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Innovation, Advances and Developments in the Water Chemistry of Pressurized Water Reactors

INNOVATION, ADVANCES AND DEVELOPMENTS IN THE WATER CHEMISTRY OF PRESSURIZED WATER REACTORS

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FOREWORD

The safe operation of pressurized water reactors (PWRs) and water cooled, water moderated power reactors (WWERs, the established abbreviation derived from ‘water–water energetic reactors’) requires, among other things, an appropriate and effective water chemistry programme. The main goals of such a programme are to support reactivity management, minimize all forms of corrosion, preserve the integrity of the fuel and reduce the buildup of radioactive material. Over the long term, excellence in water chemistry management helps prevent unplanned and earlier-than-expected replacements of major plant components, thereby helping to control operational expenses within the defined overall plant business plan. It is also a crucial element of a plant life cycle management programme and a key factor in achieving safe and cost effective operation of existing plants that have transitioned to long term operation.

In the context of ongoing research efforts and the increasing use of advanced data technologies, this publication presents innovations, advances and developments in the water chemistry practices and technologies applied in existing PWRs and WWERs that have led to (or are likely to lead to) improved performance in nuclear safety and asset value retention. Where relevant, ongoing research efforts are also presented.

This publication shares operating experiences and lessons learned from established operators pursuing excellence or transitioning to long term operation beyond their plants’ originally intended operational periods, providing valuable insights for other experienced operators seeking continual improvement. It is also intended for operators with less experience or with limited access to the newest technologies, as well as for newcomers and operators of newly commissioned plants, to help them take appropriate steps at an early stage of operation. Additionally, designers of new reactor types can refer to this publication to consider incorporating the latest operating experience and practices from existing plants into their designs.

The IAEA is grateful to all the experts involved, and their Member States, for their contributions. The IAEA officer responsible for this publication was L. Bourdonneau of the Division of Nuclear Power.

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CONTENTS

1. INTRODUCTION

1.1. BACKGROUND

Good performance in the water chemistry of a nuclear power plant (NPP) is an element of nuclear safety. This is underpinned by IAEA Safety Standards Series No. SSG-13 [1] and WANO guideline on the conduct of chemistry at nuclear power plants [2]. While seeking performance improvements in water chemistry, operating organizations of existing PWRs and WWERs face several typical challenges as follows:

- Accessing, evaluating, and assessing to relevance the latest technologies and recent operating experience from around the world;
- Adapting the current water chemistry programme to comply with evolving regulations and addressing the possible disappearance of:
  - Suppliers of nuclear-grade chemical products and chemical analysis equipment;
  - Historical technical support organizations with expertise in the technical basis for the water chemistry programme;
- Identifying and balancing technical options that enhance performance in areas such as nuclear safety, radiation protection, and environmental discharge, without causing adverse effects in other areas or impacting resources and organization at the NPP;
- Aligning the entire organization across the NPP with the technical objectives of a good (ambitious) water chemistry programme;
- Obtaining funding for improvement projects in chemistry, especially for projects that only benefit plant performance on long term.

1.2. OBJECTIVE

This publication is intended to:

- Expand upon recommendations and guidance contained in IAEA Safety Standards Series No. SSG-13 [1];
- Identify the latest innovations, advances and developments in the water chemistry of PWRs and WWERs that have led to visible and tangible performance improvement or are likely to lead to performance improvement. In addition, where relevant, on-going research efforts are also presented. However, it is not claimed that every recent innovation, advance, development and research is captured;
- Help operating organizations of existing PWRs and WWERs address some of the challenges they face – see Section 1.1 – and maximize asset value while developing, implementing and revising their water chemistry programme or planning for refurbishment of their chemistry monitoring systems.
- Offer a balanced, fact-based discussion of best practices and guidance provided by various organizations and associations alongside technical information and operating experience from operators affiliated with those organizations and associations.

1.3. SCOPE

The publication describes innovations, advances and new developments in specifying and controlling the water chemistry of PWRs and WWERs, and presents technological transformations in areas such as:

- Simulation modelling;
- On-line and automated monitoring methods and techniques;
- Use of robotics.

This publication also addresses innovations, advances and new developments following changes in NPP operations, such as the introduction of flexible operation, transition to long term operation and operation after steam generation replacement.

The typical timeframe for the implementation of the innovations, advances and new developments covered in this publication is 5 years.

In this publication:

- Innovations refer to new and changed chemistry processes, simulation models, monitoring methods and techniques implemented in NPPs that bear a certain degree of novelty. This aligns with the definition of innovation according to ISO standard 56000 [3]: a "new or changed entity, realizing or redistributing value" that "can be a product, service, process, model, method".
- Advances refer to technological improvements or augmented knowledge of existing chemical processes, models, methods and techniques that have become more accurate or more capable as a result of the advances, potentially leading to performance improvements.
- Developments refer to the expansion of existing technological solutions, approaches and good practice that have led to or are likely to lead to performance improvements in chemical processes, models, methods and techniques in NPPs. Developments that have confirmed previous operating experience are also included.

When relevant, this publication presents on-going research, defined as on-going investigations and experiments to verify new or revised theoretical models and to check practical applications before implementation at NPPs.

For areas where different strategies are pursued by operators, this TECDOC provides context and background information while presenting some details of these strategies.

This publication does not discuss existing technical solutions and specifications for the water chemistry of PWRs and WWERs that have already been published by organizations within the nuclear industry sector.

This publication is primarily intended for nuclear power plants operating organizations wishing to improve their performance in water chemistry and for designers developing new reactor types or planning the construction of advanced PWRs and WWERs.

1.4. STRUCTURE

The main body of this publication is divided into six sections, including the introduction in Section 1 and the summary and perspectives in Section 6.

Section 2 addresses innovations, advances and developments in the water chemistry of the primary system of PWRs and WWERs, Section 3 in the secondary systems and Section 4 in the auxiliary systems. Section 5 discusses on-line monitoring systems, chemistry information systems and use of robotics at NPPs, and presents innovations, advances and developments in those areas.

2. PRIMARY SYSTEM WATER CHEMISTRY

The primary goals of the primary system water chemistry are to minimize general corrosion of structural materials and fuel cladding, to avoid local corrosion as much as possible, to contribute to the reactivity management, and to reduce the build-up of radioactive material. The key success factors of an effective programme include selecting the most appropriate conditioning products, monitoring specified conditions, limiting impurities and monitoring them, and choosing the most suitable practices and procedures for operation. The typical aspects operating organizations ought to consider are as follows:

- Monitoring of the boron concentration in the primary coolant (the moderator), with a specific focus on the ^{10}B content of the total boron;
- Optimization of the potential hydrogen (pH) to mitigate the adverse effect of the total boric acid concentration in the coolant by injecting alkaline compounds such as lithium or potassium hydroxide;
- Addition of hydrogen to maintain reducing conditions and suppress oxidizing species produced by radiolysis, while balancing the risk of stress corrosion cracking (SCC) initiation and propagation;
- Dosing of a compound of zinc to mitigate general corrosion and reduce the release of species into the primary coolant. This helps change the chemical characteristics and thickness of fuel cladding deposits, decrease the source term (mostly due to^{58}Co and ^{60}Co, by lowering the dissolution rate of Ni and Co from structural materials) and mitigate SCC affecting nickel-based alloys;
- Improvement of operational procedures (especially during shutdown and start-up phases for existing plants and at commissioning for new builds), supported by simulation modelling to understand dissolution, transport and deposition mechanisms of corrosion products.

All these aspects are discussed throughout Sections 2.1 to 2.9 as follows:

- Section 2.1: Developments in the use of enriched boric acid for enhancing pH control in PWRs;
- Section 2.2: Innovation and advances in hydrogen management for controlling reactor coolant chemistry in PWRs and WWERs, including a discussion on target concentrations;
- Section 2.3: Developments in silica removal and control for protecting nuclear fuel in PWRs;
- Section 2.4: Control of source terms for reducing worker exposure, with a specific focus of the benefits of zinc injection and a presentation of surface contamination measurement campaigns in PWRs and WWERs – Section 2.9 further expands on advances in simulation modelling of surface contamination;
- Section 2.5: Advances in the control of parameters and discharges to environment in flexible operations in PWRs;
- Section 2.6: On-going research on the replacement of lithium hydroxide by potassium hydroxide in a Western design PWR;
- Sections 2.7 and 2.8 explore advances and developments in optimizing chemistry throughout commissioning, shutdown, outage and start-up.

As a reminder, general technical guidance for primary chemistry control programmes is given in chapter 4 of Refs [1] and [2][1]. Detailed technical guidance is given in Refs [4–6], depending on the specific reactor design. Note that chapter I.C of Ref. [7], published in 2002, identifies the EPRI chemistry guidelines that were made available to all WANO members at that time. Some technical elements specific to WWERs are presented in chapters 3.1.2, 4.4, 6.2, and 8.1.1 of Ref. [8].

2.1. DEVELOPMENTS IN THE USE OF ENRICHED BORIC ACID FOR ENHANCING pH CONTROL

This section presents the operating experience gained at NPPs that use enriched boric acid (EBA). Deployed in 1997 in Siemens-designed PWRs in Germany and Switzerland with positive operating experience, EBA is also used in recently commissioned (between 2018 and 2025) third generation PWRs of type European pressurized reactor (EPR) that confirmed the benefits of using EBA as identified by the operating organizations of Siemens-designed PWRs. This section also presents developments in the management and measurement of the ^{10}B isotope that apply at all PWRs and WWERs, irrespective of whether they use EBA or not.

Boric acid is widely used in operating PWRs and WWERs to control the reactivity of the core over a fuel cycle. Only the ^{10}B isotope absorbs thermal neutrons and, thereby, contributes to reactivity control through the $^{10}\mathrm{B}(\mathrm{n},\alpha)\text{-}^{7}\mathrm{Li}$ reaction. Natural boric acid contains ^{10}B at 19.8 at.% (atomic percentage). At the development of most PWRs and WWERs currently in operation, natural boric acid was used. When waste water was produced, the practice was to discharge boron to the environment. This implied the boric acid of the primary coolant had to be regularly refreshed to avoid the depletion of ^{10}B (i.e. replaced by fresh boric acid with boron at the natural $^{10}\mathrm{B}/^{11}\mathrm{B}$-ratio or at a higher ratio).

Increasing the amount of ^{10}B in the boric acid increases the ability to control reactivity while maintaining a moderate total boron concentration. The benefits of using EBA, typically at 30 at.% of ^{10}B, are:

1) Enabling operation at a higher $\mathrm{pH_T}$ throughout a fuel cycle, especially when fuel cycles are extended to 18–24 months;
2) Reaching the target $\mathrm{pH_T}$ earlier in the cycle;
3) Increasing shutdown margins when mixed oxide fuel or more highly enriched fuel is used.

Benefits 1 and 2 mitigate general corrosion and reduce the risk of fuel cladding corrosion. They might also reduce the risk of axial offset anomaly by reducing the fuel crud[2] deposits for the PWR units having steam generator tubes of nickel base alloys 600 and 690TT. Benefit 3 was the driver when Siemens-designed PWRs in Germany and Switzerland converted their plants to EBA and introduced reprocessed fuel elements with mixed oxide, to improve fuel economy [9]. Decisive was the advantageous feature of the design that allows for boron to be recycled through the liquid waste system and removed through the solid waste system.

Other operating organizations, like EDF in France where the boron in effluents is strictly regulated, did not opt for EBA for their existing fleet as it was not profitable and would have required to empty all systems containing boric acid, which would have posed long term challenges to discharge limits.

For new plants, the option of enriched boric acid ought to be considered at the design stage [10, 11].

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[1] Not publicly available but made available to all WANO members.

[2] Defined sometimes as the abbreviation for corrosion-related unidentified deposits or Chalk River unidentified deposits, referring to Chalk River research reactor in Canada – see https://www.nrc.gov/docs/ml2018/ml20182a653.pdf.

2.1.1. Enhanced pH_T control in pressurized water reactors

2.1.1.1.Background: B-Li coordination strategies

From beginning on of the PWR industry, it was found that the alkalization of boric acid containing coolant is indispensable to minimize the fuel crud deposits. Based on field experience, it was learned that increased fuel crud causes higher radiation fields, decreased core reactivity, and increased fuel cladding corrosion. Therefore, the main strategy of the alkalization was to establish a pH_T value for the minimum solubility of the coolant corrosion products (at the bottom of the core), so that the crud transport in the core area and thus the fuel deposits would be minimized. In the 1960s and 1970s it was believed that the chemical composition of the passive layers on the reactor coolant system structural materials (source of the coolant crud) is magnetite. Magnetite has a solubility minimum at pH_T of 6.9. This pH_T value could be achieved by addition of LiOH throughout the whole fuel cycle of one year, without violating the lithium concentration limit of ≈2.2 mg/kg specified worldwide by fuel vendors; the so called 'coordinated chemistry' with constant pH_T value was introduced (see line 1 in Fig. 1 and definition as in Ref. [12]). However, later in 1980s during the root cause analysis of damaged steam generator tubes, it was found that the passive layers consist of nickel ferrites instead of magnetite. The nickel ferrites have their solubility minimum at pH_T of 7.0–7.4 (depending on the temperature), which could not be adjusted for the whole cycle (especially at the beginning of the fuel cycle) without exceeding the specified lithium concentration limit. Alternatively, the so called 'modified chemistry' was introduced, starting the fuel cycle with a constant lithium limit value, till the target pH_T value of 7.4 is reached at lower boric acid concentrations close to the end of cycle. Then the lithium concentration is reduced in coordination with the boric acid concentration (see line 2 in Fig. 1) – Section 5.1.4 discusses automated lithium injection to effectively achieve B-Li coordination.

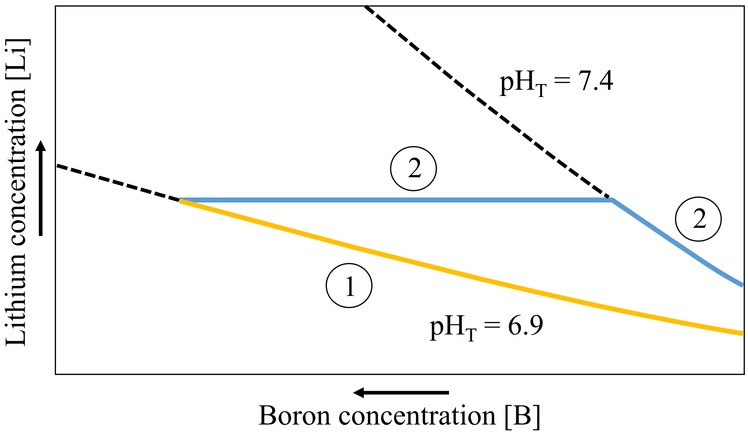


FIG. 1. Representation in principle of the 'modified chemistry' (line 2) and the 'coordinated chemistry' (line 1) – Definitions as in Ref. [12].

In the beginning of 2000s after introducing the more corrosion resistant fuel cladding materials, the fuel vendors started to allow operation at higher lithium concentrations, starting at 3.5 mg/kg up to recently 6 mg/kg in some PWRs, depending on their core duty design. This type of coolant chemistry is called 'coordinated chemistry at elevated pH_T'. A lithium concentration of 6 mg/kg at the beginning of the fuel cycle enables to operate throughout the whole fuel cycle with a constant pH_T at 7.4.

All EDF NPPs (except one) have been transitioning since 2008 to a specific 'EDF modified chemistry' that combines a B-Li coordination at lower boron concentration with a target of $pH_T = 7.2$ (with $T = 300°C$), a constant lithium concentration of 2.0 mg/kg until boron concentrations around 900 mg/kg, and then a B-Li coordination with a target pH_T of 7.0 until a lithium concentration of 3.4 mg/kg – see figure 3.2 in Ref. [8] or figure 1 in Ref. [13].

In CGN fleet in China, a first plant – Daya Bay NPP – switched from the 'EDF modified chemistry' to the 'elevated lithium chemistry' in 2023 (see definition in figure 3.2 in Ref. [8] or figure 1 in Ref. [13]). All CGN PWRs of type Chinese pressurized reactor 1000 are planned to follow this move.

2.1.1.2. Operating experience of enhanced pH control with the use of enriched boric acid

The operating experience gathered at Siemens-designed PWRs showed that, after switching to EBA at 30 at.% of ^{10}B, the target pH_T was reached earlier in the cycle and the period of constant pH_T was longer [12, 14]. For example, Fig. 2 [12] shows that, after the switch to EBA in the outage 1998, a pH_T of 7.4 was achieved 2 months earlier than in the previous fuel cycle and that the stabilization of the xenon effect was achieved at lower boron concentration (600 mg/kg vs 1,000 mg/kg) in a German plant.

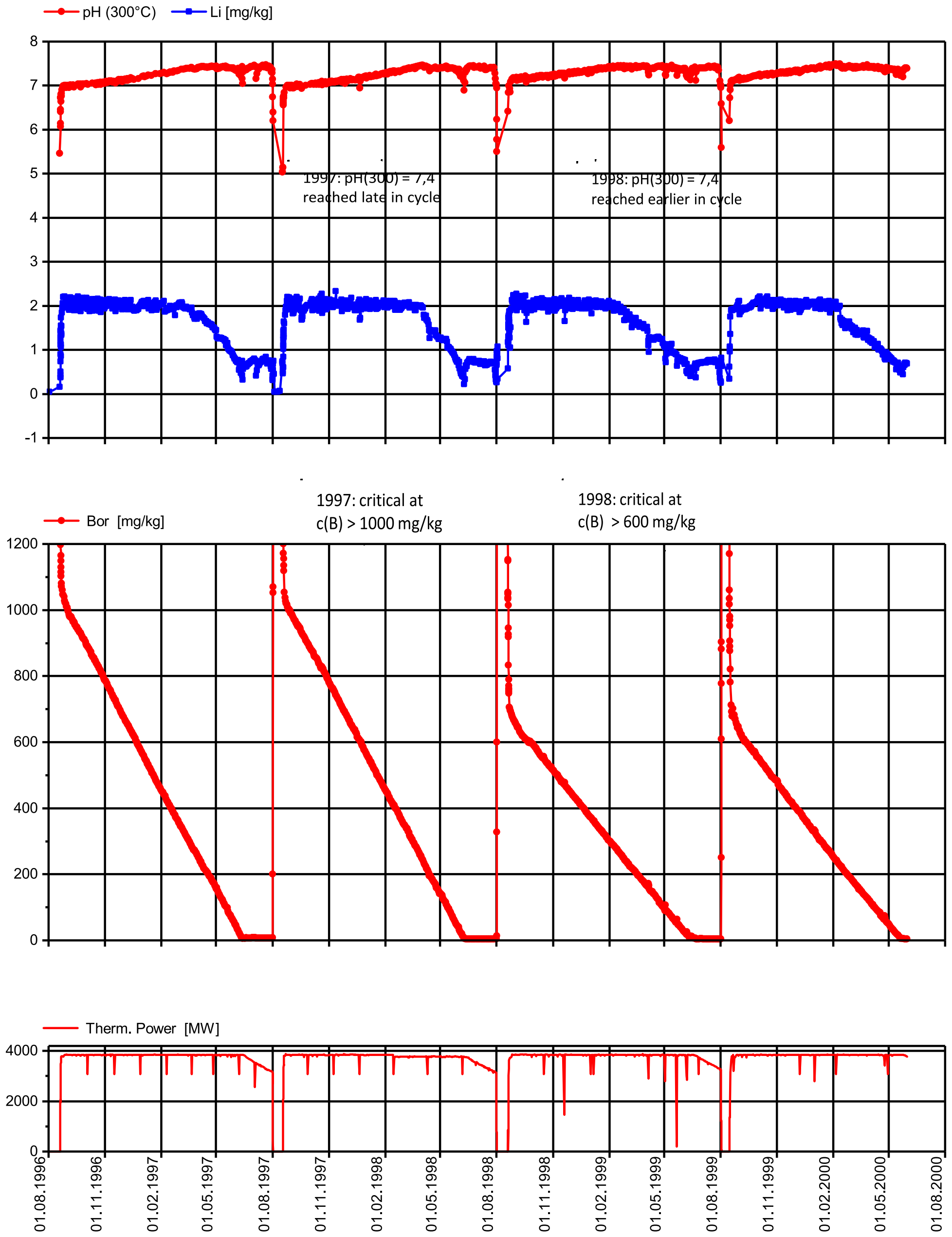


FIG. 2. pH_T, boron concentration and thermal power over 4 fuel cycles at a German plant that switched to EBA after their 1998 outage (reproduced from Ref. [12] with permission).

As the pH_T value has a significant impact on transport, deposition and activation of corrosion products and thus on the source term, operating experience at the same plant – equipped with steam generator tubes made of alloy 800 – showed a slightly positive influence on the concentration of ^{60}Co (Fig. 3) after the switch to EBA in 1998.

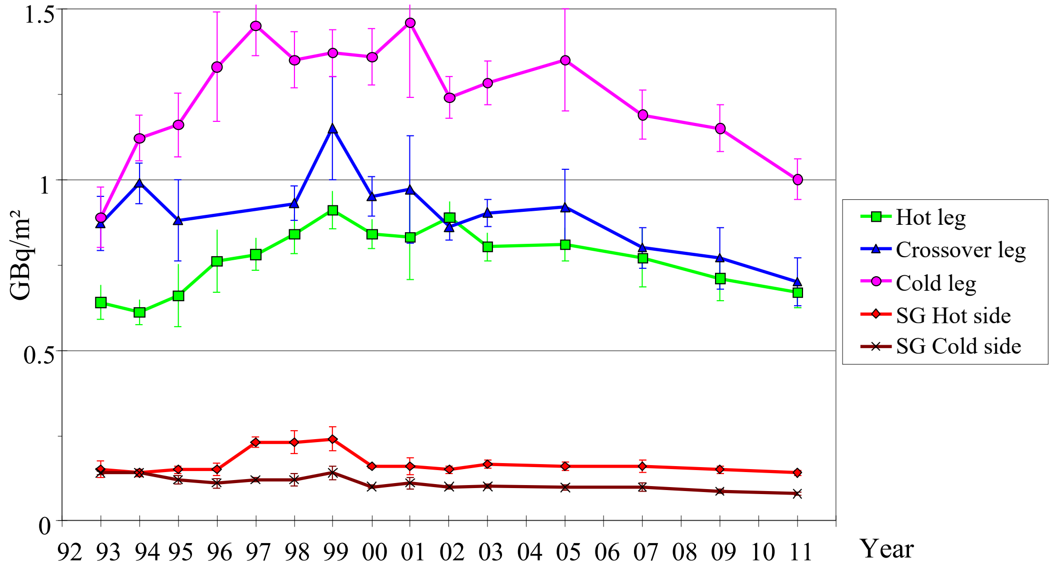


FIG. 3. ^{60}Co surface activities at different measuring points before and after a German plant switched to EBA in 1998 (reproduced from Ref. [12] with permission).

At Taishan NPP which uses EBA from the design stage, the total gamma radiation and ^{58}Co levels in the reactor coolant system (RCS) during forced oxidation in outage were significantly lower than those observed in the first 2–3 outages of Chinese pressurized reactor 1000 units. During normal operation, Ni and Cr concentrations in the RCS are below detection limit. Although the use of EBA is not the sole success factor, Taishan NPP operating organization confirmed that EBA played a pivotal role in this performance by enabling the pH to reach 7.2 at 300°C from the beginning of cycle.

2.1.2. Discussion of the other benefits of enriched boric acid in pressurized water reactors

The upper lithium concentration in PWRs was previously limited to ≈2.2 mg/kg by fuel vendors for zircaloy 4 fuel cladding alloy due to risk of concentrating lithium hydroxide on fuel cladding beneath the fuel crud deposits and thus increasing the risk of fuel cladding corrosion. This was of concern due to potential release of fission products and alpha particles. After introducing more corrosion resistant fuel cladding alloys, fuel vendors started to allow operation with increased lithium concentrations [13]. For example, PWRs in some cases have operated with lithium up to 6 mg/kg.

However, some benefits of a lower lithium concentration can be considered. Laboratory investigations conducted by EDF confirmed that a decrease of the lithium concentration from 3.5 mg/kg to 2.2 mg/kg can increase the initiation time of irradiation assisted stress corrosion cracking (IASCC) of stainless steel 304 by a factor 1000 (see [15]).

Additionally, a lower lithium concentration decreases the zirconium oxide thickness, see figure 5.6 in Ref. [8], while a higher pH_T – which necessitates a higher lithium concentration – decreases the amount of crud deposition on the fuel elements, see figure 6.15 in Ref. [8]. With EBA, beneficial effects on the zirconium oxide thickness and IASCC risk can be expected as a higher pH_T is achieved while keeping lithium concentration far below fuel vendor limitations.

Corrosion products that precipitate on the fuel elements do not only influence the source term and the integrity and heat transfer properties of the fuel but can also have a negative impact on the axial power distribution, especially when boron is accumulated in the deposits [13, 16]. There are still discussions on whether there is a linear corelation between the boron deposited on fuel, and the total boron concentration and the lithium concentration in the primary coolant, noting that the effect of less boron atoms on the fuel cladding could be counteracted by the higher enrichment of ^{10}B.

At the first fuel inspection caried out at Olkiluoto-3 NPP in 2024, an EPR commissioned in 2023 which uses EBA, there was no finding related to the effect of EBA on the fuel cladding.

2.1.3. Management and measurement of ^{10}B over the fuel cycle

The reaction ^{10}B(n,α)-^{7}Li results in a decreasing ^{10}B/^{11}B-ratio in the primary coolant over the fuel cycle and consequently in the connected systems. The decreasing ^{10}B/^{11}B-ratio necessitates the deployment of a boron management in both PWRs and WWERs – see for example experience at Koeberg NPP in Ref. [17], including when EBA and a boron recycle plant is used – see Refs [18, 19]. The key features of a boron management programme include a set of operational procedures aimed at preventing the ^{10}B concentration from dropping below the require levels, which will challenge the reactivity control, and a strategy for conducting accurate measurements of the ^{10}B concentration.

Operating experience at a 1400 MW$_e$ PWR using EBA at 30 at.% of ^{10}B at beginning of cycle, with no primary coolant leak, shows that the boron ratio decreases by less than 1 at.% over a one-year cycle. The strategy to compensate the loss is to keep the target ^{10}B/^{11}B-ratio in the boric acid storage tanks (often the tanks with the highest boron concentration) at 2–3 at.% above the requirement by adding EBA at 95 at.% of ^{10}B in the tanks. During shutdowns and load reductions, the boric acid concentration in the primary coolant is increased by injecting EBA from the boric acid storage tanks and, thereby, its isotope ratio is increased.

^{10}B concentration would be enough to be specified in the technical specifications. However, ^{10}B is always accompanied by ^{11}B and the solubility of total boron (sum of ^{10}B and ^{11}B) is limited to about 8000 mg/kg at room temperature. Therefore, some organizations specify the maximum total boron concentration and the minimum ^{10}B concentration [18], whereas other operators specify the range (upper and lower limit) of the total boron concentration and the isotope ratio in the systems. The isotope ratio as well as the total boric acid concentration may not be the same in all systems. Especially in safety systems of PWRs, which are not mixed with other systems during outages like the safety injection system, the values might differ significantly to increase safety margins.

Regarding the measurements of the ^{10}B and the total boric acid concentration, strategies are as follows:

- ^{10}B:
  - Inductively coupled plasma mass spectrometry (ICP-MS) for grab analysis;
  - On-line meter using the principle of the neutron absorption – see Section 5.1.3;
  - On-site laboratory measurement using the principle of the neutron absorption.
- Total boric acid concentration:
  - Manual titration for grab sampling;
  - On-line titration – see Section 5.1.3;
  - Calculation from ^{10}B-meter using the principle of the neutron absorption – see experience from Bohunice NPP below;

As a reminder, the isotope ratio (isotopic abundance of ^{10}B in at.%) is the ratio between ^{10}B concentration in mole/kg and the sum of ^{10}B and ^{11}B concentrations in mole/kg.

To measure the boron ratio, many plants use ICP-MS [20] for grab analysis in the plant laboratory. Due to the significant relative mass difference between ^{10}B and ^{11}B ions in the argon plasma, strong space charge effects lead to a non-linear response of the calibration curve, necessitating a thorough calibration strategy. An effective strategy includes bracketing the expected sample ratio with two ‘standards’ (reference solutions for calibration) that have higher and lower boron isotope ratio. Independent control standards, with their isotope ratios close to the sample isotope ratio, ought to be measured regularly to detect disturbances such as drift or instrument contamination. Contamination can lead to high blank values (count rates), ought to be eliminated or at least mitigated by thoroughly rinsing the instrument. Some plants have defined upper tolerable blank count rates. When done properly the uncertainty of such analysis is less than 0.1 at.%. It is recommended that laboratories participate in round robin tests.

Grab analyses are necessary whenever new boric acid is prepared, typically from natural boric acid and highly enriched boric acid (e.g. 95 at.% of ^{10}B). This also applies when borated water from different systems is mixed, e.g. during outages and before start-up. Since the isotope ratio slowly changes in the RCS during power operation, many plants perform the analysis in the RCS approximately once a month, and even less frequently in the other systems, such as the spent fuel pool (SFP).

When determined by titration (in mole/kg as boric acid), the total boric acid concentration is adjusted to mg/kg (as boron) using the molecular weight corresponding to either the target ^{10}B isotopic abundance (per definition, however, in this case the isotope ratio has to be measured at least once), or the last measured value (recognizing the isotope ratio only changes slowly). Quality control measurements are typically carried out with natural boric acid. Differences in the stoichiometric factor (molecular weight of EBA and natural boric acid) can be considerable and could result in safety issues, when mixed. Laboratories are advised to take adequate mitigating measures, such as clear labelling of standards and clear indication, printout and documentation of the stoichiometric factor used in the instrumental analytical device (electronical titration unit).

As an alternative to titration, Bohunice NPP (a WWER using natural boric acid) installed a laboratory ^{10}B-meter for additional comparative measurement of boric acid concentration in the RCS and other systems such as safety systems, boric acid tanks, liquid radioactive waste and liquid samples (for identification of boric acid presence). The measurement is based on neutron absorption. The high activity source ^{241}Am/Be is used as a neutron source. The instrument consists of a measurement unit with neutron source (Fig. 4), a semi-automatic sample filling station and a control unit. Same technology had already been used in 9 European WWERs and in Ringhals NPP, see details in Ref. [21].

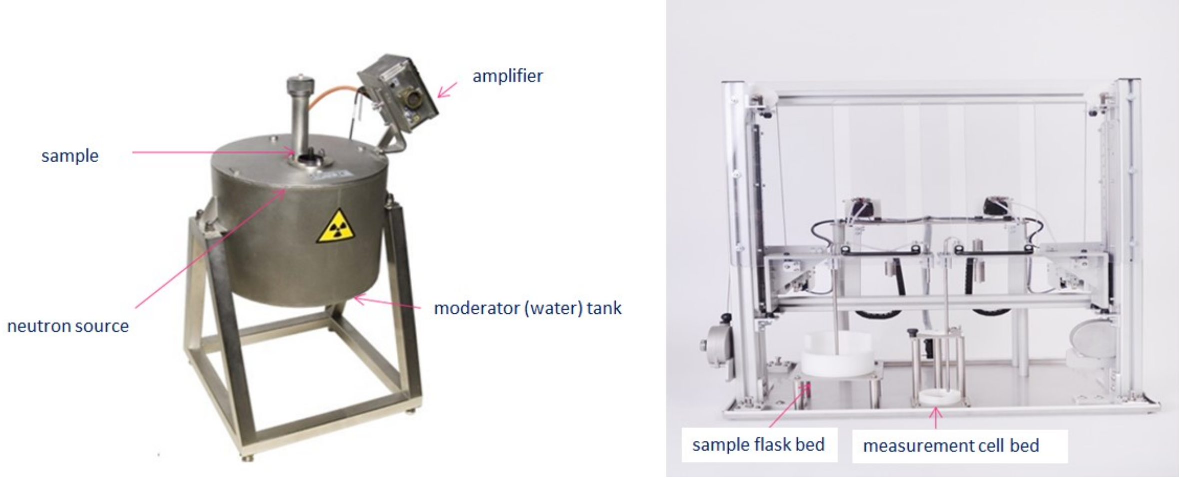


FIG. 4. Laboratory neutron ^{10}B-meter (measurement unit, left) and semiautomatic filling station (right) (courtesy of Slovenské elektrárne, a.s.)

As a result of the measurement, the content of ^{10}B (in mg/kg) is determined and recalculated to gain the total boric acid concentration. The calculation of boric acid concentration is based on the calibration curve from certified standards measured in special calibration cells. The concentration range of calibration curve is 0–50 000 mg/kg (boric acid). The measurement uncertainty is ±60 mg/kg for the concentration range of 0–10 000 mg/kg. In the range 10 000–50 000 mg/kg, the uncertainty is 1.7% (k=2). To assure consistent statistical accuracy of the results across the entire concentration range, the complete measurement consists of 53 single measurements. The duration of a complete measurement sequence is 15–45 minutes, depending on the boric acid concentration in the sample.

2.2. INNOVATION AND ADVANCES IN HYDROGEN MANAGEMENT FOR CONTROLLING REACTOR COOLANT CHEMISTRY

Dissolved oxygen in the RCS during power operation has a significant effect on the degradation mechanisms of structural materials. To suppress oxygen, hydrogen is added to the primary system as a scavenger. PWRs and WWERs have adopted strategies to control dissolved hydrogen concentration in the reactor coolant. The strategies include setting the target hydrogen concentration, dosing of hydrogen and sampling for analysis. WWERs utilize radiolysis of injected ammonia instead of dosing hydrogen in PWRs, which adds another degree of complexity to the controls.

This section presents:

- Advances in defining the target hydrogen concentrations in the primary coolant (Section 2.2.1), whereas further research is still needed to fully understand the effects of low and elevated hydrogen strategies (for example, the effects of elevated hydrogen concentration on critical welding materials);
- Innovation in injecting hydrogen into the RCS using high-pressure cylinders (Section 2.2.2);
- Advances in ammonia dosing for controlling hydrogen concentration in the RCS of WWERs (Section 2.2.3).

2.2.1. Advances in defining target hydrogen concentrations in the primary coolant

The main factors that ought to be considered when “determining the optimal dissolved hydrogen (DH) concentration are as follows: (i) the effect of dissolved hydrogen on primary water stress corrosion cracking (PWSCC) initiation and growth, (ii) general corrosion, and (iii) fuel crud deposition”, Ref. [22]. EPRI guidelines for PWR recommend a concentration 25–50 ml/kg in the RCS, where some authors advocate the advantages of a reduced concentration down to 5 ml/kg, Ref. [23]. Ammonia and hydrazine are used in WWERs as an alternative for generating hydrogen, at concentrations usually of 30–60 ml/kg. Hydrazine decomposes thermally to ammonia and nitrogen. Then ammonia is radiolyzed to produce hydrogen and nitrogen [24].

Higher DH concentrations (more reducing environment) enhance the stability of metallic Ni on behalf of NiO and other nickel-containing oxides, mitigating general corrosion, figure 4 of Ref. [25]. A lower stability of oxides of nickel may lead to increased corrosion rate of nickel-based alloy of steam generator tubing. Hydrogen is also believed to be one of key factor to influence PWSCC. It is also a fact that the phenomena of PWSCC itself is not yet completely clear [25].

Based on the crack propagation studies, there are suggestions to increase DH concentration in some PWRs. Crack growth curves, showed in figure 14 of Ref. [26] and also reproduced in figure 6.22 of Ref. [27], summarizes the benefits with respect to crack growth of an increase of the hydrogen content at 325°C for both alloy 600 and alloy 182. The maximum crack growth rate obtained at corrosion potentials equivalent to the Ni/NiO stability line shifts to lower hydrogen concentrations when the temperature decreases. Many utilities are already operating closer to the higher specification limit than before, Ref. [27].

As per Ref. [28], research suggests that peak PWSCC crack growth rates of Ni-based alloys occur at a reactor coolant hydrogen concentration of about 20 ml/kg H_2O. A decrease of DH concentration should be accompanied by a decrease of PWSCC rate, but also with a risk of insufficient suppression of radiolysis and increased corrosion of structural materials. Therefore, EPRI research has focused on quantifying the benefit of operating at elevated hydrogen as high as 80 ml/kg on SCC mitigation. The average concentration in the plants monitored through the EPRI database between 2000 and 2006 was about 35 ml/kg and increased by 11% through 2021 [29]. Recently EDF in France moved its target to 35–45 ml/kg to limit the crack growth rate. In Japan, the range is typically 25–35 ml/kg. There have been only a couple plants world-wide that have operated DH concentrations above 50 ml/kg. EPRI suggest a structured approach for the case of introducing of increased DH concentration, i.e. in conservative steps of 10 ml/kg. In parallel with the start of plant implementation, laboratory and in-reactor loop tests at the extremes of elevated hydrogen are also recommended to acquire more data and screen for unexpected results.

Beside the expected positive effect of elevated hydrogen concentration on PWSCC, it will likely change the solubility of iron and nickel in the RCS which could lead to increased crud deposition in the core. This in turn could enhance the cladding corrosion rate under the deposit. Also, during cycle startup, elevated hydrogen may increase the peak coolant nickel concentration, which will lead to accelerated deposition of metallic nickel on cladding surfaces. Metallic nickel can act as a ‘window’ for hydrogen, especially on fresh fuel with only a thin protective oxide layer. Therefore, a detailed analysis of the potential changes of coolant chemistry, such as solubility effects and crud deposition, ought to be performed by water chemistry experts, and laboratory tests are recommended for assessing the effects due to elevated hydrogen [28].

While investigating DH concentration optimization strategies, some authors advocate the advantages of a reduced DH concentration during operation down to 5 ml/kg, Ref. [23]. To assess the threshold value of DH for achieving effective reducing condition, experiments and radiolysis model calculations were performed. According to these, this threshold value is significantly lower than the current control level in PWRs. This provides a margin for some decrease in hydrogen concentration to suppress PWSCC rate. A follow-up research including a measurement of electrochemical corrosion potential of structural material, while varying dissolved hydrogen levels, is desirable in the future to compensate for the uncertainty of the model calculation [23] [25].

2.2.2. Innovation in injecting hydrogen in pressurized water reactors

Hydrogen in the RCS of PWRs is typically dosed in the volume control tank of the chemical and volume control system (CVCS). In some PWRs, such as the German Konvoi, the injection point was a pipe directly connected to the RCS. Sanmen NPP adopted a different approach while injecting hydrogen using hydrogen cylinders at 44 MPa (see Fig. 5).

The advantage of the direct hydrogen dosing is a decrease of time needed to reach the target hydrogen concentration. The calculation formula of adding hydrogen volume and dissolve hydrogen concentration is as follows, Eq. (1):

$$C_{H2} = \frac{F_{H2}}{F_S+F_B}\left(1 - \mathrm{e}^{-\frac{F_S+F_B}{M}t}\right) \tag{1}$$

Where F_{H2} is the flow rate of added hydrogen, F_S the flow rate of pressurizer spray, F_B the flow rate of CVCS outlet, M the RCS volume, C_{H2} the increase in hydrogen concentration and t the injection time.

A similar approach was also considered for some WWERs in the past but no plant implemented the change, see chapter 2.2.2 of Ref. [24].

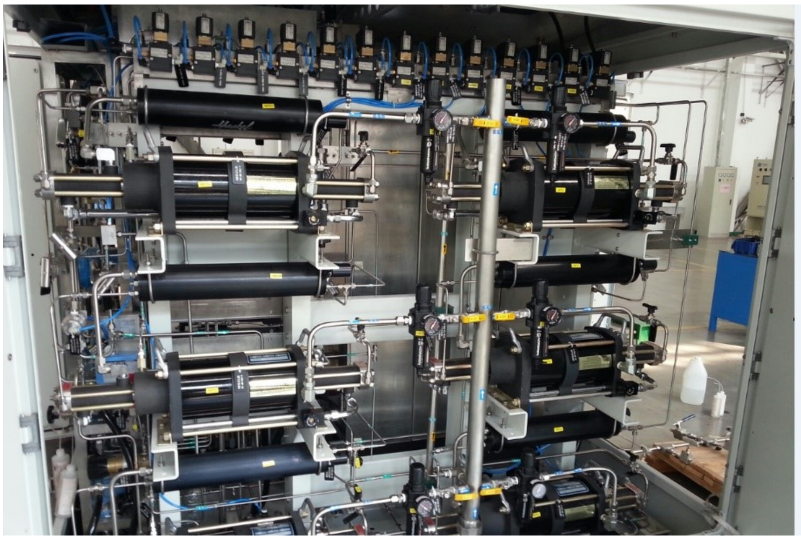


FIG. 5. Hydrogen cylinders used at Sanmen NPP to inject into the RCS (courtesy of CNNP).

2.2.3. Advances in ammonia dosing for hydrogen control in water-water energetic reactors

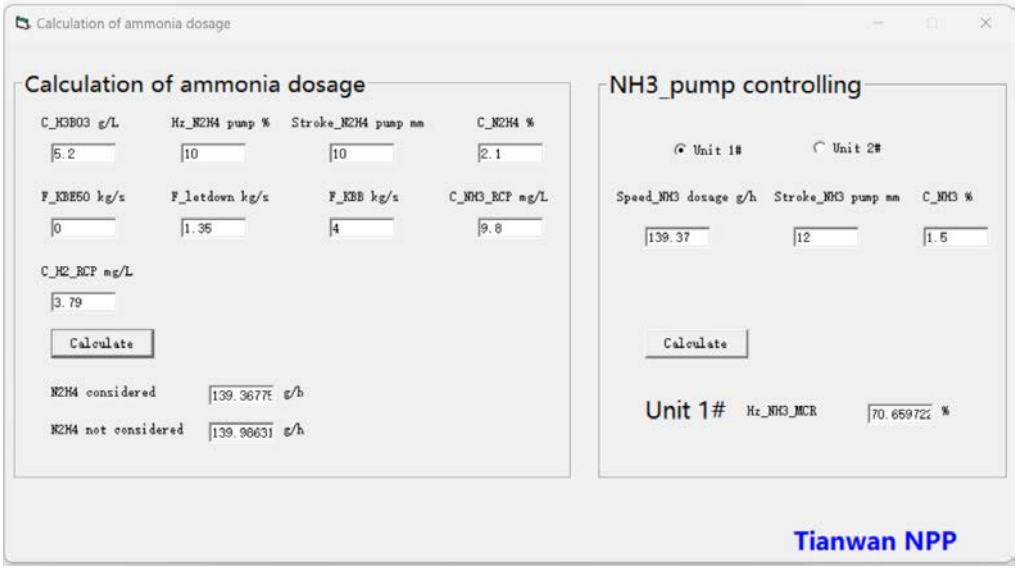
Ammonia dosing control in WWERs involves periodically injecting a quantity of ammonia calculated based on the actual ammonia concentration and the target concentration. Operating experience at Tianwan NPP showed that such intermittent dosing resulted in some fluctuations in concentration of RCS species. The resin-based primary coolant purification system operates continuously at saturation of ammonia and potassium. Since the adsorption capacities of ammonia and potassium are similar, intermittent injection resulted in fluctuations of ammonia concentrations which could consequently lead to the partial elution of potassium ions from the purification bed into the primary coolant. These fluctuations in RCS chemistry parameters are more frequent when demineralizers are in operation. Any inaccurately calculated or non-untimely adjusted ammonia dosing can cause significant fluctuation, especially at the end of the fuel cycle.

To improve the dosing pattern, Tianwan NPP explored the quantitative relation between a dosed amount of ammonia and concentration of ammonia and hydrogen. By using both materials' balance theory and operational experience, they developed a software to support optimized ammonia dosing (Fig. 6).

Considering the concentration of ammonia, alkali metal ions (potassium, sodium, lithium) and hydrogen, the amount of ammonia to be injected (in g/h) is described by an equation specific to 1000 MW$_e$ WWERs, Eq. (2):

$$M_{NH_3} = \left[\left(C_{NH_3} + C_{Alk} \times 17\right)\left(z + \frac{0.8 + x \times \frac{8.3-z}{8.3}}{0.8+x} \times \frac{y}{0.8+x+y}\right) + C_{H_2} \times \frac{17}{3} \times (0.8+x)\right] \times 3.6 \qquad (2)$$

Where C_{H2} is the actual hydrogen concentration (mg/L) in the system, C_{NH3} is the actual ammonia concentration, C_{Alk} is the total alkali metal ion concentration (mmol/L), 0.8 is the primary pump seal water flowrate (kg/s), x is the let-down flowrate (kg/s), y is the alkali metal ion removal system flowrate (kg/s), and z is the primary coolant purification system flowrate (kg/s).



C_H3BO3 g/L: 5.2
Hz_N2H4 pump %: 10
Stroke_N2H4 pump mm: 10
C_N2H4 %: 2.1
F_KBE50 kg/s: 0
F_letdown kg/s: 1.35
F_KBB kg/s: 4
C_NH3_RCP mg/L: 9.8
C_H2_RCP mg/L: 3.79
N2H4 considered: 139.3677 g/h
N2H4 not considered: 139.98631 g/h

● Unit 1# ○ Unit 2#
Speed_NH3 dosage g/h: 139.37
Stroke_NH3 pump mm: 12
C_NH3 %: 1.5
Unit 1# Hz_NH3_MCR: 70.659722 %

FIG. 6. Software interface for defining ammonia mass flowrate at injection point at Tianwan NPP (courtesy of CNNP).

After implementation of the software at Tianwan-1 NPP in 2013 (in the 6th fuel cycle), the total alkali metal ion concentration throughout the ammonia dosing sequences became more stable and remained within the control band, see Fig. 7.

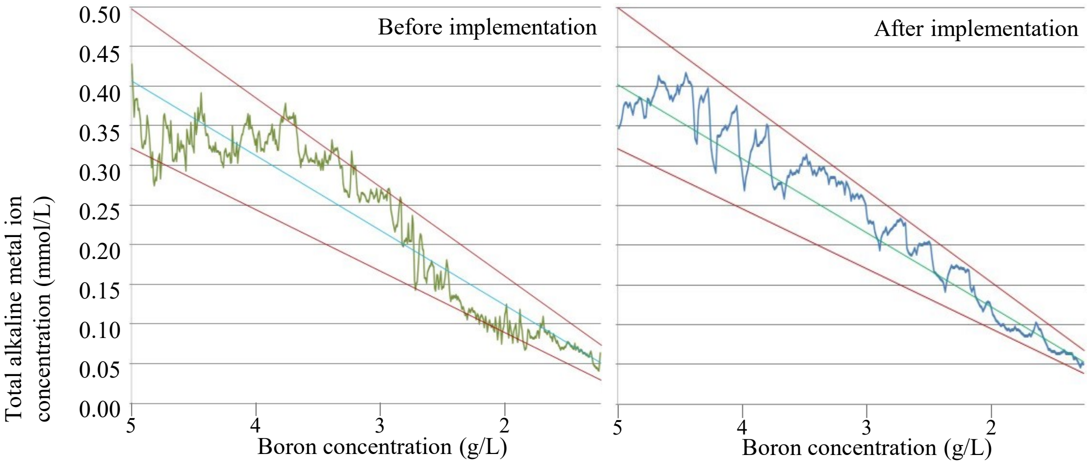


FIG. 7. Total alkali metal ion concentration vs boric acid concentration throughout a typical ammonia dosing sequence, before (3rd fuel cycle, left) and after implementation (6th fuel cycle, right) of a software for defining NH_3 mass flowrate to be injected at Tianwan NPP (courtesy of CNNP).

2.3. DEVELOPMENTS IN SILICA REMOVAL AND CONTROL FOR PROTECTING NUCLEAR FUEL

Silica is considered an impurity of concern in the RCS and auxiliary systems of NPPs. In combination with other impurities like calcium, magnesium, aluminium and zinc (all zeolite-forming ions) and/or conditioning agents, elevated silica concentrations might lead to deposits on the fuel cladding. Chemically, silica concentrates similarly to boric acid. Unlike usual impurities, silica is not removed by the most common water treatment plant resins nor by CVCS resin. This is why silica may continuously accumulate over the years and can become a major concern in systems with higher boric acid concentration such as the SFP (especially when feed and bleed are not practical because of limitations on boron discharges) and, when boron is recycled, in the boron recycling tank. Reference [30] discusses the effects of high silica concentration on corrosion product deposition on fuel and on zinc silicate precipitation when associated with zinc injection (see description of practices in Section 2.4.2), and presents a model of zinc transport in the RCS. Some operating organizations stop zinc injection in case of elevated silica concentration – see examples of applicable requirements in Table 1 of Section 2.3.1.

Typical sources of silica reported by NPPs include:

- Glass fibre filters in RCS purification systems – EDF considers that 90% of the silica in its NPPs originates from filters;
- Conditioning products, especially boric acid;
- Boric acid recovery plant;
- Degradation of the neutron-absorbing materials used in the racks of the SFP;
- Make-up water of the water treatment plant, to a lesser extent.

Additionally, operating experience from Czech WWERs indicates that dust ingress during refuelling outages is a measurable source of silica.

Strategies to control silica concentrations include:

- Reduction of source terms, such as:
  - Use of filters free of glass fibres and implementation of procedures for rinsing filters before connecting them to the main systems;
  - Replacement of racks in the SFP with neutron-absorbing materials containing less silica;
- Removal of silica:
  - Replenish of systems with low-silica water (‘feed and bleed’). However, this leads to discharging boron into the environment (see discussion in Section 2.1);
  - Installation of fixed or mobile silica removal systems connected to the SFP or the boric acid storage tanks, using technologies such as reverse osmosis and nanofiltration – see developments in Section 2.3.2;
  - Use of hybrid ion exchangers – see an example of innovative use in Section 2.3.3.

Recent operating experience from China has showed that silica removal systems effectively remove silica from RCS and its connected systems. Further examples of silica removal experience are provided in Refs [31–33]. A specific strategy for plants recycling boron, such as EPR, is presented in Ref. [19].

2.3.1. Advances in expected silica concentration in the primary coolant

Silica concentration is seldom a parameter that, when exceeded, leads to raising limiting conditions of operation (LCO) against the technical specifications for operation. An expected value[3] of 0.6 mg/kg and a limit value[4] of 1.0 mg/kg in PWR primary systems were considered good practice from 2000 to 2010 – see table 3.3 in chapter 3.1 of Ref. [8]. Examples of typical expected silica concentrations and limit values applied recently in NPPs are provided in Table 1.

Some operating organizations, such as at Temelín and Dukovany NPPs, have recently (2023) increased the action level related to silica concentration to 2.0 mg/kg at Temelín and 1.5 mg/kg at Dukovany, considering EPRI work – Refs [30] and [34] – and laboratory tests on the formation of zeolites and other substances containing aluminium silicate.

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[3] The target value below which the plants are ideally operated, as far as achievable.

[4] Action level or threshold that requires responses as per the technical specifications for operation.

TABLE 1. EXPECTED AND LIMIT VALUES FOR SILICA CONCENTRATION AT A SELECTION OF NUCLEAR POWER PLANTS

NPP	Typical and expected silica concentration (target) (mg/kg)	Limit value (mg/kg)
Armenian-2	(actual) 0.5 in RCS	0.015 in the make-up water system
Ascó-1 and 2	(actual) < 0.2 in the RCS (actual) 0.4 in the SFP	1.0 – if exceeded, zinc injection is stopped
DayaBay-1 and 2	0.6 in the RCS 1.0 in the SFP 0.05 in the make-up water	1.0, each Al, Mg, Ca < 0.05 3.0, each Al, Mg, Ca < 0.10 0.1, each Al, Mg, Ca < 0.05
EDF plants	0.6 in the RCS	1.5 and 1.0 in case of zinc injection and high duty core
	1.0 in the SFP	3.0
	0.1 in the make-up water	0.2
Koeberg-1 and 2	(target) < 1.0 in the RCS	1.5 –zinc injection is stopped when the concentration > 1.0
Krško	(actual) < 0.4 in the RCS (actual) < 0.5 in the SFP	< 1.0 (expected value)
Loviisa-1 and 2	(actual) 0.2 in primary system at mid-cycle, 2.0 at startup, 6.0 when boric acid is injected before shutdown.	
Olkiluoto-3	(actual) 0.5 in the RCS	1.0 – if exceeded, Al, Mg, Ca, and Zn are monitored
Ringhals-3 and 4	(target) 0.2 in the RCS	1.0
	(target) 0.5 in the SFP	-
	(target) 0.010 in the make-up water	0.050
	(target) 2.0 in boric acid tanks	5.0

2.3.2. Development of silica removal systems at Chinese nuclear power plants

A silica removal system using nanofiltration technology was installed in 2017 at Tianwan-1 (Figs 8 and 9). A suitable nanofiltration membrane (main material: polysulfone) was selected to separate boron from silica based on the differences in molecular weight and charge between the boric acid and the silicon dioxide in the solution. This allows for the recovery of boric acid while removing silica. The system is composed of two stages (stage #1 and stage #2). The process steps are as follows:

1) Boric water from the systems to be treated enters receiving tank #1 and is treated by membranes, batch by batch
2) The solutions from stage #1 enters tank #2 and either returns to the systems or are treated by stage #2 as needed.
3) The concentrated liquid with high boron and silica concentration can also be treated by stage #2 or discharged as wastewater.

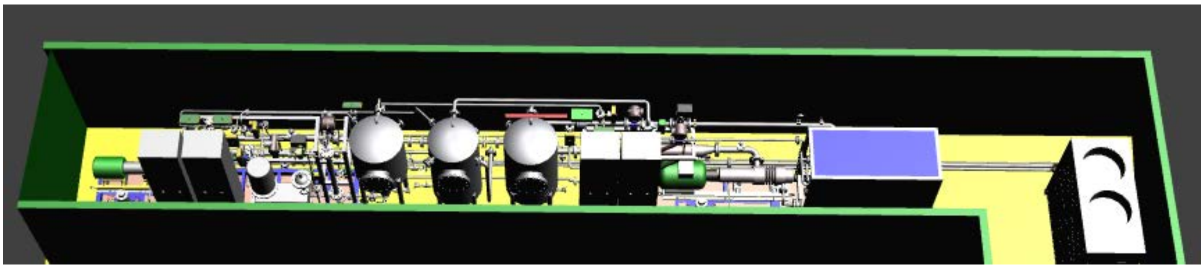

FIG. 8. 3D-model of the silica removal system at Tianwan NPP (courtesy of CNNP).

FIG. 9. Picture of the silica removal system installed at Tianwan-1 (courtesy of CNNP).

The technology achieves boric acid recovery above 99.8%, without introducing any impurities. The equipment features one-click-start, automatic operation and fault diagnosis functions. The technology did not alter important system functions and did not require a nuclear safety assessment. The silica concentration in the SFP decreased from 2.0 mg/kg to less than 0.4 mg/kg in one year (Fig. 10).

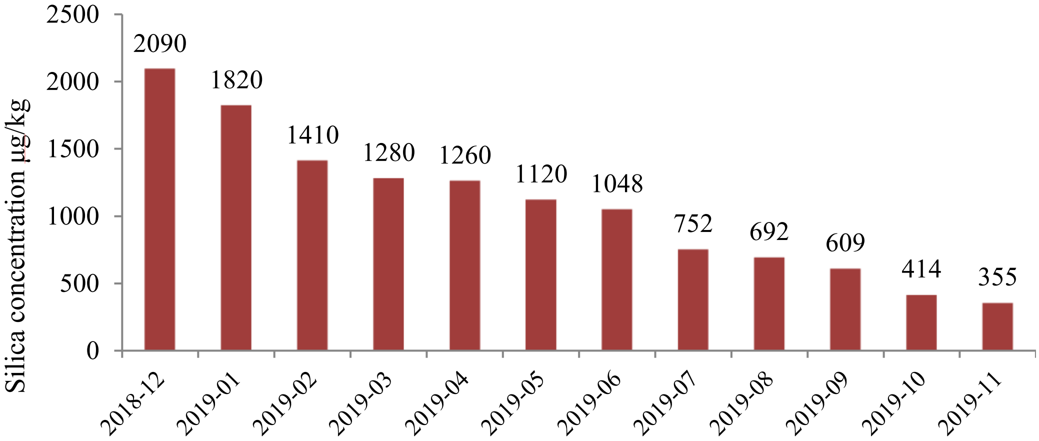

FIG. 10. Decrease of silica concentration in the SFP system at Tianwan-1 (courtesy of CNNP).

A silica removal system using the same technology was also installed in 2022 at Qinshan-I (Fig. 11) where the silica concentration was 2.0 mg/kg. After several months of operation, the concentration decreased to 0.4 mg/kg. The performance of the membrane was as follows:

- Silica removal rate: 97%;
- Boron recovery: 98%.

The membranes are thought to be capable of treating 10 000 m^3. The criterion for replacement is the silica removal efficiency. The membranes can then be replaced and compacted. It is assumed the old membranes will be low activity waste as they will not retain radioactive isotopes. The membranes can be cleaned by backflushed with demineralized water or water from the pool. A typical treatment batch is 30 m^3. When not in use, the membranes are soaked with demineralized water or water from the pool.

Less than 0.15 m^3 of silica concentrated solution are generated as waste after each batch. As the dose rate at equipment surface is low, specific shielding or zoning is not required.

FIG. 11. Qinshan-I filtration system to remove silica in borated water. (courtesy of CNNP).

The silica removal system was further promoted and implemented at the commissioning of Fangchenggang-3 to remove silica from the in-containment refuelling water storage tank, containing 1,900 m^3 of borated water at 1.3–1.4 mg/kg. The silica concentration was decreased from 1.1 mg/kg to less than 0.6 mg/kg in about 2 months.

Nanofiltration technology is further discussed in Section 4.3.3.

2.3.3. Use of innovative hybrid ion exchange resins for removing silica

During the hot functional test (HFT) of Olkiluoto-3 NPP, silica concentration in the RCS occasionally increased up to 1.5 mg/kg. While silica concentration is limited to 1.0 mg/kg to allow zinc injection, the operating organization together with the NPP vendor investigated options to overcome the issue. One option was to introduce silica-sensitive strong basic ion exchange resins (IXR) and use hybrid ion exchangers. Hybrid ion exchangers contain, in addition to the strong basic anion exchange resin, an embedded adsorbent (in this case, iron oxide-hydroxide) to support the removal of silica in all its aggregate forms (ionic, colloidal, particulate). The qualification of these hybrid ion exchangers showed a removal efficiency up to 80%. During the qualification tests, it was determined that an ion exchanger of 300 litres was sufficient to reduce the peak concentration in the whole primary system from 1.5 mg/kg down to 0.5 mg/kg. The actual layout allows for such an ion exchanger to be installed as a temporary mobile solution, which could be operated in bypass to the RCS purification system.

2.4. CONTROL OF SOURCE TERMS FOR REDUCING WORKERS' EXPOSURE

A significant part of the occupational dose in NPPs comes from the dose rate caused by activated corrosion products (ACP) on the inner surfaces of the primary circuit (and some auxiliary systems). By establishing an optimized water chemistry, the amount of these can be reduced and thus the worker exposure. Section 2.4.1 provides background information and an overview of developments that support a reduction in occupational exposure. Section 2.4.2 addresses the advances and developments in the injection of zinc (using the corrosion inhibition properties of zinc), highlighting the subsequent decrease of ^{58}Co after steam generator replacement and the good performance expected at NPPs that inject zinc since commissioning. Section 2.4.3 presents examples of RCS surface contamination measurements, that form a solid technical basis to understand the effectiveness of improvements in the water chemistry. Specific steps taken at startups and shutdowns are presented in Section 2.7.

2.4.1. Background and overview of developments

Useful background information for PWRs and WWERs is provided in chapter 3 of Ref. [35] and chapter 5 of Ref. [36], both publicly available.

ACP of particular concern are:

- ^{58}Co activated from ^{58}Ni, mainly originating from the steam generator (SG) tube material;
- ^{60}Co activated from ^{59}Co contained in structural materials and equipment;
- ^{51}Cr activated from ^{50}Cr and ^{59}Fe activated from ^{58}Fe making the stainless steel and nickel-based alloys used in all components and equipment.

^{58}Co and ^{60}Co typically contribute to more than 80 % of the radiation fields in most of PWRs, see chapter 2.4 of [37]. Similar experiences are reported by WWERs, whereas ^{54}Mn is also a significant contributor.

Strategies and improvements that support reduction of ACP are as follows:

- Enhanced pH_T control in the RCS. For WWERs, enhanced control strategies include applying enhanced potassium-ammonia coordination to achieve a typical pH_T of 7.15–7.35 and shortening transitions from normal operation to shutdown and vice-versa. For PWRs, enhanced control strategies include (see also Section 2.1.1 and Ref. [38]):
  - Increasing lithium concentration;
  - Improving lithium hydroxide management (e.g. flexible addition via chemical sampling return lines, gradual reduction at each operating shifts rather than daily schedules);
  - Using EBA when achievable.
- Zinc injection for PWRs – see Section 2.4.2;
- Enhancement of corrosion resistance of materials in valves, piping, steam generators, reactor pressure vessel internals and fuel cladding, and replacement of cobalt-base alloys (see for example chapter 3 in Ref. [36]);
- Removal of ACP by ultrasonic cleaning of fuel assemblies, chemical cleaning of auxiliary system piping or heat exchangers, and targeted decontamination of hot spots during reactor outages;
- Use of highly effective filtration and purification systems so that corrosion products are removed before being activated (e.g. use of ultra-small mesh filters of 0.1 µm) – see examples of advances and developments in chapter 13.4 of [39] and, for reactor status other than power, Section 2.7;
- Improvement of procedures in the frame of comprehensive source term optimization strategies and management programme (see an example in Ref. [40]), covering in situ measurements, assessment, training, research, stringent application of a tight limit on the cleanliness of any components in contact with the RCS.

2.4.2. Advances and developments in zinc injection in pressurized water reactors

Zinc is injected into the RCS of PWRs with the primary aims of reducing out-of-core dose rates, in-core deposit thickness and/or mitigating PWSCC, Refs [41, 42][5]. Since the early 1990s, the effect of zinc under PWR conditions has been extensively studied. Test loop experiments generally show a reduction in ^{60}Co incorporation and a decrease in corrosion [45]. Typically, zinc acetate solutions and in some cases zinc oxide solutions are injected to reach the target zinc concentrations, which are determined in

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[5] Slide 13 of Ref. [42] shows the schematic of how zinc migrates into the corrosion film as a function of exposure to zinc. Other publicly available recent publications of interest are e.g. Refs [43, 44].

consultation with the fuel vendors. It has been found preferable to use a compound depleted in ^{64}Zn to prevent the increase in ^{65}Zn due to the ^{64}Zn(n,γ)-^{65}Zn reaction, where ^{65}Zn is a gamma emitter (at 1.1 MeV) with a 243.8-day half-life. Reference [30] discusses the effects of high silica concentration on zinc silicate precipitation on fuel cladding surfaces when associated with zinc injection.

However, operating experience at NPPs indicates that the expected effects may not be significant, and could even be negative for surface contamination by ^{60}Co – see Refs [46, 47] and chapter 3.1 of Ref. [39] – and for crud on fuel rods, e.g. see Ref. [48], at least over the first cycles after zinc injection. These adverse effects are attributed to the higher release of nickel from the SGs during the first zinc injection cycle (as the oxide layer gets thinner) and to the antagonistic effect induced by zinc, which reduces ^{60}Co contamination of the inner oxide layer (chrome-rich) while increasing contamination of the outer oxide layer (nickel and iron-rich) where this contamination may eventually decrease as the oxides in the outer layer are dissolved or eroded. This antagonistic effect is supported by calculations using the OSCAR code, see Refs [49, 50] and Section 2.9 for presentation of the code.

These adverse effects are likely to diminish with the corrosion-reducing effect of zinc, especially if the surfaces exposed to zinc are new. Indeed, zinc has a clear effect on reducing the corrosion of replacement SG tubes made from alloy 690TT.

Compared to SG replacements (SGR) without zinc injection, injecting zinc leads to a greater release of nickel during the first cycle after a SGR, resulting in a higher peak of ^{58}Co at shutdown (more crud on fuel rods); subsequently, it leads to a rapid decrease in the ^{58}Co peak in the cycles following SGR due to the acceleration of the formation of a very protective passive layer (very low corrosion rate), see chapter 3.1 of Ref. [39].

Thus, zinc injection is beneficial for ^{58}Co surface contamination when the exposed surfaces had not been already oxidized to the primary coolant conditions, which is the case for reactors that have undergone SGR [47] (see Fig. 12 for experience from EDF fleet) and for reactors being commissioned. This is why zinc was injected during the hot functional tests (HFT) of Flamanville-3 [51, 52] and Sanmen-2 NPPs (see Section 2.8). Operating experience from SGRs with zinc injection shows that it is advisable to monitor ^{60}Co surface contamination over the first cycles after SGR.

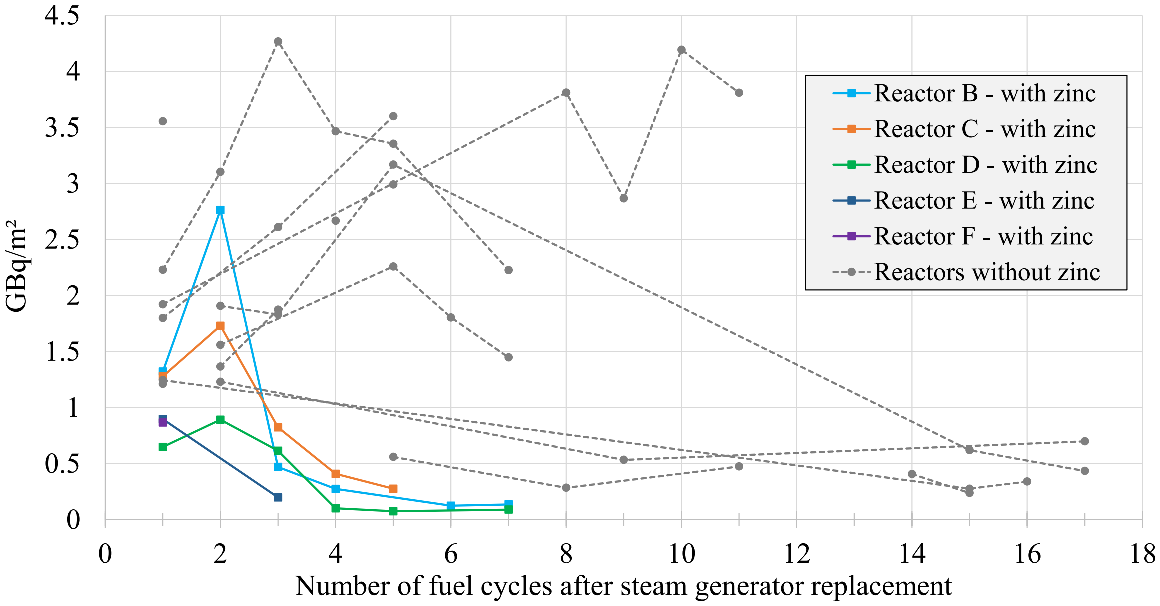

FIG. 12. Evolution of ^{58}Co surface activities (average values) in the steam generators of EDF fleet after their replacement, with and without zinc injection (courtesy of EDF).

The operating experience gained at Koeberg NPP is presented hereafter, as an example. Since 2014–15 (21st fuel cycle for both units), depleted zinc acetate has been added to the RCS at Koeberg NPP. The specification, developed for Koeberg NPP in consultation with the site reactor fuel specialists, is 5 µg Zn/kg in the RCS. Zinc was first detected in unit 1 RCS 42 days after commencement of injection of zinc acetate and 35 days after injection in unit 2. Zinc injection corresponded to an increase in ^{58}Co in the RCS and an increase in dose rates on the CVCS filters on both units, see for example Fig. 13 for unit 2. This demonstrated the effectivity of the zinc atoms preferentially taking-up the lattice positions thereby releasing the cobalt into the coolant water and preventing its incorporation. As a result, the radionuclide ^{58}Co is removed by filtration and IXR and therefore not accumulating on plant surfaces as source term.

During the time of commencement of zinc injection, both units were experiencing measurable steam generator leak rates (SGLRs)[6], well below the technical specification limit settings on the plant ^{16}N detectors. The observation was made in the immediate cycles after adding zinc that SGLRs progressively increased in the following cycles, being more pronounced at the start of each cycle. During cycles that followed, the baseline SGLRs deteriorated progressively, Fig. 14. The yellow dashed line in Fig. 14 shows when zinc injection was initiated. The peak SGLR values observed during start-up showed a similar increase cycle on cycle. This is better illustrated on unit 2 than on unit 1, as attempts to reduce/minimize the start-up SGLR peak were made on unit 1, but not on unit 2.

On unit 1, where the effect challenged the technical specifications, zinc injection was temporally suspended and the SGLRs were controlled by maintaining pH$_T$ at 6.9 after start-up. This allows corrosion products to deposit in crack crevices decreasing leak rates. Once leak rates stabilized, lithium was allowed to grow in 'naturally' until the target pH$_T$ was achieved, taking several days. This practice of controlling the pH$_T$ relatively low was successful in controlling the SGLRs with sufficient margin against exceeding the limits. Once this practice was mastered, zinc injection was resumed in the cycle before SGR. Another practice was to carefully control start-up reactor power ramp rates which included plateaus (power hold points) at specific power/temperature points. Investigations so far concluded that zinc injection did not increase crack growth nor initiated indications on SG tube surfaces.

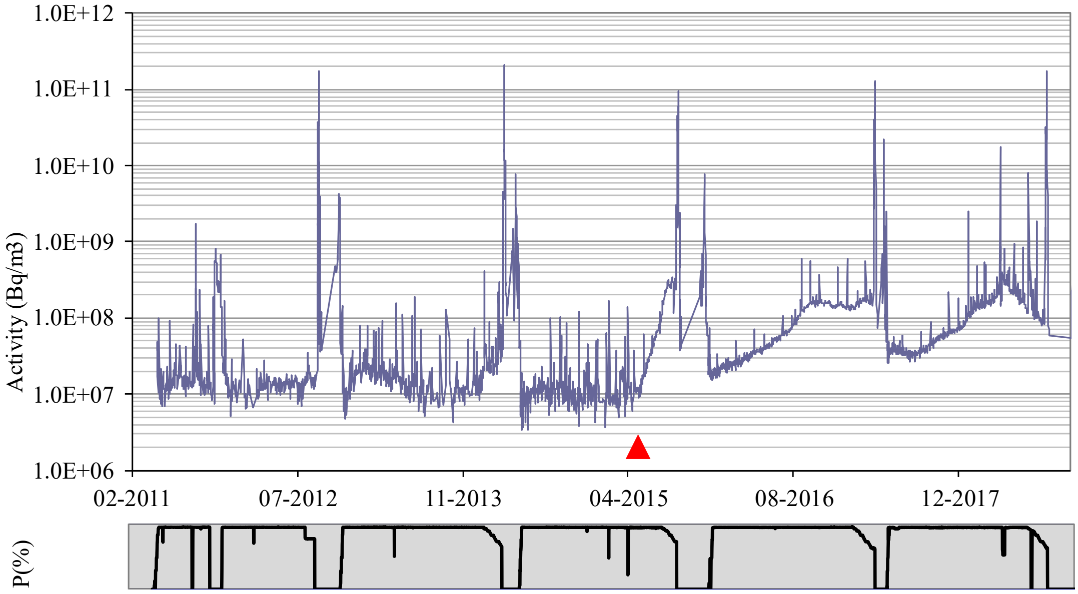

FIG. 13. Increased ^{58}Co activity in RCS of Koeberg-2 after zinc injection initiated – see red mark (courtesy of Eskom).

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[6] Note that, in 2024 (cycle 26 for both units), all SGs were replaced, with no more detectable tube leaks.

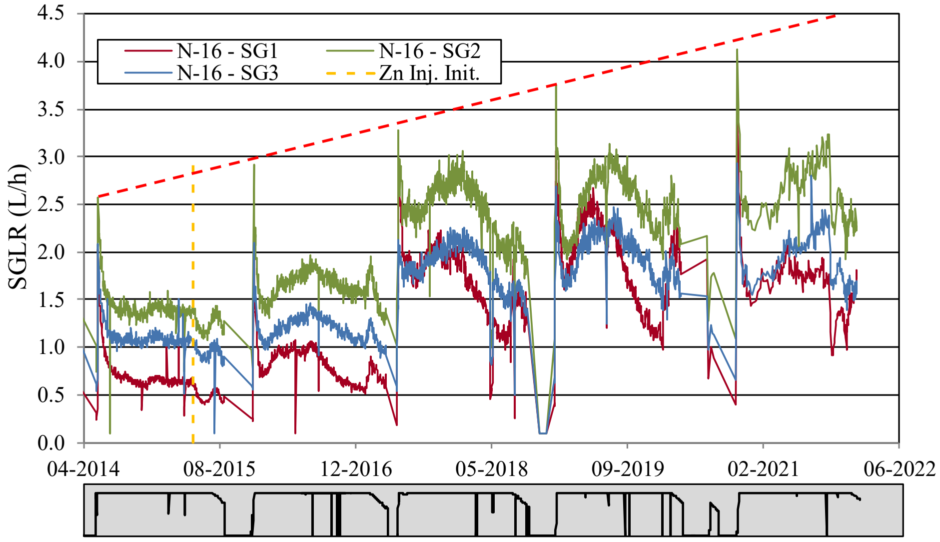

FIG. 14. Increasing steam generator leak rate in the 3 SGs at the beginning of Koeberg-2 cycle (red dotted line) after zinc injection initiated (amber dotted line) as read through ^{16}N detectors (courtesy of Eskom).

The dose rate index for a unit consists of the sum of the contact dose rates on each of the hot legs (bottom of pipe), cross over legs (side of pipe) and cold legs (bottom of pipe), as recommended in EPRI standard radiation monitoring programme – see Section 2.4.3. Dose rates were measured on contact with insulation covers 12 to 16 hours after shutdown to survey the index. Zinc injection gradually reduced the source term at most standard radiation monitoring points, indicating successful implementation advancement, evidenced by a slightly decreasing index on unit 2 (no data for unit 1, because Zn injection was temporally halted to manage increasing SGLRs – see above). Furthermore, lower dose rates inside the SG water boxes were surveyed, see Figs 15 and 16 [53].

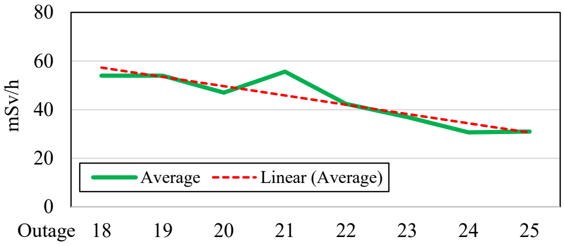

FIG. 15. Average contact dose rate on the SG tube plate (hot leg) at Koeberg unit 2 (reproduced from Ref. [53] with permission courtesy of Eskom).

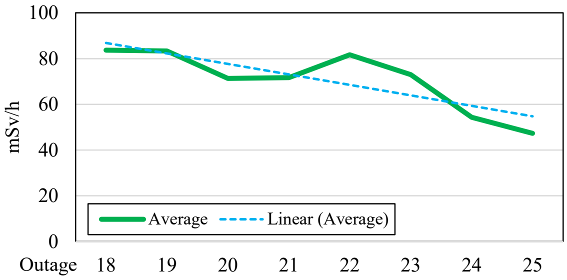

FIG. 16. Average contact dose rate on the SG tube plate (cold leg) at Koeberg Unit 2 (reproduced from Ref. [53] with permission courtesy of Eskom).

2.4.3. Developments in measuring surface contamination by activated corrosion products

This section presents operating experience with the measurement of ACP surface contamination inside RCS, due to both particle deposition and ion precipitation. Data on contamination and its evolution is a valuable input to improve operational procedures and guide design options for new reactors.

As an operator of a large fleets of PWRs, EDF has been collecting surface contamination data before and after forced oxidation through gamma spectrometry measurement campaigns for 40 years. These campaigns, termed 'EMECC'[7], are performed by the French Commissariat à l'Energie atomique et aux énergies Alternatives (CEA) using a high purity germanium detector [54]. The surface activities spectrum obtained from the campaigns typically shows ACP such as ^{58}Co, ^{60}Co, ^{51}Cr, ^{110m}Ag, ^{124}Sb, ^{59}Fe, ^{54}Mn, ^{95}Zr, ^{95}Nb, ^{65}Zn. Fission products, such as ^{134}Cs, ^{137}Cs, ^{131}I, ^{132}Te, are sometimes detected. An example of an EMECC measurement is given in Ref. [47].

The measurement points are located as follows:

- RCS: primary coolant piping (hot, crossover and cold legs) and SG tube bundles;
- Auxiliary systems: heat exchangers and pipes of the CVCS, reactor heat removal system, nuclear sampling system (NSS), etc.

EMECC measurements are used to:

- Assess the impact of operating practices and parameters – dissolved H_2 concentration, zinc injection, B-Li coordination – on the surface contamination and indirectly on the radiation field;
- Understand contamination mechanisms and elaborate strategies to address these mechanisms, either through preventive or corrective actions;
- Identify the origins of impurities and develop strategies to mitigate their production, such as material replacement and design changes;
- Support the development, calibration and validation of the OSCAR code used to model and predict surface contamination – see Section 2.9.

As an operator of WWERs, Temelín NPP employs a similar programme that includes both spectroscopy of filters and in situ measurements during refuelling outages. ^{76}As, while not a corrosion product, is included in the programme for reference. The measurements are carried out at three strategic points across all four loops of the RCS – see Table 2.

TABLE 2. CORROSION DEPOSITS ON INNER SURFACES OF THE PRIMARY SYSTEM MONITORED DURING REFUELLING OUTAGES AT TEMELÍN NUCLEAR POWER PLANT

Parameter	Location	When
ACP deposited in the filter (Bq/filter), in situ	High pressure primary coolant purification system - filters	1) before and after washing the filter and 2) without washing the filter
ACP deposited on surface, in situ	Main system – hot and cold leg	
ACP deposited on surface (Bq/cm^2 and µSv/h)	SG – primary lid of hot and cold collector – 4 spots	Before decomposition of the samples
Non-ACP deposited on surface (mg/cm^2)	SG – primary lid of hot and cold collector – 4 spots	After decomposition of the samples

Figures 17–18 show the average specific activities for the selected radionuclides at Temelín NPP. Radionuclides such as ^{51}Cr, ^{76}As and ^{122}Sb are deliberately removed from graphical representations to

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[7] The acronym stands for French 'ensemble de mesures et d'études de la contamination des circuits', a set of measurements and surveys of the contamination in systems.

avoid visual distortion, highlighting the careful balance between comprehensive data collection and clear, interpretable presentation of results.

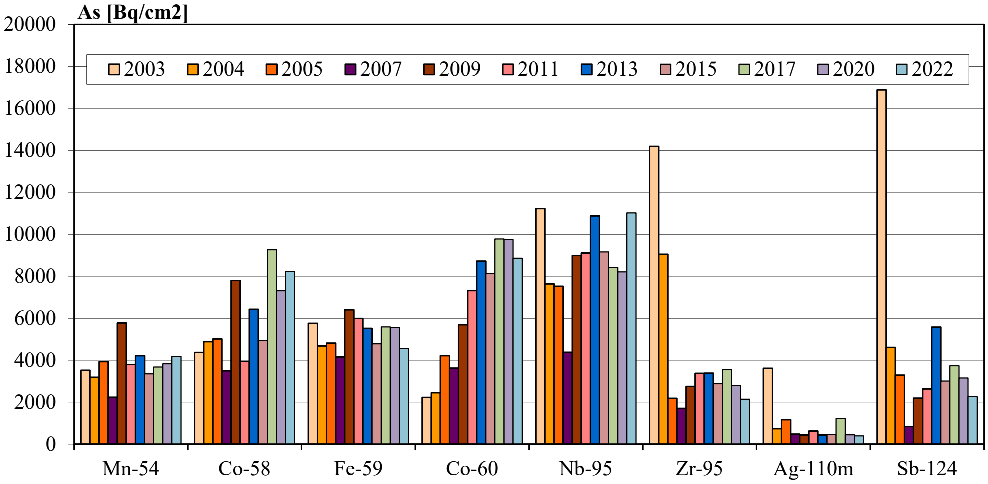


FIG. 17. Average specific activities from all loops and branches of Temelín-1 (courtesy of CEZ).

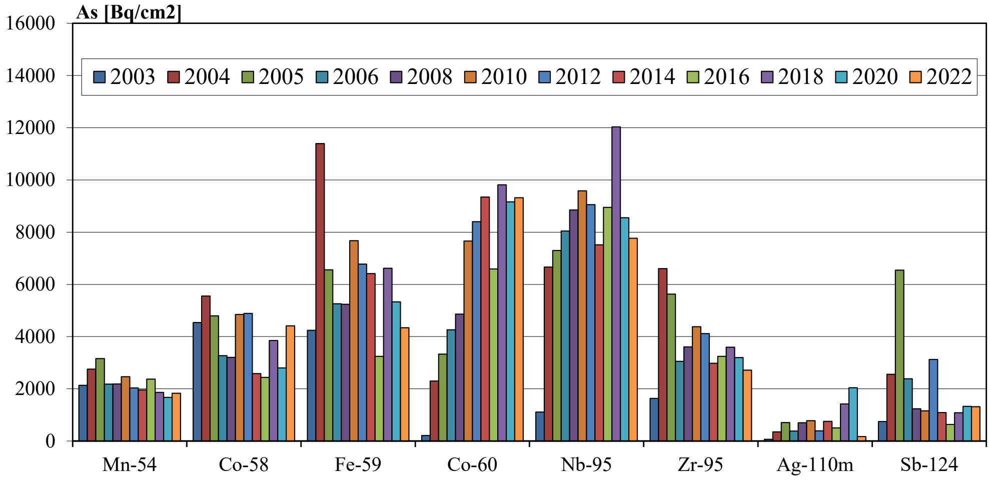


FIG. 18. Average specific activities from all loops and branches of Temelín-2 (courtesy of CEZ).

Other relevant operating experience is presented in Ref. [55] for the practice at Belgian NPPs, Ref. [56] for the practice at PWRs that follows the EPRI standard radiation monitoring programme, and chapter 5 of Ref. [35] for an overview of practices in other designs.

2.5. ADVANCES IN THE CONTROL OF PARAMETERS AND DISCHARGES TO ENVIRONMENT IN FLEXIBLE OPERATIONS

Historically, most NPPs have operated in base-load mode at a constant full-power level. In few countries, such as France and more recently the United States – Ref. [57], NPPs have been adapted for flexible power operation (FPO) [58]. This section presents advances in the control of chemistry parameters and discharges due to RCS boration/dilution sequences at PWRs operated in FPO.

Flexibility usually refers to large down-powers agreed between grid and plant operators to balance demand and production, known as ‘load following’, and limited down-powers for grid frequency control, known as ‘primary and secondary frequency control’. With the development of renewable energy sources, NPPs are increasingly required to operate flexibly to accommodate grid demand fluctuations and intermittent renewable generation, considering economic aspects.

To control core reactivity, besides using control rods, boron concentration in the RCS is adjusted. Power reductions require adding boric acid, and power increases require diluting it in the RCS. Thus, FPO necessitates using larger volumes of make-up water than base-load operation, and transients can impact the control of chemistry parameters – see generalities in chapter 5.2.8 and annex I−4.8 of Ref. [58].

Concerns and challenges related to the chemistry parameters posed by FPO are related to:

- Lithium concentration adjustment within the boron/lithium control band to ensure the correct pH in the RCS. Some NPPs use software tools to help them predict the variations in boron and lithium concentrations for planned down-powers and anticipate the required operating adjustments in lithium. Additional sampling for lithium measurements may be needed to verify that the lithium concentration is correct after the variation in power [57]. Some reactors are equipped with on-line boron and lithium monitoring with automated lithium addition to make pH_T control easier, especially during flexible power operations (see Section 5.1.4);
- Hydrogen control: In French reactors, dissolved hydrogen is continuously monitored on-line to make sure the concentration stays within the control band during transients due to flexible operation (see Sections 2.2 and 5.1.2);
- Surface contamination by ACP: EMECC campaigns showed that FPO does not have a negative effect on circuit contamination [59].

Regarding the impact on the quantity of chemicals needed to ensure a correct treatment of the water in the different systems, on the effluents generated and on the liquid and gaseous discharges to the environment, methodologies were developed by EDF and EPRI.

The methodology developed by EDF, Ref. [60], consists in estimating the increase in volume of effluents and chemicals due to FPO for the following:

- Liquid radwaste, taking into account the part of the effluents which are recycled to the RCS and the part which is subsequently discharged;
- Chemicals needed to ensure a satisfactory treatment of the primary water (fresh boric acid, lithium hydroxide, zinc acetate);
- Liquid wastes from the conventional island;
- Chemicals needed to ensure treatment of the secondary water (amines, ammonia, hydrazine);
- Make-up water needed to compensate for the water removed from the system;
- Gaseous radwaste (flowrate).

EDF analyzed more than 6,800 down-powers of at least 15% during more than 2 hours or at least 20% whatever their duration over a 4-year time period. The results of the assessment are summarized below.

Regarding liquid radwaste, FPO caused on average about 20% of the total volume generated across the fleet (Fig. 19), 5% to 30% of the fission products and ACP annual discharge to the environment (Fig. 20), and 10% to 20% of the iodine annual discharge (Fig. 20).

Regarding gaseous radwaste, FPO caused on average 7% to 25% of the total volume generated across the fleet (Fig. 21), 0% to 30% of the fission products and ACP annual discharge to the environment (Fig. 22), 0% to 30% of the iodine annual discharge, and 7% to 30% of the noble gases discharge (Fig. 22).

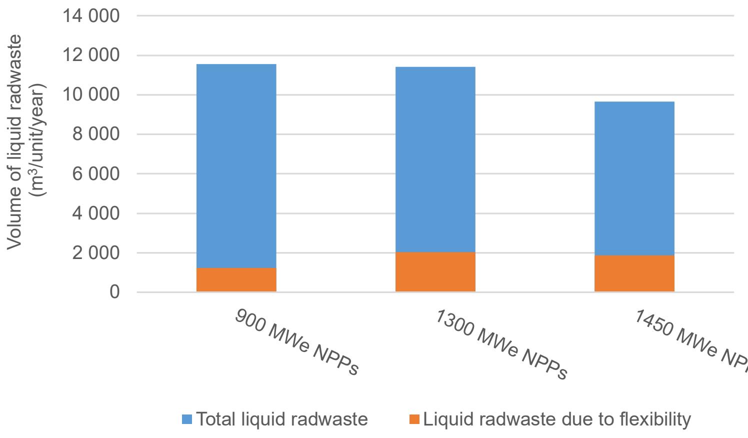


FIG. 19. Mean annual volume of liquid radwaste generated across EDF fleet and part of effluents due to FPO (reproduced from Ref. [60] with permission courtesy of EDF).

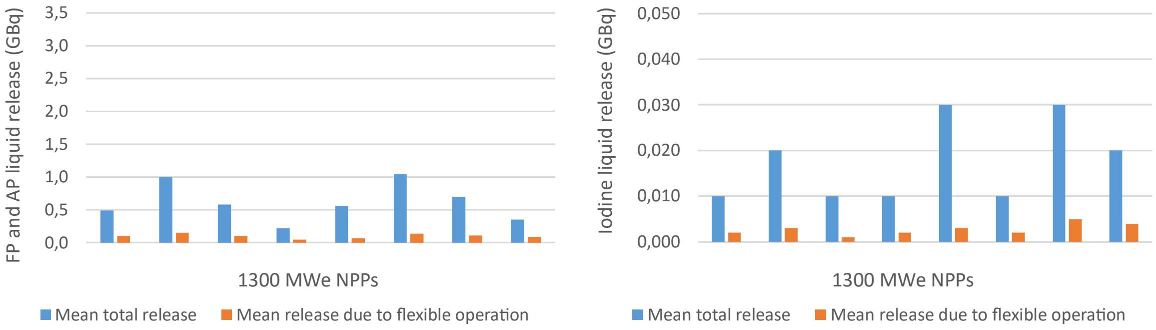


FIG. 20. Mean annual liquid release of fission products and ACP (left), and ^{131}I from the 8 EDF 1300 MWe NPPs of 2 and 4 units (reproduced from Ref. [60] with permission courtesy of EDF).

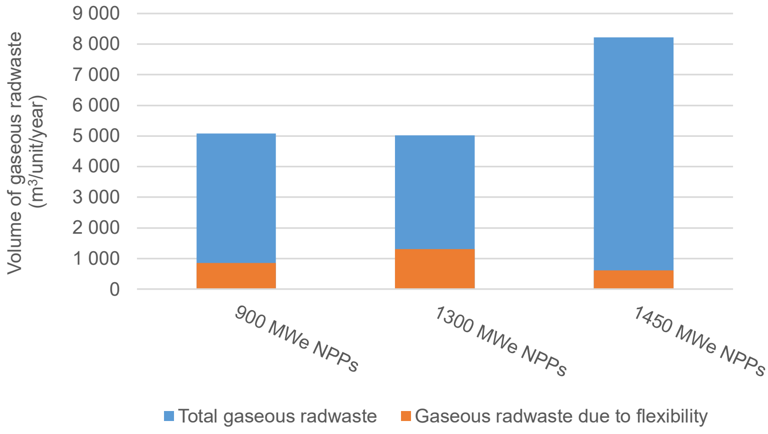


FIG. 21. Mean annual volume of gaseous radwaste generated across EDF fleet and part of effluents due to FPO (reproduced from Ref. [60] with permission courtesy of EDF).

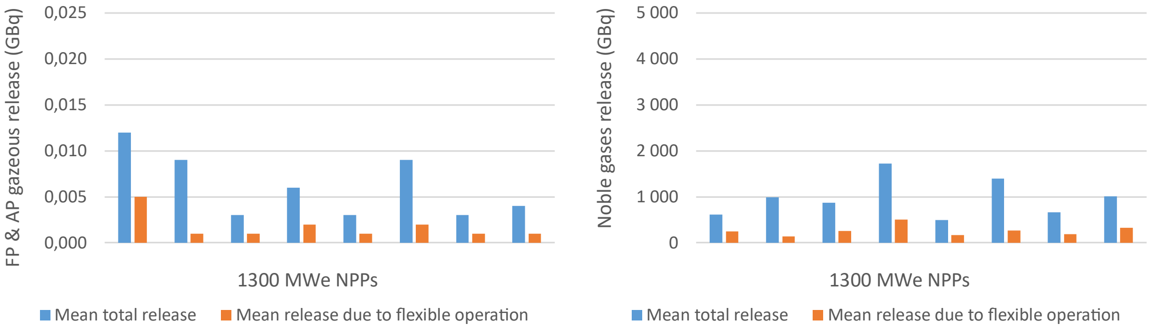


FIG. 22. Mean annual gaseous release of fission products and ACP (left) and noble gases (right) from the 8 EDF 1300 MWe NPPs (reproduced from Ref. [60] with permission courtesy of EDF).

Regarding the annual volume of demineralized water used in the French reactors, the increase was not significant (≈4%).

Regarding the effluents generated from the conventional island, there was no impact.

Regarding additional needs for boric acid, no significant impact of flexible operations was found because factors such as boron recycling, silica management in the primary and auxiliary systems and design of the boron make-up system (tanks available volume) can have a greater impact. Particularly, feed and bleed operations to decrease silica concentration have a greater impact on the effluents generated.

Regarding additional need for lithium hydroxide and zinc acetate, FPO could lead to an increase of ≈15–35% and less than 3% respectively.

EPRI also studied the impact of FPO on chemistry, solid radwaste and liquid and gaseous effluents [36, 37]. Calculation suggests increases in liquid radwaste volumes, depending on down-power frequency and timing. However, limited US plants data (as of the writing of those reports) shows minimal impacts on liquid radwaste, wet solid radwaste and liquid effluents from a few cases of FPO.

EDF operating experience and EPRI calculations indicate liquid radwaste discharges are likely to increase with FPO, depending on down-powers number, depth and time in core life. Greatest impacts occur with power reductions at the fuel cycle's end and when power is significantly reduced, since more water for boron dilution is required. Small power changes early in the cycle have no significant impact. Down-powers duration does not significantly affect effluents because water make-ups are usually performed soon after the beginning of the transient.

EDF's study of its 58 reactors and 6,800 down-powers shows similar trends for gaseous radwaste. EPRI theoretical analysis indicates that, as most radionuclides are proportional to power and neutron flux, FPO is unlikely to increase gaseous effluent radioactivity. Operational chemistry data does show some cases of increase of radiocobalt and iodines in the coolant which could contribute to gaseous radwaste radioactivity. However, these increases are expected to be small compared to the capacity for gaseous waste processing system. As of writing of the EPRI reports, operational effluent data from US plants does not show correlation between flexibility and gaseous effluent radionuclide concentrations, but EPRI emphasises that available plant data is very limited. Additional data and analysis will be needed to understand the difference between the results obtained from EDF and EPRI studies. Depending on the time down-powers happen during core-life and on the power reduction depth, EDF plants data show that down-powers can have very limited impact on the volumes of gaseous effluents generated, especially if they happen at the beginning of a fuel cycle.

Hence, increasing FPO may challenge plants with little margin in their liquid effluent treatment process or capacity of effluents hold-up or control tanks [36, 37]. Plants considering increasing FPO may need to evaluate potential impacts, ensure sufficient effluents processing capacities (e.g. collection tanks, process rate, release/effluents tanks, release rates) and develop specific water and effluents management plans, considering scenarios such as low river flow scenario that made discharges difficult to perform.

Concerning ^{3}H and ^{14}C emissions, EDF assessed that FPO would not contribute to their increase as both are generated according to neutron flux and power. EPRI used updated models to estimate ^{3}H and ^{14}C generation for various FPO scenarios. EPRI verified that the changes in total neutron flux spectrum was linearly scaled with power reduction and that the total production of ^{14}C over a fuel cycle scaled linearly with the cycle effective fuel power years. For ^{3}H, EPRI found that the production of ^{3}H in PWRs has a near linear relationship with fuel cycle effective fuel power years, with a 10% maximum difference with a perfect linear relationship [61]. Hence, ^{3}H and ^{14}C generation during a fuel cycle subject to flexible power operation are expected to be lower than during a full-power cycle of equal duration.

2.6. ON-GOING RESEARCH ON THE REPLACEMENT OF LITHIUM HYDROXIDE BY POTASSIUM HYDROXIDE

‘Western-design’ PWRs, i.e., those that are based on Westinghouse, Babcock & Wilcox, or Combustion Engineering designs and their licensed derivatives, use lithium hydroxide enriched in ^{7}Li ($^{7}LiOH$) for primary side pH_T control, which is a long accepted, standard practice. This section presents on-going research by EPRI and implementation progress at the Sequoyah NPP, operated by Tennessee Valley Authority (TVA), of the replacement of LiOH by potassium hydroxide (KOH), successfully applied for decades in WWERs.

The control of pH_T in the accepted range (i.e., ≥ 7.0) supports the three principal goals of primary water chemistry as described in EPRI’s guidelines [4]: (1) assure primary system pressure boundary integrity; (2) assure fuel-cladding integrity and achievement of design fuel performance; and (3) minimize out-of-core radiation fields. Lithium enriched to ^{7}Li at > 99.94% is used to eliminate the significant production of ^{3}H from ^{6}Li, see chapter 17 of Ref. [39].

The US government accountability office published, in 2013, a report documenting concern that the required ^{7}Li may at some point be in short supply [62]. The supply constraint reportedly became a real issue starting near the middle of 2015 with several utilities reporting an inability to procure the required $^{7}LiOH$ (although this supply constraint reportedly subsided by the next year) [39] [63]. Subsequently, in 2022, the US department of energy published an evaluation summarizing the key elements of the US energy supply chain in which enriched ^{7}Li was identified as the second most important and fifth most important supply chain issue for the current large reactors and the advanced nuclear reactors, respectively [64].

EPRI initiated a significant programme to evaluate the addition of KOH for PWRs. in lieu of $^{7}LiOH$ addition as in WWERs. Some work was completed ca. 2000 [24] [65] evaluating KOH for PWRs, but more recently (2015) a feasibility evaluation – leveraging this earlier work – was undertaken leading to the identification of technical gaps in need of evaluation. This feasibility evaluation was later summarized in 2016 [63] [66]. In addition to eliminating vulnerability to the enriched ^{7}Li supply noted above, other benefits supporting KOH addition include cost savings – based upon an informal industry survey completed in 2016 indicating approximately $100 000/year/unit savings based on median values for price and use; and asset protection–based upon some evidence that potassium may reduce certain corrosion processes compared to lithium and may be a potential mitigation strategy for crud induced power shift due to its much higher solubility with boron as compared to lithium [39].

2.6.1. Technical assessments (pre-application)

The scope of technical assessments planned by EPRI was outlined in 2018. This scope was the result of significant industry review and input by an EPRI KOH advisory committee comprised of industry experts from several different disciplines (chemistry, fuels, materials, radiation safety) and from several different utilities (both PWRs and WWERs) as well as nuclear steam supply system and fuel vendors. The following assessment scope, grouped by discipline, has been described in some detail [39] [67]:

- Chemistry and Radiation Safety:
  - Assessment of controlling pH_T with more than one alkali in the RCS.
  - Development of important potassium species to effectively model high temperature potassium chemistry.
  - Analysis of the radionuclides that could be generated from the activation of the added potassium (and sodium as an impurity in KOH) and the potential impact on plant radiation fields, effluents, and radioactive waste issues.
- Fuels: Assessment of the relative effects of potassium hydroxide chemistry versus lithium hydroxide chemistry (each with boron) on: (1) clad temperature under crudded conditions, (2) cladding corrosion rate in the presence of a highly concentrated chemistry, and (3) potential crud morphology and composition changes.
- Materials: Impact of K chemistry versus Li chemistry (each with boron) on the SCC behaviour of RCS materials. Further details regarding the planned testing were outlined in chapter 7.3 of Ref. [39].

The results from several of these EPRI assessments have been reported in the literature such as chapter 18.6D of Ref. [39] for the modelling, and Refs [68–74]. Other researchers have also published relevant assessments of interest in chapters 6.2 and 7.4 of Ref. [39].

Focusing on chemistry and the production of new radionuclides in the RCS (i.e., due to KOH addition), an activation analysis was performed and reported by EPRI in chapters 6.2 and 7.4 of Refs [72], [75–77]. This considered both naturally occurring potassium (the neutron activation and nuclide decay chains are depicted in Fig. 23) and its principal impurity of consequence – sodium.

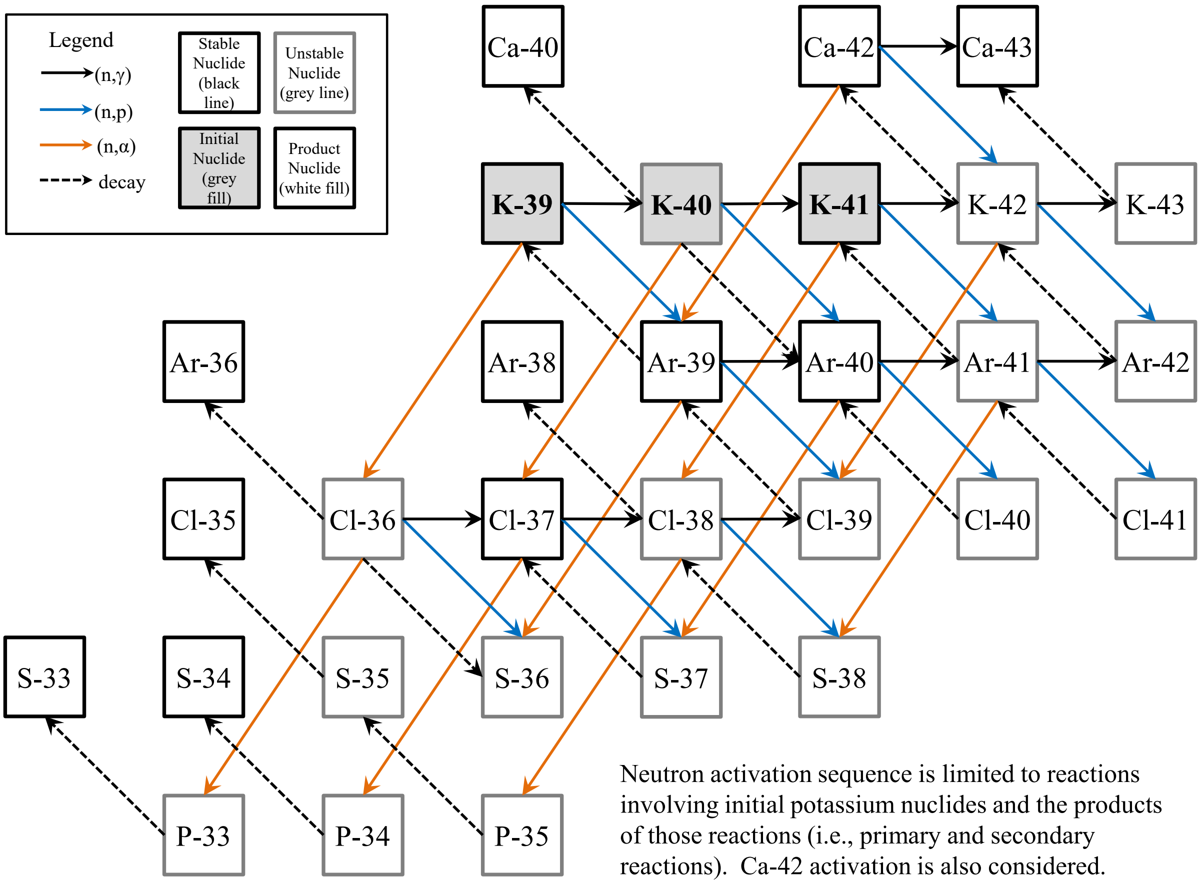
The consequential impacts on RCS activity, resin activity and gaseous activity are summarized based upon the modelling assumptions described in Ref. [72]. Further considerations for plant application are described in Ref. [78], including identification of the radionuclides of concern.

2.6.2. Planned application at Sequoyah nuclear power plant

EPRI and TVA are continuing to partner in the development for, and planned implementation of, three cycles of KOH application at the Sequoyah NPP [72]. Some details describing the efforts in preparation for implementation are as follows [78].

2.6.2.1. Change Management Process

In September 2021, Sequoyah NPP completed their engineering scoping document, which precedes the safety review in accordance with national regulation. The engineering scoping document is the first step of the TVA change management process, allowing stakeholders to ascertain the overall project scope and determine the tasks needed to implement the planned 3-cycle KOH monitored campaign. Then, in July 2022, the safety review was initiated. This allowed review and consideration of the more than 20 relevant EPRI reports to begin. These reports provide the technical basis to assess the safe implementation of the 3-cycle KOH monitored campaign (including work addressing chemistry, source term, and other radiological technical gaps). Completion of the safety review is the last input to the engineering change package that has to be completed. TVA will use the engineering change package to implement the change from LiOH to KOH addition.



Neutron activation sequence is limited to reactions involving initial potassium nuclides and the products of those reactions (i.e., primary and secondary reactions). Ca-42 activation is also considered.

FIG. 23. Neutron activation and nuclide decay for natural potassium used for modelling high temperature potassium chemistry (reproduced from Ref. [72] with permission).

2.6.2.2.Stakeholder Engagement

A team of EPRI and TVA stakeholders was assembled to evaluate the technical scope of work in support of KOH implementation at Sequoyah NPP. Questions and concerns were collected and categorized according to the disciplines most affected – radiation protection, chemistry, materials, and nuclear fuel. The stakeholder groups have been meeting periodically, approximately every quarter, to discuss and address these items, to develop consensus action plans and deliverables for successful implementation.

Some of the topical discussion items by discipline were described and are summarized here:

- Radiation Protection: Accurately measure and assess the impact of the new radionuclides from KOH addition on environmental conditions and worker dose, and to account for them appropriately for regulatory compliance. It was recognized that this will result in two separate radiological environments at the site because the other unit will continue with LiOH addition for some time (i.e., not yet implement KOH addition). Nevertheless, it was noted that no significant change in overall radiological conditions in the plant is anticipated.
- Chemistry:
  - Control of CVCS mixed bed will change from one alkali (Li) to the use of an equivalent lithium concentration (using both K and Li), since both K and Li impact pH_T in the same fashion.

    It was noted that the strategy for the outage leading into the first KOH cycle will differ from the strategy for the later cycles with KOH. Sequoyah NPP typically uses a new standby mixed bed demineralizer for end of cycle deboration, with the cation in the alkali form.

However, it was noted that the intent is not to allow any potassium into the system until the start of the next cycle (i.e., the first cycle with KOH). To eliminate the possibility of this occurring, it was reported that the new mixed bed demineralizer will be replaced during the refuelling outage in preparations for unit startup ahead of the first cycle with KOH addition. In the cycles following the first cycle with KOH in the system, Sequoyah NPP will then be able to use its typical outage strategy, i.e., use the new mixed bed demineralizer to deborate at the end of the cycle, without any concern regarding possibly adding some potassium to the RCS (other than maintain proper pH$_T$ control).

  - RCS monitoring and sampling will need to add both potassium and sodium (with commensurate instrumentation and methods). This will be addressed with the interim guidance to EPRI’s ‘PWR primary water chemistry guidelines’ issued for the three-cycle KOH application.
- Materials: It was noted that the TVA materials engineering team has been kept informed and has been providing feedback on the EPRI materials testing programme. The testing that has been published, which has been focused on bounding materials over a robust scope of PWSCC testing – both initiation and crack growth, indicates satisfactory results. Final testing, evaluating PWSCC in a crevice chemistry – consistent with chemistry that could be present within the radial gap between the pressurizer heater and support plate – was reportedly under way (as of late 2023).
- Nuclear Fuels:
  - It was also noted that the TVA nuclear fuel reliability team has been coordinating with EPRI. Testing published to date indicates satisfactory results from both the autoclave testing [70] [71] and the first set of ‘WALT’[8] loop testing. The final loop testing still needs to be completed.
  - It was noted that fuels exams will be conducted as part of the three-cycle KOH implementation. There are three fuel exam campaigns planned, starting immediately prior to the first addition of KOH (baseline cycle). The fuel exams will reportedly include one or more of the following: visual examinations, oxide measurements, crud scrapes, grid vane harvesting, etc. The fuel exam scope was reported to be different among the three campaigns, targeted to optimize the examinations needed while minimizing the impact on outage schedule.

2.6.3. Summary

A significant and robust programme of technical assessments, including laboratory testing, is being completed by EPRI in support of the application of KOH at Sequoyah NPP. EPRI and TVA are working together in support of a three-cycle application at one of the units. The technical assessments are nearly complete and more than 20 EPRI reports provide the technical basis to determine safe implementation of KOH for the three-cycle monitored campaign – underpinning the TVA process for implementation (their engineering scoping document, safety review, engineering change package). EPRI and TVA are engaged in coordinating and completing actions toward implementation, which is expected to begin in the near future (as of the time of writing this Publication).

2.7. DEVELOPMENTS IN OPTIMIZING CHEMISTRY FOR START-UPS, SHUTDOWNS AND OUTAGES

The main goal of RCS start-up chemistry is to create a reducing environment and maintain an appropriate pH$_T$. Optimizing planned maintenance and the chemical aspects of the procedure for the actual shutdown is crucial to minimize radiation doses to workers during outages [1]. The main objective of RCS shutdown chemistry is to prepare the RCS for safe reactor head lift and efficient refuelling. In

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[8] WALT stands for Westinghouse advanced loop tester, see Ref. [79].

the event of a nuclear fuel leak, shutdown chemistry steps are carefully implemented or adjusted to the extent of fuel damage. This section reviews key steps in startup chemistry (Section 2.7.1) and shutdown chemistry (Section 2.7.2) and discusses advances in ^{110m}Ag clean-up strategies (Section 2.7.3) and post-SG replacement chemistry strategies (Section 2.7.4) in PWRs.

2.7.1. Water chemistry of the primary coolant system during startups of pressurized water reactors

For PWRs, start-up steps include removing oxygen from the RCS, purifying water with ion resin, reducing boron concentration, adding hydrogen and lithium hydroxide to establish reducing and alkaline conditions before reactor start-up. As an example of steps towards reducing and alkaline conditions in the RCS of Krško NPP before start-up is shown in Fig. 24.

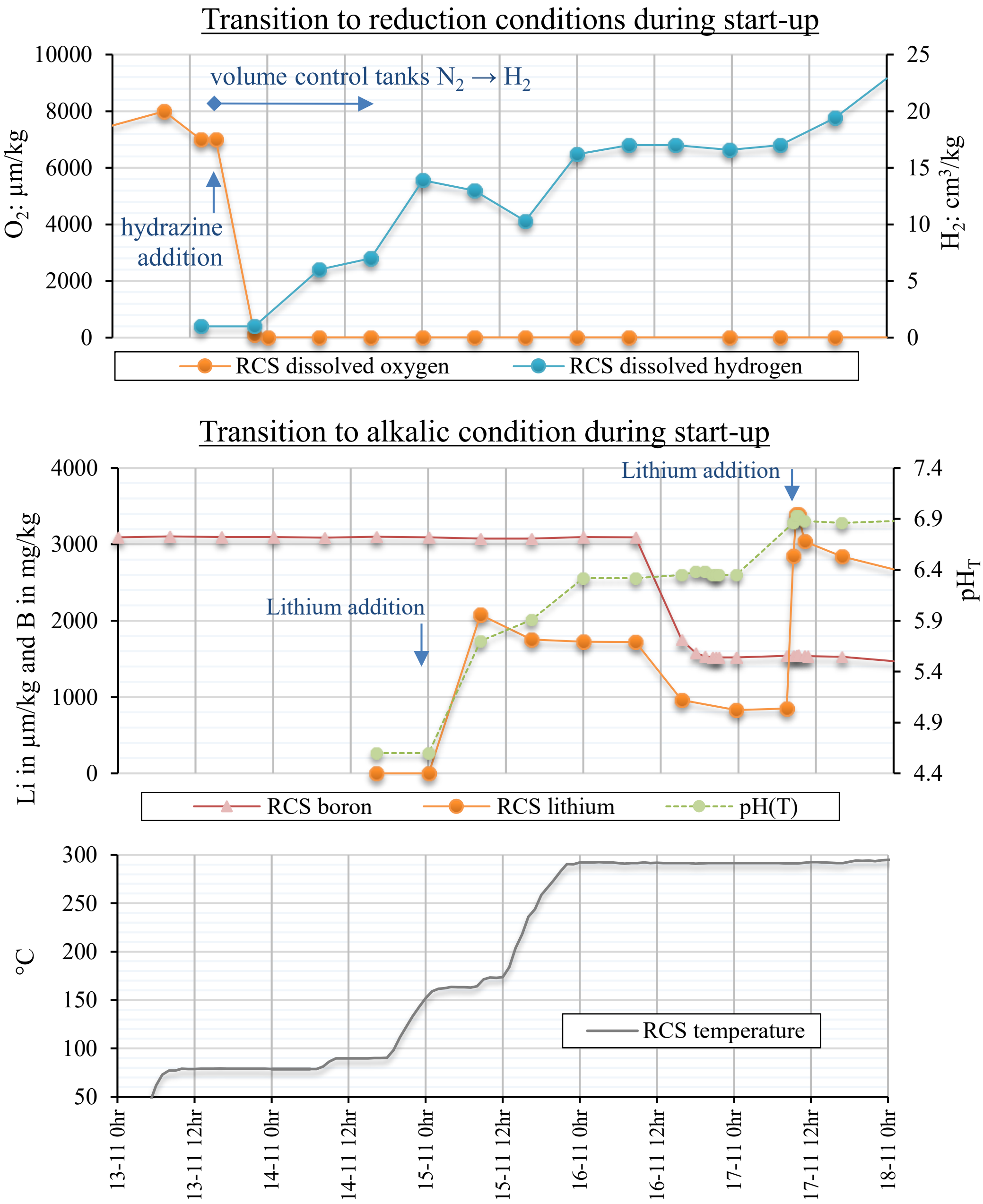

FIG. 24. Trend of RCS chemical parameters during start-up at Krško NPP in 2023 (courtesy of NEK).

Based on experience [2], activities included in NPP start-up plans to enhance chemistry control are:

- Start hydrogen injection as soon as the coolant reaches the required temperature in two-phase conditions in the pressurizer, subjected to operational readiness (e.g. 93°C at Krško NPP). It is good practice to include this step in the outage schedule;
- Add zinc as soon as conditions allow (considering silica concentration). Align the zinc dosing skid systems to warm up with startup and start injecting once temperatures meet normal values;
- Ensure filter demineralisers, deep bed polishers and the reactor water cleanup system are ready for service at start-up.

2.7.2. Water chemistry of the primary coolant system during shutdowns

The main steps in a shutdown procedure are as follows. First, hydrogen concentration is reduced to avoid explosion risks when the RCS will be open and oxygen will enter. Power is then decreased, boric acid is injected to prevent criticality as the RCS is cooled during refuelling. Before opening the reactor pressure vessel, the RCS is put under vacuum to remove gaseous fission products, and, in most PWRs, hydrogen peroxide is added for forced oxidation – Note that Some operating organizations of PWRs and most operating organizations of WWERs as surface contamination are usually lower than in PWRs consider 'natural' oxidation at the opening of the RCS is sufficient, and thus, do not carry out this step. Finally, the RCS is opened.

During this procedure, chemistry conditions change drastically. Initially alkaline reducing, the conditions become acid reducing after boric acid injection and, finally, acid oxidizing when oxygen is added, either naturally (when opening the RCS) or via hydrogen peroxide. This change impacts the oxide layer, causing corrosion products to dissolve. These products are removed by filters and IXR through the CVCS in PWRs or equivalent systems in WWERs, typically with purification let-down flow rates at a maximum. Reference [80] reviews RCS purification practices at Hongyanghe NPP.

Forced oxidation and effective management of the resulting cobalt peak are crucial to outage dose control in PWRs, especially in the first cycles after zinc injection, if any (see Section 2.4.2). It is important to add sufficient amount of hydrogen peroxide at a low temperature to avoid redeposition of corrosion products. EPRI and CEA recommend adding hydrogen peroxide to the RCS (incl. the pressurizer) in water-solid state at less than 82°C (EPRI) or 80°C (France), with at least one reactor coolant pump operating, preferably more, until the ^{58}Co concentration peak is detected.

Some operating organizations of WWERs, such as at Bohunice and Mochovce NPPs since 2007, add boric acid partially neutralized by potassium hydroxide into the RCS (where potassium is injected in the borated water supply tank) to achieve acidic reducing conditions at refuelling boron concentration. This mitigates the negative effect of decreasing pH on the magnetite passivation layer and reduces demand on the purification systems. No adverse effect on the activity removal during shutdown had been observed so far. Loviisa NPP pursued another approach and installed an additional purification pump used for outages in 2019.

In case of nuclear fuel leak, it is essential to control containment purge flow rates to prevent exceeding radioactive release limits, use fans and ventilation hoses to direct volatile species into permitted waste pathways, adjust waste gas decay tank strategies, delay the release of fission gases until RCS pressure decreases, plan for additional mechanical degassing and address potential elevated alpha contamination.

2.7.3. Optimized ^{110m}Ag clean-up strategy during forced oxidation in pressurized water reactors

Reference [1] recommends considering programmes to replace silver and antimony in components, as these materials are easily activated and could impact collective doses during outages. Alternatively, optimizing the shutdown chemistry regime can help abate ^{110m}Ag.

Key findings from the 'EMECC' campaigns (described in section 2.4.3) related to the behaviour of ^{110m}Ag include [81]:

- During oxidation, ^{110m}Ag dissolves from primary surfaces and precipitates on cold parts of auxiliary systems before dissolving slowly from these cold parts. It leads to a sharp increase in dose rates near these areas (see also the comprehensive literature survey in Ref. [82]).
- Due to the precipitation in the NSS, ^{110m}Ag sampled via the NSS is not representative of its volume activity in the RCS.
- In oxidizing and acidic conditions, silver is effectively trapped by cation exchange resins. However, in reducing conditions, silver is insoluble (colloids) and thus not trapped.

Due to its precipitation, ^{110m}Ag contamination can significantly impact dose rates in the shutdown cooling system, clean-up system heat exchangers and downstream components to the clean-up system. The silver peak activity generally appears up to 15 hours after the ^{58}Co peak – see the description of the specific measurement campaign carried out at Civaux NPP in 2019 in Ref. [83] and investigations carried out at Ringhals NPP in Ref. [84]. There is no clear correlation between the ^{110m}Ag activity peak and other corrosion products. A practical rule to assess whether a PWR unit at EDF has an issue with silver is when ^{110m}Ag shutdown peak is higher than 0.5 GBq/m^3 measured in RCS samples. Behaviour of silver, mostly assessed through gamma-ray spectroscopy over multiple outages, can be seen sometimes as unpredictable.

For ^{110m}Ag removal, some operating organizations have had success using macroporous resins under acidic and oxidizing conditions, in combination with 0.1 µm-mesh filters.

Sanmen NPP that experienced damage of a normal residual heat removal system gasket developed a prediction model and optimized their purification methods as follows:

- Increase coolant pump speed to accelerate the release of Ag and ^{110m}Ag;
- Operate two filters in parallel to increase purification flow;
- Increase hydrogen peroxide concentration to 8 ppm.

As a result, purification time is controlled, and actual ^{110m}Ag volume activity is accurately predictable against the model (see Fig. 25).

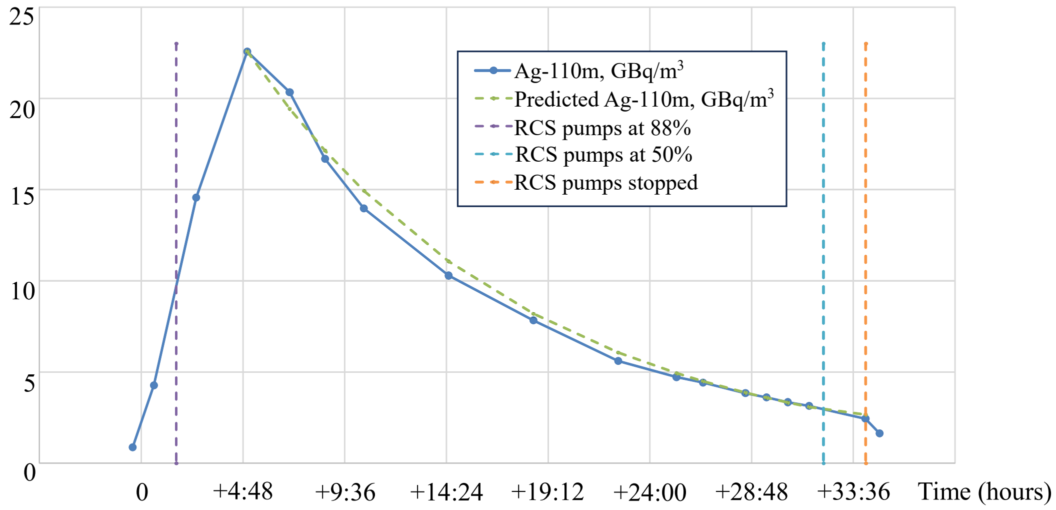

FIG. 25. ^{110m}Ag volume activity in Sanmen-1 RCS (GBq/m^3) during the 30-hour forced oxidation at unit's third outage in November 2022 (courtesy of CNNP).

2.7.4. Optimized chemistry after steam generator replacement

Most PWRs and some WWERs have replaced their SGs without the ‘preconditioning’ phase been performed prior to the return to service. Operating organizations eventually observed high levels of dissolved metals, mainly nickel, and ACP such as ^{58}Co, ^{60}Co, ^{51}Cr, during the first few cycles post-steam generator replacement (SGR). The magnitude of the ACP activity peak after forced oxidation and the variation in ACP activity levels compared to pre-replacement cycles and outages varies from between plants [85]. This section presents post-SGR experiences at Krško and Paluel-2 NPPs.

At Krško NPP, where SGs were replaced after the 16th fuel cycle (2000), shutdown chemistry follows standard EPRI instructions. The nickel inventory increased due to the larger surface area of the new tube bundle and the power uprate. In the years after SGR, the NPP extended the duration of fuel cycles from 12 to 18 months. These factors, alongside with the new un-passivated surfaces, likely contributed to higher specific cobalt activity and dose rates after the forced oxidation. Eventually, ^{58}Co and ^{60}Co specific activities returned to pre-replacement level 7 cycles after replacement. ^{60}Co decreased due to a lower proportion of cobalt in the tube bundle (Fig. 26).

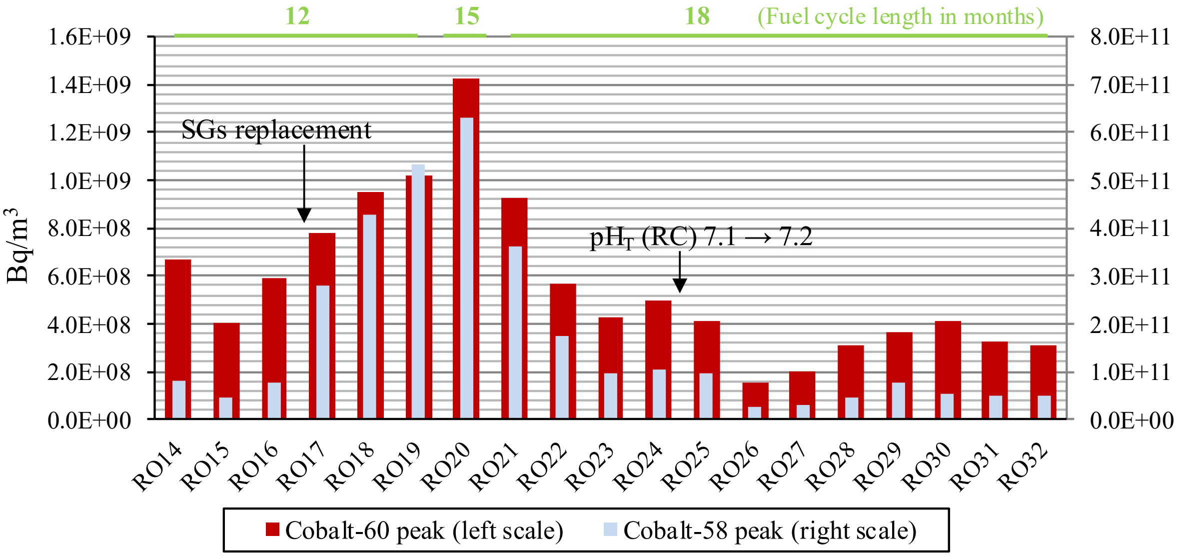

FIG. 26. ^{58}Co and ^{60}Co peak data during shutdown at Krško NPP (courtesy of NEK).

The amount of hydrogen peroxide added, and hydrogen removal and pH strategies had no effect on limiting these impacts. The use of macroporous resin in combination with standard H^+/OH^- ionic gel-type resin was effective for removing released ACP in colloidal form during shutdown chemistry.

In 2018, the first SGR at an EDF 4-loop reactor was performed in Paluel-2. At the end of the first subsequent cycle (cycle 23), 74 fuel assemblies exhibited significant corrosion product deposits and crud-induced localized corrosion was found on 3 leaking fuel assemblies. This is the only instance of crud-induced localized corrosion in EDF plants to date. One key root cause was the high corrosion product source term due to the SGR. Concerning chemistry, two aggravating factors were identified: a $pH_{300°C}$ below 6.9 for about 60 days at the start of cycle 23 (see Fig. 27) and the absence of zinc injection during that cycle [86].

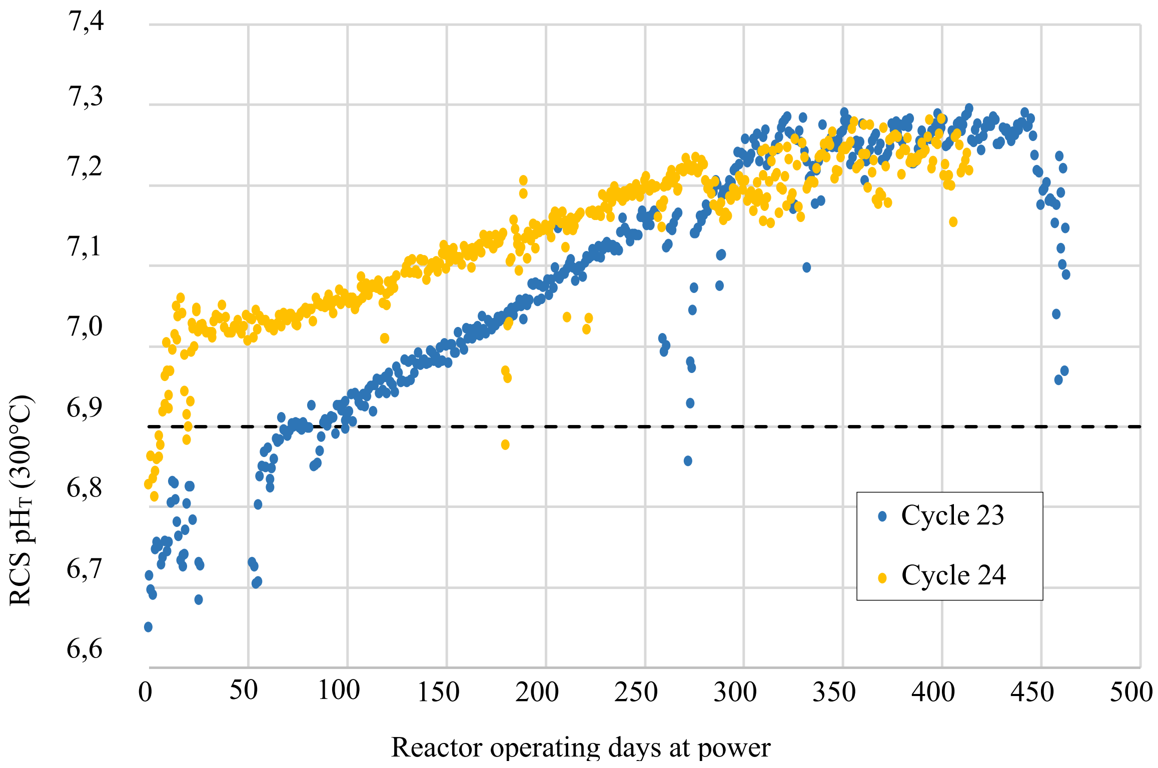

FIG. 27. Evolution of the pH_T (T = 300°C) over Paluel-2 fuel cycles 23 and 24 (reproduced from Ref. [86] with permission).

EDF subsequently implemented an optimized chemistry control programme and a specific chemistry and radiochemistry monitoring programme for Paluel-2, which was then deployed at all other units undergoing an SGR.

Hence, lithium concentration at the beginning of the fuel cycle was increased. Over Paluel-2 cycle 23 the lithium concentration was limited to 2.2 mg/kg; it was eventually increased to 2.4 mg/kg at the beginning of cycle 24 crediting Zircaloy-4 fuel assemblies. For the subsequent cycles and for the other units concerned by an SGR, the lithium concentration can be increased up to 3.5 mg/kg, enabling a $pH_{300°C}$ greater than 6.9.

In addition, EDF strengthened the chemistry and radiochemistry monitoring programme, including metallic species (nickel, iron, chromium and aluminium) in the programme [86]. 'Hold points' and 'step points' were defined. Step points are set to verify the trend in the chemistry parameters; hold points intend to ensure that no adverse trend is observed in the chemistry parameters, otherwise extended purification time is necessary (see figure 6 of Ref. [86]).

Implementing those actions enabled to better control the release of corrosion products during the start-ups after SGR and ensure their removal before criticality. Figure 28 shows ACP concentrations during startup after the implementation of an optimized chemistry programme.

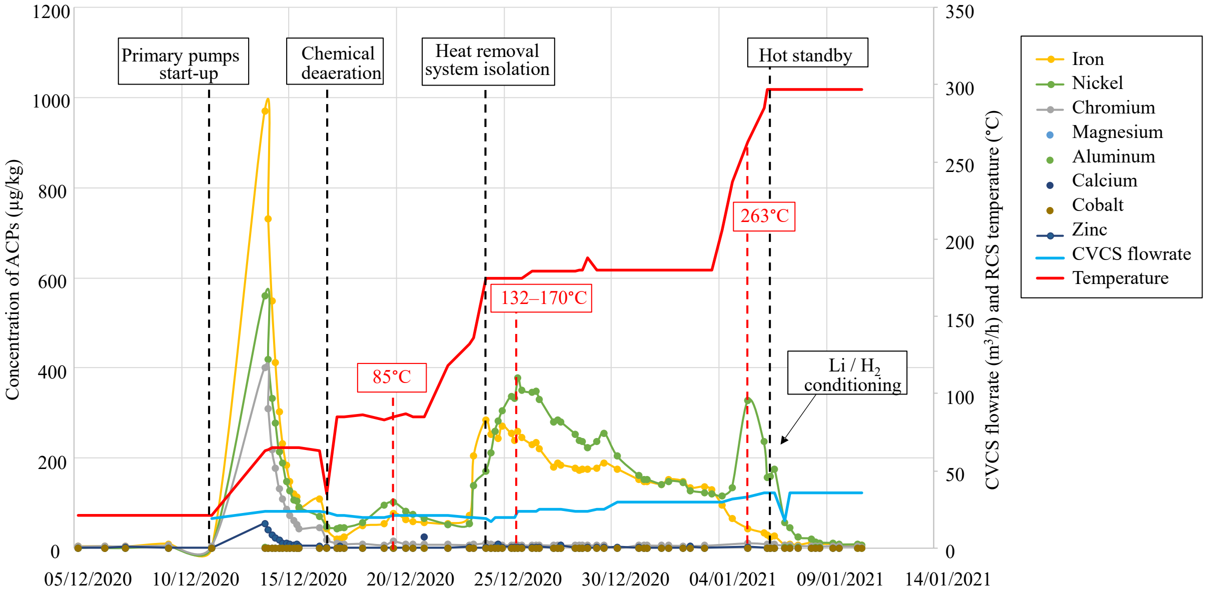

FIG. 28. ACP monitoring during Paluel-2 start-up at the beginning of cycle 24 (reproduced from Ref. [86] with permission).

2.8. ADVANCES IN COMMISSIONING CHEMISTRY

Before commissioning of new reactors, chemistry requirements and their surveillance should be defined [1]. Commissioning tests transition the reactor from construction to normal operation and are usually performed in several steps. First, pre-operational tests check systems and components individually at room temperature and pressure, including rinsing and hydrostatic tests. Next, pre-core loading tests, including cold functional tests and HFT, are conducted. The cold functional tests are carried out at room temperature but at pressure, to perform the hydrostatic pressure test of the RCS [87]. During HFT, temperature and pressure are raised to operating conditions. After the first core loading, pre-criticality tests are performed at room temperature and pressure, followed by tests at operating conditions. After the first criticality, final commissioning tests are performed during power escalation.

This section presents experiences at Flamanville-3 and Sanmen NPP. Experience during pre-core HFT at Taishan-1 is detailed in chapter 10.2 of Ref. [39], publicly available.

2.8.1. Recent experience at Flamanville-3 nuclear power plant

During the commissioning of Flamanville-3, a PWR of the EPR type, chemistry was treated as a plant system. A ‘pseudo-system’ called ‘chemistry and radiochemistry of fluids’ was created, with commissioning procedures written similarly to those for physical plant systems. Chemistry and radiochemistry requirements were defined based on the tests performed and system conditions, for systems of the nuclear island – RCS, CVCS, safety injection system, high concentration boron safety injection system, SG main feedwater, SG blowdown system – and for auxiliary systems connected to the nuclear island – boron and water makeup system, in-containment refuelling water storage tank, boron recycle system, gaseous waste treatment system, component cooling system, electrical building chilled water system, condensate extraction system. Chemistry requirements related to nuclear safety, equipment integrity, hazard mitigation, environment protection, and radiation protection were indicated. Interfaces with system commissioning procedures were also documented and requirements for the availability of specific equipment and systems were established, such as the purification equipment (filters and demineralizers), the degassing systems, the supply of gases (i.e. H_2, N_2), the supply of chemicals (i.e. boric acid, lithium, hydrazine, ammonia, amines, phosphates), the chemical injection systems, the sampling systems, the on-line chemistry monitors.

During systems pre-operational tests, requirements ensured the quality of the water used for system rinsing, hydrostatic tests, and lay-up. Impurities such as halides were monitored, and hydrazine and/or amines were added to scavenge dissolved oxygen or reach the target pH. depending on temperature and materials.

During cold functional tests, systems remained at room temperature and no chemical conditioning was required. However, impurities in fluids were strictly limited and controlled. SGs were in dry lay-up conditions.

As impurities (Cl, F, SO_4, Na, Fe, Ni, Mg, Ca, Al, Si, Cr, Zn, suspended solids) had to be monitored and minimized in the primary, secondary and auxiliary systems during the pre-core tests, the purification systems (i.e. CVCS, boron recycle system, reactor cavity and spent fuel pit cooling and treatment system, SG blowdown purification stations) and the sampling systems (i.e. NSS, feedwater chemical sampling system) were available along with local sampling points. During HFT, chemicals were added to minimize corrosion and, in some cases, to passivate the components surfaces, so the availability of chemicals and their injection systems had to be verified beforehand. Resins used for RCS purification were saturated with boron during RCS conditioning, even though this was not a requirement as there is no criticality risk during HFT. One resin was also saturated with lithium to achieve optimal pH_T.

HFT during commissioning of a new reactor are a major opportunity to passivate RCS surfaces, especially SGs [88]. The first contact with high temperature water forms the oxide layer, and appropriate conditioning enhances the formation of a protective oxide layer that reduces further corrosion products release from primary surfaces.

For the RCS, lessons learned at Flamanville-3 include – see Refs [87], [89] and [51]:

- Inject zinc into RCS at a high concentration (40–60 µg/kg) when there is no fuel in the core, to optimize passivation during HFT once the temperature reaches 120 °C;
- Maintain pH ≈ 7.2 (300°C) by adding boron and lithium once the temperature reaches 120°C;
- Remove anionic impurities and dissolved oxygen whenever the temperature exceeds 120°C. Hydrazine was injected when there was a risk of oxygen ingress, such as when water from the in-containment refuelling water storage tank or the safety injection system was injected to simulate incidental or accidental conditions (in addition to having the degassers in service);
- Keep the CVCS purification operating at the highest possible flowrate to minimize impurities and corrosion products (nickel and iron). Due to high nickel solubility at low temperature, it is important to remove it before reaching 120°C.

During HFT, a plateau of 300 hours was maintained at ≈304°C to facilitate zinc injection and surface passivation at $pH_{300°C} \approx 7.2$.

This differs from Olkiluoto-3, where zinc was injected to achieve a lower concentration in the RCS (5–40 µg/kg), $pH_{300°C}$ was maintained at 7.8, and hydrogen was added for 4 days to ensure more reducing conditions [88]. In Olkiluoto-3, coupons of 304L austenitic stainless steel and alloy 690TT were placed in the RCS before HFT and analyzed afterwards. The oxide layer formed on the coupons exhibited a continuous, thin oxide layer enriched in chromium, with zinc also found in the oxide on both coupons.

Thanks to the use of fibre-glass-free filters and silica-free products (or products with low silica levels), no significant silica concentration was observed in the RCS during HFT. Similarly, since the aluminium content in the coating materials was reduced and the use of aluminium oxide was removed from the SG manufacturing procedures, no significant aluminium impurities were observed (Fig. 29) [51].

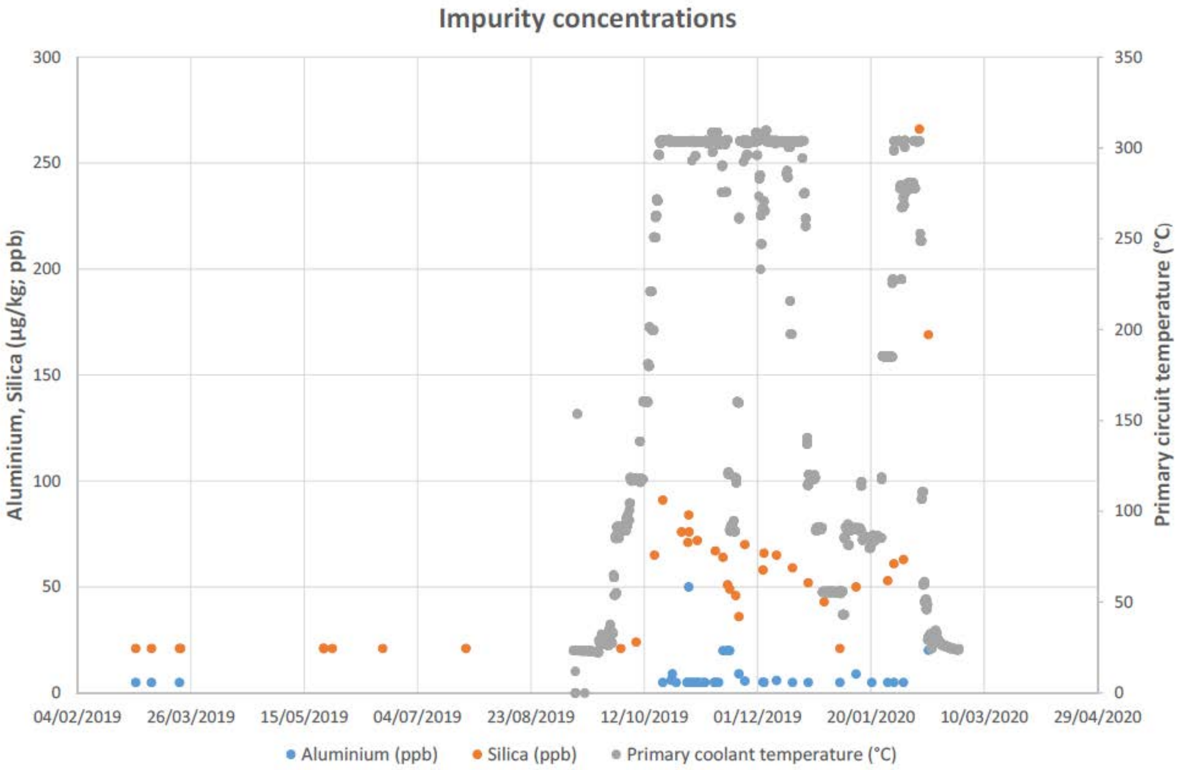

FIG. 29. Evolution of silica and aluminum concentrations in Flamanville-3 EPR primary coolant during the Hot Functional Tests (reproduced from Ref. [51] with permission).

At the end of the HTF in Flamanville-3, as well as in Taishan-1 and 2, and Olkiluoto-3, specific cleaning was performed to optimize the corrosion products dissolution in the RCS. During cooling, boric acid was injected and lithium was removed to achieve acidic conditions. Below 80°C, hydrogen peroxide was added for forced oxidation. The solubilized corrosion products were purified through CVCS demineralizers and filters. In the absence of radiation, it seems boron addition was more effective in solubilizing corrosion products than the forced oxidation.

Given the EPR-specific design of the gaseous waste treatment system and delay beds, the efficiency of these beds (filled with activated charcoal) was checked to ensure to ensure compliance with environmental regulations [89]. The delay beds are dedicated lines delaying releases to the stack and to the environment, similar to decay tanks in other NPP designs.

Concerning the secondary systems, operating conditions during HFT were as follows:

- About 10 days before filling the SGs, 2 of the 4 auxiliary feedwater tanks were filled with demineralized water dosed with hydrazine to scavenge the dissolved oxygen and with ammonia to achieve a $pH_{25°C}$ of 10–10.5. Once the dissolved oxygen was below 100 µg/kg and the pH was in the correct range, the 4 SGs were filled and kept under wet lay-up conditions;
- The main feedwater system was conditioned with ammonia (3–5 mg/kg) and ethanolamine (0.3–1.2 mg/kg) to reach a $pH_{25°C}$ above 9 (target > 9.5), and hydrazine was added (< 500 µg/kg) to maintain dissolved oxygen below 100 µg/kg;
- Once the chemistry parameters were correct in the main feedwater system and the temperature was above 120°C, the SGs were connected to the main feedwater system;
- In the SG blowdown (SGBD) system, cation conductivity and sodium concentration were expected to be below 4 µS/cm and 100 µg/kg respectively. However, because of reduced

flowrate during some HFT periods or inappropriate sampling (flowrate, pressure or filter clogging issues), these limits were occasionally exceeded.

Among issues faced during the HFT, key findings and lessons learned include [90]:

- Grab sampling was necessary in some cases due to unavailable or inappropriate conditions of the sampling systems (e.g. due to issues with flowrate, pressure, and temperature, clogging, resins saturation upstream the on-line cation conductivity monitors, calibration). However, for industrial safety, sampling systems had to available and be used when temperature exceeded 60°C and pressure 1 MPa(abs);
- Measurement inconsistencies were found between on-line instruments and laboratory analyses (i.e. lithium concentration in the RCS calculated from the on-line conductivity meter, and dissolved hydrogen determined with on-line chromatography downstream the sampling system degasser);
- Due to the unavailability of the boron recycle system evaporator, boron and demineralized water management had to be adapted to limit water consumption and boron discharge (in form of enriched boric acid). Temporary storage tanks may be considered for future reactors to ease boron discharge management;
- Minimizing air in-leakage (e.g. at water seals of some tanks), especially in the gaseous phase of systems with H_2/O_2 mixtures, and proper monitoring of those gaseous phases are crucial;
- Accurately assessing needs and securing consumable inventory to ensure enough filters and IXR are available.

Before storing the first fuel assemblies in the SFP, relevant systems[9] were filled with borated water. Then, total B and ^{10}B concentrations in these systems were analyzed to check for homogeneity at different depths in the pools and prevent local dilution. Impurities in the SFP water were also monitored and the water regularly purified.

Once HFT were completed with satisfactory results, fuel was loaded into the reactor core.

Other lessons learned from recent reactors commissioning include:

- Ensure sufficient qualified chemistry staff;
- Ensure redundancy for key chemistry analysers, to perform appropriate calibration and consistency checks between instruments (i.e. for dissolved H_2 measurement in different locations or for ICP-MS vs boron measurements with on on-line ^{10}B-meter and conversion into total boron concentration);
- Ensure availability of purification during the first fuel loading, as suspended solids may increase in the pools (SFP, reactor pit), to maintain water quality and visibility in the pools;
- Consider the needs for lithiated IXR to limit lithium consumption and to prevent pollution risk by saturating them on site;
- Avoid leakages between systems (i.e. from boron or water make-up system into the RCS), which may alter the required chemistry conditioning.

It is also recommended to perform some phases of HFT after core loading with appropriate chemical conditioning of the systems (i.e. $pH_{300°C} \approx 7.2$ and hydrogen injection into the RCS).

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[9] safety injection system, reactor heat removal system, in-containment refuelling water storage tank, boron recycle system, boron safety injection tank, boron make-up system.

2.8.2. Recent experience at Sanmen nuclear power plant

During HFT at Sanmen NPP, steps were implemented as follows:

- Start-up deoxygenation using the degasser;
- Adding lithium hydroxide, to achieve a target pH_T of 6.9–7.4;
- Adding hydrogen;
- Adding high concentration of zinc acetate (depleted in ^{64}Zn);
- Adding boric acid following the passivation phase;
- Adding hydrogen peroxide once temperature is below 82°C.

To determine the optimal zinc concentration, Sanmen NPP conducted lab tests on passivation of 316L and 690TT coupons under HFT conditions, measuring electrochemical impedance, electrochemical corrosion potential, and using scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). Finally, Sanmen-2 adopted a zinc concentration of 50–100 µg/kg during HFT, see Fig. 30.

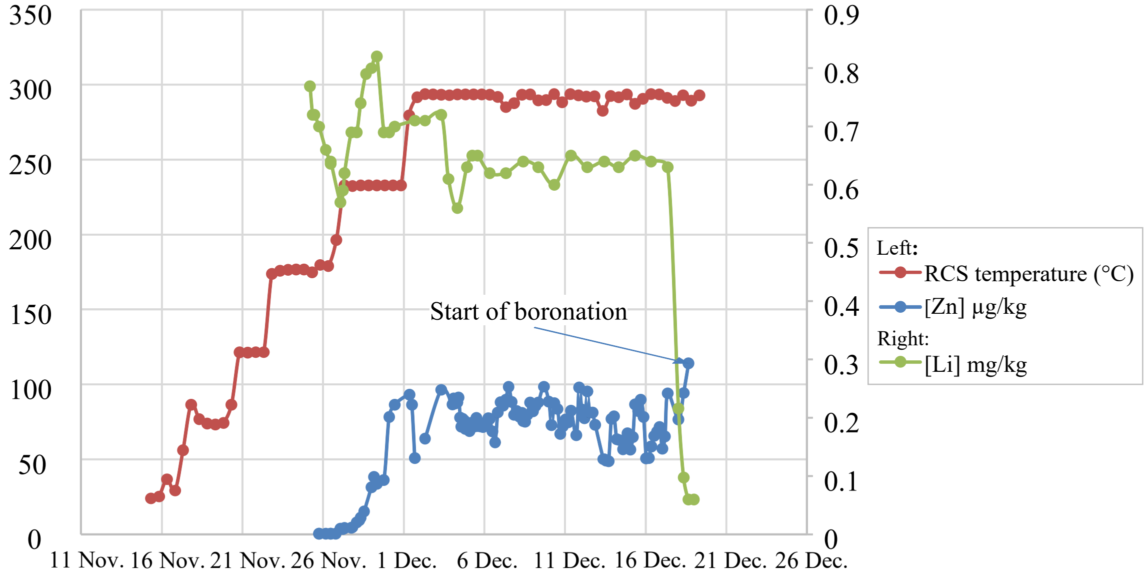

FIG. 30. Zinc concentration in Sanmen-2 RCS during HFT (courtesy of CNNP).

The biggest difference between passivation during HFT at Sanmen-2 and Sanmen-1 is the zinc concentration. Effectiveness of this increase is evidenced by comparing the collective dose and the magnitude of ^{58}Co activity peak for the first refueling outage at both units, Figs 31–32. The collective dose of the first refuelling outage at Sanmen-2 was 182.5 man.mSv (-50% compared with Sanmen-1) and the ^{58}Co activity peak was 11.8 GBq/m^3 (-87%). Note that experience with RCS chemistry during pre-core HFT at both Sanmen-1 and Haiyang-1 is presented in chapter 10.1 of Ref. [39].

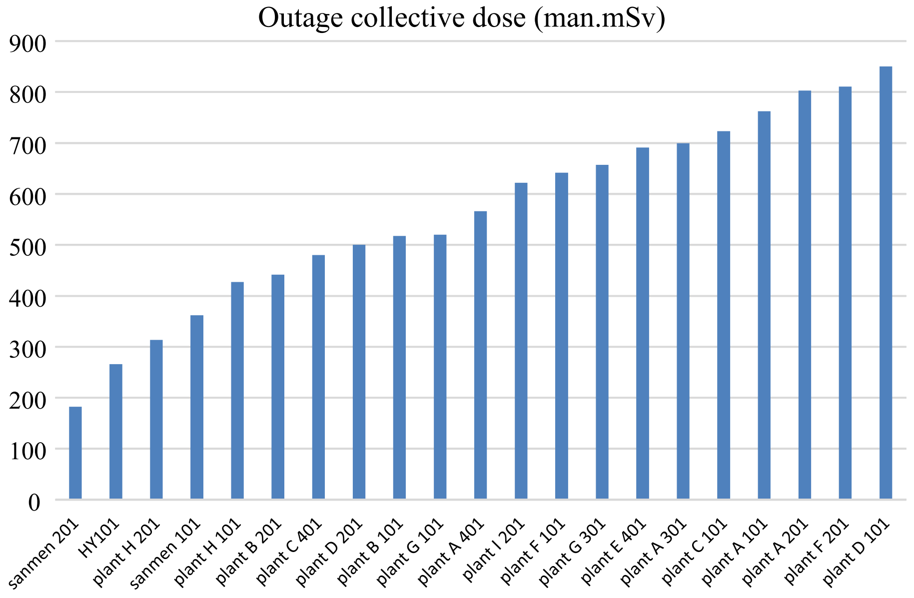

FIG. 31. Collective dose at the first refuelling outage of CNNP NPPs (courtesy of CNNP).

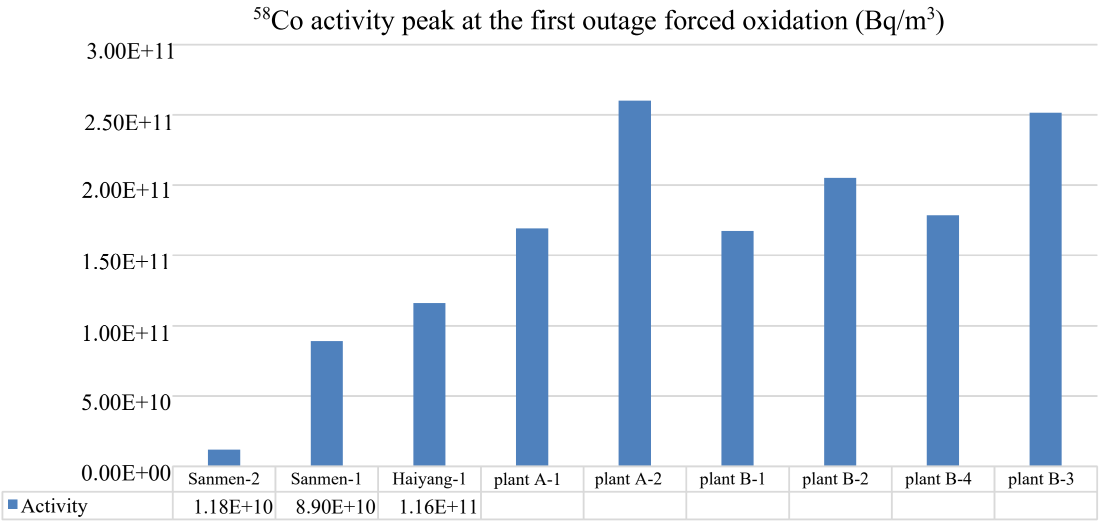

FIG. 32. ^{58}Co activity peak at the first refuelling outage oxidation at CNNP NPPs (courtesy of CNNP).

2.9. ADVANCES IN SIMULATION MODELLING

Modelling codes are used to estimate practically immeasurable high-temperature chemical properties at power aiding researchers and operating organizations in decisions related to water chemistry (e.g. optimal pH_T), operations (e.g. guidelines and technical specifications), and plant issues diagnosis (e.g. related to PWSCC, intergranular and transgranular SCC, deposits on nuclear fuel). These codes calculate the composition, pH, and electro-chemical (redox) potential of aqueous solutions at elevated temperature and pressure, and use thermodynamic equilibrium constants to determine the concentrations of aqueous species and the identities of precipitates. Code owners continuously refine the models – for example, EPRI plans to revise the model for ionization constant of water [90], for the boric acid to include a new activity coefficient model for neutral boric acid, and has updated the behaviour of silica and zinc [34].

For shutdown chemistry, codes are used for simulating surface contamination in RCS and specific radionuclides activity trends – such as predicting ^{110m}Ag, see Section 2.7.3. Another example is the use EPRI shutdown calculator to estimate clean-up time for RCS based on average ^{58}Co peak concentration over the fuel cycle. A study by Korea Hydro & Nuclear Power [91] confirmed the calculator's reliability to estimate clean-up time and that modelling can accurately support shutdown chemistry plans.

Other noticeable advances have been made in improving the OSCAR[10] code for simulating surface contamination in RCS. Developed by the French technical support organization CEA, in cooperation with EDF and the vendor Framatome, the code predicts the contamination of nuclear island systems by corrosion products, ACP, fission products, and actinides, at power and in shutdown. Initially developed for PWRs [92, 93], the code has also been used for decommissioning studies of WWERs [94].

The code considers chemical and physical mechanisms relevant to activity transfer across nuclear systems, such as corrosion, release, oxides formation, dissolution and precipitation, deposition and erosion, activation, decay, convection. It covers a wide range of conditions, including temperatures from 20°C up to 340°C, oxidizing to reducing conditions, and acid to alkaline conditions. The OSCAR code can simulate the life of a power plant (e.g. tens of operating cycles) and study transients on a second-by-second basis. The currently released version is OSCAR v1.4.a.

An OSCAR simulation begins by discretizing the systems in control volumes, each defined by its geometric, thermal, neutronic and hydraulic characteristics, and its base metal. Up to six different media can be defined in each control volume: the base metal, the inner oxide layer, the deposit/outer oxide layer, particles, ions (species in solution) and purification media. For each isotope (i) in each media (j), the mass balance Eq. (3) equation is solved.

$$\frac{\partial M_i^j}{\partial t} = \sum_{Sources} J_m - \sum_{Sinks} J_m + \dot{m_{in}} - \dot{m_{out}} \quad (3)$$

with M_i^j the mass of the isotope (i) in a given medium (j) in kg, t the time (s), $m_{in} - m_{out}$ the convection term (in kg.s^{-1}) and J_m the mass flux between two media (in kg.s^{-1}).

The OSCAR code uses comprehensive models to describe the numerous, complex interactions underlying activity transport. The deposition mechanism is crucial for activity build-up. Recently, as a non-negligible proportion of particles in the RCS of PWRs exists under colloidal size[11], a deposition model including surface interactions, which are predominant for the deposition of small particles/colloids over volume interactions, has been added [96]. The model uses the theory developed by Derjaguin, Landau, Vervey and Overbeek, Ref. [97], relying on the zeta potential of particles and surfaces to predict whether deposition occurs. The zeta potential, the potential at the slipping-plane of the particle in the fluid (i.e. the plane at the interface separating mobile fluid from fluid that remains attached to the surface), is often used as an approximation of the surface. The knowledge of the zeta potential values of the corrosion products generated in the primary system is required to compute the electrical double layer interaction and in turn the value of the potential barrier to overcome for deposition to happen.

Using this model and experimentally determined zeta potential values of typical corrosion products [98], OSCAR predicted contamination in a 1300 MWe PWR which underwent a SGR. One cycle after SGR, gamma spectrometry measurements with the EMECC device (described in Section 2.4.3) [54] showed a 10-fold higher ('preferential') ^{58}Co contamination in the crossover leg compared to the hot leg. This preferential contamination could not be reproduced with the previous model (v1.4.a) but was successfully replicated using the new deposition model considering surface interactions – see Fig. 33.

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[10] The acronym OSCAR stands for French 'outil de simulation de la contamination en réacteur', a tool for simulating contamination in reactors.
[11] See for example a comprehensive literature review on colloids in Ref. [95].

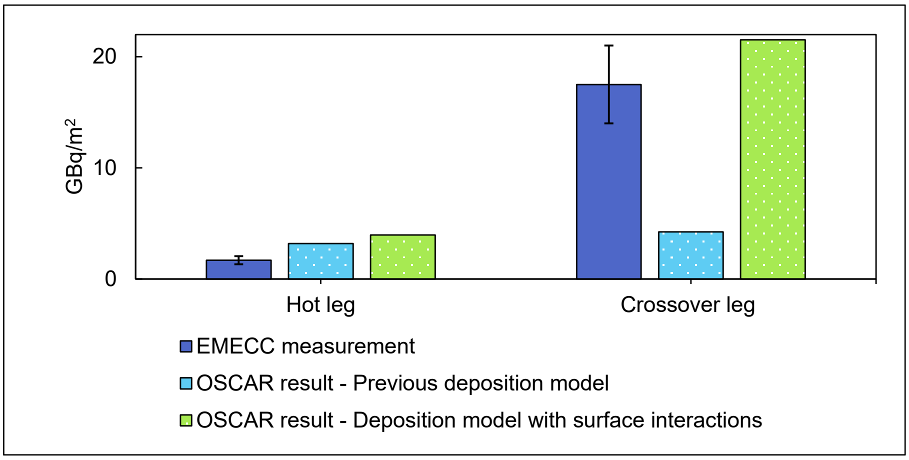

FIG. 33. Comparison of ^{58}Co surface activity measured with the EMECC device, calculated using the previous model (OSCAR v1.4.a) and calculated using the new deposition model considering surface interactions (courtesy of CEA).

3. SECONDARY SYSTEMS WATER CHEMISTRY

The main objectives of secondary systems water chemistry are to minimize corrosion, fouling, and materials degradation such as cracking. Secondary systems comprise various equipment – main steam pipes, moisture separator reheaters (MSR), turbines, condensers, feedwater reheaters and pipes, SG – made of different materials – carbon steels, low alloy carbon steels, stainless steels, cooper alloys, nickel-based alloys – operating at temperatures typically between 25–270°C in liquid and/or steam phases. Chemistry controls adopted at a NPP are specific to its materials, system features (incl. for purification and chemical additive injection), and operational conditions, often requiring a compromise.

Four key areas require attention from operating organizations:

- Cleanliness in the SG, especially in PWRs, to prevent tube degradation by impurities (e.g. sodium, sulphate, chloride, lead), tube support plate (TSP) clogging, and sludge deposition on top of the tube sheet (TTS) by iron particles, maintaining tube integrity and achieve high heat transfer – see chapter 4 of Ref. [99] for details;
- Minimization of flow accelerated corrosion (FAC) in carbon steel components in feedwater and main steam systems, to avoid wall-thinning that poses risk to workers' safety and equipment integrity – see chapter 4.5.4 of Ref. [99] for details;
- Fouling of equipment such as moisture separator reheaters and venturi nozzles in the feedwater system which affects the reliability of feedwater flowrate measurement;
- Impact of chemical additives and by-products on personnel health and the environment.

Hence, the typical measures operating organizations ought to consider are as follows:

- Achieve a high $pH_{25°C}$, as suspended iron and FAC decrease with increasing pH, and select appropriate alkalizing agents for that – Section 3.1 discusses background and developments in using amines like (mono)ethanolamine (ETA) as alkalizing agents, along with ammonia. This goes with accurate pH measurement and independent verification methods, such as ion chromatography or conductivity, associated with robust methods for calculating pH from conductivity or concentration data;

- Further minimize ferrous corrosion phenomena (formation/release of suspended iron from condenser up to feedwater that can redeposit on surfaces, especially in the SG) by:
  - Applying adequate lay-up and conditioning;
  - Protecting surfaces with film-forming substances (FFS) like octadecylamine (ODA) during shutdown/start-up – Section 3.2 covers advances and recent experience with FFS;
  - Considering oxygen injection in the water cycle (see chapter 5.3.2.1 of [99]) to favour the formation of a protective layer of hematite on surfaces, which, being much less soluble than magnetite, provides protection against FAC and minimizes iron transport to the SG;
- Remove ferrous corrosion products (Section 3.3) either by:
  - Mechanical filtration, including using magnets and magnetic traps to remove suspended forms from condenser to feedwater – Section 3.3.1 presents innovative upgrade of magnets in condensers;
  - Mechanically cleaning (incl. sludge-lancing) deposited forms, mainly from SG – Section 3.3.2 presents the development of SG lancing at a WWER and Section 3.3.3 presents advances in SG sludge characterization in PWRs – or using dispersants – Section 3.3.4 present experience with the use of polyacrylic acid as a dispersant;
- Inject hydrazine upstream of the SGs to scavenge dissolved oxygen (DO), maintaining reducing conditions to protect SG nickel-alloy tubes from intergranular attacks and SCC in PWRs. Hydrazine also decomposes into ammonia at temperature, supporting operation at high $pH_{25°C}$ – However, hydrazine poses personal safety and environment risks. Section 3.4 explores alternatives to hydrazine;
- Apply best techniques to minimize introduction of impurities (e.g. minimizing impurities from the demineralization plant) and remove them by chemical/ electrochemical filtration;
- Implement a comprehensive chemistry programme involving all NPP departments – Section 3.5 highlights good practices and attributes of an effective start-up chemistry programme.

As a reminder, general technical guidance for secondary chemistry control programmes is given in chapter 4 of Ref. [1] and in Ref. [2], not publicly available but made available to all WANO members. Detailed technical guidance is given in Refs [6], [99–102] and chapter 6.2.7 of Ref. [27], depending on the specific reactor design. Note that chapter I.C of Ref. [7] identifies the EPRI chemistry guidelines made available to all WANO members in 2002. Reference [103] offers a comprehensive review of corrosion control mechanisms in PWR SG.

3.1. DEVELOPMENTS IN THE USE OF AMINES TO CONTROL pH

This section presents developments in the use of amines (organic derivatives of ammonia) as volatile alkalinizing agents to control pH in the secondary systems of NPPs.

The most significant degradation mechanism in secondary systems' pipes is FAC. Carbon steels, especially with less than 0.1–0.15% Cr, are susceptible to FAC. Key factors contributing to FAC include materials composition, fluid velocity, temperature, and water chemistry – see chapter 4.5.4 of Ref. [99] for details. As FAC decreases with increasing pH, it is generally agreed that $pH_{25°C}$ ought to be maintained at 9.8 or higher in feedwater, with 10.0 being optimal. This reduces the transport of corrosion products, decreasing deposit accumulation in SG – see Section 3.3 for fleet performance on iron. Moving away from the original phosphate treatment, mostly in PWRs, or neutral treatment in some WWERs, and the solely use of ammonia (either added by injection or produced by thermal decomposition of injected hydrazine), operating organizations have tested and implemented various amines for achieving a high $pH_{25°C}$ strategy.

The selection of amines bears challenges. Amines decompose to organic acids elevated temperature, challenging high $pH_{25°C}$ and steam cation conductivity limits imposed by steam turbine vendors. Amines affect the performance of IXR – see Section 3.1.6 for further discussion. ETA has been widely selected by operating organizations. According to the EPRI database [29], ETA is the only amine used in 63% of the NPPs monitored by EPRI, and one of the amines used in 15% of other NPPs. In systems containing copper alloys and brass, typically the condenser tubes, the target $pH_{25°C}$ in feedwater is lower due to ammonia induced corrosion, and specific chemistry controls are applied.

ETA has a higher alkalinity than morpholine at the temperatures found in the secondary systems, requiring lower concentrations to reach the target $pH_{25°C}$. Additionally, as ETA is less volatile than morpholine and ammonia (due to having a lower distribution coefficients – see Fig. 38 in Section 3.2.1), a higher pH can be reached in the liquid phase throughout the water-steam cycle. Thus, using ETA improves FAC mitigation in specific parts of the secondary systems (two phase regions containing drains, and MSR) and performs as morpholine in feedwater low pressure reheaters. Furthermore, ETA is thermally more stable and generates fewer by-products compared to morpholine, which helps reduce discharges to the environment, chapter 11.1 of Ref. [39].

Sections 3.1.1 throughout 3.1.5 presents practices and recent experience with use of ETA at selected PWRs and one PHWR, with Table 3 providing an overview of applied amines and their concentration in the feedwater (this updates chapter 5.1.3 of Ref. [99] – note that ammonia is added in most strategies). Practices at 3 Eastern European WWERs are also briefly presented below, with Ref. [102] outlining practices and target concentrations at Russian WWERs.

TABLE 3. HYDRAZINE, AMMONIA AND AMINE CONCENTRATIONS IN THE FEEDWATER OF SECONDARY SYSTEMS AT SELECTED NUCLEAR POWER PLANTS

NPP	Target $pH_{25°C}$	Hydrazine (μg/kg)	Ammonia (mg/kg)	Morpholine (mg/kg)	ETA (mg/kg)
EDF with copper alloy	9.4	20	0.5	5–6	-
Bohunice	9.4	20	< 0.2	-	1–2
Koeberg	9.65	70–100	1–2 (added)	-	2.5–3.5
Qinshan-III	9.7	20-40	2–5 (added)	15–25	-
Paks	9.7	3–5	2–5 (added)	-	-
Daya Bay	9.7	50–100	2-5 (added)	-	2
Hanul-6	9.85	40–60	0.8–2.0	-	10
EDF without copper alloy	10.0	50–100	1.5 (added)	-	4

WWERs historically operated with ammonia-hydrazine chemistry, balancing ammonia concentration to suppress FAC and avoid corrosion in brass condensers and saturation of full-flow cation polishers. Some plants, like Dukovany and Temelín NPPs, had stainless steel or titanium heat exchange tubes, allowing higher ammonia concentrations and operating condenser polishers as needed. Other plants switched to ETA, like Bohunice (2007–08) and Mochovce (2011), to benefit from its distribution in liquid and two-phase flow, enabling the use of brass condensers and achieving high $pH_{25°C}$ across the water-steam cycle. Experience with ETA automatic dosing at Bohunice NPP is described in Section 5.1.6. Paks replaced brass with carbon steel over 2005–2008 and kept ammonia-hydrazine chemistry at high $pH_{25°C}$ (9.6–9.8). In 2022, hydrazine concentration was reduced from 20–25 μg/kg to 3–5 μg/kg, without change in the oxygen concentration.

3.1.1. Experience at EDF nuclear power plants

The target $pH_{25°C}$ in the SG feedwater is ≈ 10.0 (‘high pH’ strategy). However, in plants with copper alloys (mainly in the condenser), the target $pH_{25°C}$ is set to 9.4 (‘low pH’) due to ammonia induced corrosion in copper alloys. When equipment containing copper alloys will be replaced, all plants will increase $pH_{25°C}$ to 10.0. Reaching the optimum pH requires the addition of a volatile amine (to date, morpholine for low pH treatment or preferably ethanolamine for high pH treatment) and ammonia.

Details of the two strategies applied in the feedwater of French NPPs are as follows:

- Low pH strategy: 5–6 mg/kg morpholine, 0.5 mg/kg ammonia and 20 µg/kg hydrazine;
- high pH strategy: 4 mg/kg ETA, 1.5 mg/kg ammonia and 50–100 µg/kg hydrazine.

Operating experience across EDF fleet showed that NPPs struggle to reach and maintain the target $pH_{25^\circ C}$ at 10.0 in the secondary system, because they have trouble achieving 1.5 mg/kg ammonia. Ammonia is generated in the secondary system through the thermal degradation of hydrazine, but a significant part leaves the secondary system with the steam from the SG. To keep ammonia at the highest, ammonia is either recycled from the condenser vacuum system (also leading to decreasing discharges of ammonia to the environment) or injected under a concentrated form.

3.1.2. Experience at Daya Bay nuclear power plant

As Daya Bay NPP faced challenges to achieve a stable high pH, ETA and ammonia for conditioning the secondary systems were selected. The adopted strategy is to dose ETA in the feedwater at 2.0–2.5 mg/kg. Similarly, the $pH_{25^\circ C}$ in the feedwater is maintained at 9.73±0.05, within the range set in the chemical technical specifications at 9.6–9.8.

Key findings following the implementation of the new conditioning strategy included:

- The $pH_{25^\circ C}$ in the MSR drains increased from ≈9.4 to more than 9.8. This led to decreasing average iron by ≈60% (from 3.5 µg/kg to 1.5 µg/kg);
- Average suspended iron in the main feedwater decreased by 20% (from 1.9 µg/kg to 1.5 µg/kg);
- ETA consumption is ≈ 1.2 t/year, while ammonia consumption decreased from 30 to 20 t/year.

3.1.3. Experience at Qinshan-III nuclear power plant

The plant initially selected morpholine as the alkalizing agent [104]. Recognizing morpholine's reduced alkalinity at lower temperatures, it was then supplemented with ammonia. Since hydrazine decomposes into ammonia, adding ammonia did not introduce a new amine. Morpholine concentrations were tested with the purpose of achieving a difference between pH_T and the neutral at-temperature pH (pH_{Tn}) – noted ΔpH_T – above 1.0 across the entire temperature range in the secondary systems.

Table 4 shows calculated ΔpH_T values at various locations at operational temperatures against morpholine concentrations, while maintaining the $pH_{25^\circ C}$ in feedwater at 9.7 with an ammonia concentration of 3 mg/kg.

TABLE 4. CALCULATED ΔPH_T IN THE SECONDARY SYSTEMS AT QINSHAN-III AGAINST MORPHOLINE CONCENTRATION

	Location and temperature	Condenser (39°C)	Deaerator (138°C)	Final feedwater (187°C)	SG (261°C)	High pressure drain (142°C)	MSR drain (167°C)	First MSR drain (200°C)	Second MSR drain (234°C)
Morpholine	5 mg/kg	2.49	1.47	1.13	0.54	1.44	1.03	1.01	0.84
	10 mg/kg	2.55	1.51	1.18	0.63	1.48	1.14	1.06	0.89
	15 mg/kg	2.56	1.54	1.21	0.69	1.51	1.22	1.11	0.93
	20 mg/kg	2.58	1.57	1.25	0.74	1.54	1.27	1.14	0.97
	25 mg/kg	2.59	1.59	1.27	0.78	1.57	1.32	1.17	1.00
	30 mg/kg	2.60	1.61	1.29	0.82	1.59	1.36	1.20	1.02

It is observed that for morpholine concentration above 15 mg/kg, the ΔpH_T increment was marginal, indicating minimal pH_T enhancement with further increases in morpholine. These calculations show that, with an ammonia concentration of 3 mg/kg, a morpholine concentration of 15–25 mg/kg is generally sufficient to maintain the liquid phase ΔpH_T above 1.0 throughout the secondary systems, except in the SGs. Despite the lower ΔpH_T in SGBD system and considering the minor proportion of carbon steel surfaces on the secondary side of the SG relative to the whole secondary systems, the plant retained a morpholine concentration of 15–25 mg/kg and an ammonia concentration of 2–5 mg/kg.

As a result of the strategy, the total iron in SG final feedwater, measured using integrated sampling on a 0.45 µm filter membrane followed by a cation exchange membrane, has decreased from 3–4 µg/kg to 0.2–0.6 µg/kg from 2017, averaging 0.4 µg/kg.

3.1.4. Experience at Hanul-6 nuclear power plant

Hanul-6 experienced a slight decrease in power output due to the fouling of the feedwater venturi nozzles, related to an increase of iron oxide in the secondary systems. While pursuing operation at high pH, Hanual-6 applied amine form operation with ETA and hydrazine (same as amine breakdown operation or amine saturation cycle) with a condensate polishing system (CSP) (see Fig. 34) in 2022.

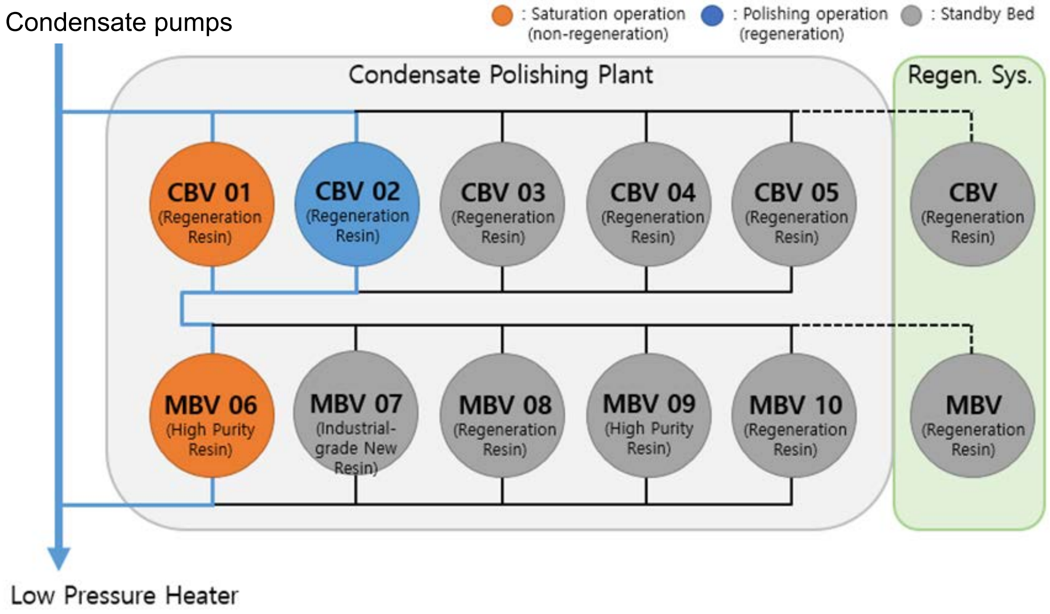

FIG. 34. Condenser polishing plant diagram in amine form operation at Hanul-6 (courtesy of KHNP)

Six representative points were selected for water quality analysis in consideration of various environmental conditions, and behaviours of chemical parameters such as iron, pH, total conductivity and chemical additive concentration (ETA, ammonia from decomposition, hydrazine) were evaluated.

The pH in feedwater was risen to 9.85 and then maintained stable at 9.8–9.9, while the iron concentration has decreased and stabilized to 1–1.5 µg/kg (see Fig. 35). Impurities concentration (sodium, chloride, sulphate) in the SG was also kept stable within the target value.

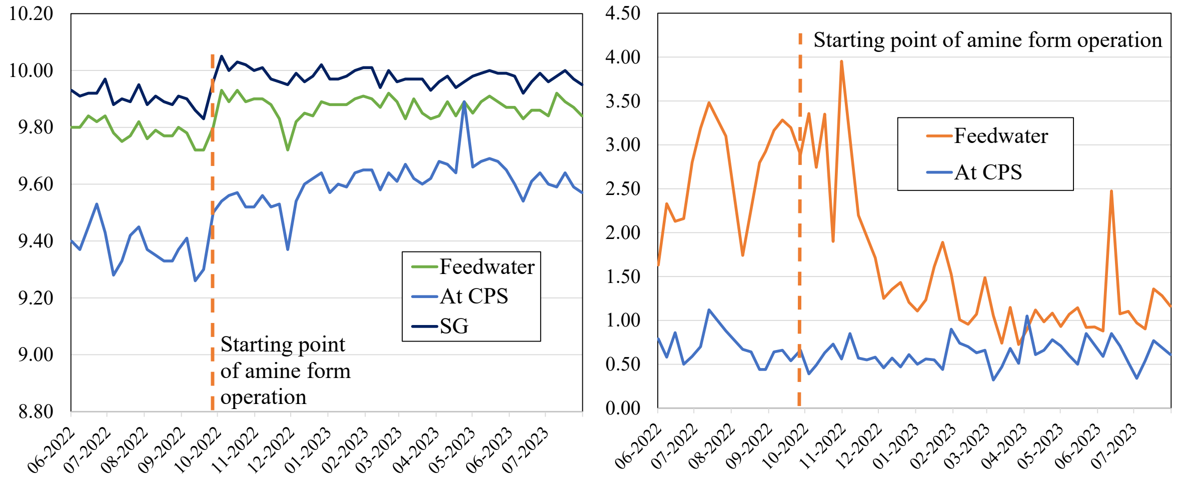

FIG. 35. pH$_{25°C}$ (left) and iron concentration in µg/kg (right) after introduction of the amine form operation at Hanul-6 (courtesy of KHNP).

ETA was slightly increased, and decomposition by-products (max concentration of organic acids: acetate 84 µg/kg, glycolate 9 µg/kg, formate 4 µg/kg) also increased (see Fig. 36), which increases cation conductivity. Some turbine manufacturers are sensitive to the possibility of corrosion caused by organic acids, where the technical review conducted by EPRI [105] confirmed there is no impact.

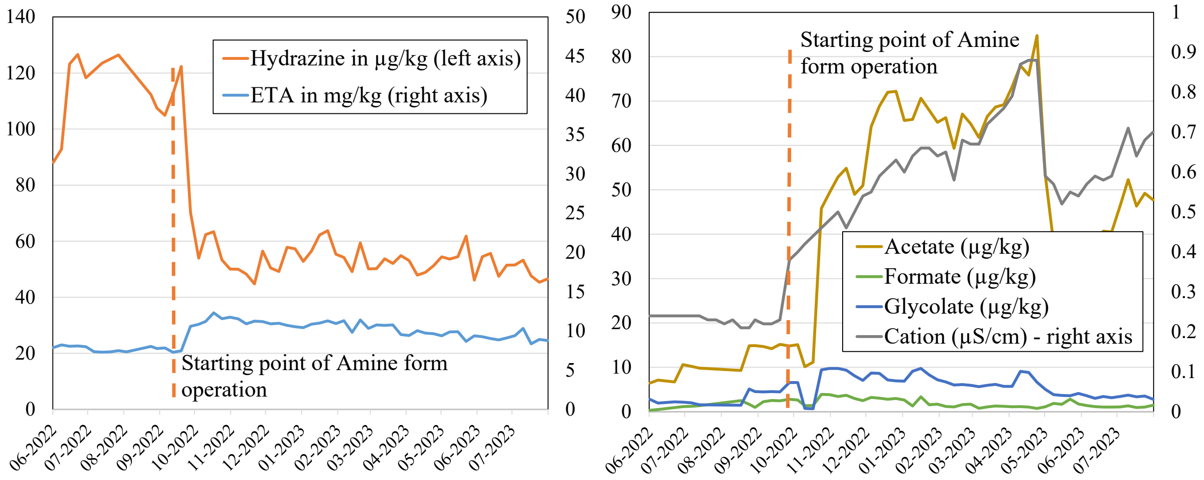

FIG. 36. Hydrazine, ETA in feedwater (left graph), organic acids and cation conductivity in SG#1 (right) after introduction of the amine form operation at Hanul-6 (courtesy of KHNP).

As a result of the new operation mode, consumption of regenerative chemicals (sulphuric acid, sodium hydroxide) has significantly dropped by 86% due to a decrease in the number of resin regenerations. Consumption of ETA has also been reduced by 79% – see Table 5.

TABLE 5. COMPARISON OF THE PERFORMANCE BEFORE AND AFTER AMINE FORM OPERATION AT HANUL-6 (FIGURES FOR 4 MONTHS)

		Before	After	Decrease
Cation resin regeneration (number and volume in m^3)	Number of sequences	24	5	-79%
	Wastewater discharge	4408	678	-85%
	Sulfuric acid	25.1	3.5	-86%
	Sodium hydroxide	27.6	3.8	-86%
Chemical consumption (t)	ETA	19.9	4.1	-79%
	Hydrazine hydrate	7.9	3.5	-56%

3.1.5. Experience at Koeberg nuclear power plant

During 2000–2001 (fuel cycle 12 for unit 1), both units of Koeberg NPP commenced advanced amine treatment by injecting ETA into the feedwater. In 2013 (fuel cycle 20 for unit 1), this regime was optimized according to Koeberg operating experience and international practices [106]. The resulting chemistry feedwater specifications are summarized in Table 6.

TABLE 6. KOEBERG FW CHEMISTRY SPECIFICATIONS USING ETA REGIME

Parameter	Units	Target value	Limit value	Analysis frequency
$\text{pH}_{25^\circ\text{C}}$	-	9.65	9.5–9.9	Continuous
Dissolved oxygen	µg/kg	< 1.0	< 5.0	Continuous
Hydrazine	µg/kg	70–100	> 20 or > 8 x FW $[DissO_2]$	Continuous
Turbidity	NTU	< 0.20	< 0.30	1 every week
Ethanolamine	mg/kg	2.5–3.5	2–4	1 every week
Ammonia	mg/kg	1.0–2.0		1 every week
Conductivity at 25°C	µS/cm	9.0–12.0		Continuous
steam generator blowdown /feedwater hydrazine ratio	-	> 1.0		1 every week
Cation conductivity at 25°C	µS/cm	< 0.20		Continuous
Total iron	µg/kg	< 3.0	< 5.0	1 every week
Total copper	µg/kg	< 0.2		1 every week
Suspended solids	µg/kg	< 10		1 every month

The corrosion product transport has reduced since implementing the ETA regime. Feedwater iron results are typically < 2.5 µg/kg and sludge removed from steam generators is reduced to around 20 kg after 18-month fuel cycles in unit 2 (see Fig. 37) compared with 60–80 kg in the earlier fuel cycles. Note that Koeberg operated with its original Inconel 600 MA SGs (only one SG on unit 1 had thermally treated alloy) until end of cycle 25, in 2022 for unit 1.

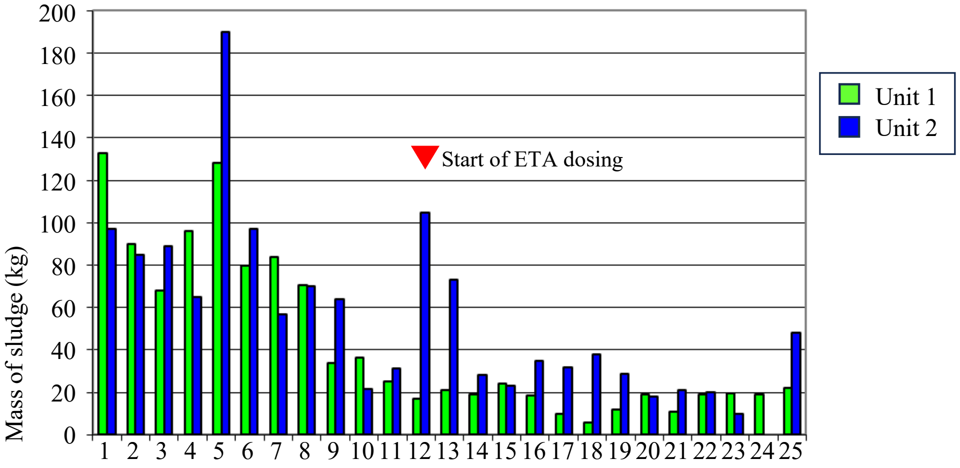

FIG. 37. Sludge mass removed at outage sludge lancing since the first fuel cycle of Koeberg NPP, where ETA dosing started in the 12th fuel cycle (courtesy of Eskom).

In 2011, Koeberg studied the distribution of ETA throughout the secondary systems and performed an organic profile which included breakdown products of ETA and natural organic matter from contamination from make-up water including total organic carbon (TOC) [107]. Chemical analysis methods were developed for ETA breakdown products as organic acids by ion chromatography. The analysis method could determine the inorganic anions fluoride, chloride, nitrite, sulphate, bromide, nitrate, and phosphate along with the organic anions glycolate, acetate, formate and oxalate. Table 7 presents the results. For both units, the CPS was on bypass, and the SGBD flowrate at 40 m^3/h.

TABLE 7. ORGANIC PROFILE THROUGHOUT THE SECONDARY SYSTEMS OF KOEBERG NUCLEAR POWER PLANT IN ETA REGIME

	Unit 1 (99.46 % reactor power and feedwater flow at 5,600 m3/h)			Unit 2 (99.49 % reactor power and feedwater flow at 5,350 m3/h)		
Sample Point	ETA (mg/kg)	Carbon from ETA (mg/kg)	TOC (mg/kg)	ETA (mg/kg)	Carbon from ETA (mg/kg)	TOC (mg/kg)
Condenser extraction	2.173	0.854	1.430	3.010	1.183	1.510
SG feedwater system	3.885	0.1527	2.420	5.200	2.044	2.580
Drains recovery system	6.587	0.2589	4.570	9.240	3.631	4.940
SGBD system	7.113	0.2795	5.843	9.840	3.867	5.740

Most of the carbon in solution is from ETA. The balance is the ETA breakdown products and organic matter added via the secondary make-up system.

3.1.6. Discussion of challenges and strategies for secondary systems purification with ion exchange resins

Two types of purification treatments are usually applied in the secondary systems:

- Mechanical filtration to remove insoluble particles;
- Chemical treatments with IXR (widely used) or electrochemical treatment with technologies such as electrodeionization (see Section 4.3.1 for experience at Ringhals-2 NPP).

Two options for designing IXR filtration systems can be adopted, either with systems like CPS (capacity at ≈50% of the feedwater flowrate) and/or with SGBD demineralizers (capacity at ≈1–3% of the feedwater). Both solutions ought to be highly reliable and available, not adding pollution risks.

When operating at elevated pH in the secondary systems (for example after switching to ETA), impurity removal capacity is reduced in the IXR. Since the pH alkalizing agents injected into the systems form cations, IXR capture them, affecting exchange capacity for other cations, depending on cationic affinity of resins as follows: $NH_4^+ > Na^+ > ETA > H^+$. Regeneration cycles or resin replacements are subsequently more frequent, increasing waste.

For example, EDF NPPs that switched to ETA increased SGBD system resin replacement frequency from every 9–12 months to every 5–7 months. Krško NPP replaces SGBD IXR when Na^+ concentration is above 0.8 µm/kg, thus every 7–8 months under normal operating conditions. This occasionally led NPPs to maintaining pH at 9.6–9.7 below the target of 9.8–10.0. Details on impurity control are provided in chapter 4.1.5.1.3 of Ref. [99].

Two strategies for saturating/regenerating IXR apply. The first one is to regenerate the cation resins when they are saturated by the alkalizing agents (this supports very low levels of impurities as sodium). When ammonia is used as an alkalizing agent, SGBD resins regeneration is inevitable[12]. The second strategy is to operate IXR saturated with the alkalizing agent to increase the lifespan of cationic resins. This required impurity concentrations to be low (thus no condenser tube leaks). Further details are provided in chapter 5.3.3.3 of Ref. [99].

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[12] It is worth noting that Qinshan-II NPP modified the SGBD purification to connect it to their CPS (of much larger IX capacity), where the SGBD purification is only operated in case of emergency.

Having a permanent (not mobile) CPS is a decision to be made at the design stage, potentially informed by cost-benefit assessment. For recent new builds, with improved materials and monitoring capacity in the secondary systems, CPS may be operated in intermittence (and thus designed to a lower capacity than for continuous operation). Continuous operation would increase consumption of chemicals and regeneration cycles, potentially degrading chemical conditions at times (due to pollution risk by the resins themselves or regeneration chemicals, and the elution of species such as Na from the resins). Intermittent operation occurs in a case of pollution at power or to swiftly remove impurities after outages (this is Krško NPP practice). CPS can also be a mobile system, connected when needed. Whatever the solution adopted, the capacity should be just considering the recent progress in condenser tube tightness and condenser leaks detection methods. Further details are provided in chapter 5.3.3.2 of Ref. [99].

3.2. ADVANCES IN THE PROTECTION OF SURFACES WITH FILM-FORMING SUBSTANCES

Film forming substances (FFS) have been referenced in the literature as both chemical substances with specific hydrophobic film forming properties and commercial products containing these chemicals. Historically, all FFS were called film forming amines regardless of whether they were amine-based or not. To avoid confusion, the International Association of Properties of Water and Steam's standardized classification from Ref. [108] is used in this section.

Section 3.2.1 outlines the properties and benefits of FFS. Sections 3.2.2 and 3.2.3 discuss the application of ODA at Krško NPP (a PWR) and two WWERs, Paks and Armenian NPP. WWERs have more extensive experience with ODA than most PWRs. FFS applications in PWR and PHWR include Embalse, Almaraz-1 – see a detailed presentation of the experience at both units in chapter 2.3 of Ref. [39], Bruce Power NPP, Blayais-1 [109], and Borssele.

3.2.1. Background

The transport of corrosion products and impurities, along with hardening substances (mainly silicate), poses a high risk of hard sludge formation on the top of tube sheet of SGs. This can lead to degradation like denting and outer-diameter SCC on affected tubes. The surface molecular film created by FFS affects corrosion susceptibility of the metal or metal oxide by altering anodic (oxidative) or cathodic (reductive) reactions involved in corrosion. A positive side effect is the mobilization of existing deposits. Even small quantities of FFS affect the structure and hydrodynamic cavitation characteristics of two-phase flows, as well as heat and mass transfer from/to the inner surfaces of the water-steam cycle. The adherent non-wettable film acts as a shield, limiting access of water and hydrated species to the metal or metal oxide surface. This barrier lowers the corrosion rate by cancelling the mass transfer to and from the surface. The film also reduces oxide dissolution and re-precipitation by coating every particle [110].

FFS are corrosion inhibitors added to water. Therefore, most use cases in NPPs are related to improving lay-up conditions, especially in extended refurbishment outages. The main concern is their thermal stability at high temperatures, and the risk of decomposition into low molecular weight organic acids which may exceed the steam cation conductivity limits set by steam turbine vendors [111].

The selected FFS ought to have sufficient volatility to ensure efficiency throughout the water-steam cycle, in both liquid and steam phases, as well as in two-phase regions. Figure 38 shows the distribution coefficients K_d (right) and dissociation constants K_b (left) of selected amines and FFS as a function of temperature. The uncertainty of K_d values of FFS at low temperatures is high due to changes in the physical properties of the solution caused by aggregate formation and the solid state of the FFS [110].

Literature shows that ODA, a long-chained saturated alkyl amine, is used in the power industry. In NPPs, the commercial product ODACON® F, a stable aqueous emulsion containing 5% by mass film amine (hydrogenated and distilled tallow amine), mainly consisting of ODA and hexadecylamine, is used. The emulsion is stable without emulsifiers and mixes easily with demineralized water.

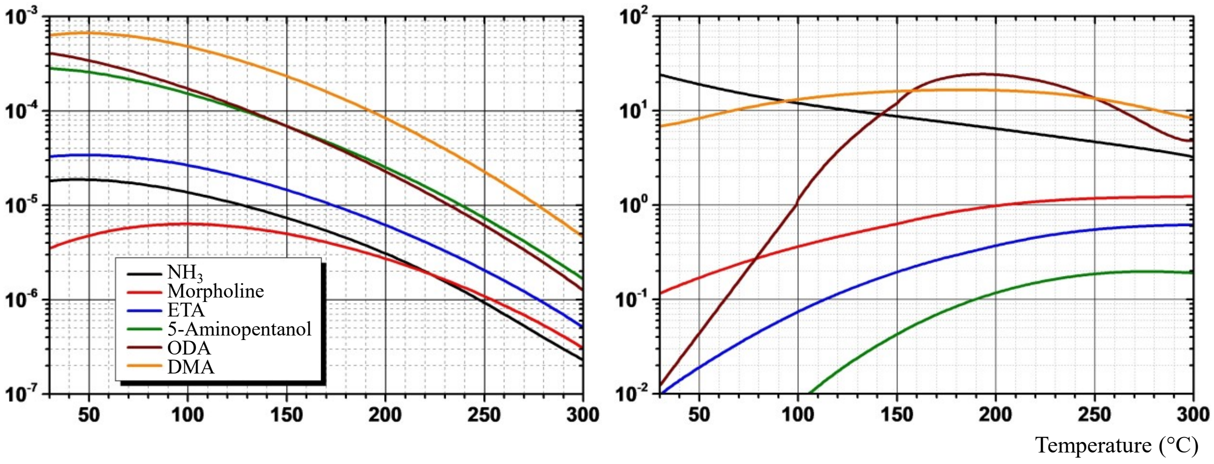

FIG. 38. Dissociation constants K_b (left) and distribution coefficients K_d (right) for different amines as a function of temperature (reproduced from Ref. [110] with permission).

Research on ODA [111] revealed the following:

- The main factors influencing ODA decomposition in secondary systems are temperature, residence time, initial ODA concentration, and applied water chemistry (conditioning);
- ODA starts forming di- and tri-ODA at ≈80°C, with complete decomposition above 450°C;
- Decomposition products, besides di- and tri-ODA, include ammonia, hydrogen, methane, carbon monoxide, hydrocarbons, but no acetic acid or other low molecular weight organic acids;
- ODA does not harm the structural materials of the secondary systems.

For reference, EPRI qualification programme is detailed in chapter 2.1 of Ref. [39].

3.2.2. Application at Krško nuclear power plant

The application at Krško NPP before the 2021 outage aimed at reducing the release and transport of particulate iron and iron oxides (hematite) from carbon steel throughout the secondary systems, where the mass balance at Krško NPP, based on the integral sampling of the secondary systems media, shows that ≈75% of the iron mass flow is measured at the outlet of the condenser, comparable to other PWRs. The NPP applies high all volatile treatment, using hydrazine and ammonia. The $pH_{25°C}$ in feedwater is specified at ≥9.80 and maintained in practice close to 10.

An external contractor with experience in similar applications at other PWRs was engaged. A feasibility study reviewed plant systems, construction materials, chemical specifications, and the chemical laboratory's analytical capabilities. It also included a review of previous FFS applications, impact assessments on non-destructive examination techniques, on-line chemistry monitoring equipment, and environmental considerations, with benchmarking at a comparable plant.

The subsequent adaptation study covered:

- Equipment set-up and dosing strategy;
- Update of the chemistry evaluation;
- Chemistry control and supervision programme;
- Interruption criteria and contingency plan;
- Analytical method for FFS determination.

The FFS application was conducted approximately four weeks before the 2021outage. ODACON®F was dosed into the condensate system over 17 days with some interruptions. The injection skid (Fig. 39), was designed and constructed following contractor recommendations and practices from other NPPs.

Krško NPP has a comprehensive on-line monitoring system, with several analysers for monitoring dissolved oxygen, hydrazine, pH, sodium, silica, redox potential, and cationic, degassed and specific conductivities. Due to the influence of FFS on measurement systems, most analysers were bypassed during application, presenting challenges for monitoring. Laboratory staff increased sampling and chemical parameters determination using portable devices also used in normal operation (ICP optical emission spectroscopy, high pressure ion chromatography, ultraviolet and visible light spectroscopy).

FIG. 39. FFS injection skid at Krško NPP, side view touch control panel (courtesy of NEK).

Figure 40 shows the concentration of ODA measured during application, with a maximum of 600 µg/kg in the feedwater system. The application of FFS coincided with a slight decrease (≈0.3°C) in reactor coolant average temperature at 100 % reactor power, resulting in slightly lower production. The calculation uses feedwater flowrate, measured by venturi nozzles. An assumption was made that FFS impacted the venturi nozzles – pending further investigations.

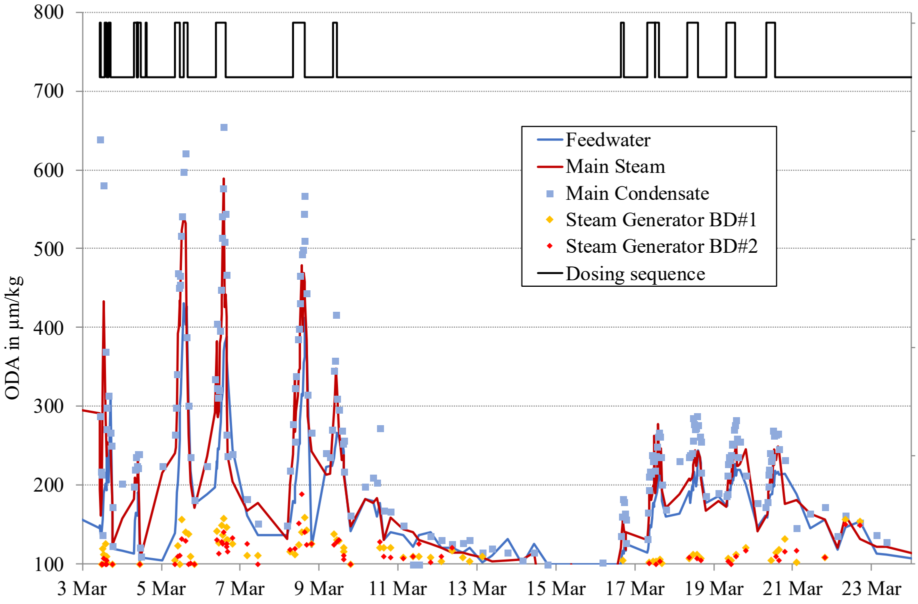

FIG. 40. Evolution of ODA concentration (above a lower limit of detection of 100 µg/kg) at different locations during its application at Krško NPP in 2021 (courtesy of NEK).

After the FFS application, visual inspections confirmed hydrophobic film formation on components such condenser, MSR and several heat exchangers (see Figs 41–43). The surfaces were cleaner and dry.

FIG. 41. Visual inspection of condenser, with support structure damaged due to corrosion and hematite layer with minor indications of rust on the upper support structure, after the application of FFS at Krško NPP (courtesy of NEK).

FIG. 42. Visual inspection of condenser internals showing water beading effect, after the application of FFS at Krško NPP (courtesy of NEK).

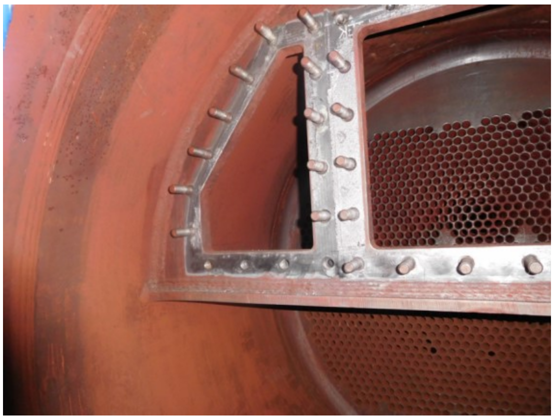

FIG. 43. Visual inspection of a heat exchanger after the application of FFS at Krško NPP, showing a hematite layer without sludge or precipitations (courtesy of NEK).

A significantly lower iron concentration was measured at the beginning of 32nd cycle (following FFS application). The ingress of particulate iron into SG was reduced (Figs 44–45). Under comparable conditions, the mass of removed magnetite by sludge lancing and inner bundle lancing decreased by 55%, at the first outage after FFS application, and was still 33% lower than at pre-application in the second outage.

In drained and emptied areas, oxygen may react with surfaces if the relative humidity in the systems is not kept below 30–40 %. This can occur from the very beginning of the shutdown, so corrosion protection ought to begin as early as possible. Using a steam-volatile FFS can effectively protect the main parts of the water-steam cycle against corrosion during shutdown. Injecting FFS before shutdown help covering most of the internal surfaces with a protective layer that remains stable during shutdown, whether or not the system is filled with water [108].

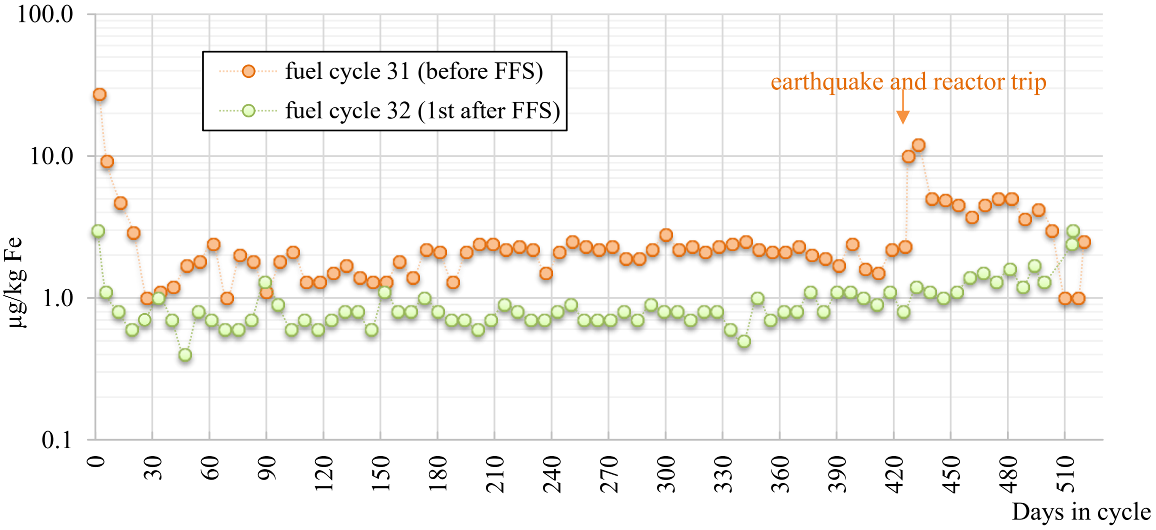

FIG. 44. Iron (>0,45 µm) concentration in feedwater, over the fuel cycle before and after FFS application at Krško NPP (courtesy of NEK).

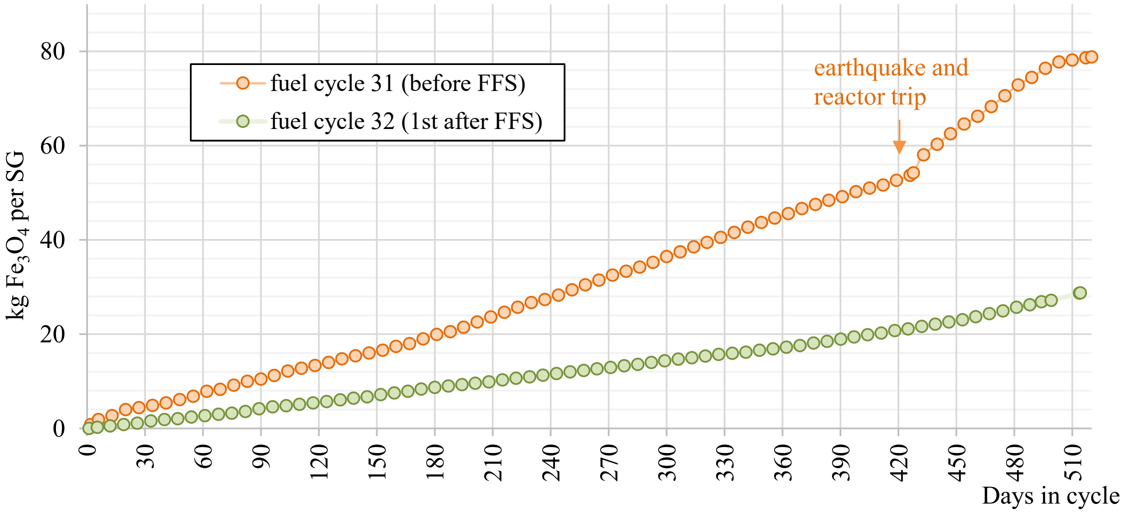

FIG. 45. Deposition of magnetite in steam generators, over the fuel cycle before and after FFS application at Krško NPP (courtesy of NEK).

An additional benefit was a reduction in hydrazine consumption for SG wet lay-up in subsequent outages (as confirmed by Almaraz and Borssele NPPs).

3.2.3. Application at two water-water energetic reactors

Paks NPP has used a 2% ODA emulsion since 1987. It is applied in shutdown between 135–150°C. After an 8-hour conservation period, the system cools to 40°C, and the ODA solution is drained. ODA is non-volatile, only working on equipment in water phase at this temperature. Challenges include residual ODA deposit in heat exchangers and compensator. The ion-exchangers of the CPS are also covered with ODA and are cleaned with NaOH in the regeneration column. At the Armenian NPP, ODA has been used since 1989 to protect unit 2 secondary systems. The application is carried out 10 days before shutdown in 3 stages over 84 hours, gradually increasing concentration from 200 to 1,200 µg/kg. This gradual increase and the duration of the application prevent deposition of ODA residues in equipment and small-diameter pipes, and avoid forming a film on IXR.

3.3. INNOVATION AND DEVELOPMENTS IN THE REMOVAL OF CORROSION PRODUCTS

There were efforts to reduce corrosion product transports across the NPP fleet that, for example, translated since 2000s in the PWR fleet monitored by EPRI by a 50% decrease of feedwater iron concentration medians to 0.6 µg/kg, Ref. [29]. However, ferrous corrosion products still deposit on surfaces, resulting in fouling, typically in SG, MSR and feedwater venturi nozzles. In SGs, the corrosion products, mainly magnetite but also other species[13], form sludge that quickly hardens under secondary side conditions. Impurities which concentrate in SG sludge and deposits contribute to pitting, TTS-denting, intergranular attack, and SCC. Corrosion product deposition on SG tube bundle ('scale') and at tube-tube support plate (TSP) intersections reduce heat transfer and lead to flow oscillations, see chapter 4 in Ref. [99], Ref. [100], and Section 3.6 on the use of a digital twin for modelling these effects.

Several techniques are available to remove these metal oxides and sludge from the secondary systems and especially from SGs:

- Capture of suspended iron by magnets and magnetic traps – Section 3.3.1 presents innovative upgrade of magnets in condensers at Chinese NPPs.
- Filtration.
- Mechanical cleaning (incl. lancing). Regarding SGs, five processes are described in chapter 5.4.2 of Ref. [99]. Along with periodic tube inspections (visual) to control the accumulation of deposits and their effects, this is the most effective measures to remove deposits on a routine basis. It consists in removing deposits from the tube sheet, the bundle or tube plates by hydraulic impact using remotely operated manipulators or static lances with high pressure water jet. Section 3.3.2 presents the first-of-a-kind SG lancing at a WWER.
- Chemical cleaning. Regarding SGs, seven processes are described in chapter 5.4.3 of Ref. [99]. Chemical cleanings are the only technique available that provides significant, immediate, and visually observable SG deposit modification and/or removal, including tube-scale and other types of deposits.
- Use of dispersants – Section 3.3.4 presents experience with the use of polyacrylic acid as a dispersant.

3.3.1. Innovative magnetic filters in condensers at Chinese nuclear power plants

Over the past decade, a significant development area at Chinese NPPs has been the enhancement of magnetic filters (Fig. 46), aimed at more effective capture of ferromagnetic and paramagnetic iron corrosion products. The corrosion products removed by magnetic filters with permanent magnetism are

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[13] Such as iron oxides, iron, silicon dioxide, lead oxide, copper and copper oxides as particles; sodium, chloride, aluminates, and sulphates as ionic species and organics; silicic acid/ colloidal silica and gases as soluble species.

ferromagnetic Fe_3O_4 and Y-Fe_2O_3, and paramagnetic α-Fe_2O3 and iron in colloidal form. Magnetic filters were sometimes installed as part of the condenser equipment or the feedwater lines downstream the high-pressure heaters, in the early industry design – see Ref. [112] for a review published in 1978.

Magnetic filters were installed around the water outlet of condenser hot well at Qinshan-III NPP [104]. The condensate passes through the magnetic filters before leaving the hot well so that the corrosion products in the water are adsorbed by the magnet – Fig. 46 – especially during start-up. The magnetic filters also act as pre-filters for the CPS and therefore reduce the demand to CPS. At each outage, the corrosion products are removed from the filters, see before/after pictures in Fig. 47. The mass of corrosion products collected is typically 6–9 kg/unit after 24 months of operation (mass dried at 105–110°C). Chemical analysis shows that the corrosion products are mainly iron oxides, with iron at 55% to 66%. Considering the quantities removed, the risk of excessive buildup and sudden release was assessed to be low.

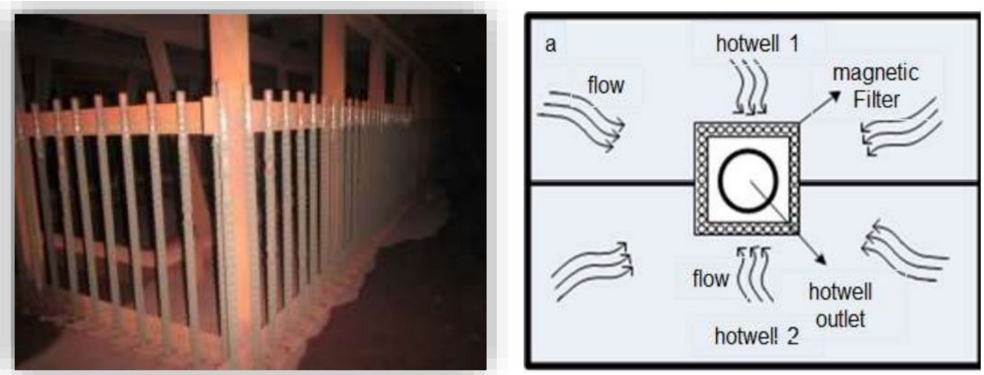

FIG. 46. Installation diagram of magnetic filters in a condenser at Qinshan-III (courtesy of CNNP)

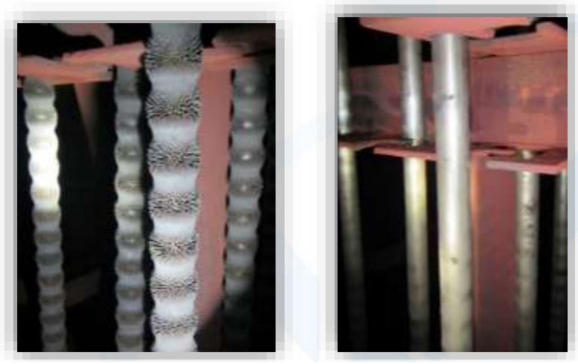

FIG. 47. Comparison before and after the corrosion product cleaned in a condenser at Qinshan-III NPP (courtesy of CNNP).

At Daya Bay NPP, horseshoe magnet filters were installed in main condenser hot wells at construction, Fig. 48. The original filters were designed mainly to adsorb corrosion products in the condenser to protect the condensate pump flow-through section but not to minimize the transmission of corrosion products to the SG, using AlNiCo magnetic material. New filters, made of $Nd_2Fe_{14}B$, were installed in 2005 and tested until 2010. Differences of characteristics are presented in Table 8 and differences in layout are presented in Figs 48–49.

TABLE 8. CHARACTERISTICS OF CONDENSER MAGNETS IN THE ORIGINAL VS. NEW DESIGN

Parameter	Original design	Modified design
Magnetic material	AlNiCo	$Nd_2Fe_{14}B$
Time of development	1930s	1980s
Magnetic remanence[14]	Br = 0.6–1.4 T	Br = 1.0–1.4 T
Maximum energy product[15]	BH_{max} = 10–80 kJ/m^3	BH_{max} = 240–400 kJ/m^3
Stability at temperature	Maintains magnetic properties up to 500°C or more	Performance drops noticeably at temperatures above 80°C
Construct of installed filters	Horseshoe shaped magnet blocks	Modular tubular construction
Effective adsorption area per filter unit area in condenser	283cm²	2,124 cm²

FIG. 48. Horseshoe magnet filters – original design in condenser of Daya Bay-B NPP (courtesy of CGN).

FIG. 49. Magnetic filters in condenser of Daya Bay NPP (Test) (Courtesy of CGN).

Tests comparing the effectiveness of modified adsorption compartments against adjacent original compartments at different locations within the condenser were carried out over one fuel cycle, demonstrating an improvement of ≈2.5–3 times – see Table 9.

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[14] Magnetic remanence (Br) in Tesla (T) is the remanent magnetic flux density in a substance when it departs from magnetic saturation by monotonic reduction to zero of the applied magnetic field strength (IEC60050 IEV 121-12-67). In other words, this is the strength of the magnetic field retained by a magnet after an external magnetic field is removed.

[15] Maximum energy product (BH_{max}) is the maximum energy density that the magnet can store. A higher value means the magnet can exert a stronger magnetic field over a greater volume or distance.

TABLE 9. COMPARISON OF IRON OXIDES REMOVED AFTER ONE FUEL CYCLE IN SINGLE LAYER FILTERS AND DOUBLE LAYER FILTERS

Area	Weight of materials retrieved (g)		Efficiency Ratio
	Original design	Modified design	
#1 (single layer)	216	648	3.0
#2 (double layer)	175	613	3.5
#3 (single layer)	142	408	2.9
#4 (single layer)	188	410	2.2
#5 (double layer)	160	424	2.7

The new magnets utilized at Daya Bay NPP were considered at the design stage of Yangjiang NPP and extensive tests and research were conducted on condenser magnetic filters at this power station. Not all locations in the condenser were equipped with filters, only half, due to cost considerations. Data on mass removed from the filters (see Table 10) are trended for reference and further benchmarking.

TABLE 10. CORROSION PRODUCTS REMOVED FROM MAGNETIC FILTERS AT YANGJIANG NPP

	Weight of materials retrieved at each fuel cycle (kg)						
	1st	2nd	3rd	4th	5th	6th	Average
Unit 1	161	120	42	35	85	32	79.1
Unit 2	144	83	59	59	56	14	69.2
Unit 3	151	62	82	44	31	n.a.	73.9
Unit 4	96	65	83	71	n.a.	n.a.	78.5

In recent years, samarium-cobalt (SmCo) magnets developed in the 1970s were also deployed at Yangjiang NPP. Their characteristics are maximum energy product BH_{max} ranging 160– 240 kJ/m³, and residual magnetic flux density (Br) between 0.9–1.2 T. They exhibit remarkable temperature stability, maintaining their magnetic properties up to 300°C. In current operational practices, SmCo magnets are preferred over $Nd_2Fe_{14}B$ magnets due to their better magnetic stability and as a way to resolve loss of magnetism observed at previous magnets used at Yangjiang NPP (see Fig. 50).

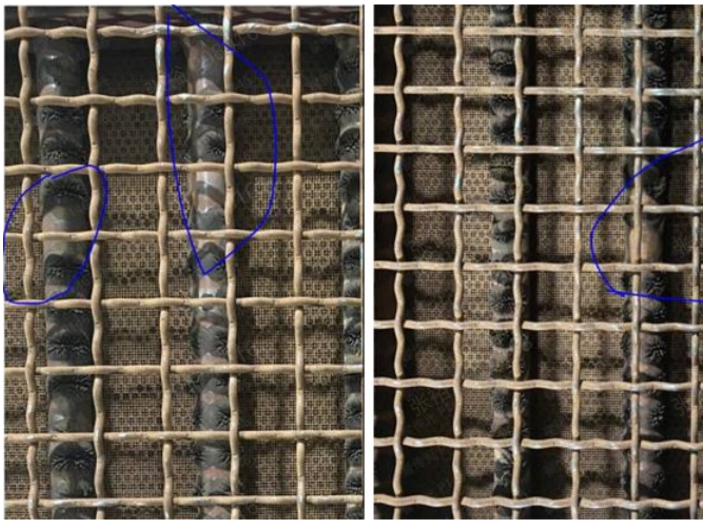

FIG. 50. Loss of magnetism in magnetic filters' bar found during an outage inspection at Yangjiang NPP (courtesy of CGN).

3.3.2. Development of steam generator sludge lancing in a water-water energetic reactor

At the design stage, no need for water lancing was expected for horizontal SG of WWER plants by some experts. The sludge in horizontal SG was expected to deposit at the bottom of the SG away from the tubes. Sludge was expected to be eliminated during shutdown maintenance in WWER SGs or by blowdown.

This expectation was not fulfilled in a SG at Dukovany NPP so that a first-of-the kind water lancing inside one steam generator was carried out in 2022 – see pictures of the sludge and a schematic view of the SG in Ref. [113]. In 2023, two other SGs were cleaned. The cleaning procedure was developed by the plant together with Skoda JS and Framatome (see Fig. 51).

FIG. 51. Steam generator lancing equipment used at Dukovany NPP during qualification tests (courtesy of Framatome).

3.3.3. Advances in steam generator sludge characterization

The characterization of the deposits that accumulate in SG is crucial to understand and predict possible material failures and the selection of the best technique for their removal. This also supports decision making about the application of strategies to minimize generation/deposition of corrosion products and impurities into the SG. The best way to obtain samples of the deposits that accumulate in the SG is to collect the sludge extracted during the sludge lancing operations or during high volume bundle flush. Once they are obtained, they are stored in high-density polyethylene bottles until characterization.

Since 2013, the Spanish research centre for energy, environment and technology (‘CIEMAT’) has performed the characterization of the sludge from the Ascó-1 and 2, Almaraz-1 and 2, Trillo and Vandellós power stations [114], based on procedures described in Refs [115, 116]. In this process, as-received deposit samples are weighted, dried and separated by sieving in three particle size sub-samples, prior to characterization. In addition, some single particles are visually selected attending to their morphology and deposit type (tube scale flakes, consolidated hard sludge collars, etc).

The physical, chemical and structural characterization of deposit samples includes following methods:

- Physical characterization:
  - Determination of the appearance and morphology of deposits sub-samples and single particles by macrophotographs and microphotographs taken by optical microscopy and SEM, respectively (Fig. 52).

  - Determination of dimensions and Vickers microhardness of single particles by optical microscopy coupled to a Berkovich diamond pyramid indenter.
- Chemical characterization:
  - Determination of the elemental composition of deposit sub-samples by different techniques such as elemental analysis technique, wavelength dispersion X-rays fluorescence, ICP atomic emission spectroscopy, ICP-MS, and flame atomic emission spectroscopy.
  - Determination of ionic species after water leaching of deposit sub-samples, recommended in case of use of FFS or dispersants in the secondary systems.
  - Determination of the composition of single particles by SEM coupled to EDS (Fig. 53).
- Structural characterization: Identification of crystalline compounds by X-rays diffraction.

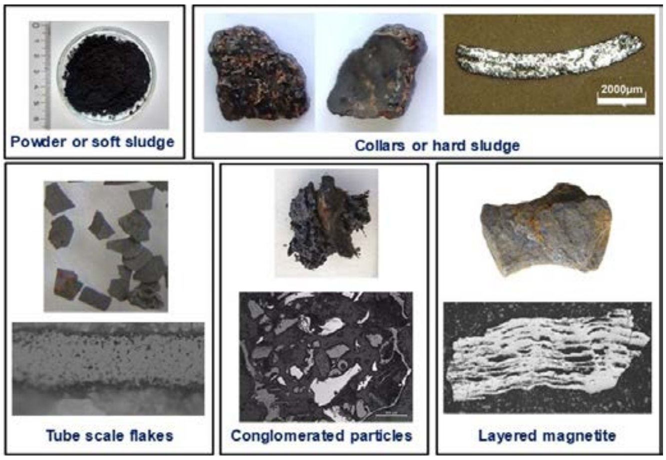

FIG. 52. Classification of deposit particles depending on their appearance and morphology (courtesy of CIEMAT).

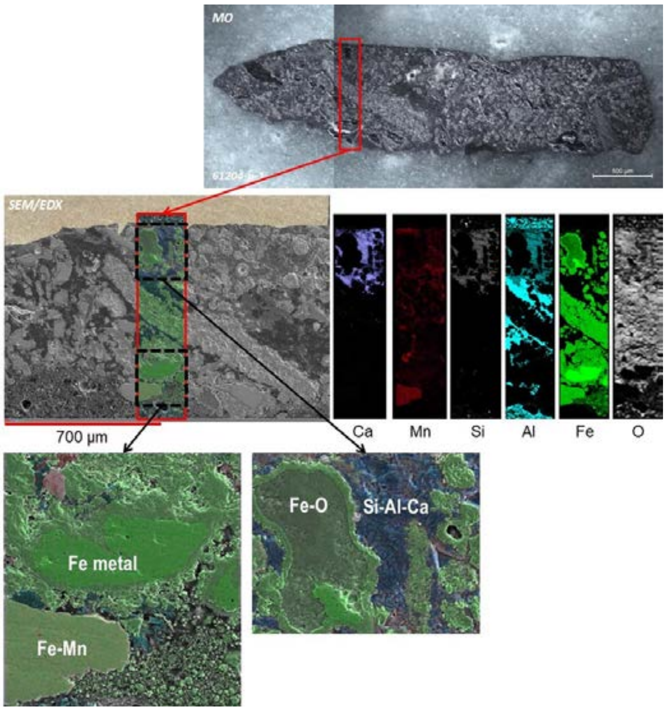

FIG. 53. Example of compositional maps of SG sludge acquired by scanning electron microscopy coupled to energy dispersive X-rays spectroscopy (courtesy of CIEMAT).

These characterization methods are used for identifying the mechanisms involved in the formation and consolidation of hard sludge – Refs [114] and [117], for designing the most appropriate sludge lancing or chemical cleaning strategies, for evaluating the effect of FFS applications (see chapter 2.4 of Ref. [39] and Section 3.3.4) and for assessing to efficiency removal of deposits, such as through chemical cleaning.

3.3.4. Use of dispersants such as polyacrylic acid in pressurized water reactors

Dispersants have been used in PWRs to reduce and control the inventory of deposits in the tube bundle. A dispersant is a negatively charged synthetic or natural organic polymer which inhibits deposit formation processes by adsorbing onto the surfaces of corrosion products particles and onto the surface of existing deposits (e.g. deposits lining the SG tubes, ‘scales’ or particles deposited on the surfaces of the SG tube support structures), resulting in a mutual electrical repulsion. This repulsion increases the likelihood that detachable deposit particles will be removed through the SGBD system, keeping these corrosion product particles in suspension.

Polyacrylic acid (PAA) is the most widely used dispersant in the NPPs since 2009. A distinction is made between free (active) PAA and PAA that has already combined with deposit particles or free iron. Free PAA remains dissolved in the aqueous phase of the SG until it combines with deposit particles (or free iron) or is removed by flushing or thermal decomposition. PAA combined with deposit particles or free iron remains suspended in the aqueous phase of the steam generator until it is removed by flushing the SG. The free PAA is not volatile but will be present in the main steam droplet carryover during normal operation (less than 0.05% of the steam mass flow rate). It is thermally degraded in about 4 hours at the saturation temperature of the secondary in normal operation. Therefore, after PAA injection is completed, its concentration decreases rapidly to undetectable levels in approximately 5 hours. It breaks down into weak organic acids and CO_2. These by-products pose no risk to the integrity of the secondary systems materials, other than slightly increasing the overall cation conductivity.

There are no operational or analytical interactions with other chemicals added to the secondary systems. Operational experience has shown that does not affect the performance of IXR present in blowdown demineralizers.

Two types of application are carried out, depending on the objective: long term on-line, which focuses on preventing ferrous corrosion products carried in the feedwater from adhering to the internal surfaces of SGs, thus increasing the efficiency of SG iron removal by the rinse stream; and off-line applications, which include SG wet lay-up and long path recirculation cleaning additives.

The most common offline applications are:

- Injection 10–24 hours prior to plant shutdown (pre-shutdown application);
- Injection into water for SG wet lay-up;
- Injection (‘addition’) in the sludge lancing water.

3.3.4.1. Overview of global operating experience

Reference [118] exhaustively reviews the experience with PAA applications up to 2014, in Belgium, France, United States and Republic of Korea. Experience at South Texas NPP that use dispersants since late 2010 (and a full-flow CPS) is discussed in chapter 14.3 of Ref. [39], showing an increase of SG outlet pressure of 0.02–0.05 MPa after application. In all applications to date, substantial increases in the blowdown iron removal efficiency have been recorded, except in one NPP in Spain.

In feedwater containing ETA and hydrazine, (low) PAA concentration is determined by ion chromatography, where PAA is resolved from a matrix using a polymer-based size-exclusion column. Water is used as the eluent to maximize sensitivity and eliminate the need for eluent preparation. PAA is detected at 200 nm with a method detection limit of ≈2.6 µg/kg in secondary water samples. This method provides a relatively simple and economical solution for NPPs to determine PAA in secondary feedwater.

Other operative experience evidenced a relation of the blowdown cation conductivity with the blowdown PAA concentration. A correlation for predicting the PAA concentration from blowdown cation conductivity can save resources as cation conductivity can be measured in real time using on-line analyzers, and PAA analyses can thus be carried out less frequently (e.g. once a week).

3.3.4.2.Operating experience from the application of polyacrylic acid at Doel-3 nuclear power plant

Due to fouling and TTS-denting in Doel-3 (operated from 1982 to 2022), it was decided to mitigate the progression of denting, while avoiding chemical cleaning. The selected solution was to use PAA in a curative manner. Based on EPRI studies, a pre-shutdown PAA application plan was set up. The aim was to remove as much ferrous sludge as possible from the SGs, especially on the TTS.

The following protocol was applied:

- Injection during the last 11–12 hours of the cycle, still at 100% power;
  - Injection of PAA into feedwater at 20 µm/kg;
  - Simultaneous injection to the 3 SGs of Doel-3;
- Stop of injection before power reduction.

Continuous on-line monitoring of cation conductivity in the SG was performed during injection. The SGBD flow rate needs to be as high as possible to evacuate as much loose sludge as possible. A filter system was used to evacuate the sludge. The filters were weighted and, a sludge lancing was performed. Compared to the average (previous) sludge lancing quantities, the pre-shutdown dispersant application and the subsequent sludge lancing removed 5 times more sludge from the SG. The resins were in bypass during the pre-shutdown application. The first application of pre-shutdown PAA injection in Doel 3 in 2012 was effective (Fig. 54) and was subsequently applied in the other units at Doel and Tihange NPPs. The protocols and results of 2012-2014 applications are detailed in chapter 5.2 of Ref. [118].

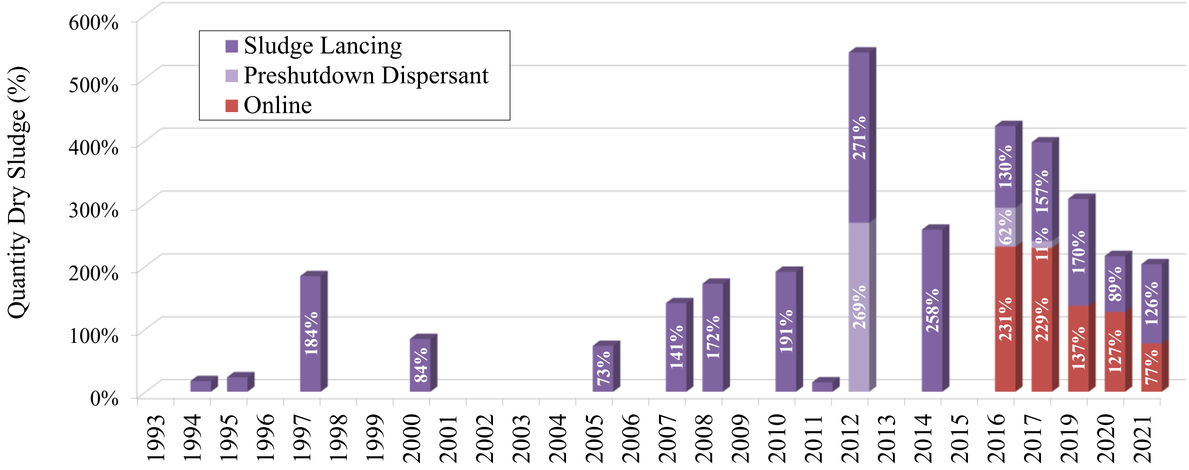

FIG. 54. Annual quantity of dry sludge removed at Doel-3 NPP 1993-2021 during PAA applications (courtesy of Engie).

After the second and third pre-shutdown applications in 2016 and 2017 in Doel-3, combined with on-line injection, sludge removal was decreased and, it was decided to apply on-line injection as preventive remediation to SG fouling – see detailed results in chapter 14.4 of Ref. [39]. Note that, during the on-line PAA application, the resins were not bypassed. The only impact the PAA application had on the resins was slight iron contamination.

3.4. ADVANCES IN THE ALTERNATIVES TO HYDRAZINE

Hydrazine is used as an oxygen scavenger and reducing agent to prevent systems from being in oxidizing conditions during operation, but also during hydrostatic tests, RCS start-up, and wet lay-up. However, hydrazine poses significant risks to worker safety and environment, and might face supply issues.

Hydrazine is a toxic and carcinogenic substance, of category 1b under Ref. [119], on the list of 'substances of very high concern' established by the European Chemical Agency. It is a candidate for authorization under European regulation Ref. [120]. In 2017, the European Union set the occupational exposure limit for hydrazine in air at 13 μg/m^3 [121], 10-times lower than the previous limit. In the future, if hydrazine is included in the list of substances requiring authorization under annex XIV of Ref. [120], European industries, including NPP operating organizations, will need to apply for authorization for use. This application would include: (i) an 'analysis of alternatives' with substitution studies for each usage, (ii) a 'chemical safety report' detailing worker exposure scenarios and mitigation measures, and (iii) a 'socio-economic analysis'.

Environmental regulations have also become stricter, requiring nuclear operators to drastically minimize hydrazine from effluents before discharge. For example, EDF has implemented devices in effluent control tanks to remove hydrazine by bubbling and stirring, which allows it to react with oxygen to form nitrogen and water. Catalysts like copper sulfate or manganese oxide can accelerate this decomposition. All these means led to significantly reducing hydrazine discharges at EDF NPPs, see Fig. 55.

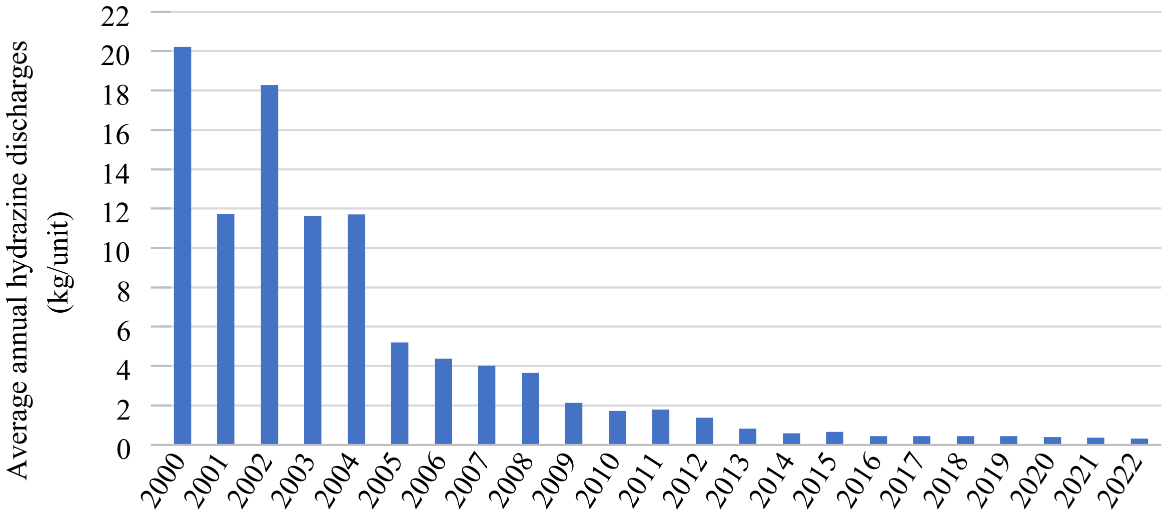

FIG. 55. Annual average hydrazine discharges into the environment from an EDF NPP unit, from 2000 to 2022 (reproduced from Ref. [122] with permission).

If industrial use of hydrazine declines, the demand from NPPs may not be enough to sustain its production, affecting supply and profitability for hydrazine producers.

In this context, various organizations worldwide are investigating alternatives to hydrazine as oxygen scavengers and reducing agents – Refs [122–131], sections 11.3 and 11.4 of Ref. [39], and posters 7C and 8B in section 18 of Ref. [39]. These alternatives are evaluated based on aspects such as supply chain, worker health and safety, systems and equipment compatibility, corrosion mitigation properties, behaviour and decomposition products, use during hydrostatic tests/operation/wet lay-up, and environmental impact.

Promising alternatives include organic compounds like carbohydrazide and diethylhydroxylamine (DEHA), either to use in the secondary systems during operation and/or for wet lay-up, while others were discarded due to toxicity (hydroquinone), corrosiveness (ascorbic acid) or pollutive decomposition products (erythorbic acid).

Carbohydrazide ($(N_2H_3)_2CO$) decomposes into hydrazine and carbon dioxide above 135°C, potentially increasing hydrazine discharges and cation conductivity in the secondary systems (because of carbon dioxide), which can hinder the detection of deleterious anions (i.e. Cl, SO_4) and lower pH. However, it does not lead to identified resins and materials compatibility issues.

Some NPPs tested carbohydrazide during operation, with mixed results:

- Kewaunee NPP: No significant impact on chemistry parameters was observed (no significant increase in cation conductivity due to acetate or formate, and pH), and carbohydrazide produced similar reducing effects as hydrazine. The plant eventually defined a target of 20–30 µg/kg hydrazine in feedwater through carbohydrazide decomposition. After several cycles of successful use, the plant reverted to hydrazine because of sodium hydroxide contamination in a supplied batch of carbohydrazide.
- Cook-1 and 2 NPP: Carbohydrazide use over 4 cycles led to increased cation conductivity in feedwater, steam, and, to a lesser extent, in SGBD system (carbon dioxide volatility may explain that), and sodium levels, likely due to impurities in supplied carbohydrazide batch. The oxygen scavenging performance was satisfactory. pH did not decrease. The NPP switched back to hydrazine after turbine replacement due to vendor requirements. This resulted in a decrease of steam cation conductivity and a (small) decrease of sodium, chloride and sulphate in SGBD.
- Summer NPP: Carbohydrazide use for several years resulted in slightly lower $pH_{25°C}$ than in comparable NPPs (9.7 vs 9.8) and significantly lower hydrazine and ammonia concentrations from carbohydrazide decomposition in SGBD system (5 times less).

During wet lay-up, at concentrations similar to hydrazine, carbohydrazide offers less corrosion protection at low temperatures due to slow oxygen scavenging kinetics. Much higher concentrations of carbohydrazide than the stoichiometric ratio and an alkalization agent are needed. Some NPPs increased refreshment to ensure adequate protection.

DEHA ($C_4H_{11}NO$) is as another potential alternative to hydrazine. It decomposes at high temperatures into various by-products such as organic compounds (acetaldoxime, acetaldehyde, acetate, formate), amines (diethylamine, ethylmethylamine), nitrites, nitrates, and ammonia. DEHA is expected to be less toxic than hydrazine and is more volatile making it well present in the steam phase. However, the carcinogenic potential of acetaldehyde, a by-product, may limit DEHA's use unless it can be shown to decompose completely into acetate before discharge. Trials at Comanche Peak-2 (1993–1995) and Doel 2 (2015–2017), Ref. [128], showed DEHA's (limited) efficiency in scavenging oxygen and achieving reducing conditions at high temperatures, while requiring higher concentrations than hydrazine. Comanche Peak-2 eventually reverted to hydrazine. At Doel-2, the significant increase in TOC was unacceptable (order of mg/kg), chapter 4.4 of Ref. [128]. However, DEHA appeared to enhance the removal of corrosion products from the SGs – a result that needs further confirmation. During wet layup, DEHA is less efficient than hydrazine at similar molar ratios to oxygen. Higher concentrations may improve oxygen scavenging and corrosion protection, but data are inconsistent. Further research is needed to understand DEHA's behaviour, decomposition, effects on electrochemical potential, and impact on plant performance and corrosion.

Other alternatives to hydrazine are being studied, including chemicals already present in NPPs: alcohols, amino-alcohols, and hydrogen.

Alcohols and amino-alcohols show promise as oxygen scavengers under radiation conditions. Two substances have been studied by Framatome:

- Methanol – Note that methanol is applied during startup in boiling water reactors, where early hydrogen addition to ensure reducing conditions is not available [132].
- ETA: Used as an alkalizing agent, see Section 3.1.

These chemicals scavenge oxygen through radical formation of the alcohol (hydroxyl) group under radiation, allowing the radicals to interact with residual oxygen to form carbon dioxide (CO_2). Methanol and ETA also act as reducing agents, maintaining required corrosion potentials in the SG feedwater to mitigate SCC of the SG tube material [133].

High-temperature loop tests under radiation confirmed this approach could be applied to all SG tube materials (600, 690, 800 nickel-based alloys and high alloyed stainless steels) in PWR and WWER, benefiting from the weak radiation field on the secondary side of SG at power. Framatome and Borssele NPP are investigating the feasibility of replacing hydrazine with a mixture of methanol and ETA [134].

Hydrogen is known for its reducing properties and already used in PWRs to ensure reducing conditions in the RCS. It is not hazardous to health or the environment but requires careful handling due to its flammability and explosiveness. Tests showed higher electrochemical potentials with hydrogen compared to hydrazine. Further work is needed to assess the potential of hydrogen as alternative to hydrazine.

For new build, technologies like gas transfer membranes may be an alternative to hydrazine if compatible with temperature and pressure conditions. Note that an example of use of gas transfer membranes in the component cooling water systems of Ringhals NPP is provided in Section 4.2.4.

3.5. DEVELOPMENTS IN IMPLEMENTING EFFECTIVE START-UP CHEMISTRY PROGRAMMES

The programme for secondary start-up chemistry is customized for each plant, focusing on protecting components, especially the SGs, from corrosion-related damages and performance degradation [2]. WANO guideline GL 2020-02 [2] offers insights for optimizing these programmes based on accumulated experience, aiming at achieving a WANO chemistry performance index (CPI) of 1.0 early in the cycle.

These insights have been integrated into the start-up plans at many NPPs and include the following [2]:

- Prior to start-up, perform system and component flushing and clean-up to avoid chemistry holds during start-up and minimize corrosion product transport to the SGs.
- Ensure condensate polishers, filter demineralizers, and blowdown purification systems are operational and ready at start-up.
- Effectively use filter demineralizers or condensate polishers to reduce corrosion product transport.
- Minimize intrusion of SG corrosion-sensitive chemicals, used for equipment cleaning and housekeeping, that can compromise feedwater purity due to thermal decomposition forming harmful species.
- Ensure a leak-tight condenser. In the event of condenser cooling water in-leakage, timely identification and correction are crucial. Utilize on-line chemistry monitors (conductivity, cation conductivity, sodium analysers) and grab sample analysis for leak detection. Effective localization may require methods like helium or sulphur hexafluoride tracing, ultrasonic testing, and other techniques. The use of dimple plugs is also effective to detect leaks. Even small

impurity concentrations can significantly impact the SGs due to high feedwater flow rates and concentrating effects.

A key success factor for NPPs to achieve a WANO CPI of 1.0 early in the cycle, as demonstrated at Tianwan-6 where a CPI of 1.0 was met in the month after commercial operation commenced in 2021, is the leading role of plant chemists. Their effective collaboration with the wider organization and the clarity of their guidance towards an objective of excellence are crucial.

Based on experience in China, areas of collaboration to be nurtured are as follows:

- With plant managers: It is crucial for chemists to communicate the importance of maintaining optimal secondary startup water chemistry for SGs. This can be materialized by the adoption by managers of a target of a CPI at 1.0 in the early stage of the cycle (only one single indicator to monitor). Success in achieving this will requires plant managers to coordinate all disciplines.
- With commissioning teams (for new build): Plant chemists ought to support these teams on secondary systems preservation and equipment cleaning/rinsing to minimize the deposition of impurities, especially iron oxides, into the SG during commissioning phase.
- With maintenance teams: Chemists play a critical role in:
  - Overseeing the use of chemicals during maintenance activities. This includes managing chemical materials that come into contact with secondary systems, monitoring usage chemicals in real time, and promptly correcting any deviations.
  - Ensuring cleanliness of spare parts before use;
  - Overseeing foreign material exclusion controls (for materials such as oil, dust, sandblasting, rags, bolts and nuts, paint chips, broken or loose parts, tools, old grinding wheels, welding slag, scaffolding hammers, tape, plastic, ear plugs, lanyards, gloves);
  - Participating in /making sure visual inspections (with specialized inspection cameras, ultraviolet light flashlights) and cleaning of equipment (flushing, wiping with cloths, vacuuming, air-blowing, and swabbing –swabs analysis provides critical information regarding the chemical cleanliness of components) after maintenance or component replacements are effectively carried-out;
  - Pre-soaking filters;
  - Overseeing resin changeovers.
- With engineering teams: Chemists closely monitor the integrity of condenser tubes at start-up and are involved in major equipment modifications (at the early stage), to prevent contamination with impurities at equipment manufacturing, transportation, and during on-site preservation.
- With operation shift teams: Chemists guide shift teams for flushing/rinsing/draining/filling complex water systems. They defined critical water quality control points on activities such as draining/filling systems, switching over from auxiliary to normal feedwater, directing MSR drains to the purification system before they enter feedwater, managing the CPS, ensuring stable operation of the SGBD system at maximum capacity, and advocating for performance beyond the sole compliance against the technical specifications for operation.

Recent experience at Chinese newly commissioned NPPs has showed that quickly achieving a WANO CPI of 1.0 during the first operational cycles (for example driving down sodium or sulphate in the SGBD system as a priority) can adversely affect iron concentration. This can lead to increased deposition in the SGs and a reduction in outlet pressure[16].

Minimizing the transport of corrosion products into SGs at start-up and therefore reducing oxidation during outages are high priorities. An analysis of 22 cycles at US plants determined 12% (and no more than 20%) of the cycle's iron transport occurs during the few days of start-up and that corrosion products

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[16] In that respect, and also because the WANO CPI does not encompass key water chemistry parameters for the RCS, WANO is working to improve the CPI basis, considering other composite indicators developed by the Institute of Nuclear Power Operations, EDF and CGN.

transported during startup are probably more oxidizing than those during normal operation, chapter 2.5.3 of Ref. [100]. Water and steam-side components are maintained in a conditioned wet-conservation state (wet lay-up with high pH and low oxygen) or dry conservation, with relative low humidity. Both methods are routinely monitored, with adjustments made when conditions deviate from the specified parameters. With the development of sophisticated wireless sensor technologies, operating organizations have deployed real time monitoring systems of conservation conditions in large components, tracking pH levels, conductivity and concentrations of impurities such as sodium, chlorides and sulphates. Lastly, application of FFS improves the protection of surfaces – see Section 3.2.

Note that experience with the secondary systems water chemistry applied at the commissioning of Flamanville-3 is presented in Section 2.8.1.

3.6. INNOVATIVE USE OF DIGITAL TWINS FOR MODELLING STEAM GENERATORS' FOULING AND BEHAVIOUR

Corrosion products deposition on the SG tubes outer surfaces can result in a decrease in heat transfer and a degradation of thermal performance. They can also accumulate in the crevice area between tubes and tube support plates (TSP) and participate in the TSP clogging (or blockage) phenomena. The TSP clogging alter the mechanical stress and thermohydraulic operating conditions of the SGs, leading to safety-related issues (excessive vibrations, risk of tube rupture, challenge to accident management procedures).

When clogging rate is high in a SG, a chemical cleaning (see Section 3.3) is performed, generating additional chemical effluents and dose for workers, impacting SGs lifetime and generating additional costs. These operations require extensive preparation (18 to 24 months in advance) and ought to be scheduled not too early, to avoid repeating chemical cleanings, and not too late to avoid operating SGs in inadequate conditions. This requires a good characterization of the clogging rate and a good control of its evolution over time.

In this context, EDF worked to identify the factors most impacting SG clogging. That work was performed based on machine-learning techniques, and proved it was possible to predict clogging evolution from one cycle to the following cycle. Among the most impacting factors in the TSP clogging prediction, the following can be cited concerning chemistry: chemical conditioning of the secondary system, corrosion products in the feedwater, size of the deposit particles and deposit surface model. The next step was to develop a SG digital twin (SG-DT). For each SG in the fleet, a digital twin model was built that reproduces its specific characteristics and history, to continuously monitor its condition and predict its evolution. This involves developing decision support algorithms, clogging prediction models, and coupling physical and chemistry models with different types of data (collected during power operation and from inspections during outages) processed using data analytics methods. Those data are used to run simulations and estimate the future conditions of SGs for different scenarios.

The tool consists of a web interface, an application server, and a database, making it modular. It includes different solvers that can be updated and modified as needed, and it is possible to extend the tool's application fields simply by adding new solvers. It is connected to operational data and can load data from other databases.

The current version of the SG-DT is used to trend TSP blockage rate and predict it evolution, infer the impact of operating parameters on clogging, and estimate SG tube cracking rate and SG clogging to optimize maintenance.

4. AUXILIARY SYSTEMS WATER CHEMISTRY

Auxiliary systems in NPPs are not unique to the nuclear industry. Similar systems are operated in fossil fuel-fired power plants and other industries. These systems face challenges specific to their functions:

- Open[17] cooling water systems: general corrosion, scaling, and biofouling of heat exchange surfaces;
- Component cooling systems: corrosion and fouling, where component specific risks apply (the stator cooling system requires ultrapure water, hence very low conductivity).
- Water treatment systems: control of impurities, e.g. for producing demineralized water or treating effluents before discharge.

Sections 4.1 to 4.3 presents innovation, advances and developments in the water chemistry of those 3 system types.

4.1. OPEN COOLING WATER SYSTEMS

In once-through cooling systems, fouling of heat exchangers, condenser tubes, filters, etc. by micro- and macro-aquatic organisms (‘biofouling’), is common. This can degrade heat exchange, cause microbiologically influenced corrosion, clogging, and leaks. Closed-loop cooling water systems are also prone to biofouling, and scaling (a fouling by inorganic matter such as calcium carbonate, typically on packing of cooling towers that decreases performance and, for packing, may lead to collapse). At the interface with plant systems, through-thickness degradation can lead to raw water ingress, pollution (incl. by dissolved oxygen) and, potentially, shutdowns. Chapter 4 of Ref. [136] details the impact of biofilms and microbiologically influenced corrosion on service water piping and systems.

Figure 56 depicts heat exchanger tubes blocked by barnacles at Angra NPP.

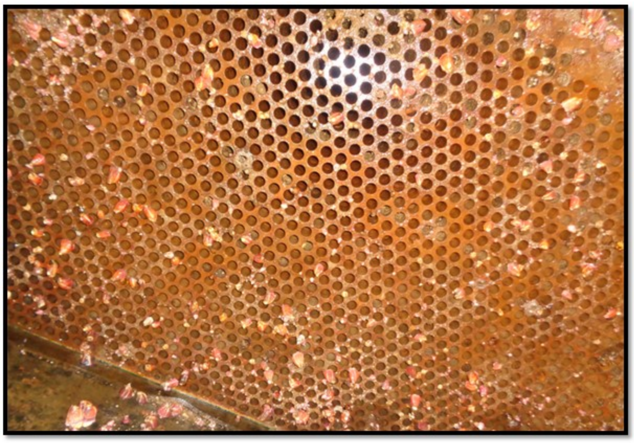

FIG. 56. Heat exchanger tubes blocked by barnacles at Angra NPP (courtesy of Electronuclear).

From a chemistry perspective, dosing biocides – such as sodium hypochlorite ($NaOCl$), chlorine dioxide (ClO_2), bromine-based compounds (e.g. $NaBr$) – prevents aquatic organisms from developing in auxiliary systems. Prevention of scaling is achieved by dosing phosphonates (also used as corrosion

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[17] In this section, open cooling water systems are those in contact with the atmosphere (EPRI terminology), opposing to most of closed component cooling systems. Hence, regarding condenser cooling, open cooling water systems cover closed-loop (or recirculating) cooling systems (with cooling towers) and once-trough cooling systems (direct discharge to open waters such as sea, lake, reservoir, river) as in the terminology of Ref. [135].

inhibitor), sulfuric acid (for pH control), and polymeric surfactants (dispersant). Injection points are typically upstream of condenser and cooling tower water pumps.

Optimal biocide and scaling inhibitor concentrations are risk/cost-informed, considering the minimum effective concentration and the maximum to meet environment permitting regulations. Dosing patterns (continuous, intermittent, cyclic, seasonal) depend on water/air temperature, species of concern, and water flowrate, with climate change affecting these patterns.

Effectiveness of dosing strategies, along with equipment and coating improvement, are evaluated through trials and 'biofouling boxes'. Examples of dosing strategies effectiveness reviews include Ref. [137] for biocide usage at British coastal NPPs, and chapter 9.4 of Ref. [39] for biocide/scaling inhibitor usage at Exelon Generation NPPs.

This section presents in:

- Section 4.1.1, developments in electro-chlorination and operating experience at two British coastal NPPs. Lessons learned for improving the design of electro-chlorination plants are also shared;
- Section 4.1.2, innovation in predicting sodium hypochlorite concentration in water intake galleries of Angra-2 NPP, using artificial neural network;
- Section 4.1.3, developments in using chlorine dioxide for biocidal dosing at St. Lucie NPP;
- Section 4.1.4, developments in using biofilm growth detectors for optimizing dosing strategies of essential service water (ESW) system ponds at Temelín NPP;
- Section 4.1.5, advances in modelling calcium carbonate in cooling towers of EDF NPPs.

4.1.1. Developments in electro-chlorination

When NaOCl is used as a biocide for condenser cooling water systems, it can be procured from external providers (and dosed via bulk tanks) or, for coastal NPPs, produced using electro-chlorination plants (see Eq. (4) for the chemical reaction), where seawater is passed through an electrolyser.

$$NaCl_{(aq)} + H_2O + energy \rightarrow NaOCl + H_2(g) \tag{4}$$

After being produced, sodium hypochlorite decomposes as per Eq. (5):

$$NaOCl_{(aq)} \rightarrow Na^+ + ClO^- \tag{5}$$

Figure 57 shows the electro-chlorination installed at Angra 2 NPP.

FIG. 57. Sodium hypochlorite production (electro-chlorination) and dosing system of Angra 2 NPP (courtesy of Electronuclear).

This section presents operating experience at two British coastal NPPs using employ electro-chlorination plants and lessons learned for improving design. Electrochemical cells operate more efficiently the higher the temperature of the influent water. Cells designed with warm-water anodes need alternative seawater sources at 15°C or greater to operate when the condenser system is out of service or during winter periods when seawater temperatures significantly drop below 10°C (typically cells do not function below 7°C). At NPPs where a warm seawater supply (for example, drawn from downstream of a condenser) is not available, special low-temperature cells are needed to avoid NaOCl supply restrictions during winter and early summer.

Seawater supply lines to the electro-chlorination plant are also protected from fouling. The main seawater strainer, filters and control valves of electrolysis units allow for by-pass operation or are doubled up to provide ease of maintenance without loss of product supply. Cells and pipework are preferably of modular, flanged design to prevent electro-chlorination plant shutdowns for minor faults.

Electro-chlorination cells need periodic cleaning, typically monthly, preferably without losing the ability to continuously dose. This can be achieved with multiple diverse streams so one can remain in service while another is cleaned. Due to the corrosive effect of NaOCl on common metals, stock tanks and pipework are usually made of high-density polyethylene, polyvinyl chloride externally reinforced with glass reinforced plastic, high density polyethylene or glass flake lined carbon steel, with spiral welded high-density polyethylene showing good performance over a 15-year life span.

Electro-chlorination plants are generally designed to be run continuously. Intermittent dosing strategies necessitate cycling of dosing/non-dosing at short intervals (minutes) which may not be compatible with the design of a continuously run electro-chlorination plant. In such cases, a tank facility allows continuous feed from the electro-chlorination plant while the dosing plant draws intermittently.

Routine maintenance is performed during periods of least fouling risk. Best practice is to conduct maintenance that prevents dosing, either (i) during plant shutdowns when dosing is not required, or (ii) when the seawater temperature is below 10°C. If this is not possible, outages are kept as short as is practicable, preferably less than 24 hours. To ensure reliable dosing during periods of highest fouling risk, outages for planned maintenance work are scheduled when dosing is unnecessary, typically over 2–4 weeks in the first quarter at the British NPPs.

Design, operating procedures and dosing strategies account for both normal and credible abnormal plant (related to cooling water flowrate) and environmental conditions. In depth investigation is essential to identify all potential scenarios requiring effective biocidal dosing (especially considering climate change), while ensuring discharge limits (regulated at the British NPPs through a total residual oxidant concentration limit at the location of the discharge of, typically, less than 0.3 mg/l) are not exceeded.

For a given biocide concentration, dosing flowrate is proportional to condenser cooling water flowrate. Adjustments are made either manually or automatically. During significant cooling water flowrate reduction (e.g. from 33–44 m^3/s regions to 9–11 m^3/s in refuelling outages) operators ensure the total residual oxidant concentration threshold is always met, even though the amount of total residual oxidant discharged into the environment is substantially lower during these periods than would be permitted at maximum cooling water flow.

Other lessons from operation include:

- Not mixing new electrodes with old on the same bank.
- Ensuring that electrodes are connected up properly and that the polarities are not reversed.
- Considering the use of hydro-cyclones on feed supply to keep sediment levels down.
- Considering new in-pipe electrolysis units for point dosing rather than adding lots of long runs of small-bore piping to the system.
- Regular acid cleaning of the generators to remove scale.

4.1.2. Innovations in predicting sodium hypochlorite concentration in water intake galleries using artificial neural network

Effective biocidal dosing necessitates that the desired biocidal concentration is met in all locations (pipes, filters, strainers, heat exchanger surfaces) sensitive to biofouling. Plant and environmental parameters that influence the local biocidal concentration include water temperature, condenser pump flowrates, NaOCl flow adjustment valves' positions. Layout and configuration of galleries upstream/downstream the NaOCl injection points also significantly influence distribution.

Angra-2 NPP employs an electro-chlorination plant to produce NaOCl which is capable to operate in automatic mode. There are 6 injection points (in each inlet gallery). NaOCl concentration is measured as residual free chlorine by colorimeters at the outlet of the heat exchangers/condenser downstream of the galleries (8 locations) – see Fig. 58.

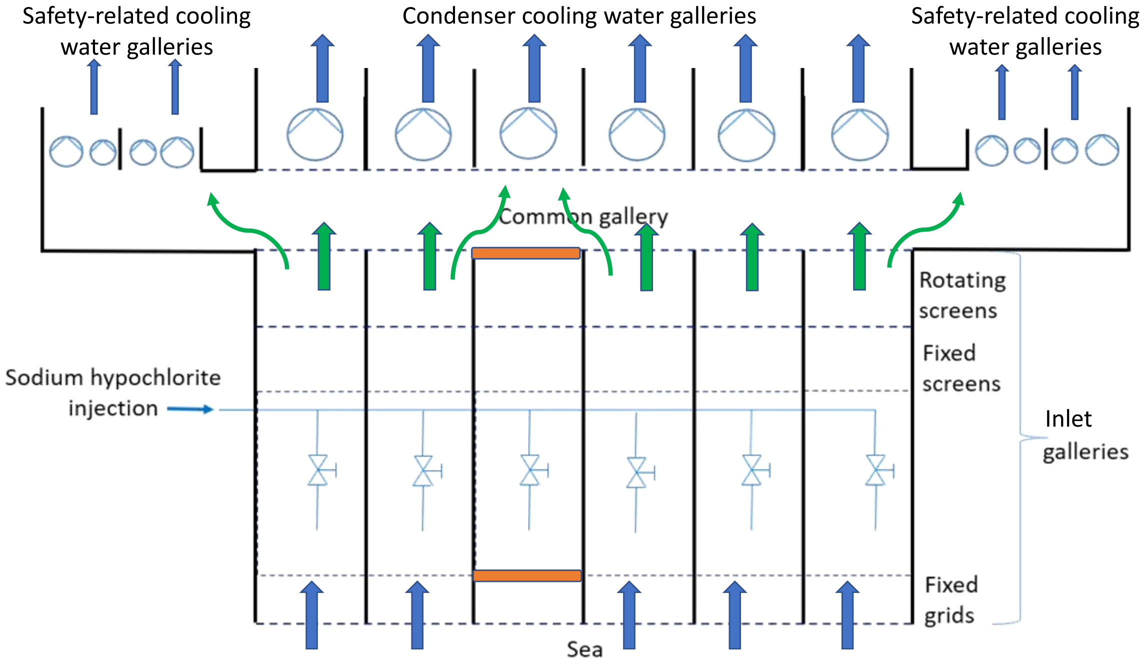

FIG. 58. Simplified layout of water intake galleries at Angra-2 NPP, with flow distribution when one gallery is isolated, and location of NaOCl injection points (courtesy of Electronuclear).

Inlet galleries can be isolated for maintenance, altering flow distribution and free chlorine concentration at the outlet of the heat exchangers/condenser (across the full operational range: 0.15–0.75 mg/kg).

To understand chlorine distribution based on configuration and parameters (15 identified), Angra-2 NPP developed an artificial neural network to predict local chlorine concentrations [138]. Predictions are used to adjust the electro-chlorination plant set points and may support future design changes for automatic control of concentrations in all downstream galleries, regardless of configuration and plant/environmental parameters.

Developing 'good' neural architecture involves identifying process variables influencing NaOCl diffusion and heterogeneity. The more complex the process and the more dosing points, the more complex the neural architecture needed to predict the actual concentrations of residual free chlorine.

Characteristics of the developed artificial neural network at Angra-2 NPP are as follows:

- 8 layers of neurons with 1 layer for input data, 6 hidden layers with 600 neurons each, and 1 data output layer. The hidden layers are interspersed with 3 layers of calculations using the rectified linear unit function as the activation function for the neurons and 3 layers for discarding inconsistent results (drop-out layer);

- Data processing from the first to the last layer;
- Error back-propagation in the opposite direction to the previous process to provide more accuracy in algorithmic calculations;
- Adam algorithm optimization process;
- Self-feeding of the algorithmic calculation process using 8000 cycles;
- Last data output layer using a linear calculation function to predict the final residual chlorine concentration.

Initial results showed excellent correlation with the measurements (average coefficient of determination of 0.934), with further training needed for some configurations, Ref. [138].

4.1.3. Developments in biocidal dosing with chlorine dioxide reactors

Chlorine dioxide (ClO_2) is increasingly used as a disinfectant in the power industry for open cooling water systems and water treatment systems. An advantage of ClO_2 over NaOCl is that it does not react with ammonia or most organic compounds, remaining effective in their presence and reducing 'chlorine demand'. Plants using ClO_2 report significant reductions in chemical deliveries compared to NaOCl or NaOCl/NaBr blends, especially in plants using reclaimed water or seawater. However, the reactants required for producing ClO_2 (sodium chlorite or sodium chlorate, sulfuric acid) and ClO_2 itself are hazardous and require strict safety measures (ClO_2 is volatile, explosive, and toxic at high concentrations).

Several NPPs in the United States (5 NPPs incl. St. Lucie) and Europe (e.g. Vandellòs-2) use ClO_2 in open cooling water systems – both St. Lucie and Vandellòs-2 NPPs are coastal NPPs. The effectiveness of ClO_2 as a biocide is consistent over the pH range normally encountered in open cooling water systems. It is less pH-dependent than NaOCl or NaOCl/NaBr blends.

St. Lucie NPP, like Vandellòs-2 NPP, uses an in situ reactor for producing ClO_2, achieving a concentration of ≈95%, see details of operating experience at this NPP in Ref. [139]. ClO_2 demand was 0.2 mg/kg vs 0.8 mg/kg for NaOCl previously. The in situ generation reactor mixes the reagents in-line within in the process water line, so ClO_2 is generated in the process water and does not come into contact with air, thus mitigating flammability risk.

Note that chlorine dioxide reactors are also used in water treatment systems at NPP such as Ascó. After 4 years of operation, Ascó NPP confirmed that no halogenated organic compounds were detected in makeup water tanks by post-ultraviolet-visible spectroscopy, which is a known drawback of NaOCl use.

4.1.4. Developments in using biofilm growth detectors in essential service water system ponds in a water-water energetic reactor

Monitoring concentrations and/or biofilms is crucial for mitigating biofouling. Temelín NPP implemented a new biocidal dosing protocol for their ESW ponds that considers on-line measurement from biofilm growth detectors (installed in 2012–2013 on unit 1, and 2016 on unit 2). The ESW system, separate from the condenser cooling water system, consists of three parallel independent trains with dedicated pump stations and spray ponds serving as an ultimate heat sink (Fig. 59). It cools safety-related equipment in reactor and turbine buildings, emergency diesel generators, and the high-pressure compressor station. ESW ponds are open to atmosphere, operating with low heat load and few concentration cycles. Clarified or raw water is used for make-up.

FIG. 59. Spray ponds at Temelín NPP (courtesy of Temelín NPP).

The biocidal dosing protocol includes a corrosion inhibitor, NaOH acting as an alkalizing agent to suppress general corrosion and decrease corrosion inhibitor dose, a stabilizer preventing slit, and a biocide (intermittent dosing) following guidance in Ref. [140].

Temelín NPP selected resin body sensors with two sets of metal electrodes made from stainless steel or titanium, see chapter 5 of Ref. [136] and figure 2 in Ref. [141], as biofilm growth detectors. The electrode sets are intermittently cathodically polarized to a preset direct current potential, which is then switched off. The electric current required to set the potential and the current after switching off are measured and proportional to the biofilm on the sensor surface. An increase in electric current signals for initiating biofilm mitigating actions. Temelín NPP developed custom software to download potential and current readings and upload them into a plant chemistry database. The NPP evaluates data and triggers biocidal dosing when currents deviate from baseline.

The installation of probes was part of an effort to optimize biocidal dosing, which proved successful in terms of budget and supplies (Figs 60–61). However, evaluation is complex as biofilm growth varies on years (depending on weather conditions, sunshine duration, etc.). Lab analysis and observations have shown no adverse effects so far.

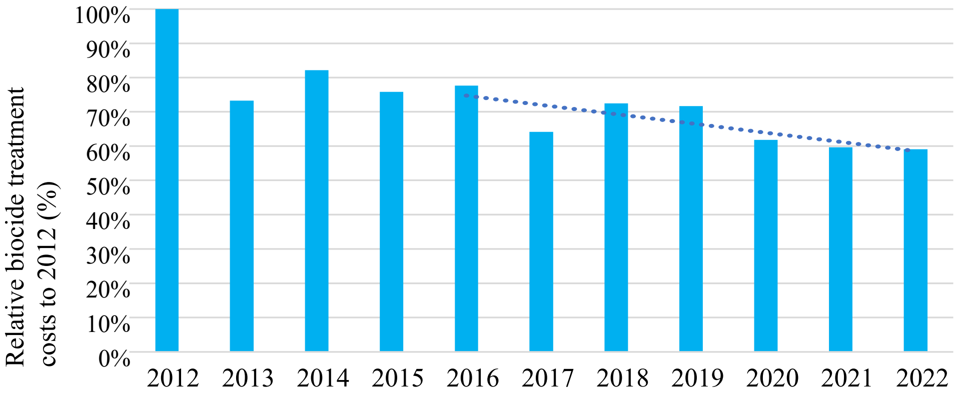

FIG. 60. ESW biocide treatment costs at Temelín NPP (in relative value vs 2012, 2022 net present value). Dotted line is a linear trend between 2016 and 2022 (courtesy of Temelín NPP).

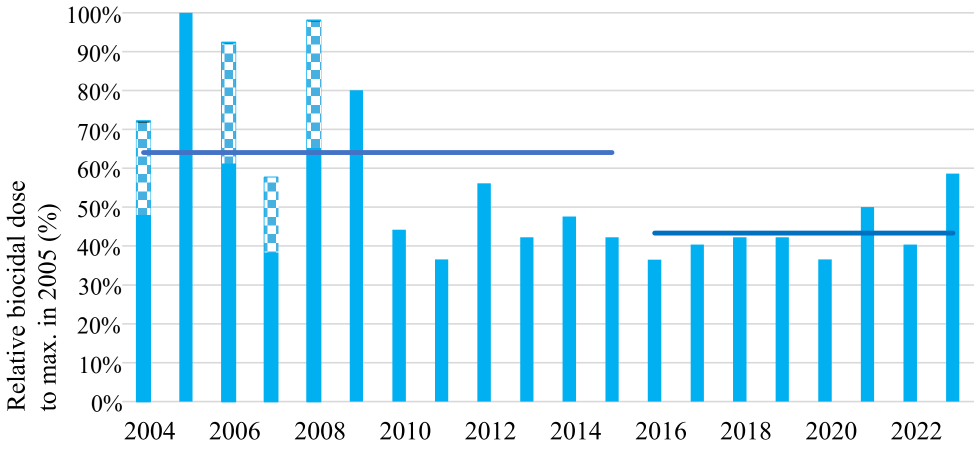

FIG. 61. Relative biocidal dose of ESW systems at Temelín NPP. The stripped bars indicate extrapolation of the dose, when only 2 of 3 ESW trains were dosed. The lines are arithmetic averages (courtesy of Temelín NPP).

4.1.5. Advances in modelling calcium carbonate in cooling towers

In NPPs with cooling towers, calcium carbonate ($CaCO_3$) can form in condenser tubes and on cooling tower packing, decreasing thermal performance, increasing maintenance and risks to packing integrity. To mitigate scaling, acid is added to shift the chemical calco-carbonic balance, polymers are used as dispersants for suspended solids, and inhibitors prevent $CaCO_3$ formation and growth.

To gain extensive knowledge of the mechanisms and optimize treatment strategies, incl. discharges to environment, EDF developed a code to simulate water cooling system at its NPPs. The code, called ‘CooliSS’ – standing for cooling system simulation, considers [142]:

- Plant design;
- Weather conditions (air temperature, humidity);
- Plant operating conditions;
- River water quality.

Calculations, in steady and unsteady conditions, consider plant data, fluid mechanics, thermodynamics and thermochemistry. Outcomes include water evaporation rates from cooling tower and temperatures across the systems. Then the code simulates the water chemical composition across the cooling system, evaluating calcium carbonate precipitation and deposits weight considering calcium concentration, pH, and chemical treatments applied.

The model was validated against experimental data obtained from laboratory and pilot plant tests – see Ref. [143] and virtual visit of the test loop[18] – representing the wide range of water qualities, plant operating conditions, and chemical treatments applied. The simulations obtained with the software were then compared to operating experience data and in situ monitoring data.

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[18] https://visite-labo360.pam-retd.fr/chatou-pericles.html

The CooliSS code is used to:

- Determine the capacity of scaling treatment facilities for new built and needed changes for existing plants;
- Identify optimal periods to pause scaling treatment and schedule outages for maintenance;
- Optimize treatment frequency during plant operation;
- Understand the causes of severe scaling (when detected);
- Simulate climate change impacts on scaling treatment strategies.

Using CooliSS led to savings. For example, adjusting pH to mitigate the risk of scaling saved 1,000 k€/year by halving the acid quantity in one unit. Another unit optimizes the acid-to-polymer ratio, reducing acid and saving ≈100 k€/year. Both cases reduced chemical discharges to the environment.

4.2. COMPONENT COOLING WATER SYSTEMS

Component cooling water (CCW) systems are totally closed. Demineralized water is typically used, with added corrosion inhibitors to prevent material degradation. Well maintained systems require infrequent water make-up and chemical adjustments. Corrosion inhibitors are chosen based on system materials, design, operating temperature, potential impurity ingress, and impurity types. Common treatments for carbon steel systems include nitrite, molybdate, chromates, phosphates, and hydrazine.

This section presents:

- Developments in dosing corrosion inhibitors such as sodium molybdate in the emergency diesel generators (EDG) cooling water system at Bohunice NPP (Section 4.2.1) and tolyltriazole with tri-sodium phosphate in the essential chilled water (ECW) system at Chasma-3 NPP (Section 4.2.2);
- Advances in stator cooling water (SCW) system chemistry based on experience at Eskom power plants (Section 4.2.3.1). Section 4.2.3.2 presents a study on the composition and microstructure of copper deposits carried out at Chinese NPPs;
- Advances in the alternatives to hydrazine in CCW systems at Ringhals NPP (Section 4.2.4).

4.2.1. Developments in using sodium molybdate as a corrosion inhibitor in emergency diesel generator cooling water systems

The original treatment of EDG cooling water systems at Bohunice NPP involved manually injecting sodium phosphate as a corrosion inhibitor, but iron concentration remained high. Drawing from Mochovce-3 NPP experience (a sister plant newly commissioned), the chemical regime was changed on EDG-1 in 2023 and all EDGs in 2024. The new product, containing sodium molybdate (Na_2MoO_4) as an active agent and additional substances, enhances passivation and corrosion mitigation, while reducing sediment layer formation (mainly iron oxide). The product is a mixture of inorganic and organic inhibitors, with alkalizing agents to adjust the pH.

The product is dosed semi-continuously or continuously into make-up or circulating water to maintain constant concentration. The initial passivation dose is higher (115 mg/kg Mo) than the operational dose (80–92 mg/kg Mo). The inhibitor concentration is kept above 50 mg/kg Mo, to prevent pitting corrosion by such anodic inhibitor. High concentrations can increase pH above 10.0, leading to copper and aluminium corrosion, so the optimal pH range is 9.0–10.0.

Concentration is monitored via laboratory measurement of molybdenum using ICP optical emission spectroscopy. Other parameters to monitor include pH, total iron, insoluble substances, total hardness, conductivity and total bacteria content. The system is flushed when total iron exceeds 5 mg/kg or insoluble substances exceed 10 mg/kg.

Initial results show more stable pH, and total iron concentration below 0.35 mg/kg, significantly lower than with the previous treatment.

4.2.2. Developments in adding tolyltriazole in essential chilled water systems

At Chasma-3 NPP, tri-sodium phosphate is dosed in the ECW system as a corrosion inhibitor, maintaining pH at 10.8–11.5. Concentration range is 100–500 mg/kg. High pH prevents ferric corrosion but can increase copper corrosion, raising water turbidity. Since the ECW system contains components with copper, minimizing copper corrosion is crucial. An assessment recommended adding tolyltriazole (TTA) in the ECW system, along with tri-sodium phosphate, to prevent copper corrosion.

In December 2021, Chasma-3 NPP began adding TTA, significantly reducing copper corrosion:

- Before TTA addition: Max copper concentration was at ≈0.64 mg/kg; average at 0.52 mg/kg;
- After TTA addition: Average copper concentration is ≈ 0.08 mg/kg.

The requirements for TTA is 5–25 mg/kg, keeping copper stable at less than 0.08 mg/kg. No adverse effects were observed.

4.2.3. Advances in stator cooling water system chemistry

Stator cooling systems use demineralized water to cool the stator which is generally made of copper. It is a fully closed system in which the water needs to be ultrapure to achieve a low conductivity. So, water is continuously purified on IXR. Corrosion of copper in these systems can lead to accumulation of deposits and flow blockage. Corrosion control is hence of utmost importance.

Stator cooling system water systems are similar for nuclear and fossil power plant electrical generators, these consist of the stator winding made up of individual stator bars with hollow conductors, stator bar hoses, manifolds, a storage tank, pumps, filters strainers, demineralizer(s), heat exchangers, piping and valves. The stator winding is generally made from copper, and most of the chemistry standards available are applicable to copper hollow conductors although stainless steel systems are also in use.

General technical guidance for water chemistry of stator cooling systems is given in WANO guideline Ref. [2]. Two options are presented. An option is to operate SCW systems at a concentration for dissolved oxygen (DO) at 20 µg/kg, with a pH at 8.0–9.0. This is the ‘low-oxygen, alkaline treatment’ option. The other option, further discussed in Section 4.2.3.1, is the ‘high-oxygen, neutral pH with no additives’ option. For both options, a low conductivity is desirable, typically less than 0.2 µS/cm for neutral pH and less than 2 µS/cm for alkaline treatment.

Further options and detailed technical guidance are given in a technical guidance document from International Association for the Properties of Water and Steam, Ref. [144], and an International Council on Large Electric Systems (known as CIGRE) technical brochure Ref. [145], both not specific to generators used in NPPs. Based on case studies, Ref. [146] provides a list of parameters to be monitored and examples of typical interpretations of stator cooling water chemistry data when they differ from the technical guidance. Figures 8 and 10 in Ref. [147] compares chemistry regimes for SCW systems adopted by some operating organizations and recommended by vendors.

This section presents experience at Eskom power plants regarding their SCW system chemistry and pH control strategies (Section 4.2.3.1), as a study on the composition and microstructure of copper deposits (Section 4.2.3.2) carried out at Chinese NPPs.

4.2.3.1.Experience at Eskom power plants regarding stator cooling water system chemistry and pH control strategies

Eskom power plants currently practise elevated pH strategy, with pH at 8.0–9.0. This significantly reduces the copper corrosion rate. Above a pH of 9.2 the copper corrosion rate again starts to increase rapidly, hence setting an upper limit of pH 9.0 provides an additional safeguard.

The drawback with elevated pH regimes is that the addition of an alkalising agent is required to the SCW system, with the attendant dangers of increased conductivity. As this could cause a trip, or worse, flashover, the sodium concentration needs to be strictly controlled. Manual addition carries the risk of overestimating how much to add at a single injection. Micro-dosing systems offer closer control of the addition rate but are subject to failure that could continue dosing after the desired pH shutoff point has been reached.

The adoption of a dual mixed bed treatment system has introduced an alkalising agent addition method that removes the risks associated with manual injection or micro-dosing. One of the mixed bed demineralisers contains cation resin in the sodium-form. Copper ions (from corrosion) entering this mixed bed replace sodium ions on the resin, thereby providing the alkalising agent. Over time, this provides sufficient sodium to achieve the target pH. If necessary manual injection may still take place initially, or after exceptional make-up, to ‘kick-start’ the ion exchange process on the sodium-form mixed bed. Risk is therefore not entirely removed but is greatly reduced. The second mixed bed contains hydrogen-form cation resin for the removal of sodium from the stator coolant to prevent the sodium concentration from becoming too high. By setting-up the flows through the two demineralisers it is possible to maintain the desired pH in the SCW system with very little further manipulation of the mixed bed flow rates.

The advantage of neutral pH regimes for SCW systems is that the cooling water is kept pure and free of additives. The disadvantage is that they are more susceptible to fluctuations during impurity ingress. Two neutral pH operating conditions have been recognized at Eskom as options for any generators that may be identified as being susceptible to crevice corrosion and for generators with stainless steel hollow conductors. For copper hollow conductors, a neutral pH regime with low oxygen (DO below 50 μg/kg) provides a lower corrosion rate than a neutral pH regime with high oxygen (DO above 2,000 μg/kg). However, this regime is extremely susceptible to fluctuations caused by impurity ingress. Air ingress will introduce CO_2, which depresses the pH to mildly acidic conditions, increasing the copper corrosion rate and increasing DO towards 200–300 μg/kg at which maximum copper corrosion occurs.

For systems operating at neutral pH but with high oxygen, a very mildly acidic condition ($pH \geq 6.7$) is desirable to minimize cupric oxide (tenorite, CuO) deposition from solution onto the tightly adherent passive layer, also CuO. This can be achieved by air sweep of the balancing/buffer/surge tank, introducing small amounts of carbon dioxide, CO_2, into the circuit. Because of the stability of the passive CuO film formed under high oxygen, this regime is less susceptible to impurity fluctuations. However, large ingress of CO_2 (from air) should be avoided as the solubility of Cu^{2+} from CuO increases rapidly under increasingly acidic conditions ($pH < 6.5$). The concentration of copper ions in solution is controlled by removal on the sidestream demineralization plant.

Operation at neutral pH is an option for any future generators that are identified as being susceptible to crevice corrosion and for generators with stainless steel hollow conductors.

4.2.3.2.Study on the composition and microstructure of copper deposits

Reference [147] presents the main equations of interest for copper species and includes graphs of calculated values vs experiments from Ref. [148]. Observations from three Chinese units indicated that chemical reaction Eq. (6) was also noticeable:

$$Cu_2O(s) + H_2(g) \rightleftharpoons 2Cu(s) + H_2O \tag{6}$$

Analysis of the deposits flushed from stator bars during outages, as well as of the cartridge retention, was carried out using X-ray diffractometer. This revealed that metallic copper is the primary component of the samples, along with minor quantities of Cu_2O and trace amounts of CuO. Figure 62 shows deposits' microstructure using SEM.

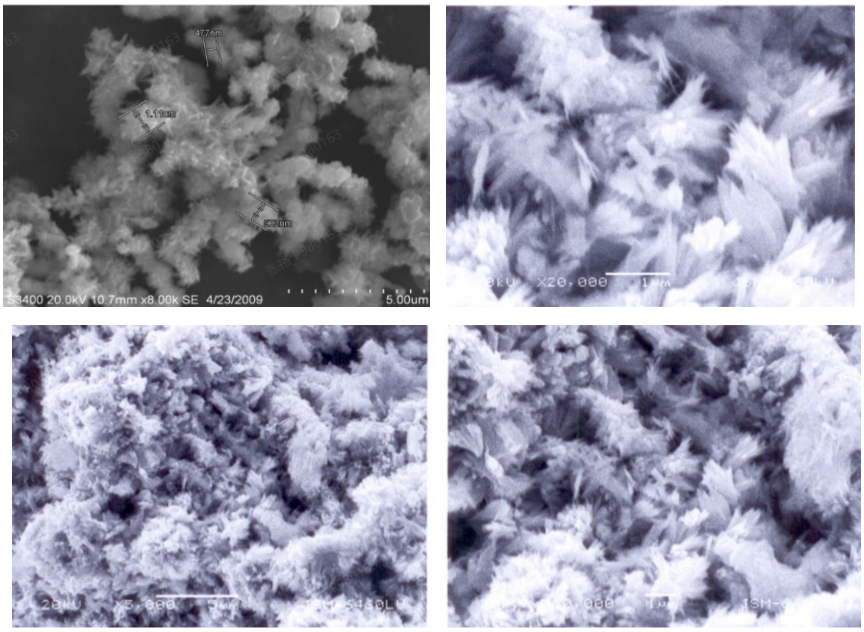


FIG. 62. Scanning electron microscope analysis of deposits flushed from stator bars during outages at Chinese nuclear power plants (courtesy of CGN)

Results from EDS analysis reflect fluctuations in the SCW system flow and bar temperatures throughout the 18-month fuel cycle – see Table 11 for deposits' composition determined with EDS after 12 months in the 18-month cycle.

TABLE 11. ENERGY DISPERSIVE X-RAY SPECTROMETER ANALYSIS OF COPPER DEPOSITS AT CGN NUCLEAR POWER PLANTS

Element	wt%	at%
C	1.90	7.48
O	8.78	25.94
Fe	1.14	0.97
Cu	88.18	65.61

Notably, two distinct phase transitions were identified during operation.

The first transition, occurring shortly after startup, is indicative of the chemical reaction Eq. (7):

$$2CuO(s) + H_2(g) \rightleftharpoons Cu_2O(s) + H_2O \tag{7}$$

The second transition, after 12 months in operation, suggests chemical reaction Eq. (8) occurs:

$$Cu_2O(s) + H_2(g) \rightleftharpoons 2Cu(s) + H_2O \tag{8}$$

4.2.4. Advances in the alternatives to hydrazine in component cooling water systems

To reduce the hydrazine demand, Ringhals NPP replaced hydrazine in some CCW subsystems with a treatment system involving ammonia for pH control, gas transfer membranes (GTM) and mechanical filters (Fig. 63). GTMs reduce oxygen, by creating a vacuum that separates oxygen from water. Nitrogen is used as a stripping gas to increase efficiency. Particle filters protect the membranes. Ammonia is added to increase pH (KOH has also been used).

For a CCW subsystem with a volume of 35 m^3, a 4m^3/h flow is distributed to two particle filters in series (5 µm and 1 µm meshes). Downstream, two gas membranes reduce DO in the CCW system, with a capacity to achieve 9,000 µg/kg to 10 µg/kg within 4 days. After oxygen reduction, the gas membranes are put in bypass mode and activated as needed. Ammonia is then added to increase pH.

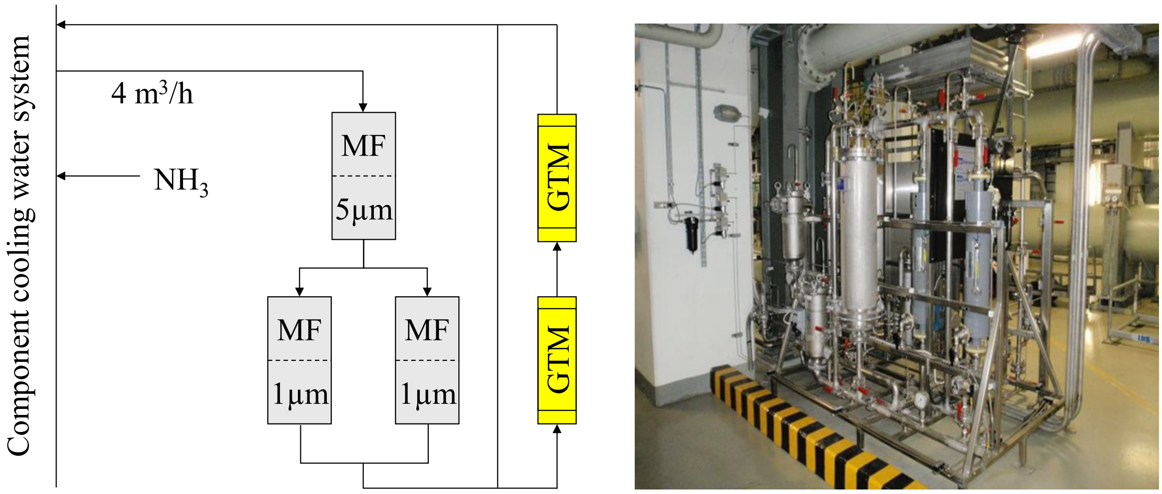


FIG. 63. Schematic process diagram (left) and picture (right) of component cooling water system treatment at Ringhals NPP (courtesy of Vattenfall).

The treatment system has been successfully used for over 10 years with no signs of increased material degradation in the CCW system compared with to previous hydrazine addition. In the first years, corrosion coupons showed no or very low corrosion rates. Normal chemistry levels for the CCW system are ammonia at 5–10 mg/kg, DO below 20 ppb (action level at 100 ppb), and iron below 50 ppb (action level above 200 ppb).

4.3. WATER TREATMENT PLANTS

Pure water (demineralized water) is used in many systems of a power plant. While potable water can be used after treatment on demineralizers (with IXR), many plants prepare themselves pure water using surface water. Traditionally, surface water was pretreated by conventional techniques such as clarification, lime-softening, filtration. More and more, pretreatment is done by using membrane technologies such as ultrafiltration and reverse osmose (RO). Ultrafiltration membranes are used to remove suspended solids and (partially) organic matters while RO removes inorganic matters (salts). Ultrafiltration and RO are often used together, completed by IXR (demineralizers) as final purification. Other trends are the use of electrodeionization instead of demineralizers, and chlorine dioxide produced by reactors instead of disinfecting agent NaOCl.

4.3.1. Developments in electrodeionization

Electrodeionization (EDI) is a continuous, chemical-free process of removing ionized and ionizable species from feedwater using DC power. EDI is typically used to polish RO permeate and can be an alternative to conventional mixed bed ion exchange as using EDI eliminates the need to store and handle the hazardous chemicals used for resin regeneration in mixed beds. And since electricity is EDI's only consumable, this method of permeate polishing does not produce a hazardous waste stream.

EDI systems create an electrical potential to drive anions towards the anodes and cations towards the cathodes of an electrochemical cell. Cation exchange membranes and anion exchange membranes allow only cations or only anions, respectively, to pass through them. Both kinds of membranes are impermeable to water. These membranes are placed in sequence to trap anions and cations in concentrated cells leaving the other cells dilute. Some EDI systems have anion and cation resin in the dilute cells in order to ensure conductivity across the system is maintained at an acceptably high level. Resin is also often used in the concentrated chamber in order to keep the chemical potential of the ions in the brine low so that a lower electrical potential is needed to drive the ions from the low concentration chambers to the brine.

A variation on EDI technology is capacitive electrochemical deionization. Capacitive EDI is an innovation that has significant advantages including selectivity to impurities, higher water recovery, and increased flow rate, as compared to conventional EDI.

Use of EDI in NPPs includes Sanmen NPP in the SGBD system to ensure the concentration of Na^+, Cl^- and SO_4^{2-} after treatment is continuously less than 0.1 µg/kg. At Ringhals-2, EDI has been successfully used for SGBD cleaning until decommissioning in 2019 – see chapter 5.3.3.3 of Ref. [99]. 98% of treated water was re-injected in condenser system and only preventive exchange of the EDI cells every 4-5 years was required.

4.3.2. Developments in reverse osmose

In RO systems, permeation is the transport of water through a membrane. RO membranes are semipermeable. This means that water molecules can permeate (pass through) the membrane, but most other substances will be rejected (i.e. do not pass through). Most power plants use flat-sheet, polyamide, thin-film composite RO membrane. The term thin-film is used because of the extremely thin salt-rejecting membrane layer. The term composite is used because a flat-sheet RO membrane is composed of three main layers. It is worth noting that the actual salt rejecting membrane layer, which is about 0.2 µm thick, a polysulfone porous support layer, which is about 50 µm thick and a polyester fabric support layer (backing material), which is about 150 µm thick.

In RO, pressurizing the higher total dissolved solids (TDS) side forces more water molecules through the membrane in the opposite direction of osmosis. The pressure on the higher TDS side required to stop osmosis is the osmotic pressure. RO occurs when the pressure on the higher TDS side is increased above the back pressures (osmotic and permeate). This forces more water molecules to permeate, or pass, through the membrane opposite to the direction of osmosis.

The percentage of feedwater that passes through the membrane as permeate is called the recovery or percent recovery. Occasionally, very high silica brackish feedwater requires operation at low recovery where only one stage is present, though this is not common. Most RO units operating at near 75% recovery in NPPs consist of two stages. The first stage recovers about 50% of the feedwater, and the second stage recovers about 50% of the 50% that was not recovered in the first stage. For very high recovery applications, three stages may be used.

Recent advances in RO technology tend to be focused on improvement and automation of monitoring of chemistry parameters and equipment performance. Routine monitoring of the RO system should include the feed, permeate, and reject flows along with on-line specific conductivity for each stream. Recovery of permeate is typically around 75% of the feed. Effluent conductivity should meet the feed requirement of the downstream polishing equipment. Reject flow may be adjusted to improve the effluent quality or the amount of permeate produced. Caustic may be added ahead of the RO to covert the CO2 to bicarbonate for removal.

4.3.3. Developments in nanofiltration

Nanofiltration is generally filtration for the 0.001–0.01 µm range of material. This range of particle size places nanofiltration generally between ultrafiltration and reverse osmosis. Nanofiltration is a liquid-phase separation process for removing solids, carried out by means of membranes. The separation takes place mainly because of diffusion of the molecules of the solvent through the mass of the membrane material, driven mainly by a high trans-membrane pressure. Nanofiltration has found application in removal of chemicals, colorants and TOC of water and simultaneous removal of sodium chloride and concentration of organics in the food and pharmaceutical industries.

At NPPs, there has been interest in its use in CVCS and for silica removal systems in PWRs (see Section 2.3.2).

5. INNOVATION AND DEVELOPMENTS IN ON-LINE MONITORING SYSTEMS, CHEMISTRY INFORMATION SYSTEMS AND USE OF ROBOTICS

On-line monitoring (OLM) systems now provide real time, continuous data on water's chemical and physical properties, enabling immediate processing and analysis. Digital sensors, now as precise as analog, allow extensive and frequent data sampling. All together, these technologies form the basis for chemistry information systems (CIS) helping operating organizations swiftly detect anomalies, assess unusual behaviours, and predict deviations, enhancing overall plant chemistry surveillance and control. These technologies are particularly beneficial for new builds, where they can be fully integrated into the digital instrumentation and control architecture, offering more opportunities for digitalizing chemistry-related processes. For operating NPPs, refurbishing monitoring and sampling systems presents an opportunity to upgrade to the latest sensor technologies, OLM systems and intelligent CIS, with robotics potentially automating tasks still performed by personnel (such as reading chemical parameters in water treatment plants and handling samples) when the refurbishment cost outweighs the benefits.

This section provides examples of developments in OLM techniques and systems (Section 5.1), innovation in chemistry information systems featuring monitoring/diagnosis capabilities (Section 5.2) and use of robotics for chemistry-related tasks (Section 5.2.2) at operating NPPs.

5.1. DEVELOPMENTS IN ON-LINE MONITORING TECHNIQUES AND SYSTEMS

OLM has several advantages over grab sampling:

- Higher frequency of data acquisition allowing early detection of anomalies;
- Continuity of surveillance between two manual samplings where unexpected, rapidly evolving situations may occur;
- Some more precisely and accurately measured parameters;
- Possibility to swifty reporting large deviations of key parameters to the main control room for immediate action;
- Trending of small deviations close to the detection limit or blank variation with grab sampling, enabling actions;
- Reduced risk of sample contamination and human errors;
- Reducing the need for resources for sample transport, preparation and analysis in the laboratory, enabling plant chemists to focus on assessing issues.

The following sections provide examples of developments in various OLM techniques and systems:

- Section 5.1.1: Ion chromatography for monitoring RCS samples in a WWER, zinc in the RCS of a PWR, and the SGBD system in a PWR;
- Section 5.1.2: Gas chromatography along with other techniques for monitoring dissolved hydrogen in the RCS of PWRs;
- Section 5.1.3: Neutron absorption for determining ^{10}B, and titration for determining total boric acid concentration in the RCS of PWRs;
- Section 5.1.4: Lithium analyzers (using conductivity measurements) and automatic injection at PWRs;
- Section 5.1.5: Sodium ion-selective electrodes for enhancing condenser leakage detection;
- Section 5.1.6: OLM and automatic dosing systems for hydrazine and ETA at a WWER.

Section 5.1.7 discusses the refurbishment of all OLM systems at Krško NPP, and Section 5.1.8 presents the test facilities used for on-line qualification of analyzers at Chinon NPP.

Another example of development of OLM systems is the project in Ref. [149] that aims at demonstrating that automated chemistry monitoring instruments in nuclear power plants can reduce costs and increase the efficacy of chemistry monitoring. The developed skids continuously measured chemistry parameters in RCS, SGBD system, and secondary systems feedwater. All skids were employed at Salem NPP (see picture in Ref. [149]).

5.1.1. On-line ion chromatography

Ion chromatography (IC) is a well established analytical method for quantitative determination of both anions and cations, often practised in laboratory. There have been several efforts to implement on-line IC for measuring ions in primary and/or secondary systems in the past. Some projects were abandoned due to (perceived) high maintenance and, low reliability. Recent experience from NPPs [150] confirms that on-line IC can be operated effectively and provide valuable information, meeting requirements for maintenance and reliability. For example, CGN NPPs have deployed reagent-free IC technology that only requires a connection to ultrapure deionized water supply, and eliminates the need for manual preparation of eluents by generating them automatically, with electrolytically-regenerated suppressors and controlled, accurate eluent/regenerant production. Also, CGN NPPs preferably installed their on-line IC in the laboratories, not modifying the in-process NSS lines but ensuring sampling flowrates allow for continuous extraction of representative samples.

The IC has been installed on the primary system of Temelín-1 and 2 since the first unit began operation in 2002. The chromatographs are used for determination of cations Li^+ and Na^+ (0–1 mg/kg), NH_4^+ (0–30 mg/kg) and K^+ (0–50 mg/kg) every 15 minutes. In 2018 the analog connection to plant systems was replaced with a digital bus. The IC shares its cooled sampling line with other chemistry measurements. Effluents from IC are dumped to plant rad-waste collection system.

Sanmen NPP also began developing an innovative on-line zinc meter in 2019, operated since September 2022 (Fig. 64, left). The non-suppressed conductivity detection method was selected, with a precision of ±10% and a limit of quantification at 3 μm/kg.

For monitoring F^-, Cl^-, and SO_4^{2-} in the SGBD system, Sanmen NPP installed an on-line IC in 2018 (Fig. 64, right) that has been operating continuously without issue.

FIG. 64. Prototype of on-line zinc meter (left) and on-line ion chromatograph used in steam generator blowdown system (right) at Sanmen NPP (courtesy of CNNP).

5.1.2. On-line monitoring of dissolved hydrogen through representative sampling

The use of hydrogen in the RCS of NPP presents challenges such as sampling and measurements accuracy, chemical reactions with materials, and safety (due to explosiveness).

Regular and correct DH sampling is crucial for trend monitoring, risk assessment, and swift response to deviations. The challenge lies in sampling coolant at optimal locations and using reliable methods for real time results. Often, the original design does not allow sampling at different points in the RCS.

To measure DH concentration in the RCS and verify results, gas chromatography and/or electrochemical and thermal methods are used. Measurement accuracy depends on sampling conditions, including temperature, pressure, and impurities.

EDF NPPs have optimized hydrogen sampling methods, using electrochemical sensors and gas chromatography in the NSS. The electrochemical sensors provide a representative capture of the RCS, allowing continuous, real time monitoring of DH. The sensors include a hydrogen section, counter-electrode, and temperature sensor. The hydrogen section has palladium and platinum filaments, where palladium and platinum have similar temperature coefficients of resistance. The platinum filament, which does not absorb hydrogen, accounts for temperature effects on the resistance. The palladium filament absorbs DH causing an electrical resistance change that also accounts for temperature. By comparing the resistance of both filaments, the system can isolate the resistance change due to hydrogen absorption.

The measurement involves three steps:

- Desorbing hydrogen from the palladium filament by electrochemical oxidation (an electric current is set through the counter-electrode and the filaments);
- For the palladium filament to absorbs DH present in the sample;
- Stabilizing the absorbed DH for accurate measurement.

On-line measurements are periodically cross-checked with manual grab samples. Samples are obtained using a phase separator which extracts dissolved gases (relative vacuum) for analysis by gas chromatography.

5.1.3. On-line measurement of boron by neutron absorption and titration

Some plants have introduced on-line ^{10}B meters [151] to continuously measure ^{10}B concentration in the RCS using the principle of the neutron absorption. These instruments are installed e.g. in CVCS and NSS of PWRs. An example of an on-line measurement system can be found in Ref. [152], publicly available.

To replace manual measurement of RCS total boric acid concentration, Sanmen NPP began developing an on-line boron meter in 2021. Titration was selected to meet the precision requirement of 0.1–0.3%. The prototype (Fig. 65) has been operated on demand (intermittent operation) since 2023 and is subjected to continuous optimization (for example, addition of a steel cask to decrease dose rate at contact).

FIG. 65. Prototype of on-line boron meter installed at Sanmen NPP (courtesy of CNNP).

5.1.4. On-line lithium analyzers and automatic injection at pressurized water reactors

Real time determination of lithium concentration is often based on conductivity measurement from an in-line sensor, considering concentrations of the main impurities in the RCS. The lithium concentration is calculated by subtracting the conductivity due to total boron (calculated from the on-line B-meter) and impurities such as Na, chlorides, fluorides and sulphates [18] [153].

Continuous lithium measurement in the NSS and automatic injection of LiOH into the CVCS were considered for lithium control at the design stage of some PWRs of type EPR (Flamanville-3, construction project Hinkley Pont C) and will undergo a test programme. Other NPPs are also testing on-line monitoring of lithium, like Salem NPP [149] [154], and Gravelines NPP, where on-going tests of conductivity measurements are showing promising results (as of 2025) – see Fig. 66.

FIG. 66. On-line lithium monitor tested at Gravelines NPP (courtesy of EDF).

Automated lithium addition helps maintain a constant pH_T in the RCS throughout the fuel cycle – this is a crucial feature for NPPs with FPO. For Flamanville 3 and Hinkley Point C NPPs, the injection device will be controlled by a feedback system comparing on-line total boron and lithium concentration measurements [153]. This system compensates for lithium dilution due to water makeups during power transients, ensuring lithium is always adjusted to boron. Additionally, automated lithium addition reduces risks of human errors since there is no manual injection. When the automated lithium addition system is not available, grab sampling will be performed for measuring lithium concentration.

5.1.5. On-line sodium analyzers to enhance condenser leak detection

The common cation conductivity measurement for monitoring condenser leakage is prone to disturbances from water quality fluctuation, and has low sensitivity (see chapter 5.3.3.1 of Ref. [99]). As an example, at Sanmen NPP, when Na concentration in condenser leakage detection system increases by 1 µm/kg (leakage at 50 mL/min), it increases by 21 µm/kg in SGBD system, triggering action level 1. However, cation conductivity in condenser leakage detection system only increases by 0.003 µS/cm, where cation conductivity is maintained at 0.1 µS/cm in the system, with a measurement precision at 0.01 µS/cm. In addition, it takes 15 minutes for the condensate water to pass through the cationic resin column upstream of the cation conductivity meter and be measured. This delayed the activation of the CPS when leaks were detected.

Thus, Sanmen NPP deployed on-line Na-analyzers in each condenser water head of both units in 2021–2022, to enhance condenser leakage detection (Fig. 67). The Na-analyzers use sodium ion-selective electrode and a reference electrode, with a sampling flow at 6 kg/h. It enables swift detection of minor condenser leaks, their localization, and thus swift operator response.

FIG. 67. Online-Na meter used in condenser leakage system at Sanmen NPP (courtesy of CNNP).

5.1.6. On-line monitoring and automatic dosing systems for hydrazine and ethanolamine at Bohunice nuclear power plant

When Bohunice switched to ETA in 2007–08, injection systems for ETA and hydrazine were refurbished. Hydrazine is dosed at 20–25 µm/kg during power operation and above 250 µm/kg during the 24-hour surfaces passivation before and after outage. Hydrazine is automatically injected into the second condensate pump suction head (Fig. 68) and measured via on-line hydrazine analyzers in the feedwater (Fig. 69) using colorimetric detection.

FIG. 68. Automatic dosing system for hydrazine at Bohunice NPP (Courtesy of Slovenské elektrárne, a.s.)

FIG. 69. On-line measurement of hydrazine in the feedwater at Bohunice NPP (Courtesy of Slovenské elektrárne, a.s.)

ETA is automatically injected into the feedwater pump suction head (Fig. 70) and measured via on-line conductivity analyzers in feedwater (Fig. 71). ETA concentrations of 1.2–1.6 mg/kg correspond to conductivity of 4.1–4.3 µS/cm in the feedwater. The target is to maintain conductivity at 4.2 µS/cm, corresponding to 1.4 mg/kg ETA.

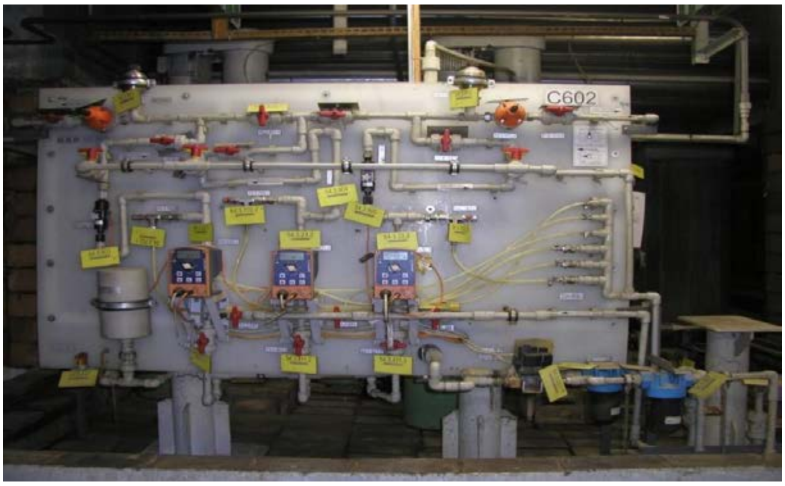


FIG. 70. Automatic dosing system for ethanolamine in the feedwater at Bohunice NPP (Courtesy of Slovenskè elektrárne, a.s.)

FIG. 71. Probe (left) and analyzers (right) for on-line measurement of conductivity in the feedwater at Bohunice NPP (Courtesy of Slovenské elektrárne, a.s.).

Results from on-line measures are automatically transferred into the CIS that covers all laboratory, on-line and in-process data. The data transfer is managed by chemistry personnel. Chemistry personnel and identified job positions (e.g. main control room personnel, system and component engineers) have access to the CIS.

5.1.7. Refurbishment of on-line monitoring systems at Krško nuclear power plant

In the 2000s, Krško NPP upgraded their OLM systems for the secondary and auxiliary systems. The refurbishment included replacing the sample cooling system and installing of 50 on-line analyzers – see Fig. 72 for an example of a new skid.

FIG. 72. One of the OLM skids at Krško NPP (courtesy of NEK).

The refurbishment improved the responsiveness, accuracy, and sensitivity of the measuring equipment and expanded the scope and range of measured parameters – see page 2 of Ref. [155] for the list (in principles) of secondary and auxiliary systems' parameters monitored on-line at Krško NPP, the locations of samples points, and the corresponding OLM techniques applied.

The project enables staff to reliably monitor chemical parameters, trigger alarms for exceeded values or inadequate analyzer responses, trend data, and implement corrective measures promptly. Over the years, the analyzers have proven reliable. After 15 years, they began systematically replacing the on-line instrumentation, about 3-4 analyzers annually. The analyzers are connected to the CIS, allowing display, data capture, and trending. This system is available in laboratories, the main control room, and on staff personal computers – see Section 5.2 for screenshots from Krško CIS.

5.1.8. On-line testing and qualification of analyzers at Chinon B nuclear power plant

To qualify analyzers for its fleet, EDF developed test facilities that are connected to operating units 3 and 4 of Chinon B NPP and to the Loire River – see Fig. 73 for location and picture of the premises.

Equipment is tested and qualified in real NPP conditions for open cooling water systems, over long time. Table 12 lists the typical parameters and reference methods used for qualifying the analyzers.

TABLE 12. REFERENCE METHOD USED TO QUALIFY ON-LINE ANALYZERS AT EDF

Parameter monitored on-line	Reference method used to validate the corresponding analyzer
pH	Portable pH-meter
Conductivity	Portable conductivity meter
Hydrazine	Colorimetric detection or IC
Silica	Colorimetric detection
Dissolved oxygen	Faraday cell for low oxygen concentrations Optical method for high oxygen concentrations
Sodium	ICP-MS
Hydrogen	Gas chromatography
Residual chlorine	Colorimetric detection

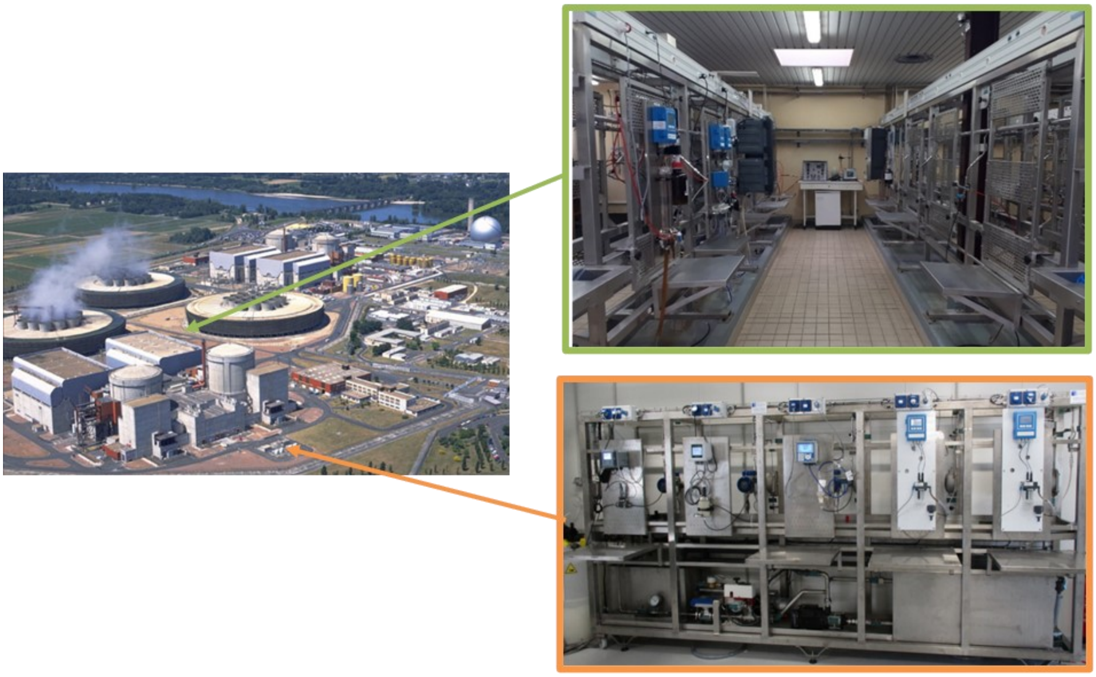


FIG. 73. Location and premises of EDF on-line testing facilities for analyzers at Chinon B NPP (courtesy of EDF).

5.2. INNOVATION IN INTELLIGENT CHEMISTRY INFORMATION SYSTEMS

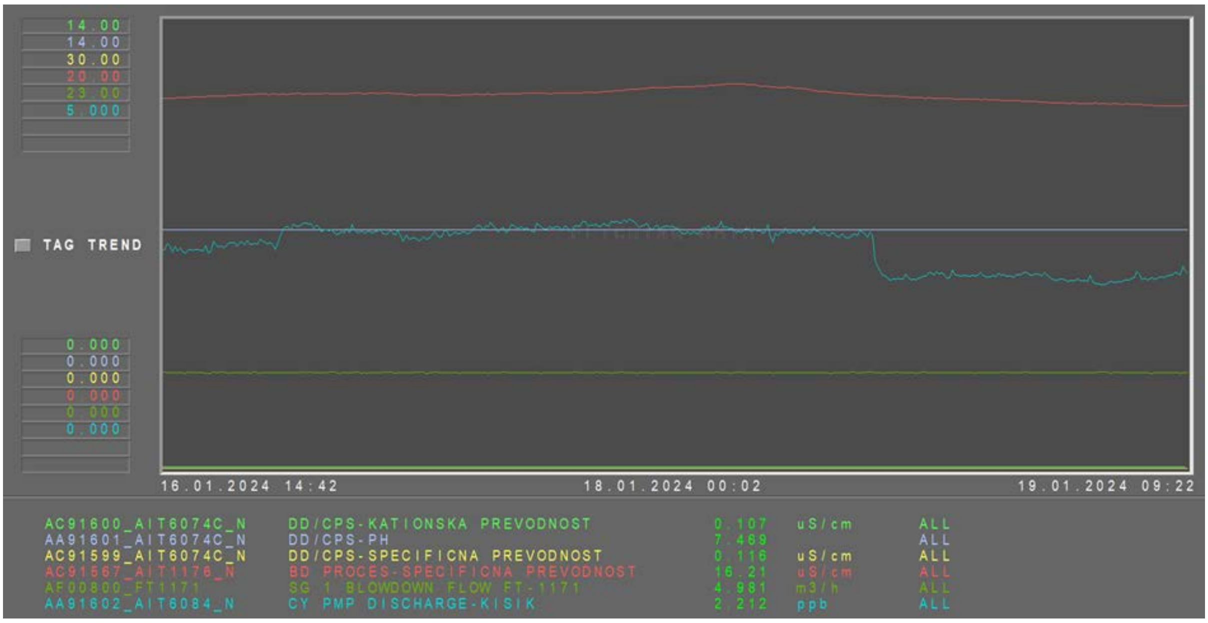
As of 1 July 2024, 66% of world nuclear fleet have been operated for more than 31 years. Some NPPs still use separated computer systems for operating measurement equipment or chemistry information systems developed in the 1990s.

When assessing the performance of their CIS and considering refurbishments, operating organizations typically determine the level of capability their CIS ought to achieve (each level adding capabilities above the previous levels):

1) Integrating and displaying data into a single system easily accessible to personnel – any use of the latest sensor technologies and OLM systems enable the deployment of such CIS;
2) Processing data to trend, statistics, exceedance of fixed thresholds;

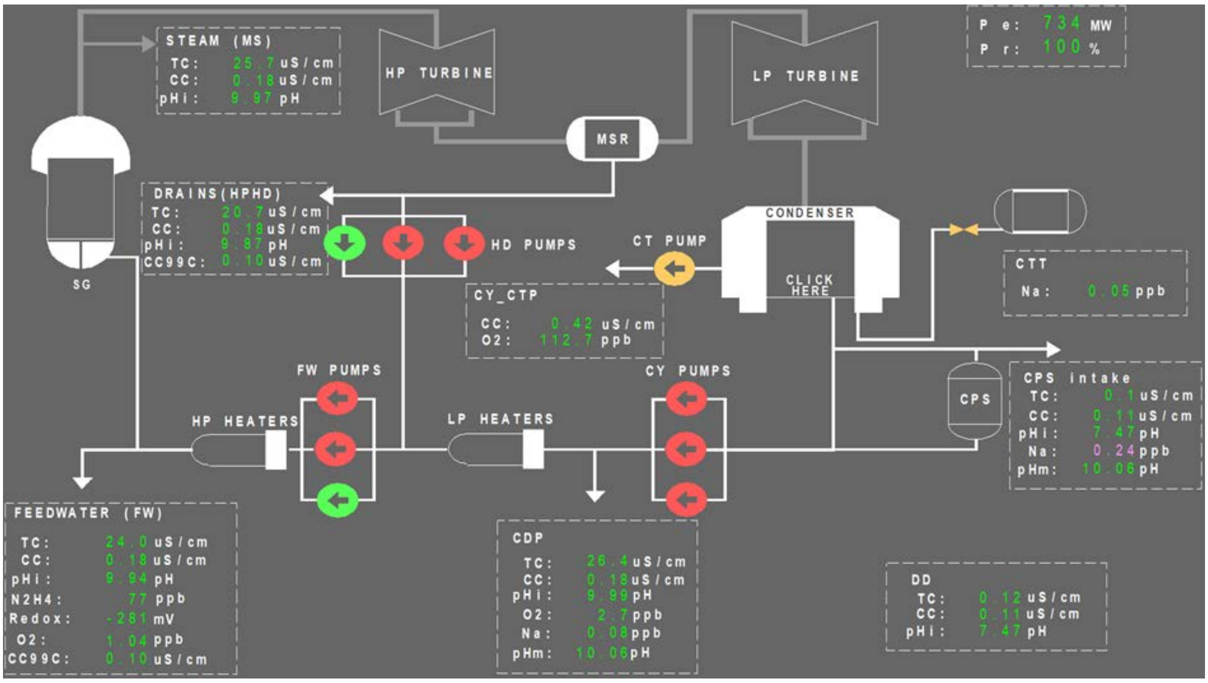
3) Having intelligent monitoring capabilities for early detection of abnormal behaviours (of parameters, sensors or chemistry-related functions/subsystems) and prediction of failures;
4) Having intelligent diagnosis capabilities for suggesting/determining causes of abnormal behaviours and suggesting actions for chemistry personnel and/or operators.

Figures 74–75 show screenshots of the user interface of the CIS deployed at Krško NPP, corresponding to a level 2 in the classification set out above.



AC91600_AIT6074C_N	DD/CPS-KATIONSKA PREVODNOST	0.107	uS/cm	ALL
AA91601_AIT6074C_N	DD/CPS-PH	7.469		ALL
AC91599_AIT6074C_N	DD/CPS-SPECIFICNA PREVODNOST	0.116	uS/cm	ALL
AC91567_AIT1176_N	BD PROCES-SPECIFICNA PREVODNOST	16.21	uS/cm	ALL
AF00800_FT1171	SG 1 BLOWDOWN FLOW FT-1171	4.981	m3/h	ALL
AA91602_AIT6084_N	CY PMP DISCHARGE-KISIK	2.212	ppb	ALL

FIG. 74. Example of displayed data/trends in the CIS used at Krško NPP (courtesy of NEK).



STEAM (MS)
TC: 25.7 uS/cm
CC: 0.18 uS/cm
pHi: 9.97 pH

Pe: 734 MW
Pr: 100 %

DRAINS(HPHD)
TC: 20.7 uS/cm
CC: 0.18 uS/cm
pHi: 9.87 pH
CC99C: 0.10 uS/cm

CY_CTP
CC: 0.42 uS/cm
O2: 112.7 ppb

CTT
Na: 0.05 ppb

CPS intake
TC: 0.1 uS/cm
CC: 0.11 uS/cm
pHi: 7.47 pH
Na: 0.24 ppb
pHm: 10.06 pH

FEEDWATER (FW)
TC: 24.0 uS/cm
CC: 0.18 uS/cm
pHi: 9.94 pH
N2H4: 77 ppb
Redox: -281 mV
O2: 1.04 ppb
CC99C: 0.10 uS/cm

CDP
TC: 26.4 uS/cm
CC: 0.18 uS/cm
pHi: 9.99 pH
O2: 2.7 ppb
Na: 0.08 ppb
pHm: 10.06 pH

DD
TC: 0.12 uS/cm
CC: 0.11 uS/cm
pHi: 7.47 pH

FIG. 75. User interface of the CIS for secondary systems at Krško NPP (courtesy of NEK).

Section 5.2.1 presents innovation in developing and using intelligent chemistry information systems that feature intelligent monitoring and diagnosis capabilities. Section 5.2.2 discusses scope and requirements for developing and installing a new CIS at a NPP, based on experience gained at Slovakian NPPs.

5.2.1. Innovation in developing and using chemistry information systems capable of intelligent monitoring and diagnosis

When the CIS at Tianwan NPP was refurbished, the chemistry engineering organization set requirements to design and deploy intelligent monitoring and diagnosis capability as follows:

- Install sufficient on-line chemistry analyzers in the primary and secondary systems to maximize digitalization;
- Deploy a network to send data from on-line analyzers, process parameters and, equipment operation status to a centralized chemistry engineering workstation;
- Develop and apply a quantifiable diagnostic method for detecting and signalling abnormal chemistry conditions on the workstation.

The workstation terminal displays real time values and historical trends of parameters (Fig. 76). Based on experience, the diagnostic method detects when thresholds are exceeded, and abnormal data trends. The magnitude of deviations, possible causes, and corresponding control measures are determined by the software and submitted to the system user for consideration.

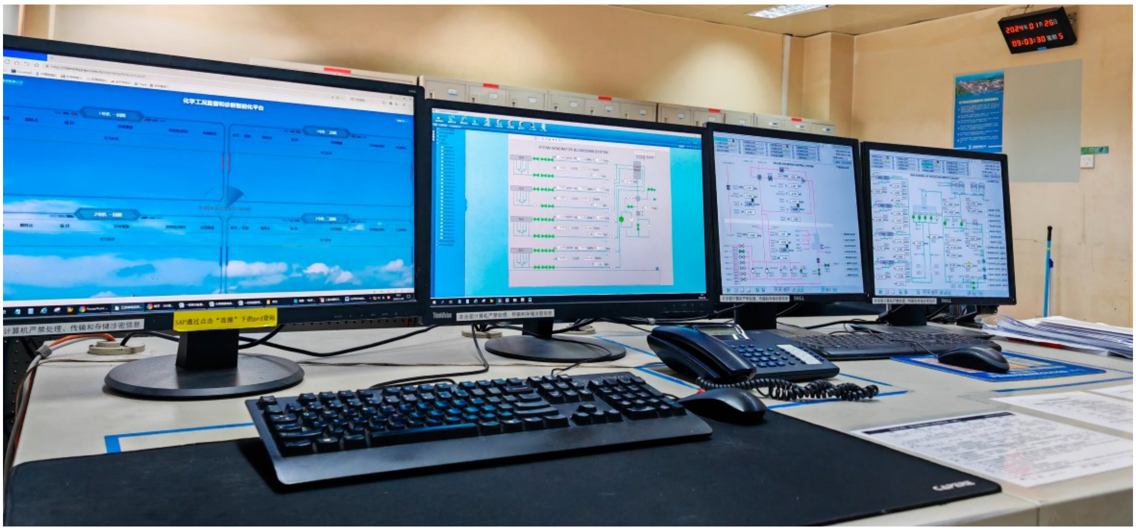


FIG. 76. Chemistry Engineering Workstation at Tianwan NPP (courtesy of CNNP).

The system deployed at Tianwan NPP consists of several modules:

- Data acquisition module: extracts chemistry relevant data from the NPP process system, such as chemical analysis data, equipment process parameters, equipment operation status, and, stores it in a database;
- Data control module: the place where chemistry engineers set criteria for identifying abnormal parameters (threshold and trends) and system performance, and define control measures for each type of abnormal parameter;
- Data processing module: automatically scans stored data against the logical relationships defined in the data control module, filters out useless data and outliers, and, after analysing, locates abnormal data, causes and corrective measures;

- Data display modules: Module 1 displays criteria for judging abnormal data and the time of occurrence. Module 2 displays the root cause and corrective measures after troubleshooting abnormal data;
- Data export module: exports criteria for judging abnormal data, the time of occurrence, root causes, and corrective measures into a report.

Sanmen NPP began developing a similar system, using artificial intelligence (AI), in 2022. Their 'expert diagnosis system', based on large language data model with self-learning from operating experience and events, includes anomaly fault trees, and is expected to start tests in 2025.

The crucial element of intelligent CIS is their ability to early detect abnormal behaviours of parameters, sensors and chemistry-related functions/subsystems. While equipment reliability programmes typically address system performance and behaviours, issues with chemistry-related parameters, sensors and functions require specific involvement from chemistry functions.

At EDF NPPs, data from in-process sensors and OLM systems are routinely collected in a database and processed by software (termed 'e-monitoring'). The software learns from historical data representing correct behaviour of the equipment or system and derives a model for expected operation. Predictive statistical algorithms estimate expected values for each parameter. E-monitoring allows real time comparison of operating data with the model – see example for hydrogen concentration in Section 1.2 of Ref. [39], helping to detect failures and identify slow drifting trends in operating data early.

If an anomaly is detected (a data point exceeds a threshold), the software automatically alerts relevant departments (via email). Slow, long term degradation of parameters is also captured. Actions from the NPPs include field inspections, specific analyses, and maintenance activities before the drift affects operation.

Thresholds are set dynamically, considering plant status and environmental conditions (e.g. seasonal variability, reactor power, periodic test). The software enables users to adjust interdependence of thresholds/signals with other parameters and plant status data as needed, offering more extensive signal processing capabilities than chemistry engineers have.

EDF 'e-monitoring' software is used for:

- Detecting fouling (see also Section 3.6 for an example of using digital twin to model steam generators' fouling and behaviour);
- Identifying defective instrumentation and control equipment;
- Detecting equipment degradation.

Examples of equipment degradation detected at EDF using the software included a hydrogen leak in the stator cooling water system, and high temperature in this system. The latest detection led to lowering the temperature setpoint to prevent alarms and power reduction and allowing for system purification before clogging the hollow copper conductors.

5.2.2. Scope and technical requirements for a new chemistry information system

This section presents the general requirements developed by Bohunice and Mochovce NPPs for their new CIS. The overall objective of the new CIS was to support safe and reliable operation in compliance with regulatory requirements and recommendations from international organizations. The main benefit is to provide a fully functional application and streamline/improve effectiveness of chemistry-related processes.

These processes include:

- Recording results of laboratory analysis, recognizing good practices, quality assurance requirements incl. for calibration and standards' quality;
- Storing on-line measurements of chemical parameters;
- Providing necessary outputs and reports to evaluate performance in chemistry for all NPP systems (requiring control of technical inputs such as materials, chemical parameters, regulations for discharges, nuclear fuel integrity controls);
- Supporting prompt initiation of actions to return within technical specifications for operation.

AI can play a key role in data analysis, modelling, and prediction, whereas programming algorithms appropriately and integrating the technology into existing nuclear power plant processes are challenging.

Key requirements for functionalities of the CIS include:

- Compliance with standards for cyber security and data integrity, enabling tracking and recording all changes to the CIS. The system uses a graded approach to access, allowing permissions (read, create, modify, execute) on a need-to-know basis depending on individual responsibilities;
- Easy data collection (ensuring data integrity) from various sources including manually recorded laboratory analysis, on-line measurements, gamma spectrometry data, and in-process parameters, imported from a file or reprocessed;
- Compatibility with multimedia files (documents, pictures, videos, hyperlinks) that can be attached to records;
- Capable of processing laboratory, in-process and calculated parameters for statistical evaluation, comparison and presentation;
- Determination of alarm levels (thresholds, trends) before breaching technical specifications, using mathematical models to predict scenarios (e.g. nuclear fuel leakage types from lab gamma-ray spectrometry), and calculates time to action;
- Take actions following diagnostics to prevent exceeding technical specification, for example informing (emailing) chemistry engineers and automatically initiating additional measurement or sampling;
- Automatic generation of NPP-specific and WANO key performance indicators (e.g. CPI, fuel reliability index, composite corrosion indicator);
- Automatic generation of graphs and reports, augmented by multimedia files;
- Management of IXR, monitoring and predicting their remaining lifespan based on the applied chemical regime;
- Management of chemicals and reference solutions (standards), including registration, labelling, consumption and disposal, with alarms when expiry dates are passed;
- Metrology control of lab instruments (incl. pipettes), with alarms for expired validity and assessment of measurement schedules;
- Detection of human errors during manual entry of lab results, using routines comparing with expected values or previous values.

5.3. INNOVATIVE USE OF ROBOTICS AT SANMEN NUCLEAR POWER PLANT

This section presents innovation in using robotics for chemistry-related tasks at Sanmen NPP. Examples cover handling of laboratory samples (Section 5.3.1) and field acquisition of data (Section 5.3.2).

5.3.1. Handling of laboratory samples

Sanmen NPP started to develop robots and robotic arms for transportation and automatic analyses of laboratory samples in 2022 – see Fig. 77 for an overview of capabilities in principles – with the objective to operate a ‘dark light lab’ in 2025. The goal was to reduce resource needs for sample transport, preparation and analysis, allowing plant chemists to focus on addressing issues and deviations.

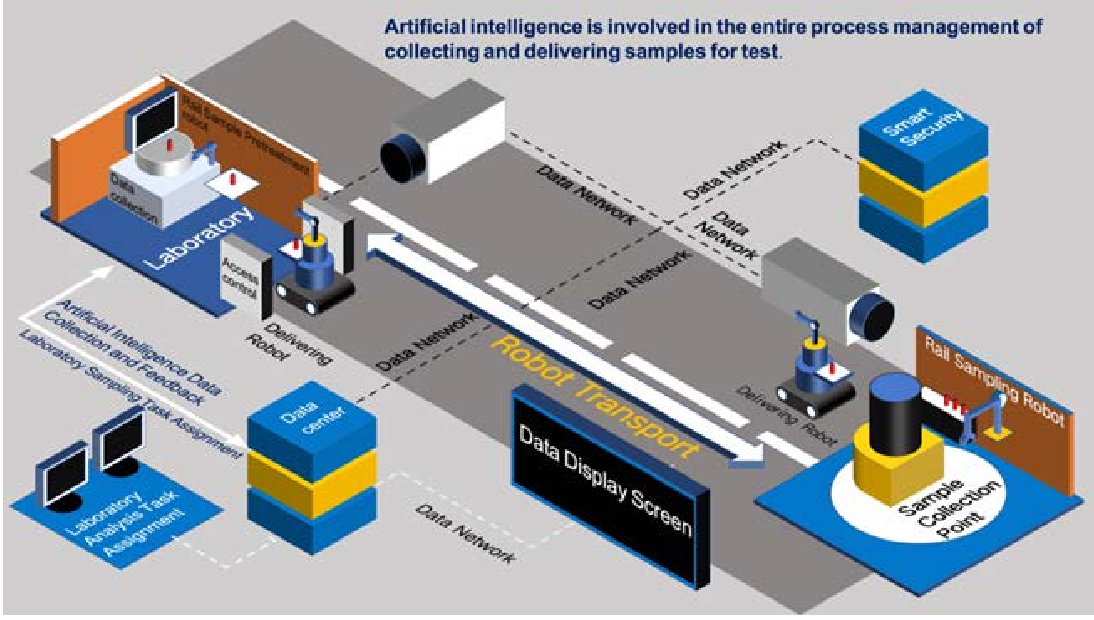


FIG. 77. Principles of the automated processing of lab sampling at Sanmen NPP (courtesy of CNNP).

Developments started with the water treatment system and include, as of 2025, robots for transporting and preparing samples (Fig. 78), performing pH measurement, liquid scintillation (Fig. 79) and operating a high-purity germanium detector (Fig. 80).

FIG. 78. Robot for transporting radioactive samples from the water treatment system (left) and preparing packages for measurement (right) being operated at Sanmen NPP (courtesy of CNNP).

FIG. 79. Robot for preparing samples for a liquid scintillation counter being operated at Sanmen NPP (courtesy of CNNP).

FIG. 80. Robot operating a high-purity germanium detector at Sanmen NPP (courtesy of CNNP).

A integration of visual sensors and lidar, combined with environmental modelling and localization, enables the robot to safely transport radioactive samples within the laboratory. Operating the robotic arms for handling samples necessitated:

- A dedicated management system;
- Establishing logical relationships between tasks, laboratory analytical instruments, robots, and analytical engineers;
- Developing human-machine interfaces, and
- Integrating force sensors with visual sensors to achieve precise operation.

5.3.2. Field acquisition of chemistry-related data

An inspection robot has been also developed at Sanmen NPP, operating since early 2024 after tests were completed. The robot (Fig. 81) is used to monitor the operating status of various instruments, including on-line chemical analyzers, flowmeters, thermometers, conductivity resin columns, pipes and valves, in the secondary sampling system, replacing field operator walkdowns. The robot rooms the premises at preset times or on demand from chemical personnel. The backend software can identify data anomalies, judge trend anomalies, system instrument anomalies, and cooperate with the AI-based expert diagnosis system for fault diagnosis.

FIG. 81. Intelligent inspection robot for field acquisition of chemistry-related data being developed at Sanmen NPP (courtesy of CNNP).

The key functional features of the system operating the robot are as follows:

- Videos collected by the robot converted into digital signals through a video image acquisition and analysis system;
- Identification of abnormal data and trends;
- Alarm automatically triggered on abnormal data and trends;
- Generation of inspection data and reports, automatically uploaded to the CIS;
- AI-based models conducting analysis and diagnosis to find the root cause of identified abnormal data and trends, learning and improving through continuous training;
- Use of image recognition techniques for:
  - Detecting leakages, comparing with previous videos;
  - Analysing resin column operation based on their colour;
  - Detecting abnormal sampling flowrates reading the flowmeters.

The benefits are:

- Under normal operational conditions, the robot can carry out more frequent and accurate walkdowns than chemistry staff;
- Under abnormal operational conditions, chemistry staff can remotely monitor the secondary sampling system in real time and focus on issue resolution.

6. SUMMARY AND PERSPECTIVES

This section summaries significant learning from examples and case studies in this TECDOC, whereas this TECDOC provides an industry overview on innovation, advances and developments in the water chemistry of PWRs and WWERs, without being comprehensive or prescriptive. Expert perspectives are included for each topic.

Regarding the water chemistry of the primary system:

- Use of enriched boric acid: Taishan NPP, commissioned 2018–2019, confirmed the benefits of EBA first identified in German and Swiss NPPs in the 1990s. The desired pH_T is achieved earlier in the fuel cycle. The reactivity margins are larger, though ^{10}B-ratio requires attention. Future operating experience from other plants using EBA will be an opportunity for further substantiate the case for the use of EBA – details in Section 2.1.
- Hydrogen management: PWRs use two practices to maintain reducing conditions. High concentrations 'better' mitigate general corrosion and PWSCC propagation in sensitive materials, while lower concentrations mitigate PWSCC initiation and metallic nickel deposition on fuel cladding. Both approaches are effective, with no recent research findings against them. Follow-up research is desirable to address PWSCC model uncertainties. Innovative practices in hydrogen management include using high-pressure cylinders in PWRs to inject hydrogen in CVCS, using gas chromatography together with electrochemical sensors for accurate on-line measurements, and quantitative models for continuous ammonia dosing in WWERs – details in Section 2.2.
- Silica control: Silica, in the presence of zinc, magnesium, calcium, and aluminium (forming zeolites), remains a concern due to potential fuel deposition. Feed and bleed operations are not widely used due to boron removal and increased waste. Recent solutions to remove silica involve nanofiltration membranes and hybrid ion exchange resins in temporary or permanent filtration systems used at power or, most commonly, during HFT for new build – details in Section 2.3.
- Control of source term and zinc injection: optimized pH_T is the main control method to mitigate the build-up of source term. Zinc injection, when initiated one cycle before and continued after an SGR, significantly reduces the ^{58}Co peak during forced oxidation from the second shutdown. However, it increases the release of ^{58}Co and other ACP in the first cycle, which necessitates appropriate countermeasures – details in Section 2.4.2. Comprehensive on-site measurements of ACP and simulation modelling are crucial for informing chemistry programmes regarding their impact to source term control – details in Sections 2.9 and 2.4.3.
- Flexible power operation: FPO increases radioactive effluents, but operating experience shows these can be managed without additional impact to environment (compared with steady operation at full power), provided storage and treatment capacity is sufficient. The same applies to chemical discharge. In FPO, pH_T adjustment in RCS ought to be easier with on-line monitoring and automatic lithium hydroxide dosing – details in Section 2.5.
- Replacement of lithium with potassium hydroxide in PWR: KOH is cheaper than lithium hydroxide and has no sourcing limitation. A comprehensive case study at a PWR explores all consequences, including analytical aspects and operator training – details in Section 2.6. The first application is expected in 2025, with operating experience to be reviewed in the coming years.
- Shutdown and start-up chemistry: During shutdowns, forced oxidation with hydrogen peroxide in PWRs is an established practice to release corrosion product (e.g. ^{58}Co) before their removal by mechanical and chemical filtration. Improved understanding and modelling ACP behaviours, such as ^{110m}Ag, throughout forced oxidation enhance abatement and filtration strategies. Adding KOH is a beneficial practice in WWERs to mitigate the negative effect of decreasing pH on the

magnetite passivation layer. During start-ups, hydrogen and lithium are injected as soon as possible in PWRs to establish reducing and alkaline conditions – details in Section 2.7.

- Commissioning chemistry: hot functional tests during commissioning of new reactors are a key opportunity for passivating surfaces reducing future corrosion products release. Good practice is to establish strict protocols during HFT, considering, for PWRs, zinc injection and hydrogen addition – details in Section 2.8.

Regarding the water chemistry of secondary systems:

- Control of pH: Using amines (mainly ETA) to achieve high pH (9.8–10.0) is now an established trend globally. Outcomes of case studies where combination of amines (ETA and others) with/without ammonia are tested ought to be reviewed, especially regarding the pH achieved throughout the secondary systems, as better products may emerge – details in Section 3.1.
- Application of film-forming substances: FFS like octadecylamine, widely used in thermal power industry but also in WWERs, are being applied in more NPPs. Optimization of their application just before outage (most beneficial application) but also over the cycle is ongoing, with further work on compatibility needed. As there are still no clear criteria to evaluate how much equipment protection is improved, experts need continue evaluating implementation cases, as better products and practices to maximize coverage could emerge – details in Section 3.2.
- Reduction of fouling and removal of corrosion products: first-of-a-kind SG sludge lancing was performed at a WWER. In PWRs, effective practices include using high-efficiency magnetic filters in condenser systems to abate corrosion product transport and developing simulation modelling of SG fouling – details in Section 3.6. The use of dispersants like polyacrylic acid as a remedy (before outage) or to keep SG clean over the cycle (through off-line application) is still to be refined for compatibility and optimal timing in off-line applications – details in Section 3.3.
- Alternatives to hydrazine: Limitation of hydrazine usage (a toxic and carcinogenic substance) is a concern in Europe. Alternatives like carbohydrazide and diethylhydroxylamine were already tested in NPPs, with mixed results at times. New applications with a mixture of methanol and ETA are being prepared. Experts agree that no alternative matches hydrazine's effectiveness as an oxygen scavenger, requiring compromises. Further research and more years of experience with alternatives are needed to fully understand what makes up the best compromises – details in Section 3.4.
- Start-up chemistry: Time and resources to achieve optimal start-up chemistry are not always of a high priority for operating organizations. Plant chemists play a critical role in convincing plant managers that expectations have to be followed. Plant managers play a critical role in coordinating all disciplines to maintain clean conditions in outages (foreign material exclusion programme, preservation, control of chemicals) and achieve a low WANO CPI, ideally 1.0, in the early stage of the fuel cycle – details in Section 3.5.

Regarding auxiliary systems' water chemistry, new treatments and technical solutions for suppressing corrosion, fouling, biofouling, scaling, etc. were developed in the non-nuclear industry and are available for NPPs. They can be considered when dealing with similar plant specific environmental and regulatory conditions or operating similar equipment and systems (e.g. cooling towers, diesel generators, generator stator, water treatment plants). NPP operating organizations ought to connect with other industries to leverage these advancements.

For all systems and analysis techniques, on-line monitoring systems now provide real time, continuous data on water's chemical and physical properties. This enables automatic dosing for better control, and comprehensive, intelligent chemistry information systems that help chemistry engineers focus on issue resolution. Further work is needed to extend automatic dosing to all chemical treatments, use AI-based diagnostic systems for automatic dosing, and transition to full digitalization of chemistry-related processes. Robotics can further optimize resource-intensive tasks, such as in on-site laboratories.

APPENDIX. REACTOR INFORMATION RELATED TO NUCLEAR POWER PLANTS REFERRED TO IN THIS TECDOC

Table 1 presents the reactor type, goss capacity and commercial operation date for the NPPs referred to in this TECDOC, as in the IAEA PRIS database[19].

TABLE 1. INFORMATION ON REACTORS AND NUCLEAR POWER PLANTS REFERRED TO IN THIS TECDOC

Reactor/Nuclear Power Plant	Reactor Type	Gross Capacity	Country	Commercial Operation Date	Operator
Angra-2	PWR Pre Konvoi	1350 MW_e	Brazil	February 2001	Electronuclear S.A.
Armenian-2	WWER V-270	448 MW_e	Armenia	May 1980	Closed Joint Stock Company Armenian NPP
Ascó-1 and 2	PWR 3 loops	1033 MWe 1027 MWe	Spain	December 1984 March 1986	Asociación Nuclear Ascó-Vandellós A.I.E. (ANAV)
Bohunice-3 and 4	WWER V-213	500 MW_e	Slovakia	February 1985 December 1985	Slovenské Elektrárne a.s.
Borssele	PWR 2 loops	515 MW_e	Kingdom of the Netherlands	October 1973	N.V. Elektriciteits Produktiemaatschappij Zuid-Nederland, EPZ
Chashma-3 and 4	PWR 1 loop	340 MW_e	Pakistan	December 2016 September 2017	Pakistan atomic energy commission
Chinon B-3 and 4	PWR 3 loops	954 MW_e	France	March 1987 April 1988	Electricité de France
Comanche Peak-1 and 2	PWR 4 loops	1259 MW_e 1250 MW_e	United States of America	August 1990 August 1993	Luminant Generation Company, LLC
Cook-1 and 2	PWR 4 loops	1131 MW_e 1231 MW_e	United States of America	August 1975 July 1978	American Electric Power Company, Inc.
Daya-Bay-1 and 2	PWR 3 loops	984 MW_e	China	February 1994 May 1994	Daya Bay Nuclear Power Operations and Management Co, Ltd.
Doel-1 and 2	PWR 2 loops	454 MW_e	Belgium	February 1975 December 1975	Engie Electrabel
Doel-3 and 4	PWR 3 loops	1056 MW_e 1090 MW_e	Belgium	1982 → 2022 July 1985	Engie Electrabel
Dukovany-1 to 4	WWER V-213	500 MW_e	Czech Republic	May 1985 March 1986 December 1986 July 1987	Czech Power Co., CEZ a.s.

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[19] https://pris.iaea.org/PRIS/home.aspx

TABLE 1. INFORMATION ON REACTORS AND NUCLEAR POWER PLANTS REFERRED TO IN THIS TECDOC

Reactor/Nuclear Power Plant	Reactor Type	Gross Capacity	Country	Commercial Operation Date	Operator
Embalse	PHWR Candu 6	656 MW_e	Argentina	January 1984	Nucleoeléctrica Argentina S.A.
Fangchenggang-3 and 4	PWR HPR1000	1180 MW_e	China	March 2023 May 2024	Guangxi Fangchenggang Nuclear Power Company, Ltd.
Flamanville-3	PWR EPR	1650 MW_e	France	Expected 2025	Electricité de France
Gravelines-1 to 6	PWR 3 loops	951 MW_e	France	November 1980 December 1980 June 1981 October 1981 January 1985 October 1985	Electricité de France
Haiyang-1 and 2	PWR AP-1000	1250 MW_e	China	October 2018 January 2019	Shandong Nuclear Power Company, Ltd.
Hanul-5 and 6	PWR 2 loops	1049 MW_e	Republic of Korea	July 2004 April 2005	Korea Hydro and Nuclear Power Co.
Kewaunee	PWR 2 loops	595 MW_e	United States of America	1974 → 2013	Dominion Energy
Koeberg-1 and 2	PWR 3 loops	964 MW_e 970 MW_e	South Africa	July 1984 November 1985	ESKOM
Krško	PWR 2 loops	727 MW_e	Slovenia	January 1983	Nuklearna Elektrarna Krško
Loviisa-1 and 2	WWER V-213	531 MW_e	Finland	May 1977 January 1981	Fortum Power and Heat Oy
Mochocve-1 and 2	WWER V-213	500 MW_e	Slovakia	October 1998 April 2000	Slovenské Elektrárne a.s.
Mochocve-3	WWER V-213	471 MW_e	Slovakia	Expected 2025	
Olkiluoto-3	PWR EPR	1660 MW_e	Finland	May 2023	Teollisuuden Voima Oyj
Paks-1 to 4	WWER V-213	506 MW_e	Hungary	December 1982 September 1984 September 1986 August 1987	MVM Paksi Atomerőmű Zrt.
Paluel-1 to 4	PWR 4 loops	1382 MW_e	France	December 1985 December 1985 February 1986 June 1986	Electricité de France
Qinshan-I	PWR CNP-300	330 MW_e	China	April 1994	CNNC Nuclear Operation Management Company Limited

TABLE 1. INFORMATION ON REACTORS AND NUCLEAR POWER PLANTS REFERRED TO IN THIS TECDOC

Reactor/Nuclear Power Plant	Reactor Type	Gross Capacity	Country	Commercial Operation Date	Operator
Qinshan-III-1 and 2	PHWR Candu 6	728 MW_e	China	December 2002 July 2003	CNNC Nuclear Operation Management Company Limited
Ringhals-3 and 4	PWR 3 loops	1128 MW_e 1178 MW_e	Sweden	September 1981 November 1983	Ringhals AB
Salem-1 and 2	PWR 4 loops	1254 MW_e 1200 MW_e	United States of America	June 1977 October 1981	PSEG Nuclear, LLC
Sanmen-1 and 2	PWR AP-1000	1251 MW_e	China	September 2018 November 2018	Sanmen Nuclear Power Co., Ltd.
Sequoyah-1 and 2	PWR 4 loops	1221 MW_e 1200 MW_e	United States of America	July 1981 June 1982	Tennessee Valley Authority
South Texas-1 and 2	PWR 4 loops	1354 MW_e	United States of America	August 1988 June 1989	STP Nuclear Operating Co.
St. Lucie-1 and 2	PWR 2 Loop	1045 MW_e 1050 MW_e	United States of America	December 1976 August 1983	Florida Power & Light Co.
Summer	PWR 3 loops	1006 MW_e	United States of America	January 1984	South Carolina Electric & Gas Co.
Taishan-1 and 2	PWR EPR	1750 MW_e	China	December 2018 September 2019	Taishan Nuclear Power Joint Venture Company Limited
Temelín-1 and 2	WWER V-320	1082 MW_e	Czech Republic	June 2002 April 2003	Czech Power Co., CEZ a.s.
Tianwan-1 and 2	WWER V-428	1060 MW_e	China	May 2007 August 2007	Jiangsu Nuclear Power Corporation
Tianwan-3 and 4	WWER V-428	1126 MW_e	China	February 2018 December 2018	Jiangsu Nuclear Power Corporation
Tianwan-5 and 6	PWR ACPR-1000	1118 MW_e	China	September 2020 June 2021	Jiangsu Nuclear Power Corporation
Vandellós-2	PWR 3 loops	1087 MW_e	Spain	March 1988	Asociación Nuclear Ascó-Vandellós A.I.E. (ANAV)

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ABBREVIATIONS

ACP	activated corrosion product
AI	artificial intelligence
CCW	component cooling water
CEA	Commissariat à l’Energie atomique et aux énergies Alternatives
CGN	China General Nuclear Power Group
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
CIS	chemistry information system
CNNP	China National Nuclear Power Co., Ltd.
CPI	chemistry performance indicator
CPS	condensate polishing system
CVCS	chemical volume and control system
DEHA	diethylhydroxylamine
DH	dissolved hydrogen
DO	dissolved oxygen
EBA	enriched boric acid
ECW	essential chilled water
EDF	Electricité De France
EDG	emergency diesel generator
EDI	electrodeionization
EDS	energy dispersive X-ray spectrometer
EMECC	ensemble de mesures et d’études de la contamination des circuits
EPR	European pressurized reactor
EPRI	Electric Power Research Institute
ESW	essential service water
ETA	(mono)ethanolamine
FAC	flow accelerated corrosion
FFS	film forming substances
FPO	flexible power operation
GTM	gas transfer membrane
HFT	hot functional tests
IASCC	irradiation assisted stress corrosion cracking
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
IXR	ion exchange resin
KHNP	Korea Hydro and Nuclear Power Co.
LCO	limiting conditions of operation
MSR	moisture separator reheater
NPP	nuclear power plant

NSS	nuclear sampling system
ODA	octadecylamine
OLM	on-line monitoring
OSCAR	outil de simulation de la contamination en réacteur
PAA	polyacrylic acid
pH	potential hydrogen
PHWR	pressurized heavy-water reactor
PWR	pressurized water reactor
PWSCC	primary water stress corrosion cracking
RCS	reactor coolant system
RO	reverse osmose
SCC	stress corrosion cracking
SCW	stator cooling water
SEM	scanning electron microscope
SFP	spent fuel pond
SG	steam generator
SGBD	steam generator blowdown
SG-DT	steam generator-digital twin
SGLR	steam generator leak rate
SGR	steam generator replacement
STP	standard temperature and pressure
TDS	total dissolved solids
TOC	total organic carbon
TSP	tube support plates
TT	thermally treated
TTA	tolyltriazole
TTS	top of tube sheet
TVA	Tennessee Valley Authority
US	United States (of America)
WANO	World Association of Nuclear Operators
WWER	water-water energetic reactor

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Consultancy Meetings

Virtual meetings: 6–7 April 2022, 5–6 June 2023
Vienna, Austria: 22–26 January 2024, 22–25 October 2024

Technical Meeting

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