Key Issues in Plant Chemistry and Corrosion in BWRs – 2016

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Contents

1 Introduction

BWRs have undergone a variety of important and improved water chemistry evolutions over the past few decades addressing issues relating to stress corrosion cracking of reactor internal materials, fuel performance, radiation fields and personnel exposure. Among the key water chemistry advancements realized include hydrogen water chemistry, noble metal chemical addition (NMCA), On-line noble metal chemical addition (OLNC), non-hydrogen technologies for SCC mitigation, iron reduction, cobalt reduction, zinc addition and improved filtration technologies. In addition, many BWRs have performed power uprates that has demanded even greater scrutiny on water chemistry effects on SCC mitigation, fuel performance and radiation field reduction.

BWR owners are striving for excellence with the use of the above mentioned technologies towards improving capacity factor, seeking inspection relief, minimizing fuel leakers, minimizing personnel exposure, while facing demanding cost reductions but still maintaining safe operation of BWR plants.

The present report summarizes, primarily, the BWR related papers from the NPC 2016 conference. The report also provides updated information with the author's critique and analysis where appropriate. The report is expected to be a comprehensive document summarizing the latest information on BWR water chemistry that would benefit the BWR operators and regulators.

The following areas presented at the oral and poster sessions of the NPC 2016 Conference are covered in this report:

1.1 BWR Plant Operating Experiences and Modeling

Iron reduction experiences, water chemistry guidelines, internal pump BWRs, chemistry intrusions related to corrosion, control rod blade leakages, hydrogen demand, radiolysis modeling, and fuel clad corrosion.

1.2 BWR Dose Rates and Radiation Field Control

Feedwater iron reduction, cobalt reduction, depleted zinc oxide (DZO) implementation and platinum addition to control plant dose rates and radiation fields are addressed in this section.

1.3 IGSCC Mitigation, Life Management and Noble Metal Related Topics

This section is dedicated to SCC mitigation technologies implemented or tested in operating BWRs, that include HWC, NMCA, OLNC and non-hydrogen technologies. It also addresses chemistry and corrosion issues related to lifetime management and countermeasures.

1.4 BWR New Builds and Water Chemistry Guidelines

Water chemistry plans for new nuclear power plants, commissioning strategies, developments in LWR plant design and materials, improvements and challenges for the operation of new plants, and water chemistry guidelines are addressed in this section.

1.5 BWR Scientific Studies

BWR related scientific studies are covered in this section that includes fundamental and laboratory studies and computer modeling efforts.

2 BWR Plant Operating Experiences and Modeling

BWR plant operators have implemented a variety of water chemistry related technologies to minimize IGSCC incidences, reduce radiation fields and minimize fuel corrosion issues. The very technologies that have been adopted to keep the BWRs operating safely with extended life have demanded more stringent water chemistry monitoring throughout the life of reactor operation since some of these technologies "might" have an adverse impact if not practiced appropriately. As an example, although HWC is a well accepted technology against IGSCC mitigation of reactor internal materials, cycling hydrogen has a negative effect on ^{60}Co release from fuel, depositing on out of core areas, causing radiation field increases. Similarly, DZO addition has been demonstrated to lower shut down dose rates, however, having higher levels of feedwater zinc has resulted in crud spallation from fuel cladding surfaces in some BWRs in the presence of elevated levels of feedwater silica. Higher levels of noble metal input in NMCA plants have not shown any discernible adverse effects, however, it is felt that an unnecessary burden of noble metals on fuel crud is unnecessary as well as expensive. Therefore, limits have been placed on the amount of allowable noble metals additions to both NMCA and OLNC plants. The adoption of at least one of the above IGSCC mitigation technologies HWC, NMCA and OLNC have been widely accepted and broadly employed throughout the BWR fleet in the US, Spain, Switzerland, Mexico, Taiwan, some in Japan and some in Sweden. Majority of the BWRs in the US, and those in Switzerland, Mexico and one of the two BWRs in Spain now operate with OLNC and low HWC. The rapid adoption of NMCA and OLNC technologies to the BWR fleet compared to HWC is shown in Figure 2-1.

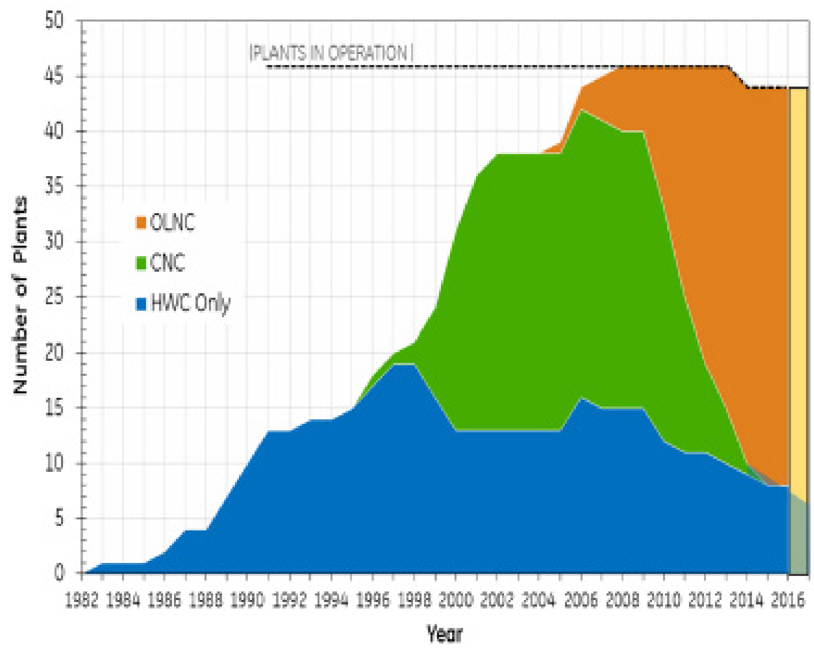

Figure 2-1: Adoption of IGSCC Mitigation Technologies in BWRs [Wells et al., 2016].

2.1 BWR Iron Reduction Experiences

Feedwater (FW) iron in a BWR is an important factor impacting the amount of corrosion products in the reactor coolant system and therefore both fuel crudding related issues and radiation field generation. In recent years there have been significant reductions in feedwater iron concentrations predominantly associated with improvements in condensate polishing systems. While the impact on radiation fields may take many years to achieve, the early impact on fuel cladding is clearly seen from lower fuel crud loading. Better filtration control has largely been achieved by installing filters upstream of condensate deep bed demineralizes (prefilters) and the use of high efficiency iron removal septa in plants with condensate filter demineralizers [Wells et al., 2016]. Figure 2-2a shows the transition for US BWRs from an industry dominated by filter demineralizers and deep beds to one where most deep beds have installed pre-filters. Figure 2-2b shows the resulting transition from only a small faction (3 units) operating with FW iron <0.3 ppb in 2004, to 2014 where more than 20 units operate at <0.3 ppb and 19 operate with <0.2 ppb and 10 operate with <0.1 ppb. This is a significant change and the effects on plant performance are only now beginning to be understood [Garcia et al., 2014].

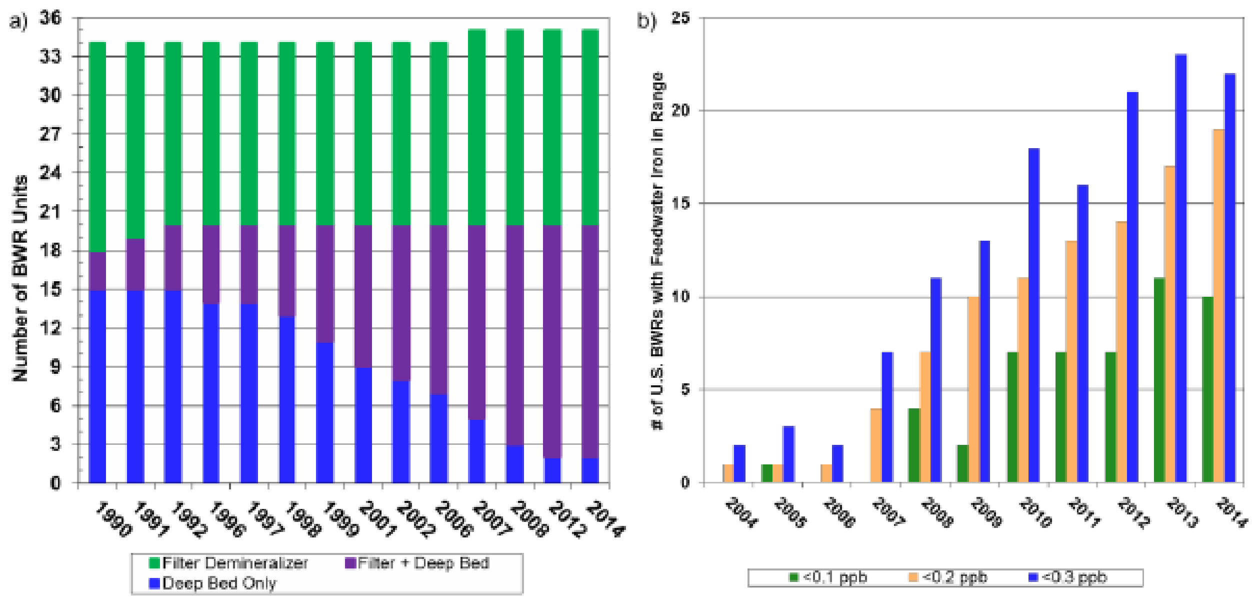

Figure 2-2: Impact of changes in BWR condensate polishing technology on feedwater iron concentration. a) shows the transition from deep bed only to operation with installed prefilters from 1990 to 2014, and b) shows the number of plants operating with FW iron less than 0.3 between 2004 and 2014 [Wells et al., 2016].

In Japan, at Tokai 2 BWR, the condensate demineralizer efficiency was improved to lower the feedwater iron concentration. After commercial operation began, the iron removal efficiency was increased with enhanced resin performance and improved backwashing (ARCS: Advanced Resin Cleaning System) as well as chemical regeneration (soaking regeneration) of the condensate demineralizer. This approach allowed feedwater iron to be lowered to 0.5 ppb with agreater than 90% iron removal efficiency.

2.2 BWR Water Chemistry Guidelines for Operating Plants

The latest revision of the Electric Power Research Institute (EPRI) BWR Water Chemistry Guidelines, was published in April 2014 in two volumes [Garcia & Gianelli, 2014]. Volume 1 contains the Mandatory, Needed and Good Practice Guidance [BWRVIP-190, 2014a], while Volume 2 documents the Technical Basis [BWRVIP-190, 2014b].

Volume 1 includes significant changes to BWR feedwater and reactor water chemistry control parameters to provide increased assurance of intergranular stress corrosion cracking (IGSCC) mitigation of reactor materials and fuel reliability during all plant conditions, including cold shutdown (≤200 °F (93 °C)), startup/hot standby (>200 °F (93 °C) and ≤ 10%) and power operation (>10%power). Action Level values for chloride and sulfate have been tightened to minimize environmentally assisted cracking (EAC) of all wetted surfaces. Chemistry control guidance has been enhanced to minimize shutdown radiation fields by clarifying targets for depleted zinc oxide (DZO) injection while meeting requirements for fuel reliability [Garcia et al, 2014a].

Volume 2 provides the technical bases for BWR water chemistry control for control of EAC, flow accelerated corrosion (FAC), fuel reliability, radiation field control, chemistry program optimization and data monitoring and evaluation. New appendices are included on the BWRVIP Mitigation

3 BWR Dose Rates and Radiation Control

The generation of radiation fields in nuclear power plants is related to many different variables including chemistry control, materials of construction, operating history, core design, and fuel design to name a few. Many instances the use of plant data to understand radiation field generation can be confounded by a lack of variable control (more than one change in a single cycle). Even comparing experimentally controlled observations to plant data can be difficult. The current model for radiation field generation begins with the corrosion and release of parent species from the wetted material surfaces (or any other "addition" mechanism). Species like nickel are transported to the core and activated to dose-contributing nuclides like ^{58}Co. These species are then released from the core and deposit out-of-core where they generate radiation fields that must be managed by utilities to minimize occupational exposure. The generation of radiation fields in high flow areas of the plant, such as the recirculation piping is thought to be primarily controlled by the incorporation (largely soluble into continually corroding materials) of activity during the cycle. Conversely, radiation fields generated in lower flow and somewhat lower temperature systems (BWR reactor water cleanup (RWCU) may be impacted by particulate deposition during shutdown or other micro-environment phenomena that are less well understood [Wells et al., 2016].

Optimized chemistry control attempts to mitigate all aspects of radiation field generation, is complicated by the multivariant aspects of the process and is challenging as the majority of the current plant data is for bulk chemistry and high flow area radiation fields. Two chemistry technologies that have been adopted in BWRs are zinc addition and noble metal addition. As data (chemistry and radiation field) for the lower temperature and flow rates systems of the plant improve, there may be an opportunity for further improvements related to chemistry control guidance for reducing radiation fields [Wells et al., 2016].

3.1 Zinc Injection for Dose Rate Control

Zinc injection is somewhat unique in chemistry control as the technology work at multiple stages of radiation field generation including reducing corrosion release, stabilizing core crud, and minimizing activity uptake. The application of this technology can be traced back to the observation of lower BWR radiation fields in plant operation with admiralty brass condensers, and first demonstration was performed at Hope Creek BWR.

Depleted Zinc Oxide (DZO) addition has been used successfully to reduce the rate of radiation buildup on BWR piping and surfaces and all US BWRs are implementing depleted zinc oxide addition for radiation field control. However, feedwater zinc limits continue to be applied in the EPRI BWR Water Chemistry Guidelines [BWRVIP, 2016a] based on concerns for the formation of tenacious fuel crud. In the presence of zinc and silicate species, zinc silicate can form and aid in the densification process of BWR fuel crud. This dense and tightly adherent, tenacious deposit on the fuel cladding surface can reduce heat transfer and can lead to the formation of a steam blanket that greatly increases fuel cladding temperature, enhances corrosion and can lead to fuel cladding failure. One symptom of this phenomenon is spalled fuel crud. This behavior is easily observed in visual observations of fuel during the outage and can be an indicator of fuel crud issues. Not only is crud spallation a symptom of potential elevated corrosion, it can also lead to cladding cool spots where hydrides can migrate and reduce cladding ductility. When the observation of crud spalling is evaluated, there appear to be a correlation between high feedwater zinc concentration coupled with high feedwater iron concentration. As such the guidance for water chemistry control has been based on these observations [Wells et al., 2016].

Feedwater iron has an indirect impact on radiation fields as higher feedwater iron requires higher DZO injection rates to suppress ^{60}Co incorporation into piping films and may result in higher particulate concentrations of ^{60}Co upon entering a refueling outage. As feedwater iron concentrations continue to reduce across the industry, it is likely that there will be an impact on target FW zinc concentrations. While FW zinc values have stabilized since the mid-2000s, the reactor water zinc concentrations have continued to increase in response to reductions in FW iron [Wells et al., 2016].

The DZO experience in operating BWRs has been extensively reported in previous documents and papers [Cowan & Garcia, 1998; Garcia et al., 2014b].

3.2 Surface Platinum Deposition for Suppression of Radioactive Cobalt Deposition

Chemical decontamination is an effective method to reduce occupational radiation exposure in BWRs when carrying out large-scale tasks such as overhauling primary recirculation pumps. During the chemical decontamination process, the oxides formed on the surface of the stainless steel (SS) piping that incorporate the ^{60}Co are dissolved with reductive and oxidative chemical reagents. The SS base metal of the piping is exposed to reactor water after the chemical decontamination and the growth rate of the oxide film that incorporates the ^{60}Co of the piping during plant operation just after the decontamination is higher than that just before it. Hence, there is a possibility that the deposition amount of ^{60}Co on the piping just after decontamination is higher than that just before the chemical decontamination. Therefore, a Pt coating (Pt-C) process was developed to lower the surface recontamination by ^{60}Co after the chemical decontamination. In the Pt-C process, a Pt layer is formed in an aqueous solution on the SS base metal of the piping using sodium hexahydroxyplatinate (IV) and hydrazine. In this study, the authors report the suppression effect of ^{60}Co deposition by Pt-C technology and confirmation of Pt-C process using 1:20 scale mock-up test as shown in Figure 3-1. The amount of Pt formation increased with increasing immersion time and reached about 1.5 μg/cm^2 after 4 h formation. The amount of ^{60}Co deposition with Pt-C specimens is about 20 % that of non-coated specimens [Kawasaki et al., 2016].

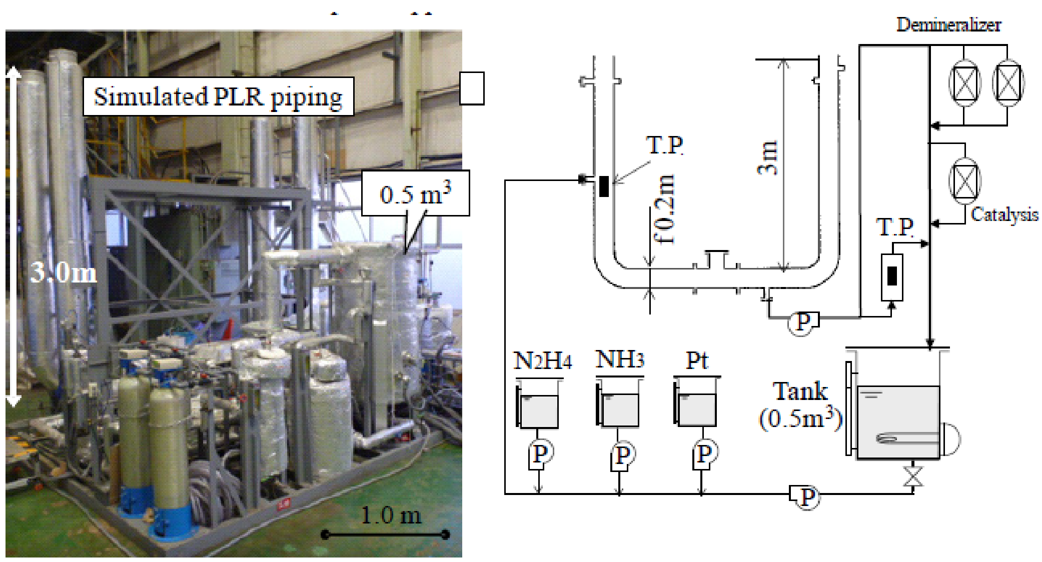

Figure 3-1: A schematic diagram and a photo of the 1:20 scale mock-up test loop apparatus [Kawasaki et al., 2016].

Figure 3-2 shows the immersion time dependency of Pt deposition amount. The amount of Pt deposit increased with increasing immersion time and reached about 1.5 μg/cm^2 Pt loading after 4 hours of immersion. In a previous report [Hosokawa et al., 2014], confirmed that even 0.1 μg/cm^2 of Pt loading amount is sufficient to suppress ^{60}Co deposition on 316SS.

4 IGSCC Mitigation and Life Management of BWRs

Environmentally-assisted cracking (EAC) of recirculation system piping and reactor internals has been, and continues to be, one of the most critical operational concerns of all water chemistry issues that impact BWR plant availability and capacity factors. The cracking mechanisms typically require a combination of inherent material properties, various stresses on that material, and the water chemistry environment in contact with the material. Over the last 35 years significant chemistry control changes have been made to reduce the frequency of, or to mitigate cracking. The chemistry regimes include the transitions from the original BWR regime of Normal Water Chemistry (NWC), followed by Hydrogen Water Chemistry and moderate Hydrogen Water Chemistry (HWC-M), original (classic) Noble Metal Chemical Application (NMCA), On-line NobleChem™ (OLNC), and Low-Temperature NobleChem™ (applied to recirculation piping surfaces) [Wells et al, 2016].

BWRs were originally designed to operate with pure-water chemistry where the chemistry is dominated by the radiolysis reactions. Water purity is largely controlled by only condensate polishing and reactor water cleanup. It was recognized in the 1970s that the residual concentration of oxidizing species (after most hydrogen and oxygen from radiolysis is carried over in the steam) contributes to crack initiation and propagation, therefore, HWC and HWC-M (depending on the dissolved hydrogen concentration in the feedwater) was introduced to reduce oxidant concentrations. However, it was realized that the reducing conditions from the elevated hydrogen concentrations lead to a problematic increase in main steam line dose rates due to increases of N-16 from the conversion of soluble nitrates to volatile nitrogen species under HWC. In order to reduce the required concentration of hydrogen and therefore lower main steam line dose rates, the addition of noble metals was introduced [Hettiarachchi et al, 1995]. The application of noble metals to the reactor wetted surfaces (either the initial NMCA technology based on Pt and Rh or the current generation OLNC and Low-Temperature NobleChem™ based on only Pt addition) is based on the catalytic reduction of oxidants on noble metal treated surfaces in the presence of hydrogen. Noble Metal Technology has been widely adopted in the BWR industry and most plants currently operate in one of these regimes with the majority now operating with OLNC [Wells et al, 2016].

The transitions and changes to BWR chemistry regimes have also had an impact on other BWR water chemistry operational issues. For radiation buildup on recirculation system piping and other out-of-core surfaces, the controlling parameter is typically the concentration of soluble ^{60}Co in reactor water during power operation. This isotope is responsible for greater than 90% of the personnel occupational radiation exposure incurred during refueling outages. This controlling parameter is applicable to all water chemistry regimes. Low ECP can convert stable hematite iron oxides to magnetite spinel oxides. If this transition occurs in the presence of a large concentration of ^{60}Co, it can quickly be incorporated into the new oxide surfaces and greatly increase radiation fields. Conversely, if the transition occurs in the presence of zinc or other non-activated species, reduction in radiation fields occur [Wells et al, 2016].

4.1 IGSCC Mitigation Monitoring Results at BWRs Following Noble Metal Treatment

Effective implementation of NMCA, in which a catalyst is applied on BWR internal surfaces require the noble metal mass loading analysis of coupons in an external sampling system. This is an approach to monitor deposition and durability accepted by the U.S. regulator as a basis to apply lower crack propagation rates for flaw evaluations or to extend inspection intervals for certain components. However, the same external deposition monitoring approach with OLNC has shown lower than expected catalyst mass loading. Consequently, the BWRVIP initiated several projects to collect data to assess the effectiveness of the OLNC process in operating BWRs [Garcia et al, 2016d]. This paper summarizes some of that data including both Pt mass loading as well as ECP monitoring of internal and external locations to prove the presence of adequate Pt catalyst on BWR internal surfaces for crack mitigation.

4.1.1 Types of Measurements

Coupons are periodically removed for surface noble metal deposition analysis after being exposed to a reactor coolant sample stream for varying amounts of times. At most plants, coupons have been installed in external Mitigation Monitoring System (MMS) skids, which receive flow from either the reactor water cleanup (RWCU) inlet or a reactor recirculation loop. One BWR-6 plant monitors coupons installed in a backup deposition monitoring system, which receives reactor coolant sample flow from the discharge of a reactor recirculation pump. Coupons have been analyzed by three separate institutions by acid stripping the oxide and analyzing the resulting solution by inductively coupled plasma – mass spectrometry (ICP-MS). In one facility, noble metal deposits are removed from coupons using a laser ablation (LA) technique and the noble metal is analyzed by ICP-MS [Garcia et al, 2016d].

A sampling tool developed by the BWRVIP is used to obtain loosely adherent and more tightly adherent deposit samples from reactor internal surfaces while in the reactor vessel or from artifacts removed and typically stored in the spent fuel pool. On-site sampling avoids the need to transport component artifacts out of containment and off-site for analysis. The tool uses a telescoping pole to lower a sampling fixture into position near a surface. The sampling fixture employs pneumatically driven paddles to hold the fixture in place while a brush or stone is applied across the sampling surface. The scraping mechanism uses a brush head to collect loosely adherent material and a harder stone head to collect tightly adherent deposits from surfaces. While the scraping is in progress, the surrounding water is pulled into sampling lines and flows through a membrane filter, on which particulate material is collected for later analysis. The filters are then dissolved in aqua regia to prepare the samples for analysis by ICP-MS.

ECP is monitored at most BWRs in the MMS skid, but seven plants have installed ECP probes at internal locations such as a reactor recirculation piping flange, the bottom head drain line (BHDL) and the Local Power Range Monitor (LPRM). ECP monitoring locations used inside the BWR power loop are shown in Figure 4-1 [Garcia et al, 2016d].

5 BWR New Builds and Water Chemistry Guidelines

5.1 UK Advanced Boiling Water Reactor Status

United Kingdom (UK) is planning the construction of an Advanced Boiling Water Reactor (ABWR) that is likely to be commissioned around 2020/2021. The UK ABWR is currently in the detailed design assessment phase [Glover et al, 2016].

Four ABWRs have been in operation in Japan for a number of years, Kashiwazaki Kariwa units 6 and 7, Hamaoka 5 and Shika 2. However, all these units have been shutdown in 2011 following the earthquake and tsunami in Fukushima. Three more ABWRs are under construction in Japan, at Shimane 3, Ohma 1 and Higashidori 1. The construction of two ABWRs in Taiwan, Lungmen 1 & 2 that began about a decade ago, has stalled due to unknown reasons.

The UK ABWR is proposing a 60 year operating life time. Unlike early BWRs, the UK ABWR utilises Reactor Internal Pumps (RIP) in place of external recirculation piping. In addition UK ABWR employs forward pumped heater drains and condensate filter demineralisers, while the reactor water clean-up (RWCU) capacity of the reference design is 2 % of the total reactor water flow. The UK ABWR is currently within Step 4 of Generic Design Assessment (GDA), having completed Step 3 in October 2015. Office for Nuclear Regulation (ONR) inspectors are currently conducting an in-depth assessment of the safety case submissions, with increasing focus on the presented evidence [Glover et al, 2016].

The selected primary water chemistry of the UK ABWR appears to be based on HWC, OLNC and DZO that reduces risks As Low As Reasonably Practicable (ALARP) for operations at power. Assessment is now currently being extended to other phases of operation (e.g. start-up and commissioning), in addition to the impact of related chemistry choices such as iron control options [Glover et al, 2016].

Horizon Nuclear Power, a UK energy company and wholly owned subsidiary of Hitachi Ltd., ia planning to operate two UK ABWRs at the Wylfa Newydd site, on Anglesey in Wales. As prospective operators of the UK ABWR, and like other new nuclear build projects, Horizon's schedule for the licensing process is running in parallel with the GDA process for UK ABWR. ONR requires Horizon to demonstrate that it is fully in control of activities on the Wylfa Newydd site, to demonstrate sufficient knowledge of the UK ABWR plant design and safety case for all operations on the licensed site; including a demonstration that Horizon has sufficient competent resource within its organisation to act as an 'intelligent customer' for any work it commissions externally [Glover et al, 2016].

ONR is focused on the following broad areas of organisational capability relating to chemistry with respect to the UK ABWR new build [Glover et al, 2016].

- ONR expect Horizon to develop a strategy to outline how the chemistry function will be developed, with the expectation that this function will ultimately evolve to the point where it is capable of delivering all of the safety related functions necessary to control the operating chemistry in the future.
- ONR expect Horizon to show that it has designed a chemistry function that can deliver this strategy. This includes identification of roles, responsibilities, specific suitably qualified and experience persons (SQEP) requirements and details of the 'intelligent customer' function.
- ONR expect Horizon to develop a chemistry work plan to set out the work that needs to be undertaken prior to licence application and granting, but also include a longer term plan post license granting including a schedule of deliverables.

Following are the details expected from a chemistry perspective [Glover et al, 2016]:

- The scope of chemistry is broad, interacting with other disciplines, and this needs to be reflected. All chemistry related hazards should be considered, and ONR may choose to sample chemistry outside of the operating chemistry of the reactor, including where chemistry is claimed as a mitigation during accidents.

- Following third-party operating chemistry guidelines for generic reactor types does not in itself constitute an adequate safety case. While these may be a relevant input, they need to be specific to the design and safety case.
- Whatever chemistry is claimed, it needs to be consistent throughout the safety case.
- Risks associated with chemistry need to be demonstrated to be ALARP, particularly where changing parameters to reduce one hazard increases another (e.g. balancing the effects on fuel, materials, doses, radioactive waste etc.)
- The safety case should clearly define what chemistry limits and conditions are necessary to safely operate the reactor; under all conditions it may operate (e.g. start-up, shutdown, operations etc.). The engineered systems should be demonstrated to be adequate to maintain the chemistry within these limits.

5.1.1 Browns Ferry Unit 1 Start-up 22 Years After Shut Down

Even though Browns Ferry Unit 1 (BF1) is not a new plant, it has gone through many of the evolutions that a new plant goes through since its start-up after 22 years of shut down. Hence, it is appropriate to look at the water chemistry responses during its start-up phase that might be of use to many of the new plants.

Tennessee Valley Authority (TVA) restarted BF1 in 2007 following a 22 year shutdown due to a significant fire in safety related equipment. Due to the long outage period, TVA had the opportunity to implement advanced technologies where they deemed appropriate. Source term elimination was an important part of the restart effort in order to lower expected dose rates due to cobalt activation. Actions taken included: recirculation pipe replacement, electro polishing surfaces, provide a stabilized chromium film and pre-oxidize the surfaces, replacement of stellite surfaces, condenser tubing change out, ultra-sonically clean already used fuel assemblies and change to depleted zinc oxide addition. Water chemistry trends and information from the BF1 restart will prove to be a valuable resource in 2016 as many Japanese Boiling Water Reactors (BWRs) are preparing to restart following extended shutdowns and new Advance Boiling Water Reactors (ABWRs) are either preparing for initial startup up or will be shortly. This paper will describe the water chemistry results of BF1's 2007 restart as well as data generated during the subsequent cycles of operation. Some information will be provided regarding system specifics including reactor water clean-up (RWCU), condensate systems, feedwater and other important chemistry systems. This information will provide valuable insight and lessons learned to plants that are planning a restart from extended outage period or new plants that are considering the early adoption of advanced dose control and stress corrosion cracking mitigation technologies [Odell et al, 2016a].

Following a plant fire in 1985 all three Browns Ferry units were shutdown indefinitely. Repairs and upgrades were made to Browns Ferry 2 and 3 and those units were restarted in 1991 and 1995 respectively. BF1 was brought back into service in 2007 and represents the most recent and modern BWR start-up and is the closest comparison to a new plant start-up in the US since the late 1980s. Over the ~20 year period from the last new plant start-up, the operating chemistry has evolved as have materials and operating practices. The BF1 data provides information on the plant response to the modern chemistry regime and is an important data set to evaluate as part of a new plant design process [Odell et al, 2016a].

Prior to restart, BF1 completed system and component upgrades to ensure radiation exposure was as low as reasonable achievable (ALARA). These activities included reducing cobalt bearing materials, replacing primary system piping followed by electropolishing and pre-oxidizing to minimize deposition of radionuclides, replacing stellite components, changing condenser material from admiralty brass to 304 stainless steel, as well as ultra-sonic fuel cleaning for fuel that was previously used and reloaded prior to the restart [Kohlman et al, 2011].

6 BWR Scientific Studies

6.1 ECP, SCC and Corrosion Related Studies

A number of basic scientific studies on ECP and SCC have been performed under both in-pile and out of pile conditions with a variety of BWR materials under a variety of water chemistry conditions.

6.1.1 Out of Pile laboratory ECP data and corrosion studies

A paper from Taiwan investigated the ECP response and corrosion currents (using polarization curves) of oxidized 304 SS and Pt treated oxidized SS in the presence of 100 and 300 ppb H_2O_2. Pt treatment was performed at 90°C and 150°C using $Na_2Pt(OH)_6$ with 100 ppb Pt [Yuan et al, 2016], much higher (two to three orders of magnitude higher) than typically used with OLNC. The Pt treatments were also done at lower temperatures of 90°C and 150°C as opposed to the BWR operating temperatures in the range of 280 to 285°C. The authors also have not described how the corrosion current density was evaluated. If an IR correction was not made when extrapolating Tafel plots to obtain the corrosion current density (no mention of IR compensation is made in the paper), the corrosion currents could have some serious errors. Hence the data from this study cannot be directly applied to understand or interpret the operating BWR plant data that have applied NMCA or OLNC.

A summary of the data obtained with Pt treatment performed at 150C is shown in Table 6-1.

Table 6-1. ECP and corrosion current density data for 150°C Pt coating and prefilmed specimens [Yuan et al, 2016].

Specimen	Temperature(°C)	H_2O_2(ppb)	ECP(mV_{SHE})	i_{corr}($\mu A/cm^2$)
Prefilm	288	100	131.85	1.41
		300	168.15	1.37
150℃ Pt coating	288	100	169.25	4.93
		300	202.65	4.63
Prefilm	250	100	152.25	2.83
		300	156.95	1.33
150℃ Pt coating	250	100	180.75	19.55
		300	189.05	2.42
Prefilm	200	100	115.95	1.08
		300	131.45	2.24
150℃ Pt coating	200	100	162.36	4.81
		300	167.85	17.33

The authors have made the general statement that, the ECP and i_{corr} of Pt coated specimens were higher than the prefilmed ones in the presence of hydrogen peroxide. However, the actual BWR plant data are in conflict with this statement, where the ECP of pure Pt was shown to be lower under NWC conditions (i.e. in the presence of both O_2 and H_2O_2) compared to those under HWC conditions [Hettiarachchi et al, 1998]. Furthermore, the plants that have applied NMCA/OLNC and measured crack growth rate of shroud ID cracks and monitored stub tube leaks in the lower plenum showed indications of crack mitigation. These plants have periodically gone through HWC/NWC transients during their operational fuel cycles, but have still shown crack mitigation [Hettiarachchi, 2009].

6.1.2 In Pile ECP Data

A paper from Japan calculated ECP through the combination of water radiolysis and an ECP model. A water radiolysis model had been applied to experiments performed in in-pile loops in the experimental reactors and applicability was confirmed. An ECP model based on the Butler-Volmer equation was also prepared. ECP of stainless steel was measured under well controlled water chemistry condition in in-pile loop in the Halden reactor, and the model was applied to evaluate ECP measured in the Halden reactor. The measured data were well explained by the water radiolysis and ECP calculations. Accumulation of in-pile ECP data are expected for further validation of the models [Hanawa et al, 2016a].

ECP of oxidized stainless steel was measured at the Halden reactor at BWR operating conditions using Fe/Fe_3O_4 based ZrO_2 electrode and a Pt electrode under both oxidizing and reducing conditions. A water radiolysis model was used to calculate the radiolytic species (both oxidizing and reducing) generation under in pile conditions. According to the calculation model, contents of O_2, H_2, H_2O_2 and other radicals was calculated along with the water flow [Hanawa et al, 2016a].

The ECP was calculated using a mixed potential model, with the metal dissolution reaction and the oxidation of hydrogen as anodic reactions and the reduction of oxygen and hydrogen as the cathodic reactions.

Figure 6-1 shows a comparison of measured and calculated ECP data plotted against O_2 and H_2O_2 concentrations. The data agrees well with previously reported data [Uchida et al, 1997] & [Wada et al, 2009].

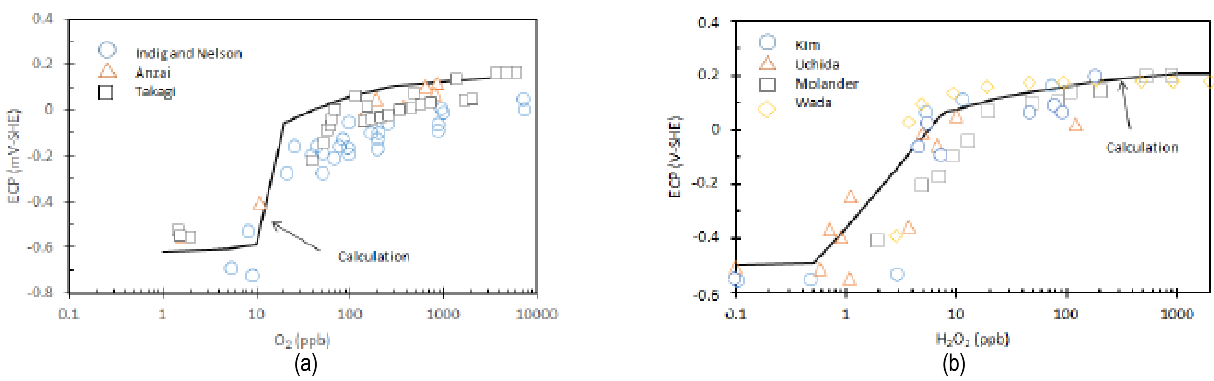

Figure 6-1: Comparison between the measured and calculated ECP against (a) O_2 [Uchida et al, 1997] and (b) H_2O_2 concentration [Wada et al, 2009].

Figure 6-2 shows the comparison between the measured and calculated ECP values. As shown in the Figure, calculated ECPs were about 100 mV higher than the experimental values in the case of O_2 injected conditions, while good agreement was observed in the case of H_2 injected conditions. Based on this comparison, the ECP calculation model applied in this study is reasonably applicable to in-pile ECP measurements [Hanawa et al, 2016a].

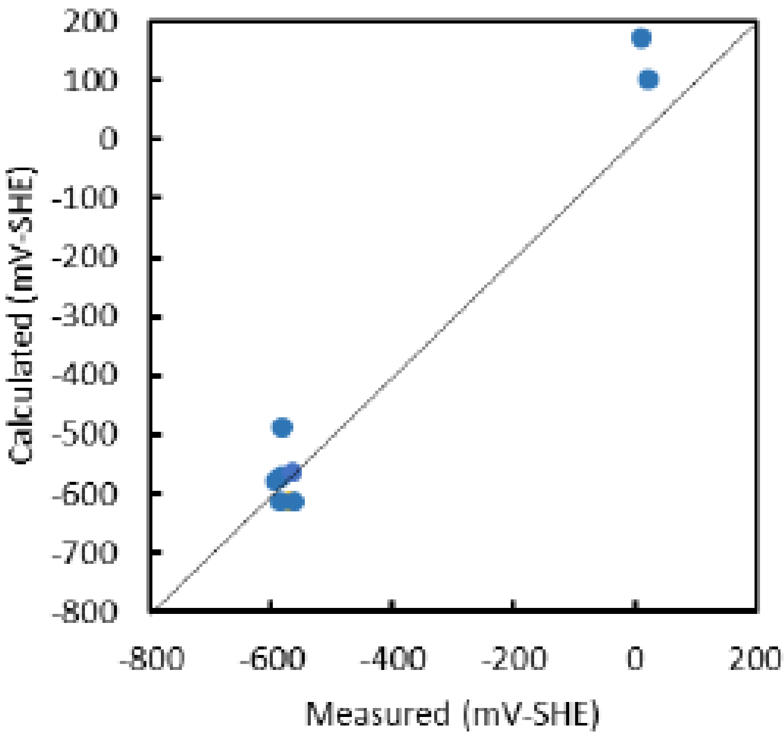

Figure 6-2: Comparison between the measured and calculated ECP under in-pile conditions [Hanawa et al, 2016a].

Another paper from Japan, proposed an ECP evaluation model introducing irradiation-induced diffusion in the oxide layer to simulate neutron irradiation effect, and predicted with this model that ECP begins to decrease from the neutron flux of about $1x10^{14}n/m^2/s$ and the decrease is about 150 mV(SHE) at the neutron flux of about $1x10^{18}n/m^2/s$ as a result of increase in anodic current density by neutron irradiation. The Japan Materials Testing Reactor (JMTR) that has in-pile loops for water chemistry experiments was used for this investigation [Hanawa et al, 2016b].

Irradiation effect on ECP in the irradiation field of the JMTR was preliminary investigated using the ECP model. ECP in the irradiation field becomes constant at about 140 mV(SHE) along the vertical direction of the irradiation capsule due to the existence of oxidizing species in the case of without neutron irradiation effect, while ECP decreased depending on the fast neutron flux by the increase of electronic conductivity of oxide film in the case with neutron irradiation effect. The predicted ECP decrease is less than 100 mV in irradiation hole in the JMTR core, but this decrease is detectable by direct ECP measurement [Hanawa et al, 2016b].

6.1.3 SCC Related Studies

For a better understanding toward stress corrosion cracking (SCC) in dissimilar metal welds with 316L stainless steel and Alloy 52, the SCC growth behaviour in the transition regions of weld joints was investigated via slow strain rate tensile (SSRT) tests in 288 °C pure water with a dissolved oxygen level of 300 ppb. Prior to the SSRT tests, samples with dissimilar metal welds were prepared and underwent various pretreatments, including post-weld heat treatment (PWHT) and solution annealing [Chen et al, 2016].

The fracture occurred at the base metal of 316L SS, which indicated that the residual stress, especially tensile stress, had little impact on the SCC behaviour in this study. The fracture surface of post-weld heat treated (550°C, 48hrs) sample exhibited transgranular SCC initiation from two sites on the edge. While the morphology of the solution annealed and the as-received dissimilar metal weld sample consisted of a large number of dimples which represented ductile fracture on the surface [Chen et al, 2016].

7 Fukushima Event and Recovery Status

On March 11, 2011, north-eastern Japan experienced a series of huge earthquakes and resulting tsunami, in which, social infrastructures including life lines and logistics were heavily damaged. A severe accident at the Fukushima Daiichi Nuclear Power Plant (NPP) from a station blackout (SBO) due to the unexpected huge tsunami resulted in core meltdowns, leakage of the primary containment vessels (PCVs), destruction of the reactor buildings due to hydrogen explosions, and the release of totally about 600 PBq of radioactive fission products (FPs) into the environment [Katsumura & Uchida, 2016].

Almost all of the fossil fuel power plants (FPPs) and NPPs along the northern Pacific coast of Japan experienced some damage to varying extents. 65% of the FPPs along the northern Pacific coast were restarted within a half year after the disaster and more than 100 % of FPPs supplied electricity in a couple of years, while NPPs in the area, including the Fukushima Daiichi NPP remained shut down.

Currently only two PWRs in Japan (Sendai 1 & 2) are in operation which meets the new regulation requirement, that requested the plant utilities to secure sufficient safety margins against the defence in depth [Katsumura & Uchida, 2016].

Many efforts have been made at the Fukushima Daiichi NPP to achieve stable cooling of the reactors and fuel pools and mitigation of further release of radioactive materials into the environment based on utility operator's roadmap toward recovery from the accident. As a result of continuous efforts, the release of the contaminated water into the environment was prevented and the radioactive materials removed from the contaminated water. The treated water containing small amount of tritium is stored in the plant [Katsumura & Uchida, 2016].

7.1 Latest Status of Nuclear Power Plants in Japan

Figure 7-1 shows the status of nuclear power plants in Japan (Note that only Sendai 1 & 2 PWRs are operating as of October 2016).

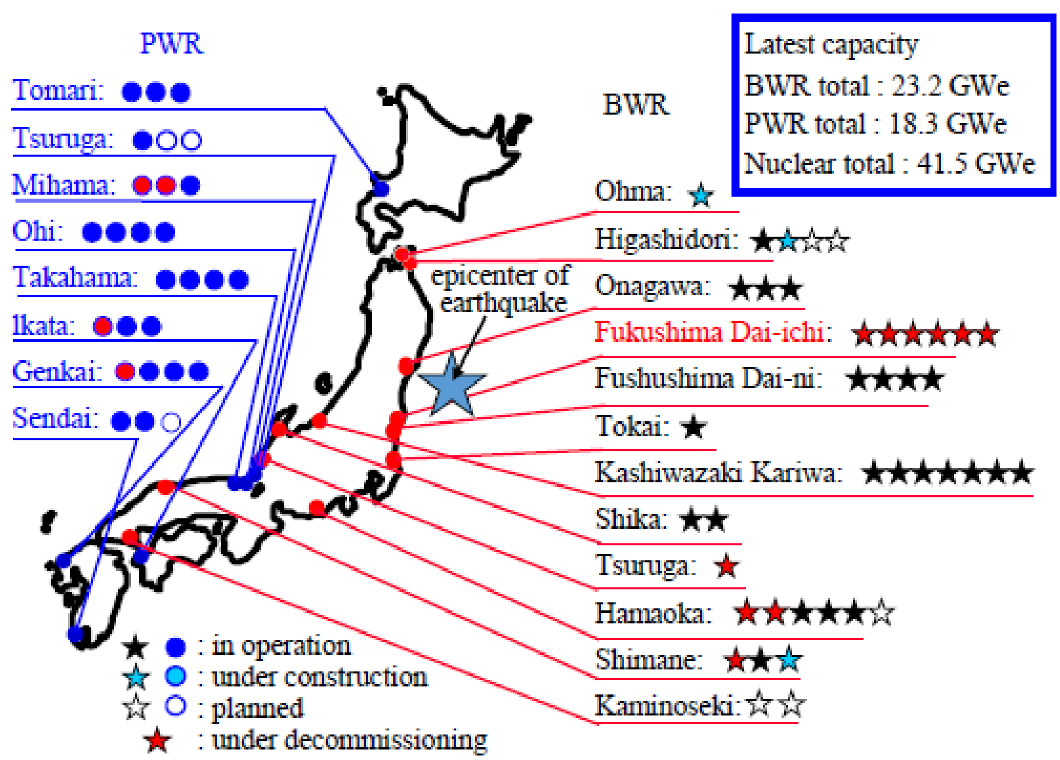

Figure 7-1: Map showing location of Japanese light water reactors [Katsumura & Uchida, 2016]. **NOTE** : As of October 2016, only Sendai 1 & 2 (PWRs) are operating.

At the time of the earthquake, 11 of 15 BWRs along the Northern Pacific Coast which were operating were scrammed to shut down. The situation of the BWR fleet along the Northern Pacific Coast is shown in Table 7-1.

7.2 Response to the Fukushima Daiichi NPP Accident

Figure 7-2 shows a multi-layered defense in depth safety measures chart that came from the investigation committee of the atomic energy society of Japan (AESJ) that reviewed the nuclear accident at the Fukushima Daiichi NPP. It was concluded that suitable countermeasures against Defense in Depth level 4 are necessary to avoid severe accidents. To achieve this, not only it is necessary to have suitable hardware for plant safety but also suitable manuals for emergency operations and sufficient training for the engineers [Katsumura & Uchida, 2016].

For levels 1-3, plants are protected by hard wares, while for level 4 plant safety should be supported not only by hard ware but also software and accident management approaches. This would include manuals addressing loss of hard ware and training of personnel for optimal behaviour under anomalous situations (Table 7-2). Even if the plant is under severe accident conditions, all effort should be focused on mitigation of radioactivity release into the environment based on the accident management procedures, described in the manuals that contain suitable countermeasures and training of personnel for rapid actions under critical conditions [Katsumura & Uchida, 2016].

Table 7-1. Status of Japan's Pacific coast NPPs after the earthquake and tsunami [Katsumura & Uchida, 2016].

Plant [tsunami height]	Units	Type	Power (MWe) [operational mode]	Earthquake scram	EPS	ACPS after tsunami	Latest status
Fukushima Dai-ichi [14-15 m]	No.1	BWR3	460 [OP]	O	all lost	all lost	core melt, H_2 explosion
	No.2	BWR4	784 [OP]	O	all lost	all lost	core melt
	No.3	BWR4	784 [OP]	O	all lost	all lost	core melt, H_2 explosion
	No.4	BWR4	784 [SD]	-	all lost	all lost	H_2 explosion affected by No.3
	No.5	BWR4	784 [SD]	-	all lost	all lost	CSD
	No.6	BWR5	1100 [SD]	-	all lost	1/3 EDGs on	CSD
Fukushima Dai-ni [14-15 m]	No.1	BWR5	1100 [OP]	O	all lost	3/3 EDGs on	CSD
	No.2	BWR5	1100 [OP]	O	all lost	3/3 EDGs on	CSD
	No.3	BWR5	1100 [OP]	O	all lost	3/3 EDGs on	CSD
	No.4	BWR5	1100 [OP]	O	all lost	3/3 EDGs on	CSD
Onagawa [~13 m]	No.1	BWR4	524 [OP]	O	1/5 line on	2/2 EDGs on	CSD
	No.2	BWR4	825 [OP*]	O	but lost in	2/2 EDGs on	CSD
	No.3	BWR4	825 [OP]	O	30 min	2/2 EDGs on	CSD
Higashidori [~10 m]	No.1	BWR5	1100 [SD]	-		2/2 EDGs on	CSD
Tokai Dai-ni [~5.4 m]	No.2	BWR5	1100 [OP]	O	all lost	1/2 EDGs on	CSD

EPS: external power supply, ACPS: AC power supply, OP: in operation,
SD: shutdown, CSD: cold shutdown, OP*: started

8 Conclusions

This report is a compiled summary of BWR papers (both oral and poster papers) presented at the NPC 2016 conference that was held in Brighton, UK, from October 1-6, 2016. It was the 20th conference in the series of "Nuclear Power Plant Chemistry" that began in Bournemouth in 1977 and is now held every other year in Europe, Asia or the United States of America. The next conference will be held in San Francisco, California, USA in 2018.

The present report summarizes critical BWR water chemistry related papers addressing a variety of topics including, BWR plant operating experiences, dose rates and radiation control, IGSCC mitigation and noble metal related topics, BWR new builds and related topics, BWR scientific studies, and Fukushima Daiichi NPP recovery status. The plant operating experiences section also includes fuel and modelling related papers as well.

The BWR plant operating experiences section, dose rate and radiation control section, and the BWR scientific studies section have an extensive coverage because of the large number of papers presented on these topics. Majority of papers in the BWR scientific studies section were poster papers. Many of these papers were on specific individual topics that helped improve scientific understanding of those specialized areas.

The coverage of papers relating to Fukushima NPP event is also somewhat detailed because it is the view of the author of this report that dissemination of knowledge base gained and resolutions achieved relating to severe accidents in nuclear power plants is crucial to the BWR owners, regulators, chemists and technologists to proactively plan adequate measures needed for safe operation of nuclear power plants. It is important to note that the situation faced by Fukushima Daiichi NPP is unprecedented because of the inability to operate the reactor core cooling systems as the pumps became inoperable due to flooding of the pump rooms, and the diesel generators became inoperable for the same reason as well. Circumventing these events are not easy as they need planning "beyond the design basis" which is always a tough task. This part of the report also summarizes the time line for decommissioning of the Fukushima Daiichi NPPs along with the activities in progress towards achieving that goal.

The report also provides a short summary of the US response to Fukushima Daiichi NPP event and actions taken for future safe operation of nuclear power plants in the US.

The major points of the NPC-2016 BWR related papers are presented and compared in this report along with the author's views and impressions where appropriate.

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Nomenclature

ABWR	Advanced Boiling Water Reactor
AC	Alternating Current
AESJ	Atomic Energy Society of Japan
AL	Action Level
ALARP	As Low As Reasonable Practicable
AREVA	French Equipment Manufacturer
ARCS	Advanced Resin Cleaning System
BF	Browns Ferry
BHDL	Bottom Head Drain Line
BRAC	BWR Radiation Assessment Control
BWR	Boiling Water Reactor
BWRVIP	Boiling Water Reactor Vessels and Internals Program
CCU	Condensate Clean Up
CER	Contact Electrical Resistance
COLA	Combined Operating License Application
CAMS	Containment Atmospheric Monitoring System
CR	Control Rod
CRB	Control Rod Blade
CS	Carbon Steel
CST	Crystalline Silico-Titanates
CUW	Clean-up Water
DTE	Detroit Edison Electric Company
DZO	Depleted Zinc Oxide
EAC	Environmentally Assisted Cracking
EDM	Electro Discharge Machining
ECP	Electrochemical Corrosion Potential
EDS	Energy Dispersive Spectroscopy
EDX	Energy Dispersive X-Ray
EFPY	Effective Full Power Years
EPRI	Electric Power Research Institute
ESBWR	Economic Simplified Boiling Water Reactor
FAC	Flow Accelerated Corrosion
F/D	Filter Demineralizer
FLEX	Flexible Safety Enhancements
FIB	Focused Ion Beam
FP	Fission Products
FPP	Fossil Power Plant
FW	Feed Water
GE	General Electric
GDA	Generic Design Assessment
HBWR	Halden Boiling Water Reactor
HES	Health, Environment and Safety
HFT	Hot Functional Test
HS-AFM	High Speed Atomic Force Microscope
HTI	High Temperature Incinerator
HWC	Hydrogen Water Chemistry
HWC-M	Moderate Hydrogen Water Chemistry
IASCC	Irradiation Assisted Stress Corrosion Cracking
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICPMS	Inductively Coupled Plasma Mass Spectrometry
ID	Inner Diameter
IGSCC	Intergranular Stress Corrosion Cracking
JMTR	Japan Materials Testing Reactor
KK	Kashiwazaki Kariwa
KKL	Kernkraftwerk Leibstadt
LA	Laser Ablation

Unit conversion

TEMPERATURE		
°C + 273.15 = K		°C × 1.8 + 32 = °F
T(K)	T(°C)	T(°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	= 3.7×10^{10} Bq = 37 GBq
1 Bq	= 1 s^{-1}

MASS	
kg	lbs
0.454	**1**
1	2.20

DISTANCE	
x (µm)	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√m	ksi√inch
0.91	**1**
1	1.10