CHAPTER 14

A. CHEMISTRY OF THE HEAT TRANSPORT SYSTEM

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ABSTRACT

Optimum control of the chemistry of the coolant in the thermalhyraulic loops assists in the achievement and maintenance of high availability, and of the safe, efficient and economic operation of nuclear powered generating stations. To achieve this optimum chemical control, it is necessary for both designers and operators to have a clear understanding of the chemical interactions between the coolant and the materials of construction and of the effects of nuclear radiations on the coolant, its additives and any corrosion products suspended or dissolved in it. The maximum benefit from this understanding is achieved when the effects of these chemical interactions are taken into account at the beginning of the design of the system.

14.1 Establishing Optimum Chemistry Conditions

There are a number of factors which the chemist has to consider in defining the optimum thermalhydraulic loop chemistry. Among the more important of these are:

i) Water corrodes most metals.

ii) There is an optimum water chemistry for the minimum corrosion rate of each material at its operating conditions.

iii) Corrosion of the loop materials is only one of the criteria considered when choosing the thermalhydraulic loop materials. For example, neutron absorption dictates the choice of in-core materials and heat transfer is an important factor in the choice of steam generator tubing. As a result, the materials used in CANDU PHWR thermalhydraulic loops include:

   a) Zircaloy-2 for fuel sheaths and Zr/2.5% Nb for pressure tubes
   b) 400 series stainless steel for pressure tube end fittings
   c) Carbon steel for feeder piping, headers and vessel shells
   d) Nickel chrome iron alloys, I-600 or I-800, for steam generator and heat exchanger tubing
   e) 300 series stainless steel tubing for instrument connections, failed fuel location and sample lines.

iv) Variations in water chemistry, temperature and hydraulic conditions affect the production, movement and activation of corrosion products in the thermalhyraulic loop. By discouraging crud deposition on the fuel surfaces, the activation of the crud is reduced and so also are the rate of increase and the ultimate equilibrium value of the radiation fields in the vicinity of the thermalhydraulic loop. Coolant chemistry can be and is optimized to minimize these radiation fields (see Section 14.3).

v) Water, when exposed to nuclear radiation undergoes radiolysis, a process in which water is decomposed to its constituent elements and the decomposition products are recombined to form water. The net radiolysis rate is dependent on the coolant chemistry. The maintenance of about 5 mL D_2/Kg D_2O is sufficient to suppress the production of dissolved oxygen to minimize corrosion of carbon steel.

vi) The use of carbon steel for the feeder piping and headers dictates a coolant chemistry with a high pH value and a low concentration of dissolved oxygen. The presence of the neutron flux dictates the use of coolant additives which do not produce unacceptable activation products. Thus lithium oxide dissolved in D_2O is used as the pH additive.

vii) Additives, while controlling one pheomenon, may, especially when concentrated on or absorbed by the system materials, aggravate another phenomenon. For example, the localized thinning of some pressure tubes where they contact some of the fuel bundle wear pads has been attributed to the locally higher temperatures boiling the coolant and so causing high concentrations (greater than 0.1 molar) of lithium hydroxide in the crevice between the wear pads and the pressure tubes. The cracking of overstressed areas of the pressure tubes at Pickering GS 'A', Units 3 and 4 in 1973/1975, was the result of the formation of zirconium deuteride (hydride) in the overstressed portions of these tubes. Thus there are limits on the maximum permissible concentrations of lithium deuteroxide and dissolved deuterium in the coolant.

viii) Additives have to be chemically stable under both neutron and gamma radiation.

Putting all of the above together leads to the chemistry specification for the PHT coolant shown in Table 1.

14.2 Effect of Non-Condensable Gases

The only non-condensable gas which is present in the coolant in any significant quantity is deuterium. The normal concentration is 3 to 10 mL D_2/Kg D_2O, the gas volume being measured at normal temperature and pressure. Gas solubility data derived from Himmelblau shows that the partial pressure required to dissolve one millilitre of deuterium in one kilogram of heavy water at the PHT operating conditions is 0.16 psi. This pressure is equivalent to about 0.05°C of sub cooling. Thus the deuterium present in the coolant will be dissolved in the coolant except for those parts of the loops where there is steam. In these areas the deuterium gas will be only a small proportion of the total vapour volume and it will be mixed with and move with the steam.

When the reactor is in the hot standby condition, the coolant has about 50°C of subcooling so the dissolved deuterium will remain in solution.

When the reactor is in the cold shutdown state (i.e., 50°C and atmospheric pressure), the Himmelblau data gives the partial pressure to dissolve one mL of deuterium in one kilogram of heavy water as 0.99 psi. The solubility of deuterium under these conditions, allowing for the heavy water vapour pressure, is about 13 mL D_2/kg D_2O so the dissolved deuterium will remain in solution. The D_2O temperature required to reach the solubility limit of 10 mL D_2/kg D_2O at 1 atm (abs) total pressure is 75°C and for 3 mL D_2/kg D_2O, it is 95°C (cf. 3.2v).

If it is assumed that there is 1 mL D_2/kg D_2O above the solubility limit in the cold shutdown state, there would be a total of 180 L of undissolved deuterium gas in the PHT coolant. Is this significant? The steam generator tubes have bend radii from about 0.1 m to 1.22 m. So a tube with the median value radius of 0.66 m and an ID of 13.64 mm requires a minimum of about 20 mL of gas to gas lock the top of the U bend. However, since there will be a differential pressure of at least 10 kPa across the inlet to outlet headers, the required volume of gas to provide a gas lock is about 230 mL per tube for a total of about 800 tubes or about 5.5% of all tubes, assuming that all of the excess gas above the solubility limit does accumulate and remain in the U bends. What this calculation shows is the advisability of keeping the dissolved gas concentration to the low end of range during cold shutdowns. The situation is not however an easy one to analyze as the solubility limit is very sensitive to the total pressure as well as the coolant temperature. At 1.5 atm (abs), the D_2O temperatures required to reach the solubility limits of 10 mL D_2/kg D_2O and 3 mL D_2/kg D_2O are 99°C and 110°C respectively.

14.3 Corrosion Product Transport Control

Although the general primary heat transport coolant chemistry requirements were established early in the 1960's, the need for improvements in the understanding of corrosion product production, transport and methods of control became apparent in the early years of operation of the Douglas Point plant. By the time the plant had accumulated 600 effective full power days of operation, the radiation fields in the boiler room were in excess of 3 R/h and still increasing. The total annual radiation dose to the operating staff was almost 2,000 rem and it also was showing a year by year increase. These conditions resulted from the presence of too high a dissolved oxygen content in the primary coolant, which led to the release of cobalt-containing corrosion products from the monel-400 steam generator tubing, which then became activated in the core and subsequently were redeposited on the out-of-core surfaces. Since Pickering GS "A" was being built of the same quality of materials as those used at Douglas Point, care was taken to ensure low dissolved oxygen contents in the Pickering GS 'A' primary coolant at all times. As a result the high radiation fields seen at Douglas Point have not occurred at Pickering GA 'A'.

The current radiation field in the vicinity of the Pickering GS 'A' steam generators is 40 mrem/h, a value which has remained relatively constant for the last 6 to 7 years. Cobalt-60 from trace Co-59 in the alloy contributes about 95% of the radiation field.

Subsequent CANDU-PHWR plants have been designed to operate with some boiling of the coolant. As the boiling is expected to result in higher levels of sissolved oxygen in the primary coolant, this resulted in the choice of steam generator tube alloys whose corrosion rates were less sensitive to dissolved oxygen corrosion. This led to the choice of low cobalt inconel-600 tubing for Bruce GS 'A' and incoloy-800 for the 600 MWe plants as the corrosion of these alloys are not affected by increases in dissolved oxygen concentrations at least up to 100 ppb.

An important aspect of corrosion product control is the activation of the mobile corrosion products. The iron solubility data by Sweeton and Baes suggests that operation at a hydroxide ion concentration above 10^{-4} moles/litre (equal to a strong base giving a pH of 10 at -25°C), will discourage the deposition of corrosion products on the fuel surfaces. Loop experiments at CRNL established that this did in fact occur. The important fact is that the reduction in the residence time of crud on the fuel reduces its activation and this in turn reduces the radiation fields in the vicinity of those parts of the primary coolant loop which are external to the calandria.

Starting with the Bruce GS 'A' plant, a concerted effort was made to reduce the cobalt content of the PHT materials. The current requirement is to achieve an average cobalt content of less than 0.015 wt% in both the carbon steel piping and the nickel alloy steam generator tubing.

The effects of these refinements on the boiler room radiation fields at Bruce GS 'A' are to average radiation fields of 2.5 mrem/h with cobalt contributing about 50% of the total.

14.4 Purification Rates

One of the results of the early Douglas Point radiation fields in the boiler room was a review of primary coolant purification rates. The initial studies on the behaviour of crud following deliberate realeases of crud from the primary system suggested crud redeposition half lives of 8 to 12 minutes with the reactor power at power and 60 to 90 minutes with the reactor shut down. As crud movement was considered to be the principle mechanism for the movement of radioactive materials within the primary system, recommendations were made for higher purification flow rates and as a result the purification half life for the initial (1972/74) 600 MWe design was set at 20 minutes with a requirement that the purification flow-rate be maintained at the maximum at all times. Since that time, operating experience from Pickering GS 'A' and Bruce GS 'A' has shown that acceptably low boiler room radiation fields can be maintained with purification half lives of 3 to 4 hours (see Section 14.3). As a result, it is now being recommended that future designs have a minimum purification half life of one hour. The control of fission product iodine is now an important factor in determining purification flow rates.

TABLE 1

CHEMICAL CONTROL PARAMETERS
FOR THE PRIMARY HEAT TRANSPORT SYSTEM

Parameter	Permissible Range	Desired Value	Minimum Recommended Sampling Frequency	Notes
pD(at 25°C)	10.3-10.8	10.45	1/day	Value as measured by pH meter
Lithium (mg.Li/kg D_2O)	0.7-2.0	1.0	1/day	
(mg.LiOH/kg D_2O)	2.4-6.9	3.4		
Dissolved D_2 (mgD_2/kg D_2O)	0.5-4.0	0.5-1.6	Semi-Continuous by Gas Chromatograph	The intent is to maintain the dissolved deuterium at the lower end of the range but high enough to prevent increases in the dissolved oxygen levels
(mLD_2/kg D_2O at 25°C)	3-25	3-10		
Dissolved O_2 (mg)O_2/kg D_2O)	<0.10	≤0.07	1/day	No rapid change should be observed Measured by Gas Chromatograph
(mLO_2/kg D_2O at 25°C)	<0.07	≤0.05		
Chloride (mgCl-/kg D_2O)	<0.2	<0.05	2/week	
Suspended Solids (mg/kg D_2O)	<1.0	0.1	1/week	
Conductivity (micromhos/cm at 25°C)	20-80	25-40	1/day	Value is dependent primarily on LiOH concentration
(mS/m at 25°	2.0-8.0	2.5-4.0		