

CHEMISTRY - COURSE 224**THE HEAT TRANSPORT AND AUXILIARY SYSTEMS**

OBJECTIVES

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

General

- 4.1 (a) State and briefly explain the primary objective of chemical control of the Heat Transport System (HTS).
- (b) State five other major objectives of chemical control of the Heat Transport System.

Standard Operation

- 4.2 State the desired operating conditions (numerical values required where indicated) and describe the method(s) regularly used to maintain these conditions for the following Heat Transport System parameters:
- (a) I-131 (desired value required)
 - (b) pH (specification values required)
 - (c) Chloride (desired value required)
 - (d) Dissolved Deuterium (specification values required)
 - (e) Dissolved Oxygen
 - (f) D₂, O₂ and N₂ in the HTS Storage Tank Cover Gas

Non-standard Operation

4.3 For each of the following Heat Transport 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.

<u># Required</u>		
(a)	(b)	(c)
1	3	2
3	2	2
1	1	1
2	2	1
2	2	3
1	1	2
3	2	4

- (i) High I-131
- (ii) Low pH
- (iii) High pH
- (iv) High Chloride
- (v) Low Dissolved Deuterium
- (vi) High Dissolved Deuterium
- (vii) High D₂, O₂ and N₂ in the HTS Storage Tank Cover Gas

Sources of Information

4.4 State two sources of information employed to monitor the Heat Transport System chemical parameters.

INTRODUCTION

The heat transport system is a heavy water system that is in a radiation flux only while the water is passing through the reactor core. It is a closed system with pressure and temperature approaching 9 MPa and 300°C, respectively. The flow rate in a large reactor is ≈ 25 kg/s per channel.

Associated with the main HTS is the D₂O storage tank and its helium cover gas system. The heavy water in this tank is essentially stagnant except for receiving bleed from the HTS during HTS swell, providing feed for the HTS during HTS shrink conditions, and receiving some D₂O from the HTS pump glands. This tank also provides make-up for normal leakage.

Figure 1 provides an overview of the heat transport system chemistry concerns discussed in this lesson.

GENERAL

Objectives of Chemical Control of the HTS

The primary objective of chemical control of the HTS is to minimize the corrosion of the various system materials/components, including:

- Zirconium alloy pressure tubes and fuel sheaths,
- Carbon steel piping, feeders, headers and storage tanks,
- Monel, Inconel or Incoloy boiler tubes.

Carbon steel is used for reasons of high strength and economy, but it is vulnerable to corrosion. Its use therefore demands careful control of the chemistry of the HTS D₂O.

Chemical control of the HTS has five other major objectives, the first of which is to control radiation fields in the HTS. This is achieved by minimizing corrosion and therefore minimizing the amount of suspended and dissolved corrosion products

224.04

Heat Transport : Controlled parameters

pH,
Dissolved D₂,
Chloride (corrosive),
I-131 (shutdown required if
over limit).

Method of Control

1. IX resins (lithiated) + LiOH (in D₂O)
addition if necessary (pH too low).

Use unlithiated column if pH too high.
pH kept at 10.3 - 10.7 to minimize
corrosion, and therefore active corrosion
products.

2. Add Hydrogen (maintains low O₂).

Storage Tank : Controlled parameters

Deuterium (explosion hazard in
the presence of oxygen),
Oxygen (increases corrosion),
Nitrogen (can cause Nitrate
production - loads IX
columns).

Method of Control

Helium purge.

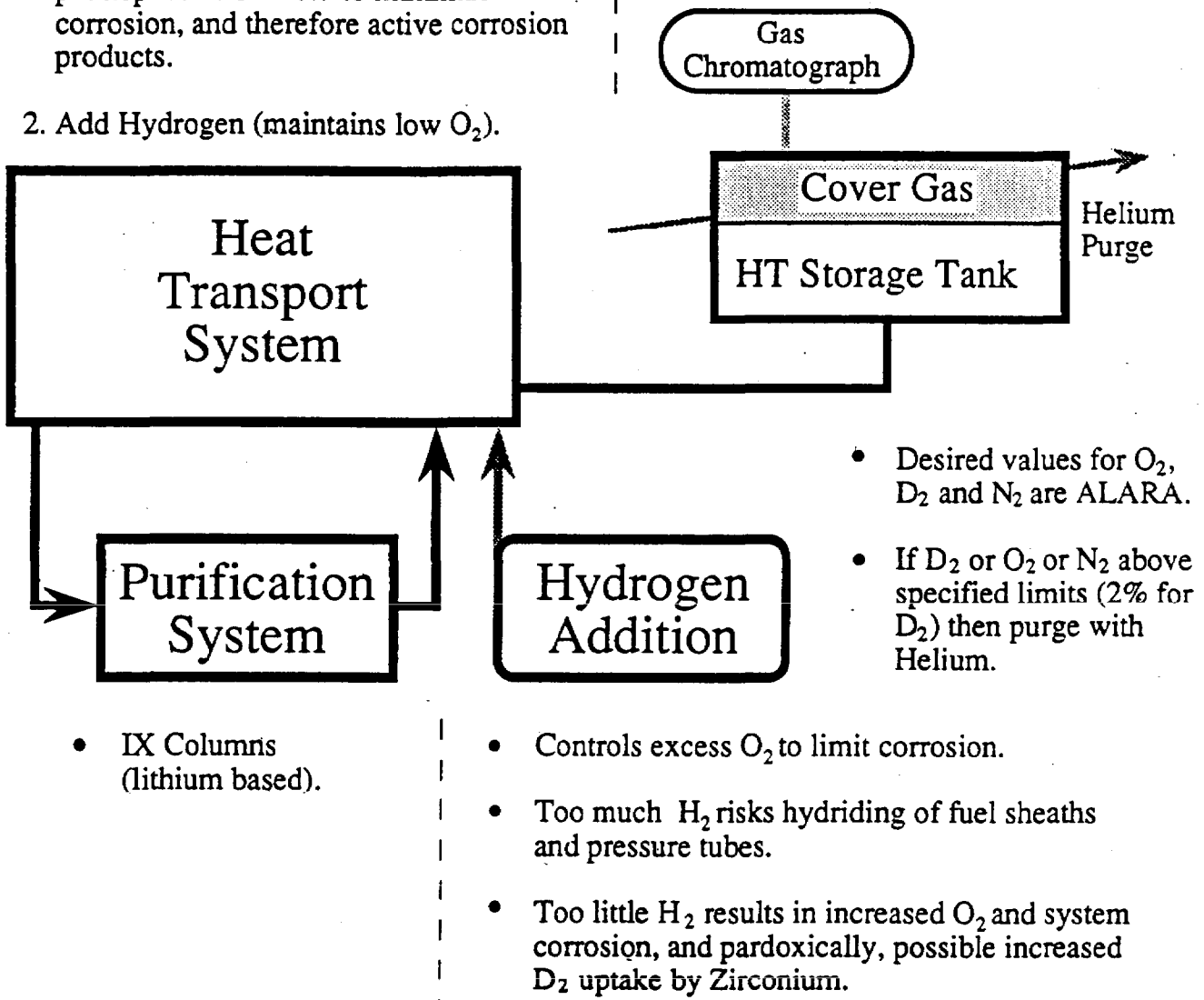


Figure 1: An Overview of Heat Transport System Chemistry

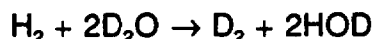
subject to neutron activation. Also, by reducing the likelihood of fuel sheath failure, the possibility of fission products such as I-131 escaping into the water are minimized. Reducing fields reduces employee exposure to radiation.

Another objective of HTS chemistry control is to maintain I-131 concentrations below the shutdown limit. This constraint is part of the station OP&Ps.

Any fission product iodines and bromines not chemically combined as halide ions are very volatile at operating temperatures and can therefore escape through even tiny holes in defective fuel sheaths. This fact, combined with the relatively long 8-day half life of I-131, makes this particular fission product especially dangerous, hence the shutdown limit for I-131.

Conditions giving rise to zirconium hydride formation in the pressure tubes must be avoided, namely too much or **too little** dissolved deuterium.

A fourth objective of HTS chemistry control is to maintain HTS storage tank cover gas hydrogen/deuterium and oxygen concentrations below explosive limits. (This is a less serious concern than for the moderator). D₂ and O₂ are present due to radiolysis of D₂O. Deuterium/hydrogen are also present because of the hydrogen added to the heat transport system to scavenge oxygen. Because of the flux, H₂ in the water carried into the reactor exchanges very quickly with the deuterium of D₂O:



As a final objective, nitrogen is also maintained ALARA because it radiolyzes to nitrogen oxides which can form nitrous and nitric acid, placing an added load on the ion exchange resins. Nitrogen can enter the system via the D₂O storage tank cover gas.

Summary

- The primary objective of chemical control of the HTS is to minimize corrosion of system components.
- Five other major chemical objectives are to:
 - Control/minimize radiation fields in the HTS.
 - Maintain I-131 concentration below the shutdown limit.
 - Ensure conditions leading to zirconium hydride are minimized.
 - Maintain HTS storage tank cover gas D₂ and O₂ concentrations below explosive concentrations.
 - Maintain nitrogen concentration ALARA to minimize production of nitric/nitrous acid via radiolysis.

STANDARD OPERATION**Control and Monitoring of HTS Operating Conditions****(a) I-131**

The desired operating condition for I-131 content in the HTS water is ALARA. (Pickering units are required to shut down if an inventory of 1000 curies is reached. The shutdown limit for Bruce and Darlington units is ≥ 500 curies for ≥ 8 hours).

Control is maintained via a feed circuit to ion exchange columns and by quick removal of defective fuel. Removal of I-131 by IX resins is possible because, in the alkaline heat transport system, most of it is present in ionic form (I^- , IO_3^-). In neutral water iodine is only slightly ionic.

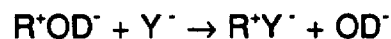
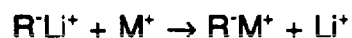
(b) pH

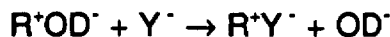
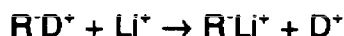
The pH specification for the HTS is 10.3 to 10.7 and the desired value is 10.3 to 10.5. This pH minimizes the corrosion of both carbon steel (especially vulnerable to acid attack) and zirconium (caustic attack above pH 13). It also helps to maintain the integrity of the protective magnetite (Fe_3O_4) layer which is formed during the chemical conditioning phase of heat transport system commissioning. Unlike rust (hematite), which is Fe_2O_3 , magnetite is tightly-adhering and non-porous, thus protecting the underlying carbon steel from the hot water and radiolytic dissolved oxygen.

The source of the alkalinity is the lithium deuterioxide in the IX resins, supplemented if necessary by LiOH (in D_2O) additions. If the pH goes above specification, it is brought down again by valving in a D-OD IX column in place of an Li-OD column.

The following equations show how these resins work:

R	represents resin polymer
M^+	represents impurity cation
Y^-	represents impurity anion

Lithium Deuterioxide Production To Increase pH:

Lithium Deuterioxide Removal To Lower pH:**(c) Chloride**

Since the chloride ion is corrosive, its desired value is ALARA. (The Cl^- specification is ≤ 0.2 mg/kg.) It is very harmful to ferrous metals, especially stainless steel (stress corrosion cracking).

Chloride concentration is kept low by the IX resins and is monitored by chemical analysis of grab samples. Recall that one criterion for declaring the resin spent or exhausted is an increase in Cl^- in the IX column effluent caused by traces of chloride in ion-exchange sites being displaced from spent resins by impurity anions. The bleed cooler temperature over-ride protects the IX resin from overheating and releasing chloride ions.

(d) Dissolved Deuterium

The specification for dissolved D_2 is 3-10 cc/kg D_2O . The desired value is 7 cc/kg D_2O . The purpose of dissolved D_2 is to scavenge radiolytic O_2 ($2D_2 + O_2 \rightarrow 2D_2O$) because the oxygen is corrosive. Oxygen also causes the zirconium dioxide layer to become thicker and more porous and therefore less protective. D_2 can diffuse more readily into the zirconium pressure tubes.

The dissolved D_2 concentration is controlled by the continuous addition of hydrogen gas, H_2 . As described earlier almost all of this H_2 exchanges isotopically to HOD because of the flux. This does not create any chemical problems and the economic penalty associated with the downgrading is less than the cost of obtaining D_2 for hydrogen addition. The addition of too much H_2 would increase the risk of hydriding in the fuel sheaths and pressure tubes.

(e) Dissolved Oxygen

Maintaining low dissolved oxygen is important for minimizing the corrosion of carbon steel and zirconium. Low O_2 concentration is also important because:

- O_2 can cause SCC of inconel boiler tubes (Bruce stations)
- O_2 increases the aggressiveness of the Cl^- ion (see 224.02)

Maintaining dissolved deuterium within specification keeps the dissolved oxygen concentration below the detection limit. Also the analysis for dissolved D_2 is less difficult than the analysis for dissolved O_2 . Therefore there is no specification for dissolved oxygen, but it is important to remember that dissolved O_2 is a very harmful impurity in the HTS system.

(f) **D_2 , O_2 and N_2 in the HTS Storage Tank Cover Gas**

The desired value for D_2 , O_2 and N_2 in the HTS storage tank cover gas is ALARA. The actual specifications are:

$$D_2 \leq 2\%$$

$$O_2 \leq 2\%$$

$$N_2 \leq 8\%$$

The cover gas is monitored by an on-line gas chromatograph and grab sample analysis. Control is by purging the storage tank cover gas with clean helium if the above specifications are exceeded.

Summary

- The following table summarizes the standard operating conditions for the HTS: Only the values marked (*) are to be memorized.

SYSTEM	PARAMETER	SPECIFICATION	DESIRED VALUE	CONTROL METHOD
Main HTS	pH	* 10.3 - 10.7	10.3 - 10.5	LiOD IX resins
	Dissolved D_2	* 3-10 cc/kg	7	H_2 addition
	Cl^-	< 0.2 mg/kg	* ALARA	IX resins. Bleed cooler temperature over-ride
	I-131	(1)	* ALARA	IX resins. Removing defective fuel.
HTS Storage Tank Cover Gas	D_2 , O_2 , N_2	$D_2 \leq 2\%$ $O_2 \leq 2\%$ $N_2 \leq 8\%$	ALARA	Purging with Helium.
(1) Pickering is required to shut a unit down if an inventory of 1000 curies is reached. At the Bruce and Darlington stations, the shutdown limit is ≥ 500 curies for ≥ 8 hours.				

There is no specification for dissolved O_2 in the main HTS because maintaining dissolved D_2 within its specification keeps dissolved O_2 below the detection limit.

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.

Chloride and high pH have Action Level 3 limits requiring shutdown within 4 hours. For I-131 the Action Level 3 specification requires immediate, controlled shutdown.

(i) High I-131

Cause/Source

The source of high I-131 is defective fuel, sometimes although rarely, in conjunction with IX resin spent on iodine.

Method of Control

Control of a high I-131 situation is achieved by removing the defective fuel, maximizing purification by IX columns and by not changing reactor power.

Consequences If No Action Taken

The consequences of high I-131 are unnecessarily high radiation fields and activity transport. If the Action Level 3 specification is exceeded, the unit **must be shut down immediately** in a controlled fashion. This limits dose to the public if a LOCA and subsequent releases outside of containment occur.

(ii) Low pH

Causes/Sources

Low pH results from one or more of the following:

(a) Spent IX resins:

When spent, the resins contain no more LiOD to be eluted into the water.

(b) Presence of lithium as carbonate rather than deuterioxide:

The carbonate has three sources:

- (i) The resin as purchased. Because of the alkalinity of the LiOH in the resin, carbon dioxide is absorbed from the air. The manufacturer will not guarantee any less than 15% CO_3^{--} in the anion exchange sites.

- (ii) Resin radiolysis by captured fission and activated corrosion products. The terminal radiolyte of organic matter in alkaline water is carbonate.
 - The relative importance of these two chronic carbonate sources is not yet known. Although alkaline, lithium carbonate is a much weaker base than lithium hydroxide.
- (iii) Carbon dioxide absorption from the air if the HTS is open during shutdowns.

(c) LiOD "hide-out" in stations with passing pressurizer valves:

Steam escapes from the pressurizer to the bleed condenser and is replaced by HTS water (LiOD solution), resulting in an increased concentration of LiOD in the pressurizer and a corresponding drop in system pH. The Pickering units do not have pressurizers.

Methods of Control

Low pH is controlled by addition of LiOH dissolved in D₂O and/or valving in fresh IX resins as required. Analyses at Pickering in 1988 show instances where > 90% of the lithium was present as carbonate rather than deuterioxide. Bruce-1 has had periods of pressurizer valves passing so badly that ½ kg LiOH had to be added twice a month.

Consequences If No Action Taken

A pH below specification increases the activity transport of corrosion products. Corrosion products are activated as they pass through or reside in the reactor core so that the amount of activated corrosion product is directly related to the amount of corrosion product in-core. Magnetite is the main corrosion product. It follows similar chemical behaviour to cobalt, manganese, and nickel isotopes, which are easily activated. At pH of 10.2, magnetite solubility increases with temperature so that little should deposit on hotter in-core surfaces. At pH 9.3 and lower, the solubility of magnetite is inverse with temperature. Magnetite is less soluble at higher temperatures and will deposit on the hotter in-core surfaces. Figure 2 shows this effect. Operation at lower pH can lead to reduced heat transfer from the fuel, fuel sheath hot spots, and fuel failure. Also increased activity generated in core will ultimately produce increased fields out-of-core.

For carbon steel, the minimum corrosion rate occurs around pH 11. The corrosion rate, however, is acceptably low for steel integrity to a pH of 7.

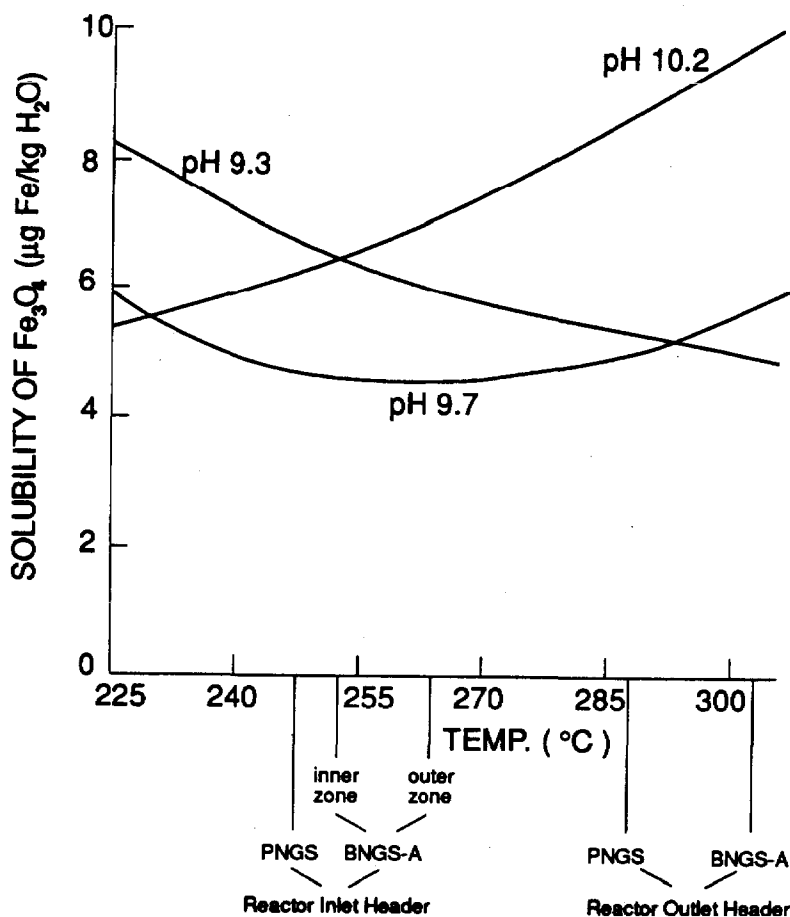


Figure 2: Solubility of Magnetite Versus Temperature for Different pH

(iii) **High pH**

Cause/Source

High pH on start-up is common in units where LiOD hide-out has occurred. When cooling down or lowering reactor power HTS shrink occurs, drawing D_2O and LiOD from the pressurizer into the HTS and causing a high pH in the HTS. This high pH is encountered on start-up as a pH excursion. On one occasion a start-up at Bruce-A produced a system pH of 11.8.

Method of Control

High pH is controlled by valving in a D-OD IX column to remove the excess lithium.

Consequences If No Action Taken

A pH above specification endangers the protective ZrO_2 layer, and enhances corrosion of the pressure tubes beneath the fuel bearing pads. Lithium hydroxide, the source of the alkalinity, can concentrate there and attack the zirconium alloy via crevice corrosion. See 224.01.

For carbon steel, the minimum corrosion rate occurs around pH 11. The corrosion rate, however, is acceptably low for steel integrity to a pH of 13.

- **Conductivity and Lithium**

Although conductivity and lithium are not controlled in the HTS and do not, therefore, have standard or desired values, they are important diagnostic parameters. As such, they are used at all Action Levels, if the HTS pH goes out of specification. If the amount of lithium present is substantially greater than the system pH would indicate, conductivity measurements of grab samples are used to help explain this discrepancy by indicating, for example, the presence of other ions, usually carbonate. Correlations between conductivity and the concentrations of ionic species are possible because the specific conductivities of individual ions are known.

(iv) **High Chloride**

Causes/Sources

High chloride is normally caused by spent IX columns. Overheated resins (unlikely) will also result in high chloride.

Methods of Control

Control is achieved by valving in fresh IX columns and by ensuring that IX resins are not overheated.

Consequence If No Action Taken

High chlorides are particularly harmful to ferrous metals, and especially so to stainless steels, eg, end fittings.

(v) Low Dissolved Deuterium**Causes/Sources**

Low dissolved D_2 is caused by insufficient H_2 addition. However it should be noted that if a unit has a significant leak, ie, a bleed condenser gasket leak, the rate of D_2 loss may exceed the flow capability of the H_2 addition system. This situation occurred several years ago at Bruce-4.

Methods of Control

Control is to increase H_2 addition and, if necessary, replace the leaking bleed condenser gasket, a shutdown job lasting several days.

Consequences If No Action Taken

Since the purpose of the dissolved D_2 is to scavenge O_2 , the result of too little dissolved D_2 is too much dissolved O_2 . Oxygen corrodes both zirconium and carbon steel, and can convert protective oxide layers into porous oxide layers. This allows attack of the underlying metals by the water, producing oxides and deuterium ($Zr + 2D_2O \rightarrow ZrO_2 + 2D_2$). In the case of the zirconium alloys, some of the D_2 resulting from this corrosion can diffuse into the metal, forming brittle zirconium hydride. This in turn can lead to hydride cracking of the metal. Thus we have the paradox of zirconium hydriding being triggered by insufficient dissolved hydrogen.

In addition, corrosion in the HTS leads to dissolved or suspended corrosion products, which become activated. High suspended solids (CRUD) often indicate a chemical shock to the system, and especially a transient to oxidizing conditions. (This condition can be controlled by stabilizing system chemistry: ensuring pH and dissolved D_2 are within specification and increasing purification flow rates). The presence of suspended solids increases activation products and therefore increases radiation fields. At Pickering, $\approx 90\%$ of the boiler room fields are produced by Co-60 (a β , γ emitter with a half-life of 5 1/4 years) which comes from traces of the natural Co-59 in the monel boiler tubes and carbon steel. High suspended solids may also plug instrument and sample lines.

(vi) High Dissolved Deuterium**Cause/Source**

High dissolved deuterium is a result of too great an H_2 addition rate.

Method of Control

Control of high dissolved deuterium is achieved by reducing the rate of H₂ addition.

Consequences If No Action Taken

If above specification, there is some risk of diffusion of D₂ into the zirconium alloy either directly from the water, or indirectly from the annulus gas after first diffusing through the end fittings. Because of this, the annulus gas has been assigned a D₂ specification (<0.1%).

High dissolved D₂ can also increase D₂ in the storage tank cover gas.

(vii) **High D₂, O₂ and N₂ In the D₂O Storage Tank Cover Gas**

Causes/Sources

D₂ - HTS dissolved D₂ is too high
- Frequent transfers to/from storage tank and main HTS.
O₂ and N₂ - air in-leakage to the storage tank

Method of Control

High cover gas D₂ is controlled by ensuring that the HTS dissolved D₂ is not above specification, lowering it if necessary by temporarily halting hydrogen addition, and purging the cover gas with helium. Helium purging also lowers N₂ and any O₂.

Consequences If No Action Taken

The consequence of high D₂ is the increased risk of explosion.

Any dissolved nitrogen carried to the main system is radiolyzed to nitric acid, placing an added load on the IX resins.

Oxygen is corrosive, and also increases the risk of explosion.

Summary

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

SYSTEM	PARAMETER	CAUSE/SOURCE	METHOD OF CONTROL	CONSEQUENCE OF NO ACTION
MAIN HEAT TRANSPORT SYSTEM	I-131 - Higher than normal	Defective fuel.	Remove defective fuel. Raise purification flow. Do not change power.	High radiation fields in HTS. High activity transport.
	I-131 - Limit exceeded	Defective fuel.	Shut down immediately, in a controlled fashion.	
	pH - Low	Spent IX resins. Lithium as carbonate not deuterioxide. LiOD Hideout.	Add LiOH (in D ₂ O). Valve in fresh resins.	Increased corrosive attack on carbon steel and magnetite layer. Increased activation products, causing higher radiation fields in HTS.
	pH - High	Hideout LiOD drawn back into HTS during cooldown but seen on start-up.	Use D-OD column to remove excess lithium.	
	Cl ⁻ - High	Spent IX columns. Overheated resins (unlikely).	Fresh IX column. Bleed cooler temperature override.	Corrosion of ferrous metals, especially SCC of stainless steel.
	Dissolved D ₂ - Low	Insufficient H ₂ addition. Possible D ₂ leak from system.	Increase H ₂ inflow. Stop bleed condenser leaks.	Too much dissolved O ₂ and increased corrosion. Hydride cracking of Zr alloys. Increased suspended, activated corrosion products.
	Dissolved D ₂ - High	H ₂ addition rate too high.	Reduce H ₂ flow.	Risk of diffusion of H ₂ into zirconium alloy pressure tubes. High D ₂ in storage tank cover gas.
Suspended Solids - High	Chemical shock to system, ie, transient oxidizing conditions.	Stabilize system chemistry. Increase purification flow rates.	Increased activation products causing higher radiation fields in HTS.	
HTS STORAGE TANK COVER GAS	D ₂ - High	HTS dissolved D ₂ too high. Frequent transfers to/from storage tank.	Ensure HTS dissolved D ₂ not above spec/lower it. Purge with He.	Increased explosion risk.
	N ₂ , O ₂ - High	Air inleakage to storage tank.	Purge with He.	Nitrogen produces nitric acid via radiolysis. O ₂ is corrosive. O ₂ increases explosion risk.

* Conductivity and Lithium are diagnostic parameters used when pH is off specification.

SOURCES OF INFORMATION

Main System

The main source of information for the main system is the chemical analysis of grab samples. Post-Pickering stations have been provided with a gaseous fission product (GFP) on-line gamma ray spectroscopy monitoring system. Among other things, this provides control room readout of I-131 concentrations.

Note: Tritium and Isotopic are also determined by the chemistry laboratory.

D₂O Storage Tank Cover Gas

The D₂O storage tank cover gas is analyzed by an on-stream gas chromatograph.

ASSIGNMENT

1. Discuss the use of carbon steel in the heat transport system with respect to the following:
 - (a) Why it is used.
 - (b) The chemical problem related to its use.
 - (c) How that chemical problem is resolved.
 - (d) Immediate and subsequent consequences of a loss of chemistry control.

2. Given that the primary objective of chemical control of the HTS is to minimize corrosion of system components, and that dissolved oxygen is an aggressive oxidizing agent, explain why there is **no** specification and no analysis done for dissolved O₂.

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J.D. Wilkinson