Chemistry - PI 24

COMMISSIONING (CHEMICAL CONDITIONING) OF THE PRIMARY HEAT TRANSPORT SYSTEM

Objective

From memory, list the basic steps in the chemical conditioning during commissioning of a heat transport system. Note briefly the purpose of each step.

The primary heat transport system pipework consists of zirconium-alloy pressure tubes and inconel or monel boiler tubes joined by tubes made of carbon steel. Of these three metals, by far the most vulnerable to corrosion is the carbon steel. The use of this strong, relatively cheap metal is made possible because of special chemistry: maintain very low dissolved oxygen levels (to minimize overall corrosion), and a pH of ten. The maintenance of pH 10:

- minimizes the corrosion of iron metal itself
- favours the formation and maintenance of a protective layer of magnetite (Fe_3O_4) on the inside of the carbon steel pipes.

It is this latter point that this Module will now discuss.

To obtain the magnetite layer, a series of steps must be performed. Before outlining these steps, let's clarify the overall purpose, ie, exactly what the magnetite layer does for us. This layer protects against:

- direct attack by hot D_2O and radiolytic oxygen
- galvanic corrosion (by insulating the pipes from the electrolyte)
- erosion by crud (but not too effectively).

Table 1 outlines the steps performed by the commissioning team.

TABLE 1

Individual Steps in the Chemical Conditioning Procedure

STEP	PURPOSE
1. Fill with demineralized H_2O or D_2O.[a]	The subsequent reaction requires water as a reaction medium; avoid scale-forming hardness and corrosive Cl.[b]
2. Purge with N_2 (nitrogen),[c] and add N_2H_4 (hydrazine).	Remove corrosive oxygen.
3. Perform a coarse filtration.	Remove large objects but leave rust.
4. Raise pH to 10 with LiOH (lithium hydroxide), deuterated if necessary.	Aids the magnetite-forming reaction to follow.
5. Heat to 200°C (by running the circulating pumps) for several days.	Triggers a reaction between the rust and the surface of the carbon steel piping: $Fe + \underset{\text{pipe rust}}{4Fe_2O_3} \longrightarrow \underset{\text{magnetite}}{3Fe_3O_4}$[d]
6. (If used H_2O) Drain; rinse and fill with D_2O.	

NOTES:

a) The use of H_2O avoids D_2O leakage costs, but involves upgrading the rinse water (step 6); with D_2O, of course, the situation is reversed. Units 1, 3 and 4 at Pickering used H_2O, while Pickering 2 and Bruce A 1 and 2 used D_2O.

b) Refers to both chlorine, Cl_2 (very corrosive to most metals), and Cl^- (chloride), the latter being harmful particularly to stainless steels.

c) The purging with nitrogen gas may be done during the filling operation. It physically displaces the bulk of the oxygen, while the hydrazine chemically scavenges the remainder:

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

d) This equation summarizes what is actually a series of reactions.

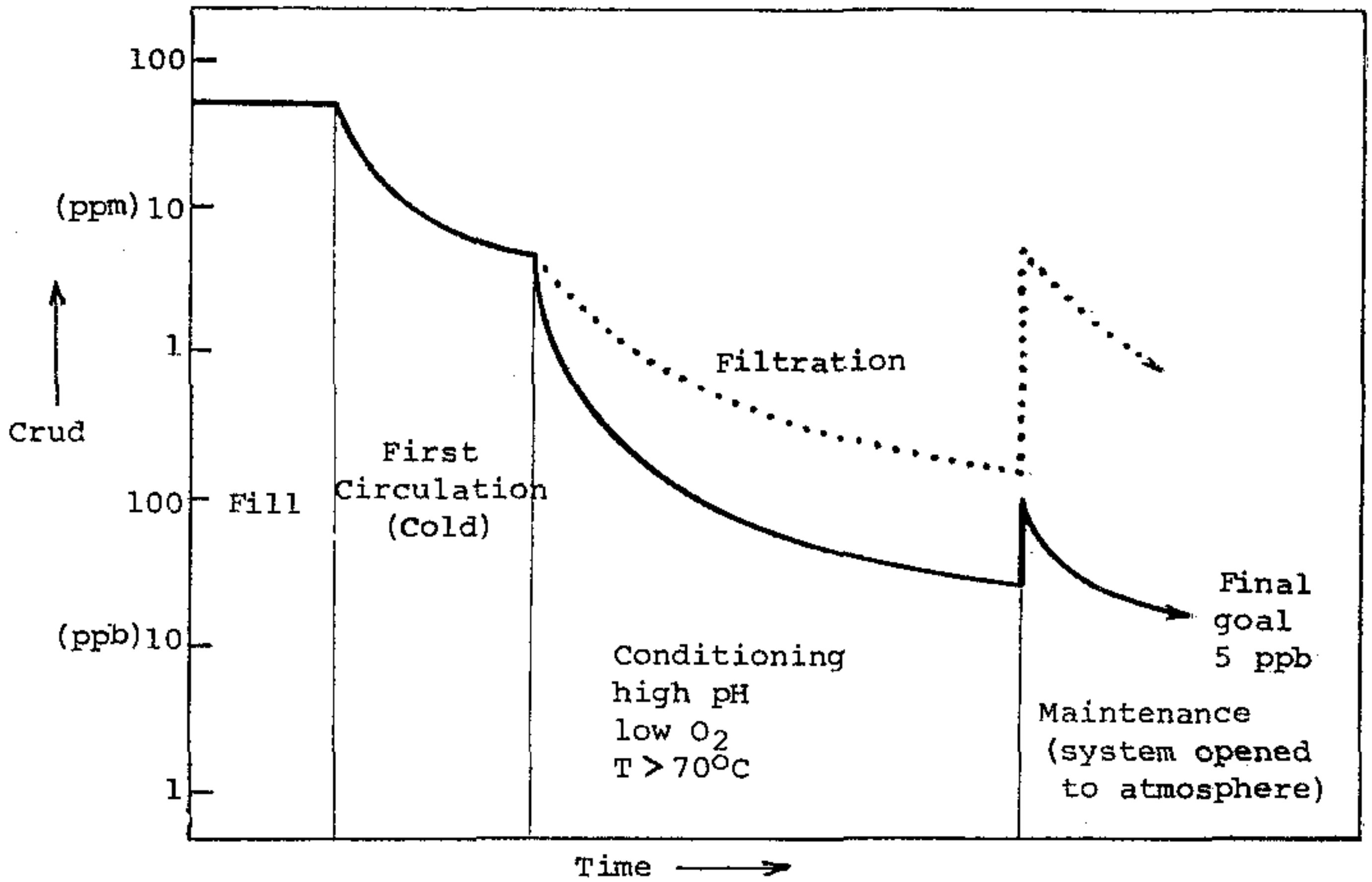
High crud levels in the system should be avoided, as they (on power) give rise to severe problems. Crud that deposits on the fuel is exposed to neutron bombardment. It will in time move through the system depositing on pipes and valves. The chemical composition of the crud is Fe_3O_4 with lesser quantities of oxides of the other metals - Cr, Co, Ni, etc. We are subject to a severe radiation problem once these materials have been activated by neutrons.

The crud deposited on the fuel restricts flow, as it makes the channel available for the coolant smaller. In addition, the heat transfer characteristics of the crud are poor compared to a pure zircaloy surface. The result is that there is a loss of cooling efficiency and hence lower power output, coupled with the danger of overheating the fuel leading to possible rupture of a fuel bundle. The crud also contributes to a wear problem.

Figure 1 gives an indication of the crud levels in a typical CANDU system during commissioning. When initially filled, the crud levels are extremely high - close to 100 ppm. As the system begins to circulate, the crud levels drop as rust goes from suspension to various surfaces that were previously clean. During conditioning, this rust is converted over to an adherent magnetite layer. Conditioning requires that the pH be kept high, oxygen low, and a temperature at least in the region of 60 - 70°C and preferably 150 - 200°C.

After a few days, the crud levels may have dropped to about 20 ppb and give all indications of continuing downward. At this stage, it may be necessary to carry out some modification or maintenance on the system. This would require opening the system to the atmosphere and allowing oxygen in. The situation is not a disaster. The crud level rises, but not that high, and it rapidly returns to a low value on startup. In time, the system heads towards a value of perhaps 5 ppb. The crud level will rise somewhat during each occasion when the system is opened to the atmosphere, but always heads down rapidly afterwards.

The situation would not have been as satisfactory had filtration alone been used to control crud rather than chemical conditioning. The crud levels would never have reached as low a level. Each time oxygen was admitted, the crud levels would have returned toward their high pre-filtration level, making it necessary to start the purification over from the starting point again.



solid line - following chemical conditioning procedures
dotted line - using filters to remove the crud

Figure 1

Typical Crud Levels in an Iron System During Commissioning

Five parts per billion may sound like a small quantity of material. It is in most cases, but not when we are talking about a system exposed to neutron bombardment. We are talking about grams of material in a very large system of hundreds of tons. It is possible to detect picograms (10^{-12}g) of some radionuclides; some highly radioactive sources contain only micrograms (10^{-6}g). One can easily visualize the problem from gram quantities circulating and depositing throughout the system.

Practice Exercise:

From memory, list the steps in chemical conditioning of a heat transport system during commissioning, briefly note the purpose of each step.

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