

# Key Emerging Issues and Recent Progress Related to Plant Chemistry/Corrosion (BWR Nuclear Power Plants)

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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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## Nomenclature

## Unit conversion

# 1 Introduction

Over the past several decades BWRs have introduced improved water chemistry changes because power plant chemistry plays a critical role in materials integrity, fuel integrity and better radiation field management. Among the key water chemistry advancements include depleted zinc oxide (DZO) addition, hydrogen water chemistry (HWC), noble metal chemical addition (NMCA), on-line noble metal chemical addition (OLNC), non-hydrogen technologies for SCC mitigation, iron reduction, cobalt reduction, and improved filtration technologies.

Safety and reliability of power plants are becoming increasingly important factors since many plants are aging and have obtained license renewal for continued power operation. Therefore, sharing plant operating experiences, sharing lessons learned, and sharing new industry research are all crucial in order to maintain the nuclear power plant fleet in a healthy condition.

The NPC conference provides a forum for utility personnel, engineers, scientists, university researchers, research institutes, and service organizations to interact and address the challenges faced by the nuclear power industry. This report summarizes the BWR related papers from the NPC 2018 conference which is designed to provide updated information with the author's critique and analysis for the benefit of the ANT/LCC customers. The report is expected to be a comprehensive summary document incorporating the latest information on BWR water chemistry related topics that would benefit the BWR operators and regulators, and those who have not been able to attend the NPC 2018 Conference in San Francisco, California, USA.

The following oral and poster sessions are covered in this report:

- Advances in BWR water chemistry and operating Experiences
- BWR SCC mitigation and guidance
- BWR dose reduction
- Noble metal technologies and future trends
- BWR water chemistry and fuel performance
- Auxiliary systems
- BWR scientific studies

The 2018 Nuclear Power Plant Chemistry Conference (NPC 2018) was held in the Hyatt Regency Hotel in San Francisco, California, USA from September 10<sup>th</sup> thro' 13<sup>th</sup>, 2018. The conference was attended by 247 participants from 22 countries. There were 51 oral presentations and 65 poster papers.

## 2 Advances in BWR Water Chemistry and Operational Experiences

This section provides a summary of the advancements made in the area of BWR water chemistry that includes relevant and available plant experiences. A main focus area at this conference was the emphasis on the future of nuclear power plant chemistry control and monitoring of key chemistry parameters with adequate and improved automation. An area of key interest is not just automated monitoring but also automated control as new monitoring technologies evolve.

One of the keynote speakers highlighted how new chemistry technologies are being evaluated, qualified, and demonstrated throughout the nuclear power industry that have the potential to significantly improve chemistry control and fundamentally alter the way water chemistry is controlled in these plants. Many of these technologies not only improve plant operation, but also improve their economic viability. In the case of BWRs, materials mitigation technologies such as online noble metal chemical (OLNC) application continues to expand throughout the industry, with utilities seeking more options including continuous noble metal injection, which would help reduce the overall cost of the application and maintenance. Demonstration of these technologies over the next few years will further help the ability of other plants to complete their own cost-benefit analysis and start utilizing the new and emerging technologies. The future of nuclear power, and specifically chemistry control in the plant, is likely achievable by balancing increased automation, implementing risk-informed plant specific programs, and the ever-expanding tool box of technologies to manage and mitigate chemistry related issues. [Wells et al., 2018].

### 2.1 Online Monitoring, Analysis and Trending

Chemistry monitoring programs at many nuclear power plants still rely on a significant amount of manual interventions. Chemistry monitoring and analysis technologies have been developed over the years, however, implementation of these new technologies to nuclear power plant applications have been slow due to the uniqueness in the nuclear industry such as the presence of radioactivity and dose rate fields. In addition while automated monitoring technologies have been applied in other industries, nuclear power plants have been slow to embrace these technologies because of their inherent conservatism [Wells et al., 2018].

In a plant environment it is customary to use manual or grab samples to monitor deleterious cations and anions, it is likely that sampling only occurs once per day. If an out of specification sample is collected, the chemistry department will likely collect and analyse a second sample to confirm the first sample, and this will likely take a few hours to complete. Considering this cycle of collection and analysis, it can take days to identify the source of the leak. If the leak is large enough, the plant could reach a point where the impurity concentration, for example chloride, reaches an unacceptable action level the plant may be required to reduce power in order to protect the plant. On the other hand, if the plant is using automated technologies to determine the concentration of chlorides, it is possible for that plant to have a new chloride concentration every 45 minutes [McElrath et al., 2018] providing identification, confirmation, and initiation of actions to mitigate the issue in a more timely manner. This type of improved response time provides a reduced risk of the plant chemistry going out of specification and the potential for lost plant power output. The major question that remains for these automated analysis technologies is the maintenance requirements. While some utilities have embraced automated analysis and some have attempted application of previous generations of these technologies, utilities generally report improvements related to asset protection but no resource savings because the instruments are maintenance intensive. It remains to be demonstrated if the newest technologies are up to the challenge of reliability without continuous maintenance or operational modification. To that end the demonstration of these technologies in actual plant conditions is of the upmost importance [McElrath et al., 2018].

If maintenance costs are found to be manageable, these technologies may ultimately help reduce the operating cost of nuclear power plants. The removal of manual sampling and analysis requirements will remove resource requirements and allow for optimization of staff resources. The use of these technologies can also help facilitate the ultimate automation of some plant operations. The designers of small modular reactors and other advanced plants are looking toward automation to help reduce the

overall cost of nuclear power plant operation, and some have included it in their design basis. Beyond alerting plant staff to a potential issue, one could envision plants of the future being able to diagnose the issue and make the necessary plant change to mitigate the problem [Wells et al., 2018].

## 2.2 BWR Water Chemistry Monitoring and Assessment Update

Electric Power Research Institute (EPRI) established the BWR Chemistry Monitoring and Assessment (CMA) database in 1997 to monitor impactful parameters. This large database, consisting of millions of discrete data points, is applied to assess trends and develop correlations to assist the industry in monitoring and optimizing the effectiveness of different chemistry control regimes, such as normal water chemistry, hydrogen water chemistry with and without noble metals, depleted zinc oxide addition, and control of impurity ingress. The data are also applied to develop chemistry control guidance to balance fuel concerns with conditions that minimize shutdown radiation fields, particularly regarding the use of depleted zinc addition. Zinc addition has been widely implemented in the BWR fleet with demonstrated effectiveness in controlling shutdown radiation fields. However, feedwater zinc concentration thresholds have been established, based on the BWR CMA database and fuel surveillances, above which there is an increased risk of fuel crud spallation that could impact fuel cladding corrosion. The application of advanced condensate filtration technologies and optimized use of ion exchange resins have resulted in significant reductions in feedwater corrosion products and ionic impurities. In recent years, many plants have consistently operated with less than 0.1 ppb feedwater iron (ultra-low iron). The EPRI BWR CMA database was used as a key resource to justify elimination of a lower limit for feedwater iron and continues to be applied in monitoring chemistry responses to ultra-low iron [Garcia et al., 2018a].

In 2017, the data base included 52 operating BWR units as shown below:

- Thirty-four U.S. BWRs
- Two Mexican BWRs (Laguna Verde 1 and 2)
- Twelve European BWRs (Cofrentes; Forsmark 1, 2 and 3; Leibstadt, Mühleberg, Olkiluoto 1 and 2; Oskarshamn 1, 2 and 3, and Ringhals 1)
- Four Asian BWRs (Chinshan 1 and 2; Kuosheng 1 and 2)

Figure 2-1 shows the worldwide regional locations of the participating BWRs.



Figure 2-1: BWR participants in EPRI Chemistry Monitoring and Assessment Database [Garcia et al., 2018a].

The main objective of the BWR CMA database was to create and maintain a central BWR chemistry database that contains information on actual plant performance, experiences, and the result of various chemistry control methods. This industry-wide BWR chemistry monitoring program establishes benchmarking standards for chemistry operation of BWRs and allows assessment of various water chemistry programs, supporting the technical guidance provided in the EPRI BWR Water Chemistry Guidelines. The database also provides plant chemistry data supporting EPRI BWR programs and initiatives [Garcia et al., 2018a].

Some of the key items in the database include the following:

- Evaluations to support revisions to the BWR Water Chemistry Guidelines
- Data summaries and reports on industry status, practices and issues based on the BWR Monitoring activities
- Annual Update Reports
- BWR Chemistry Technical Strategy Group
- Industry radiation field reduction efforts
- BWR Vessel and Internals Program (BWRVIP) Mitigation initiatives (input, computation, analysis and correlations) to support BWRVIP guidance on the implementation of technologies for intergranular stress corrosion cracking (IGSCC) mitigation, such as hydrogen water chemistry
- (HWC) and noble metal technologies, for asset preservation and inspection relief.
- BWR Shutdown and Startup Experience and Sourcebook
- BWR Shutdown Radiation Field and Chemistry Summary
- BWR Startup Electrochemical Corrosion Potential (ECP) Reduction
- BWR Vessel and Internals Application (BWRVIA) Radiolysis and ECP Model
- benchmarking
- Fuel Reliability Program Initiatives
- Platinum deposition modeling with On-Line NMCA (OLNC)
- BWR flexible operations evaluations of impacts on chemistry, fuel performance and radiation fields.

## 2.2.1 BWR Water Chemistry Advances and SCC Mitigation

Advances in BWR water chemistry have resulted in effective methods for mitigating materials degradation, reducing fuel performance concerns and reducing radiation fields [Garcia et al., 2018a].

Three methodologies have been used to mitigate IGSCC in BWRs. They are,

- 1) Hydrogen Water Chemistry (HWC) first used in a US BWR in 1983 to lower the Electrochemical Corrosion Potential (ECP) of reactor internal materials below -230 mV(SHE).
- 2) Noble Metal (Pt+Rh) Chemical Application (NMCA) first implemented in a US BWR in 1996 to lower the ECP of reactor internal materials below -230 mV(SHE) with low levels of feedwater hydrogen ( $\leq 0.4$  ppm H<sub>2</sub>). This technology is applied when the plant is in hot standby mode and resulted in lower main steam line operating dose rates compared to operating with moderate HWC.



### **3 Status of Noble Metal Technologies and Future Trends**

#### **3.1 BWR SCC Mitigation Guidance with Noble Metal Chemistry**

This paper discussed the technical bases and resulting advancements in BWR chemistry control and monitoring guidance for IGSCC mitigation. Specific guidance was developed to assist BWRs in assuring accurate hydrogen injection rate monitoring and achieving a minimum value of reactor coolant excess dissolved hydrogen, which is recognized as a key chemistry control parameter for plants applying noble metal addition + hydrogen water chemistry. The interpretation and use of ECP measurements in the mitigation monitoring system (MMS) are clarified in comparison to ECP monitoring sensors mounted within the reactor coolant system (local power range monitor, LPRM; bottom head drain line, BHDL; or flanges on the reactor recirculation system, RRS or reactor water cleanup piping, RWCU) [Garcia et al., 2018g].

##### **3.1.1 BWR IGSCC Mitigation Status with HWC, NMCA and OLNC**

The progression of US BWR chemistry regimes using hydrogen injection or hydrogen plus noble metal addition to mitigate intergranular stress corrosion cracking (IGSCC) is shown in Figure 3-1. Implementation of Hydrogen Water Chemistry (HWC) required feedwater hydrogen concentrations of 1 – 2 ppm to mitigate IGSCC of reactor internals by achieving an ECP of  $<-230$  mV(SHE), with the undesirable side effect of increasing main steam line dose rates by a factor of 3 – 5 higher than with normal water chemistry. HWC plus noble metal applications requires 0.2 – 0.3 ppm feedwater hydrogen to provide the same level of mitigation as HWC with reactor coolant hydrogen: oxidant molar ratio  $>2$ , while main steam line dose rates are remain unchanged from those measured under normal water chemistry conditions. All but three US BWRs currently operate with HWC plus On-line Noble Metal Chemical Addition (OLNC). Several European BWRs also operate with HWC plus OLNC, including Mühleberg (KKM), the first BWR to adopt the OLNC chemistry regime in 2005, Leibstadt (KKL) and Cofrentes. This paper focuses on the HWC + OLNC process and Plant experience [Garcia et al., 2018g].

A key issue with OLNC involved the interpretation and use of electrochemical corrosion potential (ECP) measurements in the external Mitigation Monitoring System (MMS) due to noble metal deposits in the MMS supply line that catalyze the reaction of hydrogen and oxygen, leading to oxygen depletion at the MMS ECP manifold when the hydrogen to oxygen molar ratio is  $\geq 2$ . The measured molar ratio is therefore not representative of the hydrogen: oxidant molar ratio in the bulk reactor coolant.

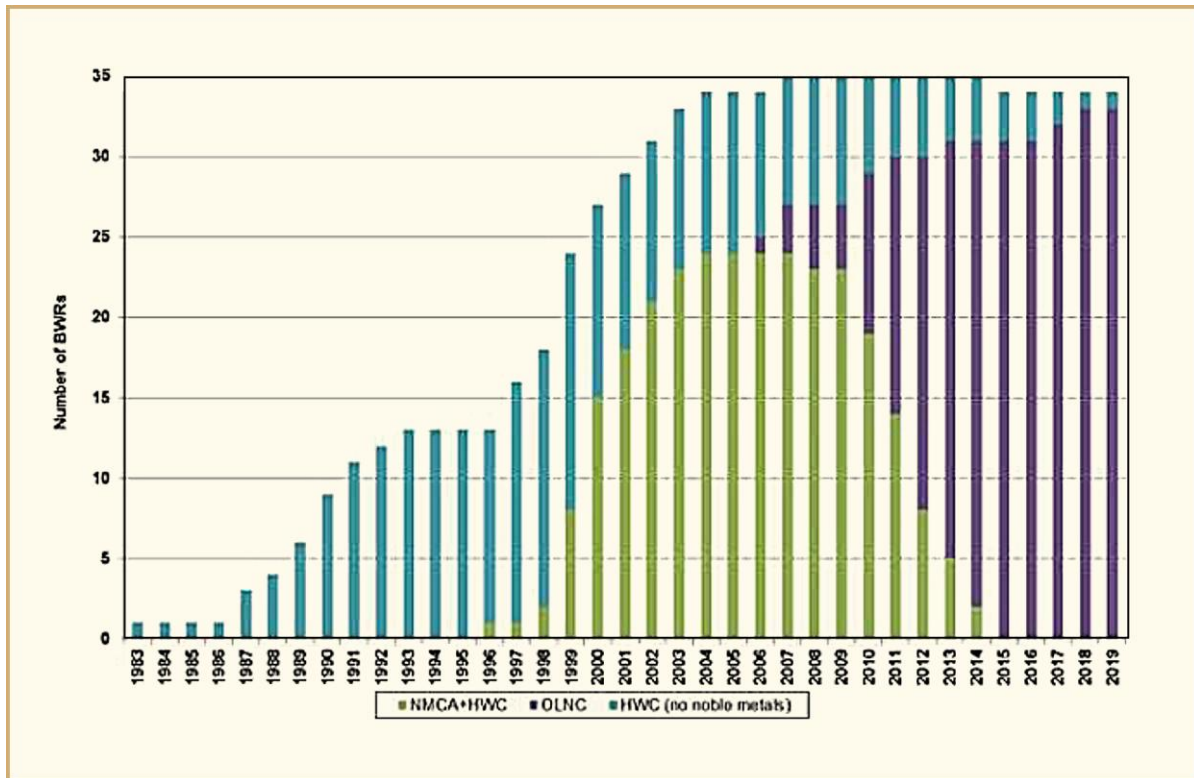


Figure 3-1: US BWR Fleet Water Chemistry Operational Regimes [Garcia et al., 2018g].

### 3.1.2 Reactor Water Excess Dissolved Hydrogen (Excess DH)

Measured concentrations of  $H_2$  and  $O_2$  will be lower in the reactor water sample than in the reactor coolant because of recombination in sample lines. Excess hydrogen is the amount of hydrogen in excess of that required to stoichiometrically recombine with the oxidant according to the equation:

Equation 3-1: 
$$\text{Excess DH, ppb} = [H_2 \text{ ppb}] - 0.126 \times [TOX, \text{ppb as } O_2]$$

where TOX is the total oxidant and  $O_2$

Excess DH of at least 12 ppb is recommended for stable and reversible platinum reference electrode response [Garcia et al., 2018g]. Excess DH > 20 ppb and a predicted hydrogen:oxidants molar ratio in the upper downcomer  $\geq 4$ , at beginning, middle and end of cycle (BOC, MOC and EOC) conditions provides the interim guidance for SCC mitigation. At 20 – 40 ppb Excess DH, main steam line radiation monitor (MSLRM) dose rate increases should be minimal [Garcia et al., 2018g].

### 3.1.3 Hydrogen Injection Monitoring

The EPRI BWR Water Chemistry Guidelines allow the feedwater hydrogen concentration to be continuously monitored by either:

- 1) measuring the feedwater hydrogen concentration using an in-line hydrogen analyzer, or
- 2) using the hydrogen injection flow rate and the feedwater flow rate to calculate the feedwater hydrogen concentration.

### 3.1.4 ECP Monitoring

ECP is a primary parameter for inspection relief and is required for hydrogen benchmark testing. It has been established that with hydrogen injection, IGSCC is mitigated when the ECP is  $\leq -230$  mV(SHE). In-process ECP provides a direct and continuous indication of catalytic activity and water chemistry at the monitored surface. BWR ECP monitoring locations are shown in Figure 3-2. Seven (7) OLNLC plants currently monitor ECP at in-process locations. The guidance here is to monitor ECP in an in-vessel location such as an LPRM, RRS, RWCU or BHD. MMS ECP monitoring is not optimal because of the hydrogen and oxidant recombination occurring along the sample line leading to the MMS ECP location. Therefore, MMS ECP values are less conservative. Should the ECP sensor becomes unavailable, need to maintain the hydrogen:oxidants molar ratio is  $\geq 2$ , proving the presence of sufficient catalyst until the next required HWC benchmark test. In-process ECP provides confirmation on the effectiveness of OLNLC applications in accordance with vendor recommendations and may be useful to validate potential future changes for process optimization.

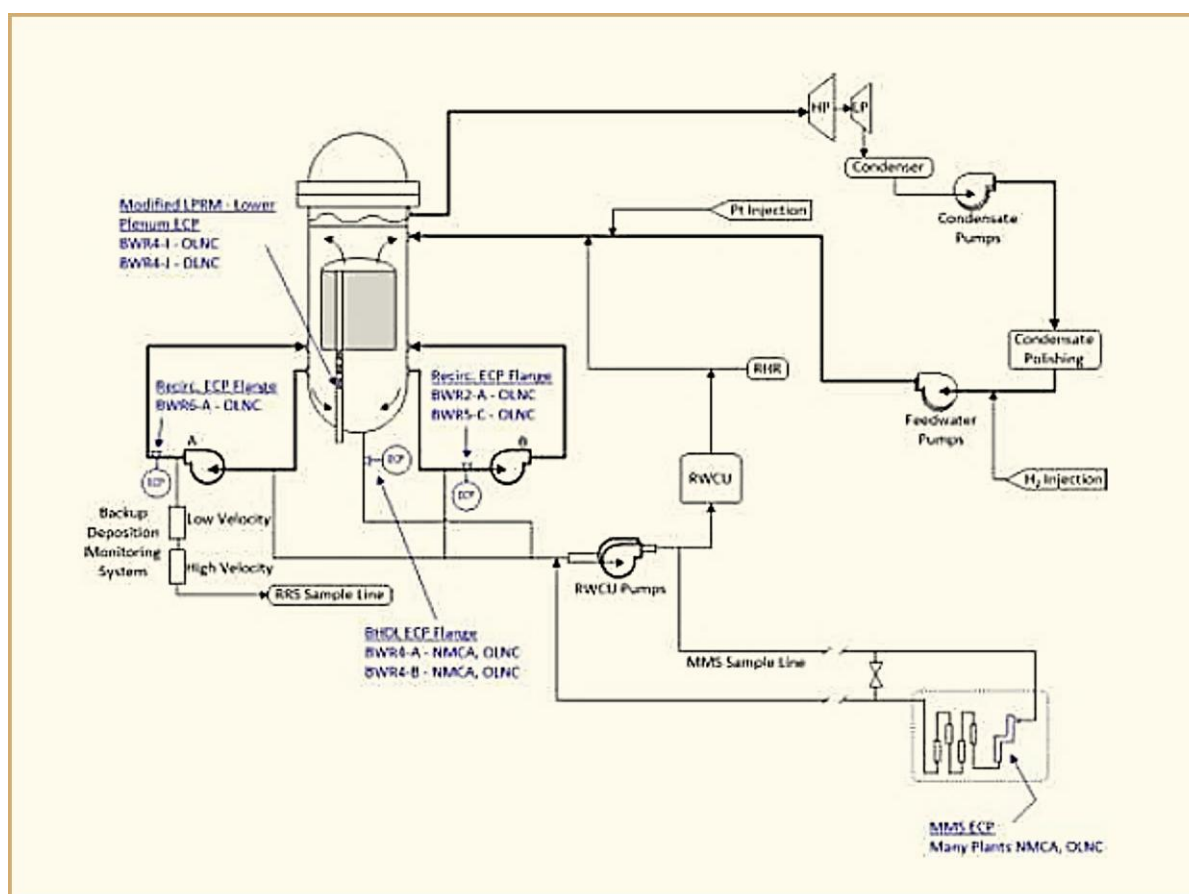


Figure 3-2: Key BWR ECP Monitoring Locations [Garcia et al., 2018g].

The rapid decrease in lower plenum ECP after the transition from HWC-M to HWC+OLNLC, is shown for a BWR-4 in Figure 3-3. This plant had no prior NMCA applications. The rapid lowering of ECP is followed by a gradual increase in ECP at constant hydrogen injection rate until the next OLNLC application, when ECP returns to  $<-490$  mV(SHE). The same Figure shows the lower plenum ECP response to the first three OLNLC applications at this Plant.

## 4 BWR Dose Rate Mitigation Technologies - Plant Operating Experiences

Following the successful IGSCC mitigation technologies employed in modern day BWRs, the focus has shifted more towards methods available for dose rate mitigation. This section describes numerous methods used for dose rate mitigation of BWRs based on plant operating experiences.

### 4.1 Fuel Cleaning for Source Term Control in BWRs

More than 30 Pressurized Water Reactors (PWRs) have implemented ultrasonic fuel cleaning (UFC) as a crud deposit reduction strategy. The process was first used in 1999 at Callaway PWR to address fuel crud buildup that resulted in core power shifts or now commonly called crud induced power shift (CIPS).

The success of PWR fuel cleaning triggered development of fuel cleaning of BWRs as a potential source term reduction technique. The results demonstrated that crud and source term could be removed from BWR fuel with no adverse impact on fuel performance. The UFC was first used at Browns Ferry 1 BWR with the first-generation fuel cleaning process. A total of 79 waste filters were generated, whereby the highest measured contact dose rate of a filter was 400 R/hr. The waste filters were stored in the spent fuel pools at Browns Ferry for approximately eight years before offsite shipping for disposal [Gregorich et al., 2018].

Ultrasonic fuel cleaning had not been pursued at BWRs since the Browns Ferry campaign mainly because of the large number of waste filters that were generated with the conventional UFC process and the associated disposal issues, and the potential impact on outage critical path work. The improvements implemented in the high efficiency UFC (HE-UFC) technology addresses these issues that prevented the process adoption among BWRs, making this technology now a viable tool for source term reduction. The anticipated fuel bundle cleaning time is about 3 times shorter with the HE-UFC technology, that is, about 2 minutes per fuel assembly [Gregorich et al., 2018].

In 2017, a BWR employed HE-UFC that included the cleaning of 260 fuel assemblies, that is, 32 once-burned and 228 twice-burned assemblies. The deployed HE-UFC setup is shown in Figure 4-1. The setup was installed in the unit's cask pit and consisted of the cleaning chamber, the all metal filter modules, a pump, and an inline dose rate detector.



Figure 4-1: HE-UFC setup used in 2017 at the deployment site [Gregorich et al., 2018].

The crud removal results are presented in Figure 4-2 in which a once-burned assembly is shown before and after fuel cleaning. The fuel cleaning was performed in the “channel on” configuration. The pictures shown in Figure 4-2 have been taken with the “channel off”.

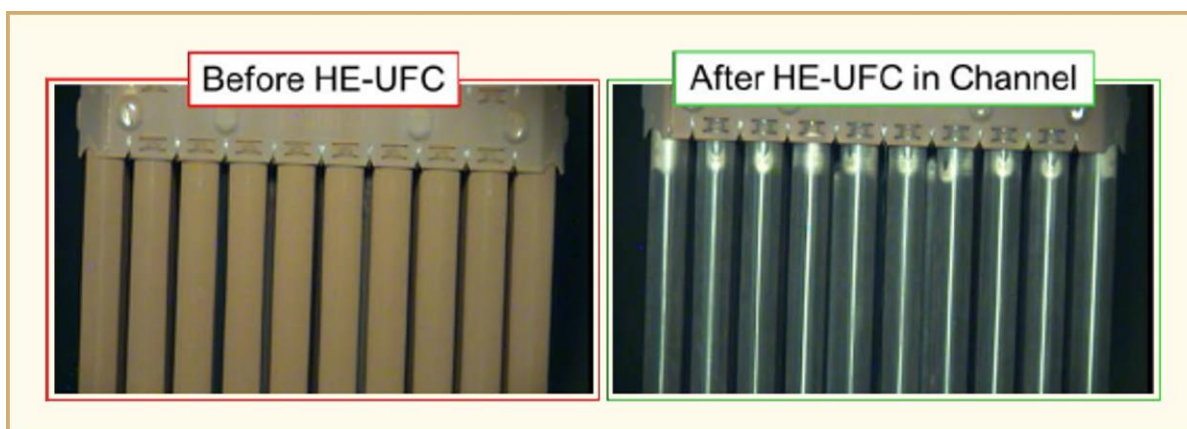


Figure 4-2: Visuals of a once-burned fuel assembly prior to and after cleaning with HE-UFC [Gregorich et al., 2018].

The amount of activity removed per each of the bundles cleaned is shown in Figure 4-3. On average, the activity removed from once-burned fuel was with 77 Ci (2849 GBq) per bundle higher than the activity removed from twice-burned fuel which was 35 Ci per bundle (1295 GBq). The higher activity levels observed and removed from once-burned fuel assemblies may be due to the preferential release of crud from peripheral assemblies or from reload assemblies in lower duty locations and deposition on higher duty leading fresh fuel assemblies. It must be mentioned that the benefits of source term mitigation strategies are seldom seen instantaneously, unlike in decontamination [Gregorich et al., 2018].

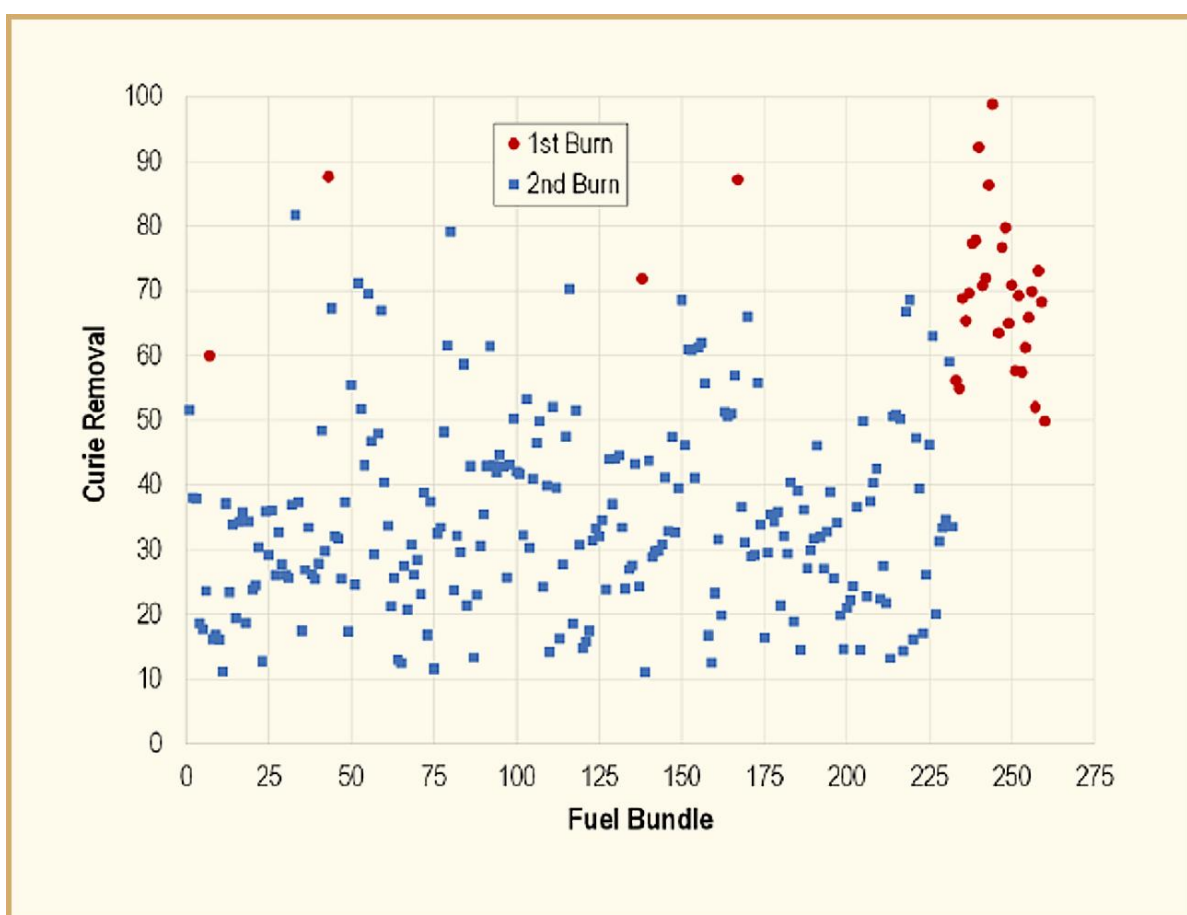


Figure 4-3: Crud activity removed from fuel assemblies – once burned are shown in red and twice-burned are shown in blue. (1 Ci = 37 GBq) [Gregorich & et al., 2018].



Fuel cleaning can reduce the radiation field source term that is available for deposition on ex-core surfaces that can be re-released during operational transients and during outage evolutions. The reduced amount of crud in fuel reduces the crud mass that can be re-released and be deposited on freshly inserted fuel [Gregorich et al., 2018].

## 4.2 Chemistry Measures for Dose Reduction at Gundremmingen BWR

In recent years, the two Gundremmingen units experienced elevated radiation levels during outages with increased man-doses. One main radiation source was identified as being due to particle mobilization from fuel surfaces (CRUD) during shut-down operation. The temperature gradient during cool down of the reactors to refueling outages was decreased from 30K/h to 10K/h in order to reduce CRUD mobilization and to clean up the reactor water thoroughly prior to water level increase and flood up for outage work. In addition, it was decided to establish a low level of zinc in reactor water with the aim to bind activation products on the fuel rods [Nowotka et al., 2018].

The operational experience with the two units in the past with brass condenser tubes was positive. With the condenser tube material change from brass to stainless steel, the zinc effect vanished and the fuel CRUD became more mobile. It was therefore decided to inject small quantities of zinc (as zinc acetate solution) into feedwater for compensation of the loss of the natural zinc source after modernization of the turbine condensers. However, this has to be accomplished by excluding any potential formation of thermally insulating Zn-silicate layers on fuel rod surfaces [Nowotka et al., 2018].

In the past, silicate levels in the two reactors were always by a factor of 2-3 higher than in other European BWRs. Therefore, it was obvious that the silicate level had to be reduced before starting zinc injection. Reduction of silica levels was achieved by three measures:

- Identification and elimination of silicate sources in the plant filter material
- Lower water purification flow rate, along with a decrease in temperature in the precoat filters by approx. 7°C, greatly improving silicate retention
- More frequent backwashes of the powdered ion exchange resin coats of the filter demineralizers in the reactor water clean-up system, approximately ten times per 11 month cycle.

These measures proved effective and resulted in a decrease in reactor water silicate concentrations by a factor of two as shown in Figure 4-4.

Reactor Water Silica / ppb	2002/ 2003	2003/ 2004	2004/ 2005	2005/ 2006	2006/ 2007	2007/ 2008	2008/ 2009	2009/ 2010	2010/ 2011	2011/ 2012	2012/ 2013	2013/ 2014	2014/ 2015	2015/ 2016
Unit B	600	640	560	600	670	590	450	680	690	570	530	400	450	340
Unit C	-	-	620	680	680	480	550	720	510	390	330	720	540	350

Figure 4-4: Reactor water silicate cycle mean values in µg/kg (ppb), as measured in Gundremmingen units B and C between 2002 and 2016 [Nowotka et al., 2018].

The following measures were implemented to improve the power station's radiologic situation while excluding any risk for the fuel assemblies:

- Reduce Fe ingress into the reactor water (recommended value < 1ppb Fe in feedwater)
- Reduce the silicate level of the reactor water (recommended value < 300ppb SiO<sub>2</sub>)
- Inject only small quantities of zinc: target concentration for reactor water is 1ppb zinc

## 5 Identification and Inspection of BWR Fuel Failures

A comprehensive review of fuel failure experience is in progress presently at Forsmark NPP. The review covers the period 2003–2018 and 43 fuel failures that have been confirmed to be caused by debris fretting in all but one case. The large number of fuel failures provides enough data to allow meaningful study of typical behaviour and possible connections that will help other BWRs. It must be noted that the main reactor coolant circulation within the reactor pressure vessel is supplied by eight internal pumps. An internal pump design means that no external circulation loops are needed unlike in US BWRs. It is possible that with this design, a relatively large amount of debris is accumulated in the pressure vessel and may contribute to fuel failures by debris fretting. Another part of the plant design that may contribute to foreign materials in the reactor is the use of forward pumping which is employed to some extent at unit 1 since 2018, unit 2 since 2011 and unit 3 since the start of operation. Forward pumping means that not all of the feed water flow is cleaned up by the precoat ion exchange filters of the condensate polishing system which will also capture the debris; forward pumped feed water heater drains enter the feed water system downstream of the condensate filters [Olsson, 2018].

Most of the fuel failures have occurred at unit 3, the most recent design with the longest history of forward pumping and the most challenging path for debris to leave the reactor. Nearly all fuel failures at Forsmark are caused by debris fretting from metal scrap that is caught between a fuel rod and a spacer. Current and future efforts to reduce the fuel failure frequency include further FME development and comprehensive debris removal from the pressure vessel of unit 3. The full fuel failure history at Forsmark 1-3 is shown in Figure 5-1.

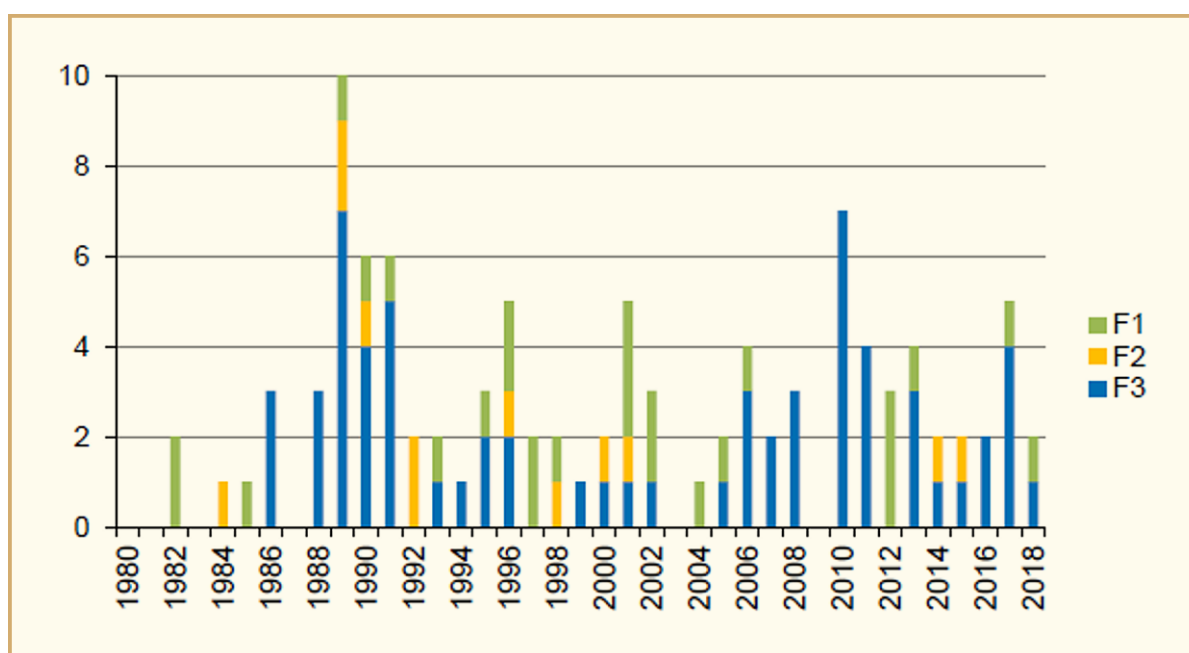


Figure 5-1: Number of fuel failures that have been removed each year, from commissioning until July 2018, from the cores of Forsmark 1–3 [Olsson, 2018].

When fuel leakers occur, the chemistry sampling of condenser offgas and reactor coolant typically include the following [Olsson, 2018]:

- The xenon and krypton isotopes Xe-133, -135, -138, Kr-85m, -87 and -88 in the offgas sampling system. The activity ratios Xe-133/Xe-135 and Kr-88/Xe-133 are especially useful to detect new fuel failures. With a Xe-133/Xe-135 ratio above 0.07–0.08 there is reason to suspect the presence of a fuel leaker.
- Iodine isotopes in the reactor coolant, especially I-131, which indicates a secondary degradation of the fuel leaker.

## 6 SCC Modelling and Electrokinetic and Platinum Deposition Modelling

This section describes three different types of models addressing 3 different areas critical to BWRs. These include, stress corrosion cracking modelling with parametric sensitivity, electrokinetic deposition modelling and Platinum deposition modelling that is useful for BWRs operating with noble metals.

### 6.1 Deterministic Model for Stress Corrosion Cracking

The main advantage of deterministic models for predicting corrosion damage in the coolant circuits of water-cooled nuclear power reactors is that their outputs takes into account the impact of all independent variables and are included in the models. The typical deterministic modelling process involves three steps [Balachov et al., 2018]:

1. Calculation of concentrations of reducing and oxidizing species in the reactor coolant based on known reactor operating parameters and principles of chemical kinetics.
2. Estimation of Electrochemical Corrosion Potential (ECP) based on calculated species concentrations, hydrodynamic conditions, and electrochemical parameters of the structural materials in reactor heat transport circuit (HTC).
3. Estimation of Crack Growth Rates (CGR) and crack depth in HTC components based on known species concentrations, ECP, material degradation parameters, and reactor operating history.

The goal of the sensitivity analysis is to define the contributions of input data variations to variations of the calculated species concentrations, ECP, and crack growth rate. The list of input parameters in sensitivity analysis (Table 6-1) includes radiolytic yields, reaction rate constants, parameters of the Mixed Potential and crack growth rate models and reactor modelling parameters, such as dose rates, coolant temperature, flow velocity and hydrodynamic diameters of the flow channels [Balachov et al., 2018].

The sensitivity of the integral parameters to radiolytic yields reveals that the yields of electrons and protons are of primary importance, followed by the yields of OH, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>. The sensitivities appear to be slightly higher under hydrogen water chemistry conditions.

The integral parameters are most sensitive to the rate constants of reactions  $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + 0.5 \text{O}_2$ ,  $\text{H}_2\text{O}_2 = 2\text{OH}$  and  $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$ . Sensitivity increases under Hydrogen Water Chemistry (HWC) conditions.

The sensitivity of the ECP (in mV) and crack growth rate (in %) have been calculated for +1% increase in input parameters under normal and hydrogen (0.5 ppm of hydrogen in feedwater) water chemistry conditions.



Table 6-1: List of input parameters for sensitivity analysis [Balachov et al., 2018].

Parameter's group	Parameter	Description
Reactor modeling parameters	Dn	Neutron dose rates
	Dg	Gamma dose rates
	Flow vel	Flow velocity
	Hydr diam	Hydrodynamic diameters
	Temp	Coolant temperature
Radiolytic yields	Yield of species	11 under gamma radiation ( $G_i$ ) and 11 under neutron radiation ( $N_i$ )
Reaction rates	Rate constants	34 chemical reactions
MPM parameters	bf H2	Tafel constants
	br O2	
	br H2O2	
	bf SS	
	E0 O2	Standard potentials
	E0 H2O2	
	E0 SS	
	Ee H2	Equilibrium potentials
	Ee O2	
	Ee H2O2	
	D H2	Diffusivity of species
	D O2	
	I0 H2	Exchange current densities
	I0 O2	
	I0 H2O2	
	I0 SS	
	I lim f H2	Limiting currents
	I lim r O2	
	I lim r H2O2	
Materials degradation parameters	K_I	Stress intensity factor
	Crack_Depth	Crack Depth
	Crack_Tip	Crack Tip Strain rate Option
	QMC	Quantum Mechanics correction for exchange current density calculation

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The ECP is most sensitive to the exchange current density for the passive electro-dissolution of stainless steel (under hydrogen water chemistry conditions), standard potentials for the oxygen and hydrogen peroxide<sup>1</sup> electrode reactions (OER and HPER, respectively) under both normal and hydrogen water chemistry conditions, and to the Tafel constants for the hydrogen (HER), OER, and HPER under both normal and hydrogen water chemistry conditions [Balachov et al., 2018].

## 7 Auxiliary Systems

### 7.1 Corrosion of Aluminium Alloys used in Containments

The performance of strainers that filter the recycled water in the reactor sump after a loss-of-coolant accident (LOCA) is vital for the continued cooling of the core. The recycled water is typically primary coolant augmented with water injected from the emergency core cooling system (ECCS), which in light-water reactors (LWRs) and CANDUs is de-oxygenated and basic for corrosion control during storage and in LWRs is also borated to control core reactivity [Huang et al., 2018].

A temperature-controlled electrochemical system was set up to investigate the corrosion of wrought aluminium alloy AA 6061, a common material used in containment, and the release of its corrosion products in borated neutral and alkaline solutions representative of the sump water chemistry after a LOCA. The electrochemical techniques employed included potentiodynamic polarization and linear polarization resistance.

The study found that [Huang et al., 2018]:

- (1) Increasing pH <sub>25°C</sub> from 7 to 9 significantly increased the Al corrosion rate.
- (2) Hydrodynamic conditions had an important influence on corrosion; they were especially significant when the electrode rotation speeds were low (and the mass transport was weak but controlling) and the solution pH was high. Special caution is therefore necessary when designing tests or using the measurements or predictive equations from the literature.
- (3) Spontaneous passivation occurred at pH <sub>25°C</sub> 7; at pH <sub>25°C</sub> 8 and 9 so-called pseudo-passivation was observed, with aluminium dissolution proceeding rapidly through a surface film that still permitted charge transfer and ionic conduction.
- (4) Localized corrosion around Fe-bearing intermetallic particles was observed on the aluminium alloy specimens corroded at pH <sub>25°C</sub> 8 and 9. These particles, which were identified by XRD to be mainly Al(Fe,Mn)Si, served as local cathodic sites and first caused trenching before being released into test solution. In reactor containments, these released particles could aggravate strainer clogging by adding to the debris bed formed.

### 7.2 Corrosion Inhibition of Aluminium Brass Heat Exchanger Piping in Sea Water Cooling Systems

In Japan, seawater is used as cooling water to cool various components at nuclear power plants. When aluminium brass piping is used in the heat exchanger as heat transfer tubes, ferrous sulphate is injected during initial film formation and normal film formation after inspection has been completed so as to suppress corrosion. Corrosion of the heat transfer tube is evaluated based on the results of eddy current tests (ECT) of heat transfer tubes during each periodic inspection [Hisamune et al., 2018].

It is generally known that aluminium brass pipes form a self-healing protective film when seawater is used as cooling water, and even when the protective film temporarily breaks down due to the passage of foreign materials, corrosion is suppressed by the formation of a new protective film over the damaged film. It has become clear that the excellent corrosion resistance of this type of aluminium brass pipe is mainly due to the iron hydroxide film that forms on its surface. It has been confirmed that ferrous sulphate injection in to brass condenser tubing is extremely effective in protecting the heat transfer surface from corrosion.

Injection of ferrous sulphate into the nuclear reactor auxiliary cooling water system heat exchangers of the Japan Atomic Power Company's Tsuruga Power Station Unit 2 was evaluated during each refuelling outage until 1991. In order to form a protective film on the heat transfer surface, ferrous sulphate was injected into the heat transfer tube of the nuclear reactor auxiliary cooling water system heat exchanger in the nuclear reactor auxiliary cooling seawater system. More specifically, when water was initially supplied following inspection of the heat exchanger heat transfer tube at the time of initial cooling, the

cooler was inspected and then an initial amount of approximately 1.0 ppm of ferrous sulphate was injected over a period of one hour once a day [Hisamune et al., 2018].

In the summer when the protective film is more likely to deposit on the heat transfer tube and in the winter when the protective film is less likely to deposit, a normal protective film formation investigation was conducted one month after initial protective film formed for one month (Test piece: outer diameter 19.05 mm, wall thickness 1.245 mm). For initial ferrous sulphate injection, the target was to set the injection amount for forming the protective film before the scale deposits when there was water passage at the beginning after inspection of the heat exchanger. It was also the intent to set the injection amount so that the protective film did not peel off due to excessive ferrous sulphate injection. In order to evaluate the corrosion protection performance of the film formed on the heat transfer tube, the natural potential and polarization resistance were measured using an electrochemical method. The criteria used for polarization resistance is shown in Table 7-1 [Hisamune et al., 2018].

Table 7-1: Evaluation criteria of polarization resistance [Hisamune et al., 2018].

Polarization Resistance	Evaluation
$<10,000\Omega\cdot\text{cm}^2$	Insufficient formation of protective film
$10,000 \sim 20,000\Omega\cdot\text{cm}^2$	Formation of protective film can be confirmed. (at the time of film formation at the normal time)
$>20,000\Omega\cdot\text{cm}^2$	Formation of protective film is sufficient. (at initial film formation)

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During ferrous sulphate injection, for the purpose of setting an appropriate injection amount so as not to remove the coating formed after initial injection, it is preferable that the flow interval in the heat exchanger be switched to once month so that the amount injected can be set to form a sufficient film. Further, the model condenser (Figure 7-1) was installed near Tsuruga-2 sea water intake port and a survey was conducted using seawater at the same temperature as the actual intake water seawater.

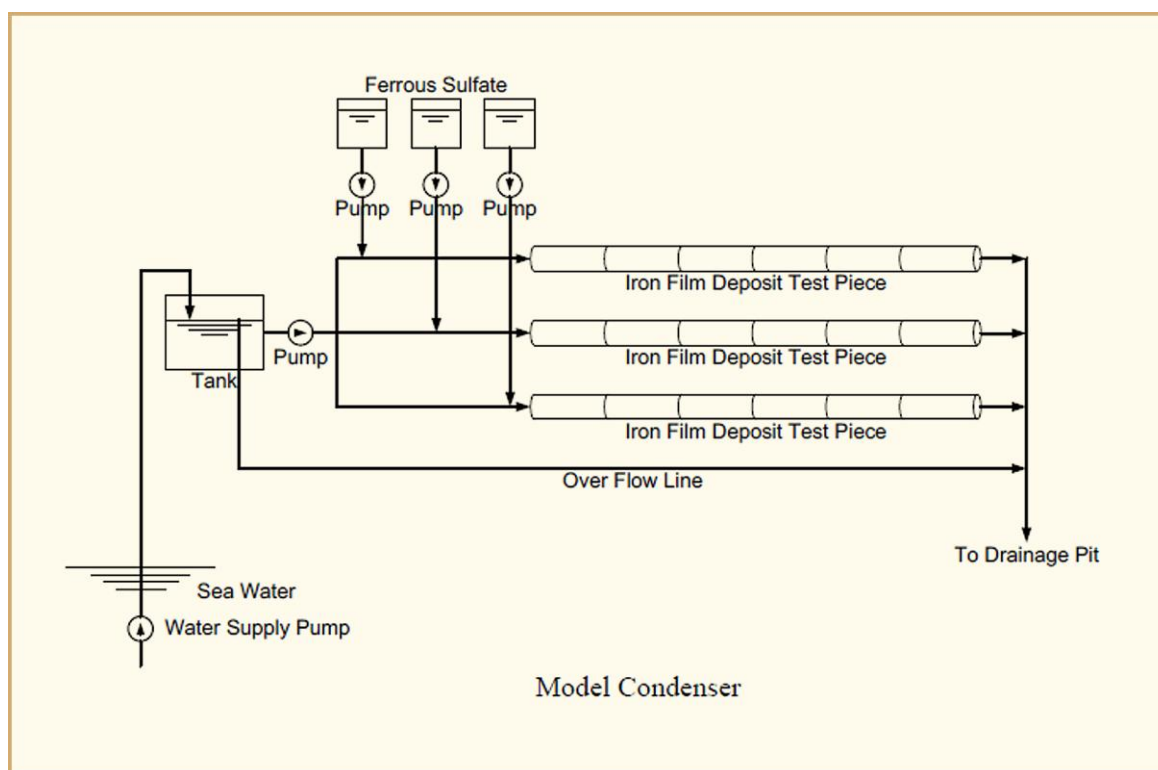


Figure 7-1: Model condenser used for the polarization resistance study [Hisamune et al., 2018].

Figure 7-2 shows the relationship between the days of ferrous sulphate injection and polarization resistance during initial film formation in summer. Figure 7-2 indicates that there was good protective film formation ( $20,000 \Omega \cdot \text{cm}^2$  or more) for 20 days at initial injection time of one hour, 15 days at two hours and 7 days at five hours.

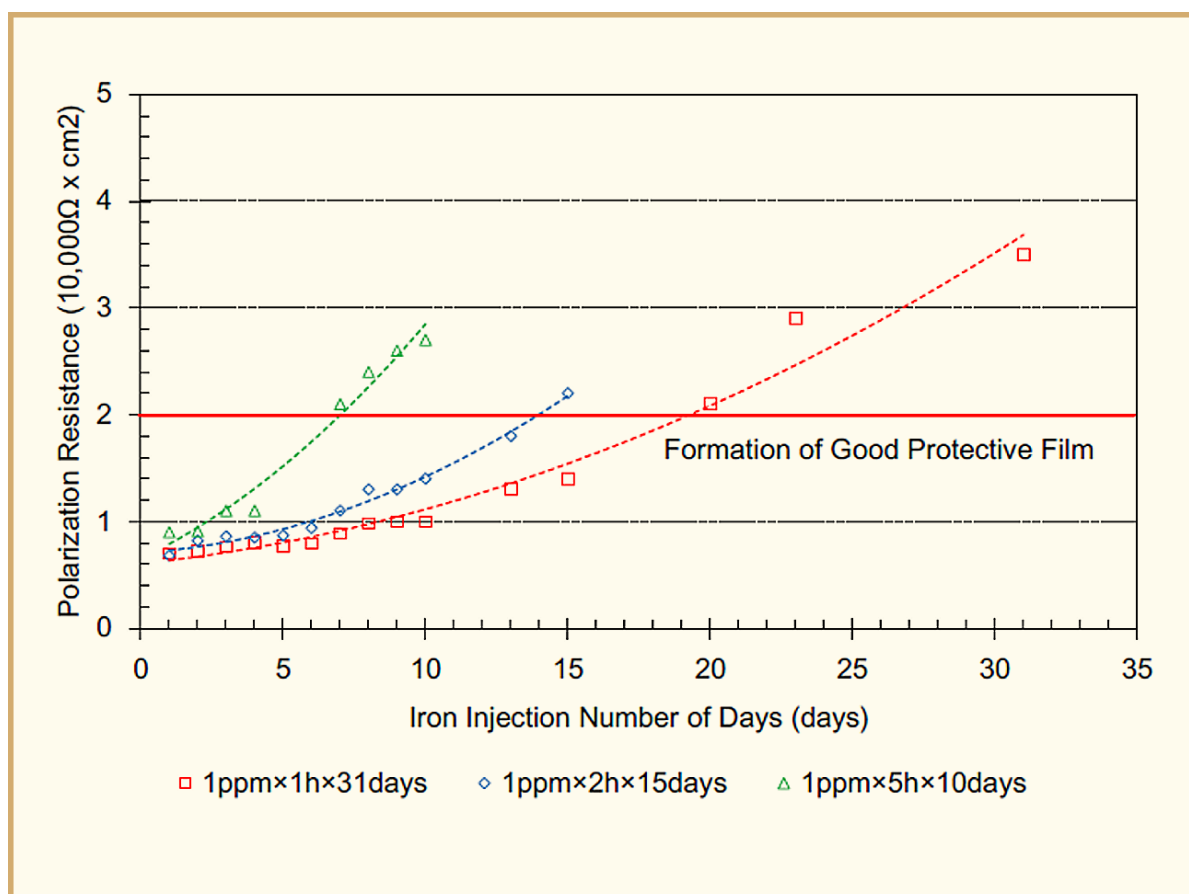


Figure 7-2: Relationship between the number of days of ferrous sulphate injection and polarization resistance during summer (at initial film formation) [Hisamune et al., 2018].

Figure 7-3 shows the relationship between the number of ferrous sulphate injection days and polarization resistance during initial film formation in winter. Figure 7-3 indicated that good protective film formation ( $20,000 \Omega \cdot \text{cm}^2$  or more) was obtained in 29 days with the initial injection one hour, 18 days in two hours and 15 days in three hours.

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## Nomenclature

ABWR	Advanced Boiling Water Reactor
ALARP	As Low As Reasonably Practicable
BHDL	Bottom Head Drain Line
BOC	Beginning of Cycle
BRAC	BWR Radiation Assessment Control
BSE	Back Scattered Electron
B-TAC	BWR Technical Advisory Committee
BWR	Boiling Water Reactor
BWRVIA	BWR Vessel and Internals Application
BWRVIP	Boiling Water Reactor Vessels and Internals Program
CANDU	Canadian Deuterium Oxide Reactor
CGR	Crack Growth Rate
CHC	Critical Hydrogen Concentration
CIPS	Crud Induced Power Shift
CITROX	Citric Acid + Oxalic Acid
CMA	Chemistry Monitoring and Assessment
CNMI	Continuous Noble Metal Injection
CORD-UV	Chemical Decontamination Technique
CP	Corrosion Products
CRD	Control Rod Drive
CRUD	Chalk River Unidentified Deposit
CRUDSAM	CRUD Sample
CS	Carbon Steel
CZT	Cadmium Zinc Telluride
DB	Deep Bed
DC	Direct Current
DH	Dissolved Hydrogen
DO	Dissolved Oxygen
DZO	Depleted Zinc Oxide
ECCS	Emergency Core Cooling System
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
ECP	Electrochemical Corrosion Potential
ECT	Eddy Current Test
EHC	Electro-hydraulic Control
EOC	End of Cycle
EPRI	Electric Power Research Institute
FAC	Flow Accelerated Corrosion
F/D	Filter Demineralizer
FE-SEM	Field Emission Scanning Electron Microscopy
F+DB	Filter + Deep Bed
FOI	Factor of Improvement
FRP	Fuel Reliability Program
FW	Feed Water
GDA	Generic Design Assessment
GE	General Electric Company
HE-UFC	High Efficiency Ultrasonic Fuel Cleaning
HER	Hydrogen Electrode Reaction
HFT	Hot Functional Testing
HPER	Hydrogen Peroxide Electrode Reaction
HPGe	High Purity Germanium
HTC	Heat Transport Circuit
HWC	Hydrogen Water Chemistry
HWC-M	Moderate HWC
IGSCC	Intergranular Stress Corrosion Cracking
IC	Ion Chromatography
KKL	Kernkraftwerk Leibstadt

## Unit conversion

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

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

MASS	
kg	lbs
0.454	1
1	2.20

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

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

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