Lecture 5 – Moderator and Auxiliary Systems

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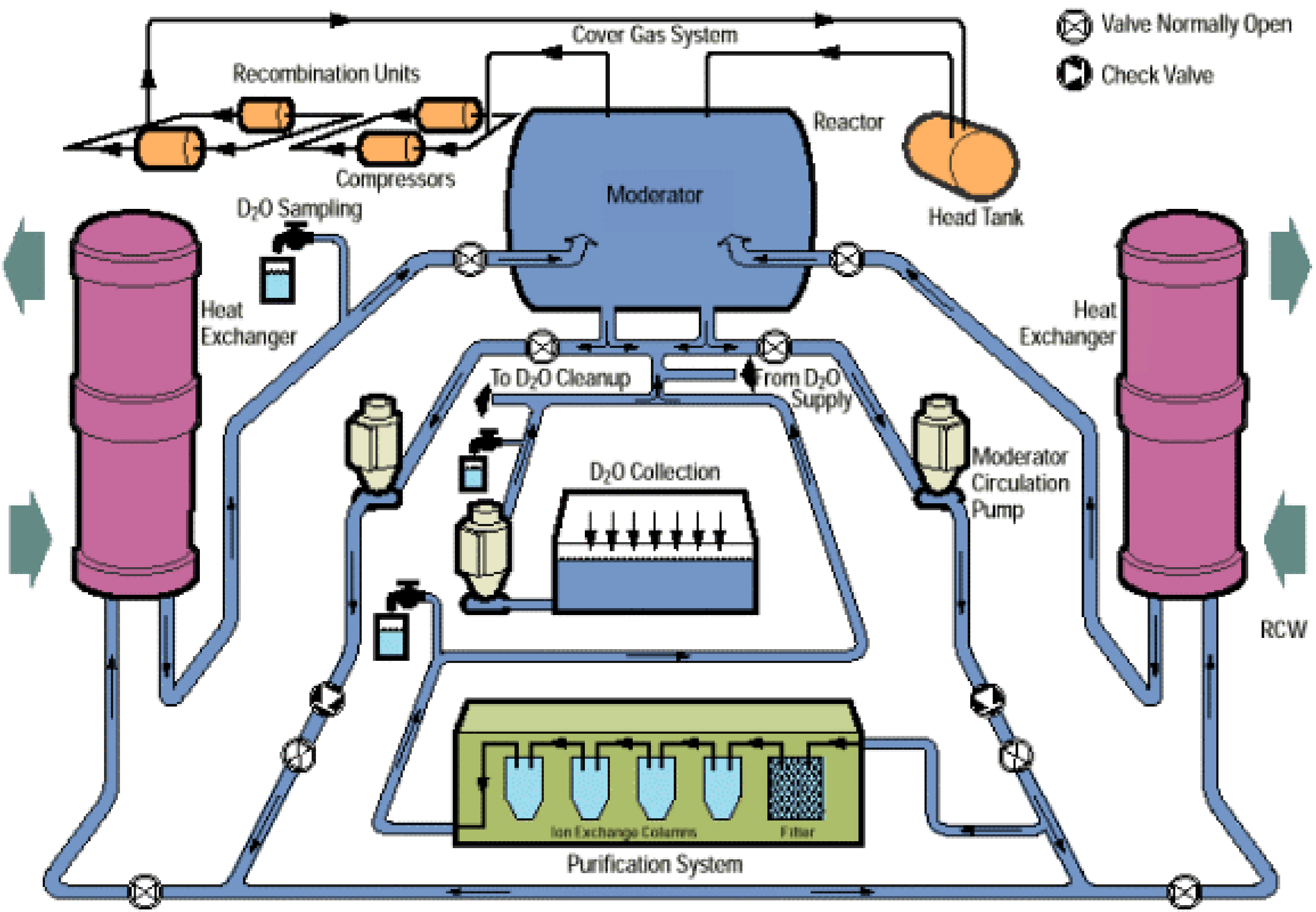
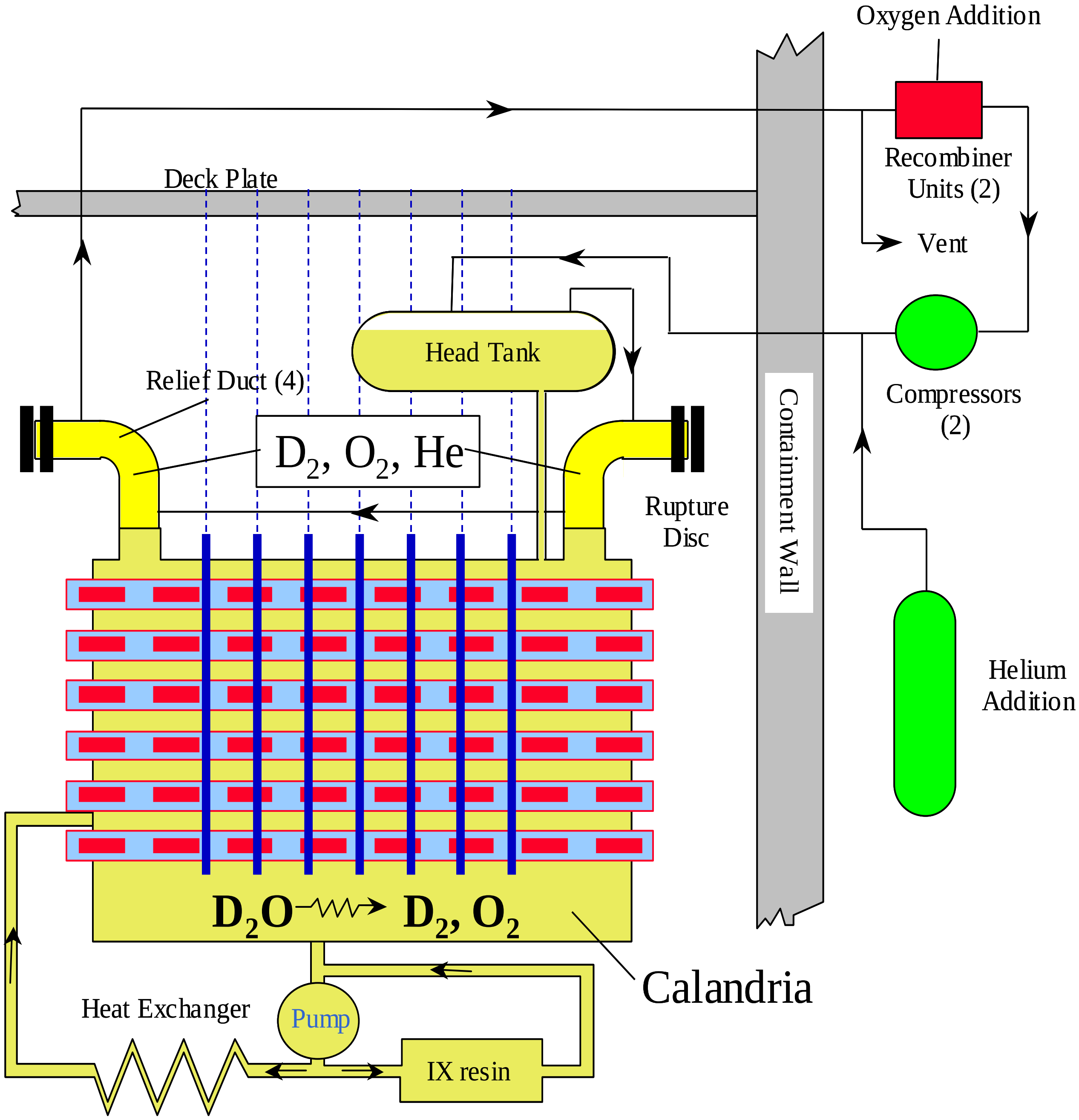
Moderator and Auxiliary Systems

Systems include:

- Main moderator circuit
- Cover gas circuit
- Purification system
- Soluble neutron poison addition system
- Liquid injection shutdown system (LISS)
- Heavy water management systems (deuteration-dedeuteration, water collection, water cleanup)


Valve Normally Open
Check Valve
Cover Gas System
Recombination Units
Compressors
Reactor
Moderator
Head Tank
D$_2$O Sampling
Heat Exchanger
Heat Exchanger
To D$_2$O Cleanup
From D$_2$O Supply
Moderator Circulation Pump
D$_2$O Collection
RCW
Ion Exchange Columns
Filter
Purification System



Oxygen Addition
Recombiner Units (2)
Vent
Deck Plate
Head Tank
Compressors (2)
Relief Duct (4)
D2, O2, He
Rupture Disc
Containment Wall
Helium Addition
D2O → D2, O2
Calandria
Heat Exchanger
Pump
IX resin

Control Parameters – Normal Operation

Parameter	Specification	Rationale
Conductivity	<0.1 mS/m	Ensure total concentration of impurities <0.5 mg/kg to minimize corrosion/cracking Minimize radiolysis
D_2O Isotopic Concentration	≥99.75 wt%	Maintain neutron economy
[B]	Station specific	B used to compensate for excess reactivity in fresh core Small amounts used for reactivity control during normal operation
[Gd]	Station specific	Gd used as soluble poison and for reactivity control
D_2 in moderator cover gas (RU in)	<2.0 vol.%	Prevent formation of flammable gas mixtures
O_2 in moderator cover gas (RU in)	$0.5<[O_2]<3.0$ vol.%	Maintain adequate O_2 to ensure complete removal of D_2 by RU

Diagnostic Parameters – Normal Operation

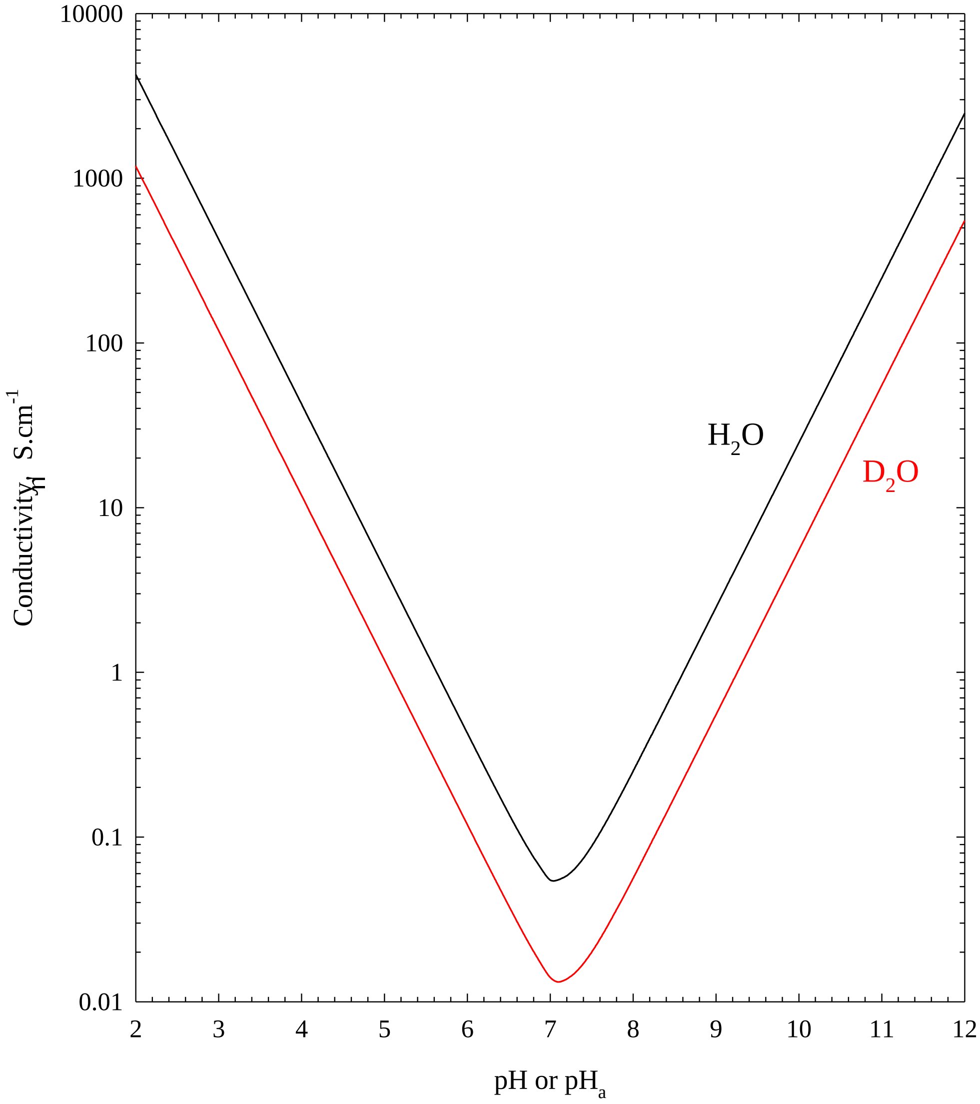
Parameter	Specification	Rationale
Dissolved D_2	<3.0 mL/kg	Reduce driving force for formation of flammable gas mixtures
pH_a	4.5-6.5	Prevent precipitation of $Gd(OD)_3$ Minimize corrosion
Total Anions (Cl^-, F^-, NO_2^-, NO_3^-, SO_4^{2-})	<0.3 mg/kg	Minimize corrosion/cracking Minimize radiolysis Determine source of conductivity changes
TIC/TOC	<1.0 mg/kg	Minimize radiolysis Minimize corrosion/cracking
^{41}Ar	<0.1	Indicative of air ingress
Radionuclides	ALARA	Minimize worker dose
D_2 (RU Out)	<0.1 vol.%	Assess RU performance
N_2 (RU in/out)	≤2.0 vol.%	Indicative of air ingress

Bulk Moderator – Normal Operating Chemistry Objectives

- Maintain heavy water as pure as possible to minimize radiolysis
  - Minimize radiolytic production of deuterium
  - Use purification system with acid-form (D^+/OD^-) mixed bed resin IRN-150 or equivalent
  - Conductivity specification is < 0.1 mS/m

Note:pH_a (pD) not measured under normal circumstances (conductivity too low).

pD vs. conductivity



Bulk Moderator – Normal Operating Chemistry Objectives

- Maintain steady-state concentrations of dissolved D_2, D_2O_2 and O_2 as low as possible

$$\mathbf{D_2O \quad \text{-Radn}\rightarrow D_2, O_2, D_2O_2}$$

- Source of D_2 in moderator cover gas is D_2 in bulk moderator water

Bulk Moderator – Normal Operating Chemistry Objectives

- Typical concentrations in the moderator under normal operation are:

D_2 $\rightarrow$ 1-3 mL/kg ($4\text{-}13 \times 10^{-5}$ mol kg^{-1})

O_2 $\rightarrow$ 1-2 mg/kg ($3\text{-} 6 \times 10^{-5}$ mol kg^{-1})

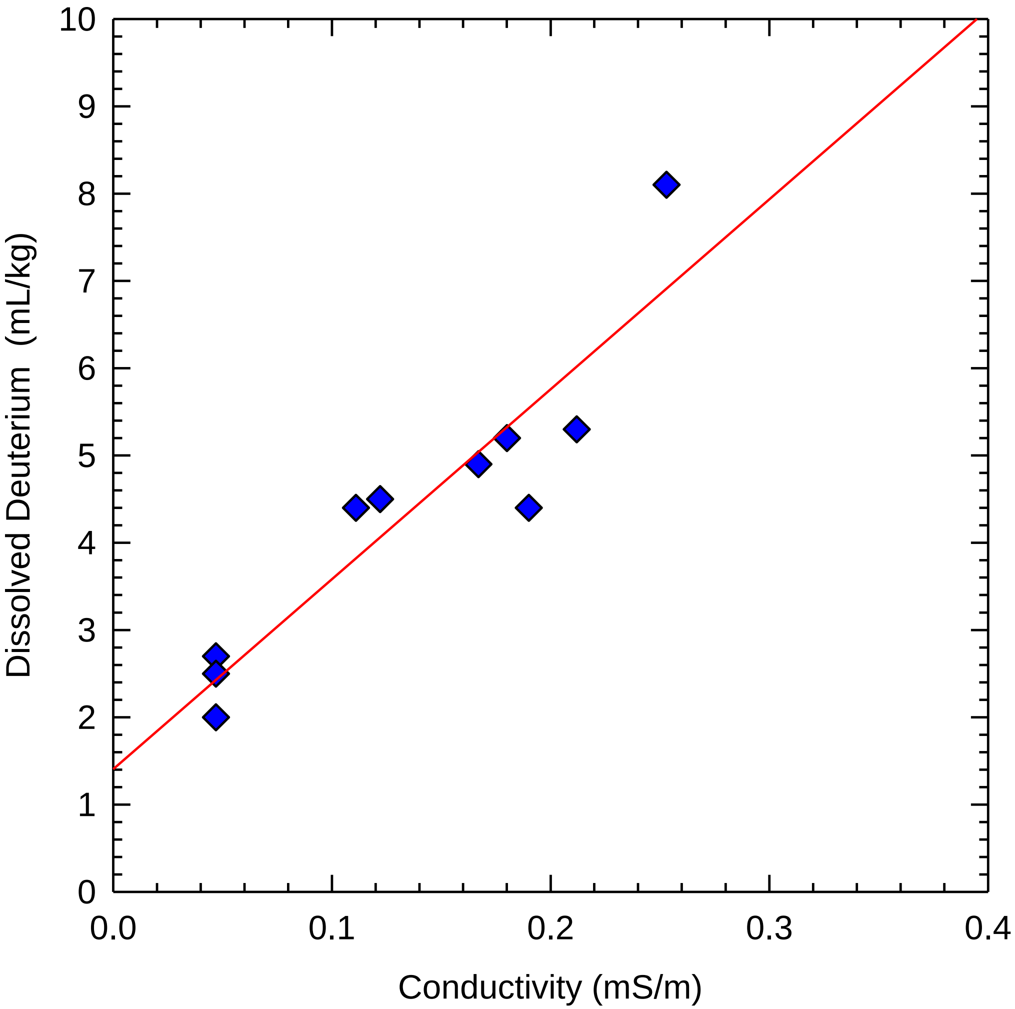
D_2O_2 $\rightarrow$ 1-2 mg/kg ($3\text{-} 6 \times 10^{-5}$ mol kg^{-1})

Bulk Moderator – Normal Operating Chemistry Objectives

- Control reactivity of core by the addition of soluble neutron poisons, e.g., gadolinium and boron
  - Important operating states include:
    - Full-power operation
    - Start-up
    - Guaranteed shutdown
  - Soluble neutron poison concentration different during each of these states

Dissolved Deuterium in the Moderator as a Function of Conductivity

(Data from a PLGS start-up in 1997 when power was greater than 8% $Gd(NO_3)_3$ is the source of the conductivity)



Sources of Impurities in Bulk Moderator Water

- Nitrate/Nitrite ion return from purification system due to breakthrough
- Leakage from poison addition and LISS system
- Nitrate/Nitrite ions $\rightarrow$ Produced radiolytically from:
  - dissolved nitrogen from air-saturated up-grader return D_2O
  - air-ingress into cover gas
- Organic compounds from resin fines, pump oil, etc.

Over-Poisoned Guaranteed Shutdown State

- Moderator system used to ensure reactor shutdown during outages

- Guaranteed Shutdown State can be achieved in two ways using the moderator:
  - Drain moderator of heavy water
    - Can lead to formation of nitric acid from moist air irradiation – leading to very low pH_a (<2) following a refill!)
  - Use Over-Poisoned Guaranteed Shutdown State (OPGSS)

    $\Rightarrow$ $Gd(NO_3)_3$ added to the bulk water

Over-Poisoned Guaranteed Shutdown State

- Only consider OPGSS in this presentation
- Concentration of Gd must be high enough to ensure that reactor is kept sub-critical in any credible event
- In Canada, worst case is a *concurrent Pressure Tube/Calandria Tube break* leading to alkaline PHTS water entering the moderator and precipitating $Gd(OD)_3$

Over-Poisoned Guaranteed Shutdown State

$$Gd^{3+} + 3\ OD^{-} \rightarrow Gd(OD)_3 \downarrow$$

[Gd] > 14-24 mg / kg in Canada

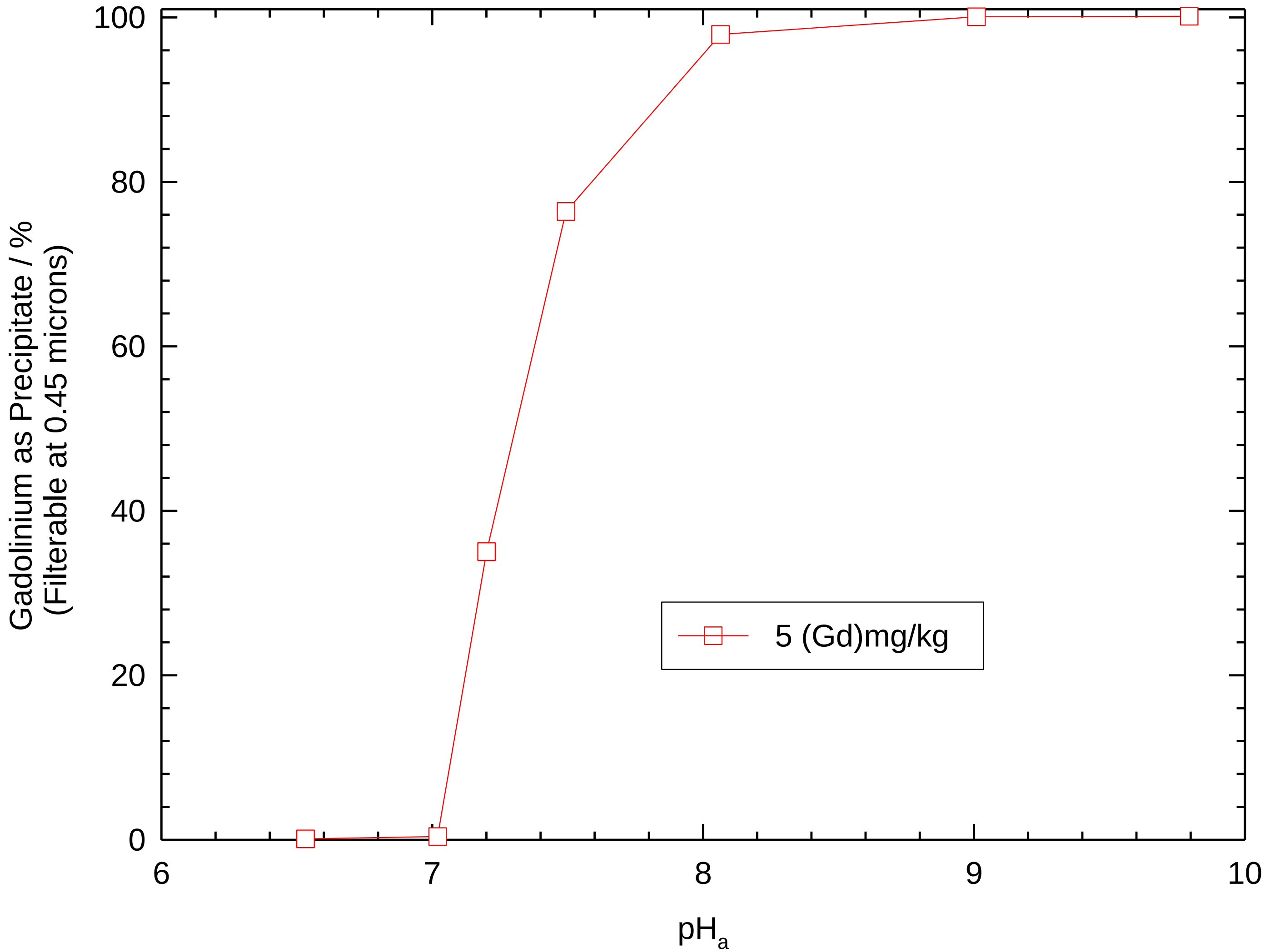
- Some off-shore CANDU 6 stations have lower values

Chemistry Control During OPGSS

- Established in a number of studies that the precipitation of $Gd(OD)_3$ only occurs in heavy water when the $pH_a > 7.0$

Precipitation of Gadolinium in D_2O as a Function of pH_a

("Gadlinium Precipitation" B.R. Nott. (1983) Unrestricted OH Report 83-7-K)



Bulk Moderator Chemistry Start-up

- Surrender of OPGSS
  - Purification System reinstated for removal of Gd^{3+} ([Gd] >14 mg/kg) to ^{135}Xe shim levels ([Gd] ~ 1 mg/kg)

- Reactor start-up $\rightarrow$ Critical $\rightarrow$ Full Power
- Reactor full power - Xenon Transient period
- Normal operation

Bulk Moderator Chemistry Start-up

Xenon Transient:

- Reactor start up after shutdown of >36 hours
  - Period of time over which ^{135}Xe has to build up in the fuel to steady-state levels

- Gd is added to moderator at start-up as a “neutron poison” to “compensate” for lack of ^{135}Xe over this period of time

Bulk Moderator Chemistry
Start-up

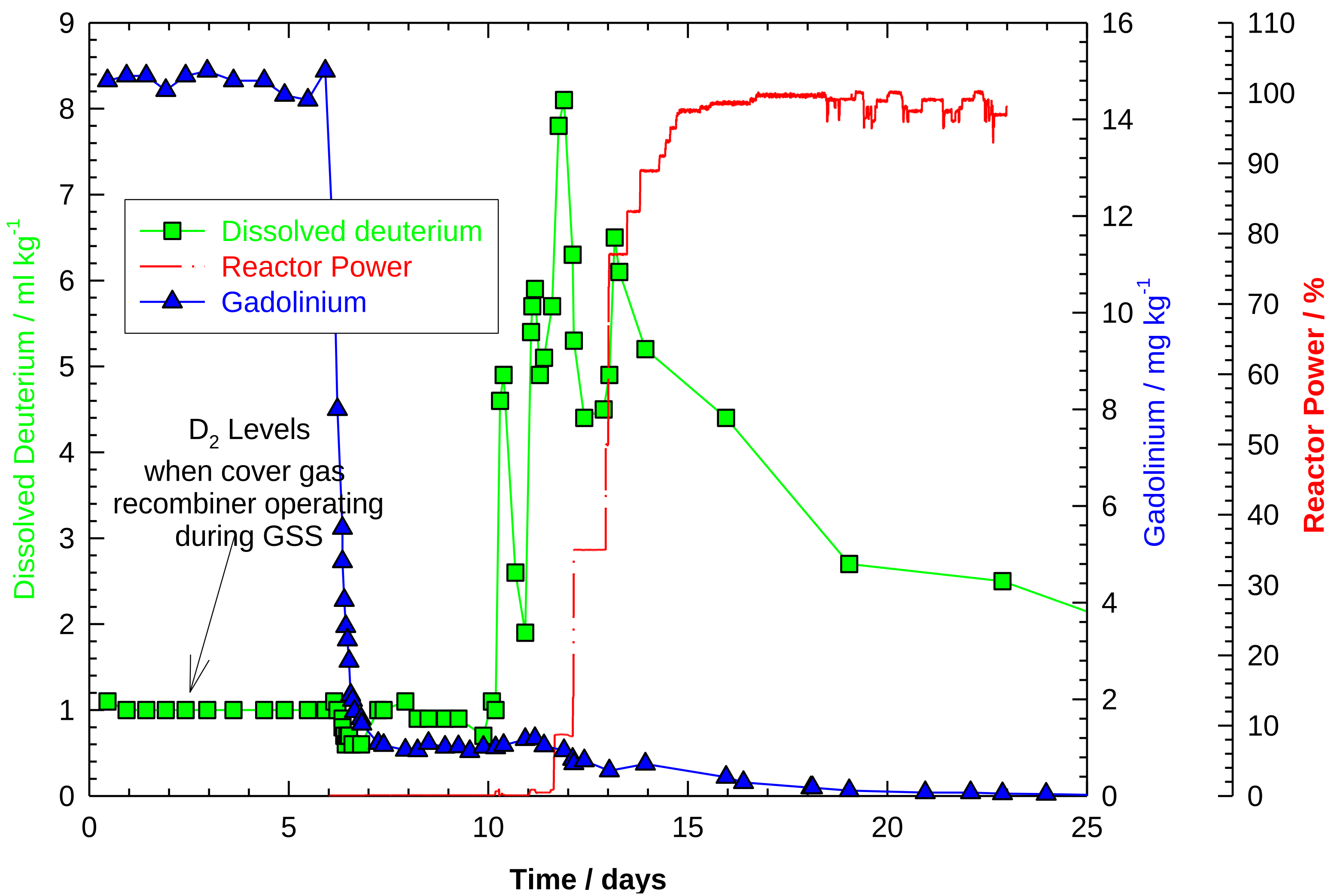
- Gadolinium "burns out" at about the same rate as ^{135}Xe builds in
  - reactivity remains balanced

Note: NO_3^- reacts with radicals and enhances radiolytic production of H_2 and O_2

What is the impact of gadolinium nitrate on H_2 concentrations in the moderator and cover gas?

Dissolved Deuterium Levels from OPGSS to Normal Operation using $Gd(NO_3)_3$ - Point Lepreau Generating Station - 1997 March

(Data supplied by T. Underhill)



Bulk Moderator Chemistry – Start-up

- Saturation limit for dissolved D_2 in bulk moderator ~18 mL/kg
  - If this value is exceeded, moderator will “degas” quickly into cover gas system, overwhelming the recombiners

- Dissolved D_2 concentration peaks observed during start-up using $Gd(NO_3)_3$ as neutron reactivity “shim” for ^{135}Xe-transient generally fall within the range 6-12 mL/kg

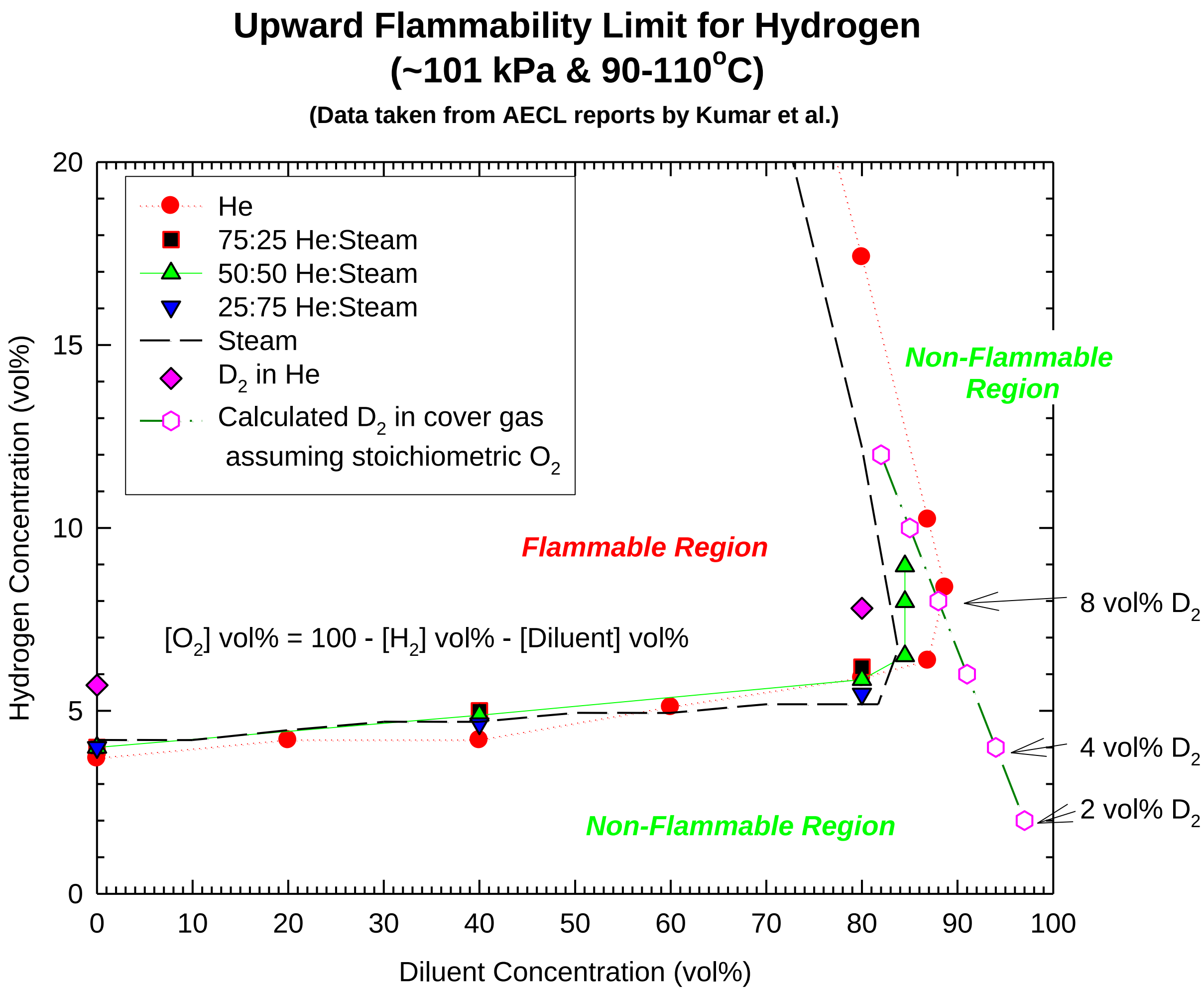
Bulk Moderator Chemistry – Start-up

- Elevated D_2 concentrations not observed when sulphate is counter ion
  - It does not interfere with the radiation chemistry
  - Dissolved D_2 levels are ~1-2 mL/kg, as observed under normal operation

Cover Gas System

- Concentration of D_2 in cover gas should be maintained below 2 vol%
  - Flammable Limit for *hydrogen* in the helium cover gas is 8 vol%
  - Assumed that limit for *deuterium* is the same. This is probably conservative.

Upward Flammability Limit



Cover Gas System

This can be achieved two ways:

1. Use of catalytic recombiner
   - However, O_2 has to be added to the cover gas
     - amount of deuterium escaping into cover gas system always greater than stoichiometric amount of O_2
   - O_2 (& Peroxide) consumed on system surfaces and in reactions involving resin

2. Purging system with helium → can lead to elevated ^{14}C and ^{3}H releases

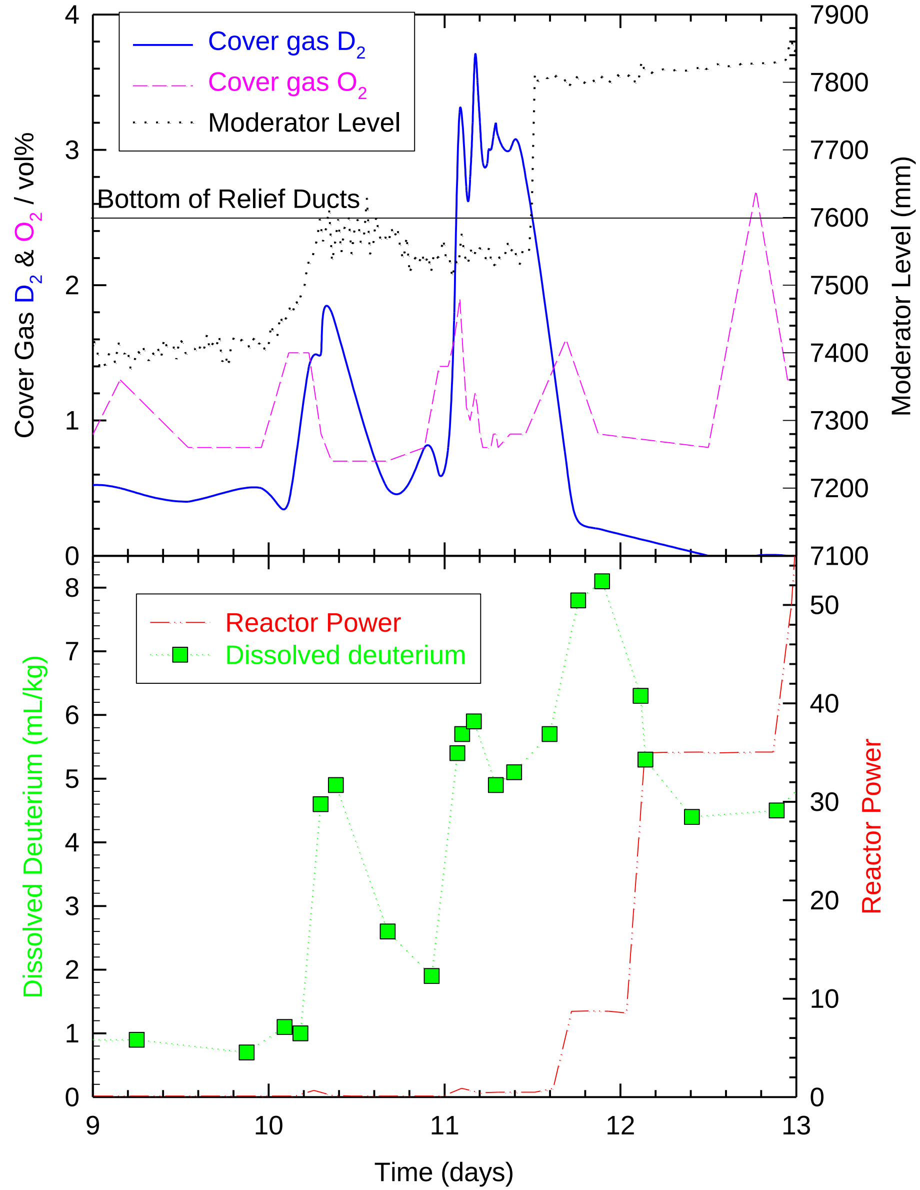
Cover Gas System

- Moderator/cover gas system in non-equilibrium state.
- Under equilibrium conditions, Henry's law predicts:
  - 1 mL(D_2)/kg in solution = 4 vol% D_2 in the cover gas

Cover Gas System

- Cover Gas System depends on the limited mass transfer of gases from moderator bulk water
  - Achieved by maintaining water level in relief ducts
  - Interfacial surface area ~0.60 m^2 when water level up in relief ducts
  - If moderator level falls below bottom of relief ducts:
    - Water/gas interfacial area increases significantly (30x for 15 cm drop in Bruce A reactor)
    - Gas dissolved in moderator partitions more rapidly to cover gas

Impact of Moderator Water Level on Deuterium Concentrations in the Cover Gas



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Other Issues

- Gadolinium Precipitation due to poor resin performance

- If NO_3^- removed more rapidly than the stoichiometric amount of Gd^{3+}
  - Potential for $Gd(OD)_3$ precipitation in column
  - Release of colloidal $Gd(OD)_3$ back into main system

$$\textbf{Resin-}(OD^-) + NO_3^- \rightarrow \textbf{Resin-}(NO_3^-) + OD^-$$

$$Gd^{3+} + 3\ OD^- \rightarrow Gd(OD)_3 \downarrow$$

Other Issues

- Some stations add layer of cation resin on mixed bed resin to ensure Gd^{3+} removed first during Gd removal (or “pull”)

- If $Gd(OD)_3$ precipitation is suspected, HNO_3 is added to main moderator system
  - Lower the pH_a and ensure re-dissolution of the $Gd(OD)_3$

Other Issues

Carbon-14 and Tritium Emissions

- Most ^{3}H and ^{14}C produced in moderator because most of the D_2O inventory resides in-core

$$^{2}H + n \rightarrow {}^{3}H + \gamma$$

$$^{17}O + n \rightarrow {}^{14}C + \alpha$$

Other Issues

- Chemical form of ^{14}C:
  - Carbonic acid/bicarbonate ($D_2{}^{14}CO_3$/ $D^{14}CO_3^-$) in moderator water
  - $^{14}CO_2$ in gas phase

$$\mathbf{D^{14}CO_3^- + D^+ \rightleftharpoons D_2{}^{14}CO_3 \qquad pK_a \sim 6.8}$$

- Equilibrium at water/cover gas interface:

$$\mathbf{D_2{}^{14}CO_3 \rightleftharpoons {}^{14}CO_2(aq) + D_2O \rightleftharpoons {}^{14}CO_2(gas)}$$

Other Issues

- Objective of ^{14}C control
  - Immobilize all $D^{14}CO_3^-$ on purification resin *& keep it there!!*

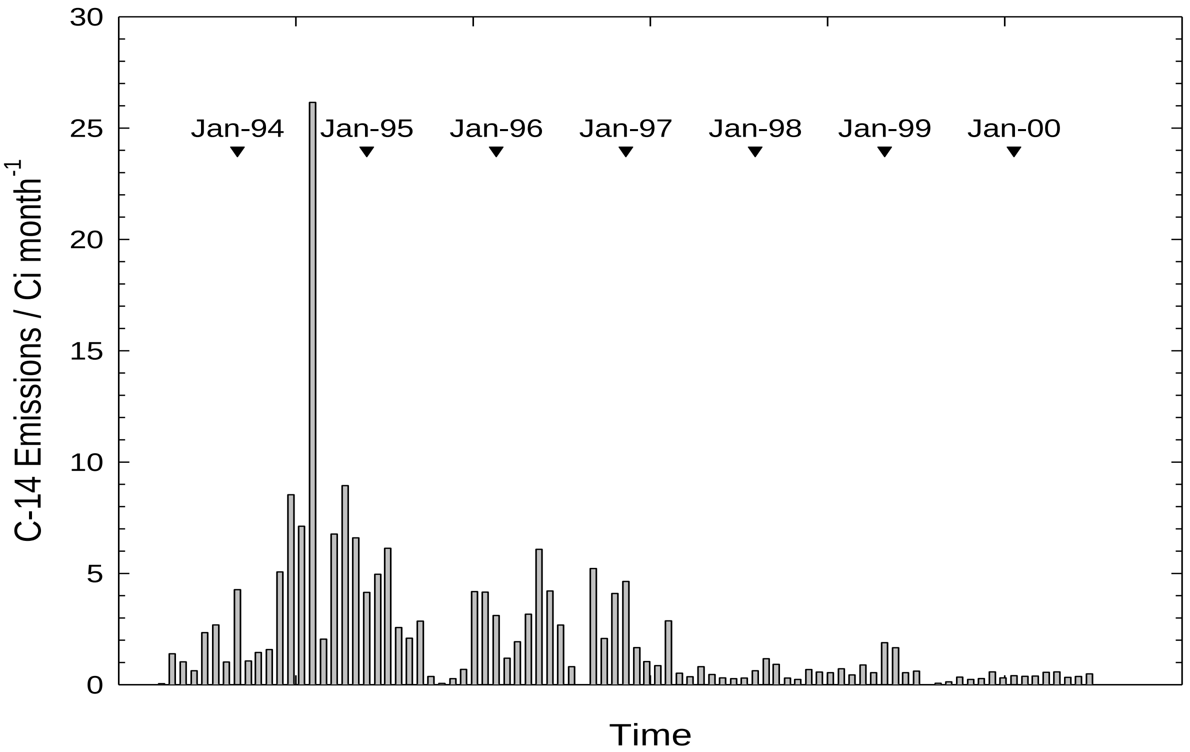
- Achieved by:
  - Change out IX-columns every 3 months
  - Never use a column which had seen previous service for $Gd(NO_3)_3$ removal

Other Issues

- Strongly absorbing anion NO_3^- will displace weakly absorbing anion DCO_3^- off the column
  - No significant increase in conductivity because the predominant form will be D_2CO_3 at moderator pH_a

^{14}C stack releases from Gentilly-2

- Instituted the above protocol
- Releases have decreased significantly.



Liquid Injection Shutdown System (LISS)

- Safety system to shut down the reactor
  - Rapid injection of gadolinium nitrate
  - Need to control the tank inventory