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FUEL DEPOSITS, CHEMISTRY AND CANDU REACTOR OPERAT

John. G. Roberts
CANTECH Associates Ltd, Burlington Ontario.
150 Willis Crescent, R.R. 1, Kincardine. Ontario.

ABSTRACT

"Hot conditioning" is a process which occurs as part of commissioning and initial start-up of each CANDU reactor, the first being the Nuclear Power Demonstration-2 reactor (NPD). Later, understanding of the cause of the failure of the Pickering Unit 1 G16 fuel channel led to a revised approach to "hot conditioning", initially demonstrated on Bruce Unit 5, and subsequently utilized for each CANDU unit since. The difference being that during "hot conditioning"of CANDU heat transport systems fuel was not in-core until Bruce Unit 5.

The "hot conditioning" processes will be briefly described along with the consequences to fuel.

1. Background

The heat transport system of a CANDU reactor is constructed primarily of alloys of steel, carbon and stainless, and zirconium. Following construction, the heat transport system is hydrostatically pressure tested to demonstrate that the systemis leaktightand will withstanddesign pressure. This hydrostatic test can be performed using either heavy or light water. For all units up to Bruce Unit 5 fuel was absent from core for the hydrostatic test. The fuel was manually loaded following hydrostatic test after draining the heat transport system.

The presence of carbon steel posed a problem;the problem being the possibility of pitting feeders following drain down as a result of pooled water remaining. Oxygen from air exposure, combined with low pH,from air exposure,would promote pitting. To offer protection to carbon steel against pitting the "hot conditioning" process evolved. This process involved heating alkaline water under reducing conditions at zero power hot and maintaining those conditions for ten (10) days [1]. Corrosion coupons, of all system materials, were installed into the (heat transport) system autoclaves for two reasons - the first to allow determination of the degree of corrosion during hot conditioning and the second to determine the quality of the magnetite layer formed by the hot conditioning process.

2. A New Process

During the 1960s the Russians had developed a process using disodium **e**thylene**d**iamene**t**etraacetic**a**cid (EDTA) to condition carbon steel surfaces of their

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nuclear reactors. AECL investigated thisprocess at the Whiteshell Nuclear Research Establishment Laboratories[2, 3]. Ontario Hydro pursued the use of EDTA for “hot conditioning” and successfully demonstrated its use at the pump test loop of the Ontario Hydro Research facility at 800 Kipling Avenue[1]. This led to Bruce Unit 4 being the first CANDU unit to use EDTA for “hot conditioning”. The chosen approach used disodium as opposed to dilithium EDTA. (Disodium EDTA was available commercially but not dilithium EDTA.) Difficulty was encountered removing the sodium at the end of hot conditioning. This was overcome by using non-lithiated ion exchange resins but consumed additional time.

Unit 6 was the next Bruce unit to be “hot conditioned” and the dilithium EDTA salt was chosen. Since commercially available dilithiumEDTA of appropriate purity was unavailable the salt was prepared on site using high purity, commercially available, EDTA and pure (analytical grade) lithium hydroxide. Examination of the corrosion coupons showed the approach to be successful [4]. The heat transport system was drained and fuel, as past practice, loaded manually.

3. Regroup?

Within hours of releasing the shutdown guarantees for Bruce Unit 6 to approach first critical, the reason for the failure of the Pickering Unit 1, G16, fuel channel was understood. The failure was due to zirconium hydride blisters forming followingfuel channel to calandria tube contact as a result of garter springs (spacers) having being incorrectly positioned. The result was that all the Bruce Unit 6 fuel had to be manually removed to allow garter springsto be located and, as necessary, relocatedto preclude similar fuel channel degradation and failure. Unfortunately, between fuel loading and subsequent fuel removal the fuel channels had been “machined” by the fuel bundle bearing pads, generating swarf or turnings. This residual swarf led to many fuel failures from debris fretting.

The observationsof swarf, and machining of fuel channels,led to the use of a shim for manual loading of fuelfor each subsequent CANDU unit. This led tothe avoidanceof such debris generation. Unfortunately the cleanliness, or build clean,execution for the construction/installation of many CANDU units has been less than desirable. A notable exception is that of Cernavoda Unit 1 which involved considerable oversight by, and on behalf of, the Client[5, 6].

On inspection, few of the Bruce Unit 6 garter springs were found in their “as designed” positions. There was a suspicion that vibration from heat transport pumped fluid flow/main pump operation was causing the “loose fitting” garter springs to “walk” and shift location. It was believed that the mass of the fuel bundles would cause the fuel channels to sag into contact with and trap, at least, the centre two garter springs thereby holding them in place. Subsequently a demonstration was performed on Unit 5 with ten channels being manually fuelled, each with 12 bundles. The position 13 (inlet) bundle location was occupied by a strainer, as had occurred for Unit 6. Following “hot conditioning” of Unit 5 the ten channels were manually defueled and it was determined that the centre two garter springs had indeed not shifted location but the outer two garter springs had, as predicted, moved.

This successful demonstration of the approach to use fuel to prevent garter spring movement led to Unit 7 fuel being loaded with fuel prior to the hydrostatic pressure test, and "hot conditioning". CANDU unitsthat have followed a similar path, includeBruce Unit 8 and the refurbished Bruce Units 1 & 2 and Point Lepreau.

Bruce Units 3 & 4 were"hot conditioned" as part of their return to service in 2003. Fuel had been loaded using fuelling machines, following spacer location and relocation. For both processes heavy water was within each heat transport system.

The EDTA process for "hot conditioning" was not used for Bruce Units 3 & 4 because the fuel channels would not have withstood remaining at $150^{\circ}C$;this was due to the total hydrogen (equivalent) contained in the fuel channels. Rather the conventional "hot conditioning" approach using lithium hydroxide and reducing conditions was used [7].

4. <u>What "hot conditioning" actually does</u>

As mentioned earlier, the "hot conditioning" process lays down a protective magnetite coat on carbon steel surfaces. The magnetite that is formed on carbon steel results from two processes, the one being corrosion of the base iron which forms an adherent, protective oxide coat. The second involves precipitation of magnetite from solution onto every surface within the heat transport main circuit, including carbon steel, resulting in a less adherent secondary coat. It is this less adherent coat which is believed to be the reason why the Bruce reactors having boilers tubed with Inconel-600 do not suffer from Co-58 radiation fields [8].The deposited magnetite offers a degree of protection from corrosion of the I-600 tubing. Co-58 is formed from neutron activation of Ni-58, released from corrosion of I-600 (steam generator tube), and has resulted in significant difficulties for US pressurized water reactor operators.

Magnetite that is precipitated from solution coats all surfaces within the heat transport system – fuel, fuel channels, endfittings, endfitting liners, feeders, headers, steam generator bowls, steam generator tubing, main pump bowls and interconnecting piping.

In summary,"hot conditioning" allows carbon steel surfaces to be offered a degree of protection from corrosion and results in reduced radiation fields from reduced corrosion of steam generator tubes.

5. <u>Approaches to "hot conditioning"</u>

Both the "conventional" and "EDTA" "hot conditioning" processes result in the same carbon steel protection and steam generator tube protection[1]. The difference lies in the benefits offered by EDTA as opposed to the conventional approach:

- The EDTA process takes a shorter time to execute (about five days total versus ten for the conventional approach) with clear economic implications;
- The EDTA approach also offers the advantage of a low concentration chemical clean (at 150^{o}C). There is but one opportunity to remove unwanted contaminants from the heat transport system prior to power operation and that is via the EDTA approach to “hot conditioning”. An example would be that of Bruce A. During the first three years of operation Zn-65 was the major contributor to radiation fields on all four units’ heat transport systems. At Bruce B zinc was effectively removed during the EDTA “hot conditioning” process and Zn-65 radiation fields were not an issue.

6. Heat Transport System Chemistry and Magnetite

Normal operational chemistry for the heat transport system utilizes high (apparent) pH (pH_a) from lithium and reducing conditions from an overpressure of deuterium. For an operating unit using within-specification chemistry the maximum solubility of magnetite is in the reactor core and is a function of temperature, pH and radiation chemistry [8, 9].

However, during the “hot conditioning” process the temperatures around the main heat transport system are, in effect, the same. This is because the significant heat input is from the main pumps whereas during power operation the significant heat input is from the fuel. The difference is that during “hot conditioning” there is neither temperature differential nor significant radiation chemistry across the fuel channel;however, a significant temperature differential (about 50°C) and significant radiation chemistry effects exist during high power operation.

Interestingly, the first CANDECON[TM] (CANDU decontamination) of a Pickering unit was considered unsuccessfulas determined by adecontamination factor (DF) of one. The ion exchange capacity requirements had been underestimated as a result of using the oxide loading on corrosion coupons removed from the heat transport system autoclaves.

The investigation,which followed, included removal of segments of inlet and outlet feeders. What was discovered was that the magnetite loading was considerably higher in some locations than indicated by evaluation of the corrosion coupons, consequently insufficient ion exchange resin had been deployed to remove the mobilized iron. Acceptable DFs were obtained in subsequent CANDECONs.

Unfortunately the reason for the unexpected higher magnetite loading was not apparently further investigated, otherwise feeder thinning might have been identified about ten years sooner!

7. Deposits on Fuel

7.1 Initial Start-up/Start-up following refurbishment

It was recognized during "hot conditioning" that magnetite was deposited onto all heat transport system surfaces, including fuel. It was also recognized that the magnetite would dissolve from in-core surfaces once normal, high power, operating conditions (associated temperature and radiation chemistry) were achieved; however magnetite would deposit in the cold leg of the steam generators.This was demonstrated in Bruce Unit 6 when the author was the first person to inspect and enter the boiler primary hot and cold heads. It was impossible to scrape oxide off the hot leg surfaces, but small amounts of less adherent oxide were able to be removed from the cold leg surfaces [10].

For Bruce Unit 7, which was the first unit to be "hot conditioned"with fuel in-core, two fuel bundles were removed following "hot conditioning" and the magnetite loading determined. This was at the request of Ontario Hydro's Design and Development division circa 1985/6;the work was conducted in the Bruce B chemical laboratory and the magnetite dissolved using Clarke's solution. This solution is very corrosive and as a consequence these two fuel bundles were not allowed back into core. They resided in the Bruce B chemical laboratory radioactive source safe for several years. The magnetite loading results were contained in a report which, so far, has proven elusive to find.

Operating experience has demonstrated that when reactors are started up andrun at low powerthe magnetite deposited during hot conditioning takes a greater duration to redissolve. This is because the fuel channel differential temperature and radiation chemistry effects are naturally lower than when the reactor is operating at high power.

Hence should fuelbe removed from core prior torefueling tomaintain of equilibrium reactivity, magnetite depositswould be expected to be observed if the reactor had not been operated at high power.

7.2 Unit Outages

All too often during unit outages control of heat transport chemistry is difficult, if not impossible, to maintain. Some CANDU reactor designsdo not allow for shutdown purification of heat transport systems whereas otherCANDU reactor designs,luckily,have this facility built-in.

7.2.1 Prescriptive Error

Even with a built-in shutdown purification capability chemistry control can be difficult to maintain. This was first demonstrated to the author in 1997, at Bruce B, when an Ontario Hydro directive prescribed that all boiler and preheatermanways would be opened simultaneously! This resulted in the maximum possible air exposure of the heat transport heavy water. The resin for one bank of purification ion exchange columns takes about four days to prepare for service. The purification bank was exhausted (from bicarbonate/carbonate as a result of air ingress) within 24 hours! So they gave up trying to control heat transport chemistry and suffered huge releases of magnetite from feeders.

"Wet scrape" of fuel channels, which had previously been most successful, had to be cancelled. This was due to the released magnetite depositing in the liner and reducing the clearance between the scrape delivery tool and the endfitting liner. The consequencewas that the delivery tool became stuck and galling occurred.

During the previous successful "wet scrape" campaign heat transport chemistry had been well controlled with insignificant release of magnetite.

7.2.2 Outage Sequencing Errors

As a result of the directive to open all boiler and preheatermanways simultaneously,at Bruce B, special bungs were procured to prevent air ingress during subsequent outages. Often during outages the staff planning and executing the work fail to grasp how fast chemistry control of the heat transport system can be compromised. Any delay in deploying bungs after boilers/preheatersmanwayshave been opened, or having too many manwaysopen simultaneously, results in loss of heat transport system chemistry control with consequential release of magnetiteand partially oxidized forms of magnetite. The correct air exclusion measures are of great importance, and not only to fuel but alsoto outage maintenance activities.

7.3 Heat Transport System Crud and Unit Start-up

Crud is underisable as it will deposit on fuel and neutron activation will follow. When the crud is released from the fuel undesirable radiation fields can result.For crud that is released from feeders during an outage it is probable that such crud, due to the lower coolant velocity, when using shutdown cooling or maintenance coolingpumps,would tend to accumulate in/on the lower areas of a fuel bundle.

Hot surfaces appear to "attract" deposits. It is therefore to be expected that following an outage during which there has been significant release of magnetite/iron oxide the hot fuel would "attract" deposits. During operation with normal chemistry and the reactor at high power the iron oxide would be reduced back to magnetite and the magnetite would, over time, dissolve off the fuel.

8. Fuel failures from deposits

The author has personally overseen the construction, commissioning and initial operation of five new CANDU units and four restarted CANDU units for a total of nine units. In each case the heat transport systems were "hot conditioned" and fuel was in-core for all but one of those "hot conditioning" evolutions. All, but one, of these units has unfortunately suffered fuel defects.In no case were any of the fuel failures the result of deposits on the fuel, rather as a result of foreign material/debris.

9. Conclusions

1. Every CANDU reactor has had its heat transport system “hot conditioned” during initial commissioning.

2. Several CANDU reactors, starting with Bruce Unit 7, have been “hot conditioned” with fuel in-core.

3. The design of some CANDU reactors does facilitate control of heat transport chemistry during outages.

4. Loss of chemistry control of heat transport system during outages results in release of magnetite from feeders.

5. On return to high power operation all iron oxide will be reduced back to magnetite and all in-core magnetite will eventually be dissolved and transported out-of-core.

6. Most CANDU reactors have experienced fuel defects following “hot conditioning” but no defects resulted from deposits on fuel.

10. References

[1] S. L. Vekris, Ontario Hydro Research Division Report. 83-117-K.

[2] B. Montford et al, “Na_2EDTAPretreatment – a possible alternative to the hot conditioning of CANDU Heat Transport MaterialsAECL WNRE unpublished report Part I – an exploratory study”, 1975.

[3] B. Montford et al, “Na_2EDTA Pretreatment – a possible alternative to the hot conditioning of CANDU Heat Transport Materials AECL WNRE unpublished report Part II – a study of corrosion, contamination and decontamination”, 1976.

[4] V.S. Chew, “Bruce Unit 6 Hot Conditioning Analysis”, Ontario Hydro Research Division Report C83-117-K, 19Oct1983.

[5] J.G. Roberts, Personal Experience, Cernavoda, Romania, 1992-1996.

[6] J.G. Roberts et al, “Short, Medium and Long Term Consequences of Inadequate Defect Fuel Management”, 11th International Conference on CANDU Fuel, October 2010.

[7] J.G. Roberts, K. Langguth, “Challenges of Restarting Bruce Units 3 & 4 from a Chemistry and Materials perspective, Canadian Nuclear Society Annual Conference 2005.

Note to reader: this paper was written to capture CANDU heat transport system tribal knowledge.

[8] D.A. Guzonas, "Activity Transport Manual for the CANDU Heat Transport System", COG-00-087.

[9] K. Burrill, email to J.G. Roberts, "Dissolution of Iron Debris in Reactor Core", 30June2006.

[10] J.G. Roberts, Personal experience, Unit 6 Bruce B, 1985.