



# Conference Paper

## IMPROVING CHEMISTRY PERFORMANCE IN CANDU PLANTS

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## IMPROVING CHEMISTRY PERFORMANCE IN CANDU PLANTS

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### ABSTRACT

There is a strong interplay between coolant chemistry and materials selection in any nuclear power plant system. To achieve the design life of reactor components it is necessary to monitor and control relevant chemistry parameters, such as ionic conductivity, pH, concentrations of dissolved ions and redox species (e.g., hydrogen, hydrazine, oxygen) and the concentrations of suspended corrosion products. Chemistry specifications are set to achieve a balance between the sometimes conflicting requirements to minimize corrosion and radiological dose and to minimize operating and maintenance costs over the lifetime of the plant.

For the past decade, Atomic Energy of Canada Limited (AECL) has taken a rigorous and disciplined approach to reviewing and updating all aspects of chemistry control in the CANDU®<sup>1</sup> nuclear power plant (NPP). This approach has included proactively reviewing chemistry operating experience from existing CANDU and other water-cooled NPPs worldwide to identify and address emerging issues, updating all of our chemistry control documentation to ensure that each chemistry parameter is linked to a specific requirement (e.g., reduce activity transport, monitor for condenser leak) and incorporating the latest results from our Research & Development (R&D) programs to ensure that all chemistry specifications are supported by a sound rationale.

The results of this review and update have been incorporated into updated chemistry specifications and, in some cases, modified operating procedures for new and existing plants. In addition, recommendations have been made for design modifications to improve chemistry control in new build plants, especially during periods of shutdown and startup when chemistry control has traditionally been more challenging. Chemistry control in new-build CANDU plants will rely increasingly on the use of on-line instrumentation interfaced directly to AECL's state-of-the-art chemistry monitoring, diagnostics and analysis system to facilitate improved chemistry control and to help staff to proactively identify and address emerging issues before they result in a loss of performance.

This paper will outline AECL's chemistry control philosophy, and provide specific examples to illustrate how changes to plant design, materials, operational procedures, and chemistry specifications are being implemented to support improved chemistry performance in existing and new-build CANDU plants.

### 1. INTRODUCTION

The target for a 60-year design life for nuclear power plants presents a significant challenge compared to earlier plants. Aging Management programs that are developed to ensure the plant both meet design life and maintain the option for life extension require rigorous chemistry

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<sup>1</sup> CANDU® is a registered trademark of Atomic Energy of Canada Limited.

control and chemistry management backed by excellent design and robust materials, while the regulator expects the plant safety margins will not deteriorate as the result of poor chemistry control.

Over the past decade, Atomic Energy of Canada Limited (AECL) has taken a rigorous and disciplined approach to reviewing and updating all aspects of chemistry control in the CANDU nuclear power plant (NPP), including a complete review of the chemistry specifications and the identification and implementation of both design and operational changes to improve plant chemistry control. This exercise started with a review of the issues affecting chemistry performance in the primary and secondary heat transport circuits of the CANDU reactor, but was later expanded to include all plant systems requiring chemistry control. Particular attention was paid to monitoring feedback on operating experience with chemistry sampling systems and chemical injection systems in both the nuclear steam supply and balance-of-plant from CANDU plants in order to identify areas for improvement that could be addressed by making improvements to the design.

The AECL philosophy of chemistry control requires that each parameter be linked to a requirement that arises from one of the objectives of the chemistry control program. In addition, there must be a sound rationale to support each chemistry specification. Thus, an important part of the exercise undertaken by AECL was to update the specifications and their supporting rationale based on feedback from the operating plants, as well as new insights arising from R&D programs funded by the CANDU Owners Group, the Electric Power Research Institute, AECL and other research organizations around the world. The updated chemistry specifications with supporting rationale, action limits (for control parameters), recommended sampling locations and sampling frequencies are documented in a Chemistry Control Design Guide which is to be updated every few years. The Chemistry Control Design Guide is delivered with each new build project, and forms the basis for the plant Chemistry Operating Manual.

In the Chemistry Control Design Guide, chemistry parameters for each system are divided into two categories: (1) control parameters, which are those parameters that must be controlled to within preset limits to achieve the objectives of the chemistry control program, and (2) diagnostic parameters, which are those parameters which provide additional information that is used to diagnose problems and assess performance. Typical examples of control parameters are the pH and the dissolved oxygen concentration, which must be maintained within well-defined limits to mitigate corrosion of system materials, while examples of diagnostic parameters include the change in conductivity across an ion-exchange resin column, which is indicative of the performance of the purification system, or the cation conductivity of the steam generator (SG) blowdown, which is indicative of the total concentration of strong acid-forming anions in the SG and is ultimately a measure of the leak-tightness of the condenser and the effectiveness of the water treatment plant. Both control and diagnostic parameters must be measured regularly at a frequency specified in the Chemistry Operating Manual, but only control parameters have defined actions that must be taken when a given threshold has been exceeded.

We present herein highlights of the initiative taken by AECL to improve the chemistry performance in CANDU plants by updating the chemistry specifications and by implementing design changes to improve chemistry control. We also describe a chemistry monitoring, diagnostic and analysis system and chemistry work management system that has been developed by AECL to enhance the ability of chemistry staff to efficiently and effectively manage plant chemistry.

## 2. UPDATED CHEMISTRY SPECIFICATIONS TO IMPROVE CHEMISTRY PERFORMANCE

### 2.1 Primary Coolant Chemistry

The Enhanced CANDU 6 (EC6) reactor is a pressurized heavy water reactor (PHWR) with a moderator circuit that is independent of the primary coolant system. The primary coolant system is used to transport the heat generated in the core to the SGs where the heat is used to boil the secondary coolant to generate steam which is sent to the turbine generator to produce electricity. The reactor fuel is natural uranium and the primary coolant is heavy water ( $D_2O$ ). The fuel elements are contained in 380 horizontal pressure tubes made of Zr-2.5 Nb. The primary coolant is transported between the core and the SGs in pipes constructed of carbon steel. The Advanced CANDU Reactor<sup>®2</sup> (ACR) is an evolutionary advancement from the EC6 in which the primary coolant has been changed from heavy to light water and the core inlet and outlet piping has been changed from carbon steel to stainless steel [1]. The fuel in the ACR is slightly enriched to make up for the increased neutron absorption cross section of light water compared to heavy water.

The current chemistry control specifications for the primary coolant for the EC6 and the ACR are listed in Table 1 and Table 2, respectively. These specifications differ from previous specifications for the CANDU 6 reactor in the following ways:

1. The control parameter for alkalinity has been switched from pH to dissolved  $Li^+$  concentration,
2. For the EC6, the upper limit for alkalinity (as measured by either  $Li^+$  concentration or  $pH_a^3$ ) has been reduced,
3. For the ACR, the alkalinity (as measured by either  $Li^+$  concentration or pH) will be increased, and,
4. The upper limits for  $Cl^-$  and  $SO_4^{2-}$  concentration have been lowered.

The control parameter for alkalinity during operation at power has been switched from pH to  $Li^+$  concentration for both the EC6 and the ACR to ensure that measurements of alkalinity are reliable<sup>4</sup>. Although the concentration of  $OD^-$  ( $OH^-$ ) in the coolant can be correlated with a measurement of the  $pH_a$  (pH) at 25°C, at high temperature the  $OD^-$  ( $OH^-$ ) concentration is more directly related to the concentration of dissolved  $Li^+$  because  $LiOD$  ( $LiOH$ ) is a strong base over the entire temperature range of interest. The parameter of interest in the high-temperature coolant is, in fact, the concentration of  $OD^-$  ( $OH^-$ ) because it controls the solubility behaviour of oxides that may precipitate in core.

The lower end of the  $Li^+$  concentration specification for the EC6 is based on data<sup>5</sup> for the control of deposition on fuel bundle surfaces measured in  $H_2O$ . The data show that operation in  $H_2O$  with a pH (25°C) above 9.75, which corresponds to a  $pH_a$  of about 10.2 (i.e., to a  $Li^+$  concentration of 0.35 mg/kg) discourages deposition of corrosion products on fuel sheaths. The upper limit for  $pH_a$  was originally set to minimize carbon steel and Zircaloy corrosion, and to

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<sup>2</sup> Advanced CANDU Reactor<sup>®</sup> is a registered trademark of Atomic Energy of Canada Limited.

<sup>3</sup>  $pH_a$  is the pH measured in heavy water by a glass-membrane pH electrode that has been calibrated using light-water buffer solutions.

<sup>4</sup> Pickup of  $CO_2$  in samples of the primary coolant has led to misleading results in the past, whereas the measurement of  $Li^+$  concentration is not subject to such interferences.

<sup>5</sup> Only scoping studies of magnetite solubility have been conducted in  $D_2O$ .

minimize activity transport. The discovery of flow-accelerated corrosion (FAC) of the carbon steel feeders at the outlet of the reactor core, however, resulted in a decision to reduce the upper limit on  $\text{pH}_a$  to 10.4 [2], corresponding to a  $\text{Li}^+$  concentration of 0.55 mg/kg.

During the design of the ACR, a decision was made to replace the carbon steel piping at the inlet and outlet of the core with austenitic stainless steel, which is immune to FAC. This change will reduce the amount of iron in the primary coolant, but may also change the precipitation behavior of corrosion products in core. The typical operating  $\text{pH}_T$ <sup>6</sup> of Pressurized Water Reactor (PWR) plants has increased over the past few decades as part of efforts to minimize activity transport, while the operating  $\text{pH}_a$  of CANDU PHWR plants has decreased to mitigate FAC of core outlet piping. As a consequence, the typical operating  $\text{pH}_T$  of PWR plants is now slightly more alkaline than the upper limit of the EC6  $\text{pH}_a$  specification. With the reduced carbon steel inventory in the ACR primary coolant, there is less concern about FAC of carbon steel and, as with PWRs, the alkalinity of the ACR primary coolant system should likely be higher than the current EC6 specification. Additional information is required before the specifications for the dissolved Li concentration, pH and conductivity can be specified for normal operation, and testing is currently underway.

**Table 1. Chemistry control specifications for the primary coolant of the EC6 during operation at power.**

Parameter	Specification	Rationale
$\text{Li}^+$ (mg/kg $\text{D}_2\text{O}$ )	0.35 to 0.55	Mitigate in-core fouling (lower limit) Reduce rate of FAC of core outlet piping (upper limit)
$\text{D}_2$ (mL/kg $\text{D}_2\text{O}$ )	3 to 10	Suppress radiolytic production of $\text{O}_2$ (lower limit) Minimize D-uptake of zirconium alloys
$^{131}\text{I}$ (MBq/kg $\text{D}_2\text{O}$ )	< 1	Monitor for fuel failure
$\text{D}_2\text{O}$ Isotopic (at. %)	> 98.65 < moderator isotopic – 0.61	Minimize the risk of certain accident scenerios.
$\text{Cl}^-$ (mg/kg $\text{D}_2\text{O}$ )	< 0.05	Minimize the risk of cracking of martensitic stainless steel end fittings
$\text{SO}_4^{2-}$ (mg/kg $\text{D}_2\text{O}$ )	< 0.05	Minimize the risk of strain-induced cracking of carbon steel
$\text{F}^-$ (mg/kg $\text{D}_2\text{O}$ )	< 0.1	Minimize the risk of corrosion and hydriding of zirconium alloys

**Table 2. Modifications to the chemistry control specifications for the primary coolant of the ACR to take account of changes in system materials from the EC6.**

Parameter	Specification	Rationale
$\text{Li}^+$ (mg/kg $\text{H}_2\text{O}$ )	To be determined	Mitigate in-core fouling for a mixed stainless-carbon steel system
$\text{Cl}^-$ (mg/kg $\text{H}_2\text{O}$ )	< 0.01	Minimize the risk of cracking of austenitic stainless steel core outlet piping
$\text{SO}_4^{2-}$ (mg/kg $\text{H}_2\text{O}$ )	< 0.02	Minimize the risk of strain-induced cracking of carbon steel

<sup>6</sup> PWR plants typically report the pH at operating temperature,  $\text{pH}_T$ , which is calculated from the measured room temperature pH using thermodynamic data on the relevant equilibrium constants of boric acid and lithium hydroxide.

The upper limits for  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  in the primary coolant of EC6 and ACR have been reduced from previous limits to further mitigate the risk of cracking of system materials. Both species can be introduced to the primary coolant from the strong-acid cation exchange resin used in the purification system;  $\text{Cl}^-$  as an exchangeable ionic contaminant left over from the manufacturing process and  $\text{SO}_4^{2-}$  from the radiolytic breakdown of sulphonate group in the resin. For the EC6, the specification for  $\text{Cl}^-$  has been reduced from  $< 0.2$  mg/kg to  $< 0.05$  mg/kg to further mitigate the risk of stress corrosion cracking (SCC) of the martensitic stainless steel end fittings [3]. Although martensitic stainless steel is generally quite resistant to SCC in high-temperature pure water, even under oxidizing conditions, its resistance to cracking decreases in the presence of  $\text{Cl}^-$  and other impurities, and it was considered prudent to reduce the allowable limit for  $\text{Cl}^-$  in the coolant even though no failures of end fittings due to  $\text{Cl}^-$ -induced SCC have occurred to date. Because austenitic stainless steels are more susceptible to SCC than martensitic steels in chloride-contaminated water under oxidizing conditions, the upper limit for  $\text{Cl}^-$  in the primary coolant of the ACR has been further reduced to  $< 0.01$  mg/kg. Sulphate has been implicated in strain-induced corrosion cracking (SICC) of low-alloy carbon steel in high-temperature water [4], thus it was considered prudent to introduce limits for  $\text{SO}_4^{2-}$  to mitigate the risk of SICC in the primary coolant system. A limit for  $\text{SO}_4^{2-}$  was set at 0.05 mg/kg for EC6, and further reduced to 0.02 mg/kg for ACR.

## 2.2 Secondary Coolant Chemistry

The secondary coolant systems for the CANDU 6, EC6 and the ACR plants are generally similar to the steam plants at PWR reactors. The condenser is tubed with either stainless steel or titanium, depending on the installation, and the CANDU design specifies a fully-expanded and welded joint at the tubesheet to minimize the risk of ingress of impurities from the condenser cooling water. All CANDU plants but one operate with a direct-contact steam-heated deaerator immediately downstream of the low-pressure feed water heaters to remove dissolved  $\text{O}_2$  from the feed water before it is sent to the high-pressure (HP) feed water heaters and, ultimately, to the SGs. The SGs are tubed with Alloy 800 NG and are designed to have a recirculation ratio of approximately 5 to promote good mixing within the tube bundle and to limit the magnitude of the local steam quality that develops at the top of the tube bundle on the hot-leg side.

The current chemistry specifications for the secondary coolant of the EC6 and ACR are listed in Table 3. All of the parameters in Table 3 are considered control parameters except condenser dissolved  $\text{O}_2$ , which is a diagnostic parameter as discussed below. The specifications in Table 3 differ from previous specifications in the following ways:

1. There is a lower limit specified for dissolved  $\text{O}_2$  in the condenser,
2. The specifications for  $\text{N}_2\text{H}_4$  in the feed water and the SG blowdown have been reduced,
3. The specification for  $\text{N}_2\text{H}_4$  in the feed water is linked to the dissolved oxygen specification at that location, and,
4. Upper limits for ionic contaminants, such as  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , in the steam generator blowdown have been reduced.

**Table 3: Chemistry specifications for the secondary coolant for power operation.**

Parameter	Specification	Rationale
<b>Condenser</b>		
Dissolved O <sub>2</sub> (µg/kg)	5 to 30	Mitigate FAC in condenser and low-pressure (LP) feed water system (lower limit) Mitigate the risk of cracking (upper limit)
<b>Final Feed Water</b>		
pH	9.5 to 10.0	Mitigate corrosion of system materials
N <sub>2</sub> H <sub>4</sub> (µg/kg)	> 5 x O <sub>2</sub>	Ensure O <sub>2</sub> is removed from the feed water before it reaches the SG
Dissolved O <sub>2</sub> (µg/kg)	< 5	Mitigate localized corrosion of SG tubes
<b>SG Blowdown</b>		
N <sub>2</sub> H <sub>4</sub> (µg/kg)	25 to 50	Maintain chemically reducing conditions in the SG
Na <sup>+</sup> (µg/kg)	< 5	Minimize concentration of strong alkali-forming cations in flow-occluded regions of the SG
Cl <sup>-</sup> (µg/kg)	< 10	Minimize the concentration of strong acid-forming anions in flow-occluded regions of the SG
SO <sub>4</sub> <sup>2-</sup> (µg/kg)	< 10	Minimize the concentration of strong acid-forming anions in flow-occluded regions of the SG

It has been well established that the rate of FAC of carbon steel is mitigated by the presence of a relatively low concentration of dissolved O<sub>2</sub> under alkaline conditions. For example, Woolsey et al. [5] showed that the rate of FAC of carbon steel at 150°C and pH<sub>25</sub> = 9.5 (with ammonia) was significantly reduced by increasing the concentration of dissolved oxygen from a concentration of less than 1 µg/kg to approximately 3 to 4 µg/kg. Similar results are reported from operating experience at the Seabrook plant, where a reduction in the condensate O<sub>2</sub> concentration from 3 to 5 µg/kg to less than 1 µg/kg resulted in an increased feedwater Fe concentration from 3 to 5 µg/kg to greater than 25 µg/kg [6]. The Fe concentration was subsequently reduced to its former value through the introduction of 2 to 3 µg/kg dissolved O<sub>2</sub> to the condenser hotwell. Thus, to avoid entering a regime where the rate of FAC can dramatically increase, a lower limit of 5 µg/kg is suggested for the dissolved O<sub>2</sub> concentration at the condenser outlet. Because dissolved O<sub>2</sub> at the condenser outlet is a diagnostic parameter rather than a control parameter, there is no defined action required if it is out of specification<sup>7</sup>. In the case of a diagnostic parameter, however, it is considered prudent to determine why the parameter is out of specification, and to assess whether mitigating actions should be taken. A value of 5 µg/kg is suggested because i) it provides a suitable margin above the concentration where the rate of FAC can become an issue, ii) the value is not so low that the reliability of the measurement can become an issue and iii) there appears to be no incremental benefit to system integrity by operating at a lower concentration.

Measurements of dissolved O<sub>2</sub> concentration in the feed water system at some CANDU plants suggest that the deaerator removes dissolved O<sub>2</sub> with an efficiency of about 90%. This result suggests that the final feed water specification of less than 5 µg/kg could be met with up to 50 µg/kg dissolved O<sub>2</sub> in the condenser. The proposed threshold for the onset of cracking of

<sup>7</sup> Dissolved O<sub>2</sub> in the final feedwater is a control parameter.

carbon steel in oxygenated water is a dissolved  $O_2$  concentration greater than  $50 \mu\text{g}/\text{kg}$  and a temperature greater than  $150^\circ\text{C}$  [7]. Thus, even though the inlet temperature to the deaerator in the CANDU feed water circuit is below  $150^\circ\text{C}$ , it was considered prudent to limit the dissolved oxygen concentration in the condenser to less than  $30 \mu\text{g}/\text{kg}$ . Therefore, assuming a removal efficiency of 90% for dissolved oxygen by the deaerator, the final feed water in a CANDU station should be within specification even with no addition of  $N_2H_4$  to remove dissolved  $O_2$ . The Gentilly-2 NPP did, in fact, operate for a period of about 10 years with no addition of  $N_2H_4$  to the feed water system to limit the concentration of ammonia in the condenser<sup>8</sup>, and throughout that period the dissolved  $O_2$  in the final feed water generally remained within specification [8]. Although operation without hydrazine resulted in a higher-than-average fraction of oxidized corrosion product in the blowdown [9], there have been no corrosion-related failures of SG tubing at the Gentilly-2 NPP and hence there is no evidence that operation without the addition of hydrazine was detrimental to the integrity of the SG tubes. The plant has since re-introduced  $N_2H_4$ , however, and maintains a residual concentration of  $N_2H_4$  in the SG blowdown that is sufficiently small to limit the concentration of ammonia in the condenser to less than  $1 \text{ mg}/\text{kg}$ .

The specification for the  $N_2H_4$  concentration in the SG blowdown and final feedwater has been significantly reduced as a result of concerns over its toxicity to both humans and aquatic species. In setting the  $N_2H_4$  specification for the final feedwater, account was taken of the fact that the feedwater deaerator removes about 90% of the dissolved  $O_2$  from the feedwater. Thus, the lower limit for the  $N_2H_4$  concentration at the outlet to the HP feedwater heater (downstream of the deaerator) is equal to 5 times the dissolved  $O_2$  concentration at that location, which analysis has shown is sufficient to remove the remaining dissolved oxygen from the feedwater before it enters the SG. The upper limit for the  $N_2H_4$  concentration at the outlet to the HP feed water heater is the concentration required to maintain the desired residual concentration of  $N_2H_4$  in the SG blowdown.

Specifications for the upper limits on strong acid and alkali-forming ions in the SG blowdown have also been significantly reduced in the updated chemistry specifications for EC6 and ACR. It should be noted, however, that high concentrations of soluble species, such as  $Na^+$ ,  $Cl^-$  and  $SO_4^{2-}$  in the SG bulk water or within the crevice regions (as a result of hideout) do not necessarily imply that the water chemistry is aggressive to the SG tube material. Lu [10] has conducted an extensive investigation, using electrochemical methods, of the effect of crevice chemistry conditions on the risk of degradation of SG tubing. The results are presented in the form of acceptable electrochemical potential (ECP)-pH zones in which the risk of SG tube degradation is minimum, such as the one shown in Figure 1 for various SG alloys at a temperature of  $300^\circ\text{C}$ .

It should be noted that the pH that develops in the crevices or flow-occluded regions of the tube-bundle is generally not determined by the volatile amine added to control the pH of the bulk water in the SG, but rather by the highly concentrated ionic solution in equilibrium with species of lower solubility that precipitate within the crevice as the result of hideout. Limiting the concentration of one or more ionic species in the SG does not necessarily imply that the SG tube material is within the recommended ECP-pH zone. However, the recommended zone does cover a broad range of pH, and provided that neither the pH or nor the ECP have reached an extreme

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<sup>8</sup> The condenser at Gentilly-2 is tubed with Admiralty Brass, and ammonia in the condenser arising from the decomposition of hydrazine was causing copper transport to the SGs to be above specification.



value, the SG tubes should be in the recommended zone. Note that the recommended zones for Alloy 690 and Alloy 800 are larger than the zones for Alloys 600 and 400. Alloy 800 NG is the reference tube material for ACR and EC6 SGs, although SGs tubed with Alloy 690 can be supplied if requested by the client.

The optimum concentration of hydrazine in the SG blowdown is that concentration which places the ECP within the recommended zone. Measurements suggest that a hydrazine concentration in the range 25 to 50 µg/kg is sufficient to maintain the ECP of the SG tube comfortably within the recommended zone.

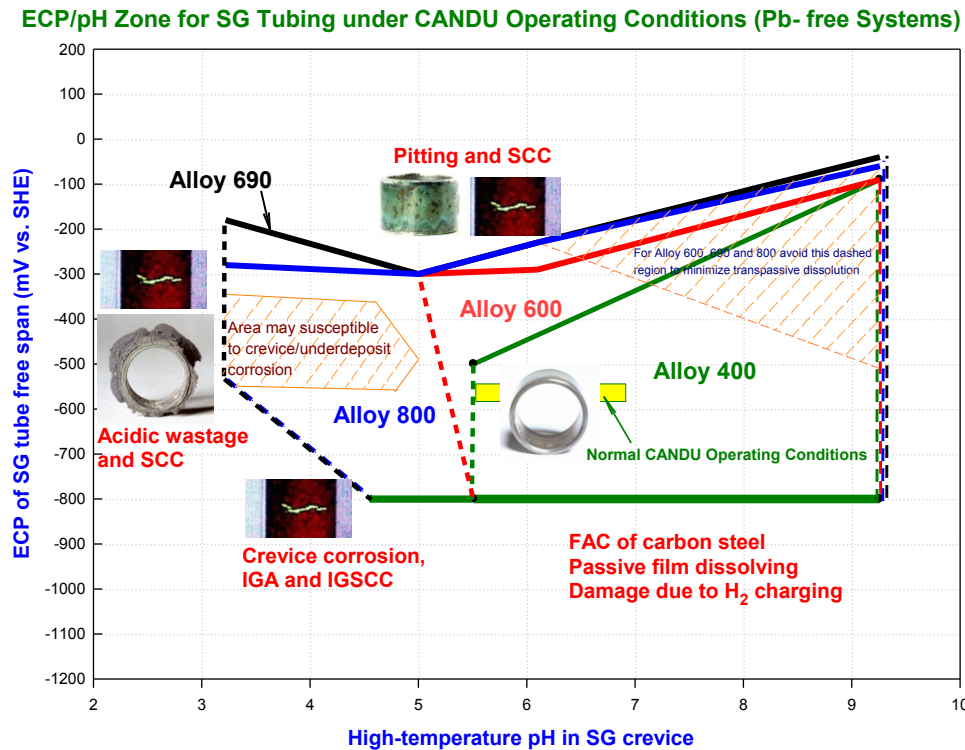


Figure 1. ECP-pH zone to minimize the risk of degradation of SG alloys at 300°C [10]

### 3. DESIGN CHANGES TO IMPROVE CHEMISTRY PERFORMANCE

#### 3.1 Primary Coolant System

##### 3.1.1 Optimizing Purification to Reduce Primary Coolant Activity

The purification system plays a major role in the control of impurity concentrations and in minimizing activity transport. The purification system can reduce out-of-core radiation fields either by removing dissolved or particulate species containing activity from the HTS before they can deposit on system surfaces, or by removing dissolved or particulate species containing the parent isotopes of hazardous radionuclides from the primary coolant before they can deposit in the core and be activated. The design of CANDU purification systems evolved from the early Nuclear Power Demonstration (NPD) design to the Douglas Point Nuclear Generating Station system (DPNGS), which incorporated some of the improvements suggested by the NPD experience, in particular the requirement that the purification half-life be as short as possible. Ultimately, a purification system with a two-hour half-life was installed in about 1970 at DPNGS

to control radiation field growth due to  $^{60}\text{Co}$  [11]. Recommendations were made to further reduce the purification half-life [12]; current CANDU 6 designs typically operate with a purification half-life of about one hour, and this is the recommended practice for the ACR and EC6.

Many PWR plants have reduced the activity in their primary coolant systems by replacing the large pore size filters in the primary coolant purification system with filters with a nominal pore size of less than 1  $\mu\text{m}$ . For example, North Anna reported a reduction in daily dose from 0.23 to 0.03 rem following the switch from 10  $\mu\text{m}$  to sub-micron filters [13].

Gentilly-2 NPP was the first CANDU plant to use sub-micron filters, introducing a filter with a nominal 0.1  $\mu\text{m}$  pore size in 1990. Other changes made as part of an aggressive campaign to reduce radiation fields [14], however, make it difficult to quantify the contribution made by the sub-micron filters to the observed reductions in radiation fields at this unit. Following replacement of their 1  $\mu\text{m}$  filters with 0.45  $\mu\text{m}$  filters, Darlington Nuclear Generating Station (DNGS) reported an increase in the amount of activity being removed by the filters and a reduction in radiation fields measured at the next outage [13]. Based on the reductions of radiation fields observed at PWR and domestic CANDU plants, it is recommended that both the EC6 and ACR pass all water that is being returned to the primary coolant system, including the water in the purification system, through a 0.1  $\mu\text{m}$  filter to reduce the development of out-of-core fields.

### 3.1.2 Narrow-Band pH Control

It has been recognized that the operation of the CANDU 6 primary coolant purification system, with its two, large volume IX columns, at maximum purification flow to reduce activity transport is not compatible with operation in a manner that would allow the system to add and remove lithium in the slow, well-controlled fashion required to maintain the pHa within the relatively narrow band 10.2 to 10.4 required to mitigate both in-core deposition of magnetite and FAC of the outlet carbon steel piping. In currently operating CANDU 6 plants, the tight control of pHa requires that one of the two columns be dedicated only to pH control, reducing the maximum purification flow and eliminating flexibility. A design that employed a larger number of smaller volume columns would be more flexible in this regard.

Several options have been explored that would add a third, smaller volume column (e.g., 14 L) containing non-lithiated cation resin to the existing purification system to improve control of the  $\text{Li}^+$  concentration over a narrow range in existing CANDU 6 plants. The remaining large columns would contain lithiated-resin to add  $\text{Li}^+$  to the coolant, as required, and remove ionic impurities. The small volume of cation resin removes the possibility of accidentally removing all of the Li from the PHT coolant. The ACR has chosen to use two large IX columns for purification and one smaller volume column for dissolved  $\text{Li}^+$  control.

## 3.2 **Secondary Coolant System**

### 3.2.1 Dedicated SG Wet Layup Loop

During wet lay-up, the pH and hydrazine concentration in the SG must be maintained within specification to minimize corrosion of the SG internals. Many plants have, therefore, retrofitted a dedicated SG wet layup loop to facilitate chemistry control and sampling during maintenance outages [8], [15]. A dedicated SG wet layup loop is proposed for the EC6 and ACR plants to improve chemistry control during wet layup, minimize emissions of water treatment chemicals to

the environment and to minimize time required to re-establish SG chemistry within acceptable limits in preparation for start up following a maintenance outage.

The wet layup loop can circulate the water in each SG one at a time or do all four SGs at once with a circulation time of several hours. The loop includes provisions for the removal of dissolved solids (resulting from hideout return) and suspended crud. This will avoid the need to drain the SG water prior to start-up, as well as the partial draining and re-filling that is generally required to get the concentrations of ionic impurities in the SG within specification before going to full power. To ensure good vertical mixing throughout the SG during layup, water is removed from the blowdown and returned to a location above the top of the tube bundle. On-line analysers for dissolved oxygen and hydrazine together with a chemical injection system for water treatment chemicals will facilitate good chemistry control during each maintenance outage. When maintenance activities permit, a N<sub>2</sub> cover gas will be established above the water line to mitigate corrosion of exposed carbon steel components.

### 3.2.2 Blowdown Recycle and Recovery

PWR plants operate with heat recovery and recycle of the blowdown water back to the condenser following removal of ionic impurities and suspended solids. Although CANDU plants have been designed to recover the heat from blowdown, the blowdown water has not been recycled but has instead been discharged to the environment following heat recovery and dilution. As a consequence, the continuous blowdown rate in CANDU 6 is typically around 0.3% of the steaming rate, whereas PWR SGs have tended to operate with a blowdown rate up to 1% of the steaming rate.

The potential for blowdown recycle has been reviewed for the CANDU design and as a result blowdown recycle is proposed in addition to heat recovery for the new EC6 and ACR plants. Recycling the blowdown will enable EC6 and ACR SGs to operate at a higher blowdown rate, reduce emissions of toxic water treatment chemicals to the environment, reduce demands on the water treatment plant and provide additional flexibility for considering advanced water treatment strategies for reducing deposit accumulation in the SGs by not discharging the blowdown to the environment. Modelling of SG fouling [16], [17] and the results of chemical cleaning have shown that about 70 to 80% of the iron that is transported to the SGs deposits on the tube bundle. Thus, reducing the rate of tube bundle fouling will have a significant impact on deposit accumulation in the SGs. Tests have shown that either addition of a dispersant [18] or the use of alternative amines [19], [20] to control pH can reduce the deposition rate on the tube bundle.

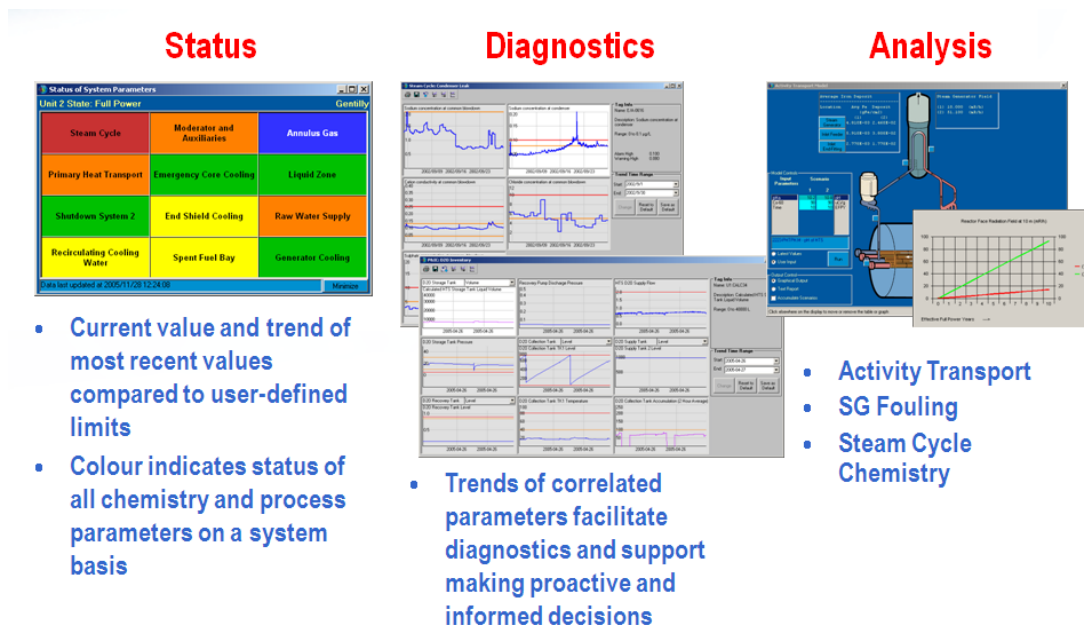
### 3.3 **Other Design Changes to Improve Chemistry Control**

Other incremental improvements have been implemented in the EC6 and ACR designs to improve chemistry control, minimize emissions to the environment and to facilitate operations to establish acceptable chemistry conditions to mitigate materials degradation prior to return to service following a maintenance outage. For example, system designs were reviewed to eliminate dead legs and to ensure that adequate provision was made to allow piping to be easily flushed following construction or maintenance activities to ensure that systems are clean before being returned to service. A review of the fire protection system has led to design changes to mitigate the growth of biological material in stagnant lines. High density polyethylene piping is now an option for some service water systems where carbon steel piping has traditionally failed. OPEX from CANDU 6 units has been used to make improvements to the chemical addition and chemistry sampling systems. Where necessary, sampling points were relocated and the location

of local sampling panels changed to ensure that more representative samples are being collected for analysis in the chemistry laboratory. The standard EC6 and ACR are two-unit stations with a single chemistry laboratory serving both units. The chemistry laboratory has been redesigned to optimize the use of available space and to provide separate work areas for the analysis of active and inactive samples. The EC6 and ACR will rely increasingly on on-line analysers to measure the concentrations of chemistry control parameters in the field. For samples that must be brought to the chemistry laboratory for analysis, instruments in the chemistry laboratory will be interfaced directly with the chemistry Laboratory Information Management System (LIMS) to eliminate errors that may arise during the manual entry of data. Finally, AECL has developed a chemistry monitoring, diagnostics and analysis system to facilitate the management of plant chemistry.

#### 4. ON-LINE MONITORING, DIAGNOSTICS AND ANALYSIS TO IMPROVE CHEMISTRY PERFORMANCE

AECL has developed an on-line monitoring, diagnostic and analysis system, known as ChemAND<sup>9</sup>, to enable chemistry staff to efficiently and proactively manage plant chemistry and to identify and resolve problems before they lead to failure of a component or shutdown of the plant [21]. ChemAND combines chemistry parameters from the on-line analysers and the LIMS to present an up-to-date snapshot of plant chemistry, identify deleterious trends and interface plant data with models to predict future performance based on current conditions. Recently, AECL has added a LIMS module to ChemAND to combine work management and reporting with monitoring, diagnostics and analysis in one software package. Examples of key displays from ChemAND illustrating the status panel, diagnostic displays and output from the model of activity transport is shown in Figure 2.



**Figure 2. Illustration of output from the status panel, diagnostic displays and the activity transport model**

<sup>9</sup> ChemAND<sup>®</sup> is a registered trademark of Atomic Energy of Canada Limited.

ChemAND provides monitoring of chemistry parameters by comparing the most recent data with user-defined limits and alerting the chemistry staff to any deleterious trends through the use of a status panel. The status panel has a tile for each system that requires chemistry control, hence it provides an overview of the status of plant chemistry in one display. The status panel uses colour coding to identify the status of each system and to direct the user's attention to where it is required, thus avoiding the requirement to systematically review all chemistry parameters from each system to detect deleterious trends. For example, a green tile means that all parameters in that system are within specification, no parameters will be trending past a predefined warning or alarm limit within a preset period of time and that there are no outstanding samples to be taken during the shift. Other colours are used to identify if one or more of the aforementioned situations applies to that system. The tiles in the status panel are active so that when one of them is selected it displays a prioritized list of parameters that have exceeded one or more of the preset limits, and directs the user to a display that has been specifically designed to facilitate diagnostics of system chemistry.

ChemAND also contains models that enable the user to evaluate the impact of chemistry or operational changes on future system performance. For example, an activity transport model can be used to predict fields at the reactor face and the SG based on operational parameters and measurements of coolant activity. A model of SG fouling can be used to predict the rate of deposit accumulation and deposit distribution in the SGs based on certain operational parameters and the concentration of iron in the feedwater. The model can be used to predict, for example, the amount of tubesheet sludge that should be removed for a given sludge lancing campaign and the total accumulation of deposit on the tube bundle for a given number of effective full power years. Using AECL's criteria of  $0.1 \text{ kg/m}^2$ , this information can be used to predict how long the plant can operate before performing a chemical clean. A model of steam cycle chemistry can be used to predict the pH of steam drain lines to optimize the amines used for pH control throughout the cycle. This same model can be used to predict SG crevice chemistry based on hideout of impurities measured in the SG blowdown.

The models are interfaced with plant data so they can run in the background, as required. Provision is also made for the user to enter the input data off-line to run 'what if' scenarios to investigate the impact of operational changes or specific system conditions on the model prediction. These models should, however, be used only in an advisory capacity. They capture the best available knowledge of specific mechanisms and phenomena, and use this knowledge to predict conditions in the plant as best as they are currently understood. The plant technical staff still needs to use their judgement to make a decision affecting management of plant assets, based in part on the output from models, but also on their knowledge of their plant and of best industry practices.

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