

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

Author

Juan de Dios Sánchez
Albacete, Spain

Reviewed by

Peter Rudling
Tollered, Sweden



A.N.T. INTERNATIONAL®

© February 2024

Advanced Nuclear Technology International
Spinnerivägen 1, Mellersta Fabriken plan 4,
448 50 Tollered, Sweden

info@antinternational.com

www.antinternational.com



Ecolabelled printed matter, 4041 0799

Disclaimer

The information presented in this report has been compiled and analysed by Advanced Nuclear Technology International Europe AB (ANT International®) and its subcontractors. ANT International has exercised due diligence in this work, but does not warrant the accuracy or completeness of the information. ANT International does not assume any responsibility for any consequences as a result of the use of the information for any party, except a warranty for reasonable technical skill, which is limited to the amount paid for this report.

Quality-checked and authorized by:

A handwritten signature in black ink, appearing to read 'Peter Rudling', is centered below the text 'Quality-checked and authorized by:'. The signature is fluid and cursive.

Mr Peter Rudling, Chairman of the Board of ANT International

Contents

1	Introduction	1-1
2	PWR Secondary Water Chemistry	2-1
	2.1 Control and Corrosion	2-1
	2.1.1 Feedwater Quality Improvements and Blowdown Management	2-1
	2.1.2 Steam Generator Corrosion and Fouling	2-14
	2.1.3 Other Components	2-19
	2.2 Hydrazine Alternatives	2-21
	2.3 Film Forming Products	2-30
	2.3.1 Application Experience	2-30
	2.3.2 FFP Research	2-34
	2.4 Dispersant Addition Experience	2-38
3	PWR Primary Water Chemistry & Radiochemistry	3-1
	3.1 Control and Corrosion	3-3
	3.2 Fuel and CRUD	3-20
	3.2.1 Fuel Experience	3-20
	3.2.2 CRUD and Coolant Chemistry	3-26
	3.3 Zinc Addition	3-32
	3.4 Potassium Hydroxide Alternative	3-43
	3.5 Shutdown Chemistry	3-49
	3.5.1 Source Term Control	3-49
	3.5.2 Specific Isotopes Control (Ag-110m, Sb-124, others)	3-53
	3.6 Post Accident Chemistry	3-60
4	BWR Chemistry & Radiochemistry	4-1
	4.1 Noble Metal Addition	4-4
	4.2 BWR Fuel and Materials	4-16
	4.3 BWR Chemistry and Radiochemistry	4-23
	4.4 BWR Secondary Systems	4-34
5	CANDU Reactors	5-1
6	Advanced Reactors	6-1
7	Auxiliary Systems Water Chemistry & Waste Treatment	7-1
	7.1 Cooling Water Systems	7-1
	7.2 Stator Cooling Water	7-7
	7.3 Radwaste	7-13
8	Maintenance & Long-Term Operation	8-1
	8.1 Chemical Decontamination	8-1
	8.2 Steam Generator Chemical Cleaning	8-6
	8.3 Spent Fuel Storage Materials	8-9
9	Monitoring updates & new developments	9-1
10	Numerical & simulation tools	10-1
	References	12
	List of Abbreviations	22
	Abbreviations for EPR Systems	27
	Unit conversion	28

1 Introduction

Safety and reliability of power plants are becoming increasingly important factors since many plants are aging and have obtained license renewal for continued power operation and also for new reactors using different technologies that are or will be in design, construction, commissioning, or start-up stage. Therefore, sharing plant operating experiences, sharing lessons learned, and sharing new industry research are all crucial in order to maintain the nuclear power plant fleet in a healthy condition as well as for new reactors using different technologies that are or will be in design, construction, commissioning or start-up stages.

For the present edition of the Key Emerging Issues and Recent Progress, ANT has collected the most relevant experiences and advanced research exposed at the Nuclear Plant Chemistry Conference NPC-2023 that took place in Antibes Juan-les Pins, France in September.

The NPC conference is the key point meeting for the nuclear chemistry and radiochemistry international community and provides a forum for utility personnel, engineers, scientists, university researchers, research institutes, and service organizations to interact and address the challenges faced by the nuclear power industry. This report summarizes papers from the NPC 2023 conference and is expected to be a comprehensive summary document incorporating the latest information on nuclear plants water chemistry related topics that would benefit the nuclear operators and regulators, and those who have not been able to attend the NPC 2023 Conference in Antibes Juan-les-Pins (France).

The 22nd International Conference on Chemistry in Nuclear Reactors Systems (NPC, 2023) took place in Antibes, Juan les Pins (France) on September 24-28, 2023, and it was organized by SFEN (Société Française d'Énergie Nucléaire). The series of conferences started in Bournemouth in 1977 and since 1992 takes place every other year, either in Europe or in Asia or in America. The previous one, NPC 2018, was hold in San Francisco (USA), The NPC-2020 was postponed due to the COVID-19 pandemic to 2021 and finally to 2023, so, it is the first conference in 5 years that the international community of nuclear chemists and radiochemists has had opportunity of meeting together. The next conference will be in Busan (South Korea), in 2025.

At NPC 2023, a total of 246 persons from 23 countries attended the conference. France with 89 attendees was the country most represented and USA, UK and Sweden had 20 or more attendees. Similarly, France was the country that presented more papers, 24 oral presentations and 19 posters, USA with 17 oral and 15 posters and Sweden with 7 oral and 7 posters follow the list of countries with more communications, 2 and 1 respectively. Despite active program on nuclear energy, there were no attendee from, Russia, Ukraine, United Emirates, etc. the first two for obvious reasons. The International Atomic Energy Agency (IAEA) took part in sponsoring this conference, as it has been the case on most of these NPC conferences.

The NPC 2023 organization divided the submitted material in the following topics and subtopics:

- Secondary Water Chemistry & Radiochemistry
 - Control & Corrosion
 - Film Forming Products & Dispersants
 - Hydrazine Alternatives
- Primary Water Chemistry & Radiochemistry
 - Control & Corrosion
 - Source Term
 - Zinc
 - BWR
 - Fuel and CRUDs
- Auxiliary Systems Water Chemistry & Waste Treatment
- Maintenance and Long-Term Operation
- Monitoring Updates
- Numerical and Simulation Tools
- Advanced Reactors

The present report has adapted slightly this index of topics.

The 10 most preferred topics by attendants to the LCC-18 seminar in April 2022 are as follows:

- PWR secondary chemistry: improving feedwater quality and managing blowdown.
- Guidance on how to use ECP (Electrochemical Corrosion Potential) to assess the reducing/oxidising conditions in the secondary circuit.
- Alternatives to hydrazine in the auxiliary Systems.
- Chemistry used in SMR concepts.
- Effects of Zn injection in PWRs including impact of zinc injection on radiation fields and also on crack growth rates in materials of construction.
- Chemistry analyses for the long-term safety purposes, for example Mo-93, during operation.
- Leakage detection - pressure boundary control and other systems.
- KOH water chemistry effects on materials
- Study of how different parameters such as material composition, preoxidation and reactor environment affect X-750 and Alloy 718 spacer corrosion.

In the text, we have emphasized these topics although, for some very specific, the submitted material has been rather scarce.

2 PWR Secondary Water Chemistry

2.1 Control and Corrosion

A miscellanea of communications was presented in this general topic. A general view of the secondary chemistry trends was presented by EPRI, confirming the general reduction of impurities in feedwater and blowdown in PWR, the generalized use of amines alternatives to ammonia and the increased number of USA plants implementing dispersant addition. In the chapter of operating experience, two Chinese communications are interesting, one on a CANDU plant secondary system ammonia-morpholine optimization for corrosion control and a second on the measurements to provide immediate action for sea water cooled plants in case of a condenser leak. Next, one statistical analysis of fleet data has allowed EPRI and its assistants to give a probabilistic value for the iron transport during flexible operation transients, an operating mode that many nuclear plants are affording of or will be in the future. Another interesting experience comes from a Swedish plant that experienced a deposition of oxides at the feedwater control valve, limiting its capacity and thus the plant output, and the role of local chemistry conditions caused by a plant modification.

An important area of research is SG fouling. EdF has made an important effort in this area from 3 different points of action: A thermohydraulic model coupled to a transport and deposition model to simulate and predict the SG tube support plate blockage, an advanced laboratory loop that reproduces PWR primary and secondary systems with the aim of study SG tube deposition, clogging and sludge consolidation and an experimental study to improve understanding of the mechanism and kinetics of transformation between different iron oxides in SG conditions. Another research in Bulgaria applied the mixed-conduction model to the experimental data of deposition and consolidation of magnetite in SG to propose a sludge deposition model.

Last, it's an update of EPRI research of possible effects of organic acid from the thermal decomposition of amines used to condition the secondary system in the turbine materials from the main manufacturers.

2.1.1 Feedwater Quality Improvements and Blowdown Management

2.1.1.1 Secondary Chemistry Trends

A general overview of the current trends in PWR secondary chemistry is presented by EPRI [Fruzzetti & Duncanson, 2023]. This organization maintains its Chemistry Monitoring and Assessment (CMA) data base collecting relevant chemistry parameters data from USA plants and from all around the world. In fact, this database contains more than 1600 cycles of valuable operating chemistry data covering all modes of operation. EPRI develops and maintains the PWR Secondary Water Chemistry Guidelines and, in support of them, performs testing, completes technical assessments, and reviews operating experience.

Regarding the essential secondary chemistry parameters at USA plants, a comparison on the data reported in 2014 to recent ones in 2023 is presented in the Table 2-1.

Table 2-1: U.S. Median Values for PWR Secondary Chemistry from EPRI's CMA data base [Fruzzetti & Duncanson, 2023].

Location	Parameter	Current U.S. Median (2014 value)	Range*		AL1
			Current Min (2014 value)	Current Max (2014 value)	
Feed Source**	O ₂ , ppb	5.73 (4.84)	0.7 (0.7)	44.0 (20.2)	> 100 ***
Feedwater	N ₂ H ₄ , ppb	105 (99.8)	22.4 (29.4)	195 (221)	< 8 x Feed Source [O ₂] or <20 ppb, whichever number is larger
Feedwater	O ₂ , ppb	0.14 (0.20)	0.015 (0.02)	1.7 (1.9)	> 5
Feedwater	pH(25°C)	9.88 (9.75)	9.30 (9.47)	10.28 (10.07)	n/a
Feedwater	Fe, ppb	0.75 (1.26)	0.15 (0.47)	3.34 (2.43)	> 5
Feedwater	Cu, ppb	0.005 (0.01)	0.0015 (0.001)	0.11 (0.11)	> 1
Feedwater	Pb, ppb	0.002 (0.009)	0.0003 (0.001)	0.015 (0.019)	n/a
SGBD	Na, ppb	0.14 (0.18)	0.04 (0.05)	0.43 (0.44)	> 5
SGBD	Cl, ppb	0.30 (0.38)	0.05 (0.05)	1.71 (1.7)	> 10
SGBD	SO ₄ , ppb	0.14 (0.40)	0.11 (0.10)	2.54 (1.41)	> 10
<p>* The range of cycle median values for each PWR considered</p> <p>** Feed Source is a new term introduced in revision 8. It is defined as the effluent from the first component upstream of the steam generator with a significant holdup volume.</p> <p>*** This AL1 value was increased in Revision 8 from 10 ppb to 100 ppb if an appropriate feedwater oxygen monitoring approach is in use and if there is no copper alloy tubed condenser and no copper alloy feedwater heaters.</p>					
© ANT International, 2024					

Each parameter has an associated Action Level 1 (AL1) that represent the threshold value beyond which data or engineering judgment indicates that long-term reliability of a secondary system component may be threatened. As can be seen, the impurity levels in the U.S. are typically well below the AL1 values, with some improvement noted since 2014 -notably regarding the median value for feedwater iron.

EPRI presented the trends for the relevant parameters [Lynch et al. 2023]. Figure 2-1 illustrates the evolution of secondary coolant (SG blowdown) chloride, sulphate, sodium and silica. We can highlight the U.S industry secondary coolant sodium median values that have remained relatively low with the median decreasing by 65% from 2000 to 2021. Silica is an important diagnostic parameter to identify programmatic problems or diagnostic, although it is not directly related to Steam Generator (SG) degradation.

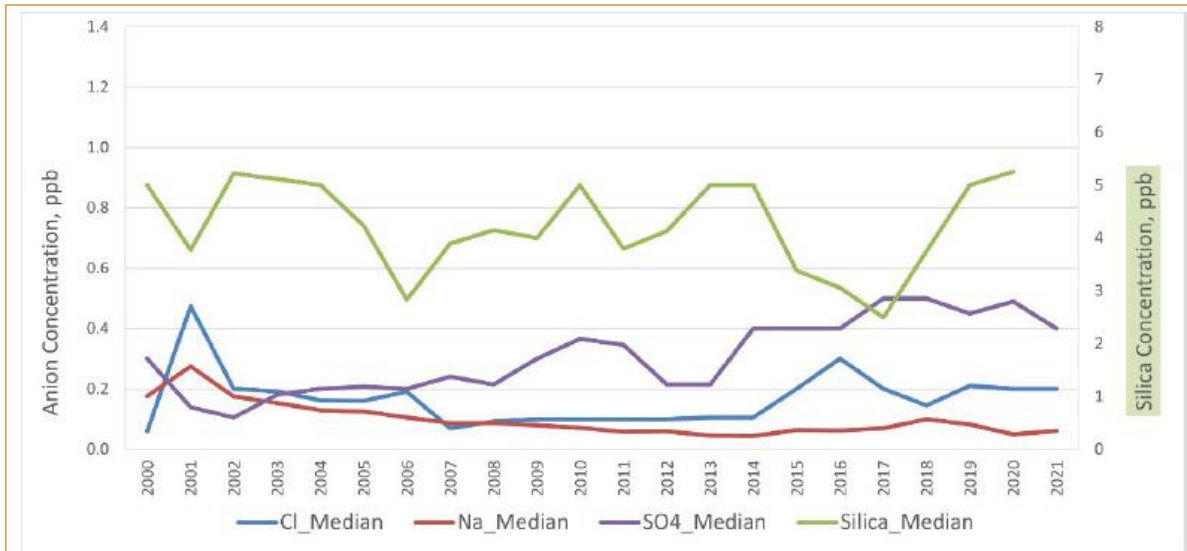


Figure 2-1: Annual U.S. Industry Secondary Coolant Impurity Concentrations [Lynch et al. 2023].

Regarding feedwater metal trends, in Figure 2-2 it is significant the reduction in feed water iron along the years and the almost absence of copper due to the removal of copper alloys in the systems.

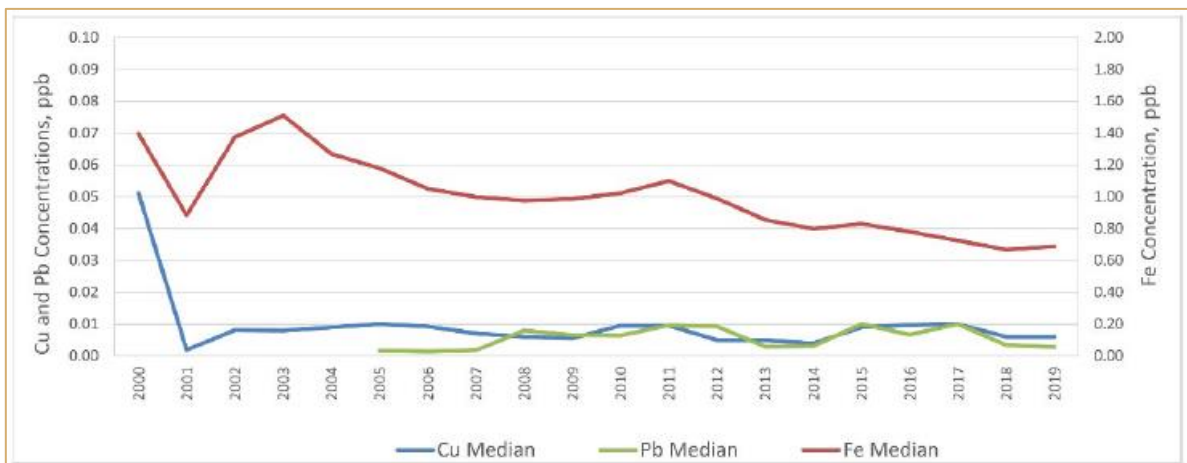


Figure 2-2: Annual U.S. Feedwater Metal Concentrations [Lynch et al. 2023].

The injection of ammonia/amine(s) to control secondary pH, to mitigate FAC and the resultant corrosion product transport to the SGs, remains plant-specific in the U.S. fleet. Figure 2-3 shows how this has varied in the U.S. from 2014 (on the left) to 2023 (on the right) based on data from EPRI's CMA database. As indicated, ethanolamine (ETA) remains the predominant chemical injected (either by itself or in combination with ammonia or another amine such as methoxypropyl-amine (MPA), morpholine, and dimethylamine (DMA)).

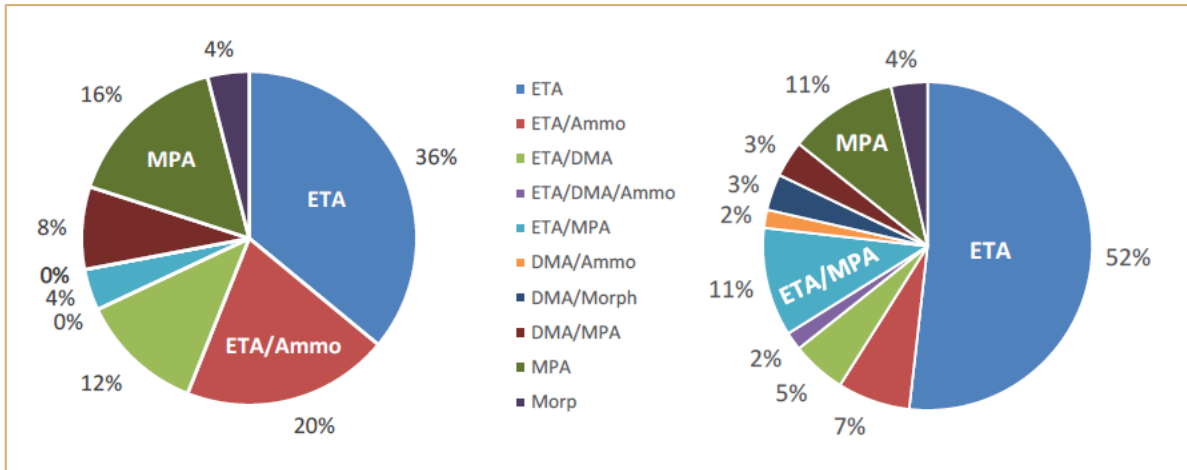


Figure 2-3: Amine/Ammonia Injection in the U.S. Based on EPRIs CMA Database (Left 2014; Right: 2023). [Fruzzetti & Duncanson, 2023].

Dispersant application it's an emergent technology that is implemented increasingly along the fleet, as it is shown on Figure 2-4.

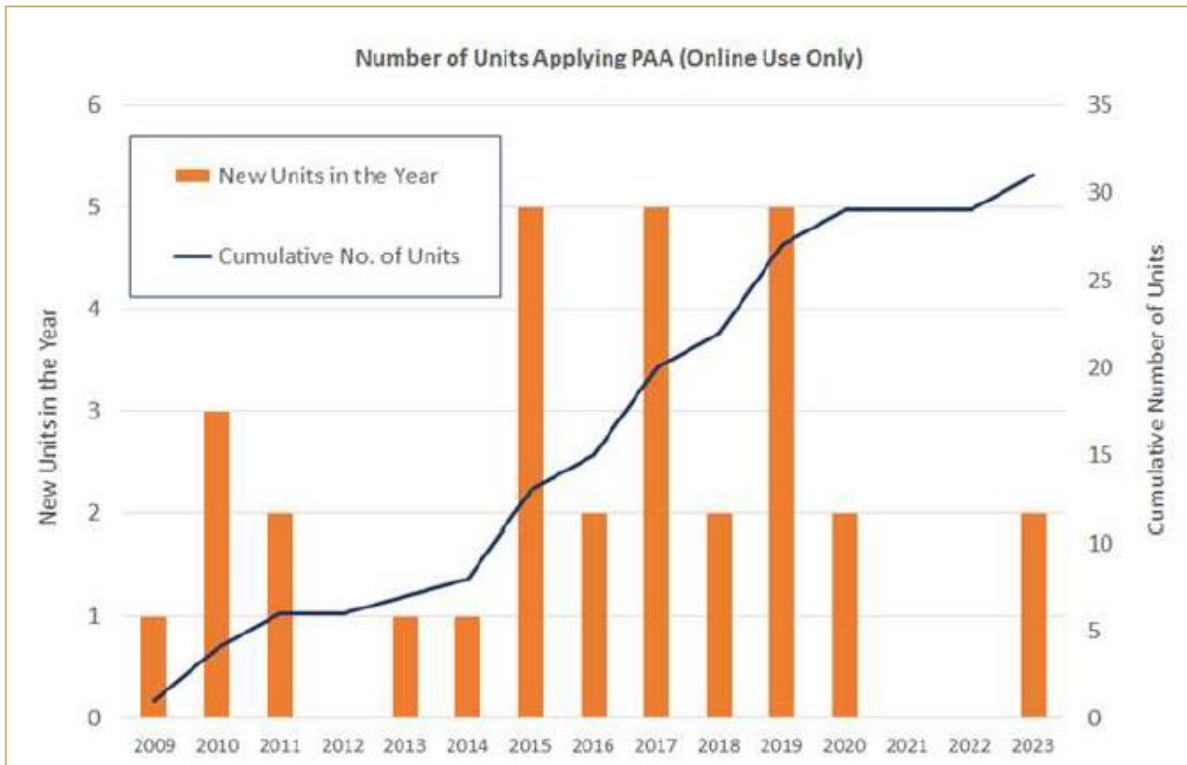


Figure 2-4: Trends in Units Implementing Dispersant Application [Fruzzetti & Duncanson, 2023].

The use of dispersants and filming products to minimize the generation, transport and accumulation of impurities in the SGs is subject to specific programs within EPRI and will be mentioned in chapters 2.3 and 2.4. Similarly, EPRI's activities to identify a potential alternative to hydrazine for the control of secondary side oxygen will be discussed in Chapter 2.2.

Finally, revision 8 of EPRI's PWR Secondary Water Chemistry Guidelines was published in 2017. Many important changes are incorporated in this revision. Of relevance, we can mention the following:

- The section describing dispersant application to mitigate SG fouling was substantively updated, summarizing technical work and significant plant operating experience since publication of Revision 7. Dispersant application is continuing to expand. New and varied operational experience and valuable technical evaluations that provide further information to optimize dispersant application are included. In addition to an interim guidance that provides palliative flexibility in monitoring dispersant concentration.
- A new section was added on filming products, summarizing the (then, 2017) current state of knowledge. As new information comes to light, a further update will be needed to provide the best available understanding of this new (to nuclear units) technology. Based on the robust program that EPRI is carrying out, this new section may be greatly expanded in the coming years. As appropriate, guidance will be added when this technology is deemed ready for more widespread application.
- The *Guidelines* already provide the opportunity to use an alternative to hydrazine when qualified by the utility. However, such alternatives—in practice—are very limited, and further substantive work is needed to identify and evaluate good alternatives. The work being done, as described above, is essential to provide needed flexibility and resources to the industry in the current circumstance of risk to continued long-term use of hydrazine.
- The term Feed Source (defined as the first component upstream of the SGs with a significant holdup volume) was introduced to more precisely prescribe the location for which the required hydrazine minimum concentration must be based relative to that location's dissolved oxygen concentration. For plants with a deaerator, this means that the deaerator outlet dissolved oxygen concentration is used (rather than the former condensate pump discharge). In practice, this reduces (likely very significantly) the hydrazine concentration requirement for plants with a deaerator.
- For plants with an appropriate feedwater oxygen monitoring approach in use and with no copper alloy tubed condenser and no copper alloy feedwater heaters, the condensate dissolved oxygen AL1 value is increased from 10 ppb to 100 ppb. This allows plants to maintain a higher dissolved oxygen concentration in the condensate as a measure, if of value, to reduce FAC in the condensate system. For plants without a deaerator, they will be limited by the corresponding hydrazine requirement. However, plants with a deaerator may find great value in this flexibility.

2.1.1.2 Operating Experience

a) Secondary System Corrosion Control Improvements at Qinshan PHWR NPP [Zhaojin Y. et al. 2023]

Qinshan III is the only PHWR NPP in China, with two 728 MWe CANDU-6 reactors that started commercial operation in November 2002 and July 2003 respectively. They are in the Qinshan Nuclear Power Base, that has got 9 operating units, in the province of Zhejiang, south of Shanghai. Each unit has a copper free secondary system with 4 SG, condensate polishing and deaerator as it's shown in Figure 2-5.

Since 2008 the plant has implemented a plan to minimize the corrosion product ingress into the SGs by adopting several actions:

- High morpholine-ammonia combination control to increase the pH_T of the overall secondary system. The initial all volatile treatment of ammonia and hydrazine as reducing agent was modified to provide an optimum pH_T to the liquid phase in all the circuit. For this purpose, an investigation was done to look for the optimum amine combination that should have the following characteristics:
 - The amine should have sufficient base strength. The pH_T value at operating temperature in all locations of secondary system shall be higher than the neutral pH value corresponding to the temperature (pH_{Tn}) by 1 unit or higher.
 - The distribution coefficient of the amine in vapor and liquid phases should be close to 1 to ensure the liquid phase surfaces in all locations of the whole secondary system are protected properly.

- The amine must have less impact on the fouling of heat transfer tube surface on the secondary side of SGs.

The result of the research was an optimal mixture of morpholine and ammonia with concentrations controlled between 15-25 ppm and 2-5 ppm respectively to increase the pH(25°C) of secondary system between 9.7- 9.9. The pH_T of secondary system waters are well controlled 1 pH unit above neutral in liquid phase, for all locations, except the SGs blowdown, ($\Delta\text{pH} = 0,74$), which is acceptable considering the small proportion of carbon steel surfaces of the secondary side of SG in comparison with the overall secondary system

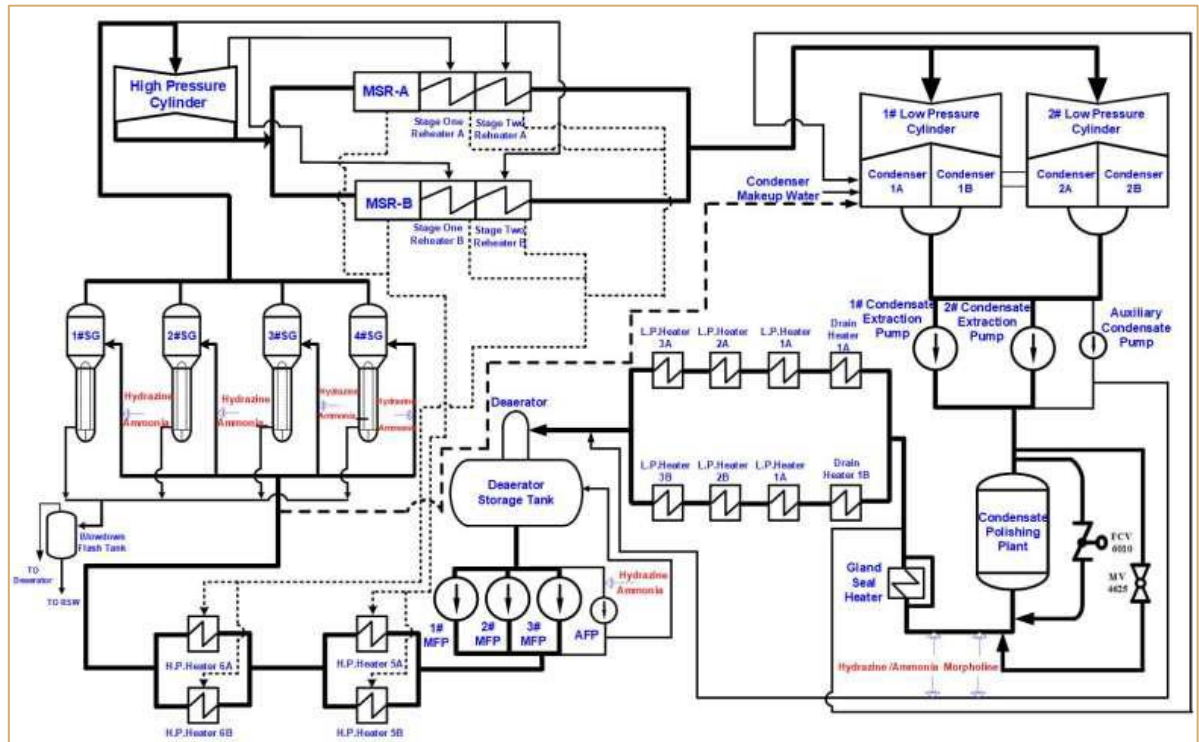


Figure 2-5: Qinshan III Secondary System Flowsheet [Zhaojin Y. et al. 2023].

Other actions taken as a consequence of the research test and the evaluation of 22 cycles of 21 nuclear plants in USA are as follows:

- Increasing Dissolved Oxygen Concentration in Condensate: In order to minimize FAC in the condensate system, a small concentration of oxygen is required. Considering thermal deaeration efficiency of the deaerator is about 90% and the dissolved oxygen in feedwater is required below 3ppb, dissolved oxygen range in condensate is conservatively raised to 5-30ppb by slightly opening the drain valve of condenser with vacuum properly maintained.
- Installing a Magnetic Filter inside the Condenser: A Magnetic grid iron-removal (MGIR) device was installed in the condensers, as is shown in Figure 2-6. The weight of magnetic deposits removed from condensers in each CANDU unit during outage is about 3.5kg (converted to 12 months' operation) which is 1/3 of PWRs' with similar condenser design in China.
- Corrosion Product Control during Startup: Apart from properly layup the steam and water sections of secondary system for the outage, during the Unit pre warm-up flushing and heat up, an optimal operation procedure was developed to establish the partial or full circulation of water, and redirect all the high iron-contained water back to condensers, and clean the water up through condensate polishers. Later, during power uptake, slightly postpone the MSR and Reheater drains pump forward and recirculate them back to condensers before the unit ramp up to 60% of full power, which could reduce a quite amount of corrosion products to get into the SGs.

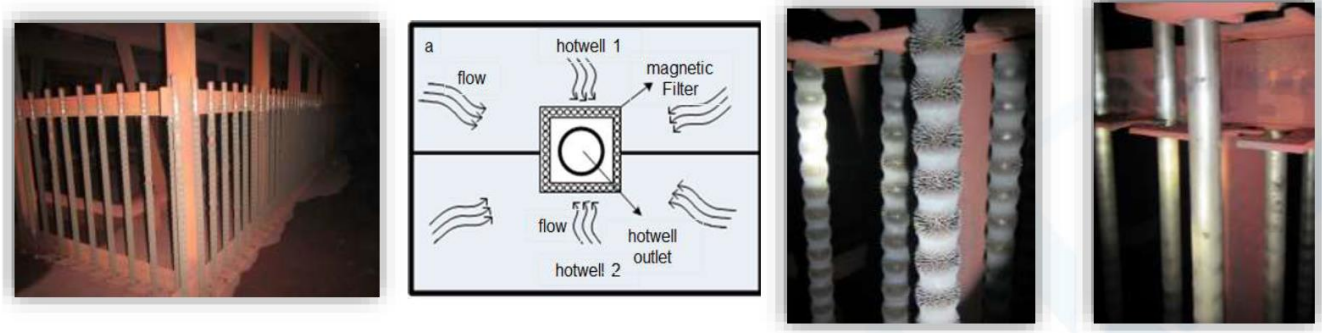


Figure 2-6: Installation diagram of magnetic grid iron-removal filter in condenser and comparison before and after its cleaning [Zhaojin Y. et al 2023].

The results of this plan are very positive, as the feedwater iron concentration is reduced to around 0,4 ppb. In-service inspection reveals that the thickness of all steam and drain system pipes are kept at the same level as the initial operation of the NPP. Converted to 12 months' operation, about 3.5 kg of magnetic deposits per unit are removed from condensers and finally, in every outage, the sludge removed by water lancing from each SG is about 0.7 kg (converted to 12 months' operation), and no visible deposits pile or deposits blockage are found on the tube support plate through video inspection. After 20 years of operation, both units are still operating at full power with no power reduction caused by the fouling of both sides of SGs, which occurred in other CANDU NPPs.

b) Countermeasures of Water Quality Affected by Seawater Leakage of Condenser in Nuclear Power Plant.

At plant located by the sea, condenser leakage occurs occasionally and affects the safety, stability and economic operation of the nuclear power plant. For this reason, a model for the influence of condenser seawater leakage on the water quality of the secondary side has been established by the China Nuclear Power Operations Research Institute [Minshun T. et al 2023]. The trends and the response time, as well as the timeliness and sensitivity of monitoring, representativeness and operation strategy of the condensate polishing are revised.

A model based on a mass balance shows that, even for a small leak, the action levels are surpassed in a short time and, if not handled properly, the nuclear power plant will quickly reach the action limit of power reduction or even shutdown. Therefore, the response time needs to be shortened. The Figure 2-7 shows a diagram with the time sequence for exceeding action levels after a small leakage of 5 and 10 kg/h of sea water:

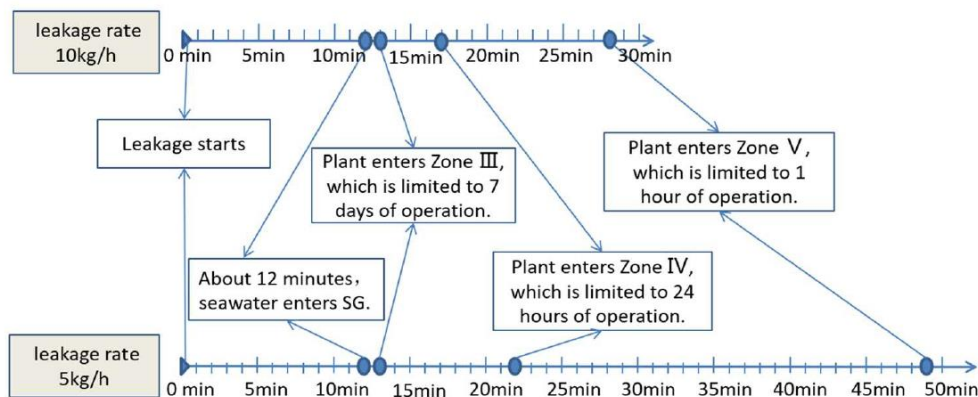


Figure 2-7: Timeframe for exceeding action levels after a condenser leakage of 5 and 10 kg/h [Minshun T. et al. 2023].

According to this time sequence, a revision of plant monitoring and operation response to a condenser leakage has led to the following proposed countermeasures:

3 PWR Primary Water Chemistry & Radiochemistry

Concerning general trends in PWR Primary Water Chemistry, EPRI presented [Lynch N. et al. 2023] some updated trend plots for the main chemistry parameters obtained from the CMA database that collects chemistry program information and operational data from participating member utilities. Current participants include 65 U.S. PWRs and 88 non-U.S. PWRs. The following data are limited to US plants.

Figure 3-1 shows the industry median values for Primary water impurities. Chloride median have decreased a 66% from 2000 to 2021, and fluoride have also a decreasing trend. Oxygen values are only reported to the data base when hydrogen level is below 15 cc/kg, according to the *Pressurized Water Reactor Primary Water Chemistry Guidelines*.

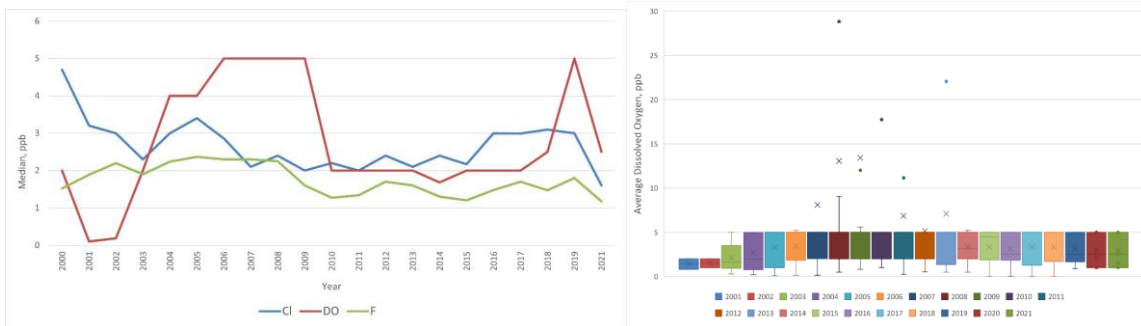


Figure 3-1: (Left) Annual industry Primary Coolant Impurity Median Concentrations. (Right) Range of Dissolved Oxygen concentration data reported to the CMA database [Lynch N. et al. 2023]

Hydrogen annual data range reported are shown in Figure 3-2. The range trends show along the years the transition of the PWR fleet to operating in the upper part of the 25 to 50 cc/kg dissolved hydrogen range as it is expected to be slightly more beneficial for the mitigation of primary water stress corrosion cracking and to minimize crud transport and deposition in the core.

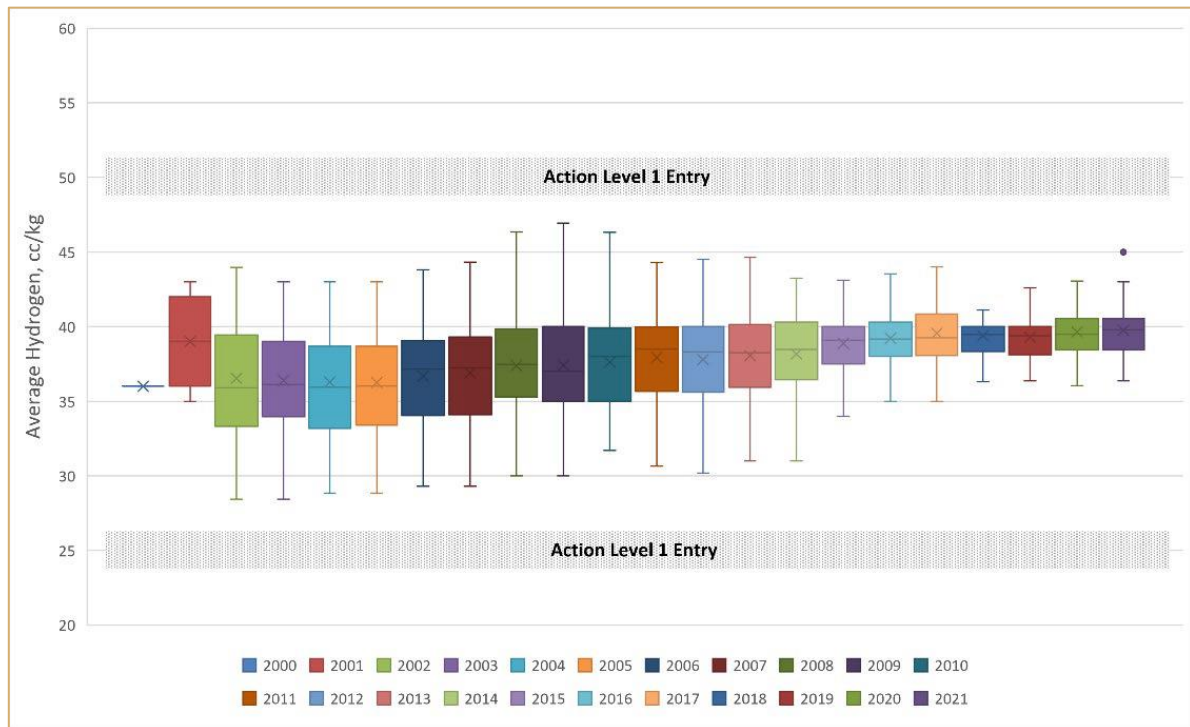


Figure 3-2: Annual Industry Primary Coolant Hydrogen Concentrations [Lynch N. et al. 2023]

With respect to Primary Coolant pH_T Control Strategy, EPRI defines a modified chemistry control strategy is defined as “a coolant pH_T control strategy in which the lithium concentration is maintained at a constant value for any portion of the cycle, thereby allowing the pH_T to increase as the boron concentration decreases”. On the other hand, a constant chemistry control strategy coordinates lithium with boron to maintain a constant pH_T throughout the entire cycle. EPRI Guidelines require that plants maintain reactor coolant $pH_T \geq 7.0$ while at full-power xenon-equilibrium conditions. The term “elevated” does not independently describe a pH_T control strategy. Therefore, it must be used in combination with a modified or constant chemistry control strategy. A constant elevated control strategy maintains a constant $pH_T > 7.2$ for the entire length of the cycle [4]. A modified elevated control strategy also has a $pH_T > 7.2$ for the entire length of the cycle, but the pH_T is not maintained at a constant value for the entire cycle. Figure 3-3 shows the distribution of PWRs operating in the specified pH_T regimes. It is clear the prevalence of elevated strategies.

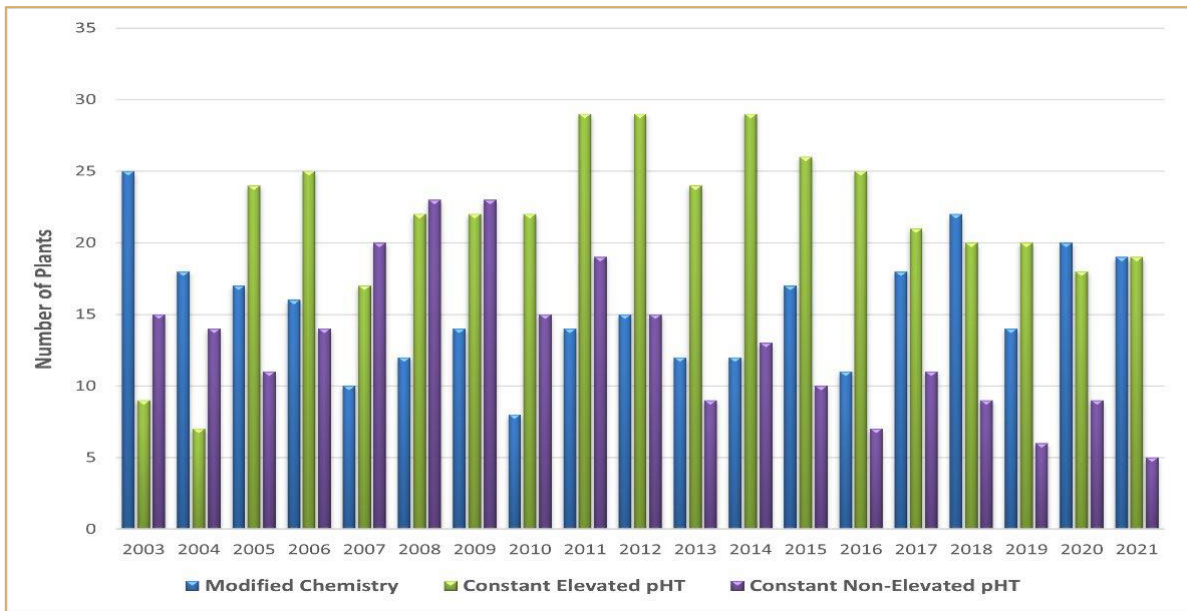


Figure 3-3: PWR fleet pH_T regimes distribution [Lynch N. et al. 2023]

Finally, regarding Zinc injection, the number of PWRs injecting zinc has risen considerably from 2000, with additional plants considering the benefits of initiating a Zinc program, as depicted in Figure 3-4.

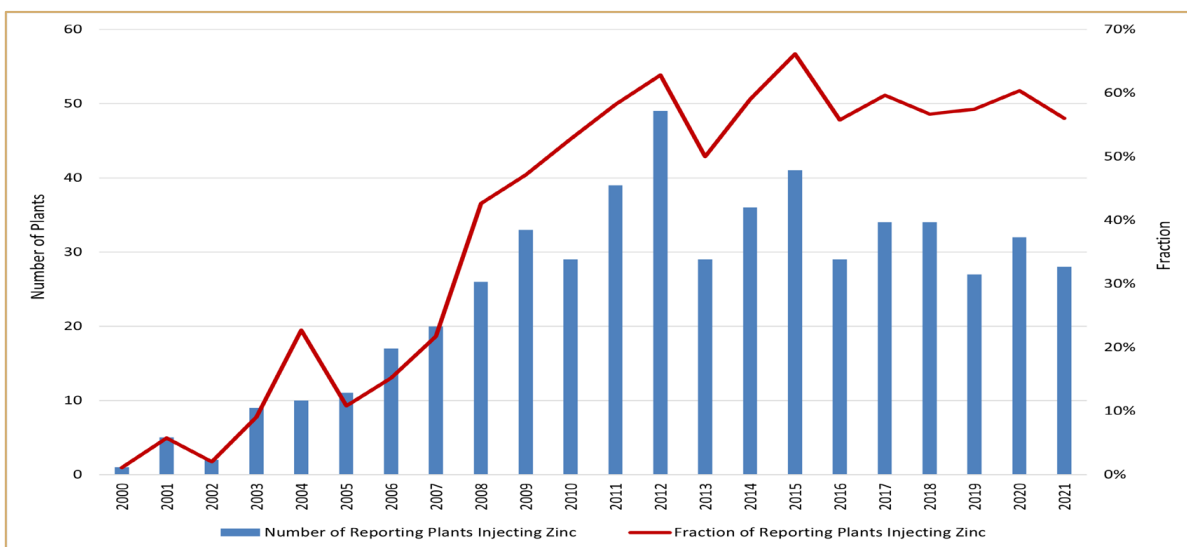


Figure 3-4: Plants reporting Zinc addition and the percentage fraction [Lynch N. et al. 2023]

3.1 Control and Corrosion

Many research communications were presented in this area, several of them focused on the effects of primary water on the corrosion layer formation and release in Alloy 690 material, that is the most common alloy of SG replacements. Surface characterization of the layer formed at primary system temperatures, in and out of the steam generator has been the focus area to provide a better understanding of some observed increased release of corrosion products after the SG replacements; also, the flow effects on corrosion has been investigated for this material. In a plant with several units, the different behaviour of CP release after SGR was investigated with interesting results. Other investigations have centred on SS304 L crack initiation and the effect of hydrogen and irradiation and on magnetite deposition mechanisms by zeta potential measurements or on the possible effects of KOH transition on SS corrosion.

a) Revision Plan for Water Chemistry Guidelines of Japanese PWR and BWR Plants

The Atomic Energy Society of Japan (AESJ) published three water chemistry guidelines and six chemical analysis standards for Japanese PWR and BWR [Kawamura H. et al., 2023]. To maintain and improve nuclear safety and reliability, these guidelines will be revised every five years, based on the latest scientific knowledge and field expertise. Accordingly, the AESJ has started the process. Regarding PWR, it has recently updated the analytical method for Boron, extending the applicable range to 10-4000 mg/l, the dissolved Hydrogen method to improve the accuracy and identify the cause of errors and the radioactive iodine methods, updating the half live of ¹³³I to 20,8 hours. They have scheduled to issue a new method for Boron Isotope Ratio in its Chemical Analysis Methods for PWR Primary Coolant. Although the ¹⁰B isotope ratios need not be measured for each cycle from a safety confirmation perspective, it is important to make safety confirmations more reliable by continuing to collect data related to ¹⁰B depletion by ¹⁰B isotope ratio analysis at specific facilities and using this data to clarify the safety margin. The ¹⁰B isotope ratio is measured by a mass spectrometer and it is important to use standard reference material with a known boron isotope ratio and measure samples repeatedly for reliable quantitative analysis.

The Primary and Secondary Water Chemistry Guidelines as well as the BWR are scheduled a revision to 2024-2025 and the respective committees are preparing the preliminary discussion.

b) Water Chemistry Effect on Stress Corrosion Crack Initiation Behaviour of Irradiated Stainless Steel 304L in Primary Water Environment.

In this research by the Ulsan National Institute of Science and Technology in Korea, the combined effect of irradiation and dissolved hydrogen (DH) of austenitic stainless steel has been studied [Ham J. et al. 2023]. To avoid the problems of neutron activation, for this study, proton irradiation has been chosen to make a radiation damage of 1 and 3dpa on SS 304L samples that will be subject to the study. For the effect of DH, two different levels have been chosen: 25 and 50 cc/kg. Slow Strain Rate Test (SSSTR) technique combined with direct current potential drop (DCPD) method has been used to detect crack initiation. The tests have been made in an experimental facility with typical PWR primary conditions, as shown in next table.

Table 3-1: Stress corrosion cracking experimental environment including slow strain rate test and direct current potential drop conditions [Ham J. et al. 2023].

Pressure [MPa]	Temperature [°C]	Boron [ppm]	Lithium [ppm]	DO [ppb]	DH [cm ³ /kg]	Current [A]	Strain rate [mm/mm/s]
15.5	325	1200	2.2	< 5	25, 50	5	1*10 ⁻⁷

© ANT International, 2024

The SS samples after irradiation have been examined by transmission electron microscope (TEM), to confirm the density of defects. Figure 3-5 shows the microstructure of the 1 and 3 dpa irradiated

specimens, confirming the presence of dislocation defects on the surface. These defects prevent the mobility of the crystal structure which may affect the material mechanical properties.

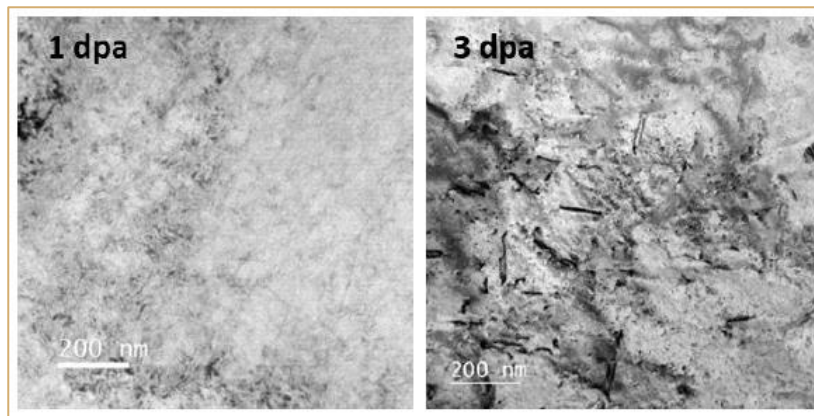


Figure 3-5: TEM bright-field images (x30,000) which show that defect density increases from 1 dpa to 3 dpa sample [Ham J. et al. 2023].

Figure 3-6 shows a typical DCPD curve used to determine crack initiation. Considering the sample dimension particularly at the gauge section, the electrical resistance of the sample will be increased uniformly. But this tendency is going to be changed when crack is initiated. The micro crack can reduce the cross sectional area of sample which causes rapid increase of electrical resistance.

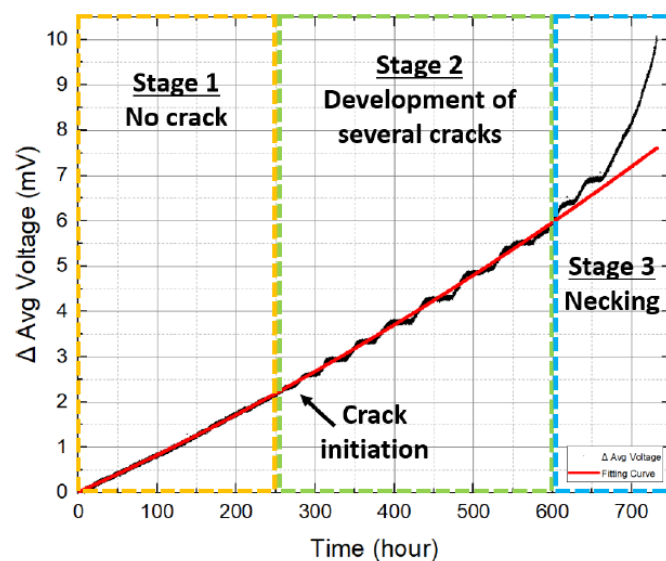


Figure 3-6: Detection method of crack initiating moment by interpreting direct current potential drop data. The data was gained from the experiment which had been conducted for 720 hours [Ham J. et al. 2023].

The results of crack initiation for the experiments made with as received samples and after irradiation, exposed to DH of 25 and 50 cc/kg clearly show the combined effect of irradiation and DH as shown in Figure 3-6. It can be seen that crack is initiated earlier with higher DH and with higher radiation damage, but it also is clear some synergistic effect of DH and radiation damage on crack initiation.

4 BWR Chemistry & Radiochemistry

EPRI presented an update of the BWR fleet chemistry performance monitoring and trends from its CMA data base [Lynch et al., 2023]. This database collects information from 31 U.S. BWRs and 8 non-U.S. BWRs: two in Mexico and 6 in Europe.

Concerning the Good Practise and Needed Values for chemistry parameters in the EPRI Chemistry Guidelines [BWRVIP-190 rev.1], Figure 4-1 shows the percentage of reactors meeting the values. Most plants do not meet the Good Practise value for reactor water soluble Co-60, and some plants operating with On-Line NobleChem™ (OLNC) exceed feedwater total zinc values, due to zinc injection rates required to achieve the reactor water Co-60(s)/Zn(s) recommendation for control of shutdown radiation fields.

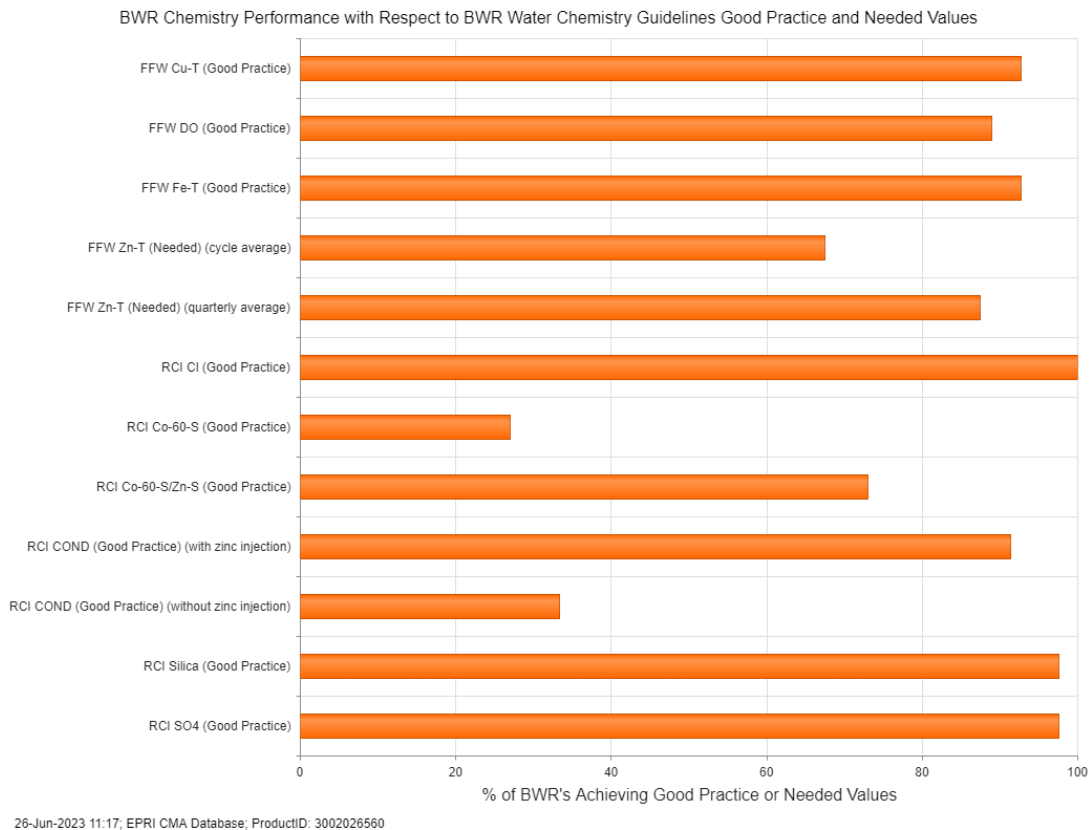


Figure 4-1: BWR Chemistry Performance with Respect to BWR Water Chemistry Guidelines Good Practice and Needed Values [Lynch et al., 2023].

Concerning chemistry regime for mitigating IGSCC, the US BWR started applying Hydrogen Water Chemistry (HWC) in the 80's, Noble Metal Chemical Addition (NMCA) at the end of 90's and On Line NobleChem (OLNC) in the late 2000's. At present, all US BWR except two units, are applying ONLC as it is shown in Figure 4-2. This technology is also applied in two units in Mexico and two GE design BWR units in Europe.

Feedwater Iron is a parameter that has experienced a significant reduction in the last years, mainly attributed to improvements in condensate polishing systems. This iron reduction is due to the installation of condensate prefilters at plants originally designed with only deep bed (DB) polishing, discontinuation of iron injection at Filter + Deep Bed (F+DB) plants, and the use of high efficiency iron removal septa at condensate filter demineralizer (CF/D) plants. Figure 4-3 shows the trends for the different type of condensate polishing plants along the years. As it can be seen in Figure 4-1, 95% of plants fulfil the Good Practise value for this parameter.

KEY EMERGING ISSUES AND RECENT PROGRESS RELATED TO PLANT CHEMISTRY/CORROSION (PWR, CANDU, AND BWR NUCLEAR POWER PLANTS)

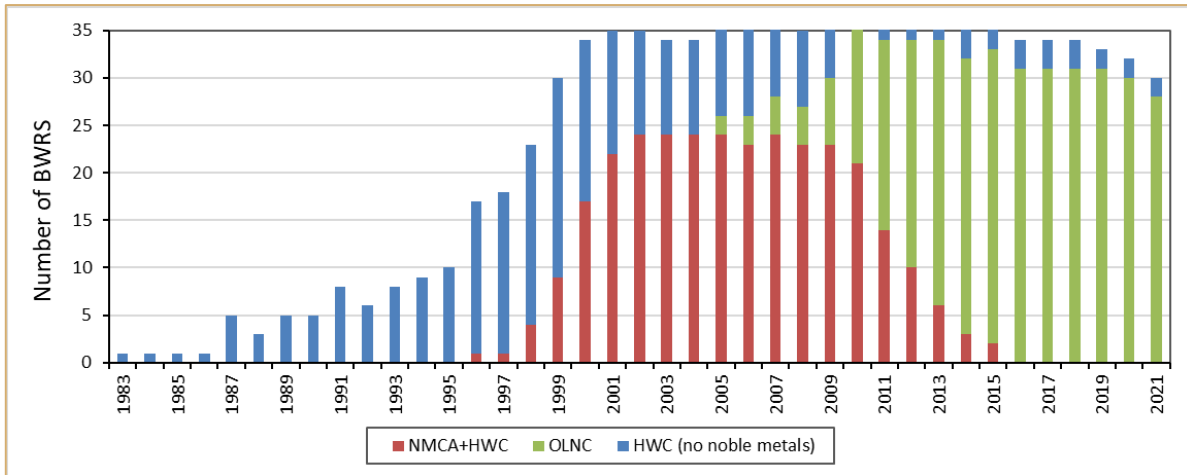


Figure 4-2: IGSCC Mitigation History at U.S. BWRs [Lynch et al., 2023].

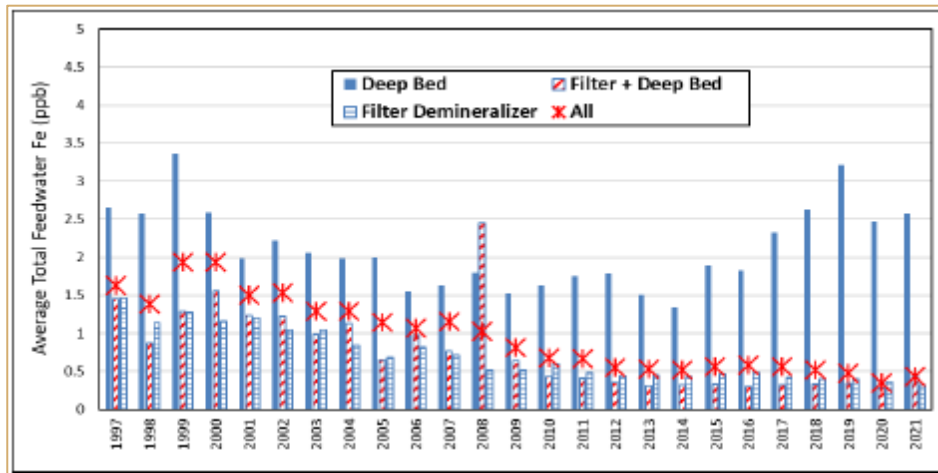


Figure 4-3: BWR Feedwater Iron from 1997 to 2021 [Lynch et al., 2023].

Regarding reactor water quality, all BWR's in the database achieve the Good Practise values of 1 ppb Chloride and all but one achieve the Good Practise of 2 ppb for sulphate. Figure 4-4 shows the average and range of values for chloride showing a significant reduction of 50% since the year 2000. Figure 4-5 also shows a similar reduction for sulphate since the year 2000, mostly due to deep bed plants installing prefilters.

4.1 Noble Metal Addition

Noble metal catalytical effect together with low addition of Hydrogen is the basic strategy for mitigating ISCC in most of BWR plants. A communication of PSI, the research institution that performed the Swiss NORA project investigation on noble metals in BWR, collects the most significant findings of this project and summarize the lessons learned. In the USA, an initiative by some plants and EPRI have developed a passive noble metal addition system that has been implemented in a plant for demonstration; a communication was presented with the results of this experience. Another presentation covers the advances in the radiolysis model BWRVIA to prepare a version to simulate this phenomenon at reduced and low power, a condition that the plants are required for flexible operation. This tool is basic for determining the amount of injected H_2 in feedwater to achieve and demonstrate mitigation with either HWC or OLN. And last, it's an update of the Hitachi efforts to develop an Fe/Fe_3O_4 ECP electrode for BWR, that are in the last performance tests before the final approval for its commercial use at BWR plants.

a) A decade of research on noble metal chemical addition at PSI – lessons learned.

Paul Scherrer Institute (PSI) presented a paper collecting some highlights from the NORA project and summarizing the main outcome with some conclusions and plant recommendations [Ritter & Grundler, 2023]. NORA stands for “**N**oble metal deposition behaviour in Boiling Water **R**eactors”, it's a joint project between PSI, the Swiss Federal Nuclear Safety Inspectorate (ENSI) and the nuclear power plants Leibstadt (KKL) and Mühleberg (KKM) in Switzerland with the objective of the investigation of the Pt deposition behaviour in BWR environment and its possible negative and/or positive impact on materials performance. The project has extended for 9.5 years (2010-2019) and has produced a set of scientific and technical communications that have been presented at different NPC conferences, among other forums.

The research has been carried out at PSI laboratory in a high temperature water loop with autoclave, as shown in Figure 4-7, at typical BWR/HWC conditions: $T = 280/270\text{ }^\circ\text{C}$, $p = 90\text{ bar}$, flow rate 10 kg/h and able to supply H_2/O_2 mixtures. The materials tested has been AISI 304L stainless steel (SS), low-alloy steel SA533, nickel-base alloy Inconel 182, Zircaloy-2. The specimens were in coupons, disks or tubes in as received (AR) or pre-oxidized (PO) for 2 weeks in BWR/HWC environment.

The Pt application rate was equivalent to the KKL typical injection rates $\sim 1.5\text{g Pt/h}$. The general application procedure was: 1 week conditioning at high temperature -> start of Pt injection ($t = 0$) -> Injection during ~ 10 days -> shutdown 3 days after end of Pt injection.

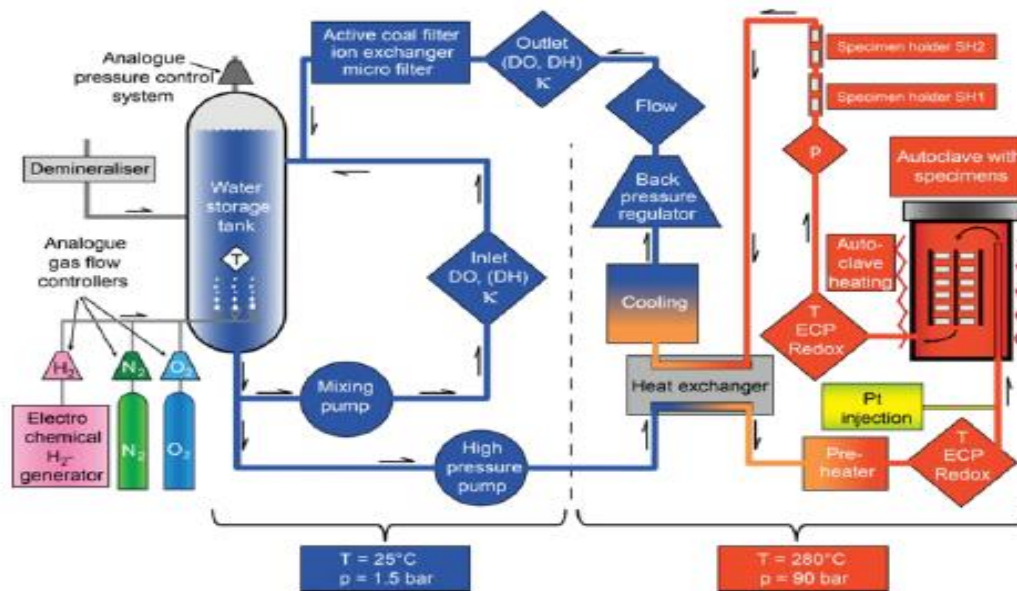


Figure 4-7: Schematic of the high-temperature water loop facility with autoclave [Ritter & Grundler, 2023].

Additional to the laboratory tests, some specimens have been exposed to the reactor water system in the KKL reactor.

Advanced electronic microscopy techniques, SEM and TEM have been used to characterize the specimen's surface and mass spectrometry with laser ablation (LA-ICP-MS) was used for quantitative elemental analysis. Figure 4-8 shows some examples of Pt treated surfaces.

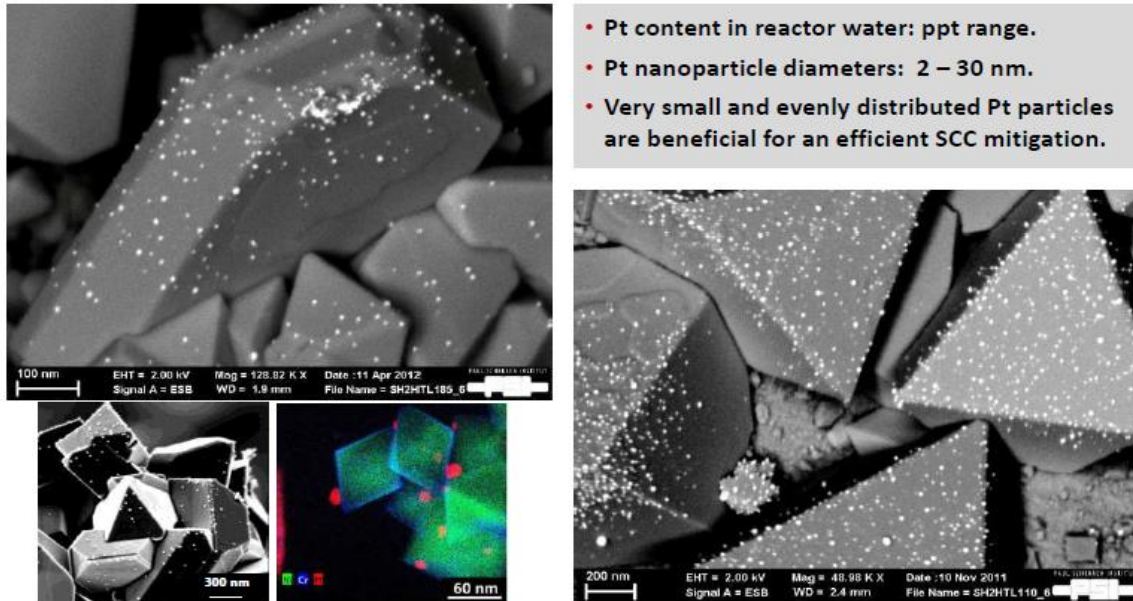


Figure 4-8: Examples of Pt treated surfaces. The SEM backscattered electron mode allows to obtain the chemical contrast that allows the vision of the Pt particles [Ritter & Grundler, 2023].

On Table 4-1 it is a list of the topics and tasks that have been systematically investigated in the project.

Table 4-1 Compilation of topics and tasks systematically investigated in the framework of the NORA project [Ritter & Grundler, 2023].

Literature Survey	Laboratory Investigations	Investigations at KKL
<ul style="list-style-type: none"> Literature study Knowledge transfer (plant to lab, lab to plant) 	<ul style="list-style-type: none"> High-resolution studies of Pt particles and Pt-oxide film interface Surface roughness and pre-oxidation Effect of Pt injection rate Effect of water chemistry and temperature Effect of different flow regimes on the Pt deposition Pt deposition in crevices Pt erosion behavior Effect of material (substrate) Effect of Pt on Zircaloy cladding behavior Spatial distribution vs. Pt loading Pt mapping by XRF (SLS) Evaluation of other analytical methods & non-destructive testing Validation of SCC initiation mitigation 	<ul style="list-style-type: none"> Exposure of coupons in the mitigation monitoring system (MMS) and backup deposition monitoring system (e.g., for validation of the OLNC technology and of the lab experiments) Assessment of the OLNC application procedure

© ANT International, 2024

5 CANDU Reactors

Several communications concerning CANDU reactors have been presented in the PWR secondary System chapter, and most of the information in that section is useful for these reactors. Unfortunately, just a few communications were presented at NPC-2023 concerning specific issues for these plants. One is concerning the Canadian regulator plan to develop and launch by 2025 a regulatory document on chemistry control program for nuclear plants. The second is the current status of CARTA, the integrated model for transport of activated and corrosion products in CANDU-6 primary heat transfer system (equivalent to PWR primary system).

a) Development of a Canadian Regulatory Document on Chemistry Control Program for Nuclear Power Plants [Gringas S. et al 2023].

The Canadian Nuclear Safety Commission (CNSC) presented the status of a regulatory document, REGDOC, on the requirements of a chemistry control program for nuclear reactor facilities.

The CNSC's regulatory framework consists of acts (laws) passed by the Canadian Parliament that govern the regulation of Canada's nuclear industry, and regulations, licences and regulatory documents that the CNSC uses to regulate the industry [Figure 5-1]. The information contained within the framework falls into two broad categories: requirements, and guidance on how to meet the requirements.



Figure 5-1: Overview of the Canadian regulatory framework [Gringas S. et al 2023].

Compliance with requirements is mandatory. Licensees or applicants must meet these requirements to obtain or retain a licence or certificate to use nuclear material, nuclear substances, or operate a nuclear facility. On the other hand, guidance provides direction to licensees and applicants on how to meet the requirements. It also provides more information about approaches that applicants or licensees may adopt to address specific topics or data to provide to aid in the CNSC review of licence applications. Licensees are expected to review and consider guidance; if the recommendations provided in the guidance are not being followed, the licensees should explain how another approach they have chosen still meets regulatory requirements. The REGDOCs contain no requirements but clarify them and provide guidance.

So far, there is not a regulatory document on chemistry control in operating nuclear reactors. There is a general requirement for it, specified in a Canadian Standard (CSA N286:12, *Management System Requirements for Nuclear Facilities*) and relevant reference documentation from the IAEA or Electric Power Research Institute (EPRI) can be used to verify the operator's chemistry program performance. Therefore, CNSC staff identified a need to specify more detailed regulatory requirements and guidance related to chemistry control which will aid with the scope of CNSC, help licensees and applicants to understand requirements related to chemistry control and clarify regulatory expectations. Finally, it is expected to assist potential license applicants for new SRM designs on chemistry control.

The Chemistry REGDOC is expected to finish its developing process, which consists of the detailed steps shown in Figure 5-2, in winter 2025 with the presentation to the Commission for its approval and publishing.

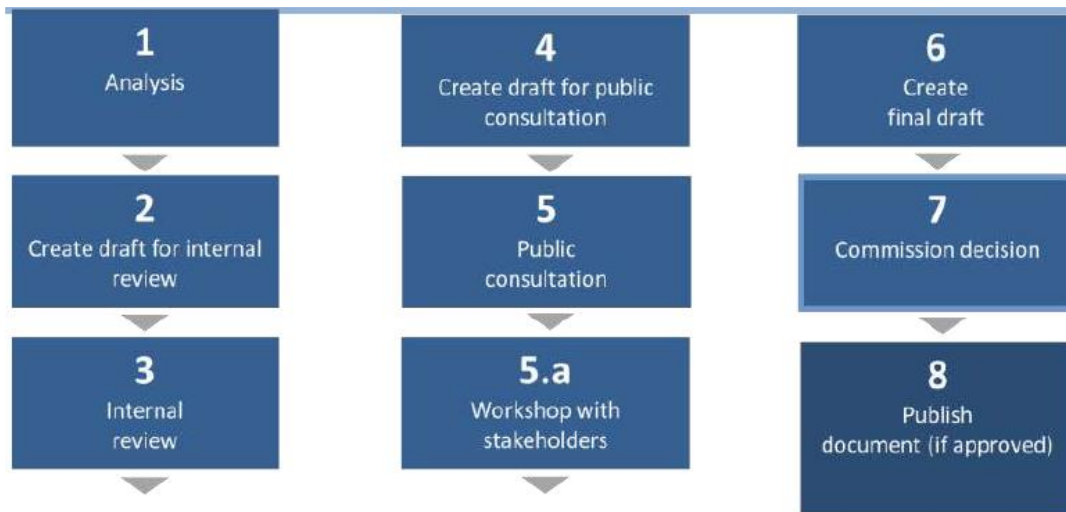


Figure 5-2: Canadian REGDOC Development process steps [Gringas S. et al 2023].

b) Radioactivity Transport Prediction Throughout a CANDU-6 Reactor Lifetime Using the CARTA Code [Baker & Palazhchenko, 2023]

Predicting radioactivity transport is crucial for the safe and reliable operation of a nuclear reactor while maintaining the ALARA (as low as reasonably achievable) principle to radioactivity, particularly surrounding station outages or refurbishment, when major changes to the materials of construction and system chemistry can occur. However, there is currently no single, mechanistic, validated simulation package for CANDU reactors that encompasses all available knowledge on material and activity transport. The attempts to use PWR predicting activity models has resulted in limited results due to the distinct CANDU water chemistry and materials of construction. There is a semi-empirical model for iron and activity transport, mainly focusing on cobalt-60 code, ACTTRACAN, developed by Atomic Energy of Canada Limited (AECL), but it is reliant on plant-specific input data to model activity transport.

The Corrosion and Radioactivity Transport Analysis (CARTA) code for CANDU reactors has been under development by researchers based out of the University of New Brunswick over the last two decades. The work presented outlines the recent advances on the previous iron transport code in simulating the transport of three additional elements, nickel, chromium, and cobalt, that are either native to the Primary Heat Transport system (PHTS) or are introduced as impurities.

CARTA is a one-dimensional, predictive, simulation package written in Python that mechanistically integrates the processes involved in corrosion and radioactivity transport within a typical CANDU-6 PHTS. The module for material and activity transport was described in a previous communication at NPC-2018 [Palazhchenko et al., 2018]. PHTS it's the equivalent to the primary system for the CANDU reactors, Figure 5-3.

6 Advanced Reactors

Some information on advanced reactors was presented. First an exercise from EPRI and NuScale for conciliation between the PWR Chemistry Guidelines, for plants with once-through SG (OTSG) and the chemistry chapter of the DCA for the NuScale modular reactor, presented to the NRC. An interesting presentation was made by EdF Energy, owner of Hinkley Point C plant, an EPR under construction in the UK, on the active participation of Operations in the Chemistry Specifications for commissioning and operation (“Chemistry specifications are not just for the chemists”). Finally, a huge information of the experience and lessons learnt from the OL-3 and FA-3 Hot Functional Tests and criticality and power escalation of the first one is presented.

a) Water Chemistry Gap Analysis for NuScale Power SMRs against PWR Guidance

Small Modular Reactors (SMRs) have recently come to the fore in terms of a nuclear-based energy resource to supply power to the modern grid. Water chemistry control technologies for nuclear power plants have been significantly enhanced over the past few decades to improve material and equipment reliability and fuel performance as well as to minimize radionuclide production and transport. As new water-cooled plant designs are considered for construction, it is important to ensure that the designs consider implementation of state-of-the-art, industry-developed water chemistry controls and also that some updates on guidelines are incorporated, based on the new plants design.

In 2022, NuScale Power received USA regulatory approval for its water-cooled small modular reactor design. In the three years prior to this decision, EPRI undertook a joint project with NuScale to assess coolant chemistry operational guidance, based upon the tenants of the current EPRI PWR Chemistry Guidelines products for both the primary and the secondary coolants [Reinders et al. 2023]. NuScale has a SMR design with enough similarities to other once through steam generator (OTSG) PWR designs that it could conceivably be controlled to the EPRI PWR chemistry guidelines with some modifications due to design differences. Figure 6-2 it's a simplified sketch of the NuScale simplified reactor.

The project to develop the chemistry guidelines for this type SMR is based on a 4 systematic step process that it's described in Figure 6-1. At present, the first two steps have been covered and EPRI has published the corresponding reports:

- NuScale PWR Design Gap Analysis: conducted to identify differences between current water chemistry control guidance (specifically the technical basis described in the EPRI PWR Water Chemistry Guidelines) and intended chemistry related operations of the new SMR nuclear power plants.
- NuScale PWR Design Gap Closure & Guidance Implementation Plan: Prioritize and develop a success path for closing gaps (those that can be dispositioned without significant effort) and recommend the PWR Guidelines Committee how the gaps should be closed.

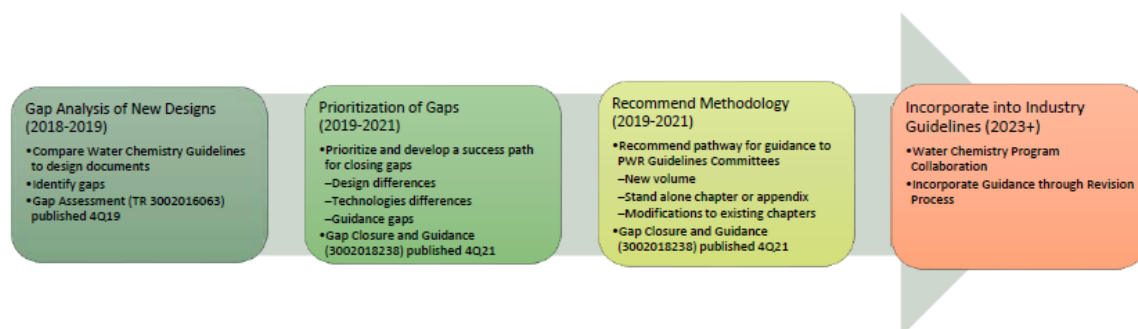


Figure 6-1: Systematic step process for the development of SRM Chemistry Guidelines [Marks, 2023]

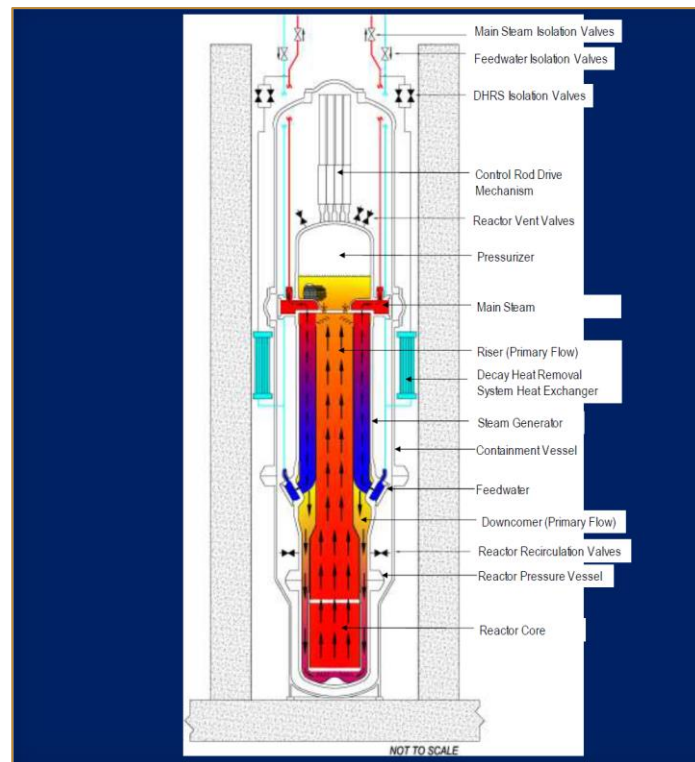


Figure 6-2: Sketch of the NuScale SMR primary system with the main components (not to scale) [Reinders, 2023]

EPRI and DEI have defined four situations when analysing the applicability of the guidelines to the SMR:

- Inconsistency: Situation in which the Primary Guidelines or Secondary Guidelines value is more restrictive or conservative than the value published in the NuScale design documents.
- Guidelines Technical Gap: Situation in which the NuScale design document is more restrictive or conservative than the Primary Guidelines or Secondary Guidelines. The guidelines revision committee will need to evaluate possible guidelines revision if the technical bases of the NuScale Design Certification Application (DCA) restrictions can be verified.
- Knowledge Gap: Situation in which more information is needed to make a determination of the effect of the NuScale design on water chemistry controls.
- Other items: Items not directly related to chemistry specifications that may need to be considered since they may affect water chemistry control practices.

The result of the gap analysis for the Secondary side guidelines is that all of the secondary side inconsistencies, technical gaps, and knowledge gaps identified in the Gap Analysis are able to be closed with minor changes to the Secondary Guidelines or the NuScale Design Certification Application (DCA). For Primary side, the results have been that there are no inconsistencies identified and there are several primary side knowledge gaps still open, but no technical gaps are identified.

The list of findings for the secondary and primary side analysis is shown in Figure 6-3

8 Maintenance & Long-Term Operation

Framatome and EdF have presented two communications on chemical decontamination of auxiliary circuits as an ALARA approach and a spray decontamination process to apply to parts of the primary system previous to a substitution work.

8.1 Chemical Decontamination

a) Chemical decontamination of RHRS and/or CVCS circuits, one of the main drivers of EDF's ALARA approach

Since 2004, EDF has been implementing chemical decontamination with the aim of reducing the radiation fields of the most contaminated units to reach the average values for their series. The deployment of an innovative methodology, based on radiological diagnosis of the units (primary and auxiliary circuits) and on the planning of heavy maintenance operations onto circuits that are candidates for decontamination (RHRS and / or CVCS), now allows the establishment of a multi-year unit remediation program for the EdF Fleet [Rocher A. et al. 2023]. Today, typically, 3 to 4 units are cleaned up every year. The characterization of the radioelements in the circuits to be decontaminated, determines the choice of the redox chemical solution to implement. Decontamination processes have been developed and qualified for materials in order to effectively dissolve the most harmful radioelements in doses integrated by personnel, principally Co-60 and / or Ag-110m.

Typically, the contamination found in the systems can be labile and fixed. For labile, i.e. hot spots, a mechanical treatment, such as flushing, rinsing, etc. is applied. For fix contamination, which main system exposed to are CVCS and RHR, a chemical decontamination is proposed and selected according to a systematic process. The selection of a system candidate to process starts when the equivalent dose indices are greater than 1,25 times the average of the candidate systems in the fleet. There are two indices for a system, one based on contact dose rate at selected locations and other based on gamma spectrums taken in the heat exchangers for both systems, taken at the previous shutdown. Then, a techno-economic study is performed to evaluate activities planned for the outage, the estimated personnel dose the expected dose savings and a comparison of the cost of man·Sievert with the cost of the decontamination process. After that, if the result is positive, a chemical decontamination is planned. Figure 8-1 shows the process described.

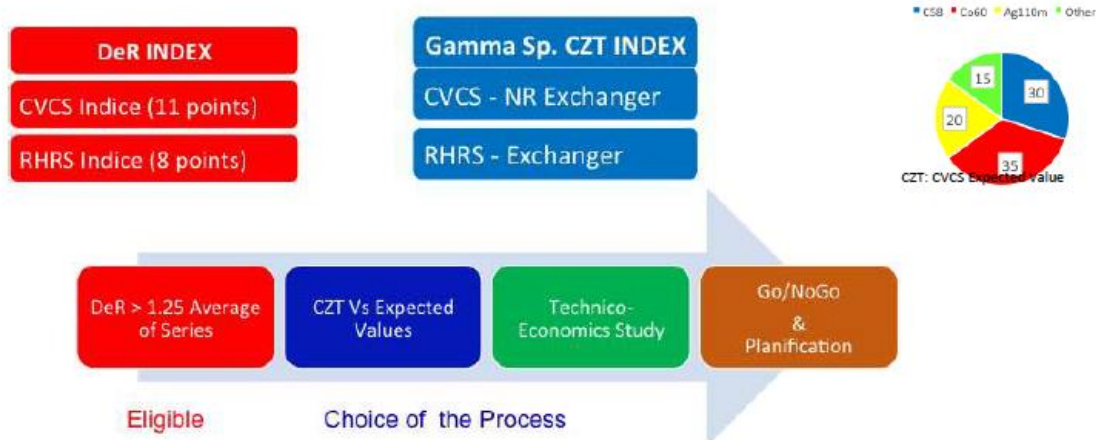


Figure 8-1: Process for decision of a chemical decontamination of a system [Rocher, 2023]

EdF has qualified up to 5 chemical decontamination processes: single oxidation-reduction phase (EMMAG), two phases (P1, P2), or three successive oxidation-reduction phases (EMMAC-POA, P3). In general, the oxidizing stage entrains nickel and silver, and the reducing phase entrains manganese and iron. Before selecting a process, the plant must check that the candidate is compatible with all the

materials in the system that will be in contact with the chemical solutions. For this purpose, tests to confirm that no significant loss of thickness, generalized and non-significant stress corrosion, unchanged surface condition and roughness etc. have been performed in coupons for the system materials.

There are two main isotopes responsible for the dose in the circuits: Co-60 and Ag-110m. The preferred decon process for elimination of Ag-110m is EMMAg and for Co-60 is EMMAC-POA. The CZT spectra taken at the end of the shutdown is crucial to determine which will be the process chosen for the specific system.

To measure the efficiency of a decontamination, a parameter is defined: the Dose Rate Reduction Factor (DRRF), that is calculated from the average of the dose equivalent rates (DeR) measured at the contact of the materials and circuits before and after decontamination. The DRRF is the following ratio:

$$DRRF = \frac{DeR \text{ before decontamination}}{DeR \text{ after decontamination}}$$

The EdF experience on decontamination from 2004 to 2019 extends a total of 23 circuits, 13 CVCS (1m³ of volume) and 10 RHR (10 m³ volume) all of them from 900 Mwe plants. The main isotopes have been 14 times Co-60 and 9 times Ag-110m, and 11 circuits were separated and 12 circuits were treated jointly.

Regarding efficiency, on figure 8-2 there is a plot of the averaged DRRF for each type of decon process that also shows the number of time that each process has been applied. It is clear that the most efficient processes are EMMAg and EMM-POA, followed by P1.

Concerning dose savings, the collective dose saved over 5 years ranges from 230 to 520 man·mSv with an average of 350 man·mSv. On the other hand, the integrated dose cost for one decontamination ranges from 14 to 31 man·mSv with an average of 25 man·mSv, a 45% of it was received by EdF personnel.

The activity removed from the systems averages 350 GBq, with a 70% being of Co-60, removed mostly in the reducing phase, whereas the of Ag-110m was removed in the oxidant phase. Regarding the two more efficient process, Table 8-1 shows the liquid effluent volume and the process duration for the two most efficient process:

Table 8-1 Averaged Effluent volume and duration of the two most efficient decontamination processes

Process	Liquid Effluent	Duration
Emmac-Poa (3 cycles)	96 m ³ (x3/EmmAg)	96 hours (x5/EmmAg)
EmmAg (1 cycle)	35 m ³	19 hours
© ANT International, 2024		

9 Monitoring updates & new developments

A miscellanea of monitoring techniques was presented, from methods for cooling water analysis of Legionella and Naegleria, to resin free cationic conductivity monitors and automated monitoring panels for the online measurement of most of the interest parameters for primary and secondary systems or the validation process applied to the online chemistry monitors for French plants.

a) Operational experience with EDI Technology for Cationic Conductivity measurements

The conductivity measurement after cation exchange (CACE) is one of the most important analytical methods in the water-steam cycle. Seven years ago, it was introduced the AMI CACE analyser by Swan Analytical Instruments to avoid the problems of the classical online determination, mainly the cation exchange resins depletion after some time, which lead to interruption of the measurements, operation that is quite frequent in high pH PWR secondary systems. Continuous removal of alkalizing agent in the sample by Electrodeionization (EDI) prior to measurement is the alternative to the conventional cation exchange.

Swan presented a poster [Gath & Nogales, 2023] to communicate the experience of use of this CACE analysers at 4 European PWR plants that operate the water-steam cycle in an AVT regime with a target pH of 9.8. A total of 66 instruments were installed and the lifetime of the modules ranges between 3 and 5 years with virtually no maintenance required. Some instruments required servicing after reduced periods of between 8 months to 1,5 years mostly after being exposed to high load of corrosion products. In summary, the instrument provides a continuous reliable measurement and gives good or even better measurements results than the conventional method.

The main substances that can shorten the module lifetime are high corrosion products (that can be prefiltered) and film forming amines.

b) Current and emerging methods for Legionella and Naegleria fowleri monitoring in cooling circuits of EDF nuclear power plants.

Cooling towers of river nuclear power plants present favourable conditions for Legionella and Naegleria fowleri proliferations. Both are human pathogens, responsible for legionellosis and amoebic encephalitis respectively. French regulation (ASN) requires the monitoring and treatment for controlling these two pathogens and has defined a regulatory method for monitoring Legionella and EdF has an internal method for Naegleria. However, there is a need for alternative methods that provide a rapid quantitative result with similar or better characteristics than the reference methods. EdF R&D is making a systematic study for evaluating the available methods with the aim to propose an alternative and to present the required validation file for them to the French authorities [Binet M. 2023].

The proposed microbiological methods must meet the following criteria:

- Speed and ease of measurement.
- Suitable detection threshold.
- Specificity
- Viability (pathogenicity)
- Applicability to cooling circuit waters and environmental waters.
- Compatibility with the presence of biocidal treatment

Following a bibliographic survey of methods, EdF R&D is testing experimentally the most promising ones on the different water qualities found in French NPPs. The survey of methods is still on going. To date, three methods are potentially to be evaluated experimentally for the enumeration of Legionella; the MICA-test method being developed by Diamidex, the flux cytometry count by RQ Micro and the Legiolert method by IDEXX. Regarding the Naegleria fowleri count, the method marketed by GENEsig based on quantitative PCR should be assessed. In the paper there is description of each one of the methods reviewed and the results of its evaluation.

c) SMART Chemistry - Automated Chemistry Monitoring

EPRI's SMART Chemistry project is an effort to develop and demonstrate automated chemistry monitoring instruments for use in nuclear power plants to reduce costs and increase the efficacy of chemistry monitoring. A paper was presented to show the last online equipment implemented, some plant experiences and the EPRI reports that collect the information [McElrath, J. et al. 2023].

In the last years (2018-20), a series of three demonstrations were conducted, at Salem, Darlington, and Nine Mile Point plants, to demonstrate online monitoring technologies. Three skids were constructed to enable ease of installation of those instruments needed to monitor EPRI Guidelines control parameters continuously in the steam generator blowdown (SGBD), the reactor coolant system (RCS), and the feedwater system (FW). Each skid connects to the plant with a common header and from that header provides flow to each instrument. The RCS skid was employed at Salem and Nine Mile Point plants. The SGBD and FW skids were used at Salem and Darlington plants. Additionally, online coolant isotopic monitoring using a cadmium zinc telluride (CZT) detector was also demonstrated at Nine Mile Point and an in-line Isotopic Gamma Emission Measurement System with HPGe detector was tested in a demonstration at the Monticello Nuclear Power Plant. The instruments installed in the skids have been previously evaluated and validates its use and reliability by EPRI and its members.

As an example, Table 9-1 provides the instruments and analytical parameters surveyed by the RCS on line skid tested in Salem plant.

Table 9-1: Instruments on RCS Skid tested in Salem NPP [McElrath, 2023]..

Vendor	Species	Sampling Frequency
Scout-Prep (ICP-OES)	Fe	1/hr
	Ni	
	Zn	
	Li (ppm)	
	Al	
	Ca	
	Mg	
	B (ppm)	
Metrohm ANCAT (combined anion and cation ion chromatograph)	Cl ⁻	1/hr
	F ⁻	
	SO ₄ ²⁻	
	Li ⁺	
	NH ₄ ²⁻	
Swan Analytical Powercon	Specific Conductivity	Continuous
Hach Orbisphere	H ₂ (cc/kg)	Continuous
	O ₂ (ppb)	
Swan Analytical AMI Silica	Si	1/30 min
Swan Analytical AMI Soditrace	Li	30/hr
Harch Turbidity 5400sc (laser scattering-based instrument)	Suspended Solids	Continuous
© ANT International, 2024		

Concerning the online coolant isotopic analysis, EPRI has tested up to five types of chambers to avoid activity buildup: Electropolished, Framatome Quartec Coated, Electropolished and passivated, EPRI stabilized Chromium process and Pt plated 304 SS. None of them are immune to buildup, but a wide

10 Numerical & simulation tools

Along the previous chapter, many numerical and simulation tools for several chemical processes have been described in some cases or mentioned its development or application and in others. In this chapter, other numerical and simulation models are presented or its application is described.

a) Water Radiolysis in PWR Fuel Crud [Arcis H. et al., 2023]

The EPRI crud chemistry model (CCM) developed by NNL has been coupled to a standalone radiolysis model to simulate the effect of radiation chemistry for a Li/B/H₂ coolant in the bulk and in the crud. The model was used to simulate the levels of oxidising and reducing species in the bulk coolant and in a generic PWR fuel crud for different fuel cycle conditions.

The FACSIMILE crud radiolysis model is a standalone radiolysis model that simulates the effect of radiation chemistry for a Li/B/H₂ in the aqueous solution within the crud. The radiolysis model uses the deposit temperatures, along with concentrations of boric acid, H₂(aq), OH⁻, H⁺ and total boron; and activity coefficients; potential gradients, liquid and vapour streaming velocities simulated by the CCM model. The radiolysis model calculates the concentrations of reducing and oxidising species within the crud deposit. The CCM programme was used to simulate the equilibrium local pH and concentrations of chemical species as a function of crud depth for a simple Li/B/H₂ PWR coolant. The model was tested using the bulk coolant conditions found in the upper half of a PWR fuel channel for middle of a cycle (MOC) conditions. As an example, the outputs of the couple model, such as the crud depth profile of boron and lithium species or the radiolytic species are in Figure 10-1.

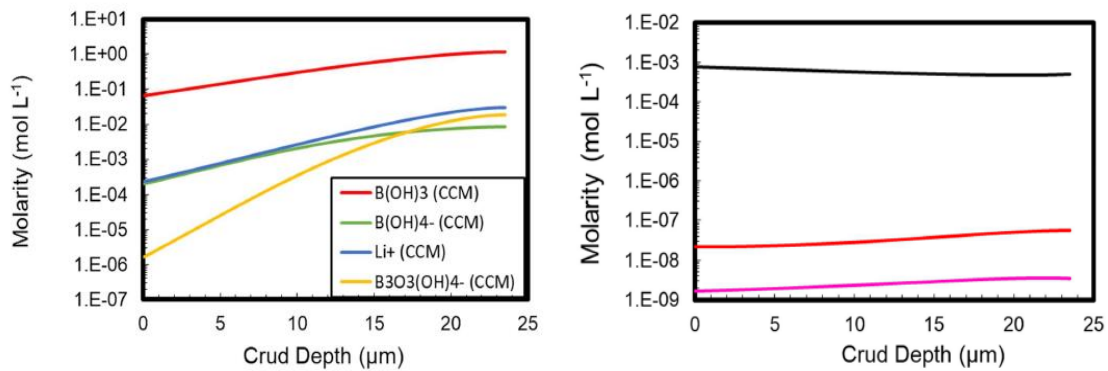


Figure 10-1: (Left) Mole Fractions of B(OH)₃, B₃O₃(OH)₄⁻, B(OH)₄⁻ and Li⁺ with crud depth (MOC). (Right) Levels of H₂O₂ (red), O₂ (pink) and H₂ (black) with crud depth. [Arcis, 2023]

The model predicts deposit temperatures, local pH and chemical species concentrating with crud depth. The model is able to predict the level of hydrogen and oxidizing species in the liquid filled crud, which could in turn be used to calculate equilibrium redox potentials and electrochemical corrosion potentials (ECP). Calculations indicate that precipitation of Li-borate salts limits the depth of deposit actually filled with water, which means that H₂ stripping into the crud steam chimney occurs over a limited depth. This depth is typically in the range of 25-35 μm for a fuel cycle based on the calculations here, meaning that hydrogen in the liquid phase remains at around 2 ppm, well above the critical hydrogen level necessary to suppress radiolysis. Consequently, oxidant levels in the coolant in the crud remain low, at a few ppb.

Future work will assess the possible effects of including Zn and Ni radiolysis for which high temperature data are recently available. It is also important to investigate situations in which no boron is present, as several new reactor designs are planning on operating boron free. The lack of boron will mean zero alpha dose rates, but the depth of liquid filled deposit will be greater meaning that greater hydrogen stripping can occur.

References

- Andgren K., Ahlford K. *Activity determination of the difficult-to-measure nuclide ^{93}Mo in low and intermediate level waste*. Paper 114. Proc. of International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023.
- Arcis H. et al. *Impact of Potassium Primary Coolant Chemistry on PWR's Operating with Fuel Crud*. Paper 079. Proc. of NPC 2023. International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023
- Arcis H. et al. *A New Boric Acid Model for MULTEQ*. Paper 041. Proc. of NPC 2023. International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023
- Arcis H. et al. *Water Radiolysis in PWR Fuel Crud*. Paper 090. Proc. of International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023.
- Astorg A. et al. *Iodide and iodate ions retention by ion exchange resins in the primary coolant circuit shutdown conditions*. Paper 156. Proc. of NPC 2023. International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023
- Atkinson C.M. *Trials of Alternative Biocidal Dosing Strategies for the Control of Marine Fouling at United Kingdom Coastal Power Stations*. Paper 166. Proc. of International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023.
- Bachet M. and Leclercq S.. *Cleaning the Primary Circuit After the First High Temperature Oxidation of Steam Generator Tubing: Why and How To Do It*. International Conference on Water Chemistry of Nuclear Reactor Systems Quebec. 2010
- Bachet M. et al. *Updated equilibrium constants for the protonation and volatility of Morpholine and Ethanolamine in the MULTEQ database*. Paper 044. Proc. of International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023.
- Baek S. H., Shim H. -S., Kim J. G., Hur D. H., *Effect of chemical etching of fuel cladding surface on crud deposition behavior in simulated primary water of PWRs at 328°C*, Annals Nucl. Ener. 116(2018) 69-77
- Baker F., and Palazhchenko O, *Radioactivity Transport Prediction Throughout a CANDU-6 Reactor Lifetime Using the CARTA Code*. Paper 097. Proc. of NPC 2023. International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023
- Balakrishnan P. and Allison G., *Some in-reactor loop experiments on corrosion product transport water chemistry*. Nuclear Technology, vol. 39, no. 2, pp. 105-120, 1978.
- Bartels D.M., *Comment on the possible role of the reaction $\text{H}+\text{H}_2\text{O} = \text{H}_2+\text{OH}$ in the radiolysis of water at high temperatures*, Radiation Physics and Chemistry 78 (2009) 191-194.
- Beal S.K., *Deposition of Particles in Turbulent Flow on Channel or Pipe Walls*, Nuclear Science and Engineering. 40 (1970) 1-11.
- Becker R. et al. *Activity release from fuel crud - An experimental study*. Paper 030. Proc. of NPC 2023. International Conference on Nuclear Plant Chemistry. Antibes-Juan les Pins, France, September 25-28, 2023
- Bengtsson B., Svanberg P., Dingee J., Pellman A., and Wells D. *Experience with High Efficiency Ultrasonic Fuel Cleaning Using a Side-Stream Sampling System at Ringhals Unit 4*. International Conference on Water Chemistry in Nuclear Reactor Systems. Sapporo, Japan. 2014
- Beslu P., *Pactole: Prédiction du comportement et de l'activation des produits de corrosion dans le circuit primaire des réacteurs à eau légère*, Centre d'études nucléaires de Cadarache, 1990.

List of Abbreviations

ABWR	Advanced Boiling Water Reactor
AC	Alternating Current
AECL	Atomic Energy of Canada Limited
AGR	Advanced Gas-Cooled Reactors
AISI	American Iron and Steel Institute
AL	Action Level
ALARA	As Low As Reasonably Achievable
ALARP	As Low As Reasonably Practicable
ANTI	ANT International
AOA	Axial Offset Anomaly
AOX	Adsorbable Organic Halogens
AR	As received sample
ATR-IR	Attenuated Total Reflectance-IR
AVT	All Volatile Treatment
AVT(O)	All Volatile Treatment with O ₂ injection at some part of the secondary circuit
BAST	Boron Addition Storage Tank
BAT	Best Available Technique
BHDL	Bottom Head Drain Line
BNDE	Bottom Nozzle Debris Elimination (by Ultrasonic Cleaning)
BOA	Boron-Induced Offset Anomaly
BOC	Beginning of Cycle
BRAC	BWR Radiation Assessment Control
BRS	Boron Recycle System
BSE	Back Scattered Electron
B-TAC	BWR Technical Advisory Committee
BWR	Boiling Water Reactor
BWROG	BWR Owners Group
BWRVIA	BWR Vessel and Internals Application
BWRVIP	Boiling Water Reactor Vessels and Internals Program
CAM	Chemistry Monitoring and Assessment (EPRI Plant Chemistry Database)
CANDU	CANada Deuterium Uranium
cc/kg	cubic centimetre (per kg): used for H ₂ concentration in RCS = ml/kg (under normal pressure and temperature)
CEA	Chemical Etching
CEA	Commissariat à l'Énergie Atomique (French Atomic Energy Commission)
CFD	Computational Fluid Dynamics
CGR	Crack Growth Rate
CHC	Critical Hydrogen Concentration (to suppress water radiolysis)
CHZ	Carbohydracide
CILC	Crud-Induced Localized Corrosion
CIPS	CRUD Induced Power Shift
CITROX	Citric Acid + Oxalic Acid

CL	Cold Leg
CMA	Chemistry Monitoring and Assessment (EPRI Plant Chemistry Database)
CNMI	Continuous Noble Metal Injection
CORD-UV	Chemical Oxidation Reduction Decontamination (Chemical Decontamination Technique incorporating UV destruction of reagents)
CP	Corrosion Product
CPS	Condensate Polishing System
CRD	Control Rod Drive
CRDM	Control Rod Drive Mechanism
CRUD	Acronym for “Chalk River Undefined Deposits”
CRUDSAM	CRUD Sample
CS	Carbon Steel
CT	Constant Tension (test for CGR determination)
CVCS	Chemical and Volume Control System
CW	Cold Worked
CZT	Cadmium Zinc Telluride
DB	Deep Bed
DC	Direct Current
DCA	Desing Certification Application
DCPD	Direct Current Potential Drop
DEHA	Diethylhydroxylamine
DEI	Dominion Engineering Inc.
DEMO	DEMONstration fusion power plant
DH	Dissolved Hydrogen
DMA	Dimethylamine
DO	Dissolved Oxygen
dpa	displacements-per-atom (measurement of material irradiation)
DW	Drywell (in GE-BWR Containment)
DZO	Depleted Zinc Oxide
EA	Erythorbic acid
EBA	Enriched Boric Acid
EBS	Electron-Back Scatter Diffraction
ECCS	Emergency Core Cooling System
ECHA	European Chemical Agency
ECP	Electrochemical Corrosion Potential
ECT	Eddy Current Test
EdF	Electricité de France
EDL	Electrical Double Layer
EDM	Electric Discharge Machining
EDS	Energy Dispersive Spectroscopy
EDTA	Ethylenediamine tetraacetic acid
EFPY	Effective Full Power Years
EHC	Electro-hydraulic Control
EIS	Electrochemical Impedance Spectroscopy
EOC	End of Cycle
EPR	European Pressurized Water Reactor
EPRI	Electric Power Research Institute, USA

ETA	Ethanolamine
ETV	Visual Inspection by TV image
F/D	Filter Demineralizer
F+DB	Filter + Deep Bed
FAC	Flow Accelerated Corrosion
FE-SEM	Field Emission Scanning Electron Microscopy
FF	Fouling Factor
FFA	Film Forming Amines
FIB	Focus Ion Beam
FOI	Factor of Improvement
FOPH	Federal Office of Public Health
FP	Filming Products
FPO	Flexible Power Operation
FRP	Fuel Reliability Program
FW	Feed Water
GDA	Generic Design Assessment
GDOES	Glow-Discharge Optical Emission Spectroscopy
GE	General Electric Company
HER	Hydrogen Electrode Reaction
HE-UFC	High Efficiency Ultrasonic Fuel Cleaning
HFT	Hot Functional Testing
HL	Hot Leg
HPER	Hydrogen Peroxide Electrode Reaction
HPGe	High Purity Germanium
HTC	Heat Transport Circuit
HTP	High Temperature and Pressure
HWC	Hydrogen Water Chemistry
HWC-M	Moderate HWC
HZ	Hydrazine
IAEA	International Atomic Energy Agency, Vienna
IASCC	Irradiation Assisted Stress Corrosion Cracking
IC	Ion Chromatography
ICP	Inductively Coupled Plasma optical emission spectrometry
IER	Ion Exchange Resin
IGSCC	Intergranular Stress Corrosion Cracking
KAERI	Korean Atomic Energy Research Institute
KKL	Kernkraftwerk Leibstadt (Swiss BWR plant)
KKM	Kernkraftwerk Mühleberg (Swiss BWR plant)
LA-ICP-MS	Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry
LAS	Low Alloy Steel
LBE	Liquid Lead Bismuth Eutectic
LLD	Lower Limit of Detection
LOCA	Loss of Coolant Accident
LPR	Linear Polarization Resistance
LPRM	Local Power Range Monitor
LTU	Long-term use

KEY EMERGING ISSUES AND RECENT PROGRESS RELATED TO PLANT CHEMISTRY/CORROSION (PWR, CANDU,
AND BWR NUCLEAR POWER PLANTS)

LWR	Light Water Reactor
MA	Mill Annealed
MAI	Material Aging Institute (French EdF research institute with international cofinancing)
MAMBA MPO	Advanced Materials/Boron Analyser
MCE	Microfluidic Capillary Electrophoresis
MCM	Mixed Conduction Model
MCO	Moisture Carryover
MCR	Major Component Replacement
MEKO	Methyl-ethyl-ketoxime
MMS	Mitigation Monitoring System
MOC	Middle of Cycle
MPA	Methoxypropyl-amine
MPO	Material Performance Optimization
MS	Main Steam
MSLRM	Main Steam Line Radiation Monitor
MSR	Moisture Separator Reheater
MSV	Main Steam Valve
MTC	Mass Transfer Coefficient
MWe	Megawatts Electrical
MWth	Megawatts Thermal
NMCA	Noble Metal Chemical Application
NMP	Nine Mile Point (USA BWR plant)
NOP	Normal Operating Pressure
NOT	Normal Operating Temperature
NPC	Nuclear Plant Chemistry Conference
NPP	Nuclear Power Plant
NRC	Nuclear Regulatory Commission (USA Nuclear Regulator)
NRU	National Research Universal
NW	Never Wet
NWC	Normal Water Chemistry
ODA	Octadecylamine
OEL	Occupational Exposure Limit
OER	Oxygen Electrode Reaction
OLNC	On Line NMCA
OPEX	Operational Experience
OPG	Ontario Power Generation (Canada)
ORE	Occupational Radiation Exposure
OTS	Operating Technical Specifications
OTSG	Once Through Steam Generator
PAA	PolyAcrylic Acid (dispersant)
PCV	Primary Containment Vessel
PHT	Primary Heat Transfer System (Reactor Coolant System of CANDU plants)
pH _T	pH at 300°C
PHWR	Pressurized Heavy Water Reactors
PIE	Post Irradiation Examination of Fuel rods
PLNGS	Point Lepreau Nuclear Generation Station (Canada)

PM	Post Morten (after exposure, at the end of an experiment)
PO	Preoxidized
ppb	part per billion = µg/kg
ppm	part per million = mg/kg
PSI	Paul Scherrer Institute (Switzerland)
PSL	Primary-to-Secondary Leak
PTFE	Poly Tetra Fluoro Ethylene
PWR	Pressurized Water Reactor
PWRCMA	Pressurized Water Reactor Chemistry Monitoring and Assessment (EPRI Chemistry Database)
PWROG	PWR Owners Group
PWSCC	Primary Water Stress Corrosion Cracking
RB	Reactor Building
RC	Reactor Coolant
RCP	Reactor Coolant Pump
RCPB	Reactor Coolant Pressure Boundary
RCS	Reactor Coolant System
REACH	Registration, Evaluation, Authorisation, and Restriction of Chemicals (EU Regulation)
RFO	Refuel Outage
RHR	Residual Heat Removal
RHRS	Residual Heat Removal System
RIHT	Reactor Inlet Header Temperature (in CANDU reactors)
RIP	Reactor Internal Pump
RIS	Radiation Induced Segregation
RP	Radiation Protection
RPV	Reactor Pressure Vessel
RRS	Reactor Recirculation System
RT	Room Temperature
RW	Reactor Water
RWCU	Reactor Water Clean-Up
SCC	Stress Corrosion Cracking
SDC	Shut Down Cooling System or mode of RHR system operation
SDR	Shutdown Release
SEM	Scanning Electron Microscopy
SG	Steam Generator
SGBD	Steam Generator Blowdown
SGR	Steam Generator Replacement
SHE	Standard Hydrogen Electrode
SMAW	Shielded Metal Arc Welding
SNB	Sub-cooled Nucleate Boiling
SRV	Safety Relief Valve
SSTR	Slow Strain Rate Test
STP	South Texas Project (USA Plant)
TEM	Transmission Electron Microscopy
TOF-SIMS	Time of Flight Secondary Ion Mass Spectrometry
TRO	Total Residual Oxidants
TSP	Tube Support Plate

TSS	Total Suspending Solids
TT	Thermal Treatment
TTS	Top of Tubesheet
UED	Ultra Ever Dry
UFC	Ultrasonic Fuel Cleaning
UK	United Kingdom
UT	Ultrasonic Testing
VGB	Vereinigung der Grosskraftwerksbetreiber (Association of Great Power Producers), Germany
VVER	Voda Voda Energo Reactor (Russian Acronym for the Russian type of PWR)
WSC	Water Steam Cycle (Secondary System in CANDU Plants)
XPS	X-Ray Photoelectron Spectroscopy
XRF	X-Ray Fluorescence
ZIRLO	ZIRconium Low Oxidation Alloy
Zry	Zircaloy

Abbreviations for EPR Systems

FA3 Coding Systems	OL3 Coding Systems	English EPR Acronym	System Name
SG-APG	LCQ	SGBS	Steam Generator – Steam Generator Blowdown System
ARE	LAB	MFWS	Main Feed Water System
ASG	LAR	EFWS	Emergency Feed Water System
HK/HR	UFA/UJA	FB/RB	Fuel Building/Reactor Building
IRWST	JNK	-	In-containment Refuelling Water Storage Tank
PTR	FAK/FAL	FPCS/FPPS	Fuel Pool Cooling (and Purification) System
RBS	JDH	EBS	Extra Boration System
RCP-PZR	JE/JEF	RCS-PZR	Reactor Coolant System-Pressurizer
RCV	KBA	CVCS-VCT	Chemical and Volume Control System – Volume Control Tank
REA	KBC	RBWMS	Reactor Born and Water Make-up System
REN	KUA	NSS	Nuclear Sampling System
RES	KUB	-	Steam Generator Secondary Sampling System
RIS/RA	JN	SIS/RHRS	Safety Injection System operating in Residual Heat Removal Mode
SGH, SGN, SGO	QJC, QJB, QJA	-	Hydrogen Distribution System, Nitrogen Distribution System, Oxygen Distribution System
TEG	KPL	GWPS	Gaseous Waste Processing System
TEP1, TEP2, TEP3, TEP4, TEP5, TEP6	KBB, KBE, KBF, KBG, KBF, KBF	CSTS	Coolant Storage and Treatment System

© ANT International, 2024

Unit conversion

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

Radioactivity	
1 Sv	= 100 Rem
1 Ci	= 3.7×10^{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 $\sqrt{\text{m}}$	ksi $\sqrt{\text{inch}}$
0.91	1
1	1.10