Key Emerging Issues and Recent Progress Related to Plant Chemistry/Corrosion in BWR Reactors

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Contents

1 Introduction

The NPC 2014 conference was held in Sapporo, Japan, from October 26-31, 2014. It was the 19th 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 and America. The next conference will be held in Brighton, UK, from October 1-6, 2016. The 2018 conference will be held in San Francisco, California, USA.

The NPC 2014 conference report is divided into two parts:

- The part relating to PWR, VVER CANDU and HPWR reactors is covered by Francis Nordmann in a separate report. The report covers topics such as type of reactors, their maintenance, fuel, future trends, auxiliary systems, wastes, etc. The total number of papers covered by the report is 122.

- The present report covers BWRs, addressing a variety of topics including, water chemistry optimization and management, BWR operating experiences, water chemistry and its impact on fuel performance, life time maintenance and plant aging, water chemistry scientific studies, and last but not the least the Fukushima Daiichi NPP accident related papers and recovery efforts. This report covers a total of 105 papers.

Both reports are intended to cover key topics of the conference that would be of use to Utility personnel, R&D personnel, vendors and Regulators. The key points of the NPC-2014 BWR related papers are presented and compared in this report along with the author's views and impressions where appropriate.

The conference had 12 oral sessions and a special session dedicated to Fukushima NPP events and recovery efforts, covering 68 and 24 papers respectively. The poster sessions had a total of 152 papers including 22 relating to Fukushima NPPs. The total number of papers is 244 with 227 written papers included in the CD-ROM.

After the opening remarks, three keynote lectures were delivered by lead scientists from USA, France and Japan giving their country's perspectives on the reactor performances and their current status.

The technical material relating to BWRs in the keynote lectures as well as material from other BWR related papers are presented and discussed in the subsequent chapters.

2 BWR water chemistry optimization, compliance management and status

2.1 BWR water chemistry improvements - overview

The keynote paper from the US recognized the importance of proper chemistry control and the value in understanding the relationship between chemistry guidance and actual operating experience [Fruzzetti et al, 2014a]. He mentioned that EPRI continues to collect, monitor, and evaluate operating data from BWRs and PWRs around the world. Operating BWR chemistry data have been collected on-line during start-up and shut down for more than 20 years.

The paper provided an overview of current trends in BWR chemistry, focusing on plants in the U.S. Important chemistry parameters were highlighted and discussed in the context of the EPRI Water Chemistry Guidelines requirements that included key topics such as materials integrity, fuel integrity and plant radiation field reduction.

The paper highlighted the evolution of BWR water chemistry improvements including the implementation of hydrogen water chemistry (HWC) to lower the electrochemical corrosion potential (ECP), for the purpose of mitigating inter-granular stress corrosion cracking (IGSCC) of reactor piping and internals. In 1986, the first U.S. BWR implemented zinc addition for the purpose of reducing plant radiation fields. Noble metal chemical application (NMCA – addition of solutions of $Na_2Pt(OH)_6$ and $Na_3Rh(NO_2)_6$) was first implemented (in the U.S.) in 1996 as the strategy to reduce the amount of feed water hydrogen required to establish the ECP needed for mitigation of IGSCC (≤ 0.4ppm instead of 1-2ppm in the feed water). This was important to markedly reduce dose impacts caused by N-16 as a consequence of moderate hydrogen water chemistry (HWC-M). In 2005, on-line NobleChem™ (OLNC) was first implemented so that smaller amounts of the catalytic material ($Na_2Pt(OH)_6$ only) could be added on-line to reduce the critical path impact during the outage as often required with conventional NMCA. More recently, a cobalt sequestration resin (CoSeq®) has been developed by EPRI as a technology to more effectively remove ionic cobalt from process streams.

The author reported that EPRI has a Chemistry Monitoring and Assessment (CMA) data base that contains data from all 35 operating U.S. BWRs and 15 non-U.S. BWRs.
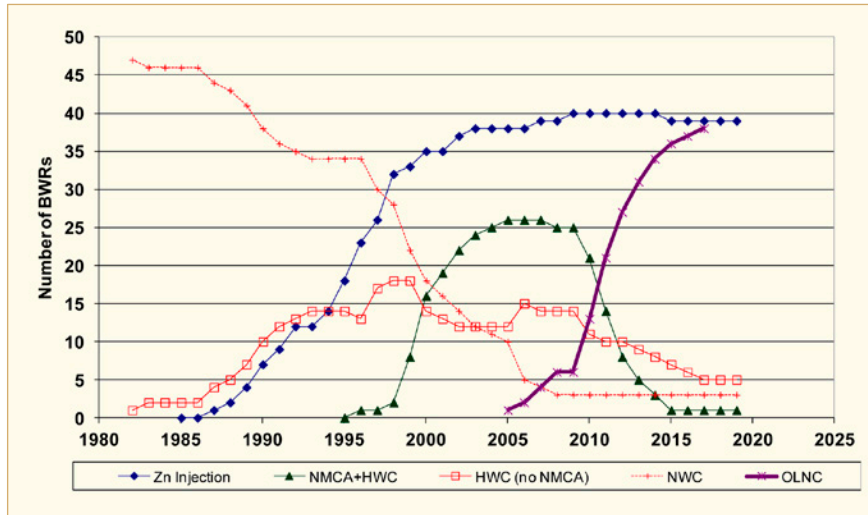
Figure 2-1 shows the application evolution of several different chemistry technologies for 48 different BWRs over the past several decades. All U.S. BWRs were injecting hydrogen as of 2004. Hydrogen availability has increased significantly in the U.S., recently averaging about 98%. Early hydrogen water chemistry (i.e., hydrogen addition when the reactor water reaches 200°F (93.3°C)) continues to be an important area of development. Since the first OLNC application in 2005 at the Mühleberg BWR in Switzerland followed by the first US BWR OLNC application, the number of plants operating with OLNC+HWC has increased dramatically. Zinc continues to be used at all BWRs in the U.S., and has been effective in reducing primary system radiation fields, as measured at the BWR Radiation Level Assessment and Control (BRAC) reactor recirculation system (RRS) locations, covering BWRs 2 through BWR 6 designs for all operating chemistry regimes (NWC, HWC-M, NMCA+HWC, and OLNC+HWC).
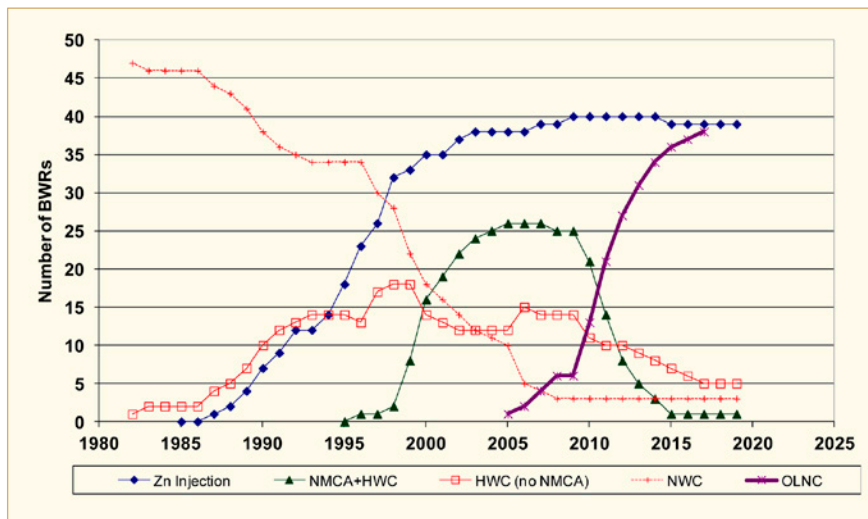
Figure 2-1:   Chemistry program history (NMCA category does not include OLNC) [Fruzzetti et al, 2014a].

2.2   Plant performance

Table 2-1 shows the latest median values for key BWR reactor water, feed water, and hot well parameters from 48 of the 49 BWRs in 2012. Table 2-1 compares the results with Good Practice and Action Level 1 (AL1) values from Reference EPRI Water Chemistry Guidelines. Good Practice values are recommendations for targets that plants may use in optimizing water chemistry in order to balance requirements for material integrity, fuel performance, and radiation control. The AL1 values represent the limit that, if exceeded, may threaten long-term system reliability as indicated by data or engineering judgment, thereby warranting an improvement in operating practices.

2.3   Cobalt sequestration for radiation control

Typically, the concentrations of Co-58 and Co-60 need to be reduced to predetermined levels before workers are allowed to enter containment and begin outage activities such as fuel moves and inspections. The more quickly those levels are reduced, the sooner the work in the containment area can begin and the sooner the plant can return to service.

A cobalt specific resin CoSeq® has been developed to have a very high selectively for cobalt from typical power plant process streams. Laboratory evaluations have repeatedly shown exceptionally high levels of cobalt removal, by a factor of about three over typical ion exchange resins. Figure 2-2 shows the soluble Co-60 removal efficiency calculated from measured bed influent and effluent activity concentrations during power operation at one BWR.

3 BWR operating experiences

3.1 Radiation level reduction in BWRs – Exelon fleet

Several studies have been conducted at Exelon Nuclei's 14 BWRs in order to understand more completely the cause and effect relationships between reactor water radioactive species and radiation levels. Between reactor water radioactive species and radiation levels [Odell & Jarvis, 2014]. Most BWRs have experienced lower BRAC (BWR Radiation Assessment Level and Control) dose rates after On-Line NMCA (OLNC). All Exelon BWRs have made significant progress in removal of cobalt containing materials, such as original equipment manufacturer (OEM) control rod blades (CRBs) containing Stellite™ pins and rollers. The reduction in OEM CRBs at the selected BWRs is shown in Figure 3-1. All original OEM CRBs have been removed at LaSalle 2 and Quad Cities 2 as shown in the Figure.

The resulting dose rate experience of these plants following NMCA is shown Figure 3-2. The dose rates decreased with CRB replacement, increased somewhat after the 2nd NMCA application. But, all dose rates decreased following OLNC except LaSalle 2. The higher dose rate at LaSalle 2 (BWR/5) is attributed to the smaller diameter (51cm) RRS piping having a different geometry compared to other BWRs (BWR/2 through BWR/4) that have larger diameter piping (71cm).
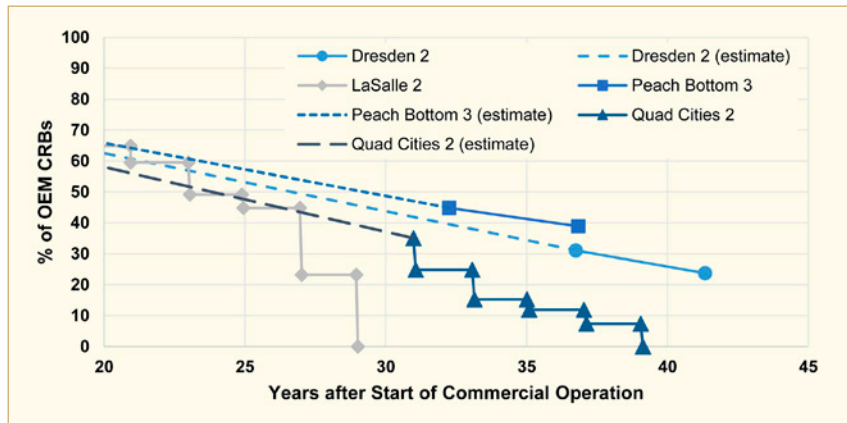
Figure 3-1:   Percent of OEM CRBs in core at selected BWRs [Odell & Jarvis, 2014].
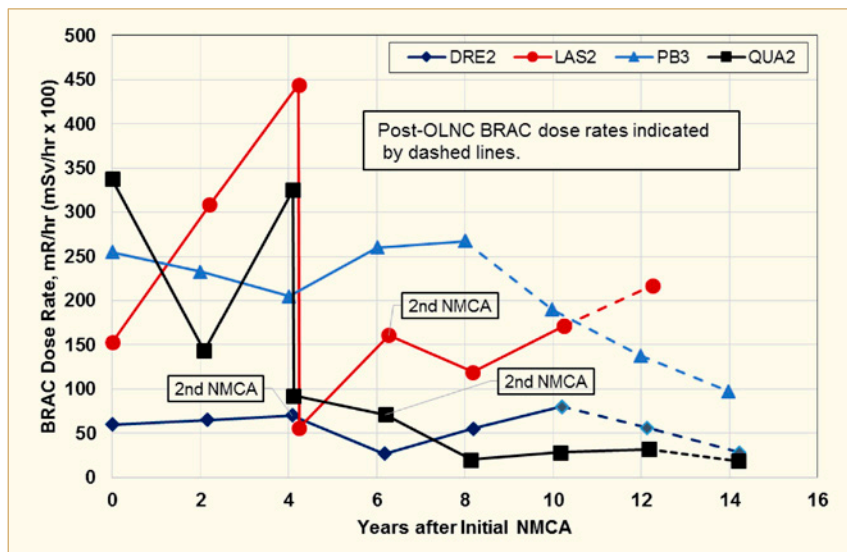
Figure 3-2:   Post-NMCA BRAC dose rate history at selected BWRs [Odell & Jarvis, 2014].

A comparison of the BRAC dose rates at the selected Exelon BWRs with the median BRAC dose rate at all U.S. BWRs having refuelling outages in the same calendar year is shown in Figure 3-3. Since 2001, U.S. BRAC dose rates have been on a decreasing trend. All U.S. BWRs inject depleted zinc oxide (DZO) for control of shutdown radiation fields and operate with HWC or NMCA/OLNC+HWC for mitigation of IGSCC.
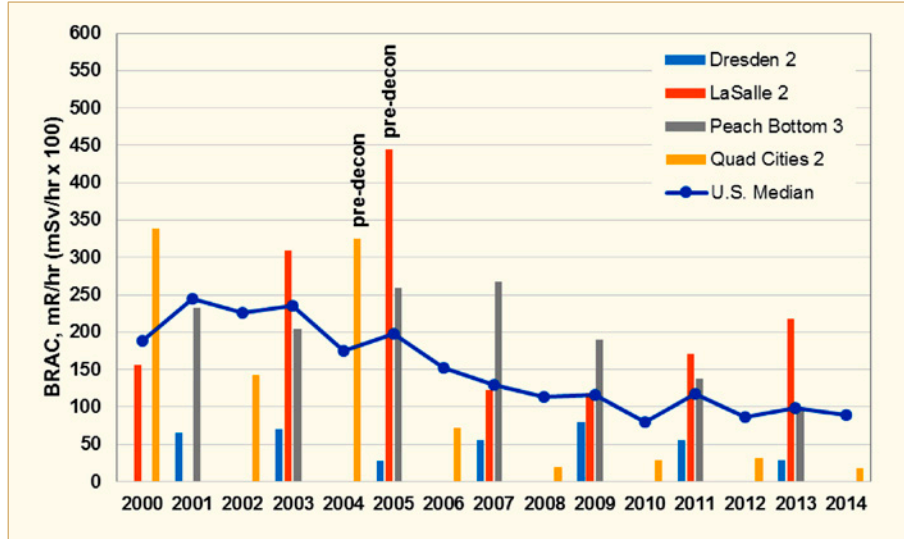
Figure 3-3:   BRAC dose rate comparison of US and Exelon BWRs [Odell & Jarvis, 2014].

All Exelon BWRs inject depleted zinc oxide (DZO) for radiation field control. Zinc injection rates are adjusted based on soluble Co-60 concentrations to maintain the reactor water Co-60(s) to Zn(s) ratio less than 2E-5µCi/ml/ppb. In some cases, feed water zinc concentrations of >0.4ppb (cycle average) or 0.5ppb (quarterly average), are required to meet the ratio when soluble Co-60 is elevated. Assessment of the risk to fuel reliability is considered when increasing feed water zinc above 0.4ppb (cycle average). The reactor water to feed water zinc concentration factor is higher at plants with lower feed water iron [1], allowing the ratio to be met at lower feed water zinc concentrations.

Cycle median reactor water zinc concentrations and BRAC dose rates for Exelon plants are shown in Figure 3-4. Increased reactor water zinc concentrations were the result of increased feed water zinc concentrations in an effort to reduce the reactor water Co-60(s) to Zn(s) ratio for radiation field control. The paper concludes that the relationship between water chemistry, Co-60, feed water iron and feed water zinc are complex factors that are not always easy to understand.
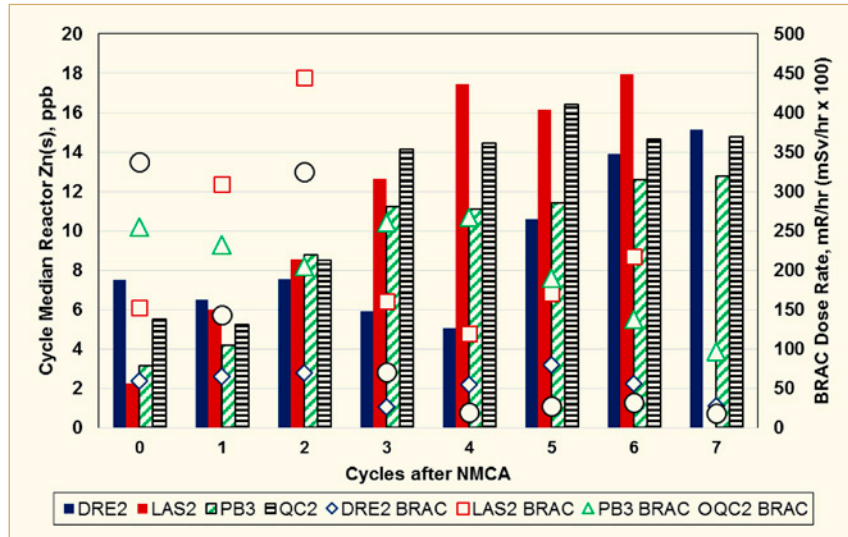
Figure 3-4:   Cycle median reactor water zinc and BRAC dose rates at selected BWRs [Odell & Jarvis, 2014].

3.2   Surface treatment methods for mitigating recontamination

Mitigating recontamination is an approach that can be used to control dose rates in NPPs. This paper describes different surface treatment methods that include, 1) Low temperature NMCA (Pt), 2) Application of a self-assembling monolayer (SAM), and 3) Pt deposition followed by SAM [Stellwag et al, 2014]. Self-assembling monolayers consist of an organic film bonded with surface active substances to the substrate. SAM films make the treated surfaces water repellent. SAM coatings also suppress transport of oxygen and other species to the underlying substrate surface. It was therefore expected that SAM coatings will also decrease the transport of nuclides and reduce dose rate build-up.

These methods were applied to carbon steel surfaces following the decontamination by the CORD CS process. Their effectiveness was tested by installing surface treated tube samples in a BWR that has carbon steel RWCU piping. The results are shown in Figure 3-5. The measured surface gamma activity values of the tube samples after six months of exposure is shown in Figure 3-6. The dominant nuclide in the oxide films is Co-60, followed by Co-58 and Cr-51.

4   Zinc addition and dose reduction in BWRs

A few papers presented in the BWR dose reduction area were covered already in chapters 2 and 3 under water chemistry optimization and compliance management, and BWR operating experiences since discussion of these papers [Fruzzetti et al, 2014a], [Odell & Jarvis, 2014], [Stellwag et al, 2014] and [Garcia et al, 2014a] were more appropriate in those chapters. This chapter will focus more on zinc addition and the impact of other chemistry controls on BWR dose rate reduction. Currently, all US BWRs, the two Swiss BWRs, the two Spanish BWRs, the two Mexican BWRs and one Swedish BWR are implementing zinc addition as depleted zinc oxide (DZO) in order to control dose rates. Several Japanese BWRs also implemented zinc addition at low concentrations before they were shut down and before the Fukushima event.

The benefits of BWR feed water zinc injection were first identified by General Electric in the early 1980s, when it was recognized that BWRs with condensate filter/demineralizers (CF/Ds) and admiralty brass main condenser tubes had lower primary system radiation fields, as measured at the BWR Radiation Level Assessment and Control (BRAC) reactor recirculation system (RRS) locations, compared to any other grouping of BWRs. These plants tended to have reactor coolant zinc concentrations above 5ppb (µg/kg) because with CF/Ds there is limited ion exchange capacity to remove soluble species, such as zinc. The zinc content of admiralty brass is about 30%, by weight. The release of zinc into the hot well from the condenser tubes occur due to general corrosion of the tubes [Garcia et al, 2014b].

Laboratory testing was performed by General Electric to confirm that the presence of zinc in the water suppressed radiation build-up. Radiation build-up (Co-60) in high temperature loop testing results, under simulated NWC and HWC conditions, (water conductivity at 0.1µS/cm) are shown in Figure 4-1 for 304 SS. The plots show lower Co-60 deposition for both the NWC and HWC cases when 5ppb to 15ppb (µg/kg) zinc is present in the water. The results suggested reduction factors of 3 to 7 under NWC conditions and up to 20 for HWC conditions (after 2000 hours of coupon exposure). The lower Co-60 build-up under HWC conditions suggested a synergistic effect with even thinner corrosion films than those occur under NWC conditions in the presence of zinc [Garcia et al, 2014b].

Boiling Water Reactors (BWRs) have been injecting zinc into the primary coolant via the reactor feed water system for over 25 years for the purpose of controlling primary system radiation fields. The BWR zinc injection process has evolved since the initial application at the Hope Creek Nuclear Station in 1986. Key transitions were from the original natural zinc oxide (NZO) to depleted zinc oxide (DZO), and from active zinc injection of powdered zinc oxide slurry (pumped systems) to passive injection systems (zinc pellet beds). Zinc addition has continued through various chemistry regime changes, from normal water chemistry (NWC) to hydrogen water chemistry (HWC) and HWC with noble metals (NMCA) for mitigation of inter-granular stress corrosion cracking (IGSCC) of reactor internals and primary system piping. The Zinc Sourcebook was prepared by EPRI to consolidate all of the experience gained over the past 25 years [Garcia et al, 2014b].

Natural zinc oxide (NZO) contains about 48% of non-radioactive Zn-64, and Zn-65 is formed from the neutron activation of Zn-64. Recognizing the radiation dose consequences of the Zn-65 release at many BWRs that implemented NZO isotopic ally depleted zinc oxide (DZO) was developed that had about 1% Zn-64 and were manufactured in a powder form similar to the natural zinc oxide powder.
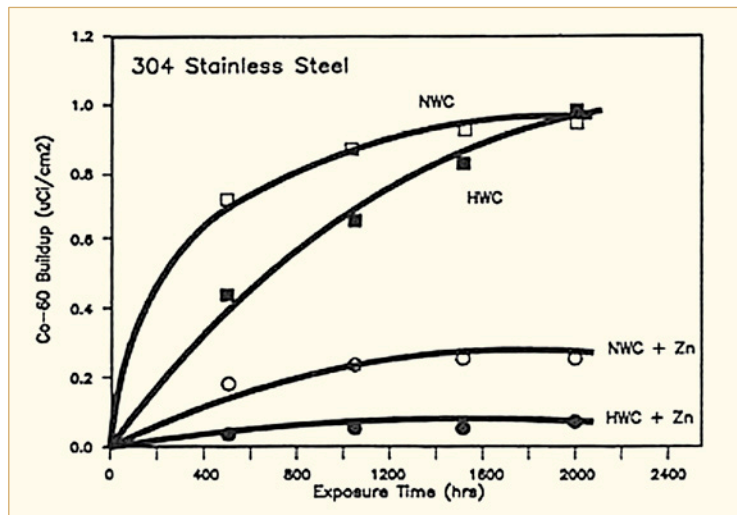
Figure 4-1:   Co-60 build-up on 304 stainless steel (in NWC & HWC) in the presence of zinc addition [Garcia et al, 2014b].

The early zinc injection system used was referred to as an "active" system that included a small tank for preparation of the zinc oxide slurry and a small metering pump to inject the zinc slurry into the feed water system. The plants experienced numerous problems associated with fouling of the pump check valves and the small diameter tubing with the zinc oxide slurry that resulted in system downtime.

In later years a "passive" zinc injection system was developed where DZO is fabricated in the form of solid pressed and sintered pellets. The major components of the system include the zinc vessel, flow control valve, strainer, flow element, and isolation valves. The typical flow path implemented at all plants is that a side stream from the discharge of the reactor feed water pump is directed towards the passive zinc system skid. Reactor feed water enters the zinc vessel at the bottom, passes through the bed of zinc oxide pellets, and exits the zinc vessel at the top. The typical design contains a strainer in the effluent piping just downstream of the zinc vessel. After the strainer, feed water passes through a flow control valve and then returns to the suction of the reactor feed water pumps. A typical passive DZO injection skid flow diagram is shown in Figure 4-2 [Garcia et al, 2014b].
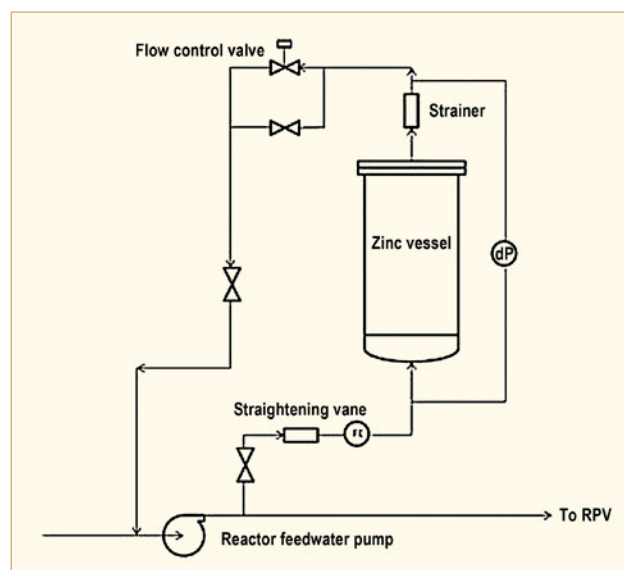
Figure 4-2:   A typical "passive" DZO injection system flow diagram [Garcia et al, 2014b].

4.1 Feed water zinc addition criteria

Feed water zinc addition criteria in BWRVIP-190 that supported avoiding crud spalling were based on fuel surveillance observations through 2007, mainly under NMCA [Garcia & Gianelli, 2014]. Data since 2007 were compiled for preparation of BWRVIP-190 Revision 1. The newer data, which were mainly from operation with OLNC, were limited; more data are needed to fully assess the effects. It was concluded that the feed water zinc cycle average and quarterly average values established previously are still effective to avoid crud spallation in OLNC plants. Also, the same guidance for limiting feed water zinc applies to all chemistry regimes. As more plants implement OLNC over the long term, with reduced FW iron inputs, it is expected that crud redistribution will be reduced and as a result less crud spallation will be observed. As a result, the following needed values of zinc apply unless cycle-specific values based on an approved fuel risk assessment or change management assessment is established:

- FW Zn ≤0.5ppb quarterly average

- FW Zn ≤0.4ppb cycle average

4.2 Post-NMCA zinc addition criteria

Following the implementation of the NMCA process by a number of plants, a correlation was developed for NMCA plants that showed that NMCA plants that reported having primary system radiation field measurements <100mR/hr (1mSv/hr) at the standard radiation survey points (the BWR Radiation Level Assessment and Control of BRAC survey points) all had a cycle median reactor coolant Co-60(s)/Zn(s) ratio <2E-5µCi/ml/ppb ($7.4E+5Bq/m^3$/(µg/kg)). The correlation plot is shown in Figure 4-3. This Co-60(s)/Zn(s) ratio appears as a "Good Practice" value in the 2004 Revision of the EPRI BWR Water Chemistry Guidelines [Garcia et al, 2014b].
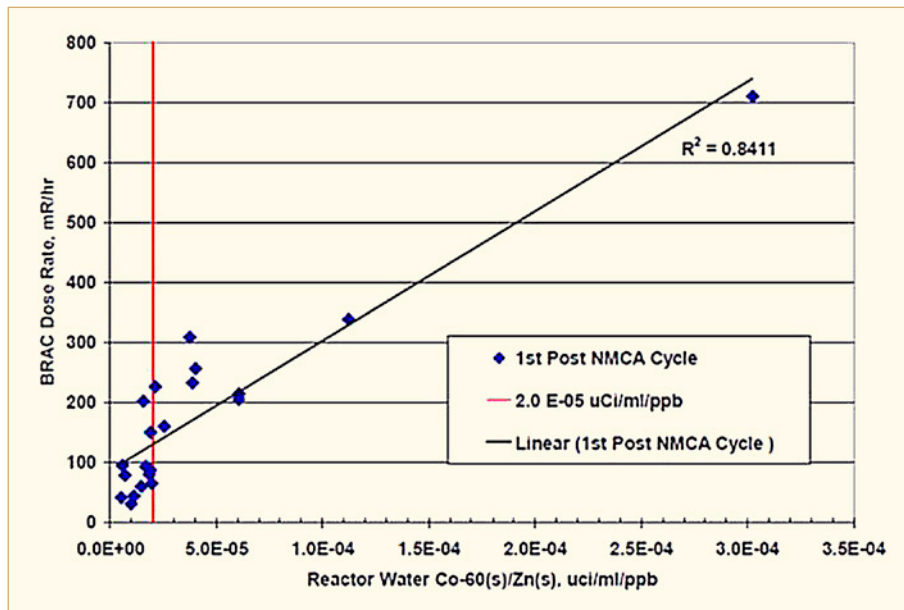
Figure 4-3:   Correlation of BRAC RRS dose rates with the Co-60(s)/Zn(s) ratio [Garcia et al, 2014b].

Low cobalt source term plants have generally no issue meeting the Co-60(s)/Zn(s) ratio goal because Co-60 levels are low. These plants can achieve the ratio operating at reactor coolant zinc concentrations as low as 3ppb to 5ppb (µg/kg) with feed water zinc levels well below 0.4ppb (µg/kg). Experience at some of the plants in this category has shown that BRAC dose rates can increase even if the cycle median value for the ratio met the goal.

5 Fuel behaviour and crud

5.1 Guidelines for improved fuel performance

EPRI's BWR Water Chemistry Guideline Report (BWRVIP-190 Revision 1, Volume 2 Chapter 4) on Chemistry Control for Fuel Reliability, summarizes the main chemistry-related fuel performance issues and information on fuel risk assessments. A Mandatory requirement in the Fuel Guidelines Revision 1 is that a crud and cladding corrosion risk assessment shall be performed for each cycle during core reload design phase. This risk assessment, which is performed by the organization responsible for nuclear fuel, covers water chemistry as well as fuel and core design and operational factors. There is also a needed requirement in the Fuel Surveillance and Inspection Guidelines Revision 2 (FSIG Rev. 2) following a significant change or anomalous event, to conduct a utility/vendor assessment to determine the need for targeted inspections [Garcia & Gianelli, 2014].

The fuel risk assessment process is used by plants when the generic needed values for feed water zinc will be exceeded to meet soluble Co-60 to soluble Zn ratio targets to control shutdown dose rates. Guidance in BWRVIP-190 Revision 1 (Volume 1 Chapter 2) is given below:

The following values apply unless cycle-specific values based on an approved fuel risk assessment or change management assessment is established:

- FW Zn ≤0.5ppb quarterly average

- FW Zn ≤0.4ppb cycle average

If any of the cycle-specific values, or the above values if cycle-specific values are not developed or are exceeded, then it is necessary to perform a fuel risk assessment in accordance with the Fuel Reliability Guidelines.

Similar guidance is given for feed water iron and feed water copper needed values.

Fuel crud layer spallation is a condition where the tenacious crud layer cracks, delaminates and spalls under stress. Although no fuel failures have been directly attributed to crud spalling, fuel performance concern exists for two reasons [Garcia & Gianelli, 2014]:

1) The Zircaloy corrosion process generates hydrogen and forms a zirconium hydride phase in the cladding, reducing the strength of material. Spallation of thermally insulating tenacious crud layers will result in cooler spots, where hydrogen in cladding will form zirconium hydrides.

2) Crud spallation may also be an indication of cladding oxide spallation.

Examples of fuel crud spallation are shown in Figure 5-1. Minimizing crud spallation is recommended to maintain good fuel performance. Therefore, it is advisable to optimize feed water iron, zinc and copper inputs to avoid or minimize crud spallation.

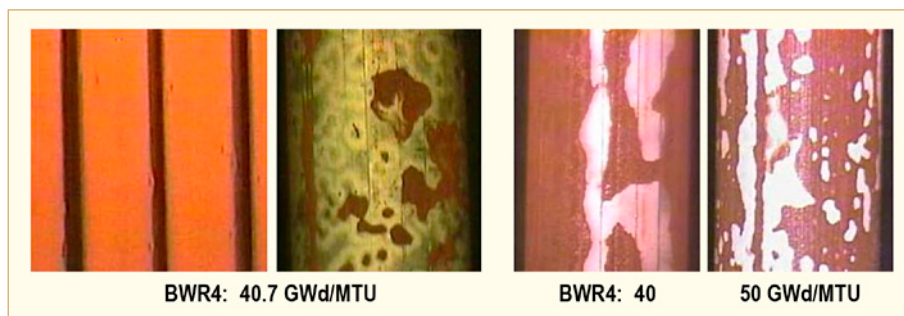| BWR4: 40.7 GWd/MTU | | BWR4: 40 | 50 GWd/MTU |

Figure 5-1:   Examples of surface fuel crud spallation [Garcia & Gianelli, 2014].

The Good Practice fuel risk assessment process has three levels:

- Qualitative Change Assessment (Level 1): Use of a simple checklist. This is the most commonly used assessment level.

- Extended Change Assessment (Level 2): Expanded evaluation using an approximate quantitative method; a qualitative method is applied for evaluating cladding corrosion effects.

- Comprehensive Effects Quantification Assessment (Level 3): More detailed quantitative evaluation of the effects of specific changes in the parameters of interest on crud deposition and crud deposition-related fuel performance effects.

Examples of other chemistry parameters that could trigger a fuel risk assessment due to potential impacts on fuel performance are:

- Cycle average reactor water sodium exceeding 10ppb

- Quarterly average steady state reactor water lithium exceeding 5ppb

- Feed water hydrogen >0.4ppm for NMCA/OLNC plants or >2ppm for HWC-M plants

- Initial application of early hydrogen water chemistry (EHWC)

- Reactor water Mn-54 less than 1000Bq/kg (2.74E-5μCi/ml) for plants operating with fuel containing either Inconel spacers or spacers with Inconel springs (indicator of iron deficiency condition)

- Effects on plant chemistry from power uprates or changes in reactor water clean-up (RWCU) capacity

- Plant Challenge Ranking changes and System Design Operation changes: Plant design or operating changes, particularly to the condensate clean-up system, that could allow higher chemical impurities in the feed water

- Other changes that may impact fuel crud and corrosion performance

5.2 BWR crud characterization

A paper from Taiwan investigated the nature of crud recirculating in the BWR heat transport circuit by analysing water samples from condenser demineralizer inlet (CDI), condenser demineralize effluent (CDE) and feed water (FW). The main reason for this investigation is that coolant-borne corrosion products create issues in the removal efficiency of condensate polisher, crud deposition on fuel cladding surface and radiation build-up on system piping and components. The single dominate corrosion product in reactor coolant is iron, approximately greater than 95%. The analysed samples basically comprised mostly of crystalline structures of hematite (α-Fe_2O_3), magnetite (Fe_3O_4), goethite (α-FeOOH), lepidocrocite (γ-FeOOH) and some non-crystallite forms under both normal water chemistry and hydrogen water chemistry environments [Wen et al, 2014].

The results from Kuosheng Nuclear Power Station (KSNPS) unit 1(BWR/6) indicate that crud in feed water is dominated by hematite as shown in Figure 5-2.
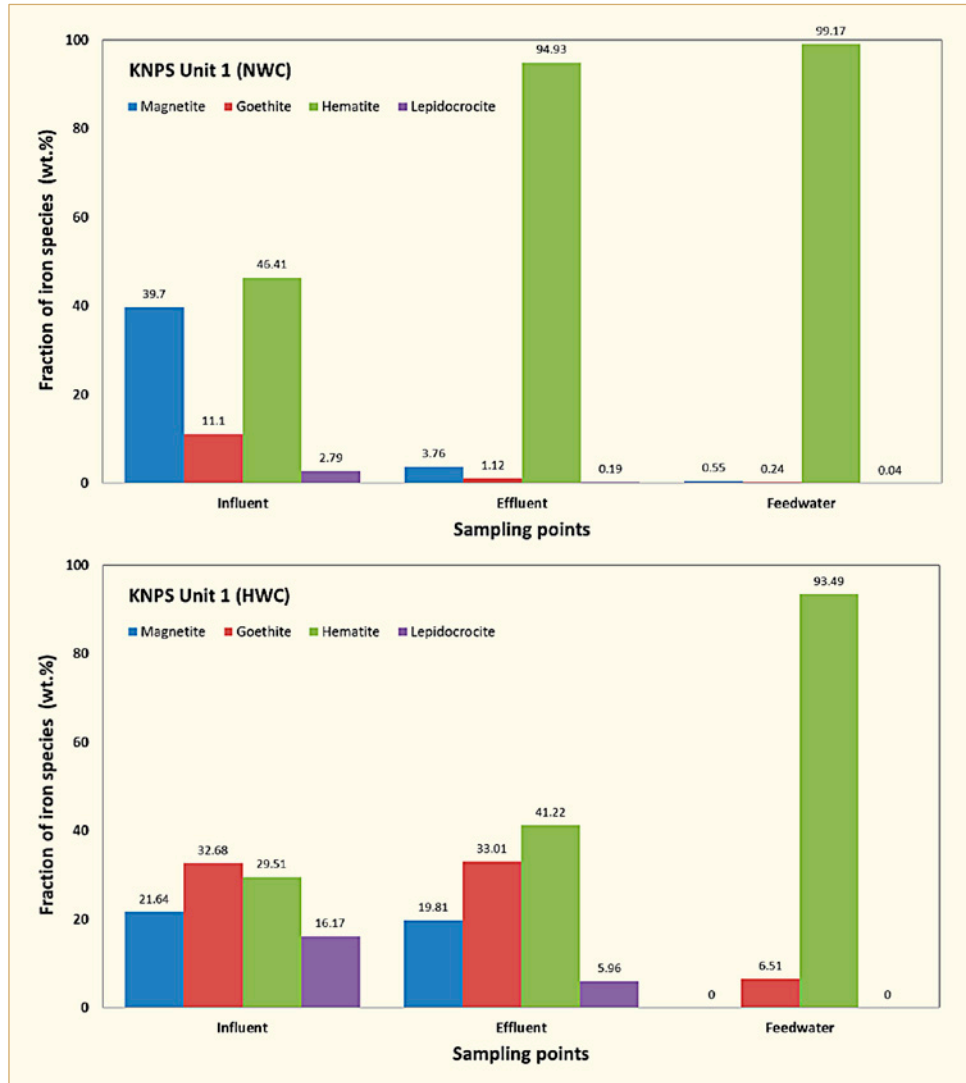
Figure 5-2:   Fraction of iron species from CDI, CDE and FW in KSNPS unit 1 [Wen et al, 2014].

Figure 5-3 shows the percentage distribution of particle size at unit1 and unit 2 of KSNPS CDI under HWC conditions via SEM photomicrographs.

The results from the crud investigation were used to explain the discrepancy of crud removal efficiency of the individual plant unit with the same design containing no pre-filters upstream of the condensate demineralizers.

6 Lessons learned from Fukushima event

6.1 The event and the early actions

On March 11, 2011, north-eastern Japan experienced a series of huge earthquakes resulting in a tsunami that caused heavy damage to the Fukushima area and surroundings. All Units except Unit 6 lost all electricity not only from the external sources but also from the emergency diesel generators (EDGs) which were damaged by flooding of the tsunami following the earthquakes. A severe accident at the Fukushima Daiichi Nuclear Power Plant (NPP) occurred from a station blackout (SBO) due to the unexpectedly large tsunami challenging the decay heat removal from the core of the Units 1 to 3 and severe core damage, core meltdowns, leakage of the primary containment vessels (PCVs), destruction of the reactor buildings due to hydrogen explosions, and the release of radioactive fission products (FPs) into the environment [Uchida et al, 2014a]. Units 5 and 6 were safely shutdown using one of the Unit 6 EDGs that was air cooled and hence was able to supply cooling water to both Units 5 and 6 [Muto, 2014].

It was shown in the official report of the Fukushima accident that 600PBq of FPs were released into the environment. Major parts of the FPs consisted of radioactive noble gases, e.g., Xe-133 & Kr-85, radioactive iodine, e.g., I-133 & I-131, and radioactive caesium, e.g., Cs-134 & Cs-137. Based on previous understanding, it was considered that Cs was released from fuel into the coolant, where some of Cs reacted with iodine to produce CsI and the rest formed CsOH. The accumulated mass of Cs in the core was about ten times larger than that of iodine. Only 10% of Cs existed as CsI and 90% was CsOH in the water [Uchida et al, 2014b]

Since the accident, efforts have been made to cool down the reactors (Units 1, 2, 3) and spent fuel pools (SFPs) of Units 1 to 4 by using fresh water or sea water. Three hundred (300) tons of water is injected to cool the cores of 3 reactors [Muto, 2014]. The water injected into the reactors leaked from the damaged reactor pressure vessel (RPV) and primary containment vessel (PCV) into the basement of the buildings. A water cooling circulation system was installed that enabled the reactor temperatures of Units 1, 2, 3 to achieve <100°C and also significantly suppress the radioactive material release. The SFP water purification system was also installed to prevent corrosion and it was possible to achieve temperatures of approximately 30°C as of June 2012 [Makihira et al, 2012].

The areas affected by flooding of the Fukushima Daiichi NPP site is shown in blue in Figure 6-1.
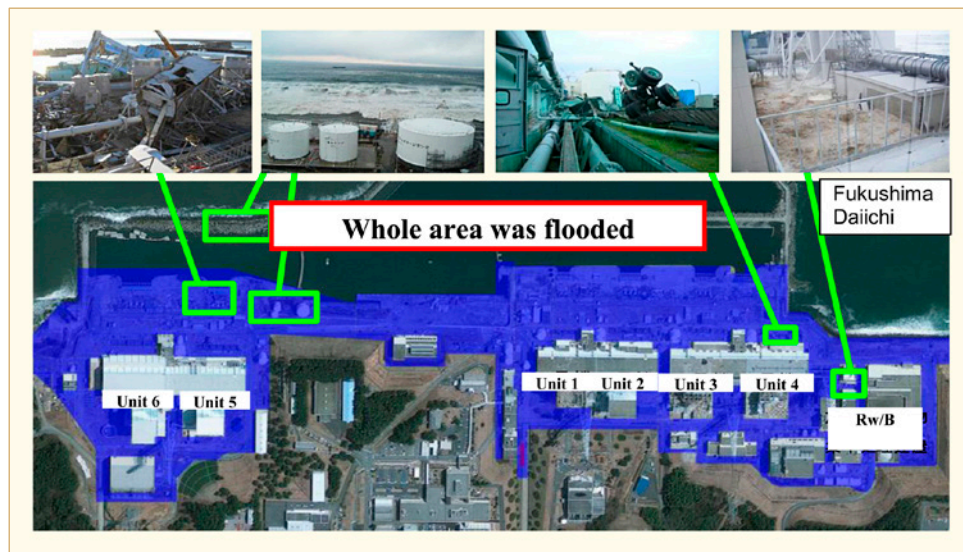
Figure 6-1: Flooded area of Fukushima Daiichi NPS shown in blue [Muto, 2014].

There are six nuclear power units in Fukushima Daiichi and four in Fukushima Daini totalling ten units. The two stations are separated by 12km with Daiichi in the north. Out of ten, seven were in operation on March 11th 2011. The plant locations are shown in Figure 6-2.

All of Fukushima Daini units were operating at the rated power. All of Fukushima Daiichi and Daini Units except for Unit 3 of Daini lost their heat sink because they lost pumps at 4m above sea level. In Daini, however, in-coming off-site power was available, and some diesel generators survived as well. The availability of power made possible for Daini to monitor reactor status and succeed in depressurizing reactors and also use make-up water pumps (MUWP) to inject water to cores as defined in accident management procedures [Muto, 2014].
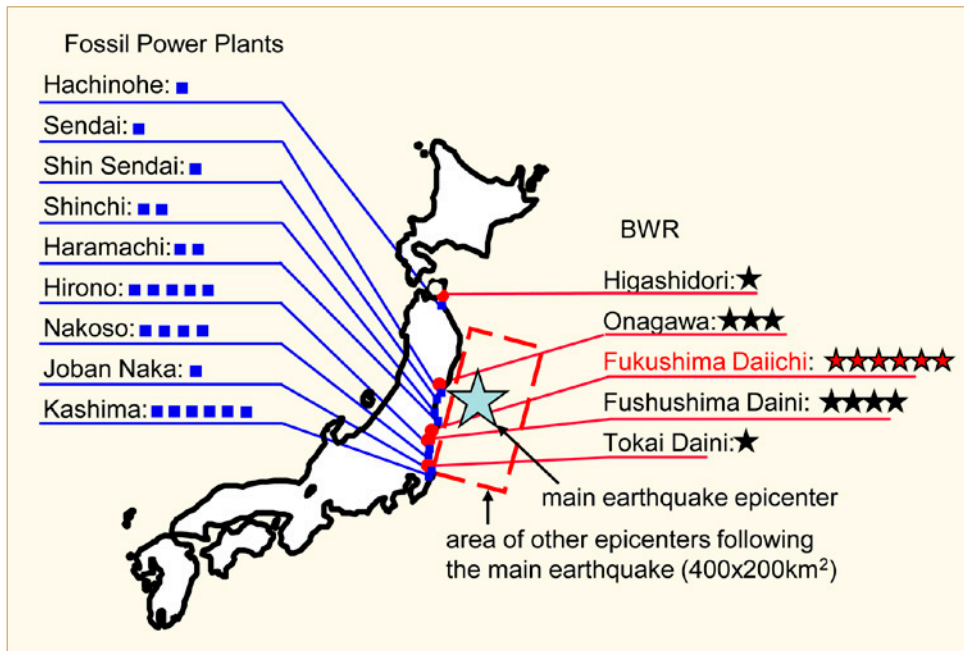
Figure 6-2:   Map showing location of the epicentre of the main earthquake, fossil power plants and BWRs along the northern pacific coast of Japan [Uchida et al, 2014a].

The Atomic Energy Society of Japan (AESJ) organized an Investigation Committee on the nuclear accident at the Fukushima Daiichi NPP to evaluate the events that led to accident and to reveal its root causes and then to propose improvements to safety. The direct causes and underlying factors of the accident are listed in Table 6-1 [Uchida et al, 2014a].

Table 6-1:   Root causes of the accident at Fukushima Daiichi NPS, after [Uchida et al, 2014a].

Direct causes of the accident	
1)	Inadequacies of tsunami countermeasures Critical information had not been applied for prevention measures. (Jogan Sanriku Tsunami and Fukushima Offshore Trench Tsunami-Earthquake)
2)	Inadequacies in severe accident management measures No effective training in measures for severe accident had been since 2002. No measures for external events as earthquakes and tsunamis.
3)	Inadequacies in emergency response, post-accident management & mitigation and recovery measures.
Underlying factors of the accident	
1)	Experts: lacked awareness not only for themselves but also for others.
2)	Utilities: lack of effort in establishing safety measures & fostering safety awareness
3)	Regulatory body: lacked awareness on safety
4)	Others: Lack of effort in learning international and domestic practices. Lack of human resources and management to support plant safety.

ANT International, 2014

6.2   Activities in progress at Fukushima Daiichi NPS

The activities in progress are categorized into the following sections [Doi, 2014]:

• Management of Contaminated Water

• Comprehensive Counter Measures to Manage Contaminated Water

• Current Status of Each Unit at Fukushima Daiichi NPP

• Mid and Long-Term Roadmap Towards Decommissioning

• R&D Activities in Support of Decommissioning and Decontamination

6.3   Management of contaminated water

The highly contaminated water in the basement of the building was processed and reused for water injection into the reactors (Units 1, 2, 3) by a "circulating water cooling system". The early system is designed to have oil separators, radioactive nuclide removal system and a desalination system as shown in Figure 6-3a [Makihira et al, 2012]. A later version of the circulating water cooling system with more details showing the caesium removal beds is shown in Figure 6-3b.

For the purpose of isolating water from contaminated sources, other additional measures taken include construction of the frozen-soil and land-side wall to prevent the groundwater from flowing into the area and contaminated water from flowing out from the area. Also, in order to prevent leakage of contaminated water into the ocean, soil improvement with sodium silicate (liquid glass) and installation of the sea-side impermeable walls are implemented [Arai & Takahashi, 2014].

7 BWR life time management and plant aging

Many approaches have been used in the past to manage the life of operating BWRs that include, HWC, NMCA, OLNC, early hydrogen water chemistry (EHWC), monitoring mitigation performance indicators (MPI), and monitoring start-up/shut down chemistry. All these methods have been employed to manage degradation of materials in the BWR environment. This chapter provides a summary of the above methods that have been utilized to manage degradation of BWR materials.

7.1 Early hydrogen water chemistry

Boiling Water Reactors (BWRs) have been injecting hydrogen into the reactor coolant via the feed water system for the purpose of controlling primary system inter-granular stress corrosion cracking (IGSCC) for over 30 years. However, plant design limitations prevent hydrogen injection until there is sufficient steam flow to support the operation of the Steam Jet Air Ejector (SJAE) system, which typically occurs at greater than 5% power. The time from when the reactor coolant temperature is heated up to 200°F (93.3°C) until hydrogen injection starts is counted as time when IGSCC is not mitigated. Laboratory data show that crack growth rates peak at intermediate temperatures [BWRVIP-190, 2014]. To address this gap, Early Hydrogen Water Chemistry (EHWC) was developed by EPRI/BWRVIP for plants that use GE Hitachi NobleChem™ to lower the ECP during early start-up [Garcia et al, 2014d].

A demonstration of EHWC performed at Peach Bottom 3 BWR in October 2011 showed that sufficient hydrogen could be injected, while condenser vacuum was being maintained using the Mechanical Vacuum Pump (MVP), before steam flow was sufficient to place the SJAE system in service, to lower the ECP to a level indicative of IGSCC mitigation. While this demonstration successfully showed that sufficient hydrogen can be injected safely to mitigate IGSCC during early start-up when temperature was between 360°F and 460°F (182°C-238°C), a reactor coolant hydrogen: oxidants molar ratio >2 was not achieved during the initial heat-up when the temperature reached 200°F (93.3°C) because a steam flow path from the reactor vessel to the main condenser had not been established. At this condition, the reactor coolant oxidant concentrations remained high, and the quantity of hydrogen injected was limited so that the hydrogen gas concentration in the reactor head space (above the liquid level) would be maintained below 4% (lower flammability limit in air). Therefore, alternative agents to enhance HWC (EEHWC) were considered [Garcia et al, 2014d].

Agents considered included:

- Reductants: Hydrazine (N_2H_4) and Methanol (CH_3OH)

- Surface Agent: Titanium Dioxide (TiO_2)

Each of these agents is discussed below.

Hydrazine

The results of laboratory tests and studies support the feasibility of using hydrazine injection during BWR heat-up and early start-up to substantially lower ECP, especially on surfaces on which noble metals have been deposited. High temperature loop tests showed that hydrazine reacted catalytically with O_2 at surfaces on which noble metals were deposited at 200°F-400°F (93.3°C-204°C) in the absence of radiation. Evaluations show the feasibility of hydrazine injection during the heat-up and low power during the start-up process.

Hydrazine would be injected as a liquid solution into the reactor recirculation system (RRS) or reactor water clean-up system downstream of the filter demineralizers or deep bed demineralizers. Injection is required only during start-up before EHWC is initiated. A controlled BWR plant demonstration would be needed to confirm the effectiveness and to evaluate other impacts of hydrazine [BWRVIP-190, 2014].

Methanol

The basis for methanol to lower the ECP would be by consuming the oxygen present in the bulk solution or catalytically at the metal surface. The injection of methanol has been proposed by AREVA as a complement to the BWR fleet's vessel internal protection programs. A European plant demonstration (approximately 75 hours) and test reactor demonstration indicated effectiveness at normal power operating temperature, and laboratory data indicate effectiveness in reducing oxidants at temperature above 80°C (176°F) in the presence of Cherenkov radiation. A controlled BWR plant demonstration would be needed to confirm the effectiveness and to evaluate other impacts of methanol [BWRVIP-190, 2014].

Titanium Dioxide (Surface Agent)

Toshiba Corporation, in collaboration with Tokyo Electric Power Company (TEPCO), has developed titanium dioxide (TiO_2) technology for stress corrosion cracking (SCC) mitigation of the BWR primary components [BWRVIP-190, 2014]. An advantage claimed for TiO_2 over noble metals is that hydrogen injection is not required. Titanium dioxide is a well-known photo-semiconductor and is excited with ultraviolet (UV) light to produce an electron and hole pair. A photoelectric current is produced that can be utilized to reduce the ECP of the structural materials in the presence of Cherenkov radiation existing in the reactor due to high radiation fields in the core. A BWR plant demonstration would have to be performed with the objective of applying titanium dioxide to reactor piping and internal surfaces to which noble metal treatments have also been applied, and to monitor the ECP during the initial heat-up and start-up to determine if IGSCC is mitigated prior to the start of EHWC [Garcia et al, 2014d].

A summary of the alternative agents considered for enhanced EHWC is provided in Table 7-1.

Table 7-1:   Summary of alternative agents for enhanced EHWC, after [Garcia et al, 2014d].

Agent	Experience	Technical gaps
Hydrazine 54mL/min 35% sol'n equivalent to 1scfm ($1.70nm^3/h$) H_2	• Effective (catalytic) at low temperature in loop tests without radiation. • Long term use in PWRs.	• Decomposition reaction stoichiometry not precisely known. • NH_3 impact on monitoring and ion exchange loading.
Methanol 65mL/min 20% sol'n equivalent to 1scfm ($1.70nm^3/h$) H_2	• Effective in loop tests at high temperature with UV radiation; non-catalytic without radiation. • Demonstrated for 14 days at European BWR.	• Interaction with noble metal surface deposits. • Low temperature ECP data. • Impact of CO_2 on condenser leak monitoring.
TiO_2 Approx. $30\mu g/cm^2$ based on application during hot shutdown.	• Effective in loop tests at high T with UV radiation. • Plant demonstration performed at a BWR in Japan for part of one cycle.	• Interaction with noble metal surface deposits. • Low temperature ECP data. • Durability.
		ANT International, 2014

A paper from Taiwan [Wang & Yeh, 2014] attempted to model the water chemistry and IGSCC mitigation propensity of selected BWR-X under EHWC conditions for four regions, the upper plenum, the outlet of the upper down-comer, the outlet of the recirculation system, and the outlet of the bottom lower plenum which approximately represent the top guide, the belt area of the core shroud (outer diameter side) and jet pump risers, the recirculation piping, and the core shroud base and support, respectively. Simulations were carried out for [H_2] FWs ranging from 0.0 to 2.0 parts per million (ppm) and for power levels ranging from 3.8% to 11.3% during start-up operations.

However, it is important to note that steam did not generate in the core region in this BWR-X until the power level exceeded 6% of the rated power. When steam is absent, the feed water pumps in a BWR are not activated and therefore, no feed water entry and hence no H_2 addition up to 6% power in this BWR. Thus, any predictions made are valid only when the reactor power exceeded 6% in this modelling study.

The study concluded that radiolysis of water still dominated the water chemistry in a BWR even at very low power levels. The HWC efficiency did not experience any significant changes when the steam had not yet generated in the core. The feed water H_2 required for reducing the ECP below the Ecrit was less than 0.6ppm at the four selected locations.

7.2 BWR shutdown and start-up chemistry experiences

From a shutdown chemistry perspective, the overall goal is to minimize crud bursts; to minimize the amount of time required to remove activity from the reactor coolant during the shutdown process prior to refuelling, and to assist plants in predicting and controlling radiation exposure during outages. From a start-up chemistry perspective, the overall goal is to show that plants are more susceptible to IGSCC during early heat-up and start-up when reactor coolant oxidants are high in concentration. Also, during the start-up phase there is a greater likelihood for chemical excursions associated with refuel outage work activities to occur, when hydrogen injection is not available because of system design limitations [Garcia et al, 2014e].

Data from over 70 refuelling outages were evaluated to determine the Co-60 change at each of the key shutdown sequences. The data are shown in Figure 7-1 [Garcia et al, 2014e]. The plot includes all the plants that are on HWC, NMCA and OLNC. The highest change in Co-60 concentration occurs during the initial cool-down when the reactor coolant temperature is lowered from the normal operating range of 545F (285°C) to about 350°F (177°C), just prior to the initial start of shutdown cooling, while the highest Co-60 concentration occurs just after shutdown cooling is placed in service.
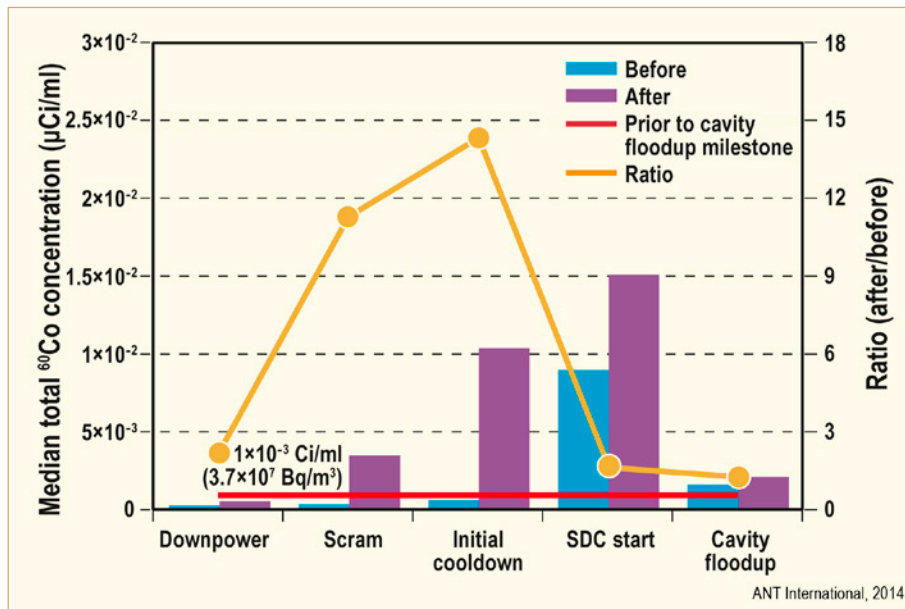

Figure 7-1:   Co-60 changes during different phases of plant shutdown, after [Garcia et al, 2014e].

8 Noble metal technology and water chemistry scientific studies

This chapter intends to summarize key areas involving noble metal chemical applications (NMCA), On-Line NMCA, and scientific studies relating oxide film formation, dose reduction and modelling.

8.1 Noble metal technology – NMCA and OLNC

A GE-Hitachi paper [Seeman et al, 2014] provided a technology update and a review of the OLNC application process including chemistry parameters typically monitored, such as reactor water conductivity and activated corrosion by product levels, and primary application progress indicators, such as ECP and Main Steam Line Dose Rate measurements. The update also presented noble metal loading and durability trends as measured from deposition coupons installed in an external reactor water sampling system exposed to numerous OLNC reapplications. Finally, new insights on more representative ECP in OLNC-treated external monitoring locations were also presented.

As of August 2014, there have been a total of 34 BWRs using OLNC technology. Of these, 27 BWRs transitioned from classic NobleChem™ to OLNC, 6 units transitioned from MHWC to OLNC, and a single unit transitioned directly from NWC to OLNC. Figure 8-1 shows the cumulative number of classic NobleChem™ and the rapidly growing OLNC applications that have been performed since 1996. The last classic NobleChem™ application was performed in 2009.
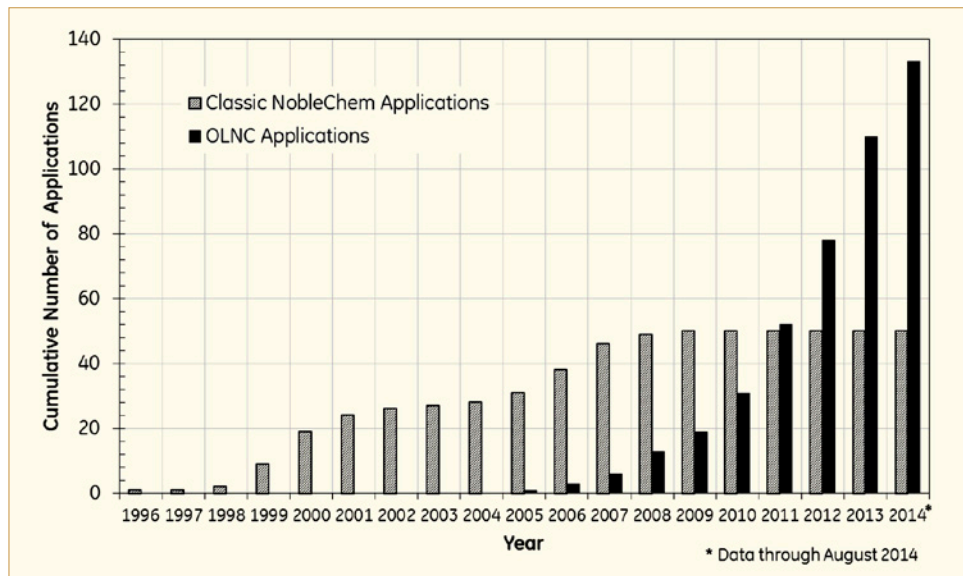

Figure 8-1: Cumulative number of classic and OLNC applications performed [Seeman et al, 2014].

The paper summarized plant experiences during OLNC applications relating to reactor water conductivity, reactor water Pt concentration, activation corrosion products, main steam line radiation monitor response, long-term durability trends and ECP monitoring. Only a few plants have made internal ECP measurements in the reactor recirculation system (RRS) or using an ECP/LPRM, the vast majority of the ECP data collected during and after OLNC applications are from a plant's mitigation monitoring system (MMS) or a similar external manifold system. One of the challenges in external ECP measurements is the catalytic sampling line that makes the oxygen concentration in the sample line very low before the water reaches the ECP measurement location. Hence, the measured ECPs tend to be more negative and do not represent the ECP of the surface in contact with the actual plant water chemistry condition. Therefore, to demonstrate the long-term durability of platinum on reactor surfaces, ECP measurements were made with dissolved oxygen (DO) addition upstream of the ECP monitoring location to better demonstrate the catalytic effectiveness of platinum on surfaces following OLNC applications.

A second GE-Hitachi paper [Varela et al, 2014] focused more on how the DO addition is being used to prove the validity of ECP measurements in an external ECP monitoring system. A typical DO addition location and the MMS ECP monitoring location are shown in Figure 8-2. The MMS supply receives water from the reactor water clean-up (RWCU) system before the clean-up beds.
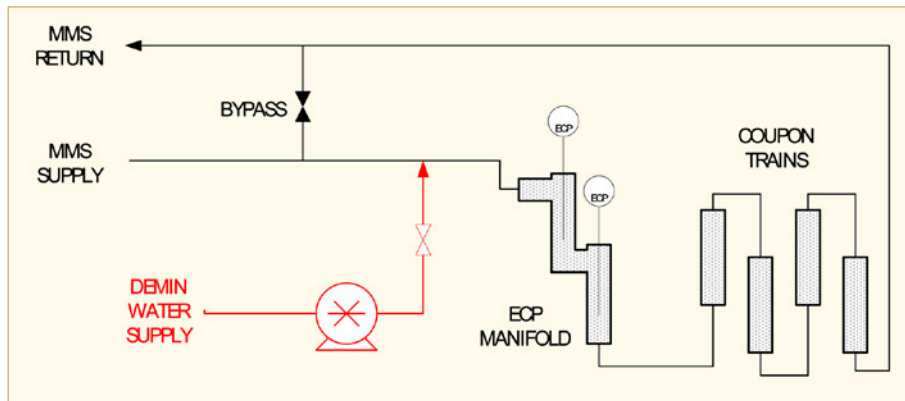

Figure 8-2:   DO addition diagram, the temporary equipment used for the DO addition is shown in red [Varela et al, 2014].

In order to show the effectiveness of an OLNC application with DO addition, a DO addition step test was performed before and after the OLNC application, and the data are compared with the response of a Pt electrode potential for the same DO addition steps. The data are shown in Figure 8-3. The Figure illustrates that the post-OLNC ECPs are more negative at each step compared to the pre-OLNC DO addition steps, confirming better catalytic activity of the treated surface due to the OLNC application. The data also shows that the OLNC treated surface is less catalytic than the Pt electrode in its response at H_2/O_2 molar ratio >2 as expected.
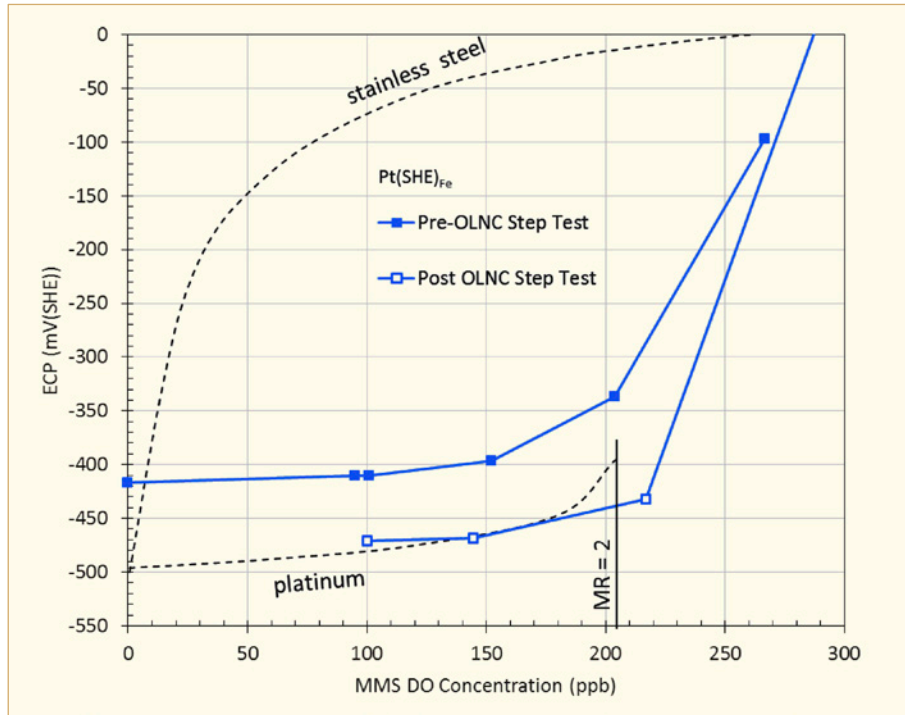
Figure 8-3:   Pt electrode ECP measured over the three phases of the project using the Fe/Fe$_3$O$_4$ reference electrode [Varela et al, 2014].

One of the key requirements with NMCA or OLNC is to prove that there is sufficient noble metal on the surfaces. One approach is to remove a noble metal deposited coupon from the coupon train shown in Figure 8-2 and analyse for the amount of noble metal on the surface. Another approach is to collect samples from artefact from the reactor or from the reactor core shroud itself and then analyse for the noble metal loading on the surface. This paper [Kohlmann & Drehmel, 2014] describes how a sampling system that was designed to collect samples from, fuel channels (Zircaloy), fuel bundle lifting bale handle (type 304 stainless steel), surveillance capsule surface (type 304 stainless steel) and surveillance capsule pigtail or spring (Alloy X-750) was used for noble metal sampling from surfaces. A nylon brush was used to remove loosely adherent particles and an alumina stone was used to remove the adherent deposits.

The total noble metal (Pt+Rh) loading analysis performed on Perry BWR surveillance capsule surface using the sampling tool is shown in Figure 8-4.
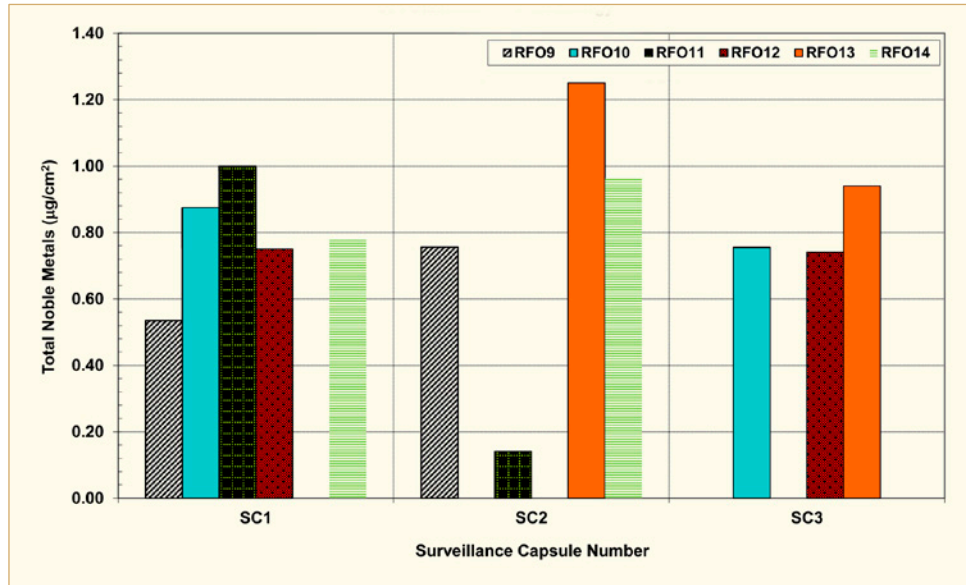
Figure 8-4:   Perry surveillance capsule noble metals trend [Kohlmann & Drehmel, 2014].

The analysis of shroud surfaces has consistently shown that the noble metal loading on the shroud is higher than the noble metal loading measured on an MMS surfaces.

Platinum deposition behaviour on stainless steel surfaces using OLNC type applications was studied by Paul Scherrer Institute (PSI) in Switzerland [Grundler et al, 2014]. Pt was imaging was done by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) and Pt loading analysis was performed by Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS).

Pt particle size was also measured as a function of the Pt injection rate, and the data are shown in Figure 8-5. It is evident that the Pt particle size depends on the Pt injection rate where low injection rate results in smaller particles and high injection rate results in larger Pt particles. This is related to the Pt concentration and its dilution factor.
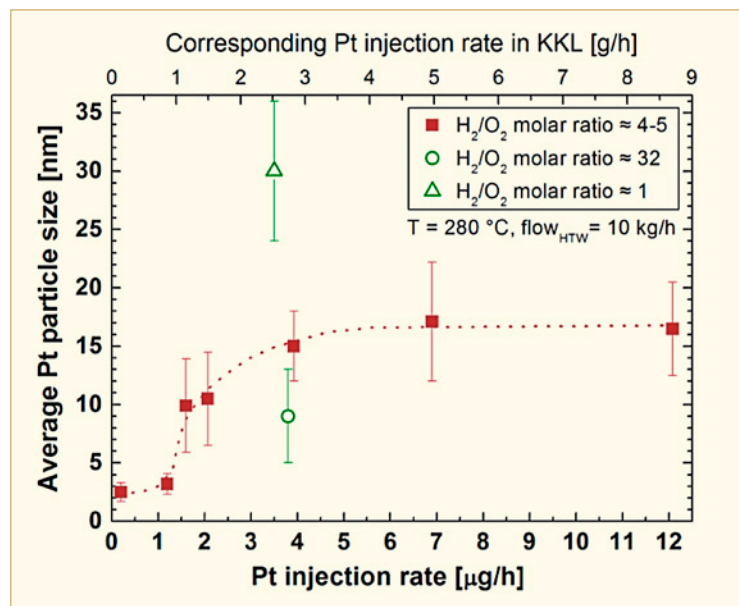

Figure 8-5:   Effect of Pt injection rate on the average Pt particle size [Grundler et al, 2014].

9 Auxiliary systems

9.1 Reactor coolant clean-up system optimization

Optimization of the reactor coolant clean-up (RWCU) systems in the boiling water reactor (BWR) environment is important for controlling the transport of corrosion products (metals and activated metals), fission products, and coolant impurities (soluble and insoluble) throughout the reactor coolant loop, and this optimization can contribute to reducing primary system radiation fields. The removal of radionuclides and corrosion products (predominately isotopes of cobalt and nickel) is just one of many functions (both safety- and non-safety-related) performed by primary reactor coolant clean-up systems.

Impurities entering the reactor vessel from the feed water system concentrate in the reactor coolant and reach an equilibrium concentration based on the feed water input rate, RWCU removal rate, surface deposition rate, and steam carryover rate. For all BWR designs, the RWCU system takes suction from the reactor recirculation system (RRS) and the vessel bottom head drain line. The flow split between the two streams may vary from plant to plant.

The RWCU process stream temperature at the outlet of the Non-Regenerative Heat Exchanger (NRHE) is reduced to <120°F (48.8°C) to allow for processing by ion exchange without thermally decomposing the resin. After the NRHE, but before the water treatment equipment, the pressure of the process fluid is reduced to about 100psig (690kPa) via a pressure control valve. The fluid is then processed through the water treatment equipment, which for the early BWRs consisted of a pre-coat filter followed by a deep bed demineralizer. Downstream of the deep bed demineralizer are the main RWCU circulating pumps. The pumps raise system pressure and transfer the treated reactor water through the Regenerative Heat Exchanger (RHE), shell side. Downstream of the RHE, RWCU returns to the primary system via final feed water for most plants [McElrath et al, 2014].

Various types of pre-coat materials are used in filter demineralizers (F/Ds). Many plants use pre-coat materials that contain in part an inert fibre, while others may use all resin pre-coat materials. Plants that have the latest generation of high integrity septa can use all resin pre-coat materials as resin leakage through the septa is unlikely. Some plants use standard resins with mass ratios high in cation resin to improve the removal of soluble activated corrosion products, such as Co-60. Some plants use specialty resins to enhance Co-60 removal.

For plants with deep bed demineralizers, underlays of anion resins are typically used along with a mixed bed layer above the underlay consisting of high capacity cation and anion resins. Some plants may further use a macro porous anion resin overlay above the mixed layer to enhance colloidal material removal [McElrath et al, 2014].

Increasing the overall clean-up flow rate by 20%, as some BWRs have done, would provide a greater benefit in activity removal than increasing the Co-60 removal efficiency of the RWCU F/Ds, say for example, from 98% to 99%. Reducing system downtime by improving system reliability, addressing mechanical seal issues for the main RWCU circulating pumps or F/D backwash and pre-coat controls, will result in greater system availability, and ultimately result in the removal of more activated corrosion products.

For a BWR, peak reactor coolant Co-60 concentrations typically occur during a shutdown, just after shutdown cooling is placed in service for the first time. Typical peak Co-60 concentrations range between 1E-2 µCi/ml and 5E-1µCi/ml (3.7×10^8Bq/m^3 to 1.85×10^{10}Bq/m^3). It is during this period when the peak concentrations occur that plants report their highest Co-60 decontamination factors (DFs) and removal efficiencies. Some BWRs with RWCU F/Ds can achieve initial removal efficiencies >99% during this period, but continued high removal efficiencies are generally limited by the small volume of available pre-coat material compared to a deep bed demineralizer.

10 Maintenance

This section deals with maintenance related items including impurity removal, ion exchange resins, Co-60 removal approaches and decontamination.

10.1 Impurity removal by filtration and ion exchange resins

Analysis and quantification of reactor water, feed water, and chemical and volume control system (CVCS) soluble metals and radioisotopes are essential for monitoring species that impact fuel performance, steam generator and heat exchanger performance, mitigation of stress corrosion cracking of reactor piping and internals, radiation fields and ensuring that dose mitigation techniques are effective. Soluble species in the CVCS, feed water, reactor water and other process sample streams are usually collected on ion exchange membranes after the sample has passed through a 0.45µm or 0.1µm membrane filter [Garcia et al, 2014h].

Membrane filters are typically cellulose esters and have no ion exchange capacity. After passing through the membrane, colloidal and soluble species are removed by ion exchange membranes. All plants utilize cation ion exchange membranes for soluble iron, nickel and copper sample collection. Cation exchange membranes are also used to collect soluble zinc in feed water and, in many cases, reactor water as well. Some also using anion ion exchange membranes to collect capture anionic species, such as chromate. The species collected on these filters are then analysed using atomic absorption (AA) spectroscopy or inductively coupled plasma (ICP) following acid digestion or filter elution or directly (no digestion) using X-ray fluorescence (XRF).

Most nuclear plants currently use cation exchange membranes from Toray Industries, Inc. Use of Toray filters became widespread in the late 1990s, remaining the ion exchange membrane of choice until the recent focus on transition. As shown in Figure 10-1, 24 of the 30 responses received during a 2012 industry survey conducted by EPRI concerning the use of cation ion exchange membranes indicated use of the Toray CP-1 cation ion exchange membranes. In late 2012, information was exchanged stating that the major suppliers of cation ion exchange membranes, Toray, Inc. and Pall, would discontinue production of ion exchange membranes currently used in nuclear power plant chemistry sampling applications, prompting evaluations by plants and utilities for alternative membranes and the associated impacts on chemistry analyses important to process monitoring [Garcia et al, 2014h].
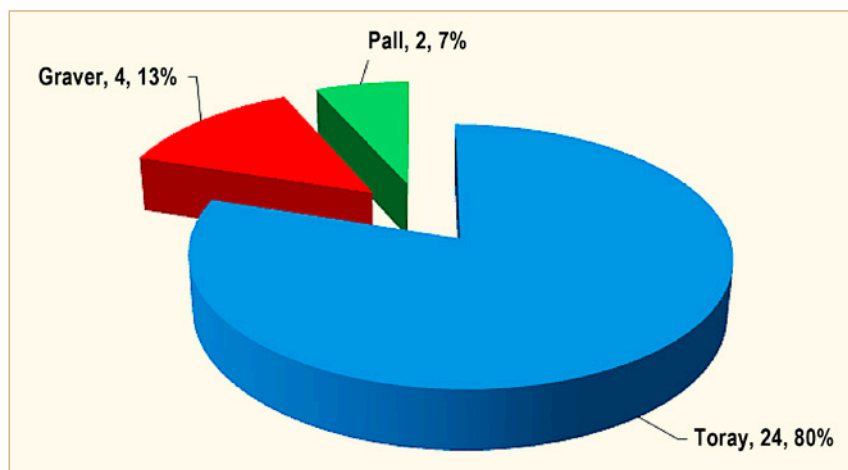

Figure 10-1:   Percentage of responses categorized according to cation ion exchange membrane manufacturer [Garcia et al, 2014h].