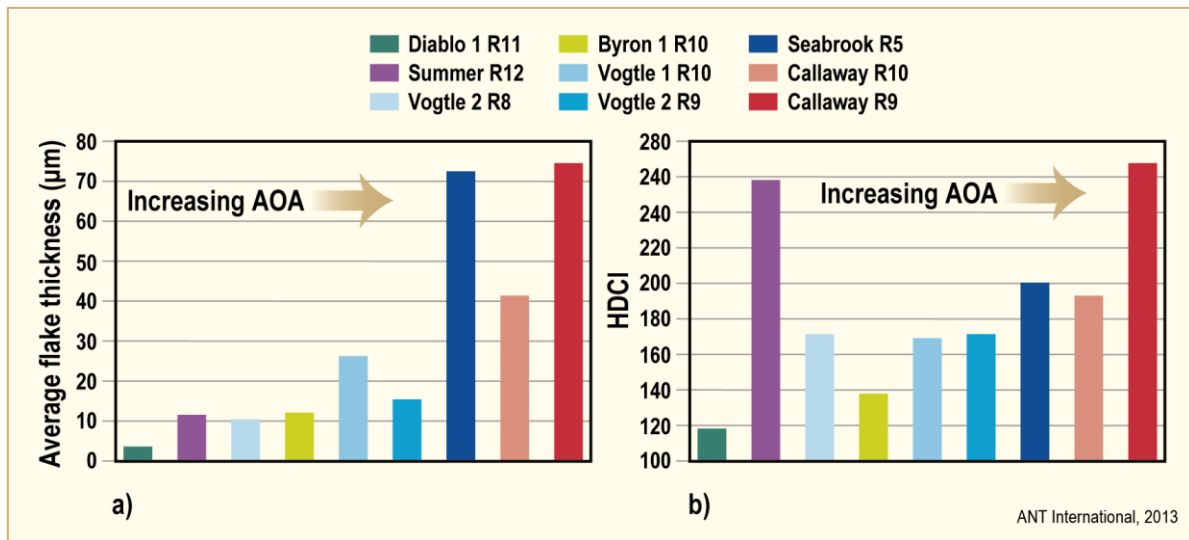


Figure 7-1: US PWRs with AOA field experience: Influence of fuel deposit thickness and high core duty, (R: Refueling cycle), [Byers & Deshon, 2004].

In this figure the increasing AOA with increasing fuel deposit thickness and increasing core power duty (indicated as HCDI: High Core Duty Index) is given, which was experienced at six different US PWR plants. In this figure Diablo 1 R11, Summer R12, even with high HCDI; and Vogtle 2 R8 did not experienced AOA. This indicates that alone high duty core design is not enough to produce AOA in PWRs with nickel base alloy SG tubing material.

In the past the precipitation of less soluble lithium-Metaborate,  $\text{LiBO}_2$  was suspected to be the real root cause for AOA mechanism due to the observed Li-HOR during power reductions at field (see Figure 7-2). However, the results of the calculations of the  $\text{LiBO}_2$  solubility to evaluate the amount of the adsorbed  $\text{LiBO}_2$  in the fuel deposits could not explain the extend of the AOA experienced at PWR Callaway in cycle 9; again, indicating that something else rather than  $\text{LiBO}_2$  was contributing to AOA occurrence. Most strong and crucial indication that  $\text{LiBO}_2$  could not be the only root cause of AOA was the worldwide first published AOA experience in the first fuel cycle at Siemens designed PWR Obrigheim: This “low dutycore” PWR plant with nickel base Alloy 600MA SG tubing was operating its first cycle with pure water without injecting  $\text{LiOH}$  and hydrogen. The result of this operation without coolant chemistry was heavy fuel deposits with extremely high nickel ( $\text{NiO}$ ) content (see Figure 7-3).

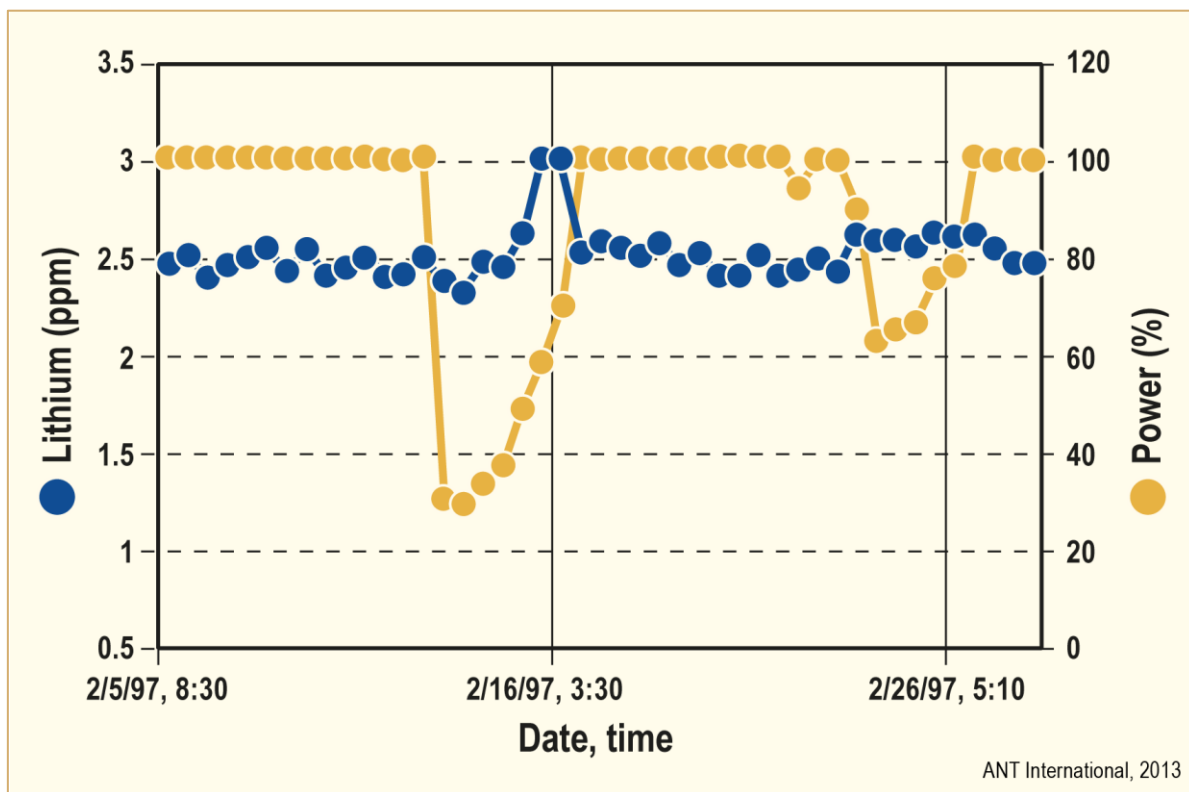


Figure 7-2: Lithium Hide-Out Return (HOR) during power reductions, [EPRI, 2004a].

In order to understand the AOA root cause, Westinghouse had investigated the fuel deposit morphology and composition from the PWRs with and without AOA experience. The cross-section SEM image and structure of Callaway cycle 9 fuel deposits with the most severe AOA experience is shown in Figure 7-4. This investigation revealed that the  $\text{ZrO}_2$  is mainly located in the mid of fuel deposit flake and not at the cladding-deposit intersection; and the cladding surface is covered by Bonaccordite ( $\text{FeNi}_2\text{BO}_5$ ). These findings indicate existence of severe beneath-deposit chemistry and thermodynamic conditions. Presence of Bonaccordite, which can be produced at temperatures above  $400^\circ\text{C}$  (see Figure 7-5), confirms the inadequate cooling of the fuel cladding surfaces. This can happen only, if the fuel deposits get extremely dense with clogged chimneys on the cladding surface.

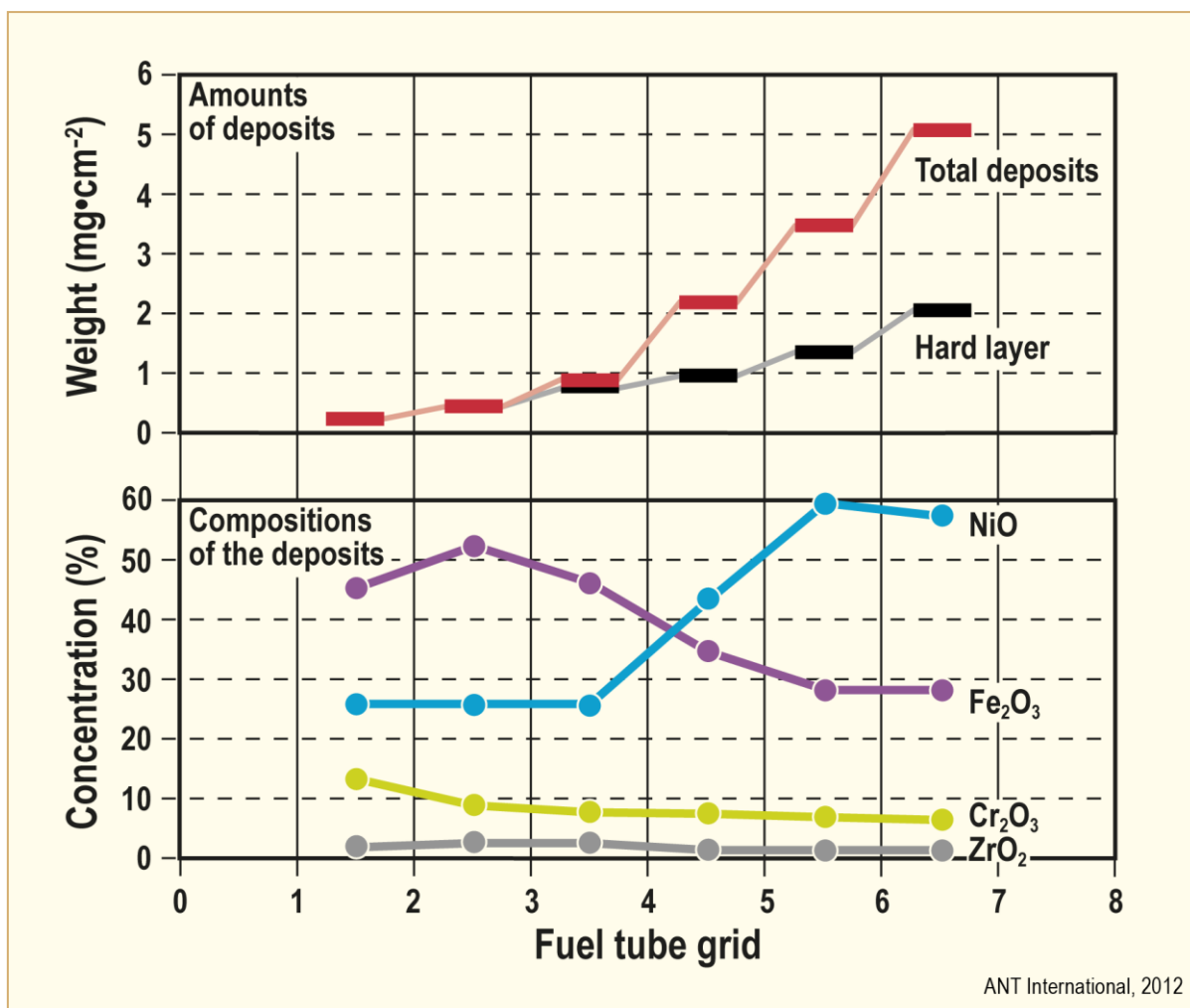


Figure 7-3: The fuel crud deposit thickness and composition at Siemens-KWU designed PWR plant Obrigheim, [Riess, 1976].

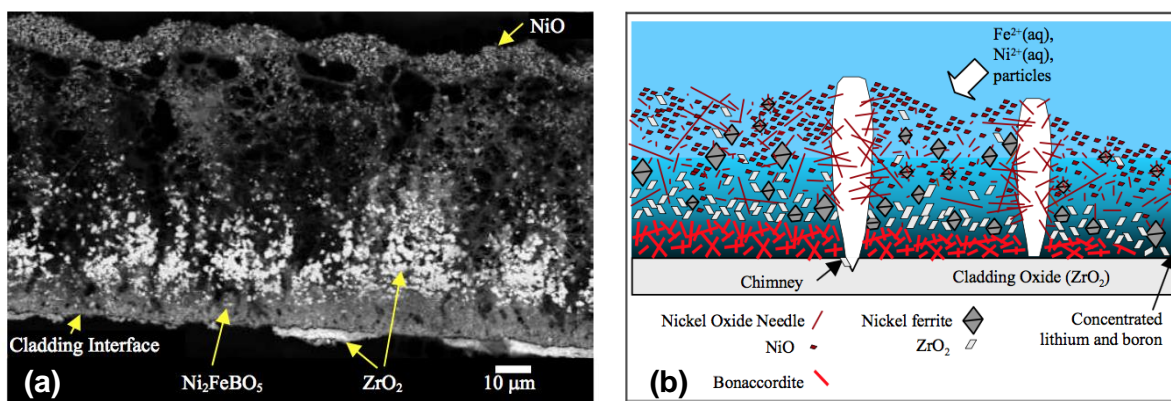


Figure 7-4: Flake of fuel deposit from Callaway cycle 9; (a): Backscattered SEM Image Crud Cross Section; (b): Crud structure with severe AOA, [Byers et al., 2006].

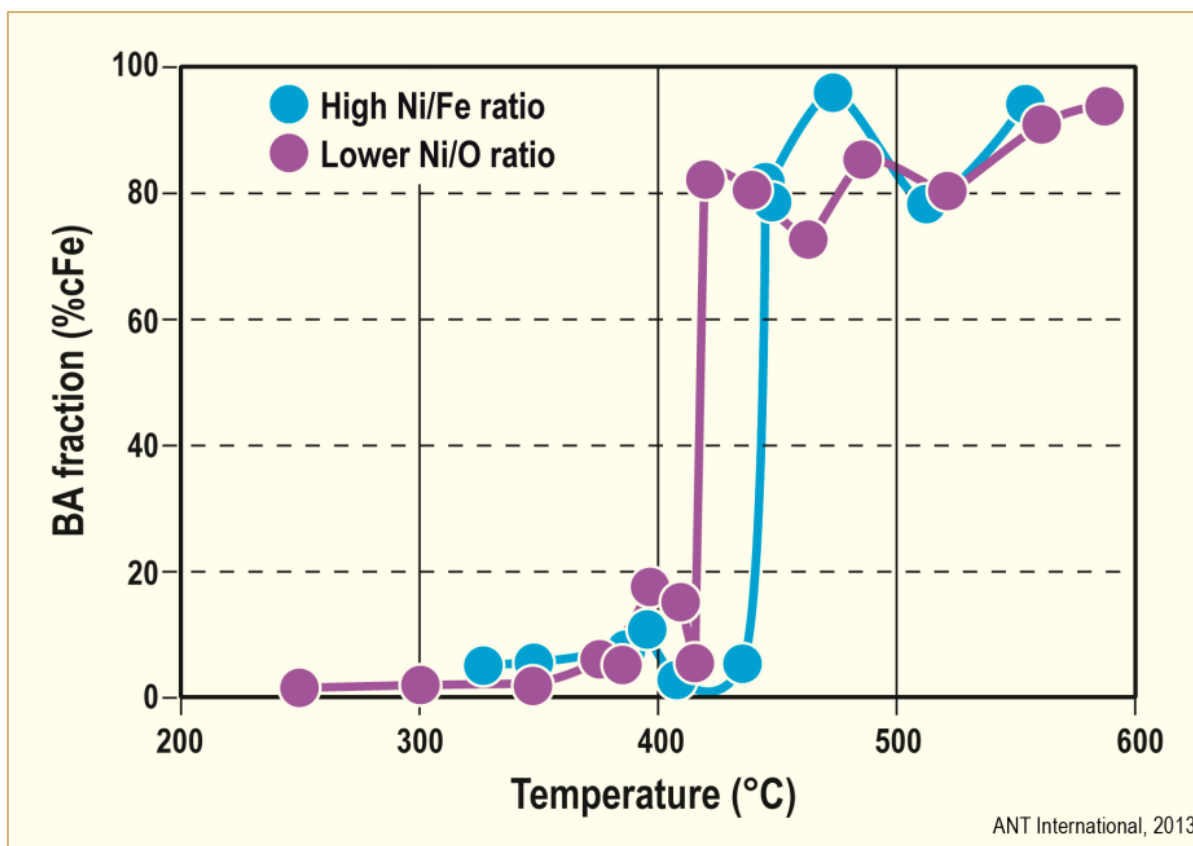


Figure 7-5: Hydrothermal production of Bonaccordite ( $\text{Ni}_2\text{FeBO}_5$ ) as a function of temperature for two different slurry compositions (red points: high Ni/Fe ratio; Black points: lower Ni/O ratio), after [Sawicki, 2002].

The adsorption of boron on fuel deposits was also investigated by Studvik under contract of Spanish PWR Industry and EPRI. Their investigations confirmed the influence of increasing nickel content on increasing boron adsorption in the fuel deposits (see Figure 7-6a). They could not find any influence of lithium on increasing boron adsorption (see Figure 7-6b; showing the Li/B ratios for  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$ ). They have also investigated the distribution of boron, nickel, lithium and iron in the fuel deposits. Their results as cross section of the fuel deposit is shown in Figure 7-7.

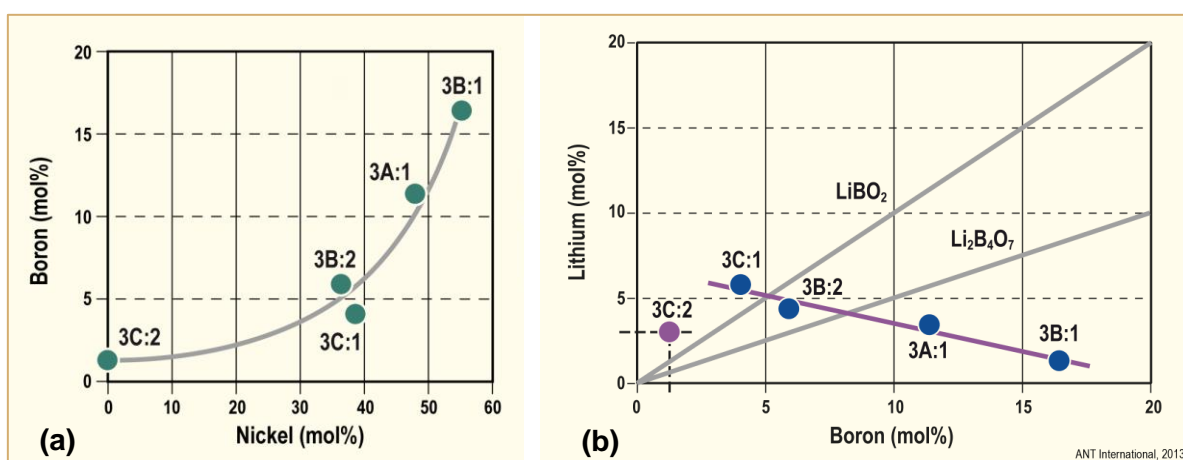


Figure 7-6: Influence of Nickel (a) and Lithium (b) on boron adsorption in fuel deposits, [Doncel & Chen, 2007].

## 8 ANT Recommendations for Coolant Chemistry

The ANT recommendations given for the reactor coolant chemistry control with respect to coolant lithium/pH<sub>T</sub> and hydrogen concentrations in the following considers the structural materials and the core design of the PWR plants:

### a) With respect to structural materials:

All PWR plants designed by Westinghouse and by their licensees (like Framatome, MHI) and by Combustion Engineering, Babcock & Wilcox (recently also PWRs built by Koreans and Chinese) are using nickel-based Alloys for their steam generator tubes (in the past Alloy 600MA/TT; later and recently only Alloy 690TT). The most of these PWR plants (especially the older ones) have nickel-based Alloy 600 in numerous penetrations of reactor pressure vessel (RPV), RPV-head, pressurizer and loop piping. Whereas, all nickel-based Alloys have excess nickel in their alloy composition, causing nickel rich fuel deposits resulting in high <sup>58</sup>Co induced radiation fields, Alloy 600 is in addition extremely PWSCC sensitive. In addition, almost all these PWRs (especially the older ones) have cobalt-based Alloy Stellites in their RCS, which contributes highly to radiation fields.

In contrast to these so-called US-designed PWRs with nickel-based Alloys, VVER plants and all Siemens designed PWRs and several CANDU plants have avoided to use nickel-based alloys in their RCS. In case of Siemens designed PWR plants the SG tubes are iron-based Alloy 800NG, and all RCS penetrations are made of stabilized austenitic stainless steels. Accordingly, entire RCS is immune against PWSCC, as it is confirmed by now almost 50 years of field experience (1970 – 2019). Same it is with VVER plants, which are designed with stainless steel steam generator tubes and RCS penetrations. Accordingly, all these PWR plants and VVER plants don't have excess nickel in their extremely few fuel deposits, if any. All VVER plants and the latest five Siemens-KWU designed PWR plants (Pre-Konvoi and Konvoi plants) are Co-free plants without stellites. Accordingly, they have extremely low radiation fields.

### b) With respect to core design:

Actually, PWR plants with nickel-based Alloys don't have very high core duty designs, if compared with most of the operating Siemens-KWU designed PWR plants. Even though, several of them are specified as "high duty core PWRs" their peak fuel rod powers with < 200 W/cm<sup>2</sup> [EPRI, 2018] is much lower than those of Siemens-KWU designed PWRs. Most of the operating Siemens designed PWR plants are real very high core duty plants with 400-500 W/cm<sup>2</sup> peak fuel rod power. In contrast to all these PWR plants, VVER plants have extremely low core duty designs!

Coolant chemistry control recommendations should consider all these plant structural materials and core design as follows:

## 8.1 Dissolved Hydrogen Concentration

Presently all coolant chemistry guidelines are specifying the dissolved hydrogen (DH) concentration in the range of 25-50 cc/kg (corresponding to 2.2 to 4.5 mg/kg due to conversion factor of 1 mg/kg = 11.2 cc/kg). VGB guidelines specify DH concentration as 1.5 to 4 mg/kg. Even though, investigations are ongoing to operate the PWRs with nickel-based alloys outside of this range with increased or decreased DH concentrations to mitigate PWSCC, these investigations are not completed yet. Accordingly, these PWRs have to operate still within this specified range. In case of PWR and VVER plants with iron-based Alloys, there is no need to operate outside of this range; because, they are immune against PWSCC. However, the selection of the operating DH concentration within this range should be selected based on the core duty design of the plant:

- **For colder plants with low core duty** it is recommended to operate in the lower range of the specified DH concentration range (2.0 to 2.5 mg/kg). Based on Japanese PWR field experience, operating with lower DH concentration has the benefit of reducing the nickel content of the fuel deposits and accordingly resulting in less <sup>58</sup>Co shutdown release and less <sup>58</sup>Co induced radiation fields.

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## List of Abbreviations

10CFR61	US-NRC Licensing requirements for Land Disposal of Radioactive Waste
AECL	Atomic Energy of Canada Limited
AISI	American Iron and Steel Institute
AL	Action Level (for Guidelines)
ALARA	As Low As Reasonably Achievable
ALARP	As Low As Reasonable Practicable
ANT	Advance Nuclear Technology
ANTI	ANT International
AOA	Axial Offset Anomaly
AR	Acidic Reducing step during plant shutdown operation
ASTM	American Society for Testing and Materials
B&W	Babcock and Wilcox
BNFL	British Nuclear Fuels plc (public limited company)
BOC	Beginning Of Cycle
BWR	Boiling Water Reactor
CANDU	CANada Deuterium Uranium
cc/kg	Cubic centimetre (per kg): used for H <sub>2</sub> concentration in RCS = ml/kg (under normal pressure and temperature)
CE	Combustion Engineering
CGR	Crack Growth Rate
CHC	Critical Hydrogen Concentration
CIPS	Crud Induced Power Shift
CP	Corrosion Product
CRDM	Control Rod Drive Mechanism
CRUD	Calk River Undefined Deposits (Coolant corrosion products observed first time in Calk River loop testing)
CS	Carbon Steel
CVCS	Chemical and Volume Control System
DH	Dissolved Hydrogen

DO	Dissolved Oxygen
dpa	Displacement per atom (unit for radiation damage)
DX-ELS	Duplex-Extra Low Sn (tin)
EBA	Enriched Boric Acid
ECP	Electro Chemical (Corrosion) Potential
EdF	Electricité de France
EDX	Energy Dispersive X-ray Spectroscopy
EFPY	Effective Full Power (operating) Year
EOC	End Of Cycle
EPR	European Pressurized Water Reactor
EPRI	Electric Power Research Institute, USA
FCC	Face Centred Cubic (cubic crystal lattice structure)
FSD	Full System Decontamination
GB/t	Giga Becquerel per ton
GW/tU	Giga Watt per tone Uranium
HCDI	High Core Duty Index
HFT	Hot Functional Test
HP	High Pressure
HPU	Hydrogen Pick-Up
HPUF	Hydrogen Pick-Up Factor
HTF	High Temperature Filter
IAEA	International Atomic Energy Agency, Vienna
IASCC	Irradiation Assisted Stress Corrosion Cracking
IER	Ion Exchange Resin
IGSCC	Inter-Granular Stress Corrosion Cracking
INCA	IN-Core Autoclave research facility owned by Studsvik
JAPC	Japan Atomic Power Company
KKG	Kernkraftwerk Grafenrheinfeld (NPP Grafenrheinfeld)
KKGg	Kernkraftwerk Gösgen (NPP Gösgen; sometimes abbreviated only with KKG)

## 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 s <sup>-1</sup>

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