Chemistry - PI 24

PRIMARY HEAT TRANSPORT SYSTEM CHEMICAL AND IMPURITY CONTROL

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1. From memory, briefly describe the effects of dissolved oxygen in the primary heat transport system which are:

   - increased corrosion
   - increased crud
   - deterioration of the protective magnetite layer

2. Briefly describe the control of dissolved oxygen using Hydrogen injection, the downgrading effects of this injection and the acceptance of this downgrading due to economic reasons rather than use of D_2 for O_2 control.

3. State that the target pH of the primary heat transport system is 10.0 and is maintained there through the use of Li-OD based resin column in the purification system; that transient conditions of high pH are usually cured through the use of D-OD based resin and transient conditions of low pH through the direct injection of Li_2O to the system.

4. State that pH 10 is chosen because:

   (a) below pH 10 acid attack occurs
   (b) above pH 10 caustic embrittlement occurs
   (c) pH 10 is the optimum pH for the maintenance of the protective magnetite layer on the carbon steel parts of the systems.

5. State that suspended solids (particulates) are removed from the primary heat Transport System by filters in the purification system, and that ionized dissolved solids are removed by the ion exchange columns in the purification system.

6. Briefly describe how IX resins are deuterated before use to remove light water and that failure to do this would lead to downgrading of the Primary Heat Transport System.

Additional Resources:

1. Film: "Corrosion In Action" (On video-tape).
2. Bruce NGS-B HTS Chemical Control Manual

Both available from the course manager on request.

The overall purpose of chemical and impurity control of the Primary Heat Transport System is to prevent it from corroding away or plugging solid with radioactive solids, and prevent solids from eroding the system. To accomplish this, the system must be put into a condition where corrosion is held to a minimum and suspended solids are kept to a minimum.

The conditions which favour low corrosion are:

- The maintenance of low dissolved oxygen to prevent simple oxidation (fancy word for rusting) of the system.
- The preservation of the magnetite layer developed during commissioning.
- The maintenance of a pH which will minimize acidic attack and caustic embrittlement which is a type of failure which occurs when the pH is too high.

The conditions which favour low suspended solids are:

- The minimization of corrosion products.
- The prevention of deterioration of the magnetite layer.
- Removal of tramp suspended solids (such as fuel dust introduced on the outside of new fuel pencils, or fragments of system components).

Dissolved Oxygen

If dissolved oxygen is present in the Primary Heat Transport System heavy water, it will have several harmful effects.

(a) Corrosion rates of system components will increase beyond design limits due to oxidation of the metals by the dissolved oxygen.

(b) There will be an increase in system suspended solids (particulates, crud*) due to the flaking off and transport of corrosion products from oxidation throughout the system.

(*CRUD - Any undissolved solid in the system).

(c) Dissolved oxygen has a harmful effect on the magnetite layer on the carbon steel components of the system. Magnetite would break off, adding to the particulates in the system, and exposing parent metal to the dissolved oxygen in the system which would lead to further corrosion.

Dissolved oxygen is removed from the Primary Heat Transport System by injecting Hydrogen gas (H_2) into the system. The following reaction occurs:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

But wait a minute; this reaction and therefore this method of control must downgrade the isotopic concentration of D_2O in the heavy water system. Right! But the cost of upgrading is less than the cost of using Deuterium gas (D_2) for oxygen control.

[Some old-timers in the nuclear business will tell you that Hydrazine (N_2H_4) is used for control of dissolved O_2. $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$. This used to be so, but the same downgrading problem exists and not only that, N_2H_4 is sold dissolved in at least 50% H_2O; so injection of the reagent alone causes downgrading].

At this point you may try practice exercise #1, or read on as you wish.

pH Control

The primary material of construction of the Primary Heat Transport System is carbon steel. The best pH to keep corrosion to a minimum is pH = 10 for carbon steel. Below pH 10, acidic attack and general corrosion is increased leading to system wastage and release of crud to the water circuit. Above pH 10 caustic embrittlement may occur leading to component failure; this is especially true for zircalloy fuel sheaths which are highly susceptible to caustic embrittlement. Furthermore, at pH 10 the stability of magnetite is highly favoured.

Under normal operating conditions, pH is controlled by passing a portion of the bleed flow through a cooler then through filters and ion exchange columns in a purification system. (For a detailed description of the purification system the reader should consult Course PI-33 or 233). The resin in the column is a mixed bed having the cation resin in the Lithium (Li^+) form and the anion resin the Deuteroxide (OD^-) form. Passage of HTS water through this type of resin will maintain a small concentration of LiOD in the water which is usually sufficient to maintain the pH at a value of 10.0 - 10.3, which is the normal operating range.

Transient conditions where the pH wanders out of the operating range may be corrected as follows.

Condition	Action
1. pH below range	1. Inject Lithium Oxide (Li_2O) dissolved in D_2O.
2. pH above range	2. Valve in a D-OD resin column temporarily.

You may now do practice exercise #2 or read ahead.

Suspended Solids

Suspended solids, or crud in the system give rise to four main problems.

(1) They may be activated in the neutron flux and then deposited outside the reactor core causing radiation problems when maintenance is required.

(2) They may deposit on fuel causing heat transfer restriction.

(3) They may accumulate and cause flow restriction.

(4) They may erode system components especially moving parts with close tolerances.

Suspended solids are removed by the filters in the purification system.

Dissolved Solids (Ionized)

Ionized dissolved solids may be corrosive or may become activated in the system. Dissolved solids are removed by the ion exchange columns in the purification system. These are the same ones used for pH Control.

You may now do practice exercise #3 or read ahead.

Ion Exchange Columns

The RESIN for use in the Primary Heat Transport System purification is purchased in the Li-OH form (or possibly H-OH) and is kept moist with H_2O. If it were placed in service directly, the H_2O and the OH from the anion component would be released into the system leading to downgrading. Prior to use, resins are flushed upflow with D_2O to purge them of light water and convert them from the Li-OH form to the Li-OD form. This process is known as deuteration. When the resins are spent and ready to go to waste management the heavy water is recovered from them by dedeuterization (passing H_2O downflow through the resin to purge out D_2O).

Practice exercise #4 deals with deuteration.

Here's What To Do:

1. Try the four practice exercises on the next few pages without using your notes.

2. Compare your answers to the sample answers on the pages following the exercises.

3. If you need further help, consult with the course manager.

Practice Exercise #1

(a) List three problems associated with dissolved oxygen in the Primary Heat Transport System.
(b) How is the level of dissolved oxygen reduced in the Primary Heat Transport System?
(c) What is the side effect of this method of control?
(d) If this side effect is harmful, how is it justified?

Practice Exercise #2

(a) State the target pH of the Primary Heat Transport System.
(b) Give three reasons why this pH is chosen for the system.
(c) Briefly outline the method for controlling this pH under normal conditions.
(d) Give one counteraction for each of:

   (i) pH well below specification
   (ii) pH well above specification

Practice Exercise #3

(a) What method is used to remove suspended solids (particulates) from the Primary Heat Transport System?
(b) What method is used to remove ionizd dissolved solids?

Practice Exercise #4

(a) Briefly outline the procedure applied to the Primary Heat Transport System IX resins before they are put in service.
(b) State the consequence of not using this procedure.

Answers to Practice Exercises:

Exercise #1

(a) The three problems associated with dissolved oxygen in the Primary Heat Transport System are:

(1) Increased corrosion of system components by simple oxidation.
(2) Deterioration of the protective oxide layers on system components, particularly the magnetite layer on the carbon steel piping which forms the major component (area-wise) of the system.
(3) Increase in crud due to the formation and sloughing of oxidation products.

(b) Dissolved O_2 is reduced by injection of H_2 gas into the Primary Heat Transport System.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

The system is monitored for dissolved H_2 and the maintenance of a slight (3 to 5 cc/kg D_2O) excess of H_2 ensures removal of O_2.

(c) The side effect of using H_2 for control of dissolved O_2 is the production of H_2O, light water which downgrades the system.

(d) One could use D_2 instead of H_2 for control

$$2D_2 + O_2 \longrightarrow 2D_2O$$

however the cost of D_2 gas is much greater than the cost of upgrading due to the presence of H_2O formed.

Practice Exercise #2

(a) Target pH of Primary Heat Transport System is pH = 10.

(b) pH 10 is chosen because

(1) Below pH 10 significant metal wastage will occur due to acid attack on carbon steel components.
(2) Above pH 10 the system metals are subject to caustic embrittlement.
(3) At pH = 10, the magnetite layer on carbon steel components is most stable.

(c) *Under normal conditions, pH is maintained at pH = 10 by* having a small concentration of LiOD (Lithium Deuteroxide) in the system. This concentration is maintained by using Li-OD based ion exchange resin in the Primary Heat Transport System purification system.

(d) (i) if pH << 10.0 then Li_2O may be injected directly.
(ii) If pH >> 10.0 D-OD resin may be used to remove excess Base.

Practice Exercise #3

A portion of the bleed flow is cooled and purified. The purification process consists of filters to remove particulates followed by ion exchange vessels to remove ionic impurities.

Practice Exercise #4

(a) Before being used in the heat transport system purification system, IX resin must have all light water removed. *This is done by passing D_2O upflow through the column.* The H_2O used to keep the resin moist "floats" to the top and the OH part of the anion resin is displaced by the OD^- in the heavy water to convert the resin from the Li-OH form to the Li-OD form.

(b) If the deuteration procedure is not followed, the Heat Transport System will be downgraded by having the light water pushed out of an IX column when it is placed in service.

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