CHAPTER 15

Chemistry in CANDU Process Systems

prepared by

Dr. William G. Cook and Dr. Derek H. Lister
University of New Brunswick

Summary:

The efficient and safe operation of a CANDU reactor is highly dependent upon the selection and proper implementation of chemistry control practices for the major and ancillary process systems such as the primary and secondary coolants and the moderator. The materials of construction of the various systems are selected in consideration of the neutron economy while keeping the proper chemical environment in mind in order to keep corrosion and degradation low and to ensure desired plant operating lifetimes. This chapter begins with an overview of the basic chemistry principles required to manage chemistry in CANDU reactors and then provides a detailed description of the chemistry control practices and the reasons behind their use in the major and ancillary process systems. The chapter concludes by examining the current practices of component and reactor lay-up for maintenance shut-downs and refurbishments and a description of heavy water purification and upgrading.

Table of Contents

1 Introduction 4
  1.1 Overview 4
  1.2 Learning Outcomes 4
2 Chemistry Principles Applied to Reactor Coolants 4
  2.1 pH, pD and Apparent pH (pH_a) 5
  2.2 Solution Conductivity 7
    2.2.1 Specific Conductivity 7
    2.2.2 Cationic Conductivity or Conductivity After Cationic Exchange (CACE) 10
  2.3 Purification and Ion Exchange Resin 11
    2.3.1 Structure of Ion Exchange Resin 11
    2.3.2 Ion exchange capacity 11
  2.4 Water Radiolysis 12
  2.5 Solubility of Gases in Water – Henry's Law 15
3 Primary Heat Transport System 17
  3.1 Chemistry Control in the PHTS 17
  3.2 Corrosion Issues in the PHTS 20
    3.2.1 Feeder Pipe FAC and Cracking 20
    3.2.2 Delayed Hydride Cracking of Zirconium Alloys 21
  3.3 Activity Transport 21
4 Secondary Heat Transport System 23
  4.1 Chemistry Control in the Secondary System 23

4.2 Corrosion Issues in the Secondary System ... 27
4.2.1 Boiler crevices ... 27
4.2.2 Flow-Accelerated Corrosion in the Feedwater and Steam Extraction Piping ... 28
5 Moderator System ... 31
5.1 Chemistry Control in the Moderator System ... 31
5.1.1 Reactor shims ... 32
Gadolinium Nitrate ($Gd(NO_3)_3$) ... 32
Boric Acid ... 33
5.1.2 Guaranteed Shutdown State (GSS) ... 33
Gadolinium Oxalate ... 33
5.1.3 Shutdown System 2 (SDS2) ... 34
5.2 Moderator Cover Gas ... 34
6 Auxiliary Systems ... 36
6.1 Calandria Vault and End Shield Cooling System ... 36
6.2 Liquid Zone Control ... 37
6.3 Annulus Gas ... 38
6.4 Emergency Core Cooling Systems ... 38
6.5 Service Water ... 39
7 Lay-up Practices ... 40
7.1 Dry Lay-up ... 41
7.2 Wet Lay-up ... 41
8 Heavy Water Systems ... 42
8.1 Upgrading ... 42
8.2 Clean-up ... 44
Tritium Removal ... 44
9 Summary of Relationship to Other Chapters ... 46
10 References ... 46
11 Acknowledgements ... 48

List of Figures

Figure 1. Temperature dependence of pK_w / pK_D and the neutral pH / pD for the dissociation of light and heavy water. ... 7
Figure 2. Simplified flow diagram of a PHT purification loop (courtesy of AECL). ... 19
Figure 3. Magnetite solubility calculated from thermodynamic data optimized to the Tremaine & Leblanc data [Tremaine, 1980]. ... 20
Figure 4. Mass balance on steam generator impurity inventory. ... 26
Figure 5. Alloy 800 Recommended Operating Envelope (Tapping, 2012). ... 28
Figure 6. Effect of steam voidage on FAC rate of carbon steel at 200°C under three chemistries (neutral, $pH_{25°C}$ with ammonia and with ETA) at a flow rate of 0.56 L/min (the effect of reduced flow rate on FAC with ammonia also indicated). [Lertsurasakda et al., 2013] ... 30
Figure 7. Normal moderator cover gas system volume and relief ducts (CANTEACH) ... 35
Figure 8. Schematic diagram of the Calandria vault and reactor assembly. ... 36
Figure 9. Locations requiring attention during maintenance outages and lay-up of a fossil plant. [after Mathews, 2013] ... 40
Figure 10. Oxide/steel volume ratios. ... 41

Figure 11. Schematic representation of a GS dual temperature absorption column (Benedict et al., 1980). 43
Figure 12. Schematic diagram of the Darlington tritium removal facility. (Busigin & Sood) 45

List of Tables

Table 1. Conductivity at infinite dilution in H_2O [CRC, 2014]. 9
Table 2. Henry's constants for select gases at 25^{o}C (calculated from IAPWS , 2004). 16
Table 3. Target chemistry parameters in the PHTS. 18
Table 4. Common radioactive isotopes and their source in the PHTS. 22
Table 5. Target chemistry parameters in the secondary system (all-ferrous materials). 24
Table 6. Comparison of delta pH for two chemical dosing strategies in a typical steam cycle. ... 29
Table 7. Target chemistry parameters in the moderator system. 32
Table 8. Typical Chemistry Parameters of the Calandria Vault and End Shield Cooling System. .. 37

1 Introduction

1.1 Overview

This chapter explains the current state-of-the-art of CANDU system chemistry. It begins with an overview of the basic chemistry principles, as relevant to the major process systems of a CANDU reactor, and goes on to describe the modes of operation of the primary heat transport circuit, the secondary heat transport circuit, the moderator system and plant auxiliary systems with respect to system chemistry. It draws on knowledge of overall system configuration and materials selection as described in chapters 2 and 11 of this text and, through examples of plant chemistry specifications, creates a detailed knowledge of the reasoning behind the combined selection of materials and chemistry. The necessity of minimizing corrosion and degradation of the auxiliary systems supporting the operation of a CANDU reactor are also highlighted along with a description of current chemistry dosing practices for these systems. Since every reactor undergoes frequent maintenance outages and a mid-life refurbishment, the lay-up practices during these outages are important factors affecting the overall lifetime of the plant; current practices are described. Finally, the isotopic degradation and tritiation of the heavy water coolant and moderator necessitate the use of clean-up and upgrading, issues that are dealt with in the final sections of this chapter.

1.2 Learning Outcomes

The goal of this chapter is for the student to understand:

- The relation between system chemistry conditions and material selection
- The current chemical dosing practices for the various cooling systems
- The primary reasoning behind specific chemistry and materials selection
- The current best practice for system layup during maintenance outages

2 Chemistry Principles Applied to Reactor Coolants

The chemistry of CANDU reactor system coolants is generally kept quite simple with the intent of maintaining highly pure water with low concentrations of chemical additives to maintain low corrosion rates on the materials in the systems. Before the specific chemistry control strategies of the various nuclear and non-nuclear coolant systems are described, it is beneficial to define several basic chemistry concepts that are particularly relevant to chemistry control in the plant. These include a reminder of the measure of acidity/alkalinity (pH) and how it is typically used in heavy water systems as “apparent pH or pH_a”, the definition and calculation of the conductivity of solutions containing dissolved ionic compounds and a discussion of water radiolysis or the breakdown of water when exposed in a radiation field. Each of these topics will be dealt with in turn to begin the chapter and will be used throughout the remainder of the chapter in describing the chemistry of the various reactor systems.

2.1 pH, pD and Apparent pH (pH_a)

The pH in a heavy water system is more correctly the pD, where D is the deuterium isotope. Before the implications of using heavy water in the CANDU systems are discussed, it is beneficial to review some basic chemistry principles. Recall that the definition of pH is:

$$pH = -\log_{10}\left(a_{H^+}\right) \tag{1}$$

where a_{H+} is the activity of the hydrogen ion in the aqueous solution, which is dependent upon the concentration of the hydrogen ion (m_{H+} - mol/kg), the activity of the standard reference state (m^o = 1 mol/kg) and the ionic activity coefficient ($\gamma_{+/-}$) as shown in equation 2.

$$a_{H^+} = \gamma_{\pm}\frac{m_{H^+}}{m^o} \tag{2}$$

Under dilute conditions, the activity of ions in solution can be approximated by their concentration since the mean ionic activity coefficient ($\gamma_{+/-}$) is dependent upon the ionic strength of solution and is nearly unity (1) for concentrations below ~ 10^{-3} mol/kg.

For neutral, light water (H_2O), there is an equilibrium established between the water molecules and the dissociation products H^+ (or H_3O^+) and OH^- as shown in equation 3.

$$H_2O \rightleftharpoons H^+ + OH^- \tag{3}$$

By definition, the equilibrium constant for this chemical dissociation reaction is given by the ratio of the activities (concentrations) of the product species to that of the reactant (H_2O); Equation 4 defines K_w, the dissociation constant or auto-ionisation constant for water, which has a value of 10^{-14} at 25 °C [IAPWS, 2007, Bandura & Lvov, 2006]. The activity of water (a_w) is typically regarded as unity in dilute solutions, thus neutral water, defined as the point where the activity of H^+ equals that of OH^-, will give a pH of 7 as calculated through equation 4.

$$K_w = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = 10^{-14} \text{ @ } 25^oC \tag{4}$$

Increasing the pH of a solution is as simple as adding hydroxyl anions from a base such as lithium hydroxide (LiOH), which will shift the equilibrium between H^+ and OH^-. Lithium hydroxide is a strong base that is essentially completely dissociated in water up to reactor operating temperatures and thus can be used at low concentrations to achieve considerable changes in pH. Exercise 1 demonstrates the calculation.

The dissociation of water (and other ionic compounds) is dependent upon temperature. The Bandura & Lvov correlation, as recommended by the International Association for the Properties of Water and Steam (IAPWS) is commonly used to relate this temperature dependence, giving the result shown in Figure 1. In the temperature range 0 – 310 °C the pK_w (defined as $-\log_{10}K_w$) decreases significantly before starting to increase again around 250°C. This implies that the neutral point of water is lowered as temperature is increased, as illustrated by simple calculation – the pH of neutral water at 250°C is ~ 5.57 and at 300°C is about 5.64.

In the heavy water systems of the CANDU reactor, the proper equations describing the dissociation of heavy water would be:

$$D_2O \rightleftharpoons D^+ + OD^- \tag{5}$$

and the pD is:

$$pD = -\log_{10}\left(a_{D^+}\right) \tag{6}$$

where a_{D+} is the activity of the deuterium ion in aqueous solution; this is analogous to the definition of pH in equation 1. As in light water, the activity coefficient under sufficiently dilute conditions is nearly unity so we can consider the activities of D^+ and OD^- to be equal to their molal (mol/kg) concentrations. Unfortunately, the direct measurement of pD is usually not possible since pH electrodes are typically constructed with light-water-based fill solutions and are calibrated using light water buffers. Thus, for heavy water systems, it is standard practice to quote a pH_a or "apparent" pH, which identifies the observed or measured pH value of the heavy water using traditional pH electrodes and buffer solutions. A general relation [Mesmer & Herting, 1978] between the dissociation of heavy water and that of light water leads to the simple correlation shown in equations 7 and 8:

$$pH_a = pD - 0.41 \tag{7}$$

or, when considering an alkaline solution such as CANDU systems adjusted with LiOH:

$$pH_a = pH + 0.456 \tag{8}$$

This equation is the direct result of the difference between the dissociation of heavy water and that of light water when considering that pOD ≈ pOH at room temperature. Also shown in Figure 1 is the pK_D expressing the dissociation equilibrium constant for heavy water [Mesmer & Herting, 1978]. It is apparent that heavy water is less dissociated than light water under equivalent conditions, leading to higher equivalent values of the neutral point of heavy water at the various temperatures. This difference results in the approximate 0.41 unit shift between pH of light water and the pD of heavy water.

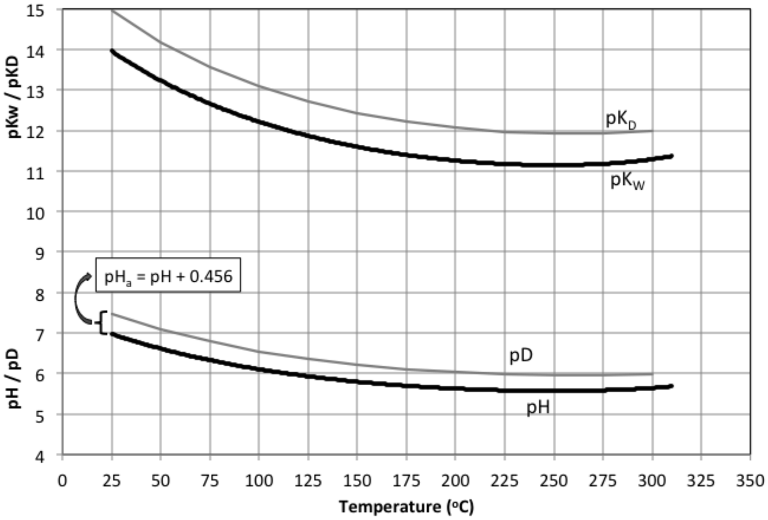

Figure 1. Temperature dependence of pK_W / pK_D and the neutral pH / pD for the dissociation of light and heavy water.

2.2 Solution Conductivity

The fact that water dissociates into H^+ and OH^- ions (equation 3) gives rise to a finite conductivity value, which means that water in its pure state can act as an electrical conductor, albeit a very poor one. We recall that the passage of current or electricity is the movement of charge measured in Amperes (A), which is the movement of one Coulomb of charge per second (i.e. 1 A = 1 C/s). Typically the charge carriers are envisaged as electrons moving down a conducting cable but the migration of ions in solution also carries charge from one point to another down a potential gradient. The conductivity (or inversely, the resistivity) of a solution is dependent upon the concentration of the charge-carrying ions in solution and their overall mobility. Thus, a measurement of the conductivity of an aqueous solution will give an indication about the quantity of the ions that it contains and, in the case of nominally pure CANDU process system water with small concentrations of additives to increase or lower the pH, this measurement should be directly related to the concentration of the specific cations and anions in the solution.

2.2.1 Specific Conductivity

The molar conductivity ($S.m^2/mol$) of an aqueous solution is given by:

$$\Lambda_m = \frac{\kappa}{c} \tag{9}$$

where κ is the specific conductance of the electrolyte (S/m or $1/\Omega.m$) and c is the stoichiometric molar concentration of the solution. Measuring the conductivity (or resistivity) of an aqueous solution is typically accomplished by placing two plate electrodes in the solution having fixed separation between them and with known cross-sectional area and then measuring the absolute resistance between them. The specific resistivity (ρ) follows from the calculation of the cell resistance shown in equation 10 and specific conductivity (κ) is related through equation 11.

$$R = \frac{\rho \times \ell}{A} \tag{10}$$

$$\kappa = \frac{1}{\rho} \tag{11}$$

The molar conductivity of the solution, and hence the solution specific conductivity, can be broken down into the sum of the individual contributions of the ions, each one of which will be dependent upon its concentration and overall mobility. Essentially, the specific conductivity of the solution is the sum of the specific conductivities of the individual ions:

$$\kappa = \sum_i \kappa_i \tag{12}$$

We define the molar conductivity of the ion in solution (λ_i) in an analogous way as the overall molar conductivity of the solution, thus:

$$\lambda_{m,i} = \frac{\kappa_i}{c_i} \tag{13}$$

In an ideal solution, the molar conductivity would vary linearly with increasing concentration (and specific conductivity); however, in reality the solution molar conductivity has a non-linear dependence on solution concentration, particularly in more concentrated solutions. This stems from the fact that ion-to-ion and ion-to-solvent interactions play larger roles in concentrated solutions. Thus, the molar conductivity for an individual ion in solution may only be truly measured if there are no other interfering ions present, i.e. in an infinitely dilute solution. Inserting equation 13 into 12 and subsequently into 9 yields:

$$\Lambda_m = \frac{1}{c} \sum_i c_i \lambda_i \tag{14}$$

If we note for a $M\nu^+X\nu^-$ electrolyte, where ν^+ and ν^- are the valences of the cation and anion respectively, that the concentration of each ion will depend upon the total concentration of the salt in solution, at infinite dilution this results in the simple relation of equation 15:

$$\Lambda_m^\infty = \nu_+ \lambda_{M^+}^\infty + \nu_- \lambda_{X^-}^\infty \tag{15}$$

The ionic molar conductivities at infinite dilution are tabulated in various sources and allow for the calculation of the solution specific conductivity directly [CRC, 2014]. It should be noted that the above equations apply for solutions at infinite dilution but may be used directly with small error up to total solution concentrations of approximately 10^{-3} mol/L. Table 1 shows the ionic molar conductivity of cations and anions relevant to the operation of CANDU reactors. Note that the ionic molar conductivity of each ion is per equivalent since the total migration of an ion subjected to an electric field will be dependent upon its charge (valence). Note also the comparatively large conductivities of H^+, D^+, OH^- and OD^-, which is due to the Grotthus "hopping" mechanism for these ions in aqueous solution where the individual ions themselves do not physically migrate but they are exchanged through the interconnecting hydrogen-bonded structure of liquid water. These ions tend to dominate the conductivity of the relatively pure CANDU process solutions.

Table 1. Conductivity at infinite dilution in H_2O [CRC, 2014].

Cations (S cm^2 mol^{-1} eq^{-1})		Anions (S cm^2 mol^{-1} eq^{-1})	
H^+	349.7	OH^-	198
D^+	249.9	OD^-	119
Li^+	38.7	Cl^-	76.31
Na^+	50.1	½ SO_4^{2-}	80.0
1/3 Gd^{3+}	67.3	HCO_3^-	44.5
NH_4^+	73.5	½ CO_3^{2-}	69.3
½ Fe^{2+}	54	NO_2^-	71.8
$N_2H_5^+$	59	NO_3^-	71.48

Example 15.1- calculating solution conductivity from pH and values at infinite dilution.

Lithium hydroxide is added to the light water in the calandria vault and end shield cooling system to control the pH and minimize corrosion of the carbon steel components. The pH specification is 9.5. Calculate the required lithium ion concentration in the water (in ppm) to attain the pH specification and estimate the solution conductivity assuming no other impurities are present.

Solution

Since the pH specification is given (9.5), the concentration of H^+ and OH^- are readily evaluated from the definition of pH and K_w:

$$\mathrm{pH} = -\log_{10}([\mathrm{H}^+])$$

thus:

$$[\mathrm{H}^+] = 10^{-\mathrm{pH}} = 10^{-9.5} = 3.16 \times 10^{-10}\, mol/kg$$

recalling the dissociation of water (K_w, eq. 4), the OH- concentration is:

$$[\mathrm{OH}^-] = \frac{K_w}{[\mathrm{H}^+]} = \frac{10^{-14}}{3.16 \times 10^{-10}} = 3.16 \times 10^{-5}\, mol/kg$$

In this case, lithium hydroxide is a strong base and completely dissociates into lithium and hydroxyl ions:

$$\mathrm{LiOH} \rightleftharpoons \mathrm{Li}^{+} + \mathrm{OH}^{-}$$

thus, the concentration of lithium must be equal to the hydroxyl concentration in the water, i.e.:

$$[\mathrm{Li+}]=[\mathrm{OH-}] = 3.16 \times 10^{-5}\ \mathrm{mol/kg}$$

Converting to ppm (mg/kg):

$$[\mathrm{Li}^{+}] = 3.16 \times 10^{-5}\ \frac{\mathrm{mol\ Li}}{\mathrm{kg\ H_2O}} \times \frac{6.94\ \mathrm{g}}{\mathrm{mol}} \times \frac{1000\ \mathrm{mg}}{\mathrm{g}} = 0.219\ \mathrm{mg/kg}$$

Ans.

To calculate the expected conductivity, combining equations 12 and 13 results in:

$$\kappa = \sum_i c_i \lambda_i$$

Conductivity values for Li+ and OH- can be attained from Table 1, and since [Li$^+$]=[OH$^-$]:

$$\kappa = c_{\mathrm{LiOH}}\left(\lambda^{\infty}_{\mathrm{Li}^{+}} + \lambda^{\infty}_{\mathrm{OH}^{-}}\right)$$

Since the units of conductivity are in cm^2, the concentration is converted to mol/cm^3 for consistency:

$$c_{\mathrm{LiOH}} = 3.16 \times 10^{-5}\ \frac{\mathrm{mol}}{\mathrm{kg}} \frac{1000\ \mathrm{kg}}{\mathrm{m}^3} \frac{\mathrm{m}^3}{1000\ \mathrm{L}} \frac{\mathrm{L}}{1000\ \mathrm{mL}} \frac{1\,\mathrm{mL}}{1\,\mathrm{cm}^3} = 3.16 \times 10^{-8}\ \mathrm{mol/cm^3}$$

Calculating the conductivity and converting to standard units of mS/m:

$$\kappa = 3.16 \times 10^{-8}\ \frac{\mathrm{mol}}{\mathrm{cm}^3}\left(38.7 + 198\ \frac{\mathrm{S\,cm}^2}{\mathrm{mol\,eq}}\right) = 7.48 \times 10^{-6}\ \mathrm{S/cm}$$

thus, the conductivity of the cooling water is expected to be 0.748 mS/m. Ans.

2.2.2 Cationic Conductivity or Conductivity After Cationic Exchange (CACE)

While the conductivity of a solution provides an indication of the concentration of impurity ions that are present, it is not species- or ion-specific; thus, there is no way of determing from a conductivity measurement what are the individual dissolved ionic species present in the solution. One way of providing a better indication of the concentration of anionic impurities in an aqueous solution is to use the cationic conductivity (or conductivity after cationic exchange - CACE) [IAPWS, 2012], which gives a direct measure of the anionic impurities in the system that may be aggressive to the corrosion of plant materials. Cationic conductivity is simply the conductivity of an aqueous solution after it has been passed through a strong acid ion-exchange column to remove the cations (such as Na^+, K^+, Ca^{2+} etc.), which replaces them with the proton (H^+). The solution that elutes from the cation exchange column will contain the same concentration of anions (Cl^-, SO_4^{2-} etc) as the original sample and can provide a rapid and direct indication of the rate of increase of these impurities. This gives a very useful online measurement of impurity ingress, specifically in the case of a condenser leak.

2.3 Purification and Ion Exchange Resin

Filter media and ion exchange resins are used extensively in the nuclear and power generating industry for removing particulate and ionic impurities from a solution. All power plants will have a water treatment plant that includes ion-exchange as a final "polishing" method to ensure extremely pure water is available for use in the various process systems and each process system will contain filters of various configurations to collect suspended solids. Ion exchange media come in many forms and can be tailored for removal of specific impurity cations or anions as appropriate. The main classes of ion exchange media are designated as strong acid, weak acid, strong base and weak base and each may be used in a water treatment plant or a purification stream in the various process systems of a nuclear power plant.

2.3.1 Structure of Ion Exchange Resin

An ion exchange resin consists of a co-polymer, typically polystyrene and divinyl-benzene that have functionalized "exchange" groups attached to each benzene ring in the polymer matrix. A strong acid resin, suitable for removing alkali earth elements and transition metals from a water stream, is typically sulfonated producing an SO_3^-/H^+ functional group on each benzene ring (note that a perfect one-to-one aromatic ring to exchange group ratio is not achievable). The proton is the ion-exchange cation that will be exchanged with other cations from the solution. Strong base resins typically consist of a quaternary ammonium exchange site attached to two or three methyl groups whereby the functional exchange site is a chloride (Cl^-) or hydroxyl anion (OH^-) that acts to exchange with the impurity anions in the process stream to be purified. For nuclear plant process systems, where water purity is paramount, the resins are typically supplied and used in the H^+ and OH^- forms, although different suppliers can provide functionalized exchange groups such a lithiated (Li^+) strong cation resin for use in particular systems such as the primary heat transport system. It is important to note that before use of an ion exchange resin in the D_2O of the primary coolant or the moderator system, resins must be deuterated to the D^+ and OD^- form by plant operators to ensure that the isotopic purity of the D_2O is not significantly affected by H_2O exchange with the resin (see discussion in Section 8.2).

Once fabricated, cation and anion exchange resins appear as small beads (typically ~0.5 – 1.5 mm in diameter) and may be slurried in and out of their process vessels for easy replacement and regeneration. Traditional resins were specified as "gel-type" as they were effectively a wrapped-up sphere of polymer chains with significant porosity and tended to break apart if continuously reused or placed in high flow rate process streams. Newer, "macroporous", resins are much stronger and have shown good resilience in harsh environments.

2.3.2 Ion exchange capacity

The purification of a process water stream depends upon the type and quantity (or volume) of ion exchange resin used as well as its capacity to remove various ions from the water. Ion exchange capacity is defined as the number of ionic "equivalents" that can be exchanged per litre of resin used. For example, a strong acid resin in the protonated form (H^+) can have an exchange capacity of around 2 eq/L; thus, for every litre of the resin used in a purification vessel two equivalents (or moles) of H^+ cations are available to exchange with cationic impurities in the process stream. If sodium (Na^+) is used as an example, one litre of this strong cation resin may remove 2 mols of Na^+ cations, or effectively 46 grams of sodium.

The exchange capacity is also dependent upon the particular cation being exchanged with higher valence cations showing the greater preference for adsorption on the exchange site. An example of cationic preference is:

$Fe^{3+} > Ca^{2+} > Ni^{2+} > Cu^{2+} > Fe^{2+} > K^+ > NH_4^+ > Na^+ > H^+$

For a strong base ion exchange resin, an example of anionic preference follows:

$SO_4^{2-} > CO_3^{2-} > HSO_4^- > NO_3^- > Cl^- > HCO_3^- > CHOO^- > CH_3COO^- > F^- > OH^-$

Thus, a ferrous or cuprous cation would tend to displace a sodium cation from the ion exchange bed or a sulfate anion would displace a chloride or hydroxyl anion. The capacity of an ion-exchange bed can be described in a manner similar to a chemical equilibrium equation, as shown in equation 17 using the exchange of the sodium cation with the proton as an example.

$$Na^+ + RH \rightleftharpoons H^+ + RNa \tag{16}$$

The equilibrium constant, in this case called the selectivity coefficient, is given by:

$$K_H^{Na} = \frac{[RNa][H^+]}{[RH][Na^+]} \tag{17}$$

where [RNa] and [RH] designate the concentration (mol/L) of the specific cation that is adsorbed on the resin and $[Na^+]$ and $[H^+]$ are the incoming sodium ion and proton concentrations in the solution to be purified. It should be noted that a fresh ion exchange column will have a fixed number of exchange sites based upon the resin's exchange capacity and the amount of resin present; the balance between the [RNa] and [RH] must always be equal to the initial total exchange capacity. Once most or all of the proton exchange sites available have been used or taken up by another cation, the resin will start to "throw" the cations of lowest selectivity back into the process water instead of removing them. This is obviously not a desirable situation as the intent of the purification system is to remove the impurity cations from the process water stream; at this point, the ion exchange column or vessel is said to be "spent".

2.4 Water Radiolysis

The chemistry of CANDU process systems is specified to protect the reactor core and steam generator materials from localized corrosion, minimize deposition of corrosion products on the fuel and limit the corrosion of system components. The pH of irradiated CANDU process systems is typically adjusted by using lithium hydroxide to produce mildly alkaline conditions and some irradiated systems are kept under reducing conditions by excluding oxygen to prevent elevated electrochemical corrosion potential (ECP) and excessive corrosion. For in-core systems, the water is continuously bombarded by an intense radiation field of high-energy gamma and neutrons, which breaks the chemical bonds and produces highly reactive radical species. This process is known as water radiolysis. The radiolysis of pure water results in the production of hydrogen (H_2) (or deuterium D_2, for heavy water), oxygen (O_2) and hydrogen peroxide (H_2O_2) (or deuterium peroxide D_2O_2 in heavy water) [Spinks & Woods, 1990]. The radiolytic production of these oxidizing species has a direct impact on the corrosion of system components; they elevate the ECP, increasing the possibility of stress-corrosion cracking of the alloy steam generator tubes and, under low-temperature shut-down conditions when the radioactive decay of in-core components and fuel still produces intense gamma radiation, they promote the pitting of carbon steel. Radiolytically generated hydrogen peroxide will also degrade ion-exchange resins.

The radiolytic production of hydrogen, oxygen and hydrogen peroxide can be managed by adding hydrogen to the system. The elementary chemical reactions and kinetics are complicated but the net result is that the added hydrogen molecules react with the radical species and mitigate the radiolytic production of oxygen and hydrogen peroxide. The basic mechanisms for these processes are explained below with the overall result being suppression of the net radiolytic production of oxidizing species. Further details of the radiation kinetics associated with water radiolysis can be found in the AECL report by David Bartels [Bartels, 2009] or in the book chapter by George Buxton [Buxton, 1987].

Upon absorbing the energy dissipated by a particle or photon, water breaks down into several radical species as primary products of the irradiation process; on a timescale of approximately microseconds, the overall result is:

$$H_2O + \text{radiation} \rightarrow e^-_{aq}, H^+, \cdot H, \cdot OH, \cdot HO_2, H_2, H_2O_2 \tag{18}$$

Reactions of these primary products can re-form water, and produce further hydrogen and hydrogen peroxide through equations 19 - 21:

$$\cdot H + \cdot OH \rightarrow H_2O \tag{19}$$

$$\cdot H + \cdot H \rightarrow H_2 \tag{20}$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{21}$$

Oxygen is produced as a secondary product through reactions of the radical species with the hydrogen peroxide molecule:

$$\cdot OH + H_2O_2 \rightarrow \cdot HO_2 + H_2O \tag{22}$$

$$\cdot OH + \cdot HO_2 \rightarrow O_2 + H_2O \tag{23}$$

$$\cdot HO_2 + \cdot HO_2 \rightarrow O_2 + H_2O_2 \tag{24}$$

As mentioned above, providing sufficient added hydrogen to the water can mitigate the net production of oxygen and hydrogen peroxide. Hydrogen reacts with the hydroxide radical forming a hydrogen atom that readily combines with hydrogen peroxide and/or oxygen, effectively removing them from the solution and mitigating their overall production as shown in equations 25 - 27. The overall effect is a chain reaction where additional hydroxide radicals are produced (eq. 27) continuing the reaction chain, provided sufficient hydrogen is present. From a kinetic standpoint, the concentration of hydrogen in the water needs to be sufficient to make its rate of reaction with the hydroxyl radical (eq. 25) faster than the rate of reaction of the hydroxyl radical with hydrogen peroxide (eq. 22). This results in the reduction of the concentration of the hydrogen peroxide molecule and effectively suppresses the conversion of hydrogen peroxide to oxygen, removing both species from the solution. When sufficient hydrogen is added to an irradiated aqueous system, the very simplified chemical relation shown in equation 28 is the net result of the radiolysis process.

$$\cdot OH + H_2 \rightarrow \cdot H + H_2O \tag{25}$$

$$\cdot H + O_2 \rightarrow \cdot HO_2 \tag{26}$$

$$\cdot H + H_2O_2 \rightarrow \cdot OH + H_2O \tag{27}$$

$$H_2O + H_2(\text{excess}) + \text{radiation} \rightarrow H_2O + H_2(\text{excess}) \tag{28}$$

The fact that added hydrogen is required in the water to promote the desired recombination reactions implies that there must be a minimum hydrogen concentration by which the overall rate of the reaction in equation 25 is just sufficient to overcome the reaction of the hydroxyl radical with hydrogen peroxide (equation 22) and hence suppress the production of oxygen. This minimum concentration is called the “critical hydrogen concentration” (CHC) and has been measured in flow loops (both fuelled reactor systems and in gamma cells) to be around 0.5 mL/kg (~2×10^{-5} mol/L). [Elliot & Stuart, 2008]. Operating with the hydrogen concentration above the CHC with no oxidants initially present leads to a system in net radiolytic suppression while operation with an initial hydrogen concentration below the CHC (or with the presence of significant quantities of oxidants or impurities in the water) leads to net radiolysis occurring within the system.

Impurities dissolved within water will influence the water radiolysis processes. For example, impurities such as nitrate and nitrite anions will interfere with the water recombination reactions since they tend to react with and consume the hydrogen atoms and hydroxyl radicals [Yakabuskie, 2010], effectively lowering their concentrations and the overall rate of the oxygen and hydrogen peroxide consumption reactions (eq. 26 & 27). This will result in an increase in the quantity of oxygen and hydrogen produced by water radiolysis in the presence of nitrate and/or nitrite ions. Chloride ions interfere with the hydrogen recombination reactions since they readily exchange their outer valence electron with the hydroxyl radicals interfering with the primary recombination reaction (eq. 19). The chloride ion is then regenerated through electron exchange with water molecules and can continuously impede the desired recombination processes. Organic impurities from compressor leaks, oil ingress from pumps or other mechanical systems will break down rapidly in a radiation field. High molecular weight organics undergo polymerization reactions, extending their size and weight leading to plugging of filters and other flow paths. Lower molecular weight organics decompose producing hydrogen and carbon dioxide that can rapidly lead to hydrogen excursions and reduction in system pH.

The chemistry specifications for a water-filled, irradiated CANDU system must therefore be designed to prevent the build-up of the water radiolysis products in the system, or the effects of water radiolysis must be continuously managed to maintain system chemistry specifications. Some systems, such as the primary heat transport system and the end shield cooling system, are operated under net radiolytic suppression by ensuring the hydrogen concentration in the water is above the CHC. Other systems, such as the moderator, liquid zone control and the spent fuel bay, are operated with net water radiolysis occurring. For these systems, the hydrogen and oxygen produced are managed by ensuring impurity concentrations are kept extremely low and by providing catalytic recombiner units in their cover gas flow paths to ensure flammable concentrations are not exceeded. Further details of the operation of each of these systems are found later in this chapter.

2.5 Solubility of Gases in Water – Henry's Law

Gases are typically sparingly soluble in water due to the vapour-liquid equilibrium established between a gas mixture covering the liquid sample. From thermodynamics, the chemical potential of the chemical species must be equal at the interface between the gas and the liquid meaning that, even though the gas solubility may be low in the liquid phase, it is finite and is an important parameter to consider in nuclear plant process streams. Many CANDU process and auxiliary systems have a head tank and/or a cover gas space that operates at a particular pressure and the solubility of the gas in the liquid phase and its mass transfer and migration to or from the cover gas space needs to be readily monitored. Using the example of hydrogen production by the water radiolysis processes described above, the continuous irradiation of CANDU coolant streams will result in the build up of hydrogen in the water that will equilibrate with its surroundings resulting in hydrogen release to the cover gas space. This needs to be continuously monitored to ensure that the hydrogen concentration is maintained below the flammability limits.

The equilibrium established between a gas dissolved in water and its partial pressure in the gas space above the liquid is given as:

$$k_H = \frac{y_{gas}}{x_{gas}} \approx \frac{p_{gas}}{c_{gas}} \tag{29}$$

where y_{gas} is the mole fraction of the given gas in the vapour space and x_{gas} is the mole fraction in the liquid phase. Since the gases of interest in CANDU process systems are sparingly soluble the mole fractions are typically equated to partial pressure (p_{gas}) and concentration (c_{gas}) for the gas phase and liquid phase respectively giving units of pressure (atm or MPa) per molarity (mol/L). Rearrangement of equation 29 shows that, under low to intermediate partial pressures, there is a linear dependence between the partial pressure of the gas above the liquid and that dissolved in it. Thus, by knowing the equilibrium constant, in this case called Henry's Law constant, the concentration of gas dissolved in water may easily be evaluated as demonstrated in Example 15.2. Henry's law constants at 25^{o}C are shown in Table 2 for some gases commonly encountered in CANDU process systems. IAPWS has released detailed correlations for determining the Henry's Law constant for various gases as a function of temperature [IAPWS, 2004].

Table 2. Henry's constants for select gases at 25°C (calculated from IAPWS , 2004).

Gas	k_H in H_2O (in D_2O) (atm/M)
O_2	775.7
H_2	1263
N_2	1522
He	2541 (2343)
CO_2	29.40
D_2	(921.0)

Example 15.2 - Henry's law calculation – D_2 in heavy water

The heavy water storage tank for the primary heat transport system contains D_2O at roughly room temperature and is purged with a helium cover gas to maintain the hydrogen concentration below 4% (by volume). The specification for dissolved deuterium in the PHTS is 3 – 10 mL/kg, calculate the equilibrium concentration that would be attained in the cover gas if helium is not frequently added and purged and the dissolved hydrogen is maintained at the upper limit of the specification.

Solution

If 10 mL/kg of dissolved deuterium is maintained in the PHTS, Henry's law can be used to estimate the equilibrium concentration in the storage tank cover gas. First the dissolved deuterium concentration must be converted to consistent units with Henry's law (i.e. Molar or mol/L) using the conversion factor that 1 mol gas = 22.4 L gas at standard temperature and pressure (STP). Thus:

$$c_{gas} = 0.010 \frac{L_{D_2}}{kg_{D_2O}} \times \frac{1\,mol_{D_2}}{22.4\,L_{D_2}} \times \frac{1000\,kg_{D_2O}}{m^3_{D_2O}} \times \frac{m^3}{1000\,L} = 4.46 \times 10^{-4}\ mol/L \quad (M)$$

$$p_{gas} = k_H\, c_{gas} = \left(921\,atm/M\right)\left(4.46 \times 10^{-4}\ M\right) = 0.411 \quad atm$$

For a cover gas operating at approximately atmospheric pressure this would amount to a cover gas concentration of 41.1%, well above the flammability limit of about 8% in helium!

3 Primary Heat Transport System

As explained in Chapter 10, the purpose of the Primary Heat Transport System (PHTS) in a CANDU reactor is to remove the heat generated from the fissioning of the reactor fuel and transport it to the steam generator for production of steam in the Secondary System. The materials of construction in the PHTS are numerous due to the different functions of the various components; the particular materials and their properties are described in detail in Chapter 14. The materials with the largest surfaces areas in contact with the heavy water coolant of the PHTS are: zirconium-based alloys in the core of the reactor (Zircaloy-4 fuel cladding, Zr-2.5Nb pressure tubes), nickel alloys for the steam generator tubing (Alloy 400 [Monel] at Pickering, Alloy 600 [Inconel] at Bruce, Alloy 800 [Incoloy] at Darlington and the CANDU-6s), type 410 stainless steel for the fuel-channel end fittings and carbon steel for the feeder pipes joining the fuel channels through the headers to the carbon-steel channel heads in the steam generators. Thus, as with any complex system, the chemistry control practices are a compromise among the optimum chemistries for each of the major materials used.

The Zircaloy-4-clad fuel bundles, Zr-2.5Nb pressure tubes and nickel-alloy steam generator tubes exhibit low general corrosion rates over a wide range of pH and temperature [Cox, 2003]. A major role of chemical control is therefore to protect against localized corrosion, in particular the stress-corrosion cracking of the steam generator tubes and the hydriding and cracking of the pressure tubes. As described earlier in the section on radiolysis, adding hydrogen maintains reducing conditions and this minimizes the possibility of nickel-alloy cracking, but to minimize the potential for hydriding of Zr-2.5Nb the hydrogen is kept within strict limits (3-10 mL/kg).

A further role of the chemical control in the PHTS is the protection of the large surface area of carbon steel. As described in Section 6.1 in Chapter 14, the general corrosion of iron produces mixed and, at low temperature, often hydrated oxides (Fe_2O_3, Fe_3O_4, FeOOH etc.) that become the thermodynamically stable phases at a pH (at room temperature) greater than 9 or so. It is well known that carbon steel corrosion is minimized in mildly alkaline, deaerated water. However, at low temperature with static water that may occur during a shut-down, oxidising conditions can induce severe pitting of carbon steel and should be avoided. Note that during reactor operation the inlet feeders in CANDUs are exposed to coolant saturated in dissolved iron because of the heat transferred producing steam in the steam generators and the consequent drop in iron solubility, so they undergo general corrosion and develop thick magnetite films as the result of magnetite precipitation from the oversaturated coolant. On the other hand, the outlet feeders see coolant undersaturated in iron because of the heating in the core and as a consequence undergo flow-accelerated corrosion (FAC), which leads to very thin magnetite films and loads the system with iron that largely deposits as magnetite in the steam generators. Oxidising conditions tend to mitigate FAC, but the greater need to avoid localized corrosion of the alloy components in the core and the steam generators dictates the use of reducing conditions.

3.1 Chemistry Control in the PHTS

As explained above, one of the primary objectives of chemistry control in the PHTS of a CANDU reactor is to minimize the corrosion of the carbon steel, zirconium and alloy surfaces, which involves operating under alkaline conditions and mitigating the radiolytic production of oxidizing species. Other objectives include minimizing deposition of corrosion products on the fuel (fouling) and minimizing and controlling the concentration of activiated corrosion products and fission products (both gaseous and dissolved) in the system. These objectives are accomplished through dosing and control of the primary coolant's pH_a and deuterium concentration through regular additions of lithium hydroxide and hydrogen gas. Also, the molecular hydrogen gas exchanges rapidly in the reactor core with deuterium in the D_2O molecules. Although the additions downgrade the heavy water slightly, this is compensated by periodic isotopic upgrading of the system's D_2O (see Section 8.1). Each individual plant maintains its own chemistry practices and operational guidelines but, in general, guidelines for these values are shown in Table 3.

Table 3. Target chemistry parameters in the PHTS.

Parameter	Typical Specification Range
pH_a:	10.2 – 10.4
$[Li^+]$:	0.35 – 0.55 mg/kg (ppm)
$[D_2]$:	3 – 10 mL/kg
conductivity:	0.86 – 1.4 mS/m (dependent upon LiOH concentration)
Dissolved O_2	< 0.01 mg/kg
$[Cl^-]$, $[SO_4^{2-}]$ etc	< 0.05 mg/kg
Isotopic	> 98.65 % D_2O
Fission products	ALARA (< 10^6 Bq/kg D_2O; monitoring I-131 indicative of fuel failure)

During steady-state operation, variations in any of the above parameters are typically small in the absence of system transients or upset conditions. Oxygen concentrations are typically non-detectable. The alkalinity is controlled through periodic additions of LiOH through the sampling system return (for elevating pH_a) or by providing a periodic bleed flow through the purification system using an ion-exchange column containing strong acid cation resins (for lowering pH_a). Lithiated mixed-bed ion-exchange columns (where the strong-acid IX resin D^+ sites have been saturated with Li^+; both acid and base resins are deuterated) are run as normal purification for the PHTS to collect cationic and anionic impurities. A simplified flow diagram for a PHT purification circuit is shown in Figure 2. The purification system keeps particulate concentration low and helps to maintain the anioic impurity concentrations below the specification to minimize the risk of SCC of the stainless steel and alloy components in the system and to minimize the risk of strain-induced cracking of carbon steel components [Turner & Guzonas, 2010]. It also serves to keep the radioacitivity of the PHT coolant low as the filters and ion exchage column may capture activiated corrosion products or ionic fission products released from failed fuel bundles.

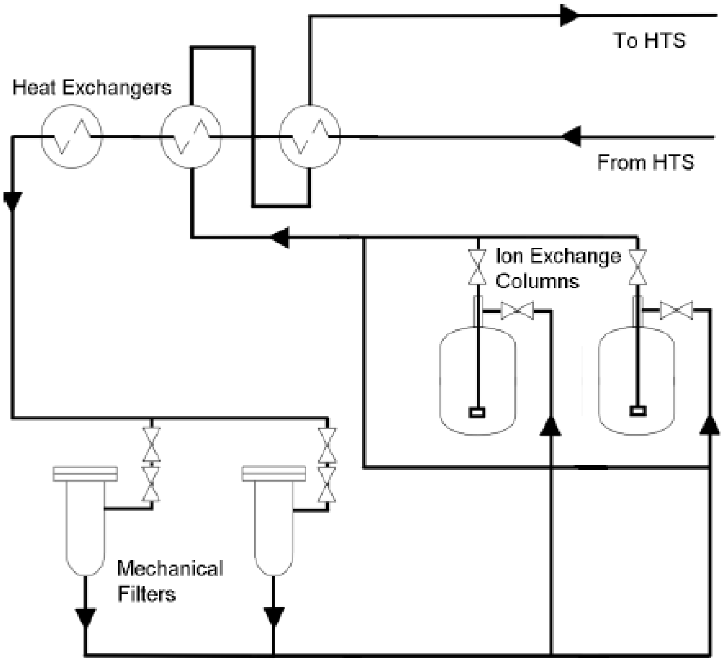

Figure 2. Simplified flow diagram of a PHT purification loop (courtesy of AECL).

Since pH_a and conductivity are directly related to $[Li^+]$, purity of the PHTS coolant is readily observed by comparing the measured values to the theoretical values as calculated using the equations developed earlier in the chapter. If the system is controlled well and has minimal impurities, then the conductivity and pH_a measured should match closely with the calculated values appropriate to the measured lithium-ion concentration. Deviations in the measured-to-theoretical value indicate ingress of ionic impurities or problems with system sampling techniques.

The above discussion seems to imply that sampling the high-temperature PHTS system is routine and simple. While it is routine, collecting and analyzing samples from a high-temperature, high-pressure system is far from simple. Take, for example, the collection of a sample in an open polypropylene jar. The sampled water must first be cooled from the operational temperature and throttled to low pressure. Each of these operations changes the state of the chemical species present in the sample. Once the valve at the end of the sample line is opened, the ideally oxygen-free coolant sample is exposed to the atmosphere and will readily absorb nitrogen, oxygen and carbon dioxide from the air. Thus, this sample is immediately not appropriate for obtaining a dissolved oxygen measurement. Additionally, the absorbed CO_2 dissociates in the sample solution to form carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions, which disturb the equilibrium chemistry established between lithium hydroxide and water. The CO_2 absorption effectively produces carbonic acid and lowers the pH (or pH_a) of the sample, rendering it compromised for system monitoring. Thus, differences in pH_a, conductivity and $[Li^+]$ from PHTS samples may imply improper sampling techniques, not problems with system chemistry and care must be taken to identify the root cause. Several standard methods and recommended practices are available to properly specify and conduct sampling campaigns including the Technical Guidance Document on corrosion product sampling recently released by IAPWS [IAPWS, 2014].

3.2 Corrosion Issues in the PHTS

3.2.1 Feeder Pipe FAC and Cracking

Recent trends for PHTS chemistry practice have focused upon “narrow-band” pH$_a$ control, within the 10.2- 10.4 range, in order to help mitigate excessive FAC on the outlet feeder pipes, which is demonstrated to increase with increasing pH$_a$ (Lister, 2002, Slade & Gendron, 2005). This observation results from the fact that the magnitude of FAC is partially controlled by the degree of corrosion-product under-saturation in the coolant, via processes described by equations 21-23 presented in Chapter 14. Consider the closed-loop PHT system and take the PHT main pump as a starting point. The temperature at this point is typically around 260^{o}C and is considered to be the “cold-leg” of the PHT circuit. In these conditions, the PHT coolant is typically saturated or over-saturated in corrosion-products (mainly dissolved iron), which leads to the precipitation of magnetite on the surfaces up to the inlet of the reactor core and promotes low corrosion rates of the carbon steel inlet feeder pipes (the precipitation actually begins within the steam generator and along the whole inlet section of feeders and headers to the core). Shown in Figure 3 is the calculated solubility of magnetite at a pH of 10.2 and 9.0 (in light water) between the temperatures of 250^{o}C and 310^{o}C, the approximate temperature of the coolant exiting the core. It is seen that for the elevated pH, the solubility increases over this temperature range, which is considered to be beneficial since this will typically prevent deposition of corrosion products in the reactor core. The coolant ultimately leaves the core in an under-saturated condition since most of the in-core surfaces contacting the coolant are zirconium alloys and this leads to a large driving force for magnetite (and metal) dissolution in the end fittings and carbon steel outlet feeder pipes. Compounding the problem is the intricate series of bends that are required for the feeder pipes to connect appropriately to the end-fittings – many outlet feeder pipes can have two tight-radius bends. This acts to increase the fluid turbulence and exacerbates the FAC phenomenon due to the action of fluid shear and mass transfer.

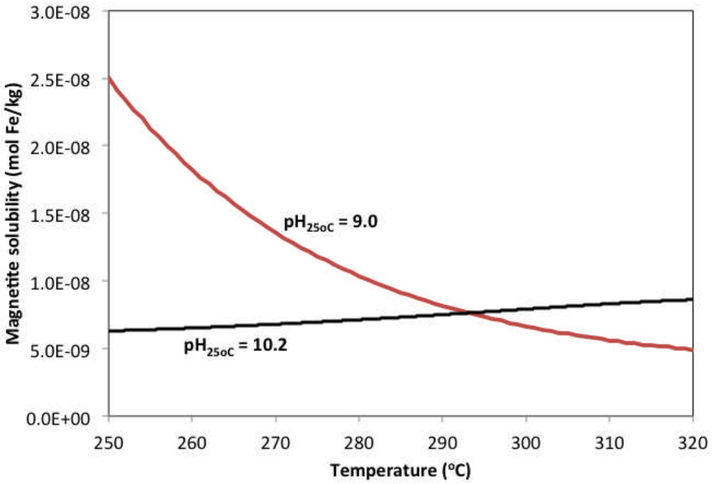

Figure 3. Magnetite solubility calculated from thermodynamic data optimized to the Tremaine & Leblanc data [Tremaine, 1980].

The Point Lepreau CANDU-6 was the first reactor to exhibit FAC of the outlet feeder pipes. The feeders were on average corroding at rates greatly in excess of what was assumed and predicted in providing a suitable corrosion allowance and many sections of outlet feeders needed to be replaced well before the end of their design lifetime. Unlike other CANDU stations that also observed FAC in the outlet feeder pipes, the Point Lepreau station also had demonstrated cracking, which necessitated many removals and replacements prior to the refurbishment outage that began in 2008. The stress-corrosion cracking (SCC) or environmentally assisted cracking (EAC) observed at Lepreau was very unexpected as carbon steel is not typically susceptible to significant cracking. Theories supporting mechanisms such as hydrogen embrittlement due to the high corrosion rates and hydrogen production associated with the outlet feeder FAC were proposed along with a detailed examination of the construction and operational history [Slade & Genderon, 2005]. Evidence pointed to high residual stresses from the bending, welding and fabrication process as a primary culprit to the cracking mechanism and the fact that none of the bends were stress relieved following fabrication. No direct evidence of a connection with hydrogen embrittlement related to FAC was found, however it is still suspected to have played a factor. The material for replacement sections of pipe, and that used for new construction and refurbishment projects, is now specified to contain a higher chromium content (~0.3 wt%) and has slightly more carbon (~0.35% vs 0.3%) which, in combination act to significantly reduce the FAC issue and increases the yield strength respectively, thereby creating more margin to protect against cracking. All new bends are also fully stressed relieved before being placed into service.

3.2.2 Delayed Hydride Cracking of Zirconium Alloys

Of the corrosion issues of most concern in the PHT system, perhaps the most critical is delayed hydride cracking (DHC) of the Zr-2.5Nb pressure tubes as they represent the physical barrier and pressure boundary of the reactor core. As described in Chapter 10, the pressure tubes in a CANDU reactor are sealed on each end through a rolled-joint connection to the 403SS end-fittings. Deuterium produced through the limited corrosion of the Zr-2.5Nb pressure tubes has been shown to accumulate within the alloy; its accumulation is readily measured through scrape samples obtained during maintenance outages. Over time, should the solution solubility limit of deuterium in the alloy be exceeded, zirconium-hydride platelets may form within the metal's lattice and between grain boundaries. The hydride is a brittle, ceramic-like material that is prone to cracking under stress as was demonstrated on several of the original Zircaloy 2 pressure tubes in the Pickering A station that were replaced as a result of DHC in the period between 1974 – 1976 [Urbanic, 1987]. The most prone locations are at the rolled joint areas on each end of the pressure tube due to the increased deuterium production and migration rate at the galvanic couple between the pressure tube and the stainless steel end-fitting – deuterium produced through corrosion of the stainless steel is free to migrate into the pressure tube due to the intimate contact resulting from the rolled-joint seal. Residual stress due to the rolling process also plays a large role in these locations.

3.3 Activity Transport

The PHTS coolant in a water-cooled reactor such as CANDU may become activated itself through the absorption of neutrons as it passes through the reactor core. This is particularly relevant in CANDU reactors where heavy water is used as the reactor coolant and moderator (in the separate moderator system described in Section 5) since neutron absorption by the deuterium atoms in heavy water will directly produce tritium (T or H_3), which is radioactive and has a 12.3

year half life. Tritium production and decay in the PHTS heavy water means that, even in the absence of particulate or ionic impurities, the coolant will be radioactive and the entire PHTS will have significant concentrations of tritium, typically of the order of 10^4 Bq/kg of heavy water. This is several orders of magnitude lower than the steady state tritium concentrations in the moderator water since only about 3% of the PHTS coolant is in the reactor core at any given time whereas >95% of the moderator heavy water is continuously being exposed to the high neutron flux in the reactor core. Thus, all reactor systems that employ heavy water as their coolant will contain significant tritium activity in all sections of the circuit.

In addition to the production of tritium, the PHTS heavy water coolant will contain trace concentrations of dissolved ions and particulates that are the result of the corrosion and wear of the system materials. These impurities, which include iron, nickel, chromium, cobalt and antimony can deposit in the core and may become activated by neutron absorption. In addition, zirconium alloy wear products released by the movement of fuel inside the fuel channel during refuelling, and fission products and actinides released from the (infrequent) failure of the fuel cladding, can be transported out of the core by the coolant. These species are easily deposited, adsorbed and incorporated into the oxide layers that form on the surfaces of out-of-core components leading to elevated levels of activity on components removed from the direct radiation field of the reactor core, the reactor inlet/outlet headers and feeders and inner surfaces of the steam generator tubes, for example.

Typical activation and fission products observed in the PHT and their half-lives are shown in Table 4. Note the relatively long half-life of Co-60, which is a major contributor to radiation fields in out-of-core components. The fission products are generally kept at very low concentrations in the PHT coolant since they are indicators of failed fuel elements, which are removed as quickly as possible once identified. The radioiodines are of particular concern since they are readily absorbed in the thyroid of humans and must be contained in the system and disposed of appropriately.

Table 4. Common radioactive isotopes and their source in the PHTS.

Activation product	Typical source	Half Life
Cr-51	Alloys	27.7 days
Fe-59	Steels and alloys	44.6 days
Sb-124	Impurity in steels and alloys – bearings and wear surfaces	60.2 days
Co-58	Nickel alloys	70.8 days
Mn-54	Steels and alloys	312.5 days
Co-60	Impurity in steels and alloys – hard-facing materials for wear resistance (e.g. Stellites)	1924 days
I-131	Fission product	8.04 days
Xe-133	Fission product	5.24 days
Xe-135	Fission product	9.1 hours
Kr-85	Fission product	10.73 years
Kr-88	Fission product	2.84 hours

4 Secondary Heat Transport System

The Secondary Heat Transport System (commonly called the secondary system or steam cycle) produces the steam necessary to drive the turbines and electrical generator. The configuration of the secondary system is described in detail in Chapter 8 but in summary it contains the condenser, a series of low-pressure feedwater heaters, a deaerator, a series of high temperature feedwater heaters, the boilers or steam generators, the steam supply piping and control systems, and the high- and low-pressure turbines with a moisture separator and steam reheater in between them. While the secondary system at each plant is unique in terms of its exact configuration and the materials used for the various components there are typically two classifications of system; all-ferrous and copper-containing. The operating chemistry for the secondary system is dependent upon the type of materials from which the plant is constructed. For example, as described in the corrosion section in Chapter 14, it is desirable for iron-based materials to operate with alkaline chemistry to promote the formation of passive oxide films and minimize corrosion. This is often done with the addition of ammonia or other volatile amines and target pH values (measured at room temperature) can be up to 10. In a copper-based system or a system that contains some copper components, copper corrosion is known to be accelerated considerably by ammonia, especially when oxygen is present, and maximum pH's must be kept to about 9.2 – 9.4 and the use of ammonia minimized or excluded all together. Reducing conditions are maintained, mainly to protect the steam-generator alloys from cracking, by the addition of hydrazine.

4.1 Chemistry Control in the Secondary System

In order to protect the entire secondary system from corrosion, a volatile pH-controlling agent is employed, i.e., one that enters the steam phase in the boilers and is carried through the entire system such that it protects the main steam lines, steam extraction lines, moisture separator and reheater and the condenser. Previously, the chemical buffer sodium phosphate was in widespread use for dosing feedwater but was effectively non-volatile and concentrated in the steam generator, where its reactions within crevices and under deposits could lead locally to either highly alkaline or acid conditions if not properly adjusted and monitored. Extended pitting or wastage of nickel-alloy steam generator tubes, especially under the "sludge pile" on the tube sheet, was a not-infrequent occurrence. Nowadays, it is common practice to use "all-volatile" treatment (AVT), with hydrazine for oxygen control and a volatile base such as ammonia to distribute the alkalizing agent around the system. Ammonia, however, is so volatile that it concentrates in the steam phase and can leave the water-touched areas unprotected, so less-volatile amines such as morpholine (the cyclic compound $O(C_2H_2)_2NH_,$ ethanolamine ($HO(CH_2)_2NH_2$) or cyclohexylamine ($(CH_2)_5CNH_2$) may be used instead of, or in combination with, ammonia. A drawback of these higher-molecular-weight organic compounds is that they break down at high temperature to simpler substances such as acetic acid and eventually carbon dioxide, which may be corrosive; their concentrations therefore have to be limited in the steam generators through strict chemistry control.

Chemistry parameters that are targets for the secondary system chemistry control and are typically measured at the high pressure feed water heater outlet are shown in Table 5.

Table 5. Target chemistry parameters in the secondary system (all-ferrous materials).

Parameter	Typical Specification Range
pH	9.5 < pH < 10 (for all-ferrous systems)
Dissolved O_2	< 0.01 mg/kg (ppm)
Hydrazine	0.020 – 0.030 mg/kg (ppm)
Na^+	< 0.05 μg/kg
Cl^- ; SO_4^{2-}	< 0.05 μg/kg

The distribution of amine retained in the water phase or stripped to the steam phase is described by the distribution coefficient, which is dependent upon both temperature and concentration. The true distribution coefficient is defined as the ratio of the vapour-phase mole fraction of volatile species (y_B) to its liquid phase mole fraction (x_B):

$$D_B = \frac{y_B}{x_B} \tag{30}$$

Note that, in the true distribution coefficient, the measure is per fraction of the volatile species. For ammonia this means the neutral species, NH_3. However, due to the dissociation of ammonia and other amines in water, the true distribution coefficient is not typically what is measured; the measurement is the "apparent" distribution coefficient. The apparent distribution coefficient accounts for the total concentration (or fraction) of ammonia-based species in the liquid phase including the dissociation products as shown in equation 31. For example, the equilibrium established between ammonia and the ammonium cation in water is given by equation 32 and its equilibrium constant in equation 33. If ammonia is stripped to the vapour phase, its liquid phase concentration will be reduced and will subsequently affect the concentration of the ammonium cation retained in solution. As with other equilibrium chemical equations that have been discussed in this chapter, the equilibrium constant for amine dissociation is temperature-dependent, as are the distribution coefficients, thus the apparent distribution coefficient is a complicated function of the true distribution coefficient and equilibrium chemistry.

$$[NH_3]_{Total} = [NH_3]_{(aq)} + [NH_4^+] \tag{31}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{32}$$

$$K_{NH_3} = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3} a_{H_2O}} \approx \frac{[NH_4^+][OH^-]}{[NH_3]} \tag{33}$$

While protection of the entire secondary system is the goal of the chemistry dosing practices, protection of the materials in the steam generators or boilers is paramount since the boiler tubes represent the physical barrier between nuclear and non-nuclear sections of the plant. A boiler contains an array of 1000's of tubes, tube support plates, tube sheet, and associated steam driers. Since dissolved species, other than the ammonia or the other amines dosed to control pH, represent impurities in the feedwater it is important to minimize (or eliminate if possible) their concentrations entering the boiler. Some impurities of particular importance in boiler feed water include iron, copper, sodium, chloride and sulphate. The iron (and copper if the system includes some copper-bearing materials) enters the boiler as corrosion products released from the predominately carbon steel components in the feed water train and, since they are not volatile will accumulate in the boiler as steam is produced. Ultimately, boiler sludge (mainly iron oxides or hydrated oxides) will accumulate on the tube sheet and tube support plates and must be periodically removed through a physical or chemical cleaning procedure. This can become difficult if significant copper is retained in the deposits.

Sodium, chloride, sulphate and other inorganic impurities can enter the feedwater system through leaks in the condenser tubes and must be kept at very low concentrations since all non-volatile species will tend to concentrate in the boiler, particularly in crevice regions in the tube sheet or around the tube support plates. The concentration of these species is kept low in the boiler through a continuous blow-down that removes a small fraction of the circulating water in the boiler. Example 15.3 demonstrates the calculation on the effectiveness of blow-down to maintain low levels of contaminants in the boiler. A simple calculation of the feedwater input flow rate divided by the blow-down rate can give a rough indication of the concentration factor (CF) that can be achieved in a steam generator crevice. For example, an individual boiler in a typical CANDU-6 plant will have an incoming flow rate of around 250 kg/s. With a blow-down of approximately 0.5% of the incoming flow (amounting to 1.25 kg/s) this shows a concentration factor of 200, meaning that any impurities entering the boiler from the feedwater will be concentrated 200 times in the bulk water of the steam generator. Regular sampling of the blow-down stream for sodium, chloride, sulphate and other impurities provides a ready indication of poor feedwater chemistry.

Impurities in the boiler cause hide-out, whereby they are absorbed and retained in the boiler crevices or in the deposited sludge piles, which can lead to aggressive chemistry conditions for the boiler tubes. Alloy 800, the choice material for recent CANDU reactor boiler tubes, has shown excellent corrosion resistance and little stress corrosion cracking over a wide range of chemistry conditions. However, if the environment adjacent to the tubes becomes sufficiently acidic or alkaline due to the ingress and hide-out of ionic impurities, chlorides, sulphate or sodium for example, the recommended operating envelope for the boiler tubes may be compromised. This situation has occurred at various nuclear plants, both CANDUs and PWRs, where boiler tubes had to be plugged due to through-wall cracking and leakage of primary system water into the boiler. This is detected by increasing radiation levels in the boiler blow-down or main steam line.

Example 15.3 - Blow-down calculation.

A sketch of a steam generator with feedwater inlet flow rate (F), steam flow rate (S) and blowdown flow rate (B) is shown in Figure 4. Assuming steady state operation, feedwater iron concentration of 5 ppb (mg/kg), feedwater flow rate is 250 kg/s and blowdown rate of 0.5% (1.25 kg/s), calculate the concentration of iron in the bulk boiler water (C_M). If the blowdown rate was reduced to 0.1%, what effect does that have on bulk boiler water iron concentration?

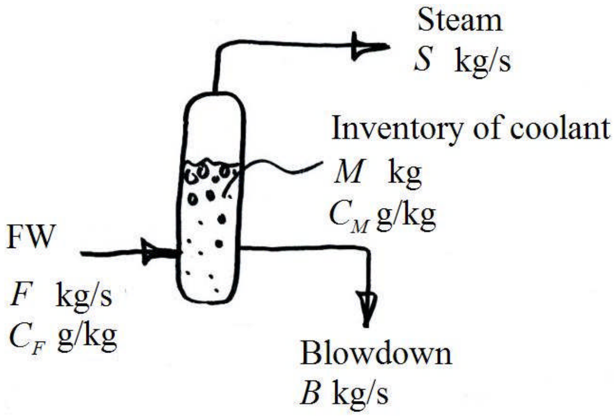

Figure 4. Mass balance on steam generator impurity inventory.

Solution

A steady state mass balance on the iron inventory using the sketch in Figure 4 results in:

$$\text{Fe In} = \text{Fe Out}$$

$$F \cdot C_F = S \cdot C_s + B \cdot C_B$$

We not that the concentration in the bulk boiler water will be the same as the blow-down concentration, hence $C_M = C_B$. Also, the iron in the boiler water is non-volatile so its concentration in the steam line will be zero. Applying these conditions and rearranging results in:

$$C_M = C_B = \frac{F}{B} C_F$$

The term F/B is the concentration factor described above and is the ratio of the feedwater flow rate over the blow-down rate. For the conditions indicated above this results in a concentration factor (CF or F/B) of 200. Thus:

$C_M = 200 \times C_F = 200 \times 0.005$ *mg/kg = 1 mg/kg* *Ans.*

Reducing the blow-down rate to 0.1% effectively increases the concentration factor by five leading to $C_M = C_B = 5$ mg/kg. Ans.

4.2 Corrosion Issues in the Secondary System

4.2.1 Boiler crevices

As described above, the steam generators represent critical locations in a CANDU plant as the boiler tubes and tube sheets are the physical barriers between the nuclear and non-nuclear sections of the plant. As a result, the operational chemistry practices in the steam generation circuit are targeted primarily at protection of the shell side of the boiler while trying to minimize corrosion issues in the feedwater train and the steam cycle. The recent material of choice for the steam generator tubing is nuclear grade Alloy 800 (~20%Cr, 35% Ni, balance Fe with ~1% each Al & Ti), which has shown excellent corrosion resistance and minimal cracking in well over 30 years of operation in CANDU plants and German PWRs. Earlier CANDUs used Inconel 600 or Monel 400, each showing poorer performance than Alloy 800 in terms of their susceptibility to underdeposit corrosion, SCC, intergrannular attack and fretting wear [Tapping et. al, 2000]. It is, however, imperative to keep the feedwater and hence boiler chemistry within specification limits for pH and oxygen, as these parameters directly affect the electrochemical corrosion potential (ECP) attained on the boiler tubes and have significant influences on corrosion and environmentally-assisted cracking (EAC). During operation, crevices in the steam generator accumulate impurities from the concentrated environment in the bulk boiler water due to the concentration factor (CF) effect as illustrated in the blow-down example above (crevices as defined here are not only the physical crevices between the boiler tubes and the tube sheets and support plates but also the tight-tolerance micro-environments that are created under boiler sludge deposits and along the tube support plates). As the power level is reduced and the CF subsequently lowered, the impurities leach out of the crevices and may be consequently removed via blow-down, a phenomenon known as hide-out return. Failure to keep impurity concentrations low in the bulk boiler water may lead to chemical imbalances in the boiler crevices and promote either acidic or alkaline pH's, both of which are detrimental to the boiler tubes from a general corrosion perspective. The presence of impurity oxygen in the bulk boiler water compounds the effect and may lead to cracking, particularly during transient operations during station run-ups or shut-downs.

AECL has developed a recommended operating environment envelope for Alloy 800 boiler tubes [Tapping, 2012]. The chart, shown in Figure 5, is the result of decades of reactor operating experience and ongoing research at the Chalk River Laboratories and elsewhere to evaluate the cracking and degradation propensity of boiler tubes in out-of-specification chemistry conditions. While a plant may be within the recommended operating envelope for the majority of its operational lifetime, there will be periods of out-of-specification chemistry due to ingress of contaminant ions or elevated concentrations of dissolved oxygen. The effects of these, hopefully short, periods need to be carefully assessed as they may be the initiating events for pitting and cracking later on in the life of the plant.

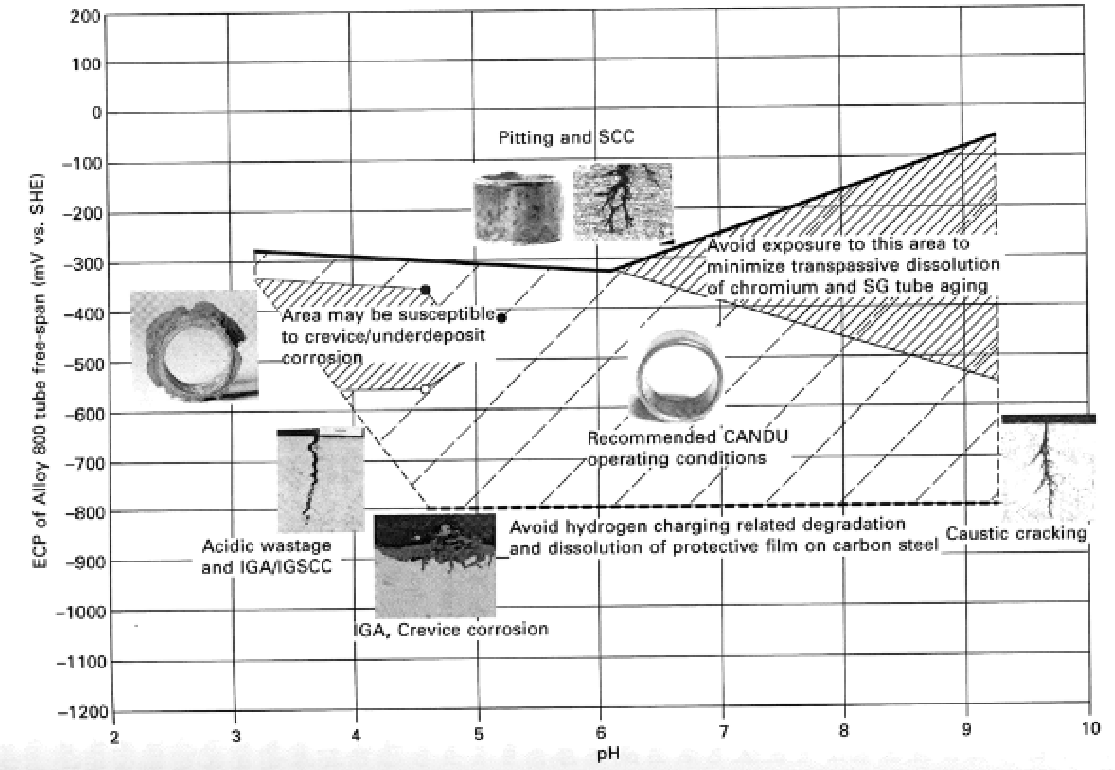

Figure 5. Alloy 800 Recommended Operating Envelope (Tapping, 2012).

4.2.2 Flow-Accelerated Corrosion in the Feedwater and Steam Extraction Piping

Protection of the boiler is the primary objective of the chemistry dosing practices in the secondary system and one of the best ways to accomplish this is to minimize the corrosion of the materials in the feedwater train and regenerative feedwater heaters. Excessive corrosion of the feedwater piping will introduce corrosion products into the boiler water, ultimately dumping the material as sludge that accumulates on the tube support plates and tube sheet in the steam generators. Flow accelerated corrosion (FAC), described in detail in Chapter 14, is prevalent in the feedwater system since the steam that condenses following the low pressure turbines is ultimately pure water with a relatively low concentration of volatile amine that has been carried through the steam cycle. This condensate water is effectively iron-free or fully undersaturated in dissolved corrosion products and is an excellent fluid for promoting FAC of carbon steel piping. The moisture content of wet steam in the moisture separator and turbine steam extraction lines will be effectively pure water and fully undersaturated in corrosion products as well, but have the additional complication of possessing small water droplets that can impinge on piping surfaces, creating a mechanical erosion mechanism compounding the FAC effect. Critical locations for FAC are typically downstream of tight radius bends, orifice plates for flow measurements or any location where turbulence is enhanced and mass transfer from the piping promoted. The solubility of the primary protective oxide film, magnetite, also plays a role in the most affected locations since it is seen to go through a maximum at temperatures between 130-150 °C as shown in Figure 7 in Chapter 14.

Management of FAC in the secondary circuit of power plants is quite advanced and relies upon computer model predictions (EPRI's CHECWORKS code for example) to assess critical locations in the plant and frequent inspections. One of the key factors in protecting the secondary side piping from FAC is to maintain a suitable alkalinity level at ***all*** locations around the steam cycle. Magnetite solubility is demonstrated to be at a minimum around a $pH_{25°C}$ of 9.5 or so and maintaining this specification at every location in the steam cycle is highly desirable to minimize pipe wall thinning by FAC. However, this is difficult to achieve in the field since chemical dosing typically occurs at a sole location in the feedwater circuit (usually just downstream of the condensate extraction pump) and the fact that the two-phase sections of the plant can have a significantly different chemical composition from that of the feedwater due to the distribution coefficient of the volatile amine used for plant pH control. In principle, the target is to maintain a delta pH ($\Delta pH = pH_T - pH_{neutral@T}$) greater than 1.0 to ensure that sufficient alkalinity is maintained at each location and the solubility of magnetite is kept to a minimum.

Table 6 shows the results of a calculation for the effect of different chemical dosing strategies on the delta pH throughout a common secondary side feedwater and steam circuit. In case 1, ammonia is used as the pH-controlling chemical and in case 2 morpholine is used, both achieving a final feedwater pH_{25C} of 9.6. Note that in case 2, 1 mg/kg of ammonia is also assumed to be present due to the decomposition of the morpholine (and hydrazine) at the higher temperature locations in the system; such decomposition typically results in a residual ammonium concentration between 0.5-1.1 mg/kg. As is demonstrated in the table, both chemical dosing strategies achieve the same target $pH_{25°C}$ and maintain a sufficient delta pH at the outlet of the HP heater, thus maintaining suitable protection of the feedwater train from FAC. However, due to the differences in volatility and distribution coefficients, the delta pH achieved with the morpholine chemistry in case 2 provides much better protection for the steam extraction lines and moisture separator.

Table 6. Comparison of delta pH for two chemical dosing strategies in a typical steam cycle.

	Case 1: 2.3 mg/kg Ammonia (pH_{25} = 9.6)			Case 2: 25 mg/kg Morpholine + 1 mg/kg Ammonia (pH_{25} = 9.6)		
Location	pH_T	$pH_{neutral}$	ΔpH	pH_T	$pH_{neutral}$	ΔpH
HP heater outlet (final feedwater)	6.71	5.68	1.03	6.87	5.68	1.19
Bulk Boiler water	5.92	5.59	0.32	6.34	5.59	0.74
HP turbine extraction to HPH2	6.29	5.67	0.62	6.80	5.67	1.14
Moisture Separator/Reheater	6.57	5.78	0.80	7.13	5.78	1.35
LP turbine extraction to DA	6.85	5.89	0.96	7.43	5.89	1.54
LP turbine extraction to LPH3	7.11	6.01	1.11	7.73	5.89	1.54
LP turbine extraction to LPH2	7.45	6.16	1.28	8.11	6.16	1.95
LP turbine extraction to LPH1	7.88	6.38	1.50	8.57	6.38	2.20
Condensate	8.73	6.83	1.89	9.49	6.83	2.65

Similar effects are realized with other amines of lower volatility, such as ethanolamine (ETA), which has a relative volatility of about 0.15 at 200°C while that of ammonia is about 5.0. Its effect on FAC compared with that of ammonia and in neutral chemistry is illustrated in Figure 6, which shows on-line measurements of the FAC rate of carbon steel in an experimental loop. The operating conditions were two-phase steam-liquid flows at 200°C with ammonia and ETA at the same $pH_{25^\circ C}$ (9.2) and with no additive. The effect of the additives on reducing FAC below that of neutral chemistry is immediately realized at zero voidage (% steam by volume) and continues up to 97% voidage. As the voidage increases from zero the FAC rates with the two additives are roughly the same and increase together. At about 80% voidage, the FAC rate with ammonia increases further as the ammonia partitions to the vapour phase, while that for ETA decreases as the ETA partitions to the liquid phase (the FAC occurs in the liquid film on the walls of the pipe or component). The diagram also shows how reducing the flow rate also reduces the FAC rate.

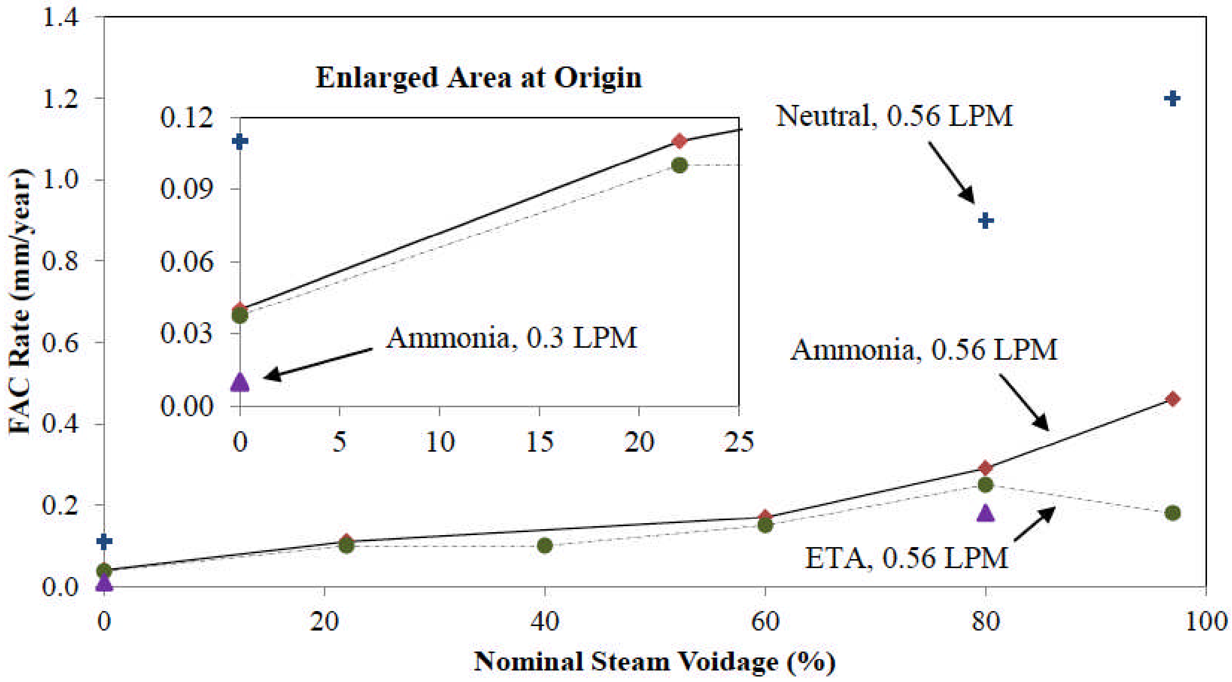

Figure 6. Effect of steam voidage on FAC rate of carbon steel at 200°C under three chemistries (neutral, $pH_{25^\circ C}$ with ammonia and with ETA) at a flow rate of 0.56 L/min (the effect of reduced flow rate on FAC with ammonia also indicated). [Lertsurasakda et al., 2013]

5 Moderator System

As described previously, the main purpose of the heavy water moderator is to slow down or thermalize the high energy neutrons produced through the fission reactions to low, thermal energies so that they more easily induce further fission reactions. A significant amount of heat is produced as a result of the high-energy neutrons losing their kinetic energy and this must be dissipated through the external heat exchanger loops. A secondary purpose of the moderator system is to serve as an additional reactivity control mechanism for the reactor, which is accomplished by dosing the heavy water with low concentrations of neutron-absorbing elements, boron or gadolinium for example. The third purpose of the moderator system is to act as a reactor safety system through rapid additions of high concentration of neutron poisons (known as shut-down system 2 – SDS 2). Thus, the moderator system encompasses a large volume of heavy water contained within the calandria vessel, the associated side recirculation loops for heat removal and purification, the moderator cover gas system for removing deuterium gas produced through the water radiolyisis, and the connections to SDS2. A schematic overview of the moderator systems is shown in Figures 4 and 5 of Chapter 8.

5.1 Chemistry Control in the Moderator System

The materials of construction in the moderator system comprise mainly stainless steel (calandria vessel, heat exchangers, etc), Zircaloy (calandria tubes) and nickel-based alloys, so the chemistry of the moderator is not specified to limit corrosion specifically since the corrosion rates of these alloys at the low temperature and pressure of the moderator system (~60^{o}C and essentially atmospheric pressure) is quite low. Thus, the heavy water in the moderator system is highly purified and the only chemicals added to the system are those used as neutron poisons for excess reactivity control or to guarantee reactor shut-down. Typically, gadolinium nitrate ($Gd(NO_3)_3$) and/or boric acid (H_3BO_3) (alternatively boric anhydride – B_2O_3) are dosed to the moderator system at low concentrations (a few ppm) and these dissolved ions make up the primary contributor to the conductivity of the moderator heavy water – so much so that system conductivity can be translated as a direct measure of reactor negative reactivity. Unlike many of the other reactor coolant systems, the moderator system is not purposely deareated to maintain low dissolved oxygen concentrations. Due to the large radiation fields associated with the reactor core, the heavy water moderator is continuously bombarded with radiation, leading to high production of deuterium and oxygen gases as the net products of water radiolysis. To avoid accumulation of these gases, they are constantly removed through the cover gas system and the deuterium is eliminated by recombination in catalytic re-combiner units, if necessary with oxygen addition.

Typical operating parameters for the moderator system are shown in Table 7. Unlike the heat transport systems where the water is kept alkaline to control and minimize the corrosion of system components, the heavy water in the moderator is kept slightly acidic to ensure that gadolinium hydroxide ($Gd(OH)_3$) will not precipitate on the surfaces of the moderator components and that SDS-2 can function if required.

Table 7. Target chemistry parameters in the moderator system.

Parameter	Typical Specification Range
D_2O isotopic	99.6 – 99.9%
Conductivity	0.005 – 0.1 mS/m
Dissolved D_2	< 3 mL/kg
pHa	4.5 – 6.5
total anions	< 0.2 mg/kg
TIC / TOC*	< 1.0 mg/kg

*Analysis for TIC/TOC has become increasingly important due to concerns for gadolinium oxalate precipitation during guaranteed shut down conditions (see Section 5.1.2).

5.1.1 Reactor shims

Gadolinium Nitrate ($Gd(NO_3)_3$)

Gadolinium has been demonstrated to be an excellent reactor shim and chemical for controlling excess reactivity during refuelling operations and to ensure reactor shut down conditions. The isotopes Gd-155 and Gd-157 are 15 and 16% abundant in nature and have huge neutron absorption cross-sections of 61000 and 255000 barns respectively, which gives them the distinction of being the naturally occurring isotopes with the largest known neutron absorption cross sections. Gadolinium nitrate hexahydrate ($Gd(NO_3)_3.6H_2O$) is easily dissolved in the heavy water moderator. Upon dissolution, the pH of the heavy water will become mildly acidic (pH_a between ~5 to 6) due to the interaction of the nitrate salt dissociation (equation 34). It is important to maintain these slightly acidic conditions within the heavy water moderator because the Gd^{3+} cations will readily hydrolyse at neutral to alkaline pH and precipitate as gadolinium hydroxide (equation 35). This is undesirable since the gadolinium must be homogeneously dispersed in the moderator system to achieve its primary goal of reactivity control.

$$Gd\left(NO_3\right)_3 \rightleftharpoons Gd^{3+} + 3NO_3^- \tag{34}$$

$$Gd^{3+} + 3H_2O \rightleftharpoons Gd\left(OH\right)_3 + 3H^+ \tag{35}$$

Gadolinum concentrations within the moderator system can range from zero to ~ 1 mg/kg under typical reactor operating conditions, leading to water conductivities of ~ 0.005 mS/m to ~ 0.10 mS/m. Care must be taken during normal reactor operation to limit the conductivity, and hence, nitrate concentration in the heavy water to below ~ 0.05 mS/m (corresponding to ~ 1 mg/kg gadolinium nitrate) since the nitrate anions may form reactive intermediate species with the water radiolysis products and promote the formation of deuterium gas (D_2) [Yakabuskie et al., 2010], which can lead to excessive cover gas concentrations and increased workload for the recombiner units (the D_2 concentration in the cover gas must be kept below 4%). Some operating reactors have used gadolinium sulfate ($Gd_2(SO_4)_3.6H_2O$) as their preferred salt, which eliminates the issues of increased deuterium production from interaction of the radiolysis products with the nitrate ion (sulfate ions do not form reactive intermediates with short-lived radiolysis products). However, the sulfate salt is sparingly soluble compared to the nitrate salt thus, if excess reactivity control is required, such as during start-ups with significant amounts of fresh fuel in the core, the preferred reactivity control shim is boric acid. Sulphur species may also promote localized corrosion of alloy components.

Boric Acid

Boron 10 is 20% abundant in nature and has a neutron absorption cross-section of 3838 barns. Boric anhydride or boric acid is soluble in water and can be an efficient alternative to gadolinium as a reactivity control mechanism. Its dissolution, however, is very slow and so boric acid is only employed in the operations of the CANDU plant when necessary. This is typically when concerns of excess deuterium production are encountered through the use of higher concentrations of gadolinium nitrate such as during startups with significant volumes of fresh fuel.

5.1.2 Guaranteed Shutdown State (GSS)

During maintenance shut-downs, the reactor is placed in a guaranteed shut-down state (GSS) whereby a soluble neutron absorbing salt (gadolinium nitrate) is injected into the moderator at high concentrations in addition to having the reactor at zero power with the shut-down rods. This provides redundancy and ensures that the reactor will be maintained in a sub-critical state until the soluble poison is removed via gadolinium and nitrate/nitrite removal in the mixed bed ion exchange columns of the moderator purification circuit, a simplified schematic of which is shown in Figure 3 of Chapter 8.

To ensure a guaranteed shut down state, gadolinium concentrations of greater than 15 mg/kg are typically required and this is the lower limit for gadolinium in the moderator during GSS. Typical concentrations are targeted at greater than 20 mg/kg and assurances must be made to the Canadian Nuclear Safety Commission that GSS is achieved and maintained. This assurance is typically accomplished by manually sampling the moderator and analyzing for gadolinium concentration at least twice per day.

Gadolinium Oxalate

In 2008 during a planned station outage at a unit of the Pickering B plant, while the unit was placed in GSS it was observed that the Gd concentration in the moderator was decreasing at an alarming rate. The over-poisoned condition for the GSS requires assurances that the Gd concentration in the moderator is maintained above 15 mg/kg at all times and the measured loss rate of Gd was approximately 2 mg/kg per day. The utility, with the assistance of experts from AECL Chalk River traced the unexpected Gd depletion to precipitation as gadolinium oxalate ($Gd_2(C_2O_4)_3$), a salt known to be very insoluble in water. Oxalate is normally not present in the moderator heavy water systems and, upon investigation, its formation was attributed to a known leak of CO_2 from the annulus gas system through the rolled joints at one of the end fittings, a condition that had been assessed in 2005 and monitored routinely through measurement of total inorganic carbon (TIC). Elevated CO_2 concentrations in the moderator heavy water produce carbonate anions, which are readily converted to oxalate through combination with primary water radiolysis radicals such as shown in equations 36 & 37.

$$\mathrm{CO_{2(aq)}} + \mathrm{e^{-}_{(aq)}} \rightleftharpoons \cdot\mathrm{CO_2} \qquad (36)$$

$$\cdot\mathrm{CO_2} + \cdot\mathrm{CO_2} \rightleftharpoons \mathrm{C_2O_4^{2-}} \qquad (37)$$

Under typical reactor operating conditions, with little gadolinium present in solution, the oxalate anions would readily decompose back to CO_2. However, under GSS with appreciable concentration of gadolinium in solution and a high enough concentration of TIC (from the ongoing CO_2 leak in the rolled joint), the oxalate anion could readily combine with the gadolinium present as quickly as it was produced, leading to precipitation of the gadolinium oxalate salt throughout the moderator system, as shown in equation 38.

$$2Gd^{3+} + 3C_2O_4^{2-} \rightarrow Gd_2\left(C_2O_4\right)_{3(s)} \tag{38}$$

The Gd depletion is of concern for maintaining the reactor in GSS but the fate of the oxalate precipitate throughout the calandria vessel and on the calandria tubes is of greater concern as it could prevent the reactor from becoming critical upon startup and must be removed. Several research programs were initiated to formulate a chemical cleaning strategy to remove the precipitated gadolinium oxalate; however, none were ultimately needed as the precipitate in-core was found to be readily oxidized and converted to the soluble nitrate salt through action of the shut-down gamma fields and ultra violet radiation (Cerenkov radiation) in the drained (air-filled) and humid calandria vessel. The remaining precipitate from out-core surfaces was easily removed through filtration upon moderator refill and reactor start up [Evans, 2010].

Oxalate production in the moderator system has also been demonstrated to occur by radiolytic processes involving total organic carbon (TOC), primarily from oil ingress. Two operating CANDU units have recently experienced issues with radiolytic decomposition of hydrocarbon lubricants within the moderator system, which will produce decomposition gases such as hydrogen and carbon dioxide as well as create particulate material through polymerization reactions that is highly efficient at plugging filters [Ma, 2010]. These issues with elevated TIC and TOC in the moderator system have led to more strict guidelines and chemistry control practices since the implications of oxalate formation have been realized.

5.1.3 Shutdown System 2 (SDS2)

Gadolinium nitrate is used in the moderator for rapid reactor shut down in the event of a station upset or trip. Shutdown System 2 (SDS2) is described in detail in Chapter 8 and comprises the poison addition tanks which contain approximately 1000 litres each of concentrated gadolinium nitrate solution (~8000 mg/kg). The poison tanks are connected to a high pressure helium gas to rapidly inject the gadolinium solution into the moderator heavy water; the systemis able achieve a reactor shut down in a matter of seconds.

5.2 Moderator Cover Gas

As described above, significant deuterium and oxygen production occurs in the moderator due to the large volume of heavy water that is continuously exposed to high radiation fields associated with the reactor core. The net water radiolysis produces the gases that are initially dissolved in the coolant but diffuse into the moderator cover gas space at the top of the calandria vessel. If the concentration of deuterium gas were not controlled, flammable concentrations would be reached in the cover gas in a matter of hours under normal operating conditions. Flammable concentrations of hydrogen (deuterium) in the helium cover gas are ~ 8%, so upper control limits are set at 4% D_2.

The head space in the calandria vessel is separated from the bulk of the moderator heavy water through a series of calandria relief ducts, as depicted in Figure 7. It is extremely important that the moderator level be maintained within the relief ducts as these provide the conduit for the deuterium and oxygen gases to diffuse into the head-space and to the helium cover gas. Since the surface area for moderator heavy water to cover gas exchange is limited when water level is maintained within the relief ducts, bulk diffusion rates can be minimized and kept within controllable margins. If the moderator level were to fall below the relief ducts a large surface area would then present itself for the D_2 and O_2 to readily migrate into the gas phase, leading to a rapid increase in cover gas concentrations and potential for exceeding flammability limits.

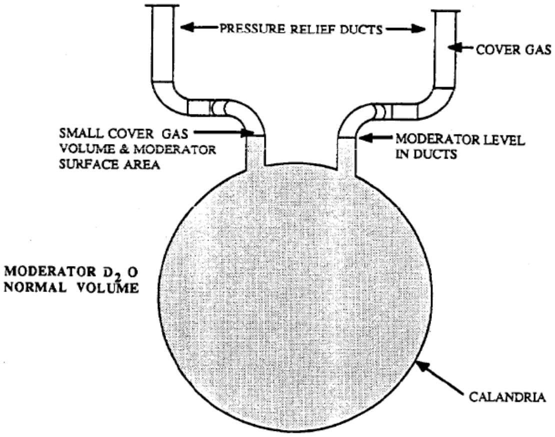

Figure 7. Normal moderator cover gas system volume and relief ducts (CANTEACH)

The helium cover gas is maintained at slightly above atmospheric pressure (~ 110 kPa absolute) and is circulated by several compressors, operating in parallel, through the head-space and on to the catalytic re-combiner units (RCUs). The hydrogen (deuterium) RCUs are usually AECL-patented components that contain a supported platinum or palladium catalyst. The re-combination reaction that ensures deuterium concentrations are kept low in the cover gas follows equation 39. As can be seen, the reaction requires a 1/2x stoichiometric concentration of oxygen in order to fully recombine the deuterium gas to heavy water; however, it is common practice to dose the helium cover gas with oxygen in excess to ensure sufficient recombination occurs. By ensuring the cover gas oxygen concentration is between 1-2%, sufficient excess is continually maintained and deuterium concentrations are kept to very low values and are often undetectable.

$$D_2 + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} D_2O \qquad (39)$$

6 Auxiliary Systems

6.1 Calandria Vault and End Shield Cooling System

The Calandria Vault and End-Shield Cooling system is a light-water system that acts as a biological shield from the gamma radiation and neutrons present in the core of the reactor. In this system, radiation energy is dissipated as heat that is removed from the water in external heat exchangers. Schematic diagrams of the system are shown in Figure 8 and the system is described in more detail in Chapter 8. The system comprises two distinct circuits; the calandria vault that surrounds the reactor calandria vessel, which is enclosed in concrete; and the end shields on either face of the reactor through which the fuel channels protrude. The end shields are packed with carbon steel balls that stop most of the neutrons and gamma emanating from the reactor core (note, in some CANDUs the end shield is a solid carbon steel plate with integral cooling ports). The system operates at nearly atmospheric pressure and contains a circulated nitrogen cover gas. Any gas that is produced from water radiolysis will diffuse into the cover gas, which needs to be purged periodically to avoid the build up of flammable concentrations of hydrogen and oxygen.

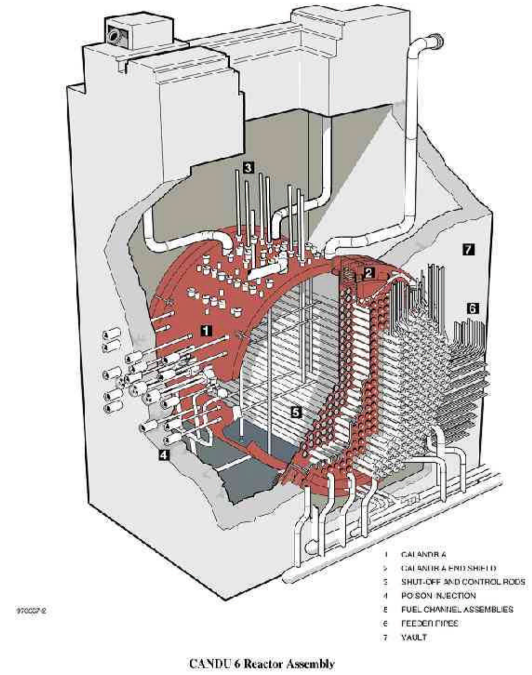

Figure 8. Schematic diagram of the Calandria vault and reactor assembly.

Typical operating specifications for the calandria vault and end shield cooling system are shown in Table 8. Alkalinity is controlled by addition of lithium hydroxide to ensure low corrosion rates of the system materials and the specifications for dissolved hydrogen and dissolved oxygen in the system are set to ensure flammability limits are not exceeded. If the nitrogen cover gas for the system reaches the control limit for hydrogen (4%), the system is purged with fresh nitrogen to ensure safe operation is maintained.

Table 8. Typical Chemistry Parameters of the Calandria Vault and End Shield Cooling System.

Parameter	Typical Specification Range
pH	9.0 – 10.0
[Li^+]	0.07 – 0.7 mg/kg
conductivity	0.24 – 2.4 mS/m
Anionic impurities	< 1.0 mg/kg
H_2 (vol. % in cover gas)	< 4%
O_2 (vol. % in cover gas)	< 2%

Under normal circumstances, the end shield cooling system operates with a small excess of dissolved hydrogen produced through the corrosion of system materials. This results in the net radiolytic production of hydrogen and oxygen being suppressed. Some CANDU reactors have had chronic issues with build up of hydrogen in the cover gas, which requires a frequent purging to ensure that flammable concentrations are not reached. The increased hydrogen production has been linked to the presence of dissolved oxygen in the water due to the addition of higher–than-normal quantities of air-saturated make-up water. Dissolved oxygen is consumed through recombination with the dissolved hydrogen, but when there is insufficient dissolved hydrogen net water radiolysis will recommence to produce hydrogen and more oxygen, which exacerbates the process. Once net radiolysis is occurring on a long-term basis, simply addressing the aerated make-up water ingress issue has been shown not to reduce the hydrogen production.

The CANDU industry has investigated the possibility of mitigating excessive hydrogen production in the calandria vault and end shield cooling system and has demonstrated that adding an oxygen scavenger, such as hydrazine, to the system will mitigate the hydrogen production and return the system to net radiolytic suppression [Stuart, 2012]. The dissolved oxygen reacts with hydrazine to form nitrogen and water, which is a process that is fast at low temperatures as it is mediated by the radiation field. Note that simply adding dissolved hydrogen to the water would also promote a radiolysis recombination reaction, however, since the Calandria Vault and End Shield Cooling system operates at atmospheric pressure, this method is not feasible and hydrazine additions are becoming common practice in operating reactors.

6.2 Liquid Zone Control

The liquid zone control system, as described in detail in Chapter 8, is designed to make fine adjustments to the neutron flux profile in the reactor. This is accomplished by varying the water level in each of the liquid-zone control tubes by adjusting the inlet water flow rate to the individual zones. The materials of construction for the liquid zone tubes are primarily Zircaloy 4, with auxiliary components being 300-series stainless steel; thus, the corrosion of the system components is minimal under a wide range of chemistry conditions. Since the purpose of the light water in the liquid zone system is to absorb neutrons to shape the reactor flux, the water is kept nominally pure with a very low conductivity. The cover gas space is occupied with helium and no direct method is used to limit the water radiolysis reactions that produce hydrogen and oxygen. Hydrogen control in the cover gas space is minimized by purging with helium as required and by recombiners. Water purity in the liquid zone system is paramount to minimize the hydrogen produced by radiolysis since impurities such as chlorides or nitrate/nitrites will interfere with the hydrogen recombination reactions and catalyze oxygen and peroxide production. Thus, nitrogen in the cover gas (indicative of air ingress) is highly undesirable, since it will produce nitrate anions in the presence of a radiation field and subsequently produce nitric acid that can lead to low pH conditions and corrosion of the system materials as well as promote high production rates of hydrogen.

The typical operating specifications for the liquid zone control system are focused on water purity as measured through liquid conductivity. For high purity make-up water, it is often possible to achieve conductivities in the range of 0.006 – 0.008 mS/m, and most utilities will try to keep the system operating within these limits or at least below 0.01 mS/m. By doing so, water radiolysis is minimized and the cover gas purge can be done as frequently as necessary to maintain the cover gas hydrogen concentration below 4%.

6.3 Annulus Gas

The annulus gas system provides a thermal barrier between the Zr-2.5Nb pressure tubes operating at temperatures between 300-310^{o}C and the low temperature (~60^{o}C) calandria tubes that separate the moderator from the primary heat transport system. The annulus space in each fuel channel provides a gap of approximately 5 mm and is continuously purged with carbon dioxide gas, thus purity of the CO_2 is a direct indication of the overall health of the system. Typical impurities in the CO_2 purge gas include deuterium (D_2), which diffuses through the pressure tubes from to the small amount of corrosion occurring on the PHT side of the tube, and water vapour (D_2O). The corrosion of the exterior surface of the pressure tubes and the interior surface of the calandria tubes is not typically an issue when the CO_2 is pure. The presence of heavy water vapour in the gas can indicate leaks from either the PHT or moderator systems. Thus, typical chemistry parameters that are monitored in the annulus gas include the volume percentages of deuterium and oxygen and the dew point (^{o}C). Gradual increases in the dew point are expected in the system since, ultimately, a small amount of heavy water will migrate through the rolled-joint seals at each end of the fuel channel. However, accelerating increases in dew point measurement provide an on-line indication of developing leaks in the system.

Oxygen may also be injected into the CO_2 annulus gas to a concentration of approximately 2-4%. This is beneficial as it promotes protective ZrO_2 films on the pressure tubes and calandria tubes and helps to ensure that the garter springs or calandria tube to pressure tube spacers (Alloy X750 – a nickel superalloy) are maintained in a suitably oxidized state, also promoting passive oxide film formation. If no oxygen is present, the garter springs can become extremely brittle as the reduced oxides or elemental nickel present under these conditions can promote cracking in the material. This is exacerbated by radiation embrittlement due to the high neutron fluxes to which the garter springs are exposed. Oxygen injection to the annulus gas also promotes the recombination with deuterium to form D_2O, helping to ensure the deuterium concentrations are kept below the flammability limits.

6.4 Emergency Core Cooling Systems

The emergency core cooling systems must be ready on a moment’s notice in the event of a loss of coolant accident (LOCA) from the PHT, thus it is imperative that the system components do not corrode excessively and accumulate particulate corrosion products that can accumulate as sludge in the normally stagnant system. Short-term decay heat removal is supplied by the high-pressure and medium-pressure ECC systems that have their own distinct water supplies. For longer-term core cooling, the emergency cooling water is supplied via a tank inside the vacuum building in the multi-unit CANDUs or from the dousing tank in the roof of the containment building of single-unit stations.

In the event of a LOCA, when a reactor PHTS is vented to the building, water from the dousing tank is sprayed into the building to condense the steam and reduce the pressure. The supply tank is connected to the sump below the reactor building that collects water draining from the system for re-injection via the emergency injection pumps. The system chemistry is maintained moderately alkaline and is deoxygenated with hydrazine, which will decompose over time to ammonia producing the alkalinity required to maintain low corrosion rates of the ECC piping and injection nozzles. Recent regulations have focused on ECC chemistry, particularly the effect of debris or corrosion products clogging the strainers of the injection pumps. Of primary concern are high-pH conditions, where the corrosion of aluminum components in contact with the ECC water (the sump strainers for example) has been the focus of considerable research effort [Edwards et al, 2010]. At too high a pH, aluminum components may corrode excessively and form precipitates that could block the strainers. For this reason, an upper limit on dousing system pH is typically set around 9.5.

6.5 Service Water

A nuclear power plant contains many subsystems that act as coolants for the primary process systems. These include auxiliary heat exchangers for the emergency core cooling systems, recirculated cooling water for the turbine/generator lubrication oil, and general service recirculated cooling water (RCW). These systems are chemically-dosed to maintain low corrosion of the piping and heat exchanger tubing by providing an alkaline environment with minimal dissolved oxygen. The RCW and TARCW (turbine & auxiliaries recirculated cooling water) systems are continuously circulated during plant operation, making their chemistry control quite simple; chemicals may be added as required to meet the pH and dissolved oxygen specifications. These auxiliary systems will typically operate with the same chemicals as are used in the feedwater circuit, but care must be taken to limit the operating pH if ammonia is used since the auxiliary systems will typically contain some copper-bearing components. In general, pH is controlled by ammonia and/or morpholine additions to maintain a value of around 9.2. Dissolved oxygen is monitored and managed through hydrazine additions at concentrations between 50 – 100 ppb, ensuring low corrosion of the carbon steel piping. Particulate corrosion products are also monitored to ensure system corrosion is low; higher particulate concentrations can be an indication of out-of-specification chemistry conditions that may be remedied by chemical addition or through a feed-and-bleed procedure to lower overall chemical and impurity concentrations.

7 Lay-up Practices

Inevitably, every power plant needs to be shut down for regular maintenance outages. In the case of a CANDU, a mid-life refurbishment outage (after ~ 25-30 years operation) is required to remove and replace the Zr2.5Nb pressure tubes that tend to stretch and sag due to the operational temperatures and high atomic displacements caused by the continuous neutron bombardment under load. A regular maintenance outage may last from 2 – 8 weeks depending upon the scope of work required and refurbishment outages are planned for at least two years. During any of these plant outages, the systems are typically depressurized and frequently drained to facilitate the required maintenance work and subsequent inspections. These maintenance activities can allow air ingress into the closed-loop systems that are intentionally kept de-aerated to minimize corrosion during operation. The duration and extent of the oxidizing conditions that are produced when the systems are shut down can play large roles in their behaviour during startup and subsequent steady power operation. Thus, it is now considered extremely important to provide a suitable lay-up condition to the plant during regular maintenance outages and is paramount for protecting non-refurbished components during an extended shut down during a mid-life refurbishment. Degradation mechanisms and problem locations in the feedwater and steam circuit of fossil plants are described by Mathews and are shown schematically in Figure 9 [Mathews, 2013]

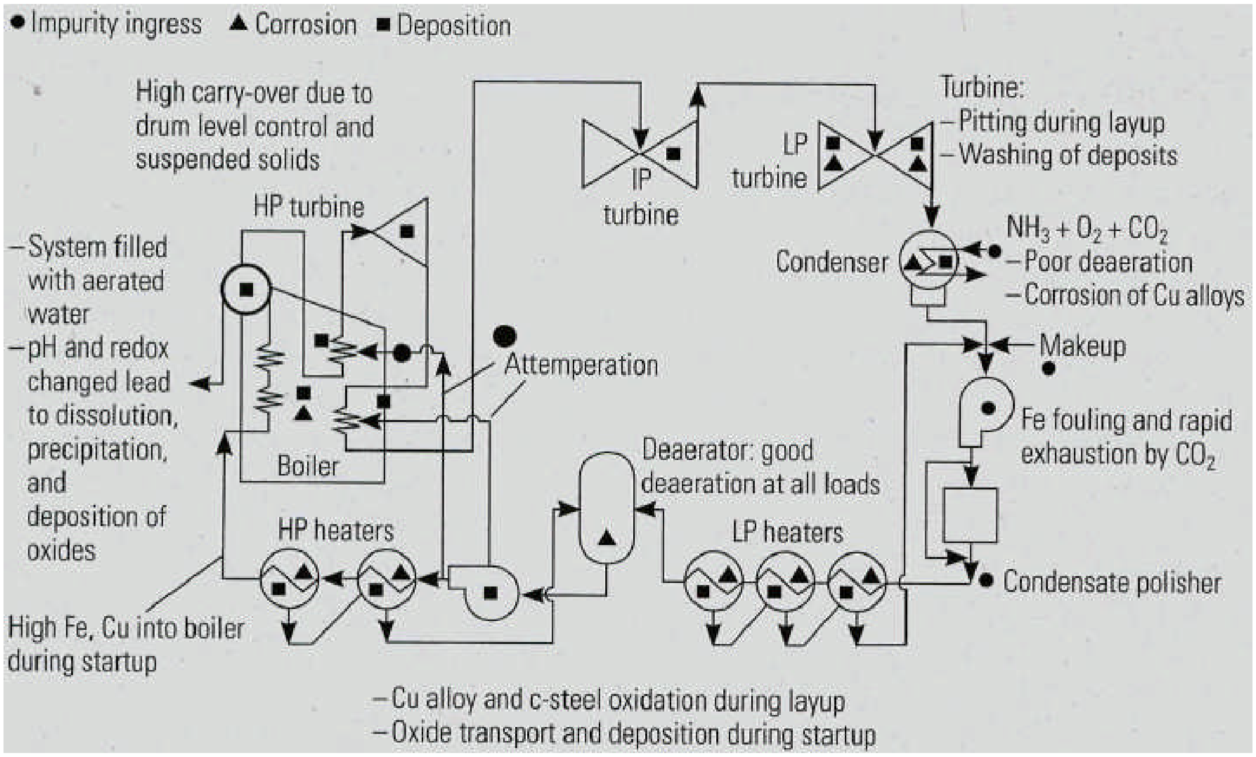

Figure 9. Locations requiring attention during maintenance outages and lay-up of a fossil plant. [after Mathews, 2013]

7.1 Dry Lay-up

It is common practice in the power generating industry to provide, at a minimum, a low humidity environment for systems that are placed in "dry lay-up". This includes the steam-carrying piping and components of the secondary system along with the condenser shells. Depending upon the duration of the maintenance outage it may be desirable not only to circulate low humidity air through the system but also to maintain an inert cover gas, typically nitrogen, to prevent oxidation of the reduced corrosion products present on the piping surfaces. If significant humidity is present, a thin water film will develop on the piping surfaces and this will be fully oxygen saturated, thus promoting general corrosion and pitting on the predominantly carbon steel surfaces in these systems. It will also convert, at least partially, the reduced protective oxide formed on the surfaces during operation (typically magnetite – Fe_3O_4) to a more oxidized form such as hematite (Fe_2O_3). This oxidation process will tend to alter the volume and thickness of the oxide films leading to poor adhesion and spallation during subsequent plant start up. Figure 10 shows the relative oxide/steel volume ratios and it is clear that the further oxidized the corrosion product the larger the volume occupied. Thus, maintaining an oxygen-free, dry environment for all system components during a maintenance outage is seen as the most prudent step in protecting the plant's assets.

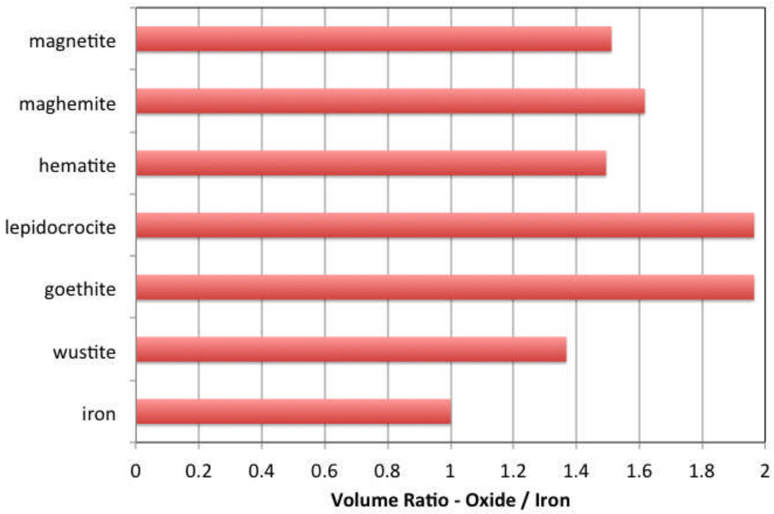

Figure 10. Oxide/steel volume ratios.

7.2 Wet Lay-up

Some systems may not be drained during a maintenance outage if work is not scheduled to be performed on the system or if parts of the system in question can be isolated. Thus, at the start of the lay-up period, the system will have the good chemistry specified for the operational period but this may be difficult to maintain, especially if the outage is extended or if the project is large in scope such as an overall mid-life refurbishment. Under these circumstances, the keys to maintaining low corrosion rates of all system materials are the same as during operation: maintain an alkaline pH condition to promote passivity of the corrosion films and maintain reducing conditions in the fluid by excluding air ingress and, typically, dosing with an oxygen scavenging chemical such as hydrazine (N_2H_4). Frequent recirculation of the laid-up system volume during the maintenance outage is recommended to promote good mixing and representative sampling.

8 Heavy Water Systems

Heavy water (D_2O) is essential to the operation of a CANDU reactor. It is used in place of light water (H_2O) as a moderator and coolant due to its superior neutron moderating properties (deuterium's neutron absorption cross-section is orders of magnitude lower than hydrogen's) making it feasible to fuel the reactor with uranium containing the natural abundance of the fissile U-235 isotope (~0.7%). Heavy water or, more specifically, the deuterium isotope, is naturally abundant in the environment at about 0.015% (atomic percentage) as both the D_2O and the HDO molecule, all in chemical equilibrium as shown in equation 40. The moderator and PHT systems both require heavy water that is greater than 98% in isotopic for D_2O. For reactor safety purposes in the event of a pressure tube rupture where the PHT water enters and mixes with the moderator, the PHT isotopic content is typically kept slightly lower than the moderator, 98.6% vs > 99% for example, which will dilute the moderator in the accident scenario lowering the overall moderation.

$$H_2O + D_2O \rightleftharpoons 2HDO \tag{40}$$

8.1 Upgrading

Separation techniques are numerous and include fractionation through distillation and various processes involving atomic exchange through chemical sorbants and equilibrium systems. All of these processes rely on the fact that the mass of the deuterium atom is twice that of the hydrogen atom, making properties such as vapour pressure slightly different from those of compounds containing the hydrogen atom alone. The separation factor for the deuterium-hydrogen isotopes is defined as the ratio of the deuterium fraction in the desired phase (liquid, x) over its fraction in the other phase (gas, y), as shown in equation 41. For a light-water/heavy-water mixture, the separation factor can be estimated through the vapour pressure of each of the components as shown in equation 42 for the normal boiling point of natural water [Benedict, 1980].

$$\alpha = \frac{x/(1-x)}{y/(1-y)} \tag{41}$$

$$\alpha_{HD} = \sqrt{\frac{p_{H_2O}}{p_{D_2O}}} = 1.026 \tag{42}$$

The primary method for heavy water production is known as the GS dual-temperature exchange process. It involves the equilibrium exchange of the deuterium atom between water and hydrogen sulfide gas in a staged absorption column as shown in equation 43. Two towers are employed whereby a fresh water feed to the cold tower, which has a higher separation factor for deuterium ($\alpha_c \approx 2.32$) since it will be retained preferentially in the liquid phase, is stripped of some of its hydrogen content to a deuterium-rich hydrogen sulfide gas (HDS), which is effectively leached of its deuterium content. The feed gas to the cold column is produced in the high temperature column, where the separation factor (ratio of the fraction of D in liquid to D in the gas) is lower ($\alpha_h \approx 1.80$), thereby producing the D-rich gas for feed to the primary, cold exchange column. The basic principles of operation of the GS process are depicted in Figure 11 (from Benedict et al., 1980). With an appropriate number of stages in the absorption columns, water can be fairly economically enriched to about 25% - 30% D_2O. From this concentration, final upgrading using conventional distillation is economically feasible.

$$H_2O + HDS \rightleftharpoons HDO + H_2S \tag{43}$$

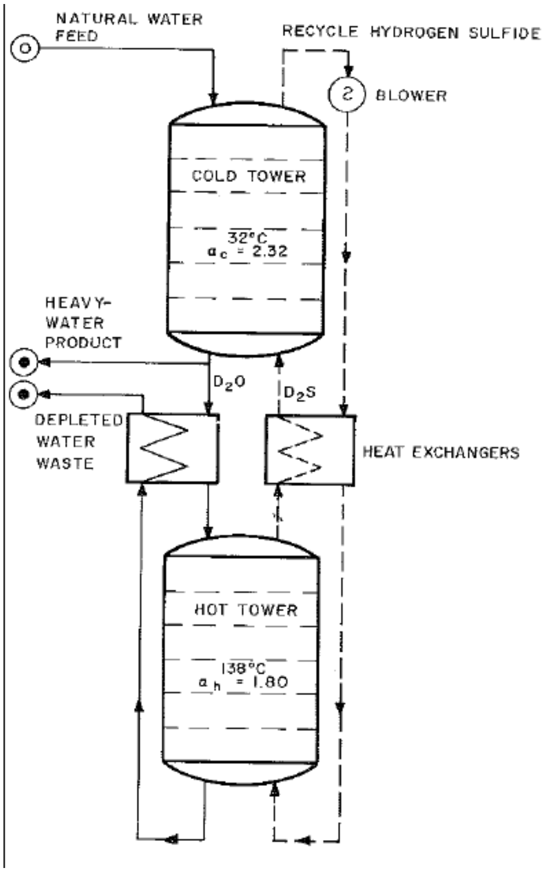

Figure 11. Schematic representation of a GS dual temperature absorption column (Benedict et al., 1980).

The distillation of water to produce a heavy water product is extremely energy intensive, since large volumes are required to compensate for the low isotopic content of natural water. Thus, once primary upgrading has been accomplished from processes such as the GS dual-temperature exchange described above, energy requirements are much reduced, particularly when conducted under vacuum conditions. All CANDU plants will contain a distillation facility for upgrading the D_2O isotopic content since it can be diluted during operation through addition of chemicals containing the hydrogen atom (H_2, LiOH, N_2H_4, NH_3 etc.) and through neutron absorption producing tritium (H-3 or T). The overall efficiency of the fission process relies upon specified isotopic content in the moderator and coolant thus the process water must be periodically upgraded.

8.2 Clean-up

Like the make-up water that feeds the secondary system and the reactor auxiliaries and is conditioned to ensure low corrosion rates of the materials of construction and adequate system lifetimes, the heavy water used in CANDU plants must be very pure. The basic methods of filtration and ion exchange all apply to heavy water as they do for light water, with the exception that the isotopic content of the heavy water must also be taken into consideration (the H_2O content in the heavy water may be considered an impurity).

As described above, D_2O production and upgrading facilities may produce heavy water at isotopic concentrations greater than 99.5% quite readily. Impurities introduced during the upgrading process may include corrosion products from the materials of construction of the distillation towers and packing columns (Fe, Ni, Cu etc) as well as contaminant cations and anions (Na^+, Ca^{2+}, Cl^-, SO_4^{2-} etc) from ingress of humidity or contamination during transfer operations. These may be removed through ion-exchange; however, it is imperative that the ion-exchange resin first be converted to a deuterated form (exchange of the H^+ sites with D^+) to minimize the downgrading in isotopic from cation exchange.

Tritium Removal

Some plants, notably the Darlington station in Ontario, include a tritium reduction facility in order to ensure low environmental releases and to minimize the tritium activity in the operating plant. Tritium removal plants follow the same isotopic removal principles as upgrading the deuterium content to produce heavy water, except that the separation factor for D/T is very close to unity under near atmospheric and/or vacuum conditions. At the Darlington facility, separation is aided by a series of catalytic exchange columns that facilitate the equilibrium exchange between tritiated heavy water and the carrier deuterium gas. The catalytic exchange process follows equation 44 and typically can reduce the tritium concentration in the input heavy water by a factor of ten [CANTEACH]. The tritium now contained in the deuterium gas stream is concentrated to >99.9% through a series of cryogenic distillation columns operating at temperatures of ~ 25 K absolute. A schematic flow sheet of the Darlington facility is shown in Figure 13. These cryogenic temperatures ensure that any humidity or traces of nitrogen and oxygen are removed (25 K is well below their boiling points) leaving a pure deuterium/tritium gas that is easily separated through the density/buoyancy effects utilized in distillation. The resulting pure tritium gas is encapsulated through reaction with titanium sponge, producing a titanium hydride and immobilizing the radioactivity. The hydride may then be stored until the tritium decays to suitable levels or sold for profit.

$$\mathrm{DTO} + \mathrm{D_2} \rightleftharpoons \mathrm{D_2O} + \mathrm{DT} \tag{44}$$

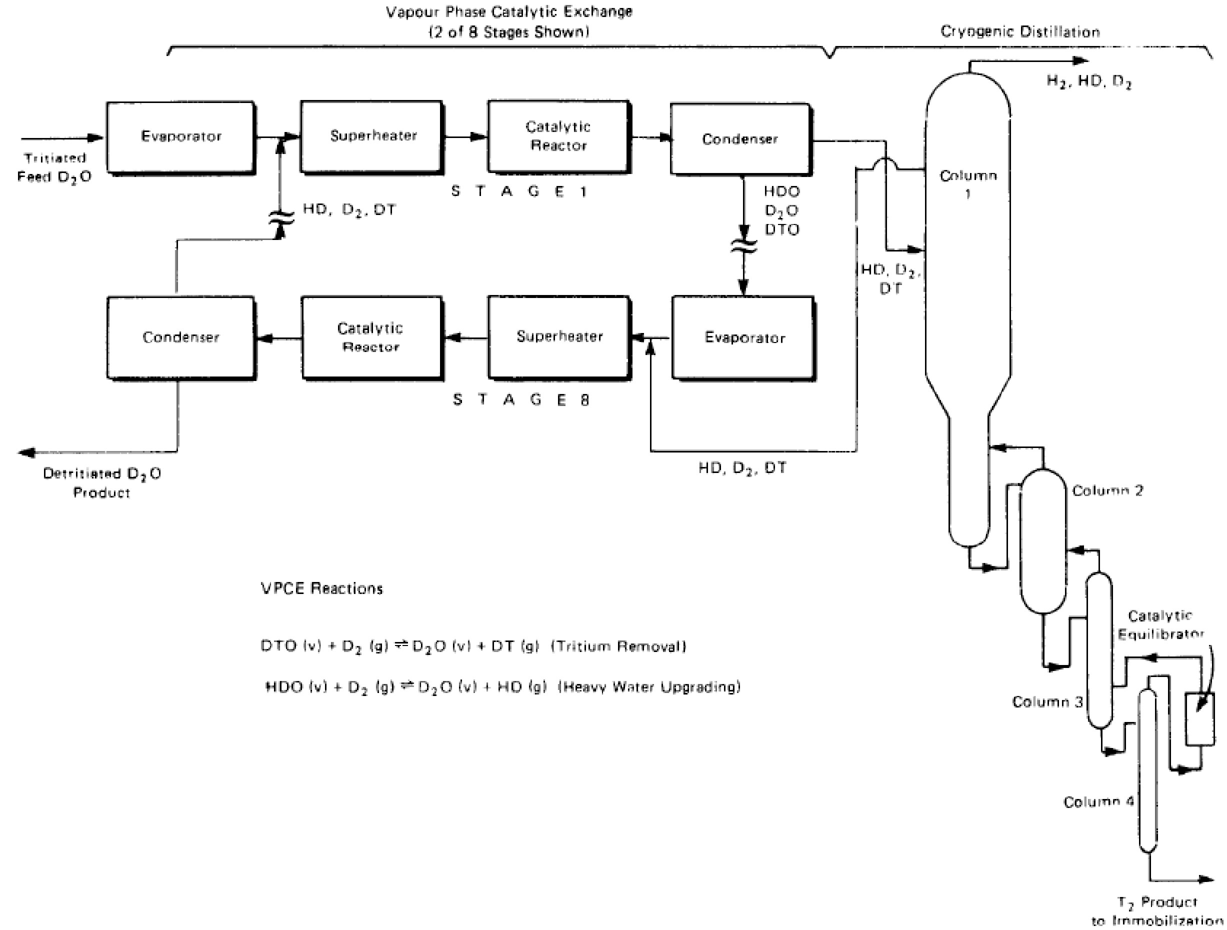

Figure 12. Schematic diagram of the Darlington tritium removal facility. (Busigin & Sood)

9 Summary of Relationship to Other Chapters

The chemistry of process systems is controlled in order to optimize the performance of the variety of materials that make up the systems. There is therefore a strong link to the Chapter 14 on Materials and Corrosion.

10 References

A.V. Bandura & S.N. Lvov, The Ionization Constant of Water over a Wide Range of Temperatures and Densitites, J. Phys. Chem. Data, vol. 25, pp 15-30, 2006.

D.M. Bartels, *The Reaction Set, Rate Constants and g-Values for the Simulation of Radiolysis of Light Water over the Range of 20^o to 350^{o}C Based on Information Available in 2008,* AECL Analyses, 153-127160-450-001, Revision 0, 2009.

M. Benedict, T.H. Pigford and H.W. Levi, *Nuclear Chemical Engineering*, Second Edition, McGraw-Hill Book Company, 1981.

A. Busigin and S.K. Sood, Optimization of Darlington Tritium Removal Facility Performance: Effects of Key Process Variables, Nuclear Journal of Canada, 1:4, pp 368-371.

G.B. Buxton, *Radiation Chemistry of the Liquid State: (1) Water and Homogeneous Aqueous Solutions,* in Radiation Chemistry: Principals and Applications, Editors: Farhataziz and M.A.J. Rodgers, VHC, New York, 1987.

CANTEACH, *Introduction to CANDU Process Systems – Heavy Water Production and Management,* available at www.canteach.ca.

CANTEACH, *The Moderator and Auxiliary Systems*, Chemistry Course 224, available at www.canteach.ca.

B. Cox, Mechanisms of Zirconium Alloy Corrosion in High Temperature Water, J. Corr. Sci. & Eng., vol.6, 2003.

CRC, *Handbook of Chemistry and Physics*, 94th Edition, CRC Publishing, 2013-2014.

M.K. Edwards, L. Qui and D.A. Guzonas, *Emergency Core Cooling System Sump Chemical Effects on Strainer Head Loss*, Nuclear Plant Chemistry Conference – NPC 2010, Quebec City, October 2010.

A.J. Elliot and C.R. Stuart, *Coolant Radiolysis Studies in the High Temperature, Fuelled U-2 Loop in the NRU Reactor,* AECL R&D Report, 153-127160-440-003, Revision 0, 2008.

D.W. Evans et al, *Gadolinium Depletion Event in a CANDU® Moderator – Causes and Recovery*, Nuclear Plant Chemistry Conference – NPC 2010, Quebec City, October 2010.

IAPWS, Guideline on the Henry's Constant and Vapor-Liquid Distribution Constant for Gases in H_2O and D_2O at High Temperatures, Kyoto, Japan, available at www.iapws.org, 2004.

IAPWS, *Release on the Ionization Constant of* H_2O, Lucerne, Switzerland, available at www.iapws.org, 2007.

IAPWS, Technical Guidance Document – 2012 Revision: Instrumentation for Monitoring and Control of Cycle Chemistry for the Steam-Water Circuits of Fossil-Fired and Combined-Cycle Power Plants, Boulder, Colorado, available at www.iapws.org, 2012.

IAPWS, Technical Guidance Document: Corrosion Product Sampling and Analysis for Fossil and Combined-Cycle Power Plants, Moscow, Russia, available at www.iapws.org, 2014.

C. Lertsurasakda, P. Srisukvatananan, L. Liu, D. Lister and J. Mathews *The effects of amines on flow-accelerated corrosion in steam-water systems.* Power Plant Chemistry, Vol. 15, No. 3, pp.181-190 (2013)

I.N. Levine, Physical Chemistry, 199??.

D.H. Lister and L.C Lang. *A mechanistic model for predicting flow-assisted and general corrosion of carbon steel in reactor primary coolants*. Proc. Chimie 2002; Intern. Conf. Water Chem. Nucl. Reactor Systems. Avignon, France. SFEN. (2002)

G. Ma et al, *Experience of Oil in CANDU® Moderator During A831 Planned Outage at Bruce Power*, Nuclear Plant Chemistry Conference – NPC 2010, Quebec City, October 2010.

J. Matthews, *Layup Practices for Fossil Plants*, Power, February 2013.

R.E. Mesmer & D.L. Herting, *Thermodynamics of Ionization of* D_2O *and* $D_2PO_4^-$, J. of Sol. Chem. Vol.7, no.12, pp.901-913, 1978.

J.P. Slade and T.S. Gendron, *Flow accelerated corrosion and cracking of carbon steel piping in primary water – operating experience at the Point Lepreau Generating Station*, Proc. Intern. Conf. on Environmental Degradation of Matls. in Nuclear Power Systems, Salt Lake City, UT. TMS. (2005).

J.W.T. Spinks & R.J. Woods, *An Introduction to Radiation Chemistry,* Wiley, New York, 1990.

C.R. Stuart, *Mitigation of Hydrogen Production in the Shield Cooling System of CANDU Reactors - Recent Changes to Chemistry Control*, 9th International Workshop on Radiolysis, Electrochemistry and Materials Performance, Paris, France, September 2012.

R.L. Tapping, J. Nickerson, P. Spekkens and C. Maruska, *CANDU Steam Generator Life Manage-*

ment, Nuc. Eng. & Design, vol. 197, pp. 213-223, 2000.

R.L. Tapping, Chapter 17: Corrosion Issues in Pressurized Heavy Water Reactor (PHWR/CANDU®) Systems, Nuclear Corrosion Science and Engineering, Woodhead Publishing Limited, London, 2012.

P.R. Tremaine & J.C. Leblanc, The Solubility of Magnetite and the Hydrolysis and Oxidation of Fe^{2+} in Water to 300°C, J. Sol. Chem., vol.9, no.6, pp. 415-442, 1980.

C. Turner & D. Guzonas, *Improving Chemistry Performance in CANDU® Plants*, Nuclear Plant Chemistry Conference – NPC 2010, Quebec City, October 2010.

V.F. Urbanic, B. Cox & G.J. Fields, *Long Term Corrosion and Dueterium Ingress in CANDU PHW Pressure Tubes*, Zirconium in the Nuclear Industry: Seventh International Symposium, ASTM STP939, pp. 189-205, 1987.

P.A. Yakabuskie, J.M. Joseph, J.C. Wren & C.R. Stuart, *Effect of* NO_3^- *and* NO_2^- *on Water Radiolysis Kinetics During* γ*-Irradtiation,* NPC 2010 – Nuclear Plant Chemistry Conference, Quebec City, Quebec, 2010.

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