

CANDU Chemistry Fundamentals

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Topics to be covered

- Units
- pH (pD, pH_a), Conductivity, H^+ (D^+), $[\text{Li}^+]$
- Overview - Radiation Chemistry of Water
- Activity Transport
- Setting Chemistry Specifications – Chemistry Rationale
- Chemistry Monitoring
- Environmental Considerations

Commonly Encountered Chemistry Units

- Research chemists prefer to work in concentration units that reflect:
 - Number of species / volume (or weight) of medium, e.g., mol/litre (molar), mol/kg (molal),
 - Number of **moles** of compound = Mass / Molecular Weight (6.022×10^{23} molecules)
- Station chemists tend to use:
 - $\text{ppb}_{\text{wt}} = \text{ppb} = \mu\text{g (x)} / \text{kg of solution}$
 - $\text{ppm}_{\text{wt}} = \text{ppm} = \text{mg (x)} / \text{kg of solution}$
 - mL (gas) / kg (soln) (or Litre)

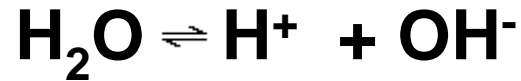
Commonly Encountered Chemistry Units

- In gas phase concentrations of gases are given in:
 - Vol%
 - ppm = ppm_{vol} (i.e. by volume or number – same)
 - Both are sensible units – reflects the molecular ratio of the gases – not the weights. (i.e., 1 ppm_{vol} H₂ means one molecule of H₂ for every 10⁶ molecules of gas).

Commonly Encountered Chemistry Units

- Conductivity (ionic) of solution:
 - Millisiemen/metre (mS/m)
 - Generally used in CANDU plants
 - Microsiemen/centimetre ($\mu\text{S}/\text{cm}$) also used
 - **NOTE:** $1 \text{ mS}/\text{m} = 10 \mu\text{S}/\text{cm}$
 - units can be confused
 - Old name for Siemen was mho (ohm reversed)
 - λ_i = specific conductivity of ion “i”

Dissociation of Light Water and pH



- Dissociation constant: $K_w = [\text{H}^+] \times [\text{OH}^-]$
- At 25°C, $\text{p}K_w = -\log_{10} (K_w) = 14.0$
- $\text{pH} = -\log_{10} [\text{H}^+]$
- At neutral pH, $[\text{H}^+] = [\text{OH}^-]$
 - At 25°C

$$\therefore \text{pH}_{25} = 7.0$$

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$$

Dissociation of Light Water and pH

NOTE: Cannot measure accurately with pH meter as the ionic conductivity is too low, i.e., <0.2 mS/m

- In neutral pure water at 300°C ,
 $\text{p}K_w = -\log_{10}(K_w) = 11.8$
- Neutral light water at 300°C , $\text{pH}_{300} = 5.9$
- Water is more dissociated at high temperatures than at 25°C .

$$[\text{H}^+] = [\text{OH}^-] = 10^{-5.9} \text{ M} = 1.259 \times 10^{-6} \text{ M}$$

Dissociation of Heavy Water and pD



$$K_{\text{D}_2\text{O}} = [\text{D}^+] \times [\text{OD}^-]$$

- At 25°C:

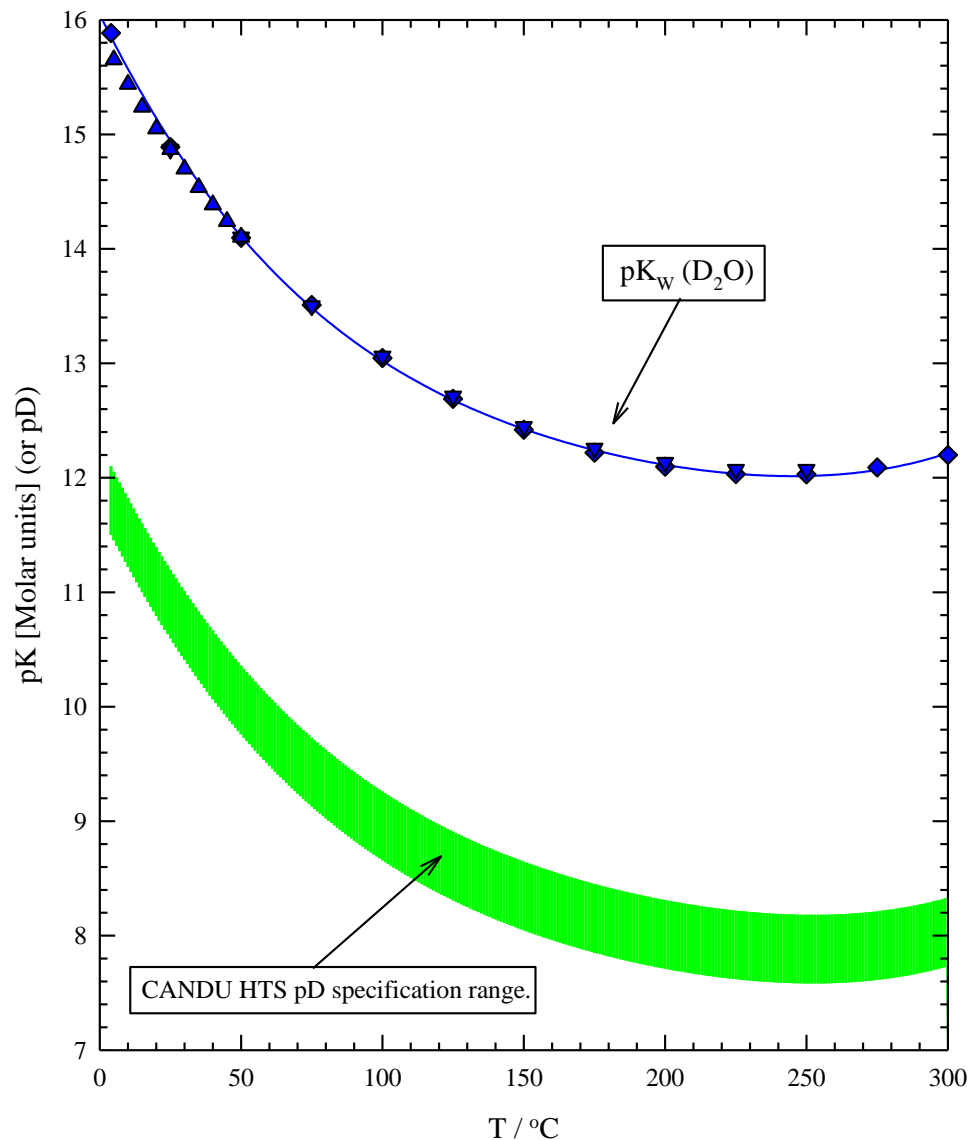
$$pK_{\text{D}_2\text{O}} = -\log_{10} (K_{\text{D}_2\text{O}}) = 14.871$$

$$(pK_{\text{H}_2\text{O}} = -\log_{10} (K_w^{\text{H}_2\text{O}}) = 14.001)$$

$$pD = -\text{Log}_{10} [\text{D}^+]$$

- At neutral pD, $[\text{D}^+] = [\text{OD}^-]$

pD changes with Temperature



Dissociation of Heavy Water and pD

- Neutral heavy water at 25°C

$$[D^+] = [OD^-] = 3.67 \times 10^{-8} \text{ M}$$



$$\text{Neutral } pD_{25} = 7.43$$

Heavy water less dissociated than Light water at the same temperature

Adjusting pH (pD)

- To increase pH → add hydroxyl ions (OH^-)
 - e.g., lithium hydroxide (LiOH) in the end-shield cooling system
- To decrease pH → add protons (H^+)
 - e.g., nitric acid (HNO_3) to the moderator
- **NOTE:** When increasing or decreasing pH, *counter ions* also added
- Control pH of PHTS using ion exchange resin in lithium form

Adjusting pH (pD)

- For chemistry control purposes
 - The pH of the solution is measured at 25°C
 - The pH at “temperature” will be different, e.g., the HTS operates at 265-310°C
- Corrosion control in ferrous systems
 - Often appropriate to adjust pH at temperature to be 1 – 2 pH units above neutral point

pD and pH_a of Heavy Water

- How is pH measured in heavy water at the stations?
 - A quantity called pH apparent (pH_a) is used
- pH_a is the pH meter reading obtained for a heavy water sample using pH electrodes calibrated with a light water buffer, all measured at 25°C

$$\text{pD} = \text{pH}_a + 0.41$$

pD and pH_a of Heavy Water

- Experimentally determined (e.g., Covington et al. Analytical Chemistry 40, 701, 1968)
- For many “chemistry” comparisons between light and heavy water in *alkaline* solutions, a simple relationship can be derived:

$$\text{pH}_a = \text{pH} + 0.47$$

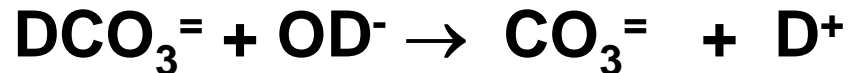
- Calculated assuming the property we are interested is the same when pOH = pOD

Alkalinity Control

- The HTS and ESC systems are operated under alkaline conditions to control carbon steel corrosion
- Currently, most CANDU stations control the PHTS coolant pH_a in the range $10.2 < \text{pH}_a < 10.4$ using LiOD as the control chemical
- **Issue** → Accurate alkalinity measurements ($\sim 0.05 \text{ pH}_a$ units) are notoriously difficult to make in the “field” due to sample contamination issues

Validation of a Measurement of pH_a

- Can be subject to errors from many sources, e.g.:
- Contamination after sampling
 - Absorption of CO_2 from the atmosphere lowers pH_a



- Inherent electrode drift
- Contamination of electrode internals with D_2O
- Electrode used for measuring pH_a in $\text{Gd}_2(\text{NO}_3)_3$ solutions (Moderator samples)
 - Precipitation of $\text{Gd}(\text{OD})_3$ in glass membrane

Validation of a Measurement of pH_a

- Need to validate pH_a measurements of D_2O in the HTS



- LiOD is a strong base
 - fully dissociated at concentrations found in the HTS in the range 25°C to 310°C

Validation of pH_a Measurements

Ionic material balance in a “pure” LiOD solution:



- When $\text{pH}_a > \sim 9$, ignore $[\text{D}^+]$ \longrightarrow $[\text{D}^+] = 10^{-9} \text{ M}$, $[\text{OD}^-] \sim 10^{-6} \text{ M}$

$$\therefore [\text{Li}^+] \approx [\text{OD}^-]$$

NOTE: Li^+ determinations least likely to be compromised

$$\text{pOD} = \log_{10}[\text{Li}^+] \quad \text{and} \quad \text{pH}_a = \text{pD} - 0.41 \quad (\text{Experimentally determined})$$



$$\text{pH}_a = \text{pK}_w^{\text{D}_2\text{O}} + \log_{10}[\text{Li}^+] - 0.41$$



Allows pH_a and $[\text{Li}^+]$ to be compared

Validation of pH_a Measurement

$$\therefore \text{In } \text{D}_2\text{O}, \text{pH}_a = 10.663 + \log_{10}([\text{Li}^+]/\text{mg}\cdot\text{kg}^{-1})$$

$$\text{In } \text{H}_2\text{O}, \text{pH} = 10.169 + \log_{10}([\text{Li}^+]/\text{mg}\cdot\text{kg}^{-1})$$

Can also relate conductivity to $[\text{Li}^+]$

$$\text{Conductivity} = [\text{Li}^+] \times \lambda_{\text{Li}^+} + [\text{OD}^-] \times \lambda_{\text{OD}^-} \quad (\lambda_i = \text{specific conductivity of ion "i"})$$



Since $[\text{Li}^+] \approx [\text{OD}^-]$ in alkaline solution

$$\text{Conductivity} \approx [\text{Li}^+] \times (\lambda_{\text{Li}^+} + \lambda_{\text{OD}^-})$$



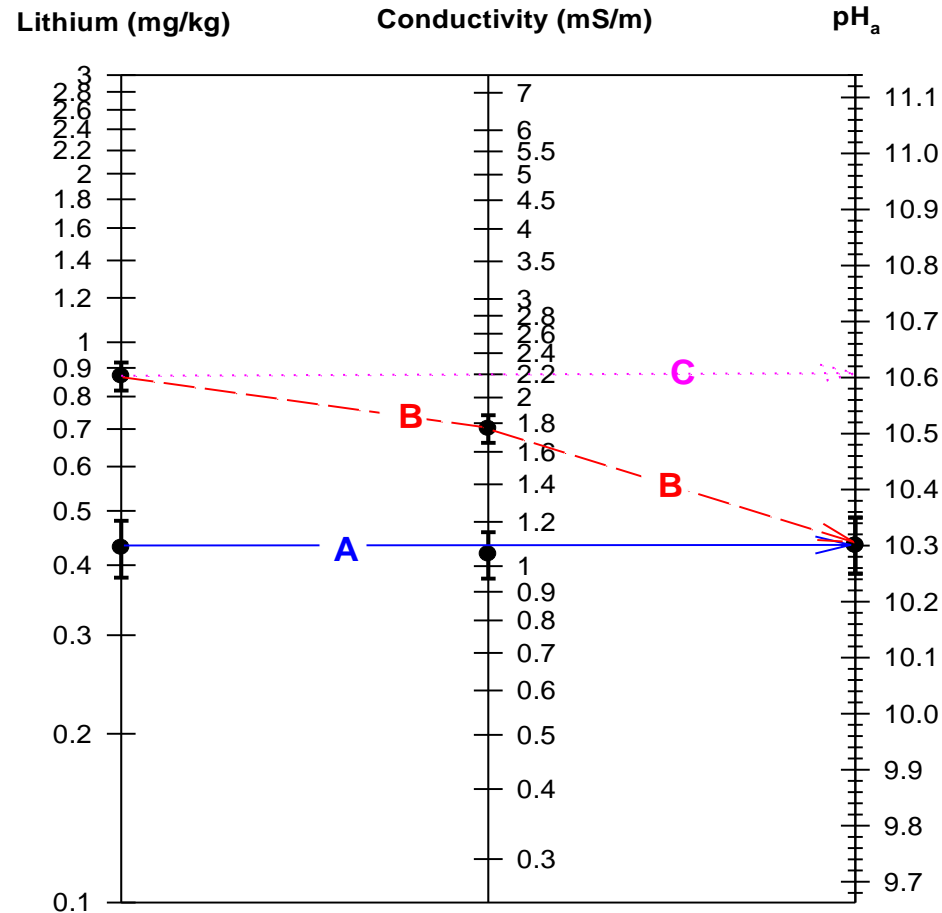
$$\text{D}_2\text{O} \quad \text{Conductivity (mS}\cdot\text{m}^{-1}) = 2.51 \times [\text{Li}^+] \text{ (mg}\cdot\text{kg}^{-1})$$

$$\text{H}_2\text{O} \quad \text{Conductivity (mS}\cdot\text{m}^{-1}) = 3.42 \times [\text{Li}^+] \text{ (mg}\cdot\text{kg}^{-1})$$

} at 25°C

Correlation of HTS Data (Heavy Water) for Lithium Concentration, Conductivity & pH_a at 25°C

(Elliot and Stuart, COG Report COG-98-097)

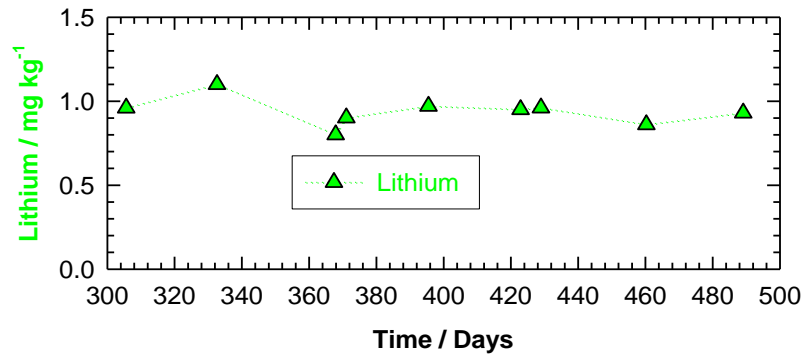
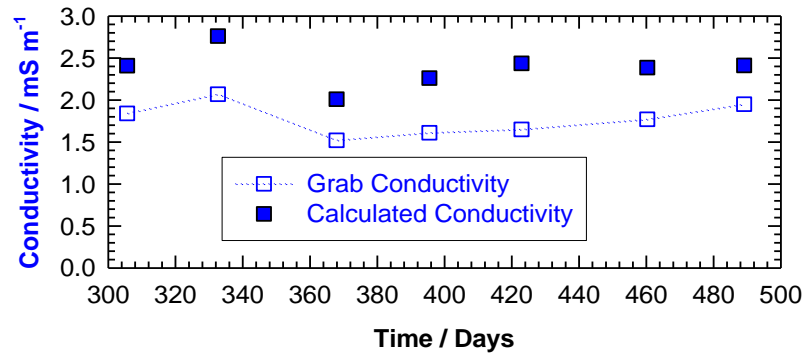
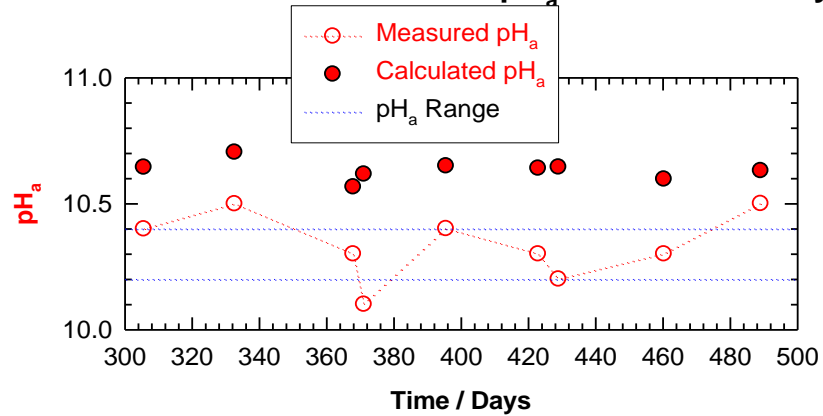


Line 'A' is an example of a correlation indicating pH_a is a valid number

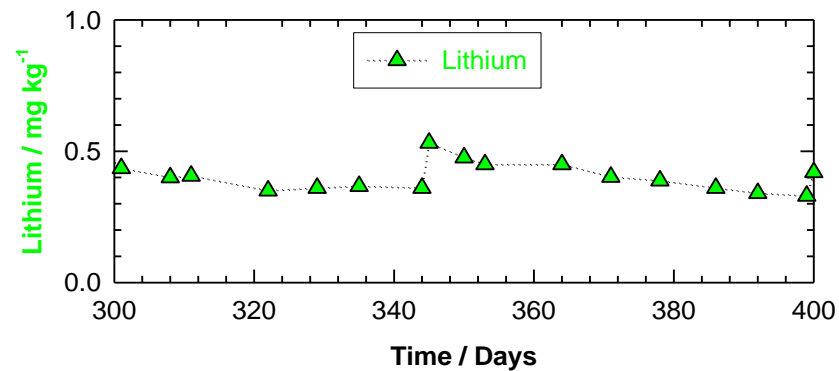
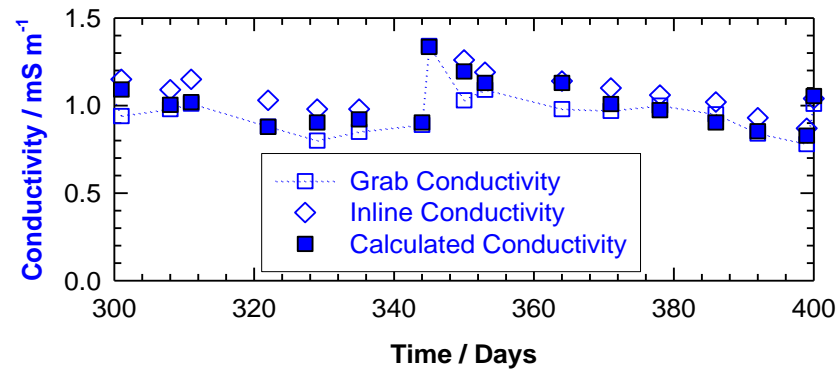
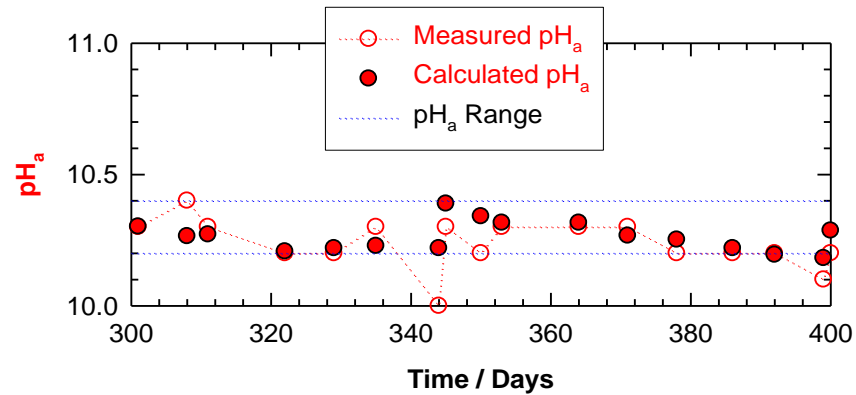
Line 'B' is an example of a correlation indicating contamination of the HTS coolant

Line 'C' indicates the pH_a calculated from the Li^+ concentration

Example of a Poor Correlation between Observed and Calculated pH_a and Conductivity



An Example of a Good Correlation between Observed and Calculated pH_a and Conductivity



Radiation Chemistry

- All the aqueous systems around the core are subjected to ionising radiation fields
 - Heat Transport System (PHTS)
 - Moderator
 - Liquid Zone Controls (LZC)
 - End Shield Cooling (ESC)
 - Annulus Gas System (AGS)
 - Spent Fuel Bay
 - Waste Storage Systems

Simplistic Radiation Chemistry View

- Reactor systems can be designed to operate in one of two steady-state modes
 - Suppression of net radiolytic breakdown of water



- Net radiolytic breakdown of water



- Transitions between these states and enhanced D_2 production via the second state can lead to unanticipated chemistry conditions in-core.

Radiation Chemistry

Heat Transport System:

- 200 tonnes of D₂O
- 265-310°C
- Dose rate: 300 Mrad/hour γ -radiation (100 rad = 1 Gy); 500 Mrad/hour fast neutron
- ~4% inventory is in-core
- Alkaline conditions (pH_a ~10.2-10.4)
- Added dissolved D₂
- Net radiolytic production of D₂ and O₂ suppressed

Radiation Chemistry

Moderator System:

- 260 tonnes of D₂O
- ~70°C
- Dose rate: 70 Mrad/hour γ -radiation;
60 Mrad/hour fast neutron
- ~92% inventory is in-core
- Slightly acid ($\text{pH}_a = 5-6$)
- Helium cover gas.
- Net radiolytic production of D₂ and O₂; gases are recombined in cover gas.

Radiation Chemistry

Liquid Zone System:

- 0.5-1 tonne light water
- ~60°C
- Dose rate: 70 Mrad/hour γ -radiation;
60 Mrad/hour fast neutron
- pH neutral
- Helium cover gas
- Net radiolytic production of D₂ and O₂; gases are recombined in cover gas.

Radiation Chemistry

Calandria Vault/End Shield System:

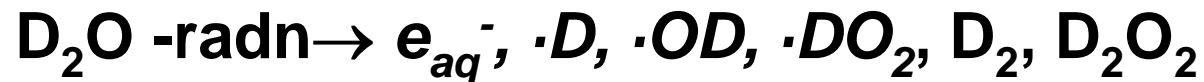
- 525 tonnes light water
- ~55-60°C
- Dose rate: <18 Mrad/hour γ -radiation;
<13 Mrad/hour fast neutron
- Alkaline (pH₂₅~10)
- Nitrogen cover gas
- Carbon steel corrosion removes small quantities of oxygen – residual hydrogen
- Net radiolytic production of D₂ and O₂ suppressed

Molecules, Atoms, Free Radicals, Ions

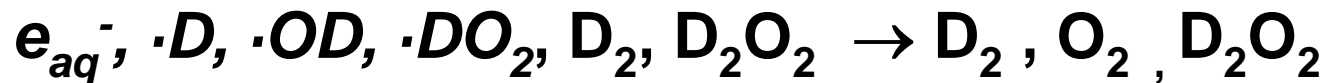
- Hydrogen Ion \rightarrow H^+
 - Stable species - also called a proton
- Hydrogen Atom \rightarrow $\cdot\text{H}$
 - Very reactive - also called hydrogen radical
- Hydrogen Molecule \rightarrow H_2
 - Stable form of hydrogen
- Hydroxyl Ion \rightarrow OH^-
 - Stable ion
- Hydroxyl Radical \rightarrow $\cdot\text{OH}$
 - Very reactive species

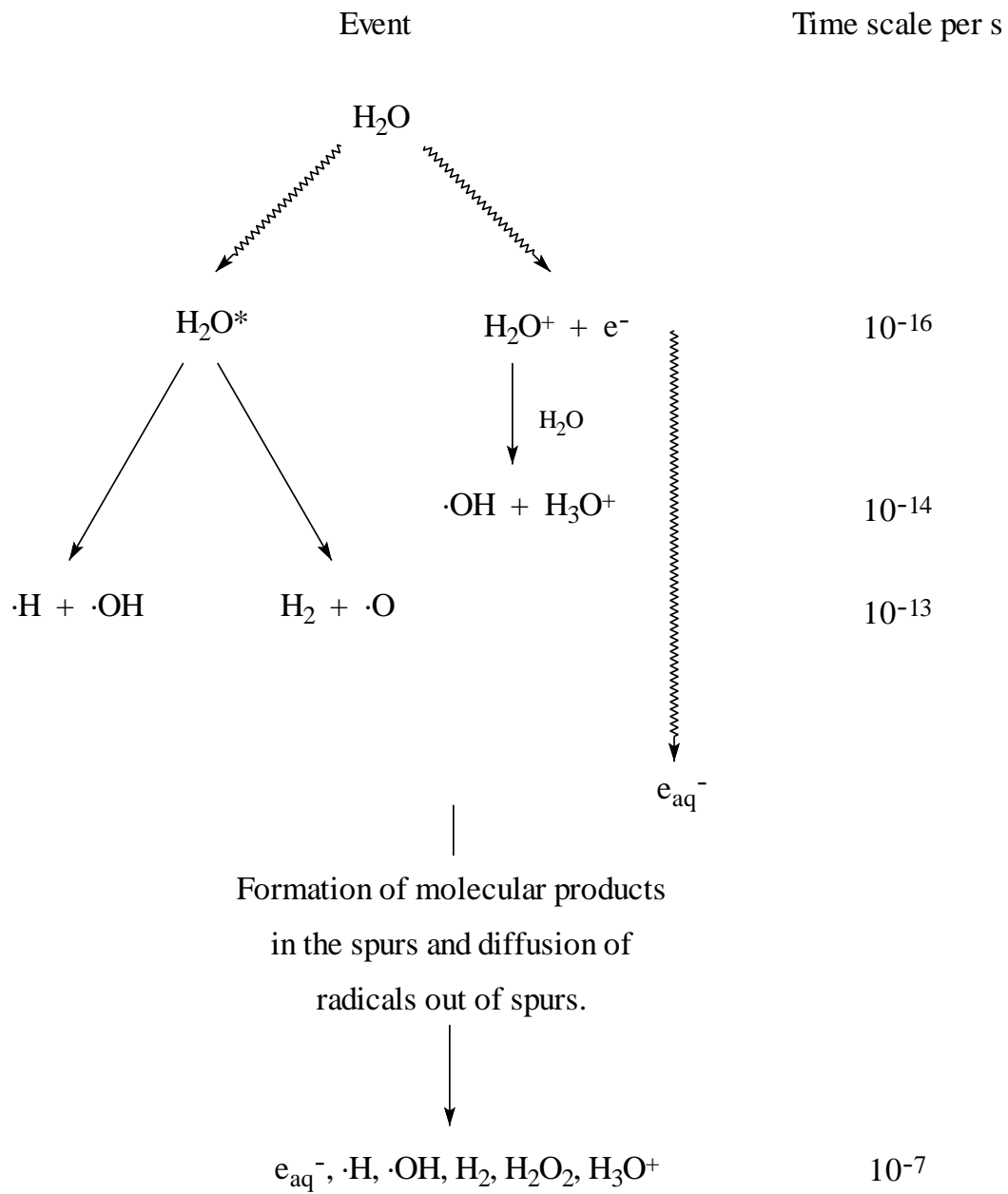
Radiation Chemistry of Neutral Deoxygenated Water (Equally valid for light and heavy water)

- Initially the ionising radiation forms short-lived ($\sim\mu\text{s}$ time scale) reactive radicals:



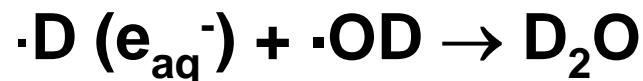
- These species react to form steady-state concentrations of stable products:



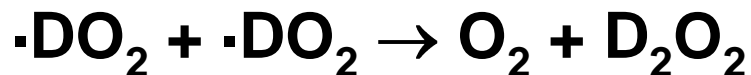
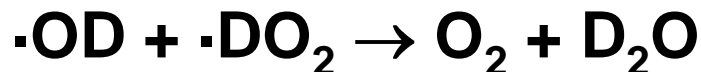
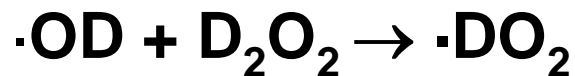


Radiation Chemistry of Neutral Deoxygenated Water (Equally valid for light and heavy water)

- *Recombination reactions to form stable products:*

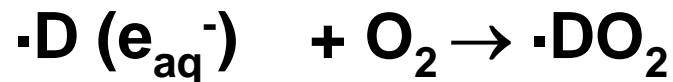
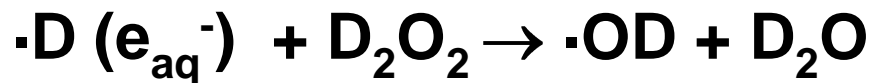
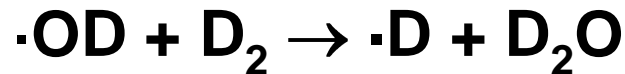


- *Oxygen production (secondary product):*



Radiation Chemistry of Neutral Deoxygenated Water (Equally valid for light and heavy water)

- *Reactions to limit build up of stable products:*

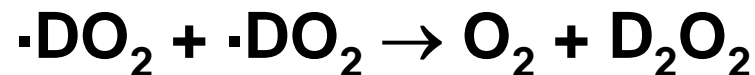
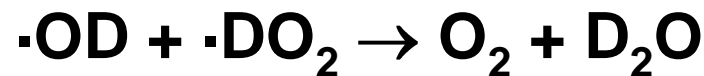


Radiation Chemistry of Neutral Deoxygenated Water (Equally valid for light and heavy water)

- HTS

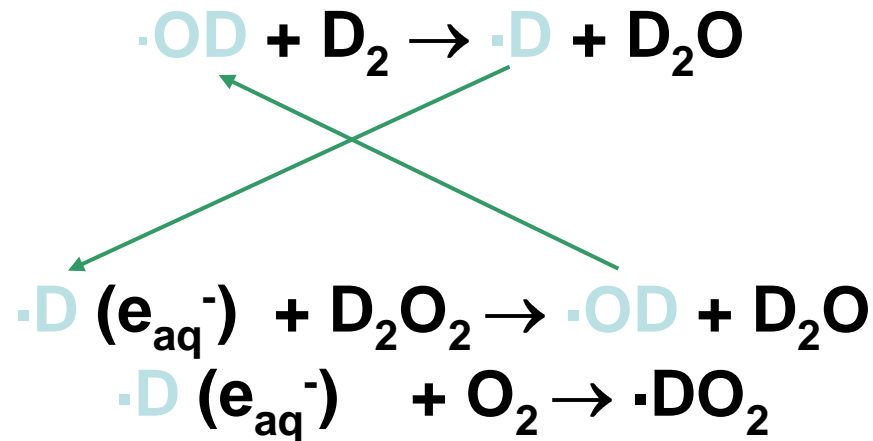
- Coolant Specification $<10 \mu\text{g kg}^{-1}$ oxygen
- Production of oxygen is suppressed by the addition of extra deuterium to the coolant

- Oxygen Production:



Radiation Chemistry of Neutral Deoxygenated Water (Equally valid for light and heavy water)

- Chain Reaction to remove Oxygen and Peroxide:



Radiation Chemistry of Neutral Deoxygenated Water (Equally valid for light and heavy water)

- Reaction of $\cdot\text{OD}$ with D_2 is made to go “faster” than reaction of $\cdot\text{OD}$ with D_2O_2 by adding excess deuterium so oxygen will not be formed

$$k_2 [\text{D}_2] \gg \gg k_1 [\text{D}_2\text{O}_2]$$

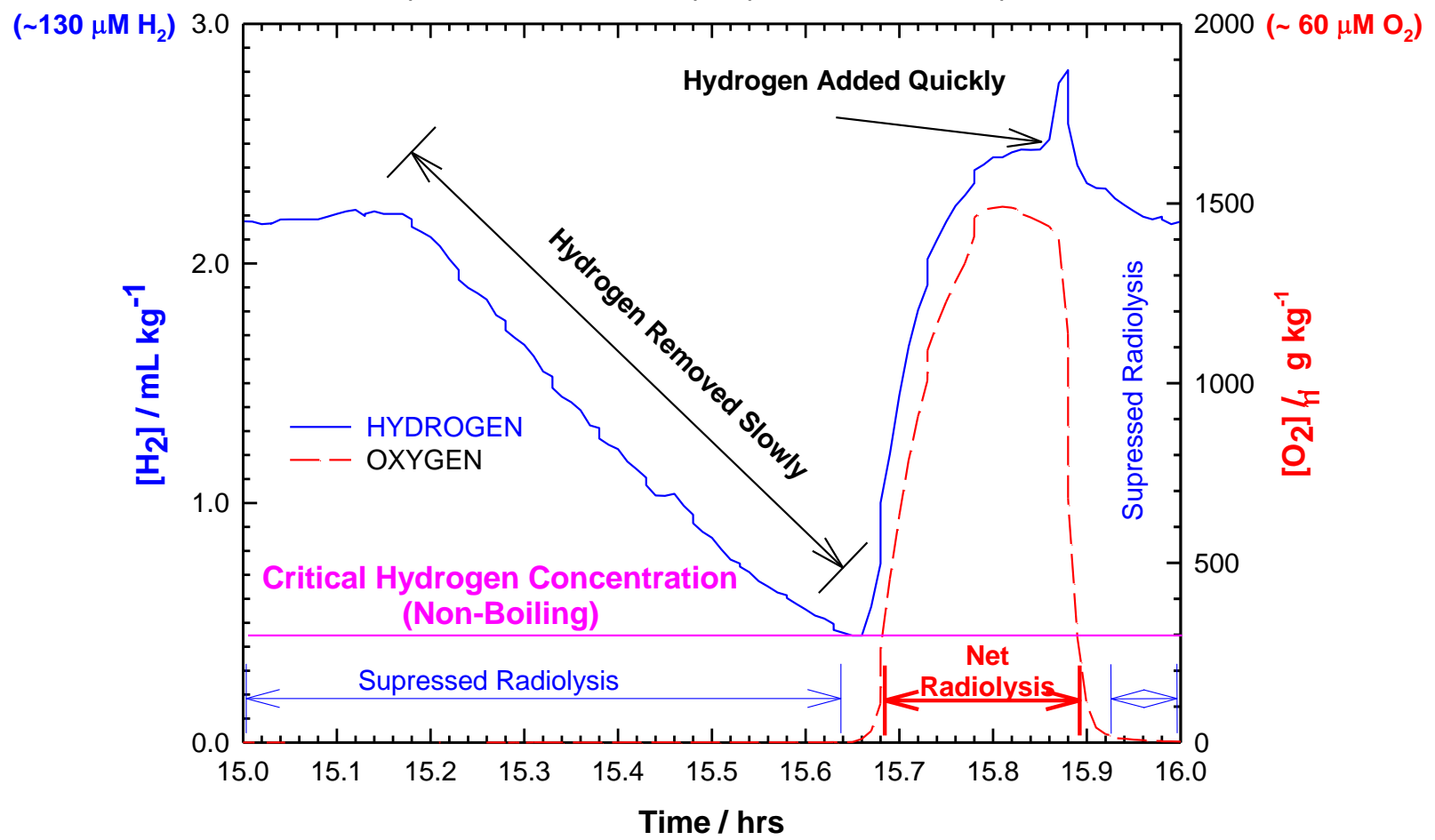
(k_i is the rate constant associated with the reaction)

There is a Critical Deuterium Concentration (CDC) required to suppress oxygen formation.

Example of Critical Hydrogen Concentration (Non-Boiling)

(Light Water, ~300°C - U2 Loop NRU - 1995)

(Elliot, Mitchel, Simmons, (1997) COG-96-610; RC-1777)



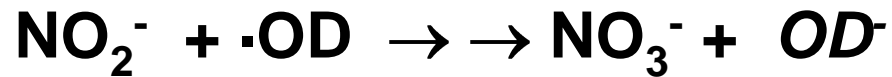
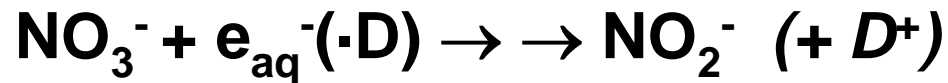
Impact of Impurities on Water Radiolysis

Two types of “impurities”:

1. Those that react with the free radical intermediates and stable products
 - Tend to increase steady-state concentrations of some or all of the stable end-products
 - Examples: Oxygen; Gd (NO₃)₃ (used as a neutron poison); ion-exchange resins fines
2. Those that do not react with the free radical intermediates and stable products so have no effect on the radiation chemistry
 - Examples: LiOH; Boric acid (used as a neutron poison); Gd₂(SO₄)₃ (used a neutron shim)

Impact of Impurities on Water Radiolysis

- Nitrate ions (NO_3^-) reacts with free radicals

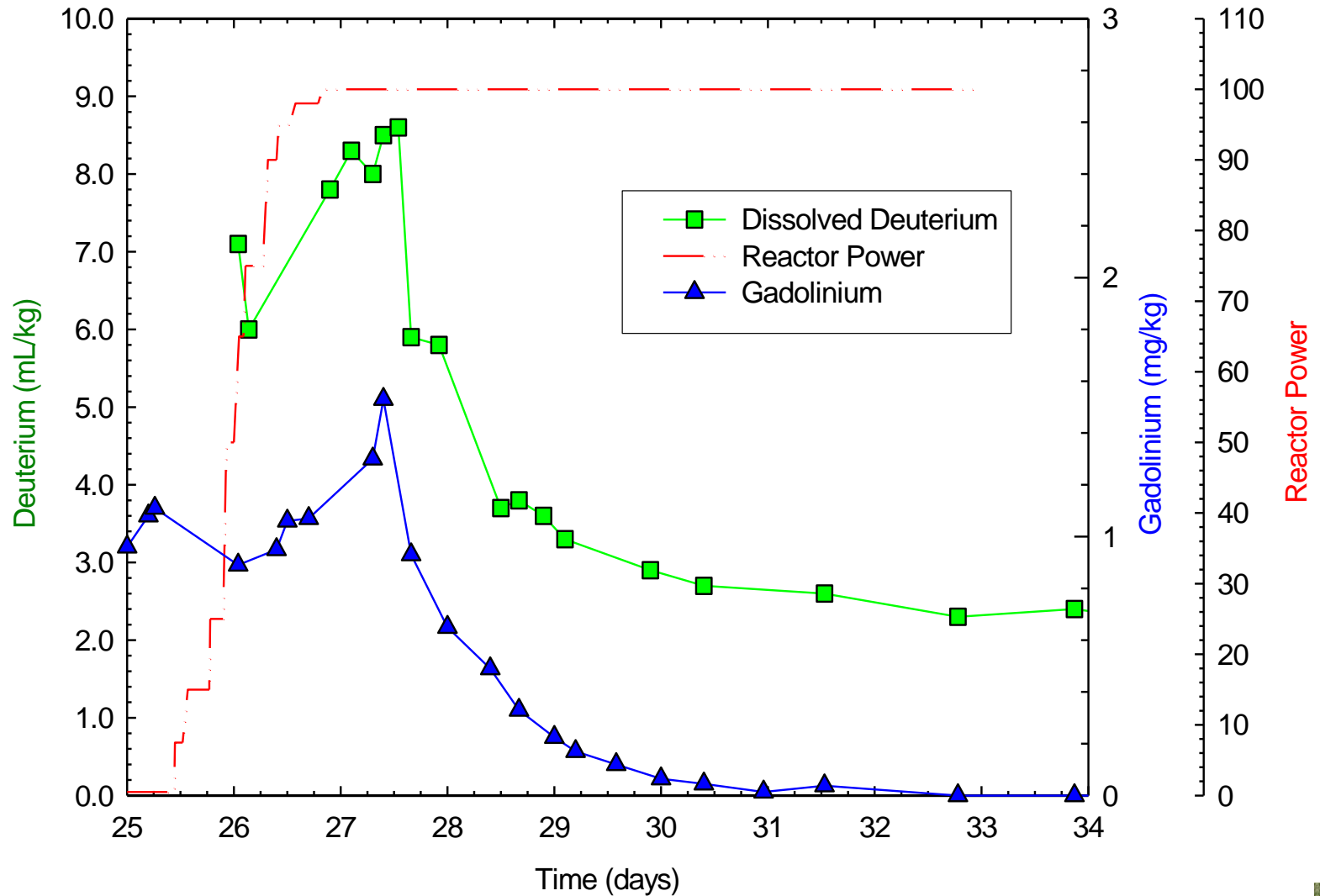


- These nitrate/nitrite reactions “short circuit” the reactions that limit build up of stable products
 - Sulphate ions ($\text{SO}_4^{=}$) do not react with radiolysis free radicals
- Ion Recombination:



- Steady state concentrations of D_2 and O_2 will be higher

Dissolved Deuterium Levels as a Function of Gadolinium Nitrate Concentration



Managing Radiolysis Processes

- In reactor systems (HTS, Moderator, ESC, LZC, AGS) we need to:
 - Control the radiolytic production of hydrogen
 - Manage the production of oxidising species
 - Minimise the radiolytic degradation of system additives
 - Assess the effects of radiolysis on proposed chemistry control modifications
- Similar considerations also exist for the storage of spent fuels and wastes

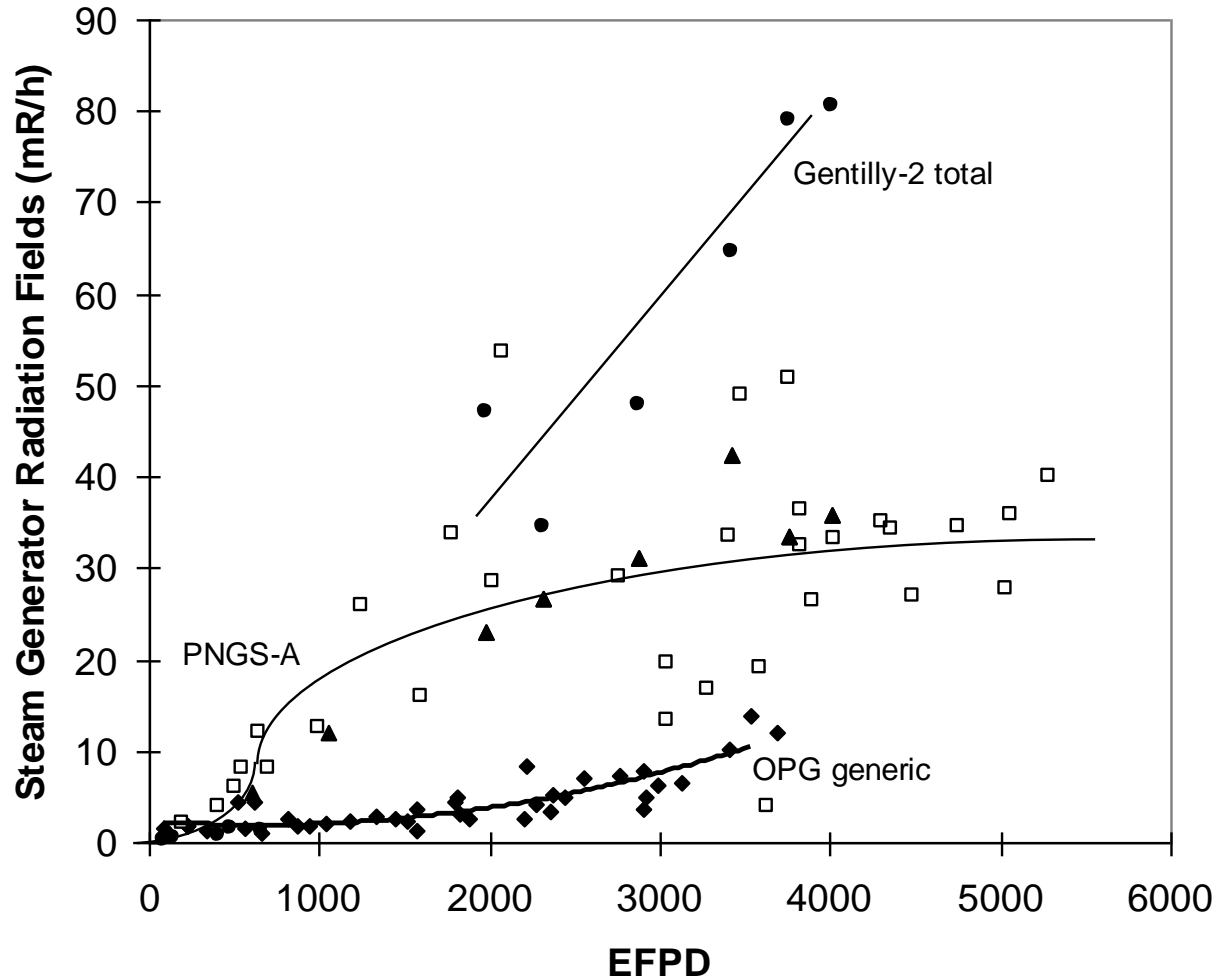
Activity and Crud Transport

- Radiation fields at CANDU stations grow as a result of radionuclide (activity) transport, contributing to worker dose
- Issue unique to nuclear industry
- Concern for any system which passes through core
- Reduce radiation fields and crud transport at CANDU stations by:
 - Identifying sources
 - Developing procedures to minimize crud and activity transport

SOURCE TERMS

- External Dose:
 - Fission products ($^{95}\text{Zr}/^{95}\text{Nb}$, ^{125}Sb , ^{103}Ru , ^{131}I , ^{144}Ce , ^{134}Cs , ^{140}Ba , ^{154}Eu)
 - $^{95}\text{Zr}/^{95}\text{Nb}$ and others (^{113}Sn , ^{94}Nb)
 - Mix of pressure tube and fuel cladding wear debris
 - ^{122}Sb and ^{124}Sb
 - ^{60}Co and Activated Transition Metals (^{54}Mn , ^{58}Co , ^{51}Cr , ^{55}Fe , ^{59}Fe)
 - Corrosion and wear products from HTS alloys
- Internal Dose
 - ^3H

Steam generator radiation fields trends with operating time



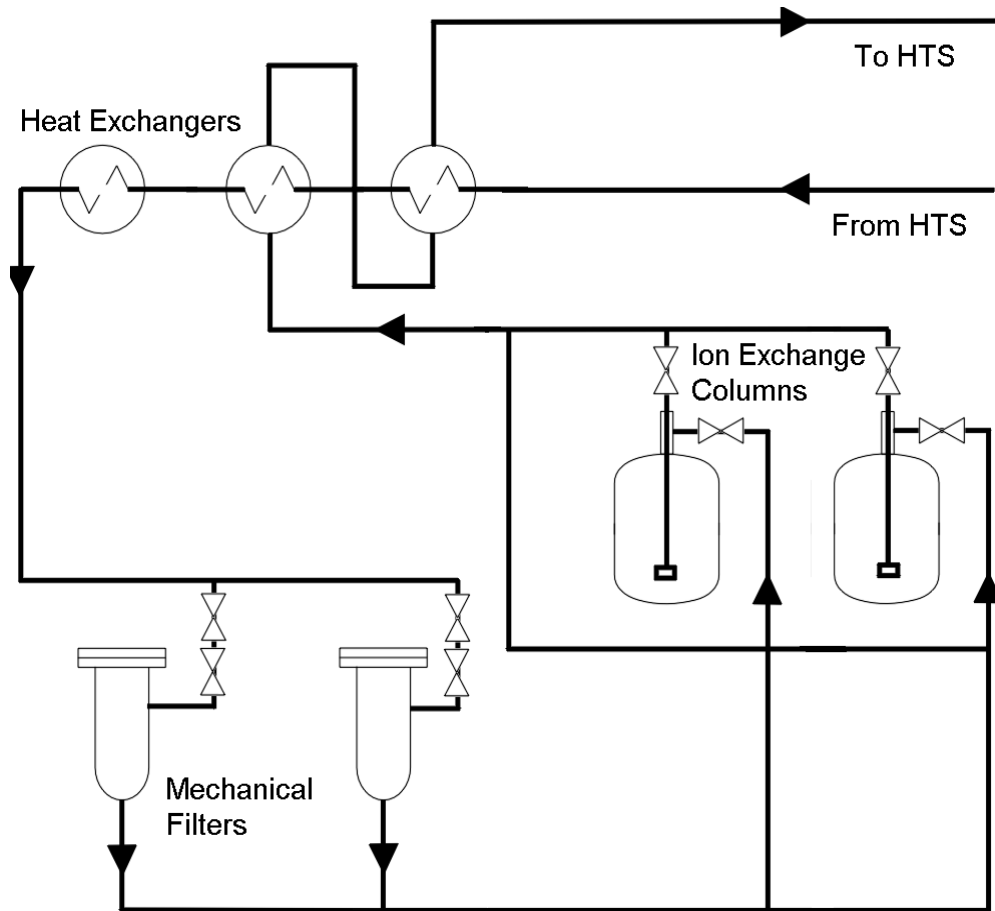
Purification

- Many systems use a purification system to:
 - Remove impurities
 - Species such as Cl^- , SO_4^{2-}
 - Radioactive species
 - Control chemistry
 - Remove Li^+ from the PHTS
 - Remove Gd^{3+} from moderator
- Can be sidestream or full-flow

CANDU 6 PHTS Purification System

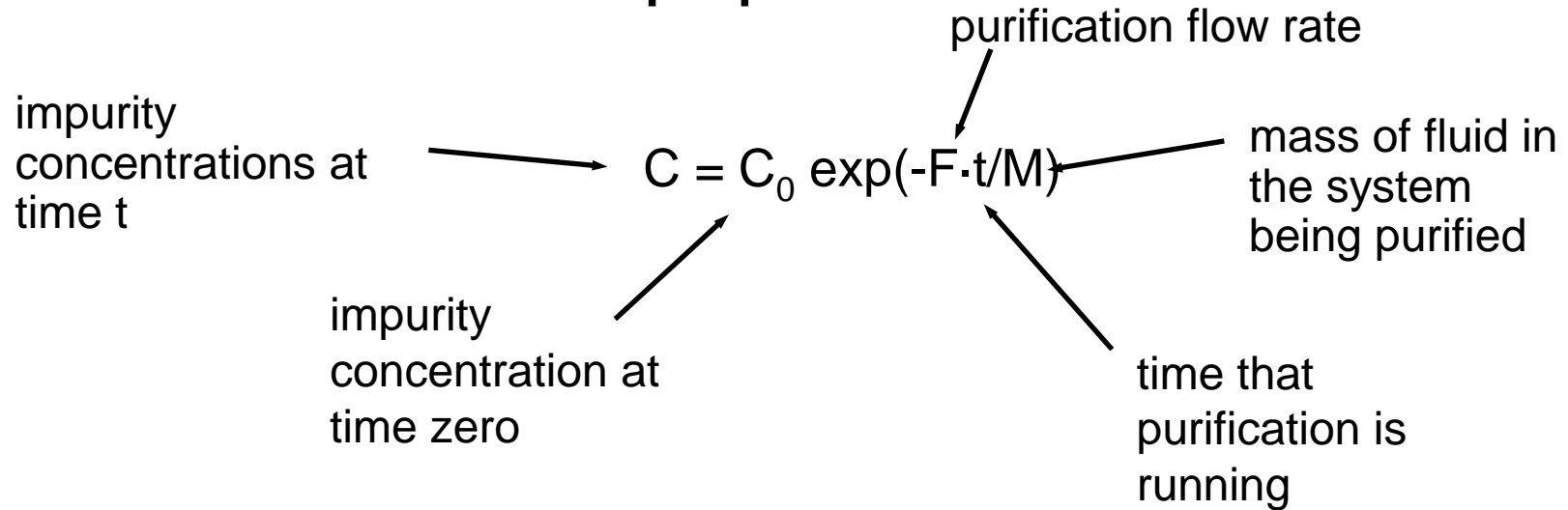
Small fraction of process stream diverted through purification system:

- Cooled
- Passed through mechanical filters
- Passed through ion-exchange columns
- Purified coolant then returned to main system



Purification Flow Rate and Purification Half-life

- Purification cleanup equation:



- **Purification half-life** \Rightarrow time required to reduce an impurity concentration by a factor of 2:

$$t_{1/2} = \ln 2 \cdot M / 60 \cdot F$$

- Ion-exchange resins must operate at $< 80^\circ\text{C}$ to avoid degradation

Ion-Exchange Resins

- Two types:
 - Cation – removes cations and replaces with:
 - D^+ (deuterated neutral water systems)
 - H^+ (neutral light water systems)
 - Li^+ (alkaline systems in both light and heavy water)
 - Anion – removes anions and replaces with:
 - OH^- (all light water systems)
 - OD^- (all heavy water systems)
 - Generally use mixed-bed (mixture of both resin types as discrete beads)

Why Chemistry Control?

Chemistry control is required for all circuits or systems through which process fluids or gasses flow and come into contact with the materials of construction of the system.

Chemistry Control

- To be fully effective, chemistry control must:
 - Start during the initial design of each system
 - Continue through:
 - manufacturing, transportation and storage of all equipment
 - construction and commissioning of each system
 - all subsequent periods of start-up, normal operation, and shutdown.

Chemistry Control

- During each of these phases, proper procedures and chemical specifications have been established and must be followed in order to:
 - Protect components from environmental attack
 - Minimize introduction of dirt and debris
 - Minimize production and transport of radioactive materials within the systems
 - Minimize release of radioactive materials from the station

Chemistry Control

- For most systems, chemistry parameters divided into control and diagnostic parameters.
- All control and diagnostic parameters must be sampled at the recommended frequency and maintained within specification.

Definitions

Control Parameters

- Parameters that require strict control in order to protect material or system integrity and to ensure that unsafe conditions do not arise.
- A control range is assigned to these parameters and appropriate measures must be taken to control the parameters within this range.
- Failure to bring a control parameter into its specified range within a specified time could force the reactor to shutdown.

Definitions

Diagnostic Parameters

- Parameters that assist in interpreting the chemistry of the system, e.g., the ingress of impurities.
- Measures such as chemical addition or changes to process parameters such as purification flow can sometimes be taken to influence their values should the parameters be outside recommended ranges.

Types of Chemistry Samples

Two types of chemistry samples:

Grab samples

Discreet volumes of cooled process fluid that may be taken to the analysis laboratory

Online samples

Analyzed directly within the process/sampling pipework

- Online samples can be further subdivided into:
 - Remote - samples cooled and depressurized before being analyzed
 - Local - samples analyzed on a sampling line at process temperature and pressure but removed from the main process flow
 - In-situ - samples analyzed at process temperature, pressure and flow conditions

Chemistry Sampling - Frequency

- Determine necessary and sufficient chemistry parameters, sampling locations and frequencies for each system in a CANDU reactor
- Optimize number of sampled parameters and sampling frequency
 - Multiple analyses can be performed on a single sample
 - Diagnostic parameters \Rightarrow use grab samples
 - Control parameters \Rightarrow use on-line instrumentation where possible

Chemistry Sampling - Frequency

- Two assumptions:
 - During upset conditions, sampling frequency and number of parameters sampled will be greater than during normal full power operation
 - When chemistry is changing rapidly, samples must be collected more frequently to provide an accurate measure of the water chemistry
 - Grab samples will be collected periodically for calibration and checks of on-line instrumentation

