INITIATIVES TO REDUCE FEEDER WALL THINNING

by

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ABSTRACT

It was recognised in 1996 that outlet feeder pipes in the Heat Transport System (HTS) of CANDU® reactors are corroding at a higher than expected rate. This degradation has been ascribed to Flow Accelerated Corrosion (FAC), a phenomenon known to affect carbon steel components exposed to turbulent flows of de-oxygenated water.

A number of actions have been devised to reduce the FAC rate of CANDU outlet feeders. One option being implemented in existing plants is the operation of the HTS coolant in the $10.2 < pH_a < 10.4$ range. A second option under development is the use of chemical treatments, applied on-line or during a shutdown, to improve the protectiveness of the carbon steel surface film. For new or replacement feeders, the use of ASME SA106 Grade B carbon steel with a Cr content of >0.20 wt% has been recommended.

In this paper, the correlation of plant feeder wall thinning measurements and life-time operating pH_a of the stations will be described along with a discussion of issues associated with operational measurement and control of pH_a in the HTS. The development of chemical treatments to reduce the FAC rate will be discussed. Finally, results of tests to demonstrate the reduction of the FAC rate through increasing the chromium content of the carbon steel will be summarised.

1. INTRODUCTION

Feeder pipes in CANDU® reactors transport coolant from the fuel channels in the reactor core to and from the steam generators where heat is extracted. Figure 1 shows the face of a CANDU-6 reactor with the feeders running laterally from each fuel channel then upwards to the inlet/outlet headers. The coolant in the outlet feeders reaches linear velocities of 8-18 m/s and a maximum temperature of ~314°C. The outlet feeders, at the point where they couple to the fuel channels, have a diameter of 2- or 2½-inches. Since the diameters of the inlet feeders are, in general, smaller than those of the outlet feeders, higher velocities are observed. However, the temperature of the coolant in the inlet feeders is lower.

The feeder pipes are fabricated from ASME SA 106 Grade B carbon steel that has a specification that allows for a Cr content of up to 0.40 wt%. However, the Cr content in feeders found in operating plants today is at the lower end of this Cr range. This is a consequence of the low AECL specification limit for Co content (<0.006 wt%), which was intended to limit the production of Co-60 in the Heat Transport System (HTS) circuit.

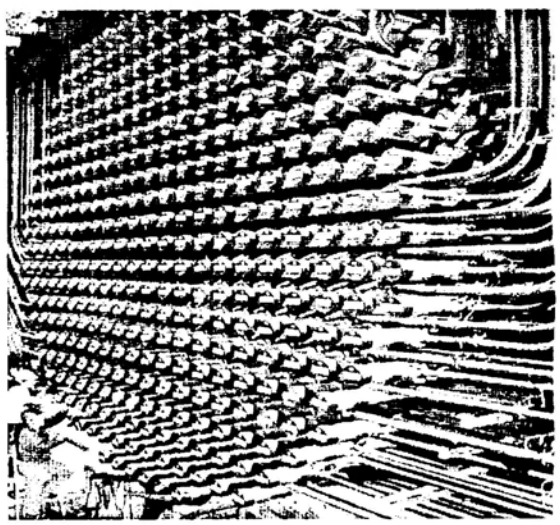

Figure 1: Face of a CANDU-6 Reactor.

In response to the observation of a significant quantity of iron oxide accumulating in the primary circuit, ultrasonic (UT) wall thickness measurements were performed at the Point Lepreau CANDU-6 station in 1996. These measurements revealed higher than expected wall thinning rates of the outlet feeders

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immediately downstream of the coupling to the fuel channels. UT wall thickness measurements at other CANDU stations confirmed that higher than anticipated rates were being experienced at all stations with the highest rates being observed at Darlington and CANDU-6 units and the lowest rates at the Pickering units.

In 1997, a section of the outlet feeder of channel S08, including the first and second bends, was removed from Point Lepreau. Examination of the inside surface of the feeder at the first bend, as shown in Figure 2, revealed a textured surface.

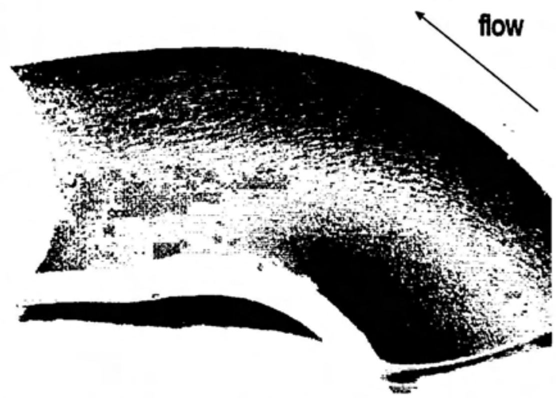

Figure 2: The internal surfaces at the first bend of S08 outlet feeder removed from Point Lepreau.

Closer examination showed scallops on the surface, as presented in Figure 3. The presence of scallops provided confirmation that the mechanism giving rise to the higher than anticipated rates is Flow-Accelerated Corrosion (FAC).

FAC is a form of corrosion that has been observed in the balance-of-plant of both nuclear and fossil power plants. This form of degradation is restricted to components, fabricated from carbon or low alloy steel, which are used to carry de-oxygenated water and water/steam mixtures under conditions of high mass transfer. Similar conditions are in found in the outlet feeders of a CANDU reactor. The HTS is operated under reducing conditions in the presence of dissolved deuterium, yielding de-oxygenated coolant. Under the conditions of the HTS, magnetite is the dominant iron oxide phase and displays an increasing solubility behaviour with increasing temperature. Hence the capacity of the coolant for dissolved iron species increases as the coolant is heated as it passes through the reactor core, which is constructed from non-ferrous materials. The first and second bends of the outlet feeders are most at risk due to their close proximity to the highly turbulent conditions at the exit of the fuel channel and due to the high mass transfer conditions expected in these small radius bends. A modified form of an oxide dissolution-based secondary side FAC model has been applied to describe the FAC at outlet feeder pipes (Burrill and Cheluget, 1998). The model includes a dependence on oxide film dissolution and on the mass transfer of dissolved iron species from the oxide surface to the bulk flow. When oxide dissolution controls the FAC process, the model predicts a linear relationship between oxide solubility and corrosion rate.

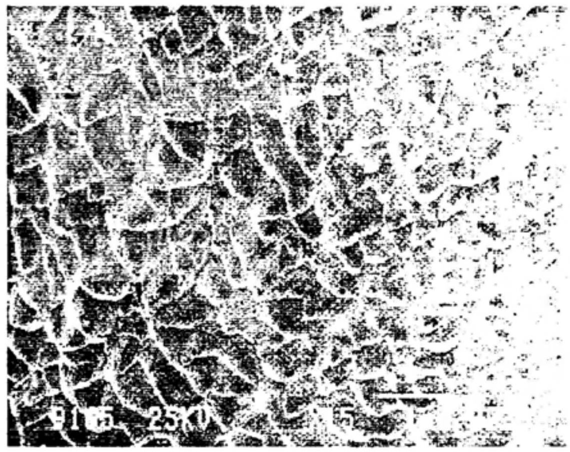

Figure 3: SEM image of scalloped surface on first bend of the S08 outlet feeder from Point Lepreau.

UT feeder wall thickness measurements have now been made at all CANDU stations to varying degrees (except the Pickering A Units). In order to calculate wall thinning rates and predict end-of-life, i.e., the time it will take feeders to thin to the minimum acceptable wall thickness, an initial pre-service wall thickness is required. Such inaugural wall thickness measurements were not made on the early CANDU-6 reactors where the majority of in-service measurements have been made. Hence, estimates have been obtained by measuring the wall thickness of spare bends, representative of those bends in the outlet feeders, at many of the CANDU-6 stations. The minimum wall thicknesses measured for 2½-inch spare bends from Gentilly-2, Point Lepreau and Embalse are presented in Figure 4, appearing on the plot at zero time. Some variation is apparent in the data collected on spare bends from the three stations. It has yet to be determined whether these differences are indicative of variations in the initial wall thickness for all the 2½-inch feeders at the respective stations or whether it represents differences in the techniques employed in making these difficult measurements.

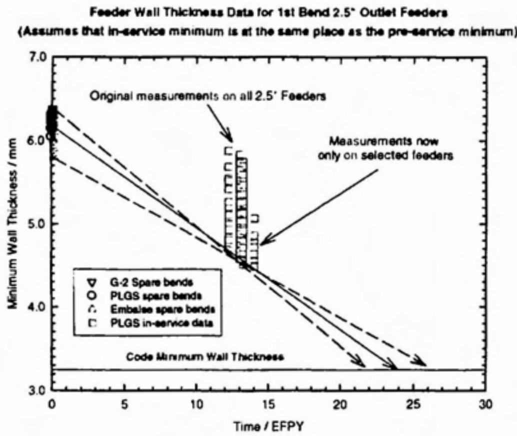

Figure 4: Minimum wall thickness data for 2½-inch feeders. Measurements at time zero from Gentilly-2, Point Lepreau and Embalse CANDU-6 stations were obtained from spare bends stored at the respective stations.

Also plotted in Figure 4 are the minimum in-service wall thickness measurements made on the first bend of 2½-inch feeders at Point Lepreau. The first few sets of measurements were made on a wide range of feeders, resulting in a large spread in the minimum wall thickness measurements. As more was learned about the variation of wall thinning rates with thermalhydraulic parameters, such as linear velocity and mass flow rate, the measurements tended to focus on those feeders experiencing the highest thinning rates. As a result, the spread in wall thickness data has decreased in the latest data reported. The time to reach the minimum allowable wall thickness, represented by the horizontal line in Figure 4, can be estimated by linear extrapolation of the data as shown. This assumes that the wall thinning rates are constant over the life of the plant. There is currently no plant data available which indicates this assumption is not valid. An estimate of the time to reach the minimum allowable wall thickness is dependent on the initial wall thickness assumed. As illustrated in Figure 4, the shortest time to end-of-life, i.e., ~22 EFPY, is achieved assuming the *maximum* initial wall thickness based on measurements of spare bends. The longest time estimated, i.e., ~26 EFPY, is obtained by assuming the *minimum* initial thickness based on measurements of spare bends.

It should be noted that as a result of the bending process, the wall thickness of pre-service bends varies axially along the bends from entrance to exit and circumferentially from extrados to intrados. The thinnest wall is found at the apex of the bend along the extrados and the thickest wall is found at the apex of the intrados. These variations, in particular the thickening of the intrados, is apparent in Figure 2. The rate of FAC is also expected to vary as the coolant passes through the bend, and these local variations in the thinning rate can further modify the wall thickness profile of the bend.

The most extensive set of feeder wall thickness data has been collected at Point Lepreau where every outlet feeder has been measured (at least once) at either the first, the second, or, in some cases, both bends. Thinning rates are calculated using the measured minimum for each feeder and an initial minimum wall thickness of 6.25 mm for 2½-inch feeders, and 5.05 mm for 2-inch feeders. These rates are found to increase with mass flow rate and linear velocity. Hence the feeders experiencing the highest thinning rates tend to be those associated with highest power channels.

2. MEASURES FOR MITIGATING FEEDER PIPE WALL THINNING

Following the identification of FAC as the mechanism responsible for wall thinning of outlet feeders, the CANDU Owners Group (COG) implemented an R&D program to investigate measures for reducing this FAC in existing plants. AECL implemented an additional R&D program to investigate means of limiting feeder wall thinning in new plants. Three strategies have emerged from these two programs for controlling the thinning caused by FAC:

(1) Optimising the coolant pH_a;
(2) Development of chemical treatments; and
(3) Specifying the use of ASME SA 106 Grade B material with a minimum Cr content of 0.20 wt%.

This last option is intended for new units or for replacement feeders in existing stations.

3.1 Optimisation of pH_a

Coolant alkalinity, or pH, is found to influence FAC under Balance-of-Plant (BoP) conditions. This is attributed to the changes in the magnetite solubility with pH (Heitmann and Schub, 1983; Bignold et al., 1986). It was therefore reasonable to expect that the wall thinning rates in CANDU reactors could be reduced by operating the HTS at a pH_a[1] which minimises the solubility difference between inlet and outlet temperature conditions. No solubility data is available for magnetite in heavy water. However, based on data available in light water (Sweeton and Baes, 1970), the solubility difference between inlet and outlet conditions is minimised at a pH of ~9.5. This is equivalent to a pH_a of ~10.0 (see Figure 5). If the coolant pH_a is lowered too much, there is concern with deposition of magnetite in the reactor core, as indicated in Figure 5. The solubility data, together with impinging jet data from laboratory experiments at Chalk River Laboratories, formed the basis for a Station Information Bulletin sent to CANDU stations in 1997 recommending that the HTS coolant be operated in the range $10.2 < pH_a < 10.4$.

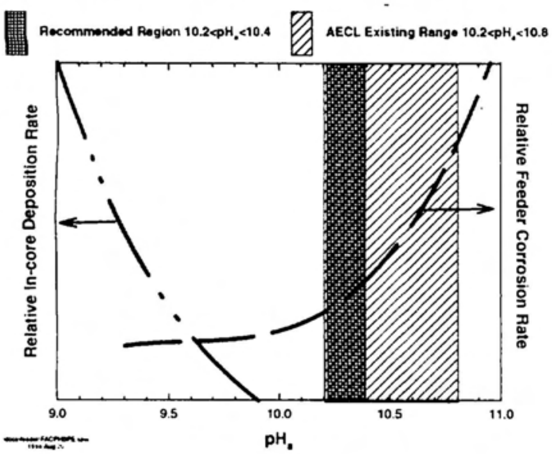

Figure 5: Schematic illustration of pH_a region to minimise FWT of outlet feeders.

Assessing the impact that this change in operating pH_a range has had on feeder wall thinning has been difficult due to the limited time that has past since stations implemented this change and the relatively large errors associated with measuring the small changes in wall thickness that have occurred during this time. However, AECL recently received lifetime operating chemistry data from the Embalse CANDU-6 station. The pH_a data for Embalse are shown in Figure 6, together with the related values for Point Lepreau and Gentilly-2. (Note - the yearly averaged pH_a values were based on pH_a values calculated from the individual lithium ion measurements (see comments in Section 2.1.1)). It is evident that Embalse has operated in a much lower pH_a regime than the other two units. The lifetime average pH_a values for Embalse is 10.2, while a value of 10.6 is observed for Gentilly-2 and Point Lepreau.

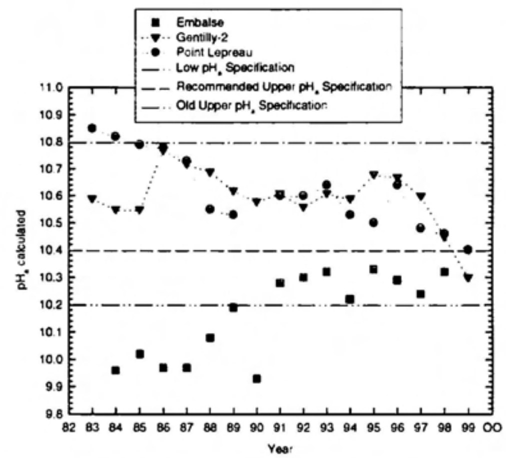

Figure 6: pH_a values, calculated from yearly average Li^+ concentrations for Embalse, Gentilly-2 and Point Lepreau.

The observed differences in lifetime average pH_a between Point Lepreau and Gentilly-2, and Embalse provide an opportunity to assess the impact of pH_a on feeder wall thinning. All three reactors are very similar in design and were constructed approximately at the same time. The feeder pipes were obtained from the same supplier and the bends were fabricated by the same manufacturer. The similarities between these units facilitate the comparison of wall thinning rates.

Wall thickness measurements have been made on all feeder pipes at Point Lepreau while smaller sets have been measured at both Gentilly-2 and Embalse. Comparing the averaged 'as-measured' wall thinning rates from Embalse and Gentilly-2 with Point Lepreau will lead to a bias since not all feeders have been measured and those measured are not the same

[1] pH_a is the 'apparent' pH, a measurement made in heavy water solutions using a pH electrode with light water buffers. It is mathematically related to pH by the expression $pH_a = pH + 0.46$.

in both cases. For example, if the measurements at one station focused only on feeders with high thinning rates, the resulting average rate would be high. It was noted that higher corrosion rates were observed for those feeders associated with higher power channels, i.e., those feeders which had higher coolant flow rates. This observation has led to one approach of estimating a corrosion rate characteristic of the reactor for the purpose of comparing data from different reactors. The corrosion rate is calculated based on an exposure time which has been scaled by a factor (QV/QV_{max}) for the feeder, where QV is the product of mass flow rate (Q) and linear velocity (V). QV_{max} is the maximum value found for the size of feeder being evaluated. This approach was developed by A. Wallace (Ontario Power Generation). The relationship between the feeder wall measurements and the normalised QV time is shown in Figure 7 for Point Lepreau. The slope of this plot, provides a 'finger print' or characteristic thinning rate for that particular station. This can be compared with the characteristic rate from other stations. It should be noted that any station to station variation in thermalhydraulic conditions will not be accounted for in this characteristic rate.

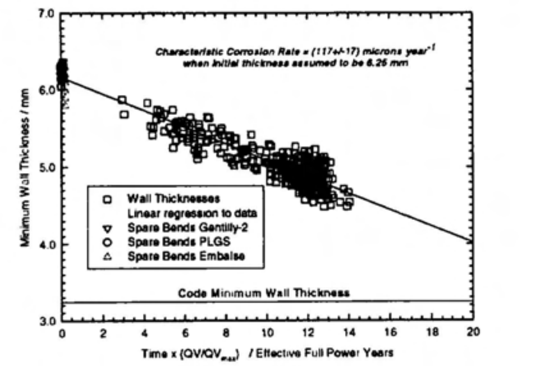

Figure 7: Correlation of FWT measurements for the first bend of the 2½-inch outlet feeders (Point Lepreau) with QV-normalised time.

Characteristic rates have been calculated for Embalse, Gentilly-2 and Point Lepreau from plots of their reported wall thinning rates against normalised QV time. These values are plotted in Figure 8 as a function of the lifetime average pH_a for the station calculated from measured Li^+ concentrations. The error bars represent one standard deviation in the calculated values. From the data, assuming an initial wall thickness of 6.25 mm for all 2½-inch feeders at all reactors, it appears that the rates at Embalse are ~10% lower than at either Gentilly-2 or Point Lepreau, presumably as a result of operating at a lifetime average pH_a of 10.2 versus 10.6. Analysis of the NUCIRC thermalhydraulic data suggests that the conditions at Embalse and Gentilly-2 are similar, while those at Point Lepreau are slightly more aggressive. However, it is not clear if this has had an impact on the characteristic wall thinning rate. Furthermore, if the differences in initial wall thickness determined from spare bends at the three stations, as indicated in Figure 4, are valid, then corrosion rates at Embalse could be lower as indicated by the open circle in Figure 8. This would increase the benefit of operating at the lower pH_a value. Additional station data is required in order to improve the certainty of these comparisons.

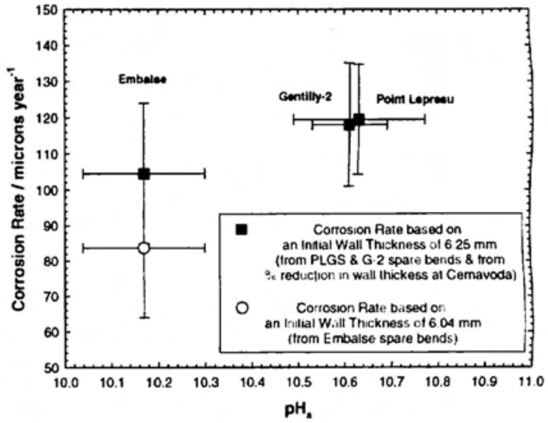

Figure 8: Plot of the characteristic feeder wall thinning rates for first bends of the 2½-feeders, determined using normalised QV values, as a function of lifetime average pH_a values calculated from measured Li^+ concentrations.

Issues Related to Operational Measurement of pH_a

The pH_a of the HTS coolant is normally measured using a pH meter with a glass electrode. The meter is calibrated using light water buffers. Hence, the value obtained from the measurement of a heavy water solution is the 'apparent pH', or pH_a. The pH_a value can be related to the pH measured for light water solutions by the following relationship:

$$pH_a = pH + 0.46$$

Although the pH_a of the coolant can be measured directly using standard pH glass electrodes, such measurements are prone to error due to the absorption of carbon dioxide during the collection, transfer and subsequent grab sample analysis. The dissolved carbon dioxide forms carbonates in the sample, thereby affecting the measured pH_a. However, as the HTS coolant is essentially a pure solution of LiOD, it is possible to calculate the pH_a using the measured Li^+ concentration. Correlation between the measured and calculated pH_a values provide confirmation of a correct or incorrect measurement.

Issues Related to Operational Control of pH_a

Historically, the normal "Permissible Range" for the pH_a of the coolant at 25°C was recommended to be $10.2 < pH_a < 10.8$, with a "Desired Value" range of $10.2 < pH_a < 10.4$. After the detection of feeder wall thinning, a chemistry committee drawn from representatives of Canadian Utilities and AECL was formed to look into chemistry options to minimise the rate of FWT. The recommendation was to operate the HTS coolant in the range of $10.2 < pH_a < 10.4$, with the possibility to lower the range even further to $10.0 < pH_a < 10.2$.

Under normal operating conditions, the HTS purification system maintains a stable pH_a level of approximately 10.7. As a result of the above recommendation, the CANDU plants, in general, decided to implement the pH_a reduction as soon as practicable, utilising existing systems and equipment. For the CANDU-6 plants, this meant utilising the HTS purification system. One method to control the pH_a was to dedicate one of the two ion exchange (IX) columns to contain a charge of mixed bed D-OD IX resin, with the other column containing the normal Li-OD IX resin. When a pH_a reduction was required, HTS coolant was passed through the D-OD containing column for a limited, defined time period, to reduce the bulk HTS pH_a.

Examination of plant operating data indicated that for normal power operation over extended time periods, the pH_a of the HTS coolant increased slowly over time. Rather than dedicating a 39 cubic feet column for pH_a control as described above, AECL has designed a small narrow band pH_a control system whose operation is basically independent of the existing HTS purification system. Its main element is a small IX column containing D-form cation IX resin, which would remove lithium ions from HTS coolant exiting the existing purification system. It would operate on a low but continual flow basis, with the flow set to maintain the HTS pH_a at a static level. For the rare events where the HTS pH_a would need to be adjusted upwards, the existing capability to add lithium hydroxide at the CANDU-6 plants would be utilised.

3.2 Chemical Treatments

Another approach to mitigating FAC of outlet feeder pipes in existing reactors is through the development of a chemical treatment. Two classes of treatments can be considered: (1) treatments applied continuously or intermittently, during normal reactor operation; and (2) treatments applied during an outage, or as part of a reactor start-up or shutdown procedure. The first class of treatments represents a change in the normal operating chemistry of the HTS. As such, this class of treatment is more restrictive since the modified chemistry must be compatible with all relevant reactor systems and processes. However, since the treatment is always present, the benefits from the treatment should persist. There are fewer restrictions on the second class of treatments, namely treatments applied during an outage, since the number of sub-systems exposed to the treatment and the length of the exposure is limited. However, the benefits of the treatments must persist for long periods in between applications. Hence the persistence of the treatment may limit the practicality of the treatment, even if it is very effective over the short term.

AECL performed a literature review of available chemical treatments in an effort to identify surface treatments to carbon steel oxide surfaces which may prove beneficial in reducing feeder wall thinning. These treatments were then assessed according to the following criteria:

a) potential effectiveness in mitigating feeder pipe wall thinning;
b) potential for long term effectiveness;
c) ease of implementation;
d) compatibility with other HTS materials and other systems.

In assessing the potential effectiveness, a solubility-dominated mechanism was assumed to be responsible for the majority of the observed feeder pipe wall thinning (Burrill and Cheluget, 1998). Hence, treatments producing macroscopic films of a dissolution-resistant oxide were considered most likely to reduce feeder pipe wall thinning.

The most promising treatment was a hydrothermal chromate treatment (HTCT). The main attributes of the HTCT is that it can be easily applied to closed water systems and produces Cr-rich oxides on carbon and low-alloy steel. The benefits of adding small quantities of Cr to carbon steel as a means of controlling FAC is well documented (Chexal et al., 1996). It is generally believed the Cr from the base metal becomes incorporated into the oxide making it more resistant to dissolution. Hence, any treatment producing Cr-rich oxides should also be beneficial in reducing feeder pipe wall thinning.

HTCT has been shown to be effective in reducing FAC through in-reactor loop experiments using the NRU reactor at the AECL Chalk River Laboratories (CRL) Site. Representative data is presented in Figure 9 which show the weight loss from two carbon steel coupons as a function of exposure time in U-2 loop. (The operating conditions where the coupons are located in the U-2 loop are similar to that of the outlet feeders in a CANDU reactor.) One of the coupons had had the HTCT applied in an out-reactor loop, while the other coupon was used as a reference. As seen in Figure 9, the corrosion rate of the treated coupon was initially reduced significantly. However, the benefit then decreased with time, as Cr was lost from the surface under these conditions. Hence, in an existing reactor, reapplication of the treatment would be necessary in order to maintain a reduced wall thinning rate.

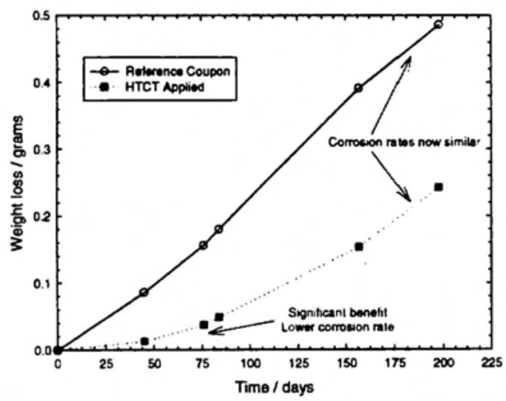

Figure 9: The impact of an HTCT application on the weight loss from a carbon steel coupon exposed in U-2 loop, NRU Reactor.

A second chemical treatment, based on Ti addition to the HTS during normal reactor operation, is also being developed by Kinectrics, formally Ontario Power Technologies. Preliminary results are encouraging. The development of both the Ti-inhibitor and HTCT is continuing.

3.3 Effect of Chromium in Carbon Steel on Feeder Thinning Rates

The benefits of small quantities of Cr added to carbon steel in reducing FAC has been well documented in the literature (Chexal et al., 1996). Prior to the measurements confirming that high corrosion rates were being observed in the outlet feeders at CANDU stations, AECL had proactively changed the Cr specification in the ASME SA106 Grade B carbon steel used in manufacturing feeder pipes to >0.20 wt% (the maximum concentration allowed is 0.40 wt%). Tests are currently underway to validate that this Cr specification will allow feeders to achieve their design intent. FAC rates have been determined from weight loss measurements of coupons exposed in the in-reactor U-2 loop, at CRL. Representative data is presented in Figure 10 comparing the corrosion rate of carbon steel containing 0.013 wt% Cr (typical of the Cr content in existing reactors) to that of steel containing 0.24 wt% Cr. Weight loss measurements collected from ~1½ years of exposure under typical CANDU HTS conditions indicate a significant reduction in FAC rate as a result of the 0.24 wt% Cr.

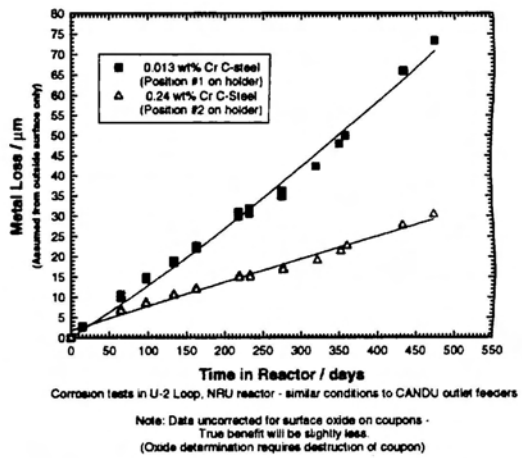

Figure 10: Plot of weight loss against exposure time for 0.013 and 0.24 wt% Cr coupons exposed in U-2 loop NRU reactor.

4. CONCLUSIONS

Wall thinning of outlet feeders have been observed at all CANDU stations with the highest rates being observed at the CANDU-6 and Darlington Units and the lowest rates at the Pickering Units. For a given reactor, the wall thinning rates have been shown to scale with the thermalhydraulic parameters of mass flow rate (Q) and linear velocity (V), as well as the product of these parameters, referred to as QV. The mechanism of feeder wall thinning has been attributed to FAC which is often observed in carbon or low-alloy steel components carrying de-oxygenated water or water/steam mixtures under conditions of high mass transfer. Without intervention, wall thinning is expected to limit the operating life of some outlet feeders.

R&D programs were initiated to develop measures for reducing the rate of feeder wall thinning. The first measure recommended was to operate existing plants with a HTS coolant pH_a in the range $10.2 < pH_a < 10.4$ as opposed to the original $10.2 < pH_a < 10.8$ specified for CANDU-6 plants. Evaluation of feeder wall measurements collected from the CANDU-6 stations at Embalse, Gentilly-2, and Point Lepreau suggests a benefit of ~10% by operating at an average pH_a of 10.2 as opposed to 10.6. Putting aside uncertainties in thermalhydraulic conditions at the three stations, if initial wall thicknesses at the first bend of the 2½-feeders at Embalse were lower than the 6.25 mm value normally used for the estimation of the corrosion rates (as suggested by the site measurements on the spare bends), then the benefit of operating in the lower pH_a range could be higher.

Correlating wall thinning rates with operating pH_a history can be hampered by the errors associated with the measurement of pH_a using glass electrodes. Much of this uncertainty can be reduced by using the calculated pH_a, based on measured Li^+ concentrations, rather than measured pH_a values. Although all available data demonstrates that operating at the lower pH_a range is beneficial, maintaining the pH_a in this range can be difficult. In response, AECL has designed a narrow-band pH_a system which can be retrofitted to existing stations to facilitate chemistry control within this range.

A second measure being considered for reducing feeder wall thinning is the development of chemical treatments. One option being pursued at AECL is a treatment which enriches Cr in the oxide film normally found on carbon steel surfaces. In-reactor loop experiments have shown that such a treatment can significantly reduce the rate of FAC, although re-application of the treatment is necessary to maintain those benefits. A second option involving Ti-addition is being developed at Kinectrics.

Based on data collected under balance-of-plant conditions, which indicated that an increased Cr content in the carbon steel reduces FAC, the AECL specification for Cr in carbon steel used for feeder pipes has been increased to >0.20 wt% (the maximum limit allowed is 0.40 wt%). Experiments currently in progress in the in-reactor U-2 loop at CRL are intended to confirm that increasing the Cr content of the carbon steel will provide the required reduction in the rate of FAC.

5. ACKNOWLEDGEMENTS

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