CHEMISTRY - COURSE 224

AUXILIARY SYSTEMS

OBJECTIVES

This lesson will address the Liquid Zone Control System and the Irradiated Fuel Bay.

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

PART A - LIQUID ZONE CONTROL SYSTEM (LZCS)

GENERAL

5.1 For the Liquid Zone Control System, explain the primary objective of chemical control of:

(a) The Main System.
(b) The Cover Gas System.

STANDARD OPERATION

5.2 State the desired operating conditions (numerical values required where indicated) and the method(s) regularly used to maintain these conditions for the following Liquid Zone Control System parameters:

Main System

(a) Zone water conductivity (specification value required)
(b) Zone water pH } diagnostic parameters
(c) Zone water chloride } diagnostic parameters

Cover Gas

(d) Cover gas H_2 concentration
(e) Cover gas O_2 concentration
(f) Cover gas N_2 concentration

NON-STANDARD OPERATION

5.3 For each of the following Liquid Zone Control System parameters, state:

(a) The possible cause(s), or source(s) where applicable, of the non-standard 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)		
1	1	3	(i)	High zone water conductivity
1	1	2	(ii)	High zone water chloride
2	3	2	(iii)	High cover gas H_2 and O_2 concentrations
1	2	3	(iv)	High cover gas N_2 concentration

SOURCES OF INFORMATION

5.4 State two sources of information employed to monitor Liquid Zone Control chemical parameters.

PART B - IRRADIATED FUEL BAY (IFB)

GENERAL

5.5 State the three major objectives of chemical control of the IFB water.

STANDARD OPERATION

5.6 State the desired operating conditions and the method(s) regularly used to maintain these conditions for the following IFB parameters:

(a) IFB radionuclide inventory
(b) IFB conductivity
(c) IFB turbidity

NON-STANDARD OPERATION

5.7 For each of the following IFB parameters, state:

(a) The possible cause(s), or source(s) where applicable, of the non-standard 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)		
1	2	2	(i)	High I-131 and other radionuclides
1	1	3	(ii)	High conductivity
2	3	1	(iii)	High turbidity

SOURCE OF INFORMATION

5.8 State two sources of information employed to monitor the IFB parameters.

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PART A - LIQUID ZONE CONTROL SYSTEM (LZC)

INTRODUCTION

The chemistry of the liquid zone system, including its cover gas, is the same as that of the moderator and its cover gas, except for the lack of poisons in the LZC. Since its function is to insert or remove negative reactivity, the LZC system uses light water (a neutron absorber). The LZC system helium cover gas is more highly pressurized than the moderator cover gas, for example from about 105 kpa(d) to 480 kpa(d) depending on the station. This relatively high, constant zone cover gas differential pressure provides the driving force required to maintain a constant flow of water out of the zones.

GENERAL

Main System

The primary objective of chemical control of the Main System is to maintain the zone water in a high purity state in order to minimize radiolytic decomposition. The light water in each of the fourteen zones in the calandria is in a high radiation field much of the time. Therefore the radiolysis of this light water cannot be prevented, but is minimized by keeping the water purity as high as possible. This is achieved by using demineralized water from the water treatment plant for the LZC system fill and makeup, and through the use of a side stream purification loop.

As is evident from its function of providing negative reactivity inside the reactor, the zone water is continually bombarded with gamma rays and fast neutrons. This radiation decomposes the light water (just as it does the moderator D_2O) into hydrogen and oxygen by the process of radiolysis:

$$2H_2O \xrightarrow{\gamma \text{ or } n} 2H_2 + O_2$$

The above equation summarizes a complicated sequence of intermediate reactions involving molecules, atoms, ions, electrons and free radicals. These reactions were described in detail for D_2O in the moderator lesson 224.03.

Again, it is emphasized that these reactions cannot be prevented and also that impurities in the liquid zone water usually aggravate radiolysis by interfering with the back-reaction $H + OH \rightarrow H_2O$. One example is chloride:

$$Cl^- + \bullet OH \rightarrow Cl + OH^-$$

The hydroxyl radical has become a hydroxyl ion, which cannot react with hydrogen atoms to form water. Thus, more hydrogen atoms are free to combine into gaseous H_2 molecules.

Finally, impurities will also increase radiation fields through activation and may be corrosive as well. It is essential therefore to keep the zone water pure.

Summary

- Radiolysis of zone water cannot be prevented.
- Radiolysis is minimized by keeping zone water pure.
- Impurities in the zone water may enhance radiolysis, and may be corrosive.
- Activated impurities in the zone water will increase radiation fields throughout the zone control system.

Cover Gas

The primary objective of chemical control of the cover gas system is to maintain concentrations of hydrogen, oxygen, nitrogen, and argon in the cover gas ALARA. The hydrogen is an explosion hazard in the presence of oxygen. The oxygen supports combustion and is corrosive. Nitrogen, which can be present due to air in-leakage, radiolyzes with water into nitric acid which increases the production of radiolytic hydrogen. Air in-leakage will also permit the ingress of argon, (1% of air) which is activated to Ar-41, increasing fields in accessible piping areas.

Summary

- H_2, O_2 and N_2 must be kept ALARA.
- H_2 is an explosion hazard.
- O_2 is corrosive, and supports combustion/explosion of H_2.
- N_2 radiolyzes and forms HNO_3.
- Argon becomes Ar-41, increasing fields.

STANDARD OPERATION

The purity of the water in the LZC main system is controlled by ion exchange and is monitored using conductivity measurements.

The liquid zone cover gas purity is controlled by controlling water purity, using recombiners, and by purging with helium, if necessary.

Main System

(a) **Zone Water Conductivity**

Conductivity is the only control parameter for zone water purity; its specification is ≤ 0.1 mS/m and the desired level is ALARA. Conductivity is a general indicator of water purity, in that it is increased by the presence of dissolved ionic substances. As long as the conductivity does not exceed specification, the water purity is high enough to minimize the formation of the H_2 and O_2 by radiolysis.

Control is achieved through the use of ion exchange resins. Should the conductivity rise above specification, a fresh IX column would be placed in service. If it is necessary to identify the reason for the high conductivity, for example to determine the presence of air in-leakage or a spent IX column, an analysis of the **diagnostic parameters**, pH and chloride, may be utilized.

(b) **Zone Water pH** (Diagnostic only)

The normally pure water is so low in conductivity that reliable pH readings cannot be obtained directly. A reproducible reading below seven would indicate HCL elution from a spent resin column. This could, in turn, be due to nitric acid from air ingress. Typical operating value for pH is 6-8.

(c) **Zone Water Chloride** (Diagnostic only)

A typical operating value for Cl^- is < 0.1 mg/kg. This is achieved using IX resins.

In addition to the above a "historical record" should be maintained through monthly analyses of chloride, pH and tritium, to provide baseline data for trouble-shooting and problem-solving.

Cover Gas

(d) **Cover Gas Hydrogen Concentration**

Hydrogen is the main control parameter. The specification is ≤ 2%. The desired value is ALARA.

In addition to water purity, control is through the use of recombination units, supplemented by purging with helium if required.

(e) **Cover Gas Oxygen Concentration**

The specification for oxygen is ≤ 3%. The desired value is ALARA.

Control is by recombination with the hydrogen to water, and by purging with helium if necessary.

(f) **Cover Gas Nitrogen Concentration**

The specification for nitrogen is ≤ 1%. The desired value is ALARA.

Control is by minimizing ingress of air and by purging with helium when necessary. This control action will also minimize the presence of argon.

Summary

The following table summarizes the standard conditions for the LZC system. Only values marked (*) are to be memorized.

PARAMETER		SPECIFICATION	DESIRED VALUE	CONTROLLED BY
Water	Conductivity	≤ 0.1 mS/m *	ALARA	IX resin.
	pH	None	Typical Value 6-8	Diagnostic parameters only.
	Cl^-	None	Typical Value < 0.1 mg/kg	
Cover Gas	H_2	≤ 2%	ALARA*	High water purity. Recombiners. Purging if needed.
	O_2	≤ 3%	ALARA *	Recombiners.
	N_2	≤ 1%	ALARA*	Minimize air ingress. Purging.

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.

There are no Action Level 3 parameters for the Liquid Zone System.

(i) **High Zone Water Conductivity**

Cause/Source

The normal cause of high system conductivity is a spent IX column. This is confirmed by checking the conductivity of the column effluent.

Method of Control

Control of high zone water conductivity is achieved by placing a fresh IX column in service. If the conductivity specification of ≤ 0.1 mS/m is exceeded, it must be restored within one week. If the conductivity rises to > 1 mS/m, it must be restored to ≤ 0.1 mS/m within one day.

Consequences If No Action Taken

If the spent IX column is not replaced, production of radiolytic H_2 and O_2 will increase. If Cl^- is the source of the high conductivity, the risk of stress corrosion cracking of stainless steel components also increases. A further potential consequence is unwanted gamma fields due to activation of the impurities in the water.

(ii) **High Zone Water Chloride**

Cause/Source

The source of high zone water chloride is a spent IX column eluting Cl^-.

Method of Control

The control of chloride is the same as for high conductivity, ie replace the spent column.

Consequences If No Action Taken

One consequence is increased radiolytic hydrogen. A further consequence is that Cl^- in the zone water increases the risk of stress corrosion cracking (SCC) of the stainless steel components in the LZC system.

(iii) **High Cover Gas Hydrogen and Oxygen Concentrations**

Causes/Sources

Two causes of high cover gas hydrogen and oxygen concentrations are:

- Radiolysis of impure zone water.
- Recombiners not functioning.

Another cause of high hydrogen may be insufficient oxygen.

Methods of Control

Control is by purifying the zone water (ensuring IX functioning properly), restoring the recombination units to service, and purging the cover gas with helium.

Consequences If No Action Taken

The consequences are possible explosion within the cover gas system and increased corrosion by oxygen.

(iv) **High Cover Gas Nitrogen Concentration**

Cause/Source

The source of cover gas nitrogen is leakage of air into the cover gas system.

Methods of Control

Control is achieved by eliminating air in-leakage and purging the cover gas system with helium.

Consequences If No Action Taken

One consequence is an increase in radiolytic H_2 and O_2. A further consequence is added HNO_3 load on the IX columns. (Radiolysis of air into NO_2 followed by dissolution into the water). Ar-41 fields may also become a problem. (Air is 1% Ar-40)

If the specification for cover gas hydrogen, oxygen, or nitrogen is exceeded, it must be restored within one week.

If the hydrogen concentration exceeds 4%, it must be restored to specification within one day.

Summary

The following table summarizes the non-standard conditions for the LZC system:

SYSTEM	PARAMETER	CAUSE/SOURCE	METHOD OF CONTROL	CONSEQUENCE IF NO ACTION TAKEN
Main System	Conductivity Above Spec.	Spent IX column	Place new IX column in service.	Increased production of radiolytic H_2 and O_2. SCC of Stainless Steels increases if due to Cl^-. Increased radiation fields.
	Chloride High	Spent IX column	Place new IX column in service.	Increased possibility of SCC of stainless steels. Increase in radiolytic H_2 and O_2.
Cover Gas System	H_2 High	Radiolysis of zone water. Recombiners not working.	Purify zone water. Check IX and recombiners. Purge if necessary with helium.	Explosion hazard.
	O_2 High	Same as for high H_2.	Same as for high H_2.	Explosion hazard. Increased corrosion.
	N_2 High	Air ingress.	Eliminate air ingress. Purge with helium.	Increase in radiolytic H_2 and O_2. Added HNO_3 load on IX columns. Ar-41 fields.

SOURCES OF INFORMATION

Main System

The only source of information for the water chemistry in the liquid zone control system is the chemical analysis of grab samples. Some stations have on-line conductivity analysis.

Cover Gas

Cover gas H_2, O_2, and N_2 concentrations are measured by an on-line gas chromatograph.

PART B - IRRADIATED FUEL BAY (IFB)

INTRODUCTION

Since the Irradiated Fuel Bay is the holding area for all irradiated fuel from the reactor, it is necessary to be able to safely observe the irradiated fuel for a long period of time. Therefore, it is essential that any leakage of radionuclides be detected immediately, that corrosion of IFB components and irradiated fuel bundle sheaths be minimized, and that the water be kept clear for maximum visibility.

GENERAL

One major objective of chemical control of the IFB water is to maintain the radionuclide inventory (especially I-131) ALARA. In the event that a defective fuel bundle is discharged to the IFB, radionuclides from the fuel will be released to the water. The most limiting radionuclide is I-131. In order to minimize this radiological hazard, it is necessary to hold the radionuclide inventory in the IFB water ALARA.

Another major objective is to maximize visibility of the irradiated fuel in the IFB, by maintaining the turbidity (cloudiness due to suspended solids) of the water ALARA.

A third major objective of chemical control of the IFB water is to minimize corrosion of the fuel cladding and of IFB auxiliary components. This will also minimize the creation of suspended solids that would reduce the clarity of the IFB water.

Summary

- Radionuclide inventory, especially I-131, must be kept ALARA.
- Corrosion of irradiated fuel sheaths and IFB components must be minimized.
- IFB water must be kept clear for fuel visibility.

STANDARD OPERATION

Control and Monitoring of IFB Operating Conditions

The purity of the IFB water is maintained by filters and IX resins and is monitored by the chemical analysis of grab samples.

(a) **IFB Radionuclides**

The I-131 specification for the IFB is ≤ 5 μCi/kg, and the desired operating condition is ALARA. As noted previously, I-131 is the most limiting radionuclide.

Control is by IX columns, and the canning of defective fuel.

(b) **IFB Conductivity**

The conductivity specification is ≤ 0.2 mS/m. The desired operating condition is ALARA to minimize corrosion of fuel bundles and IFB auxiliary components and maintain an essentially neutral pH. Corrosion by oxygen is not a concern in the ambient conditions of the IFB.

Control is by IX resins. Monitoring of the IX column outlet, by the conductivity measurement of grab samples, indicates when the resin is spent.

(c) **IFB Turbidity**

The turbidity of a fluid is a measure of the amount of solids in suspension. Turbidity control is usually achieved via filters in the purification loop.

The turbidity specification is ≤ 1 Formazen Turbidity Unit (FTU). The desired operating condition is ALARA. The NTU or Nephelometer Turbidity Unit is also used in station chemistry laboratories. 1 NTU = 1 FTU.

Summary

- Desired condition for I-131 radionuclide inventory, IFB conductivity and turbidity is ALARA.
- Control of I-131 and conductivity is by IX columns and canning defective fuel.
- Control of turbidity is usually via filters.

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.

There are no Action Level 3 parameters for the IFB.

(i) **High I-131 and Other Radionuclides**

Cause/Source

The source of I-131 and other radionuclides is defective fuel bundles in the bay.

Methods of Control

Control is by canning defective fuel to prevent releases to the IFB. If necessary, hydrazine (N_2H_4) is added to the IFB water to convert iodine into non-volatile iodide which can be removed **later** by the IX columns. The following equation shows that the hydrazine ionizes to $N_2H_5^+$ in water, and would be removed by the IX columns if they were not valved out (isolated) before the hydrazine is added.

$$N_2H_4 + H_2O \rightleftharpoons OH^- + N_2H_5^+$$

The volatile Iodine is converted to non-volatile Iodide by the hydrazine via the following chemical reactions:

$$I_2 + H_2O \rightleftharpoons H^+I^- + HOI$$

and $$2HOI + N_2H_4 \longrightarrow 2H^+ + 2I^- + 2H_2O + N_2$$

When the IX columns are put back into service, the resins remove the hydrogen iodide (H^+I^-) and any excess hydrazine from the IFB water.

IFB fixed area gamma monitors and/or semi-portable air samplers are used to monitor for I-131.

If the I-131 Action Level 1 specification of >5 µCi/kg is exceeded, it must be restored within 1 week. The second action level is at >25 µCi/kg and requires restoration within one day.

NOTE: Pickering has in place a procedure under certain conditions to suppress iodine volatility by raising the pH of the IFB to heat transport system levels. The reaction is as follows:

$$6\ I_2 + 12\ OD^- \rightarrow 10\ I^- + 2\ IO_3^- + 6\ D_2O$$

This also facilitates removal by IX by converting all the iodine to ionic species. The station is considering keeping the IFB alkaline at all times.

Consequences If No Action Taken

Consequences include both increased radiation fields in the IFB area and the increased potential for release of radioactive material.

(ii) **High Conductivity**

Cause/Source

The cause of high conductivity is any ions, radioactive or otherwise, that enter the IFB water.

Method of Control

Control is by IX resins in the purification loop. Spent IX columns are detected by measuring the conductivity of grab samples of the column effluent.

If the conductivity specification of 0.2 mS/m is exceeded, it must be restored within one week. The second action level is at 4 mS/m and requires restoration within one day.

Consequences If No Action Taken

High conductivity will result in increased corrosion of fuel bundles and of IFB components, eg, pipes and pumps. Fuel bundles will fail from corrosion, resulting in increased radionuclide inventory in the water, and higher radiation fields. Increased turbidity, due to suspended corrosion products, as water purity falls, will impair viewing irradiated fuel.

(iii) **High Turbidity**

Causes/Sources

Any suspended solids, such as corrosion products or fuel particles suspended in the IFB water will increase turbidity. Poor quality make up water can cause turbidity and on occasion, algae growth has also been a problem.

Methods of Control

The primary control is by maintaining high water purity through IX columns. Filters are also used at most stations. Algae may require the use of a biocide.

If the turbidity Action Level 1 specification of >1 FTU is exceeded, it must be restored within one week.

Consequence If No Action Taken

Any increase in turbidity will decrease the visibility of the fuel stored in the IFB.

Summary

The following table summarizes the non-standard conditions for the IFB:

PARAMETER	CAUSE/SOURCE	METHOD OF CONTROL	CONSEQUENCE IF NO ACTION TAKEN
High I-131 and other radionuclides	Defective fuel bundles in IFB.	Canning defective fuel. Add hydrazine to form non-volatile iodides and remove iodides later by IX.	Increased radiation fields. Potential for activity release.
High Conductivity	Any ions entering IFB. Poor quality makeup water.	IX resins. Control source.	Increased corrosion of fuel bundles and IFB components. Increased radionuclide inventory and higher radiation fields. Increased turbidity.
High Turbidity	Any suspended solids. Poor quality makeup water. Algae.	IX columns. Filters. Control source. Biocide may be required.	Loss of visibility of fuel bundles stored in IFB.

SOURCE OF INFORMATION

The source of information employed to monitor the IFB control parameters of I-131, Conductivity and Turbidity is the chemical analysis of periodic grab samples.

Fixed area gamma monitors and/or semi-portable air samplers are used to monitor the IFB air for I-131.

ASSIGNMENT

Part A LZC System

1. (a) State the two primary objectives of chemical control of the Liquid Zone Control System.

   (b) Describe briefly how these objectives are achieved.

2. State the consequences if the objectives you listed in question 1(a) are not met.

Part B IFB System

1. State the primary objective of chemical control of the IFB and explain its significance.

2. State the two other objectives of chemical control of the IFB water.

3. (a) Describe briefly how the objectives listed in 1 and 2 are achieved.

   (b) State the consequences if these objectives are not met.

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