CHEMISTRY - COURSE 224

THE MODERATOR AND AUXILIARY SYSTEMS

OBJECTIVES

On completion of this lesson the trainee will be able to:

General

3.1 (a) State and briefly explain the primary objective of chemical control of the Moderator System.

(b) State **one** other objective of chemical control of the moderator.

3.2 Describe the process of radiolysis indicating why D_2, O_2 and D_2O_2 can result from the radiolysis of D_2O.

Standard Operation

3.3 State the desired operating conditions (numerical values required where indicated) and describe the method(s) regularly used to maintain these conditions for the following Moderator and Cover Gas System parameters:

(a) Moderator conductivity (specification value also required)
(b) Moderator pH (desired value required for guaranteed shutdown state)
(c) Moderator chlorides
(d) Moderator fluorides
(e) Moderator nitrates
(f) Moderator organics
(g) Dissolved D_2
(h) Cover gas D_2 (alarm level required)
(i) Cover gas O_2
(j) Cover gas N_2
(k) Poison addition tank pH
(l) Poison injection tank pH

Non-Standard Operation

3.4 For each of the following Moderator and Cover Gas System parameters state:

(a) the possible cause(s), or source(s) where applicable, of the nonstandard condition,

(b) the method(s) of control,

(c) the consequence(s) if no action is taken, including approximate time factors where required.

# Required (a)	(b)	(c)		
4	3	1	(i)	High moderator conductivity.
3	4	2	(ii)	High moderator pH.
2	3	2	(iii)	Low moderator pH.
1	1	2	(iv)	High moderator chlorides (Cl^-).
1	2	1	(v)	High moderator fluorides (F^-).
2	2	2	(vi)	High moderator nitrates (NO_3^-).
1	2	1	(vii)	High moderator organics.
1	2	1	(viii)	High dissolved deuterium.
3	3	1	(ix)	High moderator/cover gas D_2 or O_2.
2	1	1	(x)	Low cover gas O_2.
1	2	4	(xi)	High cover gas N_2 and Ar.

Cover Gas

3.5 For the moderator cover gas state:

(a) typical action levels, and the action required, for D_2, O_2, and N_2

(b) the lower explosive limits for D_2 and O_2

(c) the shutdown limits for D_2

Startup and Shutdown

3.6 (a) (i) State the major chemistry-related concern for the Moderator and Cover Gas Systems on startup.

(ii) Explain six factors which affect the rate of buildup of D_2 and O_2 in the moderator cover gas system and state how each is controlled.

(b) Regarding a guaranteed shutdown:

(i) Briefly explain the major concern with respect to gadolinium nitrate concentration in the moderator.

(ii) State and briefly explain the requirements for moderator pH, and cover gas D_2 concentration.

(iii) Briefly describe how gadolinium nitrate concentration, moderator pH and cover gas D_2 concentration are kept within specification.

Sources of Information

3.7 State two sources of information employed to monitor the moderator and cover gas chemical parameters.

Poison Addition Tank and SDS2 Poison Injection System Chemistry

3.8 Explain why gadolinium nitrate concentration and pH in the Poison Addition Tank and the SDS2 Poison Injection System are of concern, and the consequences if these parameters are abnormal.

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INTRODUCTION

Whenever there are liquids and gases in contact with metals, as in the moderator system, corrosion and other chemistry related concerns will exist.

Figure 1 illustrates that there may be corrosion concerns for the calandria body, calandria tubes, reactivity mechanisms, liquid zone tubes, cleanup circuits, heat exchangers, and any other metal surfaces exposed to the moderator.

The moderator system is also a concern because of the gas space above it. The high radiation fields within the calandria can cause the moderator D_2O molecules to decompose into D_2 and O_2 gases. Note that the bulk of the moderator is exposed to radiation fields all of the time the unit is in operation, and to some continuing gamma fields after shutdown. In the correct proportions, D_2 and O_2 form an explosive mixture. In the case of the moderator cover gas, the risk of explosion is of more concern than the effects of corrosion.

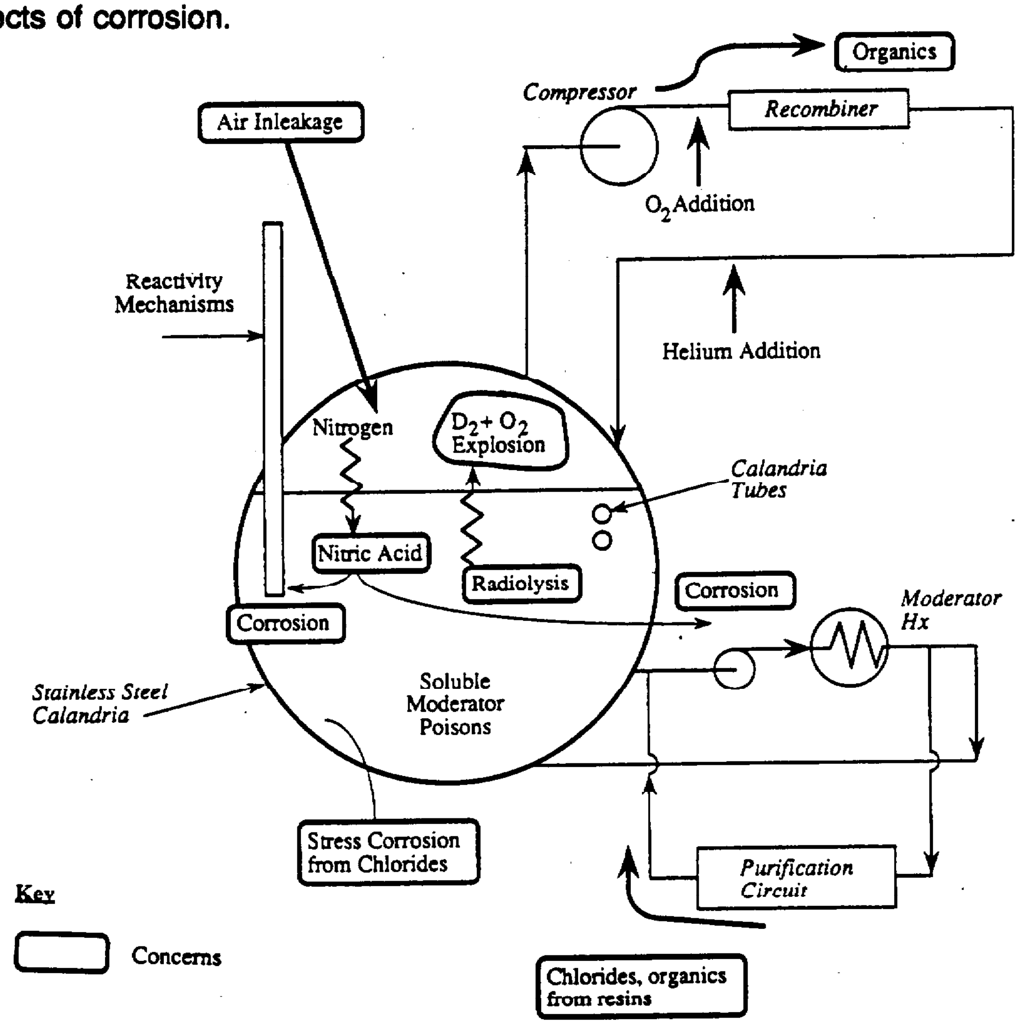

Figure 1: The Moderator System

GENERAL

OBJECTIVES OF MODERATOR CHEMISTRY CONTROL

The primary objective of chemical control of the moderator is to **minimize the radiolysis of D_2O**. This is essential in order to minimize the production of gaseous D_2 and O_2 and thereby prevent any possibility of a D_2/O_2 explosion in the moderator cover gas.

Preventing corrosion of system components is another objective of chemical control of the moderator system. Since the calandria is stainless steel, and is therefore relatively immune to corrosion, the main concern is with respect to corrosion of the heat exchangers (if copper alloys were used in their construction) and associated equipment, eg, pipes, pumps, valves. The major source of corrosion is nitric acid formed from the oxides of nitrogen produced by radiolysis of nitrogen from air which has entered the system. The nitric acid lowers the pH of the moderator, promoting corrosion, and worst of all, also enhances the radiolysis of the D_2O.

Minimizing corrosion also minimizes the creation and spread of activated corrosion products which can cause high radiation fields around moderator system equipment.

Summary

- Radiolysis in the moderator system produces gaseous D_2 and O_2, and oxides of nitrogen.
- Gaseous D_2 and O_2 represent a serious explosion hazard in the moderator cover gas.
- Oxides of N_2 form nitric acid, a major source of corrosion in the moderator system.
- Nitric acid enhances radiolysis of the D_2O.
- Minimizing corrosion helps limit the production and spread of activated corrosion products.

RADIOLYSIS

Radiolysis is the chemical decomposition of molecules by gamma rays (γ) and fast neutrons (n). Since the moderator is continually bombarded by this radiation, radiolysis of the moderator D_2O cannot be prevented. The following **unbalanced** equation simplifies and summarizes what is actually a complex sequence of intermediate reactions involving molecules, atoms, ions, electrons and free radicals.

Note that it also shows that aqueous recombination occurs and is impeded by impurities in the moderator.

$$D_2O \underset{\text{Aqueous Recombination (Impeded By Impurities)}}{\overset{\text{n or } \gamma \text{ Production}}{\rightleftharpoons}} D_2 + O_2 + D_2O_2$$

Free radicals are groups of atoms containing an unpaired electron; they are very reactive. The free radical is shown by the element symbol and a raised dot, eg, D•, •OD. The raised dot represents the single (unpaired) electron of the free radical. Thus D• is a deuterium atom, •OD is a deuteroxyl radical and both are free radicals.

These free radicals can combine in any of three ways:

D• + D• ⟶ D_2 (Deuterium Gas)

D• + •OD ⟶ D_2O (>99% when moderator water is pure)

DO• + •OD ⟶ D_2O_2 (Deuterium peroxide)

D_2O_2 is a concern because it is an oxidizing agent which can attack the organic resins in the IX columns.

Figure 2 illustrates radiolysis in the moderator/cover gas system. D_2 and O_2 gases can stay dissolved or can come out of solution into the cover gas. Alternatively, D• and •OD radicals can recombine spontaneously in the moderator to form D_2O. This is called "aqueous recombination" and is also illustrated in Figure 2. Some impurities in the moderator interfere with aqueous recombination.

The presence of excessive amounts of D_2 (and O_2) in the cover gas is a **cover gas deuterium excursion**, commonly called a deuterium excursion. Such excursions can occur very quickly.

An important feature to note about deuterium excursions is that they can occur not only from an increase in the radiolysis rate, but also from a decrease in the aqueous recombination process. Deuterium excursions can also occur if some other factor changes to cause the gases dissolved in the moderator to come out of solution more rapidly than before.

The factors which affect the rate of buildup of D_2 and O_2 in the moderator cover gas are discussed in detail under startup and shutdown.

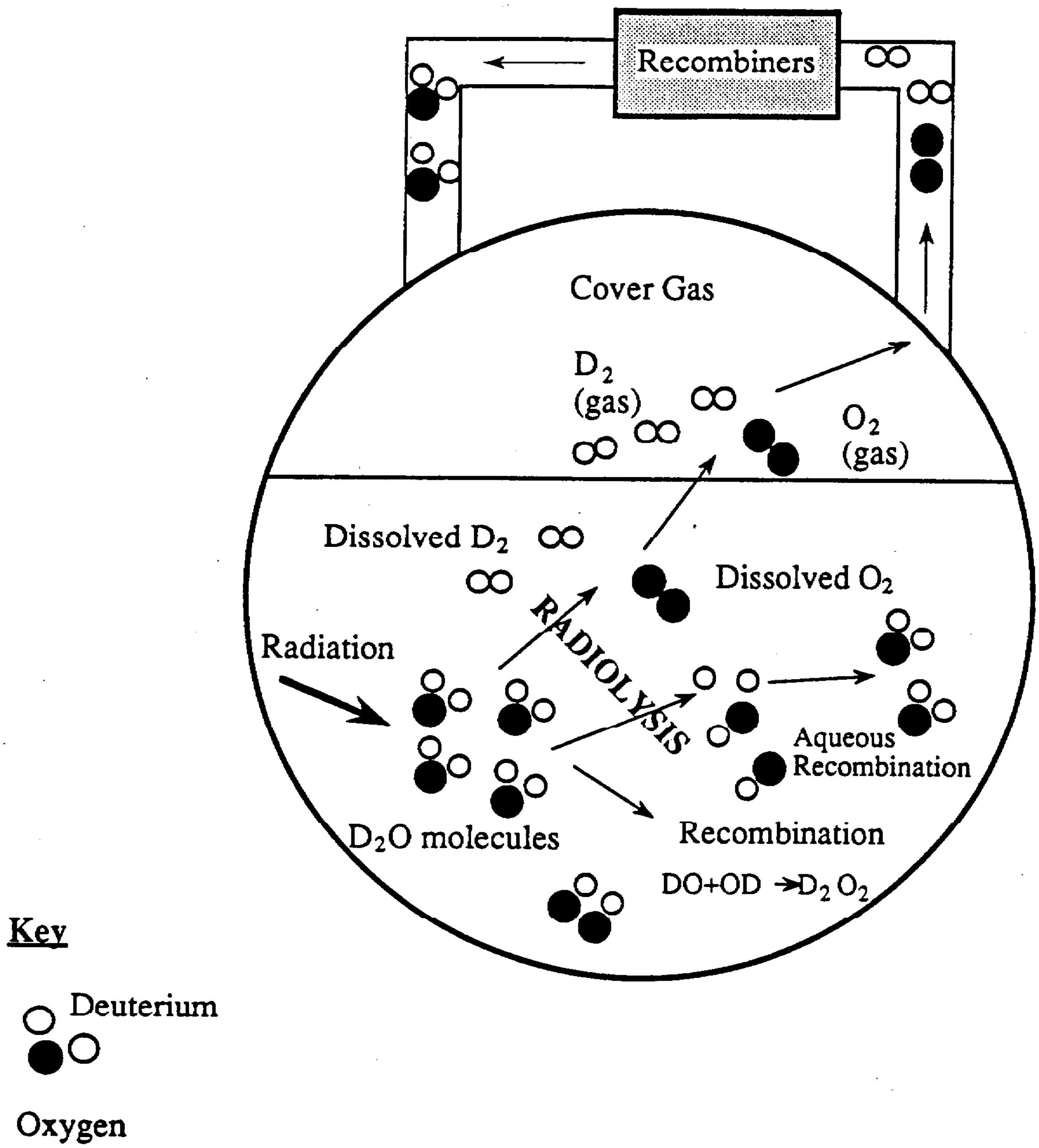

Figure 2: Radiolysis in the Moderator System

Summary

- Radiolysis is the chemical decomposition of molecules by radiation.
- Some impurities in the moderator interfere with aqueous recombination.

- At steady power, equilibrium is reached between the production and recombination of D_2 and O_2 in the moderator.
- During power increases, recombination may be less than production of D_2 and O_2 and a cover gas deuterium excursion may occur.

STANDARD OPERATION

Control and Monitoring of Moderator Operating Conditions

The purity of the moderator water is controlled by ion exchange and is monitored using on-line conductivity meters and routine grab samples.

The cover gas D_2 and O_2 concentration is controlled by recombiners, oxygen addition, control of radiolysis, and purging, if necessary, with helium. D_2, O_2 and N_2 concentrations are monitored at the inlet and outlet of the recombination units, via on-line gas chromatographs.

(a) **Moderator Conductivity**

The desired operating condition for moderator conductivity is ALARA, because a low conductivity indicates high moderator water purity, which in turn will minimize the production of D_2 and O_2 by radiolysis.

Many soluble impurities interfere with aqueous recombination, and thereby have the effect of accelerating radiolysis. Most water impurities in a power station are ionic. Thus conductivity is usually a good indication of water purity; for the moderator it is in fact excellent.

The situation with respect to moderator poisons is as follows:

<u>boron</u>: boric acid contributes little to conductivity, and not at all to the radiolysis of water.

<u>gadolinium</u>: although the gadolinium ion does not affect the production of radiolytic D_2, nitrate does. The relationship between salt concentration and conductivity is linear.

Moderator conductivity is the only control variable for the moderator. It is controlled, using IX columns, to a specification of ≤ 0.1 mS/m.

(b) **Moderator pH**

Conductivity increases as the pH of the moderator moves away from neutral, in either direction. Consequently, the desired operating condition to minimize conductivity, and therefore radiolysis, would be close to pH 7. A neutral pH is also desirable to minimize corrosion of moderator system components such as pumps and heat exchangers.

Moderator pH is controlled only in conjunction with conductivity using IX columns to remove impurity ions, and replace them with OD^- and D^+ ions, ie, D_2O. If the **conductivity** of the moderator is held very low it consists of essentially pure D_2O which ionizes very slightly. Therefore, because of the lack of ions, the pH meter will read erratically although the moderator is essentially neutral, ie, no OD^- or D^+ ions present. Thus when the moderator conductivity is very low, the pH meter is unusable but the pH is accepted as 7. Therefore, pH is analyzed on power only for troubleshooting high conductivity.

Again, an exception to the above occurs whenever gadolinium nitrate is present in the moderator D_2O. Gadolinium nitrate is the salt of a strong acid and a weak base and therefore a solution containing it has an acidic pH, ie less than 7. The pH specification during the guaranteed shutdown state is 4 - 6. At some stations, 1/7th of the column is catexer to ensure that pH will go acidic on spent columns.

(c) **Moderator Chlorides**

The desired level is ALARA (ppb level for conductivity < 0.1 mS/m).

Any chlorides in the moderator would be removed by fresh IX resins.

(d) **Moderator Fluorides**

The desired level is ALARA. Teflon is a source of fluorides when irradiated, and therefore is banned from the nuclear side.

Fluoride ions **cannot** be removed by ion exchange because they are smaller than hydroxyl ions, but are removed by the on-line upgrader distillation towers. Fluoride is an impurity in the gadolinium nitrate poison.

(e) **Moderator Nitrates**

The desired level is ALARA.

Control of nitrates is by removing them using IX resins.

(f) **Moderator Organics**

The desired level is ALARA.

Control of organics in the moderator is essentially by prevention. Dual screens in the IX columns hold back resin fines, and compressor and pump design makes oil contamination highly unlikely. Any organics appearing in the moderator would be radiolyzed, through a series of steps, into dissolved carbon dioxide (CO_2) which would be removed by the IX resins. There is no other method of removing organics from the moderator.

(g) **Dissolved Deuterium**

The desired level is ALARA.

Free deuterium in the moderator/cover gas system appears first dissolved in the moderator. Deuterium excursions occur when D_2 migrates **quickly** into the cover gas. If the dissolved D_2 concentration is low (typically 3 cc/kg D_2O), the likelihood of an excursion is small.

Control is by maintaining the moderator at high purity.

Note: Although not chemical parameters, isotopic (%D_2O) and tritium analyses are performed by the Chemical Laboratory.

(h) **Cover Gas D_2**

The concentration of D_2 in the moderator cover gas is held ALARA in order to minimize the possibility of fire or explosion. The alarm level is $\geq$ 2%.

The production of D_2 is controlled by minimizing radiolysis. Also D_2 is removed from the cover gas by recombining it with O_2 in the recombiners. Oxygen is added to the cover gas for this purpose. D_2 may also be removed by purging with helium.

(i) **Cover Gas O_2**

The desired oxygen content in the moderator cover gas is no more than that required to combine with the D_2, ie, one oxygen molecule per two deuterium molecules. Remember that oxygen supports combustion and promotes corrosion.

Control of oxygen is by addition of small batches of oxygen to the cover gas at the recombiner inlets for the purpose of combining with deuterium in the recombiners.

(j) **Cover Gas N_2**

The concentration of N_2 in the cover gas is maintained ALARA because N_2 and O_2 radiolyze into nitrogen oxides. One of these oxides, nitrogen dioxide, NO_2, dissolves in water to form nitrous and nitric acid, DNO_2 and DNO_3 respectively, both of which enhance radiolysis and cause increased corrosion.

Control is maintained by holding the cover gas pressure at ≈ 1¼ atmospheres, ie, ≈ 25 kPa(g), in order to minimize air in-leakage, and by purging with helium as required. Purging will also reduce both O_2 and D_2 in the cover gas.

(k) **Poison Addition Tank pH**

The poison used may be boron or gadolinium nitrate, depending on the station. Boron does not precipitate out at any pH. Above pH 7, gadolinium ions will precipitate out of solution.

Where gadolinium nitrate poison is used, a pH of approximately 4 results from the concentration used in the solution. The poison addition tank pH is monitored by the chemistry laboratory. If the pH is abnormally high, the solution is replaced.

(l) **Poison Injection Tank pH**

At the ≈ 2% gadolinium nitrate concentration used for this solution, the pH is about 3. This is monitored by the chemistry laboratory. If a tank is found with abnormally high pH the solution is replaced because this would be an impairment of SDS2.

Poison addition and poison injection are described in a later section.

Note: The Atomic Energy Control Act stipulates that the isotopic distributions in moderator poisons are unaltered, ie, are those that occur in nature. (Neutron-absorption ability varies between isotopes).

Summary

The following table summarizes the standard operating conditions for the moderator and cover gas systems:

PARAMETER	DESIRED CONDITION	CONTROLLED BY
Conductivity	ALARA (≤ 0.1 mS/m)*	IX resins.
pH	Neutral	IX resins; only in conjunction with conductivity.
pH - in guaranteed shutdown state	4-6	See later section, startup and shutdown.
Cl^-	ALARA	IX resins.
F^-	ALARA	No Teflon. Upgraders.
Organics	ALARA	Screens prevent release of IX beads.
Dissolved Deuterium	ALARA	Keep moderator purity high.
Nitrates	ALARA	IX resins. Keep air out.
Cover Gas D_2	ALARA (< 2%)* Alarm level is ≥ 2%	Recombiners. Purging.
Cover Gas O_2	Min: ½ D_2 concentration Max: 3%	Manual addition. Recombiners.
Cover Gas N_2	ALARA (≤ 2%)	Prevent ingress. Purging.
Poison Addition Tank pH	≈ 4	Replacement of solution if pH is incorrect.
Poison Injection Tank pH	≈ 3	

* Numerical values in brackets are NGD Divisional Chemical Specifications.

NON-STANDARD OPERATION

The causes or sources, methods of control and consequences if no action is taken are discussed in this section for a number of variables under non-standard conditions.

The only Action Level 3 parameter for the moderator system is high cover gas D_2 concentration.

(i) High Moderator Conductivity

High conductivity is the only control parameter for the moderator water.

Causes/Sources

Four causes of high moderator conductivity are:

- Air inleakage producing nitric acid, via radiolysis.
- Spent IX columns, allowing impurity ions to pass into the column effluent.
- Addition of gadolinium nitrate for reactivity control. (All stations except PNGS-A)
- Other impurities (eg, fluoride, or dissolved corrosion products).

Methods of Control

High conductivity is controlled by eliminating air inleakage and ingress of contaminants. Control is also achieved by purging the cover gas when N_2 concentration is high, eg, after system has been opened, and by ensuring IX columns are not spent.

Consequence

The most significant consequence is the probability of a cover gas deuterium excursion. D_2 excursions can occur very quickly, ie, in minutes. If the moderator conductivity rises to 1 mS/m (≈ 10X specification), it must be restored to its normal range within 24 hours. At, say, 5 mS/m, a cover gas deuterium excursion will most likely have already occurred and caused a unit shutdown on high deuterium (≥ 4%).

(ii) High Moderator pH

Causes/Sources

Any of the following will cause high moderator pH:

- Inadvertent use of heat transport system resin (lithium based) in an IX column.
- Too much anexer in the IX columns so they are short of catexer and therefore stop removing Gd^{+++} ions but continue to remove NO_3^- ions.
- Contamination of the moderator by alkaline sources such as heat transport system D_2O or lithium hydroxide.

Methods of Control

High pH is controlled by ensuring there is no HTS resin in the IX columns and no contamination in the moderator from alkaline sources.

Control is also by ensuring there is adequate catexer in the IX columns. This is diagnosed by analysis of the column effluent showing Gd^{+++} but not NO_3^-. Replacing spent IX columns so that properly functioning IX columns will eventually remove the contaminants also controls high pH. Note that IX columns made up of excess cation resin will spend on anions. Hence a column will still remove Gd^{+++}, but not nitrate. The effect is to lower pH and can cause a D_2 excursion.[1]

Consequences

The major consequence of high pH is the conversion of any gadolinium present to insoluble gadolinium hydroxide. This substance would be present as a colloidal suspension, not removable by filtration. Its tendency to settle out would be unknown. This would represent a serious situation, because of the lack of control of this negative reactivity.

A second consequence might be increased production of radiolytic deuterium.

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[1]Not applicable to PNGS-A which uses boron.

(iii) **Low Moderator pH**

Causes/Sources

The most likely cause is air inleakage to the cover gas. By radiolysis, the nitrogen in the air can form nitric acid:

$$N_2 + O_2 \rightsquigarrow 2\ NO \xrightarrow{O_2} 2NO_2$$

$$2NO_2 + D_2O \rightarrow DNO_3 \text{ (nitric acid)} + DNO_2 \text{ (Nitrous Acid)}$$

An acid, by definition, has a low pH, and therefore lowers the pH of the moderator.

Too much catexer in the IX columns will also cause low moderator pH because the columns are short of anexer and therefore stop removing NO_3^- ions.

Methods of Control

Low pH is controlled by minimizing air in-leakage. Properly operating IX columns will return the moderator pH to neutral. Purging the cover gas when N_2 concentration is high, eg, after system has been opened, also controls low moderator pH.

Consequences

If the acid formed is not removed, it will increase radiolytic production of D_2 and O_2. In severe cases, corrosion of the heat exchangers can result.

(iv) **High Moderator Chlorides**

Cause/Source

Although high chlorides are not a likely problem, the most credible chloride source is spent resin in an IX column.

Method of Control

Control is by ensuring proper IX column operation to remove chlorides.

Consequences

High chlorides increase the likelihood of stress corrosion cracking of stainless steel components, including the calandria. In addition, radiolytic production of D_2 and O_2 will increase.

(v) **High Moderator Fluorides (F^-)**

Cause/Source

Since the banning of teflon from nuclear side equipment, the only source of F^- is the traces (ppm) found in the gadolinium nitrate poison.

Method of Control

Fluoride concentration reaches an equilibrium level because of removal in the on-line upgrader distillation towers. Control is also achieved by excluding substances containing fluorides from the system.

Consequences

The levels of F^- presently found in the moderator are not harmful. Higher levels might lead to zirconium corrosion.

(vi) **High Moderator Nitrates (NO_3^-)**

Causes/Sources

Some nitrates are introduced stoichiometrically as part of the poison, gadolinium nitrate. Inleakage and radiolysis of air also produces nitrates in the moderator.

Methods of Control

Nitrates introduced with the gadolinium poison are removed by the IX columns during startup. Nitrates produced by radiolysis of air are removed by IX resins during operation. Prevention of air in-leakage is an important control factor. Grab samples are analyzed for nitrates if the conductivity is above specification, and during startups.

Consequences

If the nitric acid is not removed from the moderator it will greatly enhance D_2 formation. In sufficient concentration nitric acid will also corrode heat exchanger tubes (especially at PNGS-A).

(vii) **High Moderator Organics**

Cause/Source

There is no likely source of organics in the moderator. The cover gas compressor diaphragms have triple seals, so oil contamination from them is unlikely. Another possibility is if IX resin fines were to get into the moderator by passing through the screens.

Methods of Control

Control is by prevention. Design almost eliminates the possibility of high organics. Organics are radiolyzed to CO_2 which is removed by IX columns.

Consequence

Contamination with organics will promote deuterium formation, but is not apt to increase conductivity.

(viii) **High Dissolved Deuterium**

Cause/Source

The source of dissolved D_2 is the radiolysis of D_2O; the cause of high dissolved deuterium is insufficient moderator purity. The concentration at steady 100% power is about 3 cc/kg D_2O.

Method of Control

Control is achieved by maintaining the moderator at high purity (see conductivity).

Consequence

The higher the dissolved D_2 concentration, the likelier a D_2 excursion becomes, and the greater its magnitude might be.

(ix) **High Moderator/Cover Gas D_2 or O_2**

Causes/Sources

Most substances or conditions that increase conductivity will also increase radiolytic production of D_2 and O_2. This includes air ingress, spent IX columns, pH greater or less than 7 and contaminants. D_2 in the cover gas migrates there from the water.

Reactor power increases, moderator impurities, moderator level decreases and cover gas pressure drops were identified previously as major causes of increased D_2 and O_2 concentrations in the cover gas.

If the recombiners are out of service, or are not working effectively, D_2 and O_2 concentrations will also increase.

Methods of Control

Control is through steady operation, ie, avoiding rapid power increases and pressure and level drops, and by ensuring that the recombiners are operational and the moderator is pure.

The moderator cover gas is purged with helium, if necessary.

Action Levels

- Action Level 2 - If $D_2 \geq 2\%$, do not increase power. Helium purge. Verify by chemical analysis. Determine cause of rising D_2. Check dissolved D_2 content with respect to saturation.

- Action Level 3 - If D_2 concentration $\geq 4\%$ and is confirmed by laboratory sampling, shut down the reactor in a controlled manner.

  - If D_2 concentration $\geq 6\%$, initiate a controlled reactor shutdown immediately, without waiting for a confirming sample.

Consequences

There is a possibility of explosion within the calandria if D_2 reaches the lower explosive limit (8%) and sufficient O_2 (> 5%) is present. A high O_2 concentration increases the risk of explosion if a D_2 excursion occurs.

(x) **Low Cover Gas O_2**

Causes/Sources

Parasitic consumption of oxygen (reaction with resin radiolytic fragments, formation of nitrate, corrosion) causes low cover gas O_2.

Method of Control

Control is achieved by adding O_2, as specified by operating manual. Do not exceed 3%.

Consequence

If the ratio of Deuterium to Oxygen is > 2:1, there will be insufficient O_2 to recombine with the D_2. This can lead to high D_2 concentrations in the cover gas.

(xi) **High Cover Gas N_2 and Ar**

Cause/Source

Air inleakage to the cover gas system is the source of N_2 and Ar in the cover gas.

Methods of Control

High cover gas N_2 or Ar are controlled by preventing air ingress by sealing leaks, and by purging the cover gas with helium. The action Level 1 - if N_2 Concentration ≥ 2% applies.

Consequences

N_2 is converted to nitric acid via radiolysis. This nitric acid must be removed by IX columns. Increased nitrate enhances D_2 and O_2 production which in turn promotes cover gas excursions. The nitric acid formed increases corrosion. Argon, Ar^{40} becomes activated to Ar^{41}, a powerful gamma emitter.

Summary

The following table summarizes the non-standard operating conditions for the moderator and cover gas systems:

PARAMETER	CAUSE/SOURCE	CONTROL METHOD	CONSEQUENCE OF NO ACTION
High Conductivity	Air ingress and $\longrightarrow HNO_3$. Spent IX columns. Gadolinium nitrate. Other impurities or corrosion products.	Eliminate air inleakage. Purge cover gas if N_2 is high. Ensure IX columns not spent.	Cover gas excursion.
High Moderator pH	HTS resin	Ensure only moderator resin is used.	Gd will precipitate out of solution, OR $Gd(OH)_3$ will form a colloid. Both effects interfere with reactivity control.
	IX column short of catexer.	Ensure adequate catexer.	
	Contamination by alkaline sources.	Ensure no contamination. Replace Spent IX columns.	
Low Moderator pH	Air inleakage and radiolysis produce nitric/nitrous acid. Insufficient anexer.	Minimize air ingress. IX columns remove acid. Purge cover gas if N_2 is high.	Acid enhances radiolytic production of D_2 and O_2. Corrosion of HX tubes.
High Chlorides	Spent resins	Ensure proper IX column operation.	Increased D_2 formation. Potential stress corrosion cracking of stainless steel components.
High Fluorides	Trace amounts in gadolinium nitrate poison.	On-line upgrader distillation towers. Exclusion of substances containing fluoride.	Possible corrosion of Zr alloy. Level presently found in moderator is not harmful.
High Nitrates	Gadolinium nitrate poison. Radiolysis of air.	Keep air out. IX columns.	Enhanced D_2 formation. Corrosion of HX tubes.
High Organics	IX resin fines are most probable source. Not a likely problem.	Prevention. Radiolyzed to CO_2 which is removed by IX columns.	Promotes deuterium formation.
High Dissolved Deuterium	Source is radiolysis of D_2O. Cause is insufficient moderator purity.	Maintain high moderator purity.	D_2 excursion.
High D_2 or O_2 in Moderator/Cover Gas	Radiolysis of D_2O. Release of D_2 and O_2 from moderator liquid. Recombiners not operational.	Avoid rapid power increases. Recombiners operating. Purge cover gas with helium. $D_2 \geq 2\%$ Do not raise power $D_2 \geq 4\%$ Shut down if confirmed $D_2 \geq 6\%$ Immediate shutdown	Possible explosion in calandria (if $D_2 > 8\%$ and $O_2 > 5\%$.) High O_2 increases explosion risk if D_2 excursion occurs.
Low O_2 in Cover Gas	Parasitic consumption of O_2. Insufficient O_2 addition.	Add O_2 as per OM (maximum 3%).	High D_2 concentrations.
High N_2 in Cover Gas	Air in-leakage.	Prevent air ingress. Purge with helium.	N_2 Radiolyzed and DNO_3 formed. Increased corrosion. Enhanced D_2 and O_2 production so cover gas excursions promoted. Ar^{40} in air $\rightarrow$ Ar^{41}, powerful γ emitter.

COVER GAS

D_2 is the gas that burns or explodes, but only in the presence of oxygen. Hence it is the D_2 concentration which is most critical. If the D_2 concentration is confirmed ≥ 4% but < 6% the reactor must be shut down in a controlled manner. At ≥ 6% D_2 concentration the reactor must be shut down immediately, without waiting for a confirming sample.

There is no shutdown limit for O_2. If O_2 is < ½ D_2 concentration, O_2 is added to the cover gas. If O_2 concentration is > 3% the cover gas is purged with helium. The action level for N_2 is ≥ 2%, at which point purging with helium is initiated, and purification flow is increased if warranted by moderator chemistry.

The lower explosive concentrations for D_2 and O_2 in helium, in the presence of each other are ≥ 8% and ≥ 5% respectively.

Action levels and the required actions are shown in the following table:

GAS	CONCENTRATION %	ACTION REQUIRED
D_2	> 0.1 But < 2	Normal monitoring for rising trend.
	≥ 2	Action Level 2: Hold power. Purge cover gas with helium. Verify gas chromatograph (GC) reading. Determine cause of rising trend. Check dissolved D_2 content. Check recombiners are operational.
	≥ 4	Action Level 3: Confirm GC reading. If ≥ 4%, shut down reactor in a controlled manner.
	≥ 6	Action Level 3: Initiate a reactor shutdown immediately. Do not wait for confirming sample.
O_2	< ½ of D_2	Action Level 1: Add O_2 to cover gas.
	½ of D_2	Normal monitoring.
	> 3	Action Level 1: Purge cover gas with helium. Start analysis of conductivity and other diagnostic parameters if necessary.
N_2	≥ 2%	Action Level 1: Purge cover gas with helium. Increase purification flow if warranted by moderator chemistry.

STARTUP AND SHUTDOWN CONCERNS

(a) Startup Concern

On startup, the major chemistry-related concern for the moderator and cover gas systems is a deuterium excursion, resulting from excessive amounts of D_2 and O_2 in the moderator.

Disturbances from a steady state tend to aggravate the radiolysis process, so it is not surprising that such a large change as a startup can initiate major disturbances in the moderator and cover gas systems.

The following six factors will affect the rate of buildup of D_2 and O_2 in the moderator and cover gas systems:

(i) **Moderator Purity/Cover Gas Condition**

It is essential that the moderator water and cover gas are in the best possible condition prior to startup. Moderator pH should be a little below 7 because of residual gadolinium nitrate which is present in the moderator for xenon simulation. This causes the conductivity to be somewhat above 0.1 mS/m. Air inleakage, that can lead to the formation of nitric acid by radiolysis, must be minimized; and the air must be purged from the system.

There is sufficient fission product gamma energy in a shutdown reactor to allow nitrogen oxides to be formed from air.

A primary startup concern is to ensure that there is not an excess of nitrate in the moderator after return to criticality, because excess nitrate (ie, nitrate from nitric acid) can result in a moderator cover gas deuterium excursion. If, prior to startup, the $Gd:NO_3$ ratio is below specification, special procedures are required to remove the free nitric acid from the moderator. This involves the use of the IX purification system to remove the nitric acid, while making periodic additions of gadolinium nitrate to the moderator to keep the reactor subcritical until the free acid is removed. Conversely, if the $Gd:NO_3$ ratio is above specification, nitric acid is added to the moderator prior to startup. Monitoring is done by analysis of grab samples.

Some impurities in the moderator can affect the buildup of D_2 and O_2 by interfering with aqueous recombination. Some of these impurities are ionic, eg, $Fe^{++(+)}$. Non-ionic impurities such as organics from oil contamination or spent resin beads can also promote buildup.

Not all ionic impurities worsen the situation. For example, Gd^{+++} does not promote the buildup of D_2 and O_2, whereas NO_3^- and Cl^- do. The ions which cause radiolysis problems are those which can exchange electrons with the non-ionized OD radical. For example:

$$\mathbf{Cl^- + \bullet OD \rightarrow Cl\bullet(Chlorine\ atom) + OD^-}$$

The Cl^- is not consumed. It is regenerated and the reaction continues:

$$\cdot Cl + DOD \rightarrow D\text{-}Cl + OD\cdot$$

$$D\text{-}Cl \rightarrow Cl^- + D^+$$

Scavenging of OD• by Cl^- prevents the aqueous recombination reaction:

$$D\cdot + \cdot OD \rightarrow D_2O$$

which is the reaction required to remove the excess deuterium. Since the OD radicals are consumed, the excess deuterium atoms form D_2:

$$D\cdot + D\cdot \rightarrow D_2$$

Dissolved D_2 content in the moderator should be monitored.

To control moderator and cover gas purity, it is essential that the IX columns and cover gas recombiners are functioning correctly. There must be sufficient O_2 addition, at all times, to ensure complete recombination. Cover gas concentration must be monitored continuously during startup.

Gas Interchange Effects

Since the moderator and its helium cover gas are in continuous contact, an exchange of gases is always occurring. The concentration of D_2 in the cover gas depends on the concentration in the moderator. Anything causing changes in the interaction of gas and liquid may lead to an excursion.

In all stations, except PNGS-A, the normal moderator level is up inside the relief ducts, so the cover gas volume is restricted to the small space above the equally small moderator surface in the ducts. However, as shown in Figure 3, a relatively small decrease in moderator volume can cause the moderator level to drop below the duct openings, with a corresponding large increase in the moderator surface area. Thus a small decrease in moderator volume can cause a significant increase in the rate of release of D_2 to the cover gas. The cover gas is therefore a rapid-response system.

(ii) **Reactor Power Increases**

As reactor power is increased during a startup, the neutron and gamma fluxes increase by orders of magnitude. As these fluxes increase, radiolysis increases and, since the flux is continuing to build, a steady state of radiolysis and recombination cannot be reached. Consequently a deuterium excursion could be initiated. Therefore, reactor power is raised slowly.

(iii) **Moderator Temperature**

Gas solubility in water decreases as the water temperature increases.

Increasing reactor power will cause the moderator temperature to rise and therefore the moderator water will degas more, releasing more D_2 and O_2 to the cover gas. The recombiners can be swamped if the release rate is too high. Proper cooling water flow to the moderator heat exchangers is essential.

Raising the reactor power in controlled steps minimizes the severity of these temperature effects and also provides sufficient time for recombination of the D_2 and O_2.

(iv) **Moderator Level (Except Units with Dump Tanks)**

If the moderator level falls below the relief ducts more liquid surface area is exposed for degassing, as shown in Figure 3. This means more D_2 and O_2 can escape from the liquid and a new equilibrium is established with a higher D_2 and O_2 concentration in the cover gas.

Moderator level should therefore be kept up inside the relief ducts to minimize surface area for degassing.

(v) **Cover Gas Pressure**

If the cover gas pressure drops from a steady state, the rate of degassing of the moderator liquid will increase, and it retains less gaseous D_2 and O_2. Therefore, cover gas pressure should be held constant or increased slowly to minimize degassing. Also, when purging, it is essential not to purge too quickly because that would reduce pressure and increase degassing of D_2 from the moderator.

(vi) **Moderator Saturation**

As the dissolved gas concentration in the moderator liquid rises, more D_2 and O_2 will be transferred to the cover gas to maintain equilibrium. A problem can arise if the moderator becomes saturated, because very large quantities of D_2 and O_2 are stored in the moderator and can be released suddenly by a pressure, temperature or level change, or simple supersaturation. In this case, the recombiners may be swamped by the

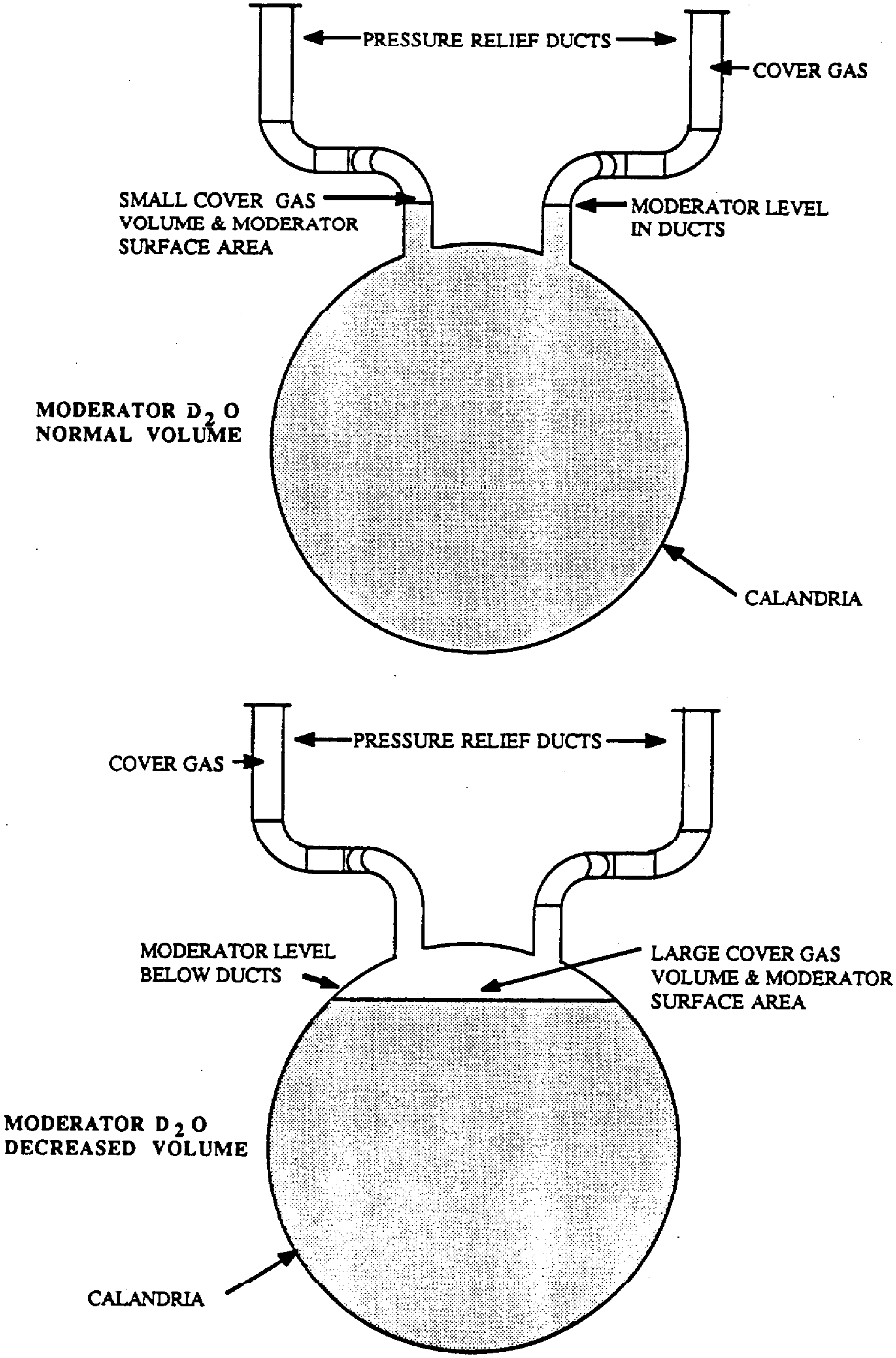

Figure 3: Effects of Moderator Volume On Cover Gas Volume and Moderator Surface Area

sudden increase in gas released, and may not be able to recombine the D_2 and O_2 fast enough to prevent a D_2 excursion.

Sudden releases of D_2 and O_2 are avoided by observing the precautions noted with the previous five factors.

Note: Two operational factors of importance with respect to D_2 and O_2 buildup are the state of the recombiner and its catalyst, and the state of the moderator purification system IX columns. Proper operation of the IX columns in the moderator purification system is essential to minimize the effects of impurities in the moderator.

(b) **Guaranteed Shutdown State (GSS)**

The principal concern, and also a Station License requirement, when the reactor is in the guaranteed shutdown state, is to guarantee that it stays sub-critical and cannot achieve criticality accidentally or unintentionally. The shutdown state is ensured by guaranteeing high concentrations of gadolinium nitrate poison in the moderator. Again the exception is PNGS-A where the moderator is drained to the dump tank for GSS. Another concern is the possible buildup of D_2 and O_2 in the cover gas while in the guaranteed shutdown state, since core gamma fields from fission products are still high.

To ensure that the reactor remains shut down in a safe condition and that D_2 concentrations in the cover gas remain at a safe level, the following requirements must be met:

(i) **Gadolinium Nitrate Concentration**

The gadolinium nitrate concentration required is that which will supply the minimum negative reactivity, as specified in the station operating documents, which will be sufficient to guarantee the reactor cannot start up.

To guarantee that the gadolinium nitrate is not removed from the moderator, the IX columns are locked out of service. Also, to ensure that the gadolinium nitrate will not precipitate out of solution, the moderator pH is held in the 4-6 pH range.

(ii) **Moderator pH**

As noted in (i) above, the moderator must be held in the 4-6 pH range, to prevent the precipitation of the gadolinium poison (High pH) without corroding system components (Low pH). If it is necessary to lower the pH, nitric acid is added to the moderator D_2O. If the pH is too low, removal of the nitric acid must await startup because the purification system is locked out during the guaranteed shutdown.

(iii) **Cover Gas D_2 Concentration**

During an extended shutdown, gases that were dissolved in the moderator D_2O continue to degas from solution. In addition, radiolysis is occurring because of fission product gamma radiation. This could lead to high D_2 and O_2 concentrations in the cover gas, whereas the requirement is ALARA (< 2%). If necessary, to maintain acceptable D_2 and O_2 concentrations, the cover gas system can be kept in service.

Summary

The following tables summarize the major chemistry-related startup and shutdown concerns and requirements.

STARTUP: Major chemistry-related concern is a cover gas deuterium excursion.	
FACTOR	HOW CONTROLLED
Moderator purity. Cover gas condition before startup. D_2 (dissolved) has been forming due to shutdown decay gamma radiolysis. Gd:NO_3 ratio.	Minimize air inleakage and purge. Monitor D_2 content in moderator. Ensure Gd:NO_3 ratio correct. Monitor cover gas concentration. Ensure recombiners operating properly.
Raising reactor power increases flux greatly, precluding equilibrium between radiolysis and recombination.	Raise power in controlled steps. This allows time for moderator and cover gas to stabilize between steps.
Increases in moderator temperature cause more degassing.	Raise power in controlled steps. Ensure recombiners operating properly.
Low moderator level increases surface area for degassing.	Keep moderator level up in relief ducts to minimize surface area. (Pickering A is exception - calandria not full)
Cover gas pressure changes affect degassing rate. Purging can lower pressure.	Maintain constant cover gas pressure or change slowly to control changes in degassing. Purge slowly.
Moderator cover gas D_2, O_2 concentration. Moderator may become saturated.	Prevent saturation and minimize changes as per above comments.

SHUTDOWN: Three Major concerns are $Gd(NO_3)_3$ concentration, Moderator pH and Cover Gas D_2 concentration.		
PARAMETER	CONCERN/REQUIREMENT	HOW CONTROLLED
Gadolinium Nitrate Concentration	Must supply sufficient negative reactivity, as specified in station operating documents, to guarantee reactor cannot start up.	IX columns locked out of service to prevent $Gd(NO_3)_3$ removal. Hold pH 4-6 to prevent precipitation of Gd.
Moderator pH	4-6 pH to prevent precipitation of gadolinium poison by high pH. Also prevents corrosion by low pH.	Lower pH by adding nitric acid. Cannot remove acid to raise pH because IX are locked out.
Cover Gas D_2 Concentration	ALARA (< 2%)	Keep cover gas system in service.

SOURCES OF INFORMATION

Various sources of information have been referenced throughout this lesson, so it is worthwhile to summarize them here.

Moderator

The moderator is monitored by on-line conductivity meters on the bulk moderator and (at some stations) IX outlets. Grab samples are used to confirm the conductivity measurements and to check IX column operation. When a problem occurs, diagnostic tests are done to pinpoint its source. Also, a historical log or "trending" of parameters is kept, as this can be very useful in identifying a problem in its early stages.

Cover Gas

On-line gas chromatographs are used to measure gas concentrations before and after the recombination units. These are verified routinely by chemistry laboratory grab samples, and also when alarm points are reached. For example, when D_2 concentration reaches 4% on the gas chromatograph, the reading must be checked by the chemistry laboratory to avoid an unnecessary shutdown, or to confirm the necessity of a shutdown if it is ≥ 4%.

Summary of Information Sources

Moderator:	On-line conductivity probes verified by chemical analysis of grab samples.
Moderator Cover Gas:	On-line gas chromatograph sampling for D_2, O_2, N_2 before and after the recombination units, verified by chemical analysis of grab samples.

POISON ADDITION TANK AND SDS2 SYSTEM CHEMISTRY

Poison Addition Tanks

Gadolinium nitrate is used for reactivity control during xenon simulations because it "burns up" at a similar rate to the xenon buildup. The poison is added to the moderator D_2O from poison addition tanks, where the gadolinium nitrate is dissolved to a predetermined concentration. The operating manual specifies a minimum concentration of poison. Since the gadolinium ions will precipitate out of solution if the pH rises above 7, the pH in the addition tank must remain below that value ($\approx$ 4) to ensure that the poison concentration will remain sufficient.

Boron is used for fuelling reactivity shim. Although the above discussion of concentration applies here also, it should be noted that boron is not subject to precipitation at any pH. Because of the difficulty in dissolving this poison, care must be taken in preparing the solution (refer to operating manual).

SDS2 Poison Injection System (PNGS-A Excepted)

It is absolutely essential that SDS2 works effectively if a poison injection is triggered. The effectiveness of SDS2 depends on its ability to inject a predetermined negative reactivity into the moderator in a given, short time span. To ensure the correct negative reactivity is available, the concentration of the gadolinium nitrate in all of the SDS2 injection tanks must always be at the specified value. Also, as indicated above, the pH of the gadolinium nitrate poison must be below 7 to prevent the gadolinium ions from precipitating out of solution and thereby reducing the poison concentration. Note that the usual pH of the SDS2 gadolinium nitrate solution in all of the poison injection tanks is approximately 3.

The consequence of a varying or unknown poison concentration in the SDS2 poison injection system is that a low concentration could impair the ability of SDS2 to shut down the reactor in an emergency shutdown situation.

Note: The pH of these solutions is monitored but is not adjusted. If the pH is higher or lower than normal the solution is replaced.

SUMMARY

- **Poison addition** tank concentration must exceed a minimum value. The degree to which the minimum is exceeded is not critical, because the operator monitors reactor power as poison is added to the moderator.
- **Poison injection** tank gadolinium nitrate concentration must equal or exceed a specified value in all tanks to ensure that sufficient negative reactivity is available for shutdown, in stations using gadolinium nitrate. (PNGS-A excepted)
- The pH in all gadolinium tanks must be below 7 to prevent precipitation of the gadolinium.

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