

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

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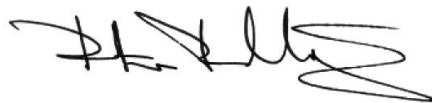


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A handwritten signature in black ink, appearing to read 'P. Rudling', with a stylized flourish at the end.

Mr Peter Rudling, President of ANT International

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Nomenclature

Unit conversion

1 Introduction

This report is related to PWRs, CANDU and similar designs while another report concerns BWRs.

In this report, we can highlight several topics of specific interest which are reported with the details of interest for LCC customers:

- Film Forming Amines in the secondary system, showing an increasing potential use;
- Several complete or specific evaluations of zinc addition in the primary coolant;
- Potential replacement of LiOH in the primary coolant of PWR units by KOH as successfully used in VVER plants;
- Hot functional Testing in new types of plants in China: the Westinghouse AP1000 and the Framatome European Pressurized Water Reactor (EPR).
- Studies on Crud deposition on the fuel, and associated parameters to this phenomenon.

The 21th International Conference on Chemistry in Nuclear Reactors Systems (NPC, 2018) took place in San Francisco (USA) on September 9-13, 2018, and organized by EPRI (Electric Power research Institute). 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 2016, was in Brighton (UK), while the next ones will be in Antibes (French Riviera), in 2020.

As shown on Figure 1-1, 247 persons from 22 countries attended the conference. This attendance reflects the fact that the some of the countries are facing a slowdown of nuclear energy with limited, if any, new NPP under construction while the countries with the largest program of construction, like China, usually do not send many attendees to such conferences. The reason is political, historical and due to language issues. In such countries, the people who are attending the international conferences are usually researchers from Institutes, but very few from the industry or NPP. Indeed, there were more attendees from Japan than from China. Despite active program on nuclear energy, there were no attendee from India, Russia, Ukraine, Bulgaria, Turkey, either for political or economic reasons. International Atomic Energy Agency (IAEA), did not take part in sponsoring this conference, as it has been the case on most of these NPC conferences.

2 Reactor Coolant System

2.1 Chemistry parameters and monitoring

Pressurized water reactors use Lithium Hydroxide (LiOH) to increase the pH of reactor coolant [Hussey et al., 2018a]. This is done to both reduce the corrosion of the primary system materials and to reduce crud deposition. The lithium has two sources. It is added in batches using the chemical addition tank at the beginning of a fuel cycle and during outages. It is also generated by the n-alpha reaction with boron that is present in the coolant in the form of boric acid.

The lithium that is added to the coolant must contain only the Li-7 isotope, since the Li-6 isotope produces tritium when irradiated with neutrons. The lithium produced throughout the cycle by the n-alpha reaction with boron conveniently produces exclusively the Li-7 isotope. The Li-7 added through the chemical addition tank must be produced by an isotope separation process, which is expensive and produces hazardous waste. There are currently only two suppliers of Li-7, and the availability of Li-7 from these suppliers is not assured. Thus, the United States government and EPRI (Electric Power Research Institute) have undertaken a program to investigate alternate sources of Li-7. This project is a subset of that program.

One source of Li-7 is ion exchange resin within the Chemical and Volume Control System (CVCS). The CVCS contains a cation bed in the H⁺ form that is used to remove Li-7 when levels get too high. It also contains a mixed bed resin that starts out in the Li-7⁺ form, and the Li-7 is replaced throughout the cycle by metal cations. However, waste mix bed resin also contains residual Li-7 which could be recovered. The recovery process involves elution of the Li-7 from the resin using either sulfuric acid or ammonium bicarbonate, followed by purification and conversion to LiOH using electrodialysis.

The purpose of this testing was to determine how effective the proposed Li-7 elution methods are in removing Li-7 from actual spent PWR (pressurized water reactor) cation resin and to what extent radioisotopes were separated from the Li-7 through elution. Cation resin from Diablo Canyon was used for the testing. Resin backwashing and elution was modelled using the procedure for laboratory testing of lithium elution from radioactive samples supplied by Finetech (now Structural Integrity Associates, Inc.). Approximately 8 mL resin fractions were eluted with either ammonium bicarbonate or sulfuric acid. The sulfuric acid regenerant is designed to rapidly elute the Li-7 in a small volume, but a portion of the radionuclides will also be eluted with the Li-7. The ammonium bicarbonate eluent should be more effective in separating the Li-7 from radionuclides such as Co-60, but the concentration of Li-7 in the recovered solution is expected to be lower. The measurements of resin capacity and settled density are meant to characterize the resin so that the effectiveness of the separations can be applied to other resin. An electrodialysis (ED) cell was used for purification and separation of the effluent streams produced through column elution.

A picture of the elution column is shown in Figure 2-1.

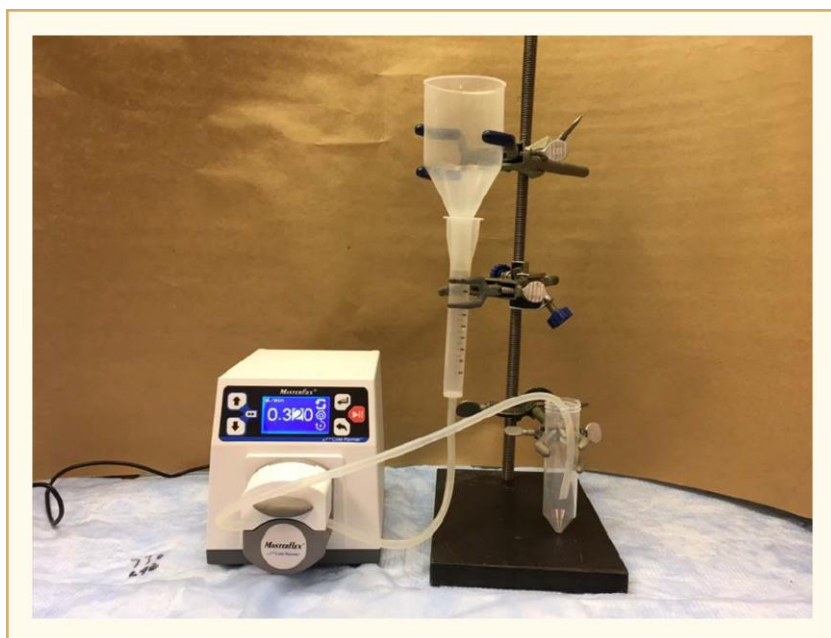


Figure 2-1: Resin Fraction Elution Column Setup [Hussey et al., 2018a].

A fraction of the backwashed resin was placed in a small column and a two (2) bed volume per hour flow rate of the ammonium bicarbonate eluent was maintained while collecting samples every 30 minutes for 10 hours. The resin was then converted to the hydrogen form using hydrochloric acid, followed by conversion to the sodium form using sodium chloride, as part of the process to measure resin capacity. Individually, three (3) runs were performed to assess reproducibility. The configuration of the column elution setup is shown in Figure 2-1. The concentration of the ammonium bicarbonate was 0.2N. Gross gamma activity, isotopic content and elemental content by ICP-OES were measured on the samples. The gross gamma activity was also measured on the column.

The 1.0 N sulfuric acid process was similar to the ammonium bicarbonate elution. A fraction of the backwashed resin was placed in a small column and a two (2) bed volume per hour flow rate of the sulfuric acid eluent was maintained while collecting samples every 30 minutes for 5 hours. The resin was completely converted to the hydrogen form using hydrochloric acid, followed by conversion to the sodium form using sodium chloride, as part of the process to measure resin capacity.

The dose rate reduction from the elution process is shown in Figure 2-2.

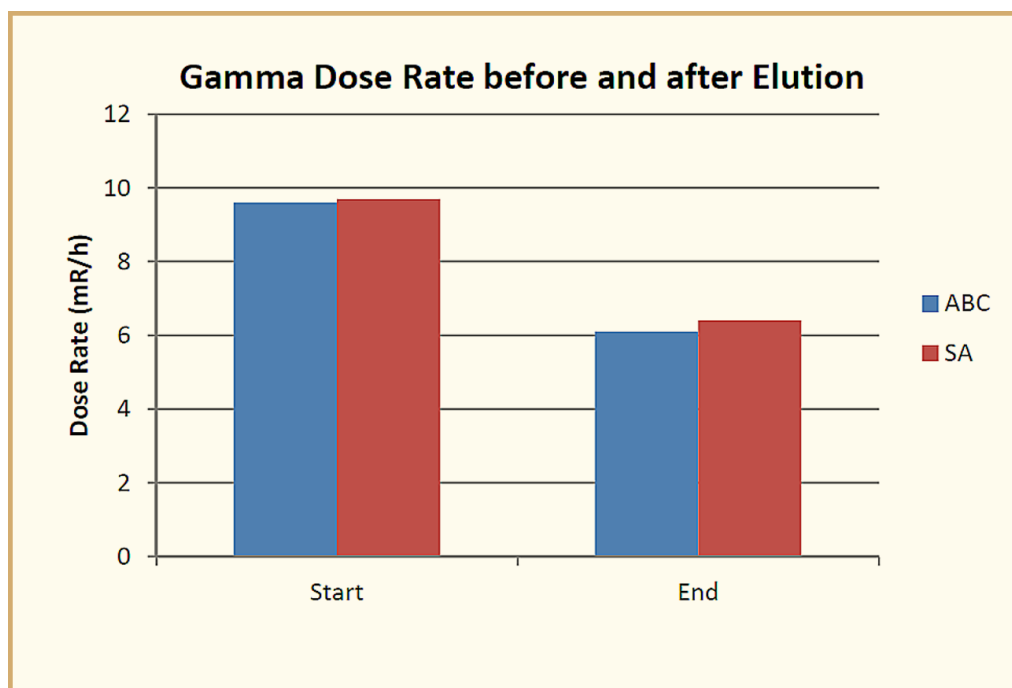


Figure 2-2: Column Dose Rate Reduction [Hussey et al., 2018a].

The lithium was mostly eluted after 390 minutes with ammonium bicarbonate, while the sulfuric acid eluent took only 210 minutes to remove the lithium.

The ED cell schematic is shown in Figure 2-3.

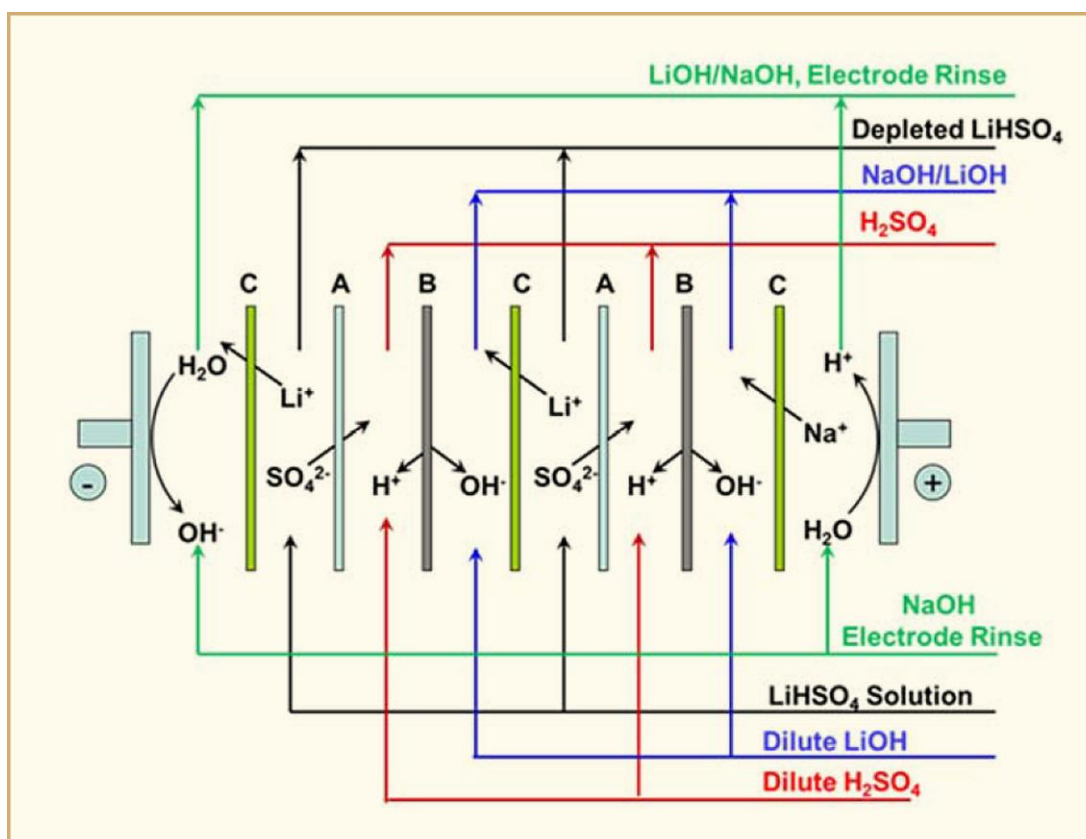


Figure 2-3: Schematic of Electrodialysis Cell [Hussey et al., 2018a].

In conclusion, the three-compartment micro ED cell was successful in separating caustic species, lithium and sodium, from the lithium sulphate feed solution with a removal rate of 98% and 96%, respectively. The low lithium recovery in the base (27%) was caused by the large ER to feed volumes and combined sodium and lithium inventory in the electrode rinse. Larger feed volume processing is required to demonstrate an improved recovery. The removal rate for the lithium bicarbonate feed was lower at 93% with 37% of the lithium inventory remaining in the ER and 41% in the base reservoir.

The results of this testing demonstrate that, if applied to all resin beds containing Li-7, a minimum of 85% of the Li-7 hydroxide monohydrate added during an operation cycle can be recovered in a purified form using the sulfuric acid elution and electrodeionization (EDI) purification process. This process, combined with recovery of Li-7 generated during the cycle, would more than cover Li-7 needs for the subsequent cycle. It must be noted that additional Li-7 may be required in the event of operational events such as substantial shifts in power or forced/planned mid-cycle outages.

Monitoring of boron and lithium concentrations in reactor coolant is one of the most important chemistry missions in the operation of PWR & VVER NPPs [Bengtsson et al., 2018]. The main driver for boron monitoring is to ensure that reactivity margins have been established post transients and shut downs, or to detect events with boron dilution in timely manner. Main driver for online monitoring of lithium is to optimize the pH-control in coolant with the purpose to protecting fuel & primary systems integrity together with lowest possible radiation built up. Boron-10 is the important isotope for nuclear use and could be monitored either specific, or indirectly as total boron (NB) with a known or expected $^{10}\text{B}/^{11}\text{B}$ -ratio. Online monitors are sometimes installed to support operators with more frequent information than ever possible with grab sampling followed by laboratory analysis. Conventional technologies for online monitoring of boron in nuclear power plants are either based on automated procedures for titration of boric acid, or the ^{10}B absorption of neutrons emitted from a neutron source. Lithium is sometimes monitored online indirectly by specific conductivity or ion chromatography (IC).

Conventional technologies for online monitoring of boron and lithium may work well, but also have several drawbacks regarding accuracy or frequency, high maintenance, use of chemicals or high sample volumes producing excessive amounts of liquid radwaste. This paper describes a small research & demonstration project at Ringhals NPP, with the purpose of evaluating alternative technologies for new boron/lithium online monitors. Technologies such as "Flow Injection Conductivity", "Continuous On/Off Titration" and "Low Field Nuclear Magnetic Resonance" (LF-NMR) was evaluated and briefly demonstrated.

Results show that alternative technologies & procedures exist that may replace conventional nuclear industry solutions, thereby supporting improved reactivity management and chemistry control during operation, transients and flexible operation. LF-NMR was chosen as the most promising solution for further demonstration and qualification. The main features with LF-NMR is the simplicity, operating within a wide range of pressurized continuous flow rate without need for chemicals, where the sample could be returned to the process without affecting primary water balances or liquid radwaste volumes. The small size without "moving" parts and low need for calibration is for NMR and vouch for high availability with low maintenance. A first demonstrations have been successful for accurate and frequent monitoring of B-11, thereby total boron with a known $^{10}\text{B}/^{11}\text{B}$ -ratio. ^{10}B and ^7Li could be measured separately by NMR as well, but less frequent than for ^{11}B and may need further development.

A conventional technology is the ^{10}B neutron absorption device. This could be installed either as "clamp on" of a pipe or as a flow through compartment with known geometry and shielding properties. The ^{10}B concentration in the sample is calculated from the neutron reduction monitored due to ^{10}B absorption when neutrons are emitted from a source on one side and detected on the other side of the pipe or compartment containing the reactor coolant. The technology has advantages of being fast with high frequency of results, chemical free and applied on a continuous pressurized flow that could be recycled. The main drawback is the comparable low accuracy with high standard deviation, without real possibility to monitor small changes in boron concentrations. Accuracy may be somewhat improved by integrating measurements over extended time frames to improve the signal/noise-ratio, but then at expense of less frequency. Costs, size and weight of an online neutron device is comparably high. Neutron devices were installed in power plants during the 90's to support the operators with rapid information in case of unexpected events with boron dilution without high need for accuracy. Other devices, such as ion chromatography, UV/VIS colorimetric etc. may be used for boron detection but in lower concentrations (ppb to ppt).

3 Secondary System

3.1 Treatment selection and optimization

3.1.1 pH and Amines

To reduce the corrosion rates of carbon steels in the secondary system, amines are widely used in several countries (USA, France, etc.). Through its Pressurized Water Reactor Chemistry Monitoring and Assessment (PWR/CMA) program, EPRI published the distribution of Plants within EPRI members, using different amines for the treatment of the secondary water in American PWR units, as reported on Figure 3-1 [Lynch et al., 2018]. The most widely used are ethanolamine (ETA) with 29 units followed by a mixing of amines with dimethylamine (DMA), methoxypropylamine (MPA) and morpholine, depending on the concerns with tube fouling and balance of plant corrosion.

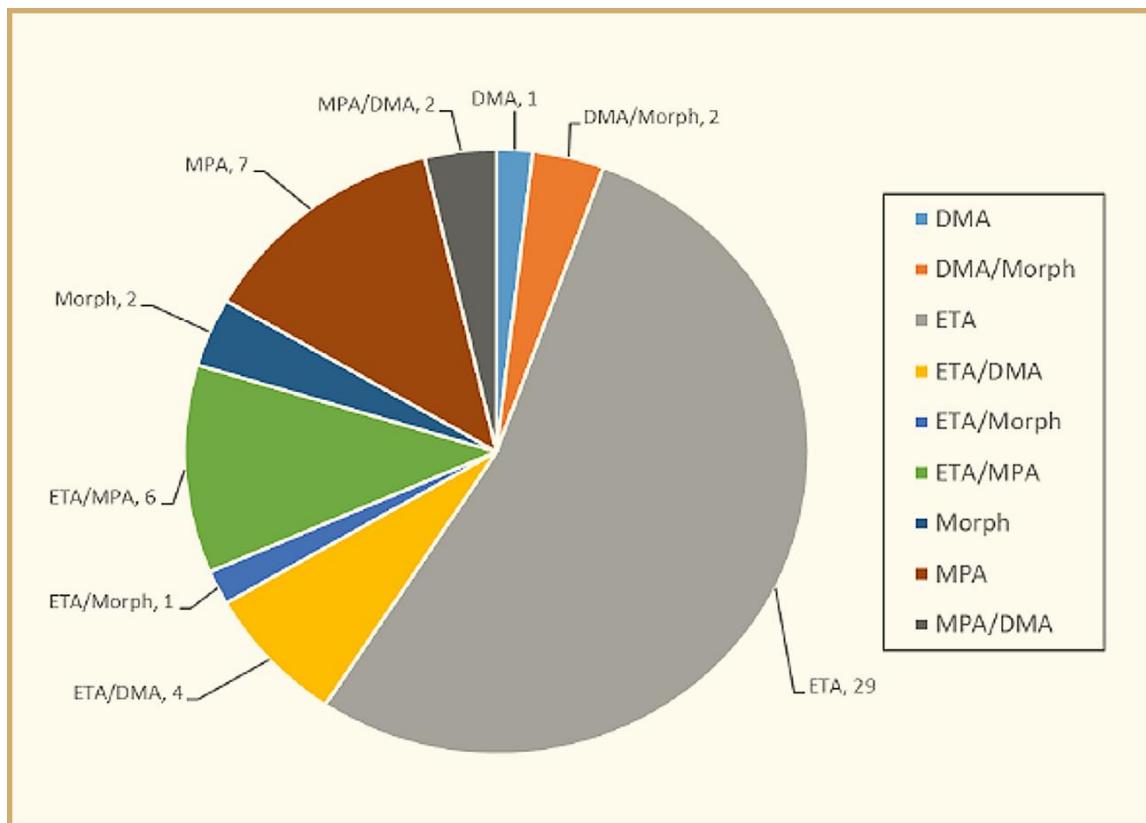


Figure 3-1: Distribution of amines used in the secondary system of US Plants [Lynch et al., 2018].

EDF is moving toward Ethanolamine (ETA) treatment to get an optimum pH at temperature for decreasing FAC and corrosion product deposition in SG [Bretelle, 2018].

A more detailed paper explained EDF strategy for moving to ETA in most of the PWR fleet of 58 reactors in operation [Gressier et al., 2018].

In order to better protect SG from corrosion, lowering Flow Accelerated Corrosion (FAC) minimizing deposits in SG at the origin of Tube Support Plate(TSP) blockage, fouling and sludge formation, EDF modifying is

- i) replacing all components with copper alloys by stainless steel or titanium
- ii) moving to ETA/ammonia (4/1.5 ppm in Feedwater), and
- iii) injecting ammonia in addition to hydrazine in the units where the target pH_{25°C} is not achieved.

EDF was keeping copper alloys at least for the condenser of some units for the bacteriostatic effect (avoiding development of amoebae) of copper. However, this copper has the negative impact of imposing a low pH in the secondary system, therefore most Utilities in the world had already eliminated copper from the secondary system. In addition, tubes with condenser are not as always as tight as condenser with titanium or stainless steel tubes. Together with the progressive elimination of copper on units that are conditioned with morpholine, EDF is moving to ETA at high pH, as shown on Figure 3-2.

Since 2009, 15 units had a condenser renewal and by 2020, almost all the units will operate at high pH_{25°C} and only 6 units should not apply ETA with the advantage over morpholine of a lower molar concentration and consequently a lower release of nitrogen organic compounds into the environment that is important in France with a very strict regulation.

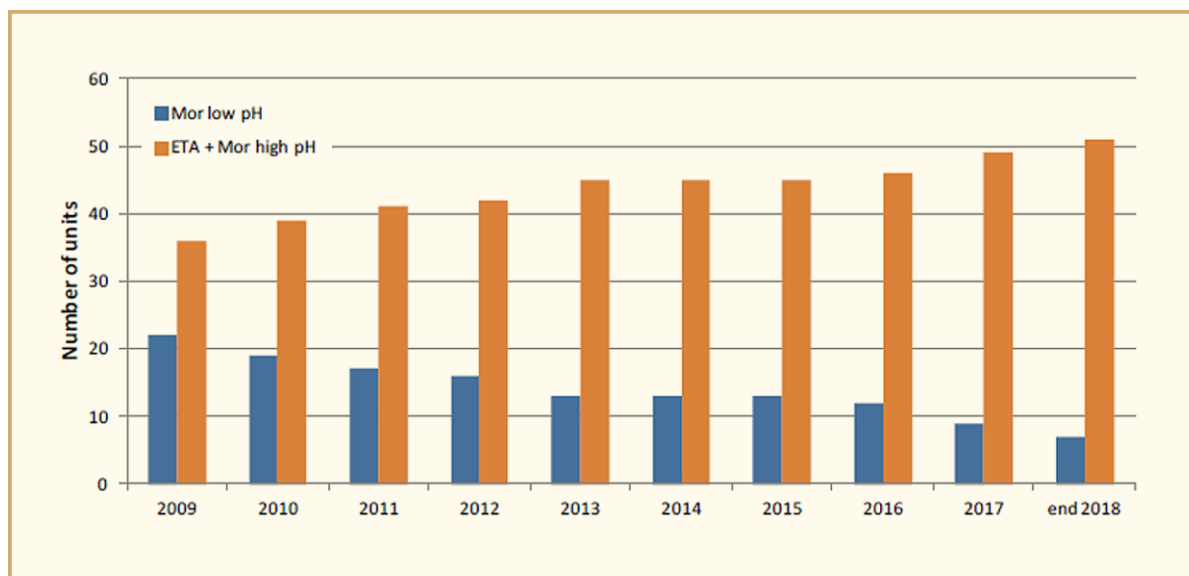


Figure 3-2: Evolution of low (morpholine) and high pH (ETA and morpholine) treatment in EDF units [Gressier et al., 2018].

The specification in Feedwater of EDF units with ETA is shown on Table 3-1. In several units, EDF decided to directly add ammonia in addition that one coming from thermal decomposition of hydrazine, to get the desired pH. As of 2018, only half of the units had the minimum expected value of 1 ppm and only 1/3 the target value of 1.5 ppm. EDF claims the necessity of increasing the pH_{25°C} with direct ammonia addition under ETA treatment, but this is highly questionable since what is important is only the pH_T and it is clear that under amine treatment, the ammonia concentration has a very limited impact on pH_T and consequently on FAC, corrosion product generation, transport and deposition within the SG. The ammonia concentration has an impact on pH_{25°C} but a very marginal one at pH_T, due to the very low alkalinity of ammonia at high temperature and its decrease of alkalinity much more significant than that of morpholine or ETA. This is also confirmed by the result given by EDF in its paper: *The data for the EDF fleet over the period 2010-2016 are summarized in Table 3-2 and show a clear impact of the pH raise from low to high pH conditioning but no clear impact of the ETA versus morpholine conditioning. The Total Suspending Solids (TSS) content is divided by a factor of 2 between high and low pH* [Gressier et al., 2018].

This confirms that the key parameter is the type of treatment with low or high pH obtained by different amine content and in a very marginal way by ammonia addition under amine treatment in the range of 1 to 2 ppm ammonia, which has almost no impact on pH_T. This is also confirmed by the TSP blockage kinetics, about twice higher for units at low pH versus units at high pH irrespective of the ammonia concentration. No difference has been observed between ETA or morpholine treatment. The only parameter identified as a key one on TSP blockage (clogging) is the negative impact of low pH (whatever the amine) or pH on pure ammonia treatment with an insufficient high pH. This is also in agreement with ANT International recommendation operating ever with amine treatment or with high AVT at a pH_{25°C} close to 10.

Table 3-1: EDF Feedwater specification for units with ETA at high pH [Gressier et al., 2018].

Parameter	Targets	Limits
pH _{25°C}	9.6 – 9.8-	9.2 - 10
ETA (mg/kg)	3.5 - 4	2 - 4
Ammonia (mg/kg)	1 - 2	<5
Hydrazine (µg/kg)	50 - 100	< 100 (expected value)
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Table 3-2: Impact of the treatment on TSS and iron over the period 2010-2016 in EDF units [Gressier et al., 2018].

Values in ppb	Morpholine low pH		Morpholine high pH		ETA high pH	
	Mean	Median	Mean	Median	Mean	Median
Feedwater TSS	12	2	7	1	5	2
Feedwater soluble Fe	3	2	3	1	2	1
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Another important information is the influence of the treatment on Ion Exchange Resins (IER) duration, which is of great importance for plants where the resins are not regenerated, as it is the case at EDF, or in presence of condensate polishing plant. EDF results show that the run time of the r IER (both cation and anion) are shortened by a factor of about 2 with ETA as compared to morpholine, but with fluctuating results, avoiding a firm conclusion. EDF considers that this may be due to the higher concentration of ETA in the liquid phase at SG blowdown and for the anionic resin by the higher alkalinity. However, EDF does not consider an important point for cationic resins [Odar & Nordmann, 2010], which is the order of affinity decreasing in the following order: ammonium > Na > ETA > Morpholine. Another confirmation is the better efficiency of macroporous resins, for sodium elimination.

One negative point with ETA has been observed on the tanks used for make up to the secondary system. In EDF plants these are treated with the alkaline reagent to decrease the need for pH and treatment regulation of the secondary system.

During the summer 2016, on one plant, a microbial development has been characterized after that the filter for total suspended solid measurement has clogged during the 2 liters sample filtration and that it showed a greasy aspect Figure 3-3. The most probable cause of this phenomenon is that ETA has favoured the development of certain bacteria in the tanks, thus creating a biofilm. The origin of the bacteria is the natural surrounding environment. The most probable metabolic degradation of ETA is ammonification with the first step leading to ammonium in solution.



Figure 3-3: Pictures of (left) the inside of make-up tank and (right) the greasy aspect [Gressier et al., 2018].

A cartography of the unit showed that the phenomenon is limited to certain systems using the make up water and that have the “good” conditions for a bacteria growth, namely ambient temperature, aerated fluid and presence of ETA. These conditions are essential for the bacteria to live and develop as what is documented in the literature. Sanitary risk is excessively limited regarding the environmental origin of the bacteria and standard personal protection devices are enough to work. Regarding the operation of the unit, the overall impact is very limited as the bacteria and biofilm are killed in deaerated conditions and by a high temperature. No specific operation issues have been reported on the unit since 2016 regarding this phenomenon.

The remediation steps were first the cleaning of the two makeup tanks with high pressure water lancing to swipe off all the biofilm. In a second step, the makeup tanks conditioning has been moved from ETA to ammonia, which is not a good substrate for microbial organism development and should prevent any major bacteria growth.

Two other aspects are listed in the improvement studies for the secondary system in EDF units [Gressier et al., 2018]:

- Improve the lay-up practices and the secondary water quality during start up, especially by a film forming amine injection in a pilot plant in June 2018.
- Hydrazine consumption minimization and substitution possibilities to comply with the REACH regulation in Europe and EDF chemical specification adjustments based on the Flamanville EPR chemical specifications that have introduced a hydrazine over oxygen ratio.

The characteristics including dissociation, vapor-liquid distribution, thermal decomposition compatibility with materials of ETA used in secondary circuit system were investigated by laboratory research and full-scale tests at Chinese NPP of Qinshan phase-I in 2009 [Zhao et al., 2018].

The laboratory test and full-scale test including dissociation, vapour-liquid distribution, high temperature thermal stability and compatibility with materials were carried out to support the first application of ETA in Qinshan Phase I nuclear power plant.

Figure 3-4 shows the pH changes in feed water, main steam, SG blow-down water, moisture separator reheater (MSR) steam and MSR condensed water after ETA is added. The pH has a first fluctuating process and then slowly stabilizes because the remaining ammonia in secondary circuit system can affect the pH in the early stage, and the pH value of each part in secondary circuit system can be controlled at 9.3~10.0 after the first fluctuating process. The full-scale test shows that the pH of each part in secondary circuit system can be well by ETA due to its enough alkalinity.

4 Auxiliary systems

4.1 Closed Cooling Water Systems

The paper “Optimization and Standardization of Closed Cooling Water Systems Chemistry Performance Monitoring in the Duke Energy Fleet” was presented by R. Thompson [Thompson, 2018]. It describes the process and the results of a rigorous evaluation to optimize chemistry monitoring in 65 closed cooling water systems in the Duke Energy nuclear fleet. The optimization process included a review of 18 years of chemistry trends (over 680 parameters) from the time period 2000 - 2017, representing 198 unit-years of operating experience. A cumulative fleet total of over 2800 specific parameter analyses per year were identified which could be eliminated.

From 2017 to early 2018 a rigorous review of long-term chemistry trends, chemistry monitoring practices, system equipment reliability classification, and system risks based on system design and operating conditions was performed to identify low value or unnecessary water chemistry sampling and analyses in the Duke Energy nuclear fleet closed cooling water systems. The elimination of, or reduction in frequency of some water chemistry analyses will improve efficiency, reduce operating costs, and will enable plant and corporate Chemistry personnel to better focus on both the plant's most important closed cooling water systems and on the chemistry parameters that are most critical to the optimum performance of every system monitored.

The Duke Energy nuclear fleet is composed of six stations: Brunswick, a two-unit BWR; and five PWR sites - Oconee (three units); Catawba and McGuire (two units each); and two single unit sites, Harris and Robinson. In the fleet are several closed cooling water systems which employ several different corrosion inhibitor chemistries, the major three being molybdate/azole, blended glycol, and nitrite/azole.

A closed cooling water system is a circulating water system that is operated above atmospheric pressure which is completely enclosed with negligible evaporation or exposure to the environment, except that it may contain an expansion or surge tank that is vented to the atmosphere. Electrical generator stator cooling water systems are subject to different industry guidelines and were not included in this review.

Component Cooling Systems

These closed recirculating systems use chemically treated water to transfer heat to the environment from the letdown heat exchangers or coolers, spent fuel pool heat exchangers, and other systems which contain radioactive or non-radioactive water. Component cooling water temperatures in the letdown coolers are greater than 66°C. There are 11 Component Cooling Systems in the Duke Energy nuclear fleet. Chromate chemistry is used in one system. Nitrite/azole chemistry is used in two systems and the remainder use molybdate/azole chemistry.

Turbine Building Closed Cooling Water Systems

These closed recirculating systems use chemically treated water to transfer heat to the environment from turbine generator accessories and related secondary plant equipment. Turbine building closed cooling water temperatures are greater than 150°F in feedwater sample coolers which are cooled by this system. There are six turbine building cooling water systems in the Duke Energy Nuclear Fleet. Nitrite/azole chemistry is used in two systems and the remainder use molybdate/azole chemistry.

Chilled Water Systems

Chilled water systems are closed recirculating systems that use chemically treated water to transfer heat from equipment, air ventilation systems, etc. to refrigeration chillers which transfer the heat to the environment (either to the air or to an open cooling water system through a heat exchanger). The water temperature ranges from ~ 7°C at the outlet of the refrigeration chiller to ~ 13°C at the inlet to the chiller. In the Duke Energy Nuclear Fleet there are five Tier 1 chilled water systems and 16 Tier 2 systems. A Tier 1 System is one which if unavailable would challenge continued plant operation, is safety-related, or supports a safety-related function. A Tier 2 System does not challenge continued plant operation if unavailable. Molybdate/azole chemistry is used in all the Tier 1 chilled water systems and

all but two of the Tier 2 systems. Nitrite/azole chemistry is used in one system and carbohydrazide chemistry is used in another.

Diesel Engine Jacket Cooling Water Systems

These closed systems circulate chemically treated water through the diesel engine block to remove heat and transfer it to the environment either through an air-cooled radiator or through a heat exchanger which transfers the heat to an open cooling water system. In the Duke Energy nuclear fleet, there are 26 diesel engines which may be classified as follows:

- Non-radiator cooled standby diesel engines with service water heat sinks. This group consists of 16 non-radiator cooled large safety-related emergency diesel generators with 2500 - 6500 kW of electrical output; and one safety-related large standby shutdown diesel generator (consisting of two engines in tandem) with 3645 kW of electrical output. Nitrite/azole chemistry is used in four of the engine cooling water systems. Molybdate/azole chemistry is used in the other 12 systems.
- Radiator-cooled standby diesel engines with blended glycol coolant. This group consists of 4 non-safety-related large standby shutdown/supplemental diesel generators with 2600 - 4000 kW of electrical output; two Tier 1 and one Tier 2 small-medium standby shutdown diesel generators with 400 - 700 kW of electrical output; one Tier 2 Security Building small standby electrical generator; and one Tier 2 diesel driven fire pump. The radiator-cooled standby diesel engines are outside the scope of this paper.

A rigorous review of five specific areas was performed for each closed cooling water system to determine what chemical analyses could be eliminated or reduced in frequency.

Long-term Chemistry Trend Review

Trends for every chemistry parameter currently being monitored in the fleet's closed cooling water systems (a total of over 680 parameters) over the 18-year period 2000 - 2017 were reviewed. These long-term chemistry trends represent an internal operating experience of 198 unit-years which provided insights into the frequency and behaviour of chemistry upsets that have occurred in these systems.

System Design and Operating Characteristics Review

A review of each system's design and operating characteristics was performed to identify both potential impurity ingress pathways and which sections of some systems where localized boiling occurs. The details of this review are discussed below.

Plant Closed Cooling Water Chemistry Strategic Plans Review

Each plant's closed cooling water chemistry strategic plan was reviewed in detail including deviations taken to the EPRI Closed Cooling Water Chemistry Guidelines. The deviations taken at some plants were evaluated for applicability at other plants in the fleet.

Industry Chemistry Guidance Review

Several documents were evaluated to determine where chemistry monitoring may be optimized. Table summarizes the chemistry monitoring frequencies of the closed cooling water chemistry guideline for systems using nitrate/azole and molybdate/azole chemistry. The details of this evaluation are discussed below.

Fleet Systems Classifications Review

Throughout the nuclear industry a graded approach is taken to equipment reliability to focus limited resources on the most important equipment and systems. A four-tier system is employed at Duke Energy in which Tier 1 is the most important. Tier 1 systems provide emergency AC power, high pressure injection, heat removal, residual heat removal, and support cooling, i.e., Mitigating System Performance Index Systems. All the emergency diesel generators and two-thirds of the component cooling systems in the Duke Energy nuclear fleet are classified Tier 1 systems.

5 Monitoring, Specifications, Strategy

14 years after a presentation at an NPC conference also in San Francisco, which explained that the lowest achievable values for some specified parameters is not always the best approach, with negative side effects [Nordmann, 2004], EPRI finally recognized that “in order to create a more sustainable and cost effective chemistry control paradigm, a critical review of the technical justification for many current chemistry control objectives, administrative or otherwise, that the industry attempts to meet, must be undertaken” [Wells et al., 2018]. This is explained by the fact that detection limits becoming lower and lower, the old ALARA principle is not always relevant, increasing operating cost without any benefit. Like the French author in 2004, EPRI is also considering that effort should focus on chemistry monitoring optimization.

Similarly, to all what was also reported in 2004 [Nordmann, 2004], EPRI understood the necessity to focus on the sole parameters that are necessary to be monitored during power operation with an intelligent optimization, to prefer on-line monitoring with immediate corrective actions if necessary, instead of waiting for confirmation by grab sample analyses [Wells et al., 2018].

EDF made an oral presentation on Hinkley Point C preparation for successful chemistry control and system operation during commissioning [Tigeras & Harrington, 2018]. Hinkley Point C (HPC) will be the fifth unit in the family of EPR reactors to be commissioned, after Taishan 1 and 2 (TSN1, TSN2), Olkiluoto 3 (OL3) and Flamanville 3 (FA3). This event represents an important appointment for EDF and the different stakeholders for demonstrating the capability of the nuclear industry to progress based on learning from Operating Experience (OPEX).

In the field of chemistry and system operation, international collaboration and continuous analysis of feedback are considered essential to define HPC commissioning procedures, for each testing phase, that are fit-for-purpose:

- Individual systems tests,
- Functional Cold and Hot tests of the primary and secondary circuits, including auxiliary system tests
- Fuel loading, pre-critical tests and power escalation.

It is often believed that chemistry (and radiochemistry) control during the commissioning period is only important during the passivation of the primary circuit surfaces during Hot Functional Testing (HFT); this paper aims to dispel this myth.

Real examples are given to show how chemistry and radiochemistry control is essential in the commissioning phases, from the end of equipment installation to full power operation. The interfaces between chemistry, radiochemistry and the different systems are explained, identifying the key activities in chronological order (for example: material preservation, rinsing of piping and equipment, SG dry/wet lay-up, hydraulic tests, additive injection in the primary and secondary circuits, as well as auxiliary systems, purification, water degassing, management of hydrogen and oxygen risks, boron management in the primary circuit, pools and tanks, radioactivity control after fuel loading to identify potential fuel failures and monitoring of corrosion and activated product source term etc.).

By capitalising on relevant OPEX for the commissioning phase of HPC, improvements can be gained in the areas of:

- Safety
- Hazard protection
- Corrosion management (with environmental and radiation protection impacts)
- Industrial constraints.

Finding the right balance between these key issues is essential for a successful commissioning phase, which is indispensable to ensuring a long plant life and good operational performance. The management of chemistry and radiochemistry plays a significant role in the decisional phases due to its numerous interfaces.

In the same way, HPC will feed its own experiences back into the international community to improve the management of chemistry and radiochemistry and system operation in the wider nuclear industry.

Hinkley Point C (HPC) is an EPR reactor to be built at Somerset (in South West England). This is the first nuclear power plant built in the UK after Sizewell B (over 20 years ago).

The OPEX from the commissioning of EDF fleet (58 reactors) and Sizewell is an essential input for Hinkley Point C. However, the advanced design and operation of the EPR leads one to consider with attention the feedback from the previous commissioned EPRs (TSN 1-2, OL3 and FA3).

Commissioning Phases

After engineering, procurement and construction phases, the commissioning is the last phase prior to the commercial operation where the previous steps are verified and validated. As detailed in [1], the commissioning programme consists of three main phases:

- Phase I: Pre-operational System Tests:
 - System Transfer Process between the erection and the commissioning
 - Test of individual Components without interaction between them.
 - System commissioning tests
 - Cleaning of circuits
- Phase II: Pre-operational Overall Systems Tests:
 - Cold Functional Tests
 - Pressure Testing of primary circuits
 - Hot Functional Tests Pre-Core Load.
- Phase III:
 - Fuel loading
 - Pre-criticality tests (Hot Functional Test Post-Core Load)
 - First Criticality and Start-up until 60% nuclear power.
 - Power escalation from 60 to 100% nuclear power.

Chemical control is required from the Phase I and radiochemistry control from the Phase III. Since chemistry and radiochemistry affect the overall plant, a “pseudo-system” called “Chemistry of Fluids” has been defined. As for any other system, procedures are developed for the pseudo-system “Chemistry of Fluids” in which the chemical and radiochemical requirements and actions are defined.

The experience shows that the commissioning phase is a very variable period with iterative steps affecting the cleanliness of the circuits and the fluid conditioning. Therefore, it is essential to define practical and achievable objectives which can be adapted to the different concerns of the plant in coherence with the evolution of the installation and commissioning phase.

The experience shows that establishing appropriate control of chemistry during the commissioning is important for long term plant operation. International standards, guidelines and best practices will be considered for HPC to provide the optimal criteria and prescriptions concerning the ensemble of activities related to the chemistry and radiochemistry:

- Monitoring of parameters defining the frequency, the means of control (sampling points, on-line devices) as well as the expected and the limit values with their associated tolerances and corrective actions.
- Injection of appropriate chemical additives during each phase as a function of objectives.
- Purification of water via commissioning and/or definitive filters and demineralisers.
- Degasification of dissolved gases and fission products.

The selection of the chemical and radiochemical criteria to be fulfilled during the commissioning phase are the result of the balance between several objectives:

- To ensure safe conditions of work for the personnel throughout each phase.
- To minimise the environmental impacts in terms of liquid, gaseous and solid discharges containing potential chemical and radiochemical species.
- To optimise the chemical conditions to contribute to the cleanliness and prevent material degradation during the plant commissioning.
- To contribute to the limitation of the future operating constraints related to chemical and radiochemical control: integrity of barriers, material corrosion, radiation protection, source term and effluents.
- To determine the initial source term of fission products (from residual tramp uranium contamination) and to detect potential fuel failures during the first start-up after fuel loading.
- To determine the initial source term of corrosion products.
- To facilitate the commissioning planning progress.

Table 5-1 shows the requirements for water in the various systems during the commissioning phase.

Table 5-1: Principles to select the type of water and preservation to use during commissioning [Tigeras & Harrington, 2018].

Material of Circuit/equipment	Type of fluid after commissioning	Type of water to be used during tests (flushing, tests of individual component, hydraulic tests) as function of test duration ('t')		Preservation Conditions	
		Test duration with water < "t" hours	Test duration with water > "t" hours	Wet preservation	Dry preservation
Carbon steel	Demineralised water conditioned with trisodium phosphate: Cooling systems	Demineralised water followed by drying.	Demineralised water with trisodium phosphate.	Demineralised water with trisodium phosphate. Periodical control of impurities, pH.	Necessity of drying following draining.
Low alloy Nickel alloys of Steam Generator (SG)	Demineralised Water conditioned with amines (ETA, ammonium, hydrazine): Conventional island systems/secondary circuit	Demineralised water followed by drying.	Demineralised water with hydrazine and amine (ETA, ammonium)	Demineralised water with hydrazine and amine (ETA, ammonium). Periodical control of impurities, pH.	Necessity of drying following draining.
Stainless steel	Demineralised water in presence of primary coolant additives (zinc, boric acid, hydrogen, lithium hydroxide, hydrogen peroxide, hydrazine: Nuclear island circuits	Demineralised water	Demineralised water	Demineralised water. Periodical control in order to verify the impurities.	No necessity of dry preservation but protection of components according to cleanliness and FME principles

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During these phases the components and systems are connected, and they are tested progressively to high pressure whilst maintaining a low temperature. The primary circuit is not chemically conditioned

6 Future Trends and Reactors

Fusion reactors are in the early phase of development and still require several studies, which include a prototype [Holmes et al., 2018].

The European DEMOnstration fusion power plant (DEMO) is currently planned for construction through the 2030s and is expected to generate electricity towards the late-2040s. DEMO is intended to be a demonstrator for fusion power plant technologies, paving the way to a first-of-a-kind commercial fusion power station, building on the scientific and technological advances of both the Joint European Torus and ITER facilities. Still, there remain several technical challenges that must be overcome to realise the deployment of fusion power plants on a commercial scale. Some of these can be addressed by drawing on the extensive operational experience of fission power plants, while the unique nature of fusion energy brings certain characteristics the industry has much less experience with, such as high magnetic fields, high-energy neutron irradiation and the resulting behaviour of advanced materials that are required to cope with these conditions. In addition, the influence of highly tritiated water, which results from tritium fuel breeding, is a further possible exacerbating factor which is less well understood.

One specific challenge relates to the irradiated water-cooling circuits in DEMO that will experience a combination of conditions; this environment has the potential to influence the performance of coolant-facing structural materials. For example, a key consideration in the development of the Breeder Blanket system is its compatibility with the operating environment, specifically the media used to transport heat away from the Breeder Blanket. Four design options for the DEMO Breeder Blanket system were originally proposed; one being the Water-Cooled Lithium Lead (WCLL) design.

In the WCLL concept, energy emitted from the fusion plasma is converted into heat by a molten lithium-lead (LiPb) system which provides both a stopping medium for the mixed radiation field and a production route for tritium to feed into plasma generation.

Irradiated water-cooling circuits in the EU DEMO fusion reactor will experience a combination of conditions which has the potential to influence the performance of coolant-facing structural materials. In common with LWR primary circuits, heat transfer plant in the Breeding Blanket, Divertor and First Wall locations will be exposed to high temperature, high pressure water within an intense neutron and beta/gamma irradiation field. The neutron energy of 14 MeV is significantly higher than thermal fission plant and components will experience significant fluencies over their expected plant lives. In addition, the influence of strong magnetic fields and highly tritiated water (due to tritium fuel breeding) are possible exacerbating factors. To ensure that the possible effects of these parameters are adequately controlled, a conceptual water chemistry programme is now under development.

Another British paper [Martin et al., 2018] with some of the same co-authors as the above paper was studying the materials properties for fusion reactors and confirms some of the above statements on the key issues in such materials behaviour in the condition of fusion reactors.

In the DEMO reactor, a cooling circuit will also be required to remove heat from the reactor walls, both from an operational perspective and to generate power through a turbine. Four designs are currently being considered for the breeder blanket cooling system of DEMO, including a helium-cooled pebble bed (HCPB) design and a WCLL system. The latter design extracts heat from the fusion plasma using a slowly circulating molten lithium-lead (LiPb) that flows through segmented modules, producing tritium and absorbing heat because of interactions with neutrons emitted from the fusion plasma. This heat is extracted by a network of embedded cooling tubes that carry a water coolant through the volume of the LiPb and out from the reactor vessel.

The steel proposed for DEMO, such as Eurofer-97, developed in Europe, contains 8.82 % Cr, 1.09 % W, 0.13 %Ta, 0.47 % Mn, 0.11 %C and Fe is the balance. These steels have a different composition and microstructure than those used in LWR and their response to corrosion will also likely differ [Martin et al., 2018].

The structural steels in a fusion reactor require high strength at elevated temperatures, while maintaining irradiation resistance, but several elements in traditional stainless steels such as cobalt and nickel can form long-lived radioactive isotopes after irradiation. Reduced Activation Ferritic-Martensitic (RAFM) steels are a class of steel developed with reduced activation properties, where the alloying

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Nomenclature

AGR	Advanced Gas-Cooled Reactors
AISI	American Iron and Steel Institute
ALARA	As Low As Reasonably Achievable
ANTI	ANT International
AOA	Axial Offset Anomaly
BOA	Boron-Induced Offset Anomaly
BWR	Boiling Water Reactor
cc/kg	cubic centimetre (per kg): used for H ₂ concentration in RCS = ml/kg (under normal pressure and temperature)
CANDU	CANada Deuterium Uranium
CGR	Crack Growth Rate
CILC	Crud-Induced Localized Corrosion
CIPS	CRUD Induced Power Shift
CP	Corrosion Polisher
CS	Carbon Steel
CRDM	Control Rod Drive Mechanism
CRUD	Acronym for “Chalk River Undefined Deposits”
CS	Carbon Steel
CVCS	Chemical and Volume Control System
DEHA	Diethylhydroxylamine
DEI	Dominion Engineering Inc.
DEMO	DEMOstration fusion power plant
DH	Dissolved Hydrogen
DO	Dissolved Oxygen
EBA	Enriched Boric Acid
ECP	Electro Chemical Potential
EdF	Electricité de France
EIS	Electrochemical Impedance Spectroscopy
EPR	European Pressurized Water Reactor
EPRI	Electric Power Research Institute, USA
FFA	Film Forming Amines
FOPH	Federal Office of Public Health
FW	Feed Water
HFT	Hot Functional Testing
ICP	Inductively Coupled Plasma optical emission spectrometry
IER	Ion Exchange Resin
IAEA	International Atomic Energy Agency, Vienna
IGSCC	Intergranular Stress Corrosion Cracking
LBE	Liquid Lead Bismuth Eutectic
LTU	Long-term use
LWR	Light Water Reactor
MA	Mill Annealed
MAMBA	MPO Advanced Materials/Boron Analyser
MPO	Material Performance Optimization
MS	Main Steam
NOP	Normal Operating Pressure
NOT	Normal Operating Temperature
NPP	Nuclear Power Plant
ODA	Octadecylamine
OPG	Ontario Power Generation ()
ORE	Occupational Radiation Exposure
PAA	PolyAcrylic Acid (dispersant)
PHWR	Pressurized Heavy Water Reactors
ppb	part per billion = µg/kg
ppm	part per million = mg/kg
PSL	Primary-to-Secondary Leak
PWR	Pressurized Water Reactor

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