The background of the cover is a photograph of a body of water with dark blue, rippling waves. At the bottom of the image, a rocky shoreline is visible, with numerous light-colored, irregularly shaped rocks and pebbles scattered across the water's edge. The overall lighting is somewhat dim, creating a moody atmosphere.

LCC9 SPECIAL TOPIC REPORT

Effects of Coolant Chemistry
on Fuel Performance

Effects of Coolant Chemistry on Fuel Performance

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1 Introduction

The deregulated market means that the nuclear utilities must reduce operating, maintenance and fuel cycle costs to remain competitive. Also reactor safety must be improved while the plant radiation build-up must be limited to cope with the change in political environment towards nuclear power. To achieve the above mentioned goals the following changes have been and are being introduced:

- Longer cycles. Longer cycles do not necessarily meet any of the goals noted above; they do however reduce licensing needs and save storage space. Two-year cycles start to be marginal in some cases economically.
- Higher discharge burnups
- Modified water chemistry:
 - e.g. elevated LiOH in PWRs,
 - increased or decreased hydrogen coolant contents in PWRs,
 - Nobel metal additions in BWRs,
 - Zn-injection in BWRs and PWRs
- Plant power uprates
- More aggressive fuel management methods

Changes in water chemistry may interact with several of the above parameters challenging the corrosion and hydrogen pickup performance of the Zr alloys being used as fuel claddings.

The fuel vendors on their part are developing new fuel designs, including more advanced materials to partly reduce the fuel cladding corrosion and hydrogen pickup rates. However, these alloys may respond differently to the parameters mentioned above. Also, very little corrosion and hydrogen pickup data exist for these new alloys.

The intent of this Report is to provide a state-of-the-art knowledge of the mechanisms of the various forms of Zr-alloy corrosion and hydrogen pickup (HPU) and how water chemistry impacts fuel performance, including corrosion and HPU. This knowledge will help the utilities to implement actions to reduce Zr alloy corrosion and hydrogen pickup.

The structure of the report is as follows:

- Section 2 gives an overview of reactor coolant chemistry in the primary circuit
- Section 3 describes the different fuel designs and materials used in the fuel assemblies
- Section 4 covers the different types of irradiation in a reactor and how it impacts structural materials and water (radiolysis).
- Section 5 provides a list of issues related to the coolant chemistry
- Section 6 describes the parameters that impact Zr alloy corrosion and HPU mechanisms and focuses on the impact of coolant chemistry and CRUD
- Section 7 gives a description of CRUD formation, transport to fuel, deposition, activation and transport to system surfaces.
- Section 8 covers AOA
- Section 9 summarises various reported cases of fuel performance issues related to coolant chemistry

- Section 10 gives a summary of the Report
- Appendix A provides information about the effects of heat treatments on growth of second phase particles

The interested reader of the topics covered in these two volumes is referred to the following references:

- ZIRAT6/IZNA1 STR on CRUD ZIRAT6/IZNA1 STR on Water Chemistry and CRUD Influence on Cladding Corrosion by Gunnar Wikmark and Brian Cox, ANT International, 2001.
- ZIRAT7/IZNA2 STR on Corrosion of Zirconium Alloys by Ronald Adamson, Brian Cox, Friedrich Garzarolli, Alfred Strasser, Gunnar Wikmark and Peter Rudling, ANT International, 2003.
- ZIRAT8/IZNA3 STR on The Effects of Zn Injection(PWRs and BWRs) and Noble Metal Chemistry (BWRs) on Fuel Performance by Brian Cox, Friedrich Garzarolli, Alfred Strasser, and Peter Rudling, ANT International, 2004.
- ZIRAT9/IZNA4 STR on Corrosion of Zr-Nb Alloys in PWRs by Brian Cox, Friedrich Garzarolli, and Peter Rudling, ANT International, 2004.
- ZIRAT12/IZNA7 STR on Corrosion Mechanisms in Zirconium Alloys by Ronald Adamson, Friedrich Garzarolli, Brian Cox, Alfred Strasser, and Peter Rudling, ANT International, 2007.
- LCC2 STR on CRUD in PWR/VVER and BWR Primary Circuits by Rolf Riess and Klas Lundgren, ANT International, 2006.
- LCC6 STR on Effect of Zink in BWR and PWR/VVER on Activity Build-up, IGSCC and Fuel Performance, by Suat Odar, Robert Cowan and Jan Kysela, ANT International, 2010.
- LCC7 and 8 STR on Introduction to Boiling Water Reactor Chemistry Volume I and II, by Robert Cowan, Wilfried Rühle and Samson Hettiarachchi, ANT International, 2011 and 2012.
- LCC7 and 8 STR on PWR/VVER Primary Side Coolant Chemistry Volume I and II, by Rolf Riess, Suat Odar, Francis Nordmann and, Jan Kysela, ANT International, 2011 and 2012.

2 General reactor characteristics

2.1 Water cooled reactors

There are essentially, 5 different types of commercial water cooled reactors (Table 2-1). By design, the water cooled reactors in operation can be separated under thermodynamic aspects into Closed Cycle Systems (PWR, VVER, and CANDU) and Open Cycle Systems (BWR and RBMK) [Riess & Millet, 1994].

The separation into “Closed” and “Open Systems” has consequences when it comes to the interaction between radiation and the coolant. In a “Closed” system, the net decomposition of the coolant can be suppressed by the addition of hydrogen or ammonia, whereas in “Open Systems” radiolysis gas is produced (see Section 4.2.1) and removed from the coolant.

Closed Cycle System reactors are operated under alkaline (pH control agent is either LiOH or KOH) and reducing conditions (as mentioned above). This basic principle is now valid since more than 30 years and it has only been modified within the established framework of specified values for pH control. Such modifications are called coordinated-, modified-, elevated-, or constant elevated Li/B-chemistries.

In Open Cycle System reactors the fundamental principle is to operate under neutral and oxygenated conditions while keeping the cycle as clean as possible. However, based on material integrity problems, the chemistry conditions have been changed in some stations to reducing conditions (Hydrogen Water Chemistry (HWC)).

Table 2-1: Design parameters in water cooled reactors.

Parameter	Western type PWR	VVER (440/1000) MW	CANDU	BWR	RBMK
1. Coolant	Pressurized H ₂ O	Pressurized H ₂ O	Pressurized D ₂ O	Boiling H ₂ O	Boiling H ₂ O
2. Fuel assembly materials (Pressure Tube (PT) materials)	Zr-4, ZIRLO, DUPLEX (DX), M5, MDA, NDA, Inconel, SS	E110, E635	Zry-4 (Zr2.5Nb)	Zry-2, Zry-4, Inconel, SS	E110, E635 (Zr2.5Nb)
3. Average power rating, (kW/l)	80-125	83/108	9-19	40-57	5
4. Fast neutron flux, average, n/cm ² .s	6-9E13	5E13/7E13	1.5-2E12	4-7E13	1-2E13
5. Temperature, °C					
Average coolant inlet	279-294	267/290	249-257	272-278	270
Average coolant outlet	313-329	298/320	293-305	280-300	284
Max cladding OD	320-350	335/352	310	285-305	290
Steam mass content, %				7-14	14
6. System pressure, bar	155-158	125/165	96	70	67
7. Coolant flow, m/s	3-6**	3.5/6	3-5	2-5**	3.7
8. Coolant chemistry					
Oxygen, ppb	<5	<10	<10	see 2.2.3 (note that the primary oxidant in the BWR is H ₂ O ₂ but it decomposes to O ₂ in sampling lines.)	<20
Hydrogen (D ₂), ppm	2-4	2.2-4.5			-
cc/kg	25-50	30-60	(3-10)		-
Boron (as boric acid), ppm	0-2200	0-1400	***		-
Li (as LiOH), ppm	0.5-6	0.05-0.6	0.4-1.1		-
K (as KOH), ppm	-	5-26			-
NH ₃ , ppm		6-30		-	
NaOH, ppm		0.03-0.35		-	
** Variation from lower to upper part of the core and from plant to plant					
*** Not in coolant but in moderator					

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The reactor types and their characteristics are described more in the following subsections.

2.2 Primary water chemistry

2.2.1 PWRs and VVERs

The Primary Coolant serves as a moderator and is the medium for transporting heat from the core to the steam generators. The role of the water chemistry in Closed Cycle Systems is to:

- Minimise the metal release of the structural materials (CRUD formation).
- Counteract any form of localized corrosion.
- Minimise the tendency of corrosion product (CRUD) deposition on fuel rod surfaces.

- Suppress the radiolytic formation of oxidising species.
- Minimise radiation fields in the primary circuit.

In the Primary Coolant of PWR/VVER, the Li/K and the H₂ concentration can be varied in a controlled manner to minimize the metal release rates of the structural materials, i.e. CRUD formation, and to avoid any type of localized corrosion.

In PWRs 25-50 cc hydrogen per kg water (2-4.5 ppm) is added to prevent the formation of O₂ and H₂O₂ to undetectable levels and thereby ensures the existence of reducing coolant conditions suppress oxidative radicals. The resulting corrosion potential (at O₂ concentrations up to 10 ppb) is about -0.4 V versus Pt, according to [Christensen et al, 1996]. In modern PWRs where sub-cooled boiling occurs¹, some H₂ can be stripped off from the water to the steam bubbles which could locally increase the oxidising environment somewhat.

PWRs contain boric acid for reactivity control (with a B-10 content of ~20% in natural boric acid.) The boric acid coolant concentration is reduced with time during a fuel cycle, usually being near zero at end of cycle. For a twelve month cycle, the initial boron concentration is typically 1500 ppm but is reduced rapidly over the first few days of the cycle to approximately 900 to 1200 ppm whilst the xenon and samarium poisons (neutron absorbers) are built up to equilibrium levels in the fuel. Thereafter the boron concentration is reduced approximately linearly at ~ 3 ppm/d. For an 18 month cycle the initial boron concentration is typically 1800 ppm dropping to 1500 ppm after a few days. Some PWRs use B-10 enriched boric acid. These plants operate with lower total B concentrations.

Because of the aggressive corrosion environment from the lowering of the pH from the boric acid additions, <6 ppm LiOH in PWRs, is added to reduce the corrosion duty of the coolant by making the coolant slightly alkaline. The LiOH strategy has changed over the years. Early specifications only limited the maximum Li content to 2 to 2.2 ppm. In the early 80's it was recognized that a more constant pH during the cycle is desirable for reducing the CRUD fuel deposition and activity buildup. Later, it was suggested [Wood, 1990], that a minimum pH of about 6.9 (at operation temperature) is required in PWRs to avoid heavy CRUD deposition on the fuel, which is undesirable for two reasons - fuel cladding oxidation may be accelerated, and activation of cobalt in the CRUD leading to high out-of-core radiation fields from deposition of Co-60. Today the optimum strategy is believed to keep the pH relatively constant between 7.2 and 7.4 and to keep the Beginning of Cycle, BOC, pH as high as possible.

Recently zinc injection has been implemented in the primary systems of some PWRs, both to reduce primary side cracking of Inconel 600 steam generator tubes (20-50 ppb Zn) and to control dose rates (5-10 ppb) [Wood, 2000].

The Russian VVERs are operating with KOH/NH₄OH/LiOH water chemistry, (LiOH build up is not allowed to exceed 0.5 ppm Li). They nominally operate with a hydrogen over pressure, but the precise hydrogen level is not clearly specified. In the Russian VVERs, NH₃ is added which decomposes radiolytically to N₂ and H₂. In VVERs hydrogen is kept between 2.6 and 5.3 ppm (30-60 cc/kg) and the NH₃ content is typically >5 ppm, [Yurmanov et al, 1997]. Also in VVERs Boric acid is added to control reactivity and to neutralise the resulting acidic coolant conditions 5-20 ppm KOH is added. None of the VVER plants is adding Zinc.

¹ Sub-cooled boiling means that boiling occurs at the cladding tube surface, where the temperature is locally above the saturation temperature due to the surface heat flux, while the bulk temperature is below the saturation temperature. This means that steam bubbles are formed at the fuel clad surface which will implode once they reach the bulk coolant.

2.2.2 PWRs/CANDUs

CANDUs are using Lithium as pH control agent. The Lithium concentration is in the range of 1 ppm. The hydrogen concentration used in the CANDU plants is also much smaller than in PWRs, well below 1 ppm and 2-4 ppm, respectively. The allowed oxygen concentration is by a factor of 2 higher than that in PWRs. Also, there is a specification for a maximum CRUD level in the CANDUs, since low alloy steel is used in the feeder pipes.

2.2.3 BWRs

The characteristic feature of the BWR design is the heat removal from the reactor core by boiling water, i.e. by a mixture of steam and water. The significant in-core boiling plus the turbine plant included in the primary loop put several restrictions on the water chemistry in the coolant that differs from the PWR conditions. The most significant differences are:

- The reactivity of the core during normal operation cannot be controlled by boron or other additives in the coolant. On the other hand, the possibility to control the void content in the core with the recirculation pumps provides an efficient way to adjust the power level.
- To reduce the risk of Intergranular Stress Corrosion Cracking (IGSCC) in structural materials of the water circuit (SSs and Inconel) reducing conditions² with a sufficient low corrosion potential in the primary loop must be achieved.
 - The traditional water chemistry in BWRs, called Normal Water Chemistry (NWC), means no hydrogen injection and therefore oxidizing conditions in the coolant.
 - Continuous injection of hydrogen to the feedwater has been introduced in many plants, so called Hydrogen Water Chemistry (HWC), in order to achieve protection corrosion potential in parts of the primary loop. Significant amounts of hydrogen are needed, and more sophisticated techniques, e.g. use of Noble Metal Chemical Addition, (NMCA), or most recently On Line Noble Chemistry (OLNC) have been introduced to improve the efficiency of the hydrogen injection and eliminate the increase in main steam line radiation levels seen with standard HWC³, see [Cowan et al, 2011] and [Cowan et al, 2012] for more details.
- The possible risk to have turbine condenser leakage calls for measures to avoid an intrusion of harmful species, e.g. chlorides, directly into the primary loop. The condensate cleanup system plays an important role in that context. This system in combination with material selection in the turbine plant is also of very large importance to maintain low levels of corrosion products in the final feedwater.

The water chemistry of the BWR plants is expected to:

- 1) Minimize IGSCC and Irradiation Assisted Stress Corrosion Cracking (IASCC).
- 2) Minimize plant radiation fields both during operation and shutdown conditions.
- 3) Maintain fuel integrity by minimizing cladding corrosion and fuel CRUD deposits.
- 4) Minimize Flow Accelerated Corrosion, (FAC), in the primary and Balance-Of-Plant⁴(BOP) systems.
- 5) Minimize the potential impact of water clarity on refuelling outage critical path.

² The (ECP) of reactor internals must be below -230 mV (SHE) to ensure protection towards IGSCC.

³ Soluble noble metal chemicals are added to the reactor during either shutdown(NMCA) or during operation (OLNC) to deposit the equivalent of a mono-layer or less of noble metal on wetted surfaces to catalyze oxidant and hydrogen recombination, resulting in zero oxidant on the catalyzed surface

⁴ The BOP is composed of several subsystems. The most important are the FW system, the steam lines, the turbine, and the condensate system.

During NWC oxidant content ($\text{H}_2\text{O}_2 + \text{O}_2$) of 125-500 ppb is measured in the reactor coolant in the water sample line before the reactor cleanup system and 20-30 ppm in the steam. These oxidants are formed by radiolysis of the water phase within the core. Because O_2 and H_2 (the other major radiolysis product) are very volatile, during boiling they are stripped to the steam phase, leaving most of the H_2O_2 behind in the water phase. Short lived radical species are also produced in the radiolysis process and they can also affect the oxidizing nature of the coolant e.g. OH , HO_2 , O_2^- , and HO_2^- . As calculations indicate in Figure 2-1, both short lived radical species and H_2O_2 may reach quite high concentrations within the fuel element. After traversing the reactor sampling lines, most of the H_2O_2 decomposes on the sample line surface to O_2 and H_2O and the measured H_2O_2 concentration is usually very low⁵. The corrosion potential in water with 300 ppb oxygen would be out-of-pile at 0 to 0.1 V, Standard Hydrogen Electrode (SHE). Within the core of BWRs with NWC even higher values have been found (0.1 to 0.3 V, SHE), which reflects the high red/ox potential of the H_2O_2 , [Indig, 1989].

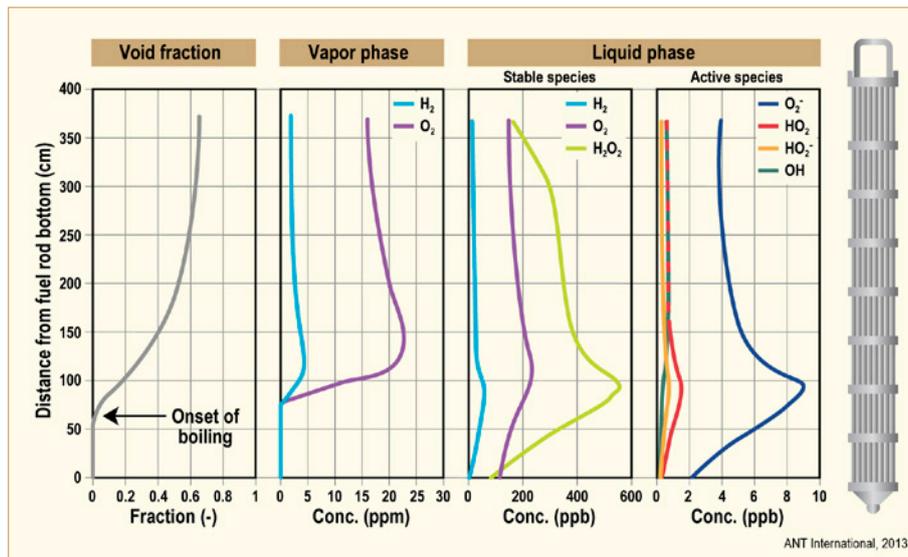


Figure 2-1: Calculated profile of radiolysis species along a fuel rod in a BWR 4 type reactor during NWC, after [Nishino et al, 1998].

Under HWC conditions the radiolytic specie profile changes with increasing feedwater H_2 additions, both inside the fuel channels (Figure 2-2a) and between the fuel channels (Figure 2-2b). H_2 additions cannot suppress radiolytic formation of oxidizing radicals due to the fact that most of the added H_2 is stripped out of the boiling water and into the steam (Figure 2-2a). Electrochemical measurements in BWRs under HWC have shown a significant reduction of the corrosion potential only in the bypass channel whereas in the boiling channel a significant reduction was only seen in the lower, non-boiling sections (Figure 2-2b), [Indig, 1989]. For BWRs utilizing NMCA or OLNLC, the conditions inside the fuel channel will be reducing only until the H_2 /oxidant ratio is reduced below 2 by boiling. Calculations show that this occurs at an elevation about 60 to 75 cm above the lower end plug.

⁵ Rooth T., Ullberg M., Karlsson E. and Persson I., *Hydrogen peroxide in BWRs: an experimental determination of the actual level*, Water Chemistry of Nuclear Reactor Systems- 5, BNES, London, 1989.

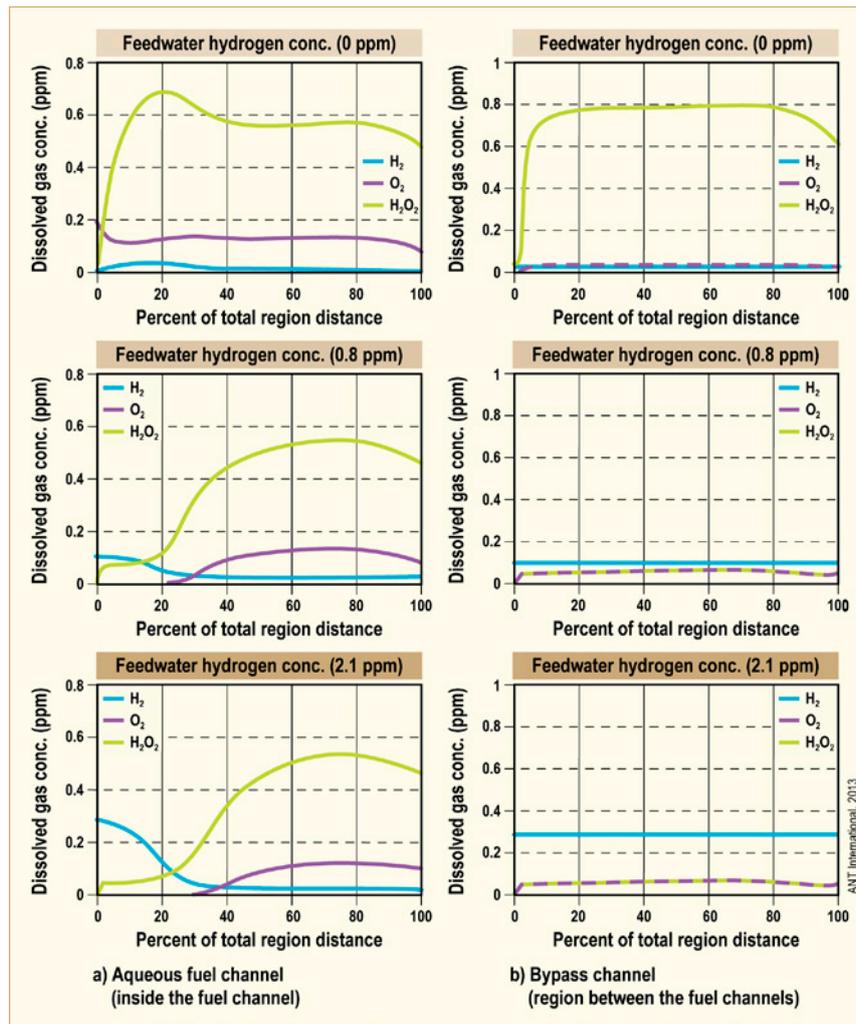


Figure 2-2: Calculated profiles of radiolytic species along a fuel rod in a BWR reactor during HCW for different H additions to the feedwater, after [Ruiz et al, 1989].

2.2.4 RBMK

The BWR of Russian design is called RBMK, what can be translated with “High Power Channel Type Reactor”. It is a water cooled, graphite moderated, nuclear power reactor, which can be operated with natural Uranium, due to the very effective moderator. It does not need a reactor pressure vessel. Each fuel bundle is enclosed in a pressure pipe, through which is passed an aliquot of the RW. The passing water is heated and the water steam mixture of a group of pressure pipes is fed into a steam collector, where steam and water are separated from each other. Because of the boiling in the pressure tubes, there is a similarity to the western BWRs.

The materials of the “RW” containing components are stabilized austenitic stainless steel types similar to AISI 321. The water chemistry is the same as in BWRs, which means demineralised pure water under oxidizing conditions.

Considerable parts of the NPP’s circulating system (especially that of the feed water drain) are made of perlitic steels, like OX 18 H10T , which have higher corrosion rates when compared to Stainless Steel (SS). Corrosion products are released from these surfaces and can be carried into the reactor core and become activated there. In order to suppress these processes, up to 200 µg/kg of oxygen is injected into the feedwater downstream of the condensate polishing plant. Further downstream most of the added oxygen is then removed from the water by the steam separator.

3 Fuel designs and Zr alloys used in the nuclear industry

There is a wide variety of different types of fuel assemblies for LWRs described more in the following subsections.

3.1 BWRs

The fuel rod array for BWRs was initially 7x7 but there has been a trend over the years to increase the number of rods so that now most fuel assemblies are either of 9x9 or 10x10 square configuration designs. An example of a BWR fuel assembly based on a 10x10 lattice is shown in Figure 3-1. The driving force in the trend toward larger number of fuel rods in each fuel assembly was the reduction of Linear Heat Generation Rate (LHGR), such changes which resulted in a number of fuel performance benefits such as lower Fission Gas Release (FGR) and increased PCI margins. However, to decrease fuel cycle costs, the LHGRs of 9x9 and 10x10 fuel assemblies have successively been increased so that peak heat generation rates are today almost comparable to those of the older 7x7 and 8x8 designs.

In all BWRs, fuel bundles are enclosed in open-ended, square tubes or “channels”. The combination of a fuel bundle (rods, spacers, tie plates and related hardware) and a channel is commonly identified as a fuel assembly. The channels are ducts for coolant flow that prevent lateral flow of coolant among the assemblies operating at different power levels. They also form the inter-assembly space into which control blades are inserted.

Fuel assemblies are positioned in a reactor core support structures at the bottom and top of each assembly. Lower tie or bottom support plates (as in Figure 3-1) are supported by a pedestal that carries the assembly weight and directs coolant into the channel. The upper ends of fuel assemblies are supported laterally by a rectangular lattice structure which bears against wear pads on the outer surface of the fuel channels. Cruciform-shaped control blades are located in the region between the channels of selected sets of four fuel assemblies. Part of the incoming coolant is diverted into the region between fuel assemblies to transfer heat from the control blades and prevent boiling.

Irrespective of the many possible different shapes, sizes and configurations, the common fuel assembly design requirements are:

- Maintain proper positioning of the fuel rods under normal operating conditions and in Design Basis Accidents (DBAs); i.e., maintain a controllable and coolable (safe) geometry during normal operation, anticipated operating occurrences and during postulated seismic events, LOCA, RIA.
- Contain or at least confine fuel materials and fission products
- Facilitate handling before and after irradiation.

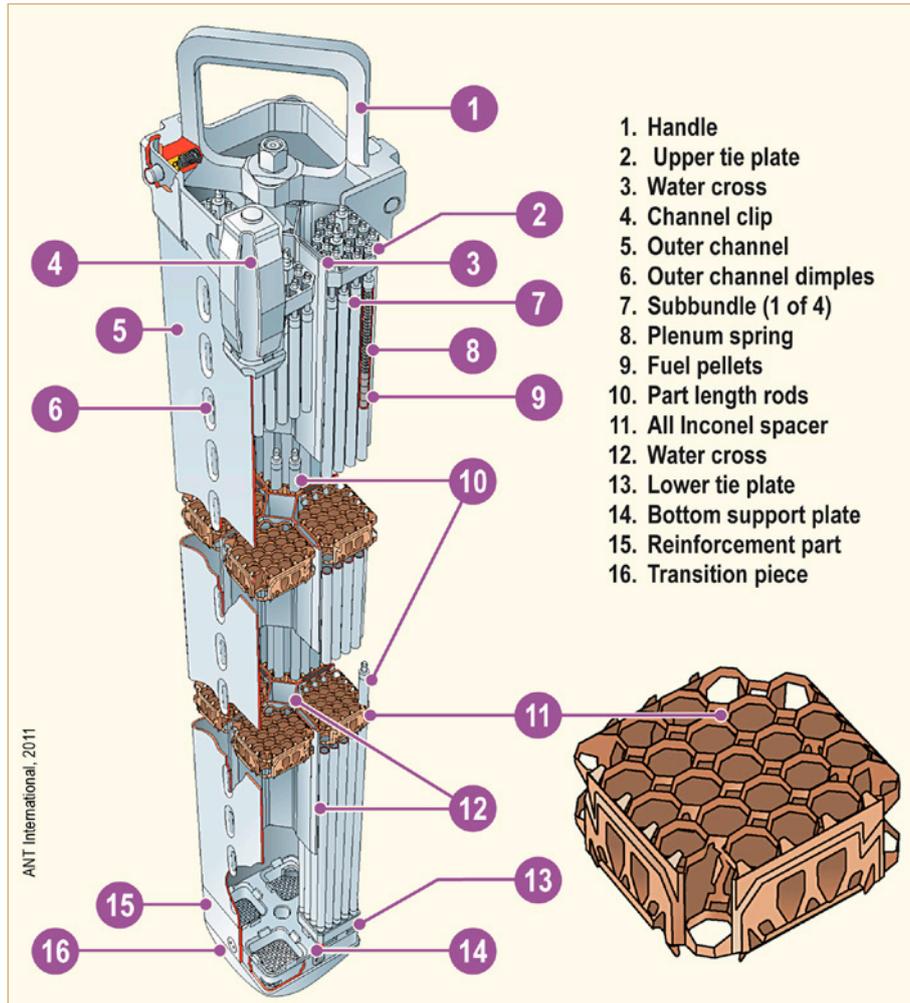


Figure 3-1: The BWR Fuel SVEA-96 Optima2, provided by the courtesy of Westinghouse Electric [Rudling et al, 2012].

3.2 PWRs

Also for PWRs there has been a trend to greater subdivision of fuel rods, e.g. from W 15x15 to 17x17 design. However, since PWRs do not have the same flexibility with core internals and control rods as BWRs, to accomplish this requires modified reactor internals. There is however, one exception namely DC Cook 1 which is switching to 17x17 by changing the reactor internals. Figure 3-2 shows the current PWR fuel rod arrays.

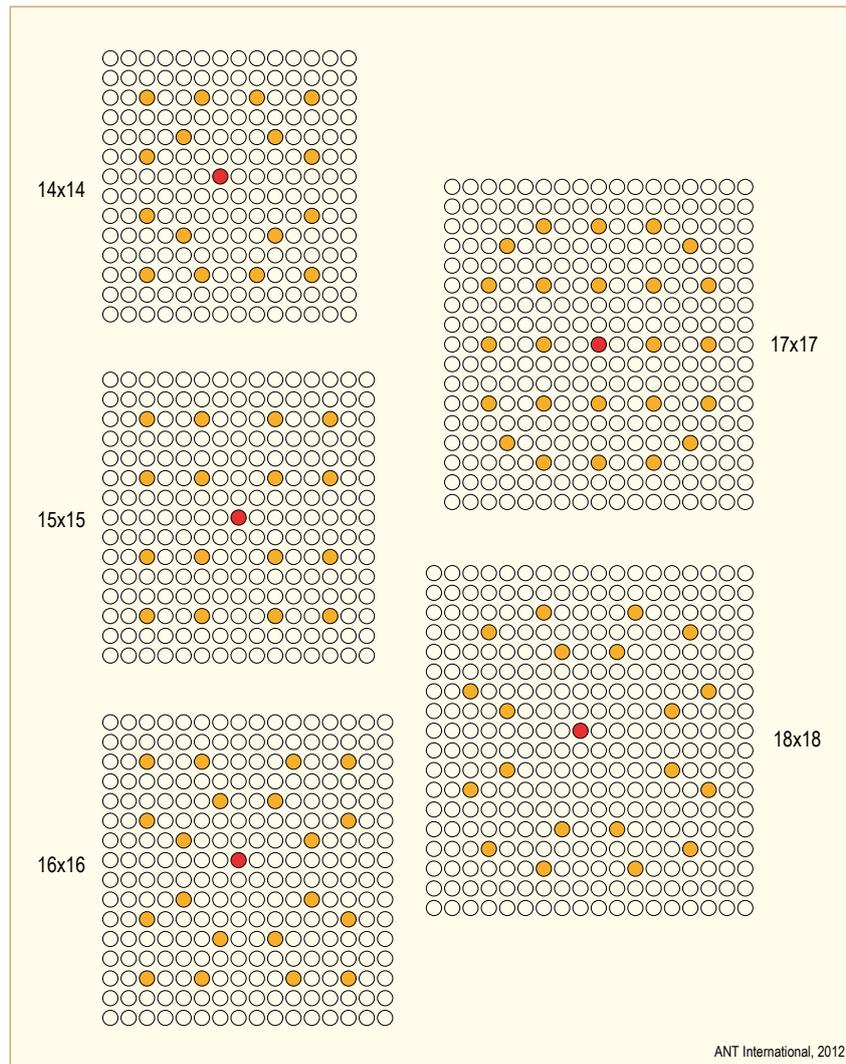


Figure 3-2: Layouts of different PWR fuel assembly arrays. Rods marked with yellow colour are GTs into which the control rod cluster is inserted. The position marked by a red filled circle is the IT position [Rudling et al, 2012].

In most PWRs, the assemblies are positioned in the core by bottom and top fittings, and the lateral clearances are restricted by the assembly-to-assembly contacts at the spacer-grid levels. PWR control rods consist of Rod Cluster Control Assemblies, RCCAs, the poison part of which moves into guide thimbles (or GTs). These guide thimbles are an integral part of the assembly structure.

As an example of a PWR fuel design, the High Thermal Performance (HTP) design (former Siemens design) is shown in Figure 3-3. The unique feature of HTP grid concept is that the fuel rods are supported along four pairs of continuous lines, providing a large grid-to-rod contact surface with coolant mixing being affected by curved internal flow channels. The HTP mid span mixing grid has no contact between the grid and the fuel rod. These grids are only used to improve thermal-hydraulic performance. The FUELGUARD bottom nozzle design (Figure 3-4), was originally designed for HTP fuel but can be used for all designs as a means for preventing debris from entering a fuel assembly with the reactor coolant.

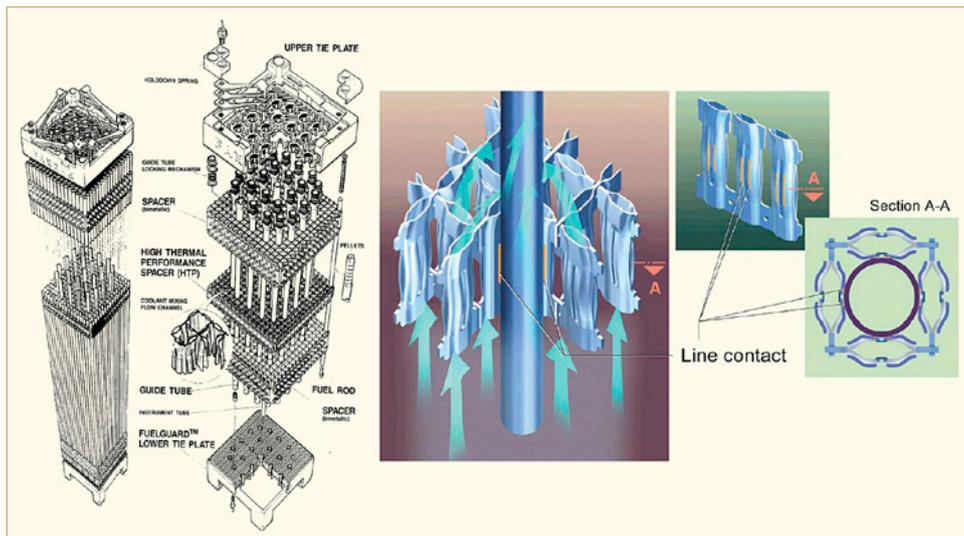


Figure 3-3: AREVA NP PWR HTP 17 x 17- HTP spacer grid design [Baleon et al, 2001].

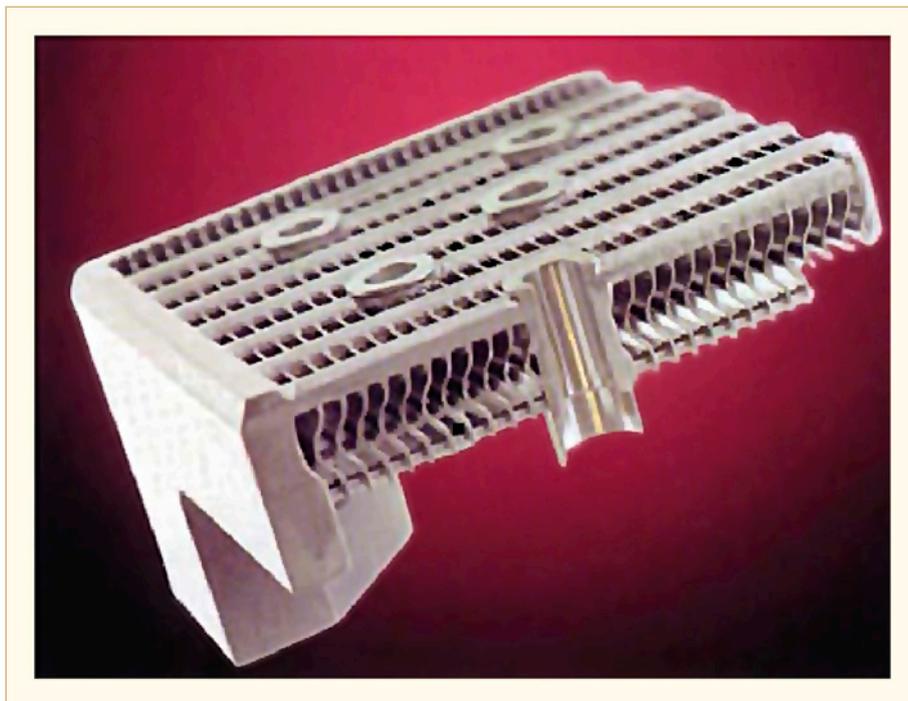


Figure 3-4: FUELGUARD bottom nozzle, provided by the courtesy of AREVA NP [Rudling et al, 2012].

3.3 CANDU

The CANDU reactor is a heavy water moderated and cooled natural uranium fuelled reactor in which the fuel bundles (50 cm long and usually 12 per fuel channel) are contained in individual pressure tubes through which the heavy water coolant flows. The number of pressure tubes varies according to the power output of the reactor (e.g. 380 in the CANDU-6 design). Reactor outlet temperatures vary somewhat, but are typically in the range of 310-315°C. The pressure tubes are separated from the “cold” (60-80°C) heavy water moderator contained in a large, horizontal, cylindrical Calandria Vessel. Each individual Calandria Tube in the Calandria Vessel contains a smaller diameter Pressure Tube. The Calandria and pressure tubes are separated by an insulating gas gap which is maintained by spacers (“Garter Springs”). There were initially 2 spacers per pressure tube, but this was increased to 4 per tube in all reactors after the failure of the G8 pressure tube in Pickering-2 as a result of the pressure tube sagging into contact with the calandria tube [Hart, 1997].

A simplified diagram of the Calandria Vessel, end shields and fuel channels is shown in Figure 3-5.

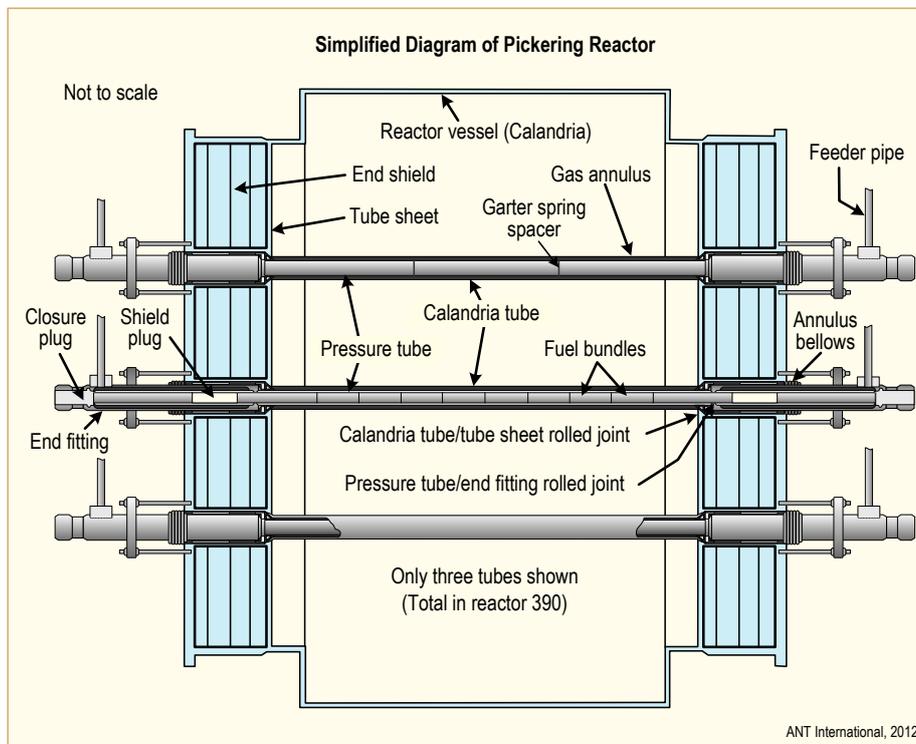


Figure 3-5: Simplified diagram of Pickering reactor showing fuel channels and garter springs [Rudling et al, 2012].

Details of an individual fuel channel showing the end fittings that the fuelling machines latch onto during on-power refuelling operations are shown in Figure 3-6. The typical appearance of the pressure tube-calandria tube spacers (garter springs) is shown in Figure 3-7. These garter springs were initially of Zr-2.5Nb-0.5Cu alloy, and were a tight fit on the pressure tube. They were subsequently changed to a loose fit, which allowed vibrations to cause spacers to move out of place during reactor construction. This movement was a major contributor to the P2-G8 pressure tube failure. A subsequent change to tight fitting Inconel 728 spacers (4 in number) resulted from this event. The gas annulus between the pressure tube and the calandria tube was initially filled with nitrogen, but this was changed to carbon dioxide to reduce deuterium uptake in the pressure tube from deuterium diffusing into the gas annulus from the stainless steel end fitting.

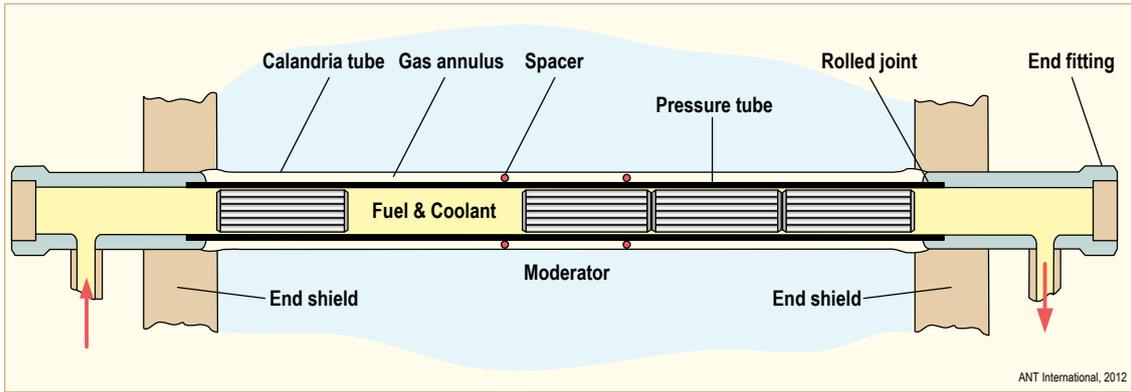


Figure 3-6: Schematic of a fuel channel for a CANDU reactor with pressurized water coolant [Rudling et al, 2012].

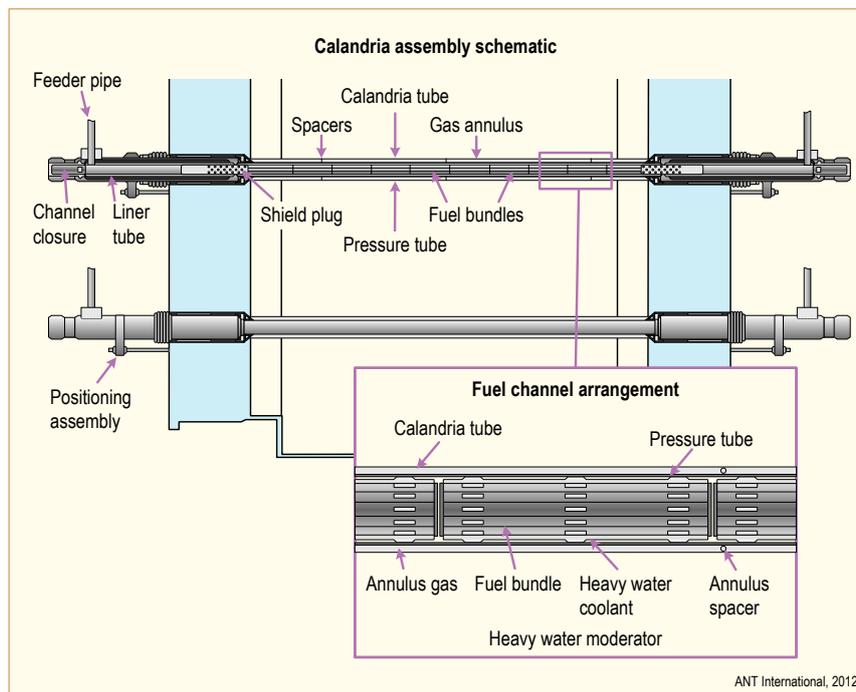


Figure 3-7: "Garter spring" spacer assembly, showing the locations of the four spacers now standard on all pressure tubes [Rudling et al, 2012].

3.4 VVER

In the early VVER-440 reactors (440 MWe), the fuel assemblies were hexagonal arrays of 126 fuel rods. The rods were clad with E110 (Zr1Nb) tubes. The assemblies contained 10 or 11 stainless steel grid spacers and were enclosed in an E125 (Zr2.5Nb) hexagonal wrapper (which performs the same function as a BWR channel) [Smirnov et al, 1994]. An example of such fuel is shown in Figure 3-8.

In some early VVER-440 fuel assemblies that were tested in reactors such as the MR or MIR, boron was added to the E125 wrappers for reactivity control. In commercial power reactors, boric acid is usually added to the coolant for reactivity control along with movable control assemblies.

The fuel is uranium-enriched up to 4.95% and is arranged in a hexagonal grid. Fuel pellets can have a central coaxial hole.

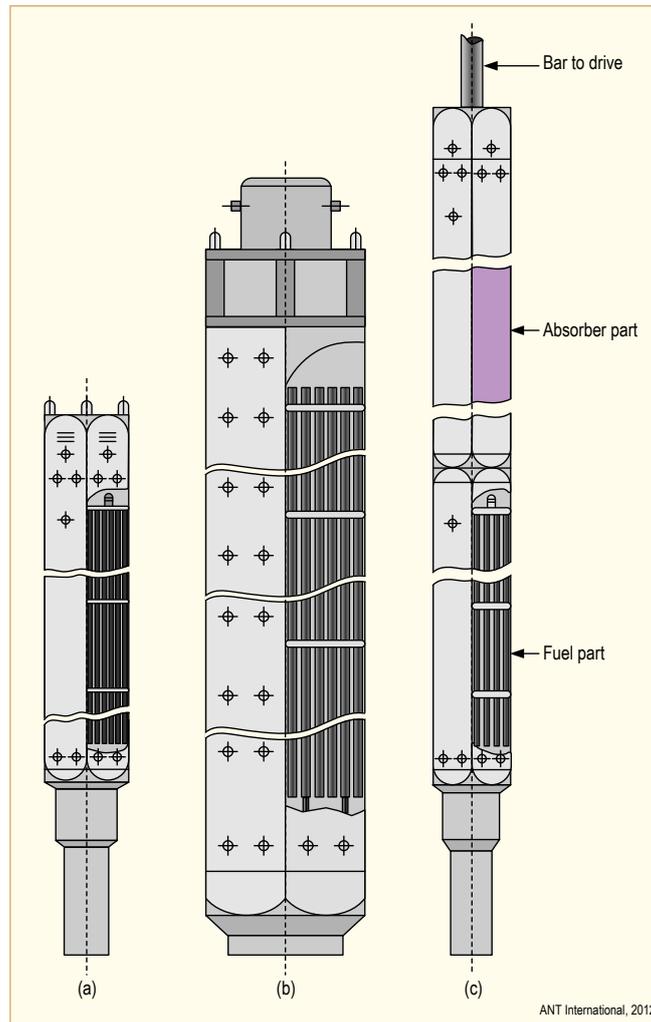


Figure 3-8: Schematic diagram of VVER fuel: (a) VVER-440 operating fuel assembly, (b) VVER-1000 fuel assembly, (c) VVER-440 control rod and fuel assembly [Rudling et al, 2012].

VVER-1000 reactor core consist of 163 FAs, incorporating the control protection system absorber rods (CPSAR). Each assembly contains 312 fuel rods, a central E125 alloy support tube and 18 stainless steel guide tubes for control and shut-down rods. VVER-1000 fuel assemblies consist of the following components: skeleton, bundle of fuel and gadolinia rods, top nozzle and bottom nozzle. The general views of two base designs VVER-1000 FA are illustrated in Figure 3-9 and Figure 3-10.

Except for the first VVER-1000 (Novo-Voronezh-5) these VVER-1000 fuel assemblies do not have wrappers; i.e., they are essentially open like PWR fuel assemblies rather than encased in a flow channels like VVER-440 and BWR fuel assemblies. Zirconium alloy E-635 ($Zr_{1.3}Sn_{1}Nb_{0.4}Fe$) is used as the structural material for the skeleton angle pieces and guide channels (GC). Alloy the E-635 is used because of better mechanical and radiation resistance properties relative to alloy E110 in the VVER-1000 environment.

4 Irradiation

4.1 Types of irradiation

In reactors the radiation environment consists of neutrons, beta (β), gamma (γ), alpha (α) and fission fragments (Table 4-1).

Neutrons are, of course, the most important form of irradiation. Not only do they allow the reactor to function, they also limit reactor performance due to their effects on corrosion, mechanical properties and dimensional stability.

Fission fragments have high energy and a very short range. They can be propelled from the fuel periphery into the inner surface of the cladding, causing hardening in a depth less than 10 μm , which can be related to microcracks forming there. The other ionizing forms (α , β and γ) cause insignificant irradiation damage compared to neutrons, but have a strong affect on the water radiolysis process, to be discussed in Section 4.2.1, and can increase the electrical conductivity of the normally high-resistance zirconium oxide, Section 4.2.2.3.

Table 4-1: Characteristics of types of radiation [Cox et al, 2006].

Type	Form	Source	Electrical charge	Relative range in metal
neutron	light particle	fission	0	long
alpha (α)	heavy particle	fission radioactive decay	+	very short
beta (β)	very light particle	fission radioactive decay compton effect pair production	-	short
gamma (γ)	wave	fission radioactive decay	0	long
fission fragment	very heavy particle	fission	+, -	very short

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4.2 Effects of irradiation

4.2.1 Radiolysis

Irradiation of water molecules with ionising radiation, primarily γ rays, interact along their pathway and produce ionized and excited water molecules. This leads to the formation of small spherical domains called “spurs” along the pathway of the ionising species where radicals and ionic species are distributed in locally high concentrations (Figure 4-1).

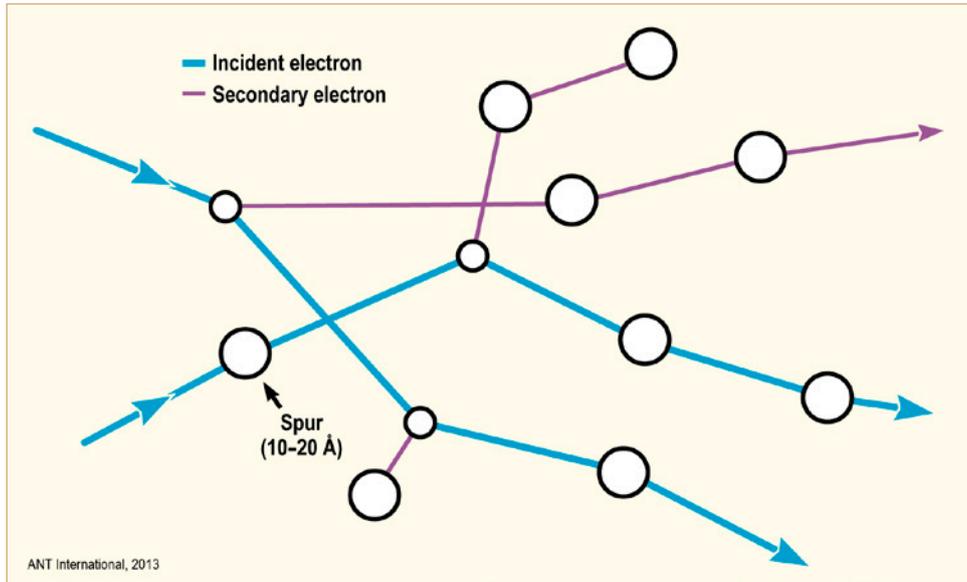
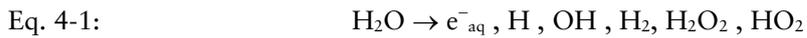


Figure 4-1: Spur formation by high energy electrons, after [IAEA, 1993].

For γ - rays or high energy electrons the primary decomposition products due to the interaction of radiation with the water molecules are:



These active species diffuse and partly react with each other to give some molecular and radical products as shown in Table 4-2.

Table 4-2: Rate Constants of Radiolysis Reactions in Water, after [IAEA, 1993].

Reaction	Rate constant at 25°C dm ³ mol ⁻¹ sec ⁻¹	Rate constant at 280°C dm ³ mol ⁻¹ sec ⁻¹
$e' + H_2O = H' + OH'$	1.6 E+1	1.65 E+2
$e' + H' = H'$	2.3 E+10	1.5 E+11
$e' + OH' = OH'$	3.0 E+10	4.05 E+11
$e' + H_2O_2 = OH' + OH'$	1.3 E+10	1.3 E+11
$2H' = H_2$	2k = 1.0 E+10	1.6 E+11
$e' + HO_2' = HO_2'$	2.0 E+10	2.06 E+11
$e' + O_2 = O_2'$	1.9 E+10	2.7 E+11
$2H_2O + 2e' = H_2 + 2OH'$	2k = 5.0 E+9	3.0 E+7
$2OH' = H_2O_2$	2k = 8.4 E+9	8.6 E+10
$OH' + H' = e' + H_2O$	2.0 E+7	6.63 E+8
$H_2O + e' + H' = H_2 + OH'$	2.5 E+10	6.22 E+9
$H_2O + e' + HO_2' = OH' + 2OH'$	3.5 E+9	8.7 E+8
$H' + OH' = H_2O$	2.0 E+10	6.0 E+11
$OH' + H' = H' + H_2O$	4.0 E+7	1.3 E+9
$H' + H_2O = OH' = H_2$	1.04 E-4	8.14 E+2
$H' + O_2 = HO_2$	1.9 E+10	1.96 E+11
$H' + HO_2' = H_2O_2$	2.0 E+10	2.06 E+11
$H' + O_2' = HO_2'$	2.0 E+10	2.06 E+11
$H_2O + e' + O_2' = HO_2' + OH'$	1.3 E+10	1.04 E+10
$H' + H_2O_2 = OH' + H_2O$	9.0 E+7	1.2 E+9
$OH' + H_2O_2 = HO_2' + H_2O$	3.0 E+7	3.7 E+8
$OH' + HO_2 = O_2 + H_2O$	1.2 E+10	2.5 E+10
$OH' + H_2O_2 = HO_2' + H_2O$	1.8 E+8	5.97 E+9
$HO_2' + H_2O = OH' + H_2O_2$	5.7 E+5	1.89 E+7
$H' + O_2' = HO_2$	5.0 E+10	5.16 E+11
$HO_2' + H' + O_2'$	8.0 E+5	3.4 E+7
$HO_2' + O_2' = O_2 + HO_2'$	1.5 E+7	4.4 E+8
$2H_2O + 2O_2' = H_2O_2 + 2OH' + O_2$	2k = 1.7 E+7	3.27 E+5
$2HO_2' = H_2O_2 + O_2$	2k = 2.7 E+6	5.2 E+7
$H' + OH' = H_2O$	1.4 E+11	1.49 E+12
$H_2O = H' + OH'$	2.6 E-5	1.33 E-1
$OH' + O_2' = O_2 + OH'$	1.2 E+10	7.7 E+10
$H_2O_2 = 2OH'$ (first order, sec ⁻¹)	2.3 E-12	1.2 E-1

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Only the molecular species have mean lives of more than fractions of a second, Figure 4-2. These ions, radicals and molecular species interact in a series of known reactions, most with low activation energies of ~3 kcal/mole, and in the absence of other added chemical species, form the molecular products H₂, O₂ and H₂O₂ [Burns & Moore, 1976], [Cohen, 1980] and [Lin, 1986]. Nevertheless, the overall stability of water increases with increasing temperature and the yields of molecular decomposition products, H₂, O₂ and H₂O₂, are correspondingly reduced.

5 Fuel performance issues related to water chemistry

There are essentially four types of fuel performance issues related to primary coolant chemistry.

5.1 Accelerated Zr alloy corrosion and/or HPU

1) Accelerated corrosion leading to fuel failures

a) Overheating of fuel cladding

- i) *CRUD related due to thermal insulation* - There have been several BWR and PWR fuel rod failures due to clad oxidation promoted by CRUD layers with poor thermal conductivity. The source of the thermal insulation has been either the CRUD thickness, density and composition or circumferential cracks in the CRUD layers. *All these failures occurred at low to intermediate burnup*, as follows:

- BWRs
 - CRUD Induced Localized Corrosion (CILC) in BWRs in 1979 and the early 80's, Section 9.3.3
- PWRs
 - TMI-1 (PWR), Cy 10, 1995, Section 9.1.3
 - Nine high peaking Fuel Rods (FRs), Zr-4 Cladding, failed after 122 days of operation
 - Seabrook (PWR), Cy 5, 1997, Section 9.1.2
 - Five one-cycle ZIRLO rods failed.

ii) *CRUD related*– failure mechanism not known:

- BWRs
 - Non-classical CILC failures occurred in Grand Gulf Cy 8 (GNF first cycle fuel), Section 9.3.5.1.1 and Cy 11 (AREVA first cycle fuel), Section 9.3.5.1.2. The failure mechanism leading to the fuel failures are not known. However, it was noted that River Bend was unique in having a combination of high copper, zinc, and iron during Cycle 11, just as in cycle 8.
- VVERs
 - Lovisa - and Paks, Sections 9.2.2 and 9.2.3, respectively
 - Several failed one cycle rods

- iii) *Excessive FR reactivity in PWRs* due to a post Axial Offset Anomaly, AOA event (AOA is treated in Section 8). The enrichment of boron in CRUD/oxide due to subcooled boiling and a significant CRUD/oxide layer thickness may cause a power reduction in the upper part of the fuel rod (AOA). At a power reduction, the boron will go back into solution which may result in excessive fuel rod reactivity (larger than anticipated by the nuclear designer) that may cause Departure from Nuclear Boiling (DNB). The DNB will increase the cladding temperature by several hundred degrees accelerating the fuel clad corrosion rate and potentially fuel failures. This failure mechanisms is suggested to be responsible for the failures that occurred in Palo Verde (a PWR), Section 9.1.4. The excessive fuel rod reactivity may also reduce the shutdown margin.
- b) *Deterioration of ZrO₂ barrier layer protectiveness*
- i) *PWRs*
- Dissolution of SPPs in Zry-4, Section 4.2.2.2
 - Increased corrosion and oxide flaking due to excessively small SPPs in Zry-4 were observed in PWRs in several reloads in late 1980's.

The second phases in Zr-Nb/ Zr-Nb-Sn/Zr-Nb-Sn-Fe alloys are more resistant towards neutron induced dissolution and up to now have not shown an increase in HPUP and corrosion rate at high burnups due to this mechanism.
 - Together with subcooled boiling, water soluble species (e.g. Li in PWRs) concentrate in the CRUD/oxide layer to such an extent that the protectiveness of the zirconium-oxide barrier layer at the Zr alloy metal/zirconium oxide interface is deteriorated. The concentration effect increases with
 - Increased degree of boiling
 - Increased concentration of the water soluble specie, e.g. lithium in PWRs
 - Increased CRUD layer thickness and decreased CRUD porosity

Failures in aggressive out-of-pile loop tests due to this mechanism have occurred. *However, no fuel failures have occurred in commercial reactors due to this failure mechanism as of now.*
- ii) *BWRs*
- Dissolution of Second Phase Particles (SPPs) in Zircalloys (Zr-Sn-Fe-Cr alloys) at high fast fluence levels (i.e., high burnups), (Section 4.2.2.2). The corrosion acceleration is preceded by an accelerated HPUF, forming a hydride rim at the oxide/metal interface and it is likely that it is this hydride rim that results in the subsequent corrosion acceleration. However, it appears that the HPUF increase rate due to SPP dissolution depends very much of the coolant chemistry, specifically it seems that increased Cu content in the coolant reduces HPUF (and no corrosion acceleration occurs) after the SPPs have been dissolved
- c) *Unknown effects.*
- i) *Enhanced spacer shadow corrosion (ESSC)* resulted in a few high burnup fuel rod failures in a Swiss BWR, Section 9.3.7.
- The mechanism is not clear but seems to be related to galvanic corrosion in an oxidising environment (thus, this does not occur in PWRs/VVERs).

- Water chemistry seems also play a role. Specifically coolant chemistry with low Fe/(Ni+Zn) ratio seems to be aggressive (provided that the cladding material shows poor corrosion performance).
- The failed Zry-2 cladding was characterized by the presence of very small SPPs. It is speculated that the reason for the failures was the complete dissolution of the SPPs and the resulting change to increased HPUF and subsequently a decrease in corrosion resistance (due to the formation of solid hydrides at the zirconium oxide/metal interface). Fuel claddings with larger SPPs were not affected by this failure mechanism. A fuel cladding material with good corrosion resistance does not result in ESSC even in aggressive water chemistry.
- Only fuel irradiated in the core for greater than four annual cycles were significantly affected in this specific case, and the failed rods had operated for 6 annual years in core.
- No CRUD was involved in the ESSC failure mechanism.

d) *Localized hydriding*

- BWRs - The failure mechanism does not seem to be perfectly clear but these failures were not related directly to accelerated corrosion and overheating, Section 9.3.6.1. Instead, the fuel is reported to have failed by localization of hydrides [Lutz et al, 2012]. Massively hydrided regions appear to have then fractured under tensile loading that arose with the accumulation of exposure during the course of normal operation. The underlying cause or causes of the corrosion and hydriding remains unknown and has been identified by [Lutz et al, 2012] as an unrecognized and previously unreported BWR failure mechanism. The failures occurred in the BWR Browns Ferry -2 and -3, as follows:
 - Browns Ferry 2 (BWR), Cy 12, 2001-2003
 - 63 FAs failed. Affected fuel was GE13B claddings that failed in their second cycle with Bu of 29-30 MWd/kgU.
 - Browns Ferry 3 (BWR), Cy 11, 2002-2004
 - 3 FAs failed. Affected fuel was GE13B claddings that failed in their third cycle with Bu of 43-47 MWd/kgU.

Failures by the same mechanism occurred in Vermont Yankee as well during the same time period.

In all three cases (BF2 and BF3 and VY), the alloy content of the high corrosion rod lots was at the “low end” of the Zr-2 specification and the fuel rods affected were the ones with highest power but the alloy effect and power cannot explain the failure mechanism. Most likely the effect of water chemistry is dominant.

- PWRs – accelerated HPU in guide tubes leading to failures, Section 9.1.1

6 Zr alloy corrosion and hydrogen pickup

6.1 Design criteria

To ensure appropriate fuel performance the fuel rod oxide thickness, hydrogen pickup and CRUD build-up should be limited according to the NRC document NUREG-0800, Section 4.3 [NUREG, 2007].

The original rationale for specifying a maximum oxide (and CRUD) thickness for fuel claddings is based on the fact that the resulting temperature increase will lower the cladding mechanical strength. If the oxide and CRUD layer thickness become too large, the resistance to heat flux will become significant and a further increase in the thickness will raise the cladding temperature further. This increase in temperature will increase the cladding corrosion rate, thus increasing the oxide thickness further resulting in an even higher cladding temperature. Such a thermal feedback situation could increase the cladding temperature and lower the material strength to such an extent that the cladding may fail due to a tensile stress.

However, in reality, mechanical failure of the fuel cladding does not occur because the stresses involved are too small. Instead, the thermal feedback effect in PWRs may cause corrosion acceleration resulting in fuel clad failure by through wall oxidation. In high power experiments (140 W/cm^2) in a PWR local perforations of the cladding wall occurred due to this phenomena at an oxide thickness of $>50 \text{ }\mu\text{m}$, [Garzarolli et al, 1979]. Figure 6-1 summarizes the experience with thick oxide layers in a diagram showing oxide thickness and heat flux for each data point. A locus curve of constant corrosion rate (approximately a hyperbola) was drawn tentatively. The area above the locus curve indicates conditions that would lead to corrosion failures due to corrosion acceleration related to thermal feedback effects. The areas beneath this curve indicate conditions not leading to any thermal feedback corrosion acceleration.

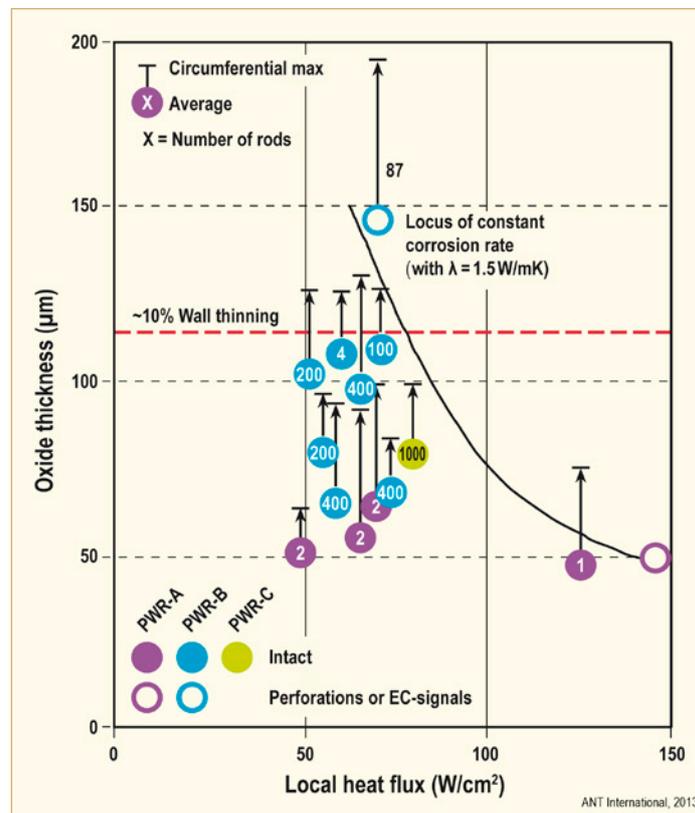


Figure 6-1: Maximum allowable uniform oxide layer thickness, after [Garzarolli & Stehle, 1987].

The maximum oxide thickness criterion used today by most regulators including the NRC for most PWR applications is 100 μm . The NRC has specified that this maximum oxide thickness is the average value along the cladding circumference in a transversal cross-section. Regulations on the uniformity of cladding oxide are also being imposed by the USNRC with the intent of constraining the formation of hydride blisters¹⁷.

The hydrogen content of zirconium alloys must be limited to prevent brittle mechanical failures due to the formation of hydrides during normal operation, handling during outage and seismic events. However, because the impact of the hydrides on ductility is strongly dependent upon morphology and cladding texture, the NRC has not given a specific maximum allowable hydrogen content for zirconium alloy cladding materials. Instead, constraints on oxide thickness and uniformity appear to be emerging as a means for limiting hydrogen concentration. Such constraints seem to be based on a relatively linear relationship between oxide thickness and hydrogen concentration in Zry-4 cladding that operates in PWRs and on the ability to assess oxide thickness and uniformity via poolside inspections. However, other regulators are applying specific limits, for example:

- France - 600 ppm H
- Netherlands - 500 ppm H
- Germany - 2000 ppm H

6.2 Introduction

The topic of Zr alloy corrosion and HPU has been covered in several ANT International published Reports. The interested reader is referred to the following Reports:

ZIRAT6¹⁸/IZNA1¹⁹ STR Water Chemistry and CRUD Influence on Cladding Corrosion,

ZIRAT7/IZNA2 STR Corrosion of Zirconium Alloys,

ZIRAT8/IZNA3 STR The Effects of Zn Injection (PWRs and BWRs) and Noble Metal Chemistry (BWRs) on Fuel Performance,

ZIRAT9/IZNA4 STR Corrosion of Zr-Nb Alloys in PWRs,

ZIRAT12/IZNA7 STR Corrosion Mechanisms in Zirconium Alloys,

Section 6 in ZIRAT16/IZNA11 Annual Report,

ZIRAT16/IZNA11 STR Performance Evaluation of New Advanced Zr Alloys for PWRs/VVERs,

Sections 2 and 3.1 in Fuel Material Technology Report Vol. II,

PZAC PWR Zr Alloy Cladding Water Side Corrosion,

LCC2 STR CRUD in PWR/VVER and BWR Primary Circuits,

LCC6 STR Effect of Zink in BWR and PWR/ VVER on Activity Build-up, IGSCC and Fuel Performance,

¹⁷ If there are large differences in the circumferential oxide thickness profile, e.g. due to local spallation of oxide, a large difference in fuel clad temperature at the outer surface may result. This situation will drive the soluble clad hydrogen to the colder spots in the cladding (where the oxide is thinnest) and when the solubility limit is exceeded form a hydride blister.

¹⁸ Zirconium Alloy Technology

¹⁹ Information on Zirconium Alloys

LCC7 STR Introduction to Boiling Water Reactor Chemistry Volume I,

LCC8 STR Introduction to Boiling Water Reactor Chemistry Volume II,

LCC7 STR PWR/VVER Primary Side Coolant Chemistry, Volume I – Technical Basis and Recent Discussions,

LCC7 STR PWR/VVER Primary Side Coolant Chemistry, Volume II – Technical Basis and Recent Discussions, (give link to sample report on our web-site),

Corrosion of zirconium alloys is a thermodynamic and electrochemically based process affected by the following parameters, see Figure 6-2:

- The microstructure of the Zr alloy-metal surface.
- The water chemistry and the hydraulic conditions.
- The Zr alloy temperature (at the metal/oxide interface).

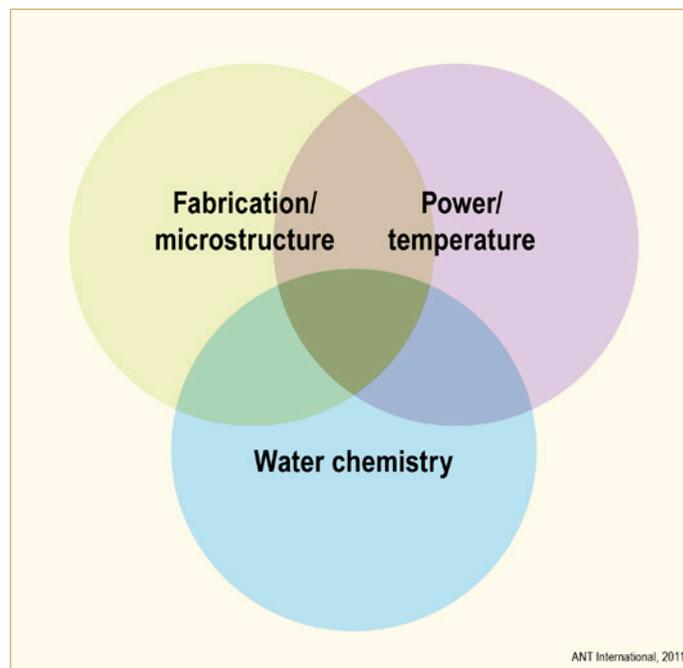


Figure 6-2: Parameters impacting corrosion performance of Zr Alloys.

During the initial oxidation/corrosion of zirconium alloys, a thin protective black oxide is formed. As the zirconium oxide grows in thickness the outer part of the oxide (facing the water/steam phase) is transformed into a greyish porous oxide. The oxide grows inwards into the zirconium alloy material.

7 CRUD characteristics

7.1 Introduction

The fuel CRUD²⁶ deposition phenomenon does include seven different steps, as follows [Berry & Diegle, 1979].

- 1) Generation (of corrosion products)
- 2) Release (of corrosion products, due to dissolution, erosion or scaling)
- 3) Transport (by the coolant)
- 4) Deposition on the fuel elements
- 5) Release from the fuel element
- 6) Transport by the coolant
- 7) Deposition on, or incorporation in, system surfaces or removal by the water treatment systems

In the following, we will discuss the steps 1. to 7 above in this listing for both PWRs, VVERs and BWRs.

7.2 CRUD Sources

7.2.1 Corrosion and corrosion release

If the solubility is low or the physical interaction force is large all or a large part of the formed corrosion products are left (or re-deposited) on the corroding metal. A special case occurs when the formed corrosion product is forming a dense and protecting layer impeding further corrosion attack. The formed corrosion film is then called a passivating film, since it hinders and in some cases almost inhibits further corrosion attack. The use of virtually every material in the LWRs is based on the principle of a passive corrosion film.

Most materials in the LWR, e.g. in BWRs carbon steels (in feed water piping, in CANDUs feeder pipes), low-alloy steels (in turbine system piping and the pressure vessel), stainless steels (in RHR and the recirculation system piping), nickel-base materials (Inconel, Alloy 600, etc. in in-core components and in the PWR steam generator tubes), Stellite (in valves), and zirconium alloys (in fuel cladding and BWR flow channels) rely on the principle of a passivating oxide film. This is also why the water chemistry of the PWR (that are operating under reducing conditions established by hydrogen addition) is adjusted with lithium due to use of boric acid as chemical shim, i.e. to have the best possible passive film and lowest possible corrosion release (of the nickel base material in the steam generators). In case of BWRs the passive oxide films are built by oxygen produced by water radiolysis. The passive films are sometimes of constant chemical composition, as for the corrosion film on zirconium alloys or a double layer, with the inner layer being a diffusion barrier (barrier layer), and the outer a protection against attack of the environment on the diffusion barrier, as for stainless steels [Robertson, 1991].

²⁶ ‘CRUD’ is the term used generally, and also in this report, to describe any solid matter that is or has been deposited on system surfaces or fuel cladding surfaces in water cooled nuclear power plants. CRUD is often interpreted as “Chalk River Unidentified Deposit”, but according to Dr. Bill Lindsay (at the EPRI Crud Related R&D meeting in Palo Alto, CA, USA, 17 - 18 Nov. 1993), the acronym CRUD appeared years after the CRUD was found and investigated in the Chalk River NRX reactor in the mid-fifties.

The passive film is in reality always a barrier against mass transport, i.e. hinders the release of oxidised ions (for all steels and nickel base alloys) or intrusion of oxidants (for zirconium alloys). The corrosion attack and corrosion release, r_{corr} , is therefore depending on the dense oxide film thickness under otherwise constant conditions. This dependence is often given by the inverse square or inverse cube of time, as shown in Eq. 7-1.

$$\text{Eq. 7-1:} \quad r_{corr} = k_{corr} \cdot t^{-n} \quad n = 0.33 - 0.5$$

A typical example is shown for Inconel in simulated BWR environment in Figure 7-1.

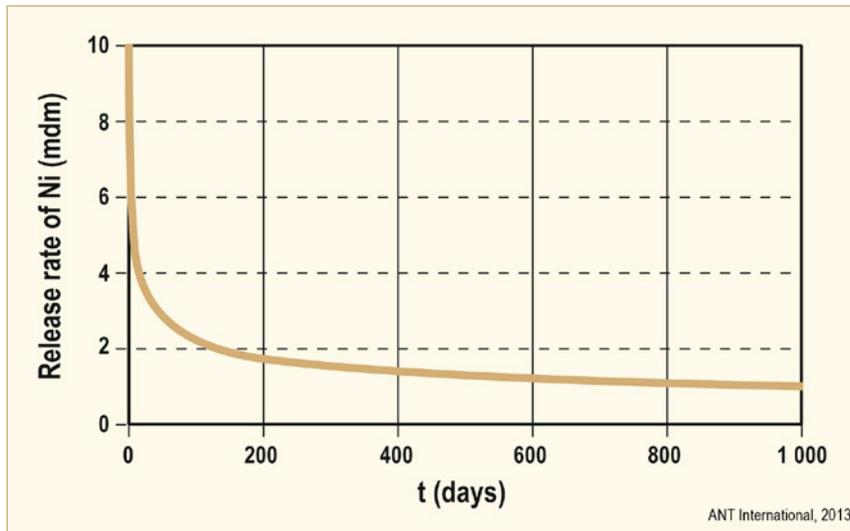


Figure 7-1: Corrosion release from Inconel X-750 in BWR environment, after [Hemmi et al, 1994].

The corrosion release from stainless steel, carbon steel, and nickel-base materials will follow a curve such as the one in Figure 7-1. This means that a much higher corrosion release is found for new surfaces, which have a very thin corrosion film (passive layers that have still pores and are not sufficiently dense). This explains why many LWR plants have had CRUD problems during the first cycle of operation and after extensive decontamination.

After a year or so in the plant, the protective oxide layers get denser and more protective. Accordingly, the corrosion and corrosion release curves, as shown in Figure 7-1, seem less and less time dependent, and the corrosion behaviour is then approximately constant. Very often, a constant value for the corrosion product formation is therefore reported in the form of “mg of corrosion product formed per month and per dm^2 ”, normally abbreviated as “mdm”.

The corrosion and corrosion release are normally similar for stainless steels and nickel base materials both in PWR and BWR environments, with values typically as given in Figure 7-1 for BWRs. For carbon steels, the corrosion rate and corrosion release is about 10 times higher [Vreeland et al, 1962] and [Brush & Pearl, 1972].

7.2.2 Materials Corroding in the LWRs

The relative surface areas of various materials for different reactor types have been reported [Berry & Diegle, 1979], see Table 7-1 and Table 7-2. This information is good to bear in mind when comparing the relative composition of the deposited CRUD and in understanding the importance of corrosion products in different reactors

The important conclusion from these listings is that even a rather small total corrosion release or a small change in the corrosion release rates could have significant consequences for the water chemistry and hence the fuel CRUD since the areas of the various materials are so large. It should also be noted that, since we have different materials, and varied physical and chemical conditions for several of the materials in the different parts of the BWR and the PWR, the impact from a physical or chemical variation will not be the same for all areas. It could even be so that a chemistry change giving reduced corrosion release in one location could enhance the corrosion release in another part or component of the plant.

Table 7-1: Estimated relative surface areas of reactor materials, after [Berry & Diegle, 1979].

Reactor Type	Material	Relative Area	Remark
US PWRs	Zry-4	20%	Fuel cladding
	Inconel 600	75%	Mainly steam generators
	Stainless steel	5%	
US BWR (GE)	Zry-2 and -4	48%	Fuel cladding and channels
	Stainless steel	44%	System piping and RPV buttering
	Carbon steel	8%	
AECL PHW (PWR)	Zircaloy ²⁷	13%	Fuel cladding
	Monel 400, Inconel 600, or Incoloy 800	77%	Mainly steam generators
	Carbon steel	10%	
AECL BLW (BWR)	Zirconium Alloys (Zry-2 and Zr2.5Nb)	18%	Fuel cladding and pressure tubes
	Carbon steel	84%	

ANT International, 2013

²⁷ Actually, both Zry-4 as fuel cladding and Zr-2.5Nb as pressure tubes are in contact with the coolant in the AECL PHW.

8 Axial offset anomalies/CRUD induced power shift (Suat Odar)

8.1 Definition and General Information

Axial Offset Anomalies (AOA), that also called CRUD Induced Power Shift (CIPS), is a phenomenon, which is caused by boron absorption in PWR fuel CRUD in the upper part of the core. The boron absorbed causes a reduction of neutron flux resulting in power reduction in the upper core region. In order to maintain overall power, the flux shifts downward in the core, resulting in uneven power distribution in the core. AOA is defined simply as difference in power between the top half of the core and the bottom half of the core divided by total core power and expressed in % as calculated by the following equation:

$$\frac{(P_t - P_b)}{(P_t + P_b)} \times 100$$

where,

P_t : Integrated power in the top half of the core,

P_b : Integrated power in the bottom half of the core

In the case of AOA incidents, Axial Offset (AO) gets negative % values due to decrease in power in the top half of the core (P_t) as can be seen in Figure 8-1 given as an example for AOA experienced in a Westinghouse designed PWR plant [Deshon, 2004].

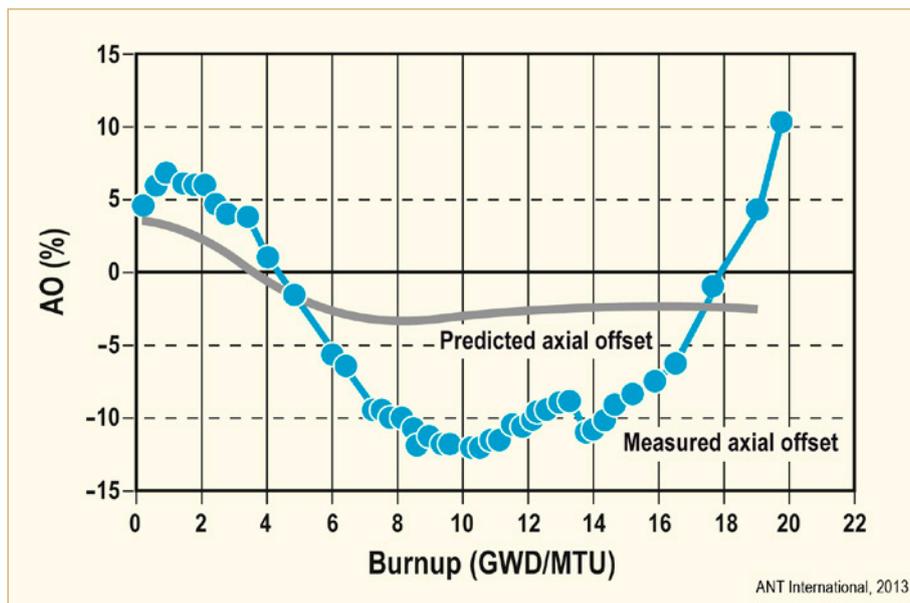


Figure 8-1: Example of AOA at a Westinghouse designed PWR plant, after [Deshon, 2004].

This phenomenon was originally known as AOA due to the observed power distortion in the measured axial offset in an operating reactor, generally at about 3% or above. So the term AOA reflects the outcome of the problem measured at a reactor, whilst CIPS refers to the ultimate cause of the power distortions by boron absorption induced by CRUD on fuel surfaces. CIPS can therefore be used to indicate any level of power distortion caused by CRUD deposition and is readily used to describe weaker or more local phenomena than AOA. However, both of the terms AOA and CIPS are widely used in the industry to refer to the same issue of CRUD induced power shifts.

Historically, it has been accepted that “core-wide AOA” occurs when the axial power distribution deviates more than 3% from the predictions got by the physics codes [EPRI, 2004a] (see Figure 8-1 as an example). However, in several PWR units of EdF-fleet, only local flux depressions have been observed on single assemblies by in-core flux trace measurements. These remarkable deformations are present on a few assemblies and lead only to moderate differences between the measured actual values of AO and their predictions. In that sense, these so-called “local AOAs” remain at the fuel assembly scale (see Figure 8-2) [Decossin et al, 2008].

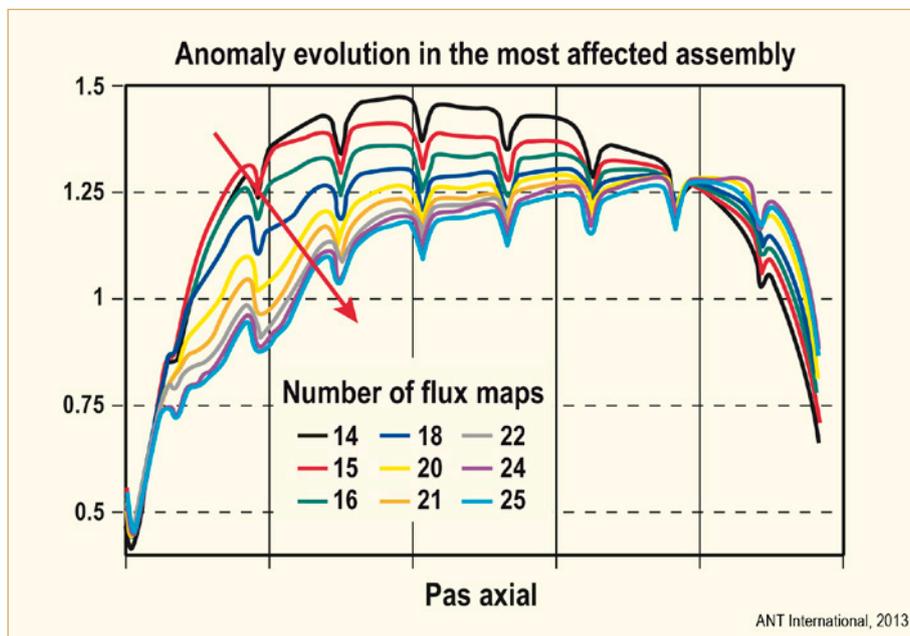


Figure 8-2: Assembly flux measurement: Progressive deformation of the flux profile (local AOA), after [Decossin et al, 2008].

8.2 Parameters Influencing AOA/CIPS Based on Field Observations

Based on field experience heavy and especially dense deposits on fuel rods that are nickel rich are the prerequisite for the occurrence of AOA. Worldwide the first reported AOA was experienced at the beginning of 1970s at Obrigheim [Riess, 1976]. This plant was actually a low duty core PWR with nickel base Alloy 600MA tubing in its original SGs; and heavy fuel deposits build-up was only due to poor coolant chemistry control without addition of lithium and hydrogen. The experienced maximum deposits was $\sim 8 \text{ mg}\cdot\text{cm}^{-2}$, which is extremely high for a PWR. It is worth to notice the highest deposit thickness and high NiO content at the top portion of the fuel rods (see Figure 9-11), which is also observed in recent AOA incidences at high duty core PWR plants with nickel base alloy SG tubes.

AOA has been experienced up to date only at PWR units with SG tubes made of nickel base alloys; mainly with Alloy 600. These units have experienced nickel rich deposits on their fuel assemblies. Also in several EdF PWR plants with Alloy 690 SG tubes (replacement SGs) in a small extent local AOA/CIPS in several fuel assemblies were experienced [IAEA, 2011] and [Bretelle, 2013]. In contrast, the PWR units with the Alloy 800NG SG tubing have insignificant amount of deposits due to remarkably less nickel release behaviour of Alloy 800 on their fuel assemblies (see Table 8-1). Accordingly these units have never experienced AOA. High temperature, heat flux and boiling are the main driving mechanism for the CRUD deposition; therefore, AOA is experienced mainly in the high duty PWR units that have nickel base Alloy SG tubes. In particular, the heaviest CRUD deposits are on the feed fuel assemblies that are operating typically at the highest relative powers. As of presence, while transitioning to longer operating cycles, AOA became a significant industry issue for PWR plants with nickel base alloy SG tubes as they increased fuel thermal duty, operated at higher peaking factors and underwent power uprates.

Table 8-1: Nickel release rates from SG tube materials exposed to simulated PWR reactor coolant, after [Riddle, 2001].

Solution, 300°C	Exposure Time [h]	pHr	Nickel Release [mg/dm ² -mo]		
			Alloy 600 (15% Cr)	Alloy 800 (21% Cr)	Alloy 690TT (30% Cr)
4000 ppm B	100	4.91	11	1.4	3.6
1000 ppm B; 2 ppm Li	500	6.96	0.24	0.14	0.20

ANT International, 2011

Most of the plant observations are based on the studies performed by [Byers & Deshon, 2004]. These studies have revealed that CRUD thickness and extent of core duty are also correlating with AOA behaviour as shown in Figure 8-3 a) and b) respectively. In this figure the cores of the first three PWR plants (Diablo Canyon Cycle 11, Summer cycle 12 and Vogtle-2 cycle 8) didn't exhibit AOA. The cores of other AOA PWR plants are arranged in order of increasing AOA severity, Callaway cycle 9 with the severest AOA. These data indicate an increase in AOA severity with increasing CRUD deposit thickness and core duty. Increased core duty with increased SNB causes severe thermodynamic conditions, which enhance the CRUD deposition on fuel rods and accordingly AOA. Especially, the presence of Bonaccordite (Ni_2FeBO_5) in Callaway cycle 9 fuel flake and unique m- ZrO_2 in the flake of Callaway cycle 9 and Seabrook cycle 5 leads to the speculations that very severe environmental conditions must have been present for the formation of these CRUD structures.

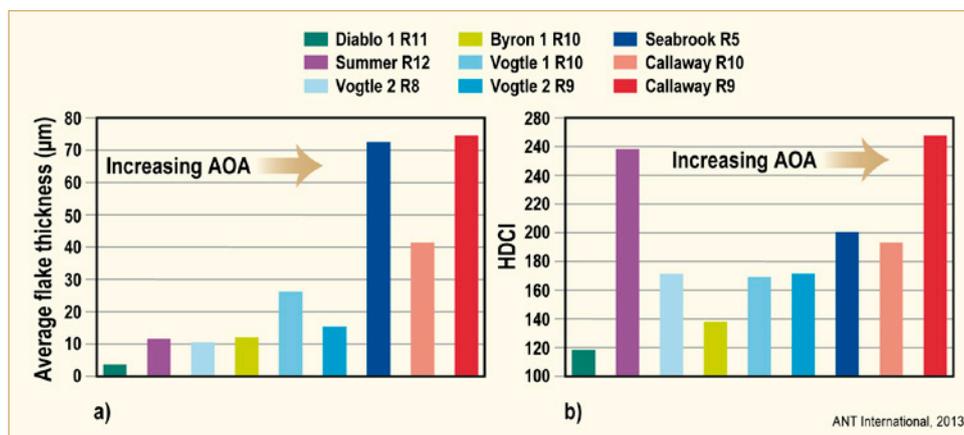


Figure 8-3: Correlation of AOA behaviour with fuel CRUD deposit thickness (a) and with core duty as HCDCI (b) based on data gained from 9 US PWR plants, after [Byers & Deshon, 2004].

9 Reactor cases of Effects of water chemistry on fuel performance

9.1 PWRs

9.1.1 Accelerated HPU in Zry-4 in PWRs – effects of water chemistry and materials (embedded SPPs)

[Pettersson et al, 2007] reported on a case when Stainless Steel, SS, particles embedded in the surface of Zry-4 guide tubes – probably bridging the barrier layer were able to pickup catalytic hydrogen⁴⁶ from the coolant during start up and only if these particles were not oxidized. Two guide tubes fractured during insertion of the control rods in the pool during the outage in Ringhals 2 due to large hydrogen contents in the Zry-4 guide tubes (Figure 9-1 and Figure 9-2). In some extreme cases, rims of massive hydrides were seen at the inner surface. The oxide thickness at the ID was about 20 μm while hydrogen content was up to 3000 ppm (average in wall thickness). This indicates that the HPUF was well above 100 % and consequently that there was another hydrogen source in addition to corrosion.

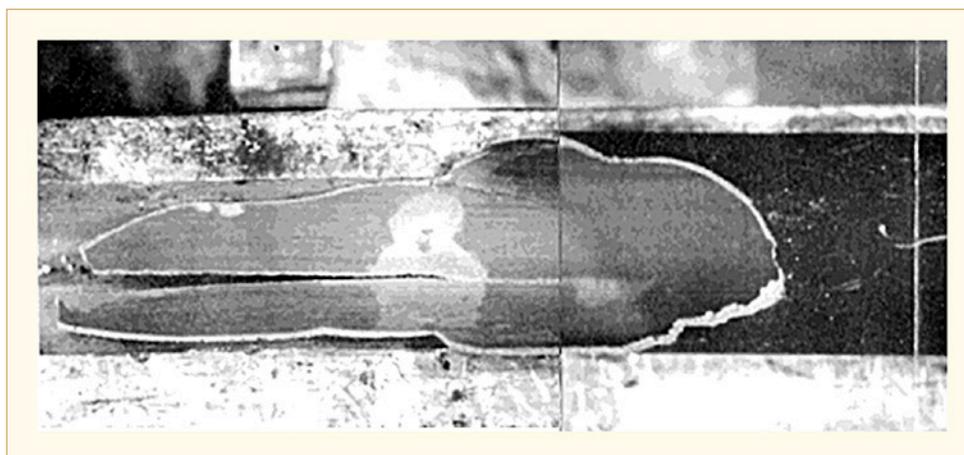


Figure 9-1: Broken piece of guide tube Q12-P10, gridspan 3-4, picture from hot cell [Pettersson et al, 2007].

⁴⁶ Pickup of hydrogen from the hydrogen molecules added to the coolant

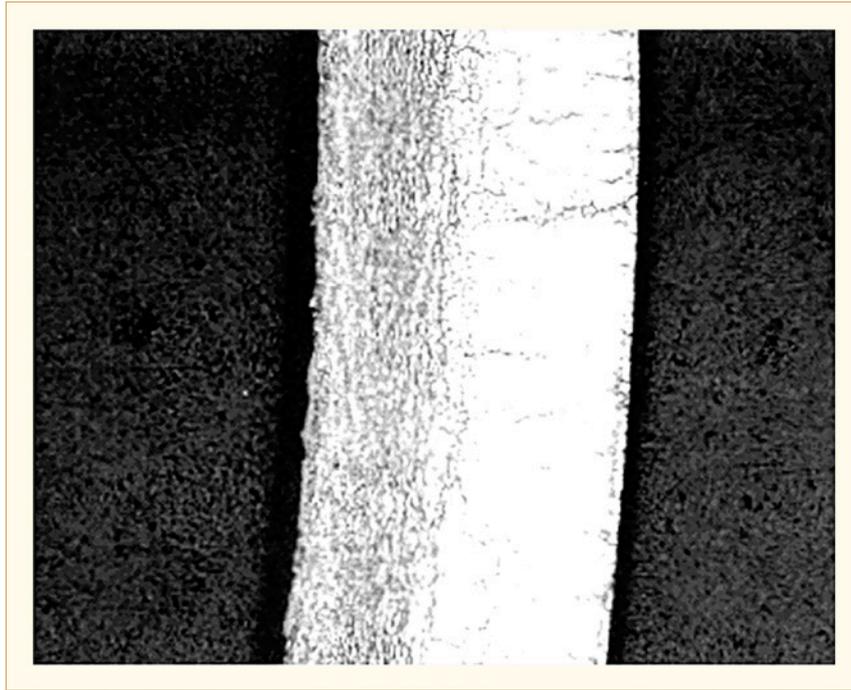


Figure 9-2: Hydride distribution in grid span 3-4 in the broken guide tube. The oxide thickness was 2-5 μm on the outside and up to 20 μm on the inside. Average hydrogen content is about 2900 ppm and the thickness of hydride rim is 150 μm (Magnification: 70x), [Pettersson et al, 2007].

The root-cause analysis revealed that the grit-blasting with the stainless steel lance being used for these guide tubes embedded small stainless steel particles at the guide tube inner surface which in-pile acted as “hydrogen windows”. Through these Ni containing particles, hydrogen was picked up catalytically after it was added to the coolant at about a coolant temperature of 150°C during the start-up procedure. Metallic nickel has the ability catalytically to breakdown the molecular hydrogen to hydrogen atoms, which then are absorbed in zircaloy matrix.

Autoclave tests were carried out successfully to simulate the increased hydrogen pickup during the PWR start up procedure. The tests revealed a significant effect on hydriding by the peak Ni coolant concentration during start-up, the hydrogen overpressure, the point in time when hydrogen was added, and the pH of the primary coolant. It was found that a prerequisite for this large HPUF was that (Figure 9-3 and Figure 9-4):

- Ni coolant concentration was large enough during the start-up phase (Figure 9-5) and,
- Hydrogen was added to the water before the formation of a protective oxide layer could prevent the hydrogen uptake.

It was also found that a “late hydrogen addition” reduced the enhanced hydriding significantly. This is because, if late hydrogen addition is applied, the soluble coolant nickel content is removed at that time by coolant purification, which would otherwise precipitate as metallic nickel on blank zircaloy surfaces without oxide layers by hydrogen addition (establishing reducing conditions).

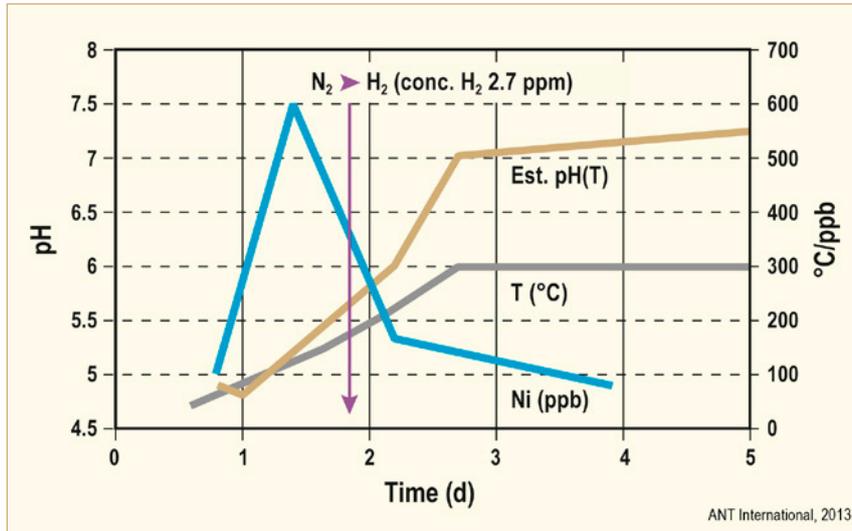


Figure 9-3: Example of start-up after which severe hydriding of guide tubes was seen, after [Pettersson et al, 2007].

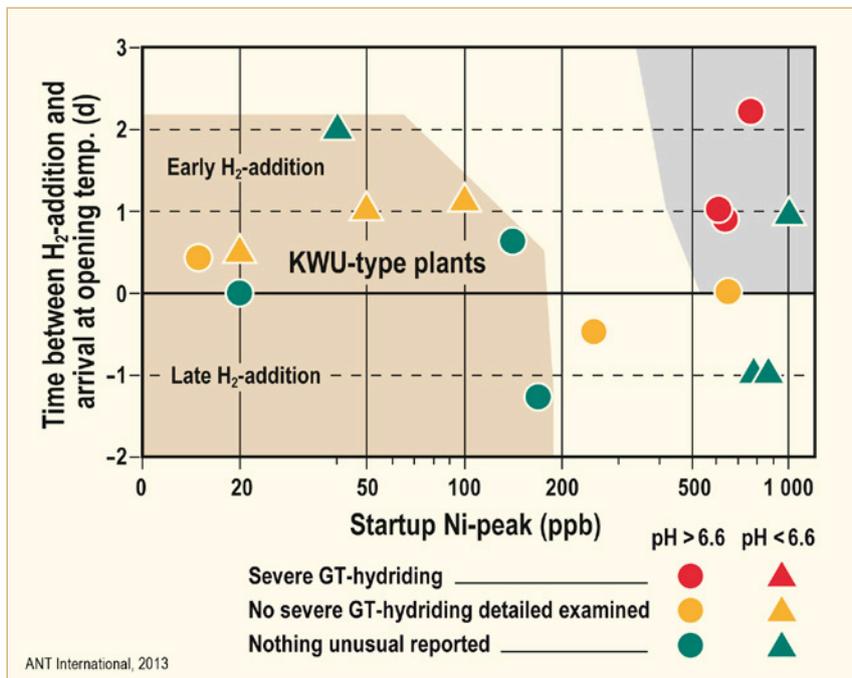


Figure 9-4: In-PWR performance experiences with guide tubes grit-blasted on ID with a stainless steel lance, after [Pettersson et al, 2007].

10 Summary

The nuclear utilities must reduce operating, maintenance and fuel cycle costs to remain competitive while maintaining or improving reactor safety. To achieve these goals there are a number of changes which may increase the Zr alloy corrosion duty. Since Zr alloy hydrogen pickup is a function of the HPUF and corrosion rate, increased corrosion duty also results in larger hydrogen concentration in the Zr alloy materials which in turn may embrittle the material. The following changes have been and are being introduced which may increase corrosion duty:

- Higher discharge burnups
- Modified water chemistry:
 - e.g. elevated LiOH in PWRs,
 - increased or decreased hydrogen coolant contents in PWRs,
 - hydrogen water chemistry coupled with noble metal additions in BWRs,,
 - Zn-injection in BWRs and PWRs
- Plant power uprates
- More aggressive fuel management methods

Corrosion of zirconium alloys is affected by the following parameters:

- The microstructure of the Zr alloy-metal surface.
- The water chemistry and the hydraulic conditions.
- The Zr alloy temperature (at the metal/oxide interface).

During the initial oxidation/corrosion of zirconium alloys, a thin protective black oxide is formed. As the zirconium oxide grows in thickness the outer part of the oxide (phasing the water/steam phase) is transformed into a greyish porous oxide. The oxide grows inwards into the zirconium alloy material.

During the oxidation/corrosion process, a certain fraction of the hydrogen in the water molecule, from the Zirconium alloy corrosion process, is picked up by the Zirconium alloy. This HPUF, depends on zirconium alloying content but also on temperature, water chemistry, and reactor start-up procedure. The total amount of hydrogen that is picked up by the Zirconium alloy is the product of the corrosion rate and the HPUF.

Due to the different FR surface temperatures and water chemistry in the different types of power reactors, such as PWR, VVER, BWR, RBMK, CANDU, corrosion of the Zr-alloy claddings and structural components proceeds quite differently in the different reactor systems.

There are different types of corrosion mechanisms: uniform, nodular and shadow corrosion

- **Uniform corrosion** (PWRs/VVERs/CANDUs/BWRs) that starts at the beginning of irradiation at a rapid rate slows quickly.

With increasing oxidation and hydrogen absorption (pickup) at higher burnup, the concentration of hydrogen in Zr alloys in PWRs can exceed its solubility limit and precipitate as hydrides which may accelerate corrosion rate.

In VVERs, there is normally no acceleration of the uniform corrosion process due to the very low hydrogen pickup. The reason for the low hydrogen pickup is due both to the (normal) use of the Zr1Nb alloy E110 and different coolant chemistry.

In BWRs, the SPPs (nickel-bearing and chromium-bearing SPPs) in Zry-2 start to dissolve already at the start of irradiation due to the fast neutron flux. At a certain fast fluence level (corresponding to a certain burnup) the SPP has completely dissolved in the matrix. When the SPPs have totally dissolved there is a dramatic increase in HPUF from 5-10% to over 100% (which means that part of the hydrogen must also come from the radiolytic hydrogen being produced) which eventually will lead to formation of a hydride rim at the metal/oxide interface and subsequent corrosion acceleration.

- **Nodular corrosion** (only occurs in oxidising environment such as in BWRs) starting after 10 to 100 days of irradiation in material with large Zircaloy Second Phase Particles (SPPs). Nodular corrosion is characterized by locally a much thicker oxide patches appearing as white spots. The corrosion rate is initially very large but levels off at high burnups. Due to the low oxidation potential in a PWR/VVER only uniform corrosion normally exists. However, if for some reason there would be an increase in the coolant oxidation potential, nodular corrosion may also occur in PWRs/VVERs.
- **Shadow corrosion** (almost only in BWRs since it requires an oxidising environment) starting after a few days of irradiation, which may accelerate at higher burnups. Although agreement does not exist regarding the underlying mechanism, shadow corrosion is frequently postulated to be a galvanic type of corrosion. Shadow corrosion has “always” been present in BWRs, but not in PWRs, primarily related to the high PWR hydrogen concentration which reduces or eliminates galvanic potentials between dissimilar alloy components. Shadow corrosion occurs in areas where a Zr alloy is in contact with or in close proximity to a dissimilar material such as nickel-based alloys (Inconel) or stainless steel, e.g. spacers in case of fuel rods and control rods in case of BWR fuel outer channels.

There is one case when a late in life oxidation acceleration occurred; viz., Enhanced Spacer Shadow Corrosion, (ESSC)⁵⁵ in KernKraftwerk Leibstadt (KKL) (Figure 6-9); see ZIRAT5/IZNA1 Annual Reports (AR) [Adamson et al, 2000/2001] for more details. The mechanism for this acceleration on oxide growth is not clear, but it may have to do with that the SPPs were dissolved at this burnup level. Effect av Fe/Zn+Ni ratio och material

Corrosion of zirconium alloys at elevated temperatures is basically an electrochemical process involving a galvanic cell. The growth of the oxide film by oxygen vacancy diffusion – through the barrier layer - is the anodic process and reduction of hydrogen ions from the water by electrons diffusing through the oxide film is the cathodic process. The corrosion rate may be limited by either the oxygen vacancy diffusion rate or the electronic conduction (or a combination of both) through the barrier layer. The limiting corrosion process is believed by most researchers to be the oxygen vacancy diffusion. The thicker the barrier layer the lower the corrosion rate. The barrier layer thickness varies in time by repeated transition building-up and breaking down the barrier layer thickness (cyclic oxide layer thickness).

⁵⁵ This corrosion phenomenon resulted in a few failed rods. This accelerated type of corrosion occurred on the fuel cladding material at spacer locations (the spacer springs in BWR fuel assemblies are made of a Ni-alloy such as X750). Water chemistry seems also to play a role. Specifically coolant chemistry with low Fe/(Ni-Zn) ratio seems to be aggressive provided that the cladding material shows poor corrosion performance. A fuel cladding material with good corrosion resistance (i.e. larger SPPs) does not result in ESSC, enhanced spacer shadow corrosion, even in aggressive water chemistry.

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