HYDROGEN EFFUSION PROBE DEVELOPMENT AND INSTALLATION AT THE POINT LEPREAU GENERATING STATION

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Abstract

Some corrosion reactions which occur in steel pipes have hydrogen as a reaction product. This hydrogen may diffuse through the steel to the outside of the pipe and escape as hydrogen gas; a process referred to as hydrogen effusion. Literature shows that the rate of corrosion can be estimated by measuring the rate of hydrogen production.

CNER enlisted the services of RPC to design and manufacture a corrosion monitor based on the principle of hydrogen effusion - the **HE*Pro***. In May 2006, an **HE*Pro*** was installed at PLGS. This report describes the success of the development and installation of the **HE*Pro***.

1. Introduction

The present report describes an endeavor conducted by the Centre for Nuclear Energy Research (CNER), and collaborators, to perform a field installation of a new on-line corrosion rate monitor at the Point Lepreau Generating Station (PLGS). This report presents concepts such as development methodology, equipment design and installation of the monitor. Initial corrosion rate data is presented however the interpretation of the results is not yet available. Further research is currently being conducted at CNER to gain a thorough understanding of the results.

1.1 Background

PLGS has a CANDU® 6 reactor which was commissioned in 1982 by NB Power Nuclear. The CANDU 6 design consists of 760 feeder pipes (190 inlet and 190 outlet feeders on each of the two reactor faces) that transfer coolant between the reactor core and the steam generators. In the early 1990's heavy deposits of magnetite were discovered in the cold leg of the PLGS steam generators [1]. This finding led to focused feeder wall thickness inspections and the discovery that wall thinning rates of all outlet feeders were in excess of what was accounted for in the corrosion design allowance [1]. Of particular concern was a location adjacent to the pressure-tube end fittings (Grayloc) near the reactor outlet where predicted rates of corrosion were in the upper range of 40 to 140 μm/yr based on estimated initial thicknesses [2]. The strong correlation between coolant velocity and corrosion rate [2] coupled with the observed scallop formations on the interior surface of the pipe [1] suggested that the mechanism of deterioration was flow-assisted corrosion (FAC). As of the 2006 maintenance outage, excess thinning has led to the replacement of six tight radius outlet feeder bends at PLGS. Feeder pipe inspections at other CANDU 6 reactors have confirmed the prevalence of this phenomenon.

1.2 Flow-assisted corrosion

FAC is a specific type of erosion-corrosion resulting in an increased rate of corrosion of carbon or low-alloy steels due to the dissolution of their normally protective oxide layer into moving water or water/steam mixtures [3]. FAC is a complex corrosion reaction and is believed to be a function of many variables including solution temperature, pH, oxygen concentration, fluid quality and flow velocity as well as the geometry and composition of the material. Table 1 outlines the normal PLGS outlet feeder operating conditions.

Table 1 PLGS normal outlet feeder conditions [1]

Property	Normal Value
Temperature	307-312°C Average: 310.7°C
Pressure	10.3 MPa
Two-phase quality	0.2-19% Average: 1.06%
Time in two-phase	0-94% Average: 49%
Average velocity	6.5-14.5 m/s Average: 12.2 m/s
pH_a	Operating 10.2-10.4 since 1999
Dissolved O_2	Specification <0.01 mg/kg
Dissolved D_2	Specification 3-10 mL(STP)/kg

The corrosion reaction of carbon steel in deoxygenated water is:

$$Fe + 2H^{+} \rightarrow Fe^{2+} + 2H \qquad (1)$$

The iron ions then react with water to form magnetite and the atomic hydrogen migrates through the steel (i.e. pipe wall) where it recombines to form hydrogen gas. Tomlinson [4] suggests that the percentage of through-wall hydrogen may be as high as 90%. In the case of outlet feeder pipes, proprietary research by AECL showed that this percentage is nearly 100%.

1.3 Hydrogen probes for estimating corrosion rate

Hydrogen that diffuses through a pipe wall can be directly measured using a hydrogen probe [5]. There are three main categories of probes used to predict corrosion rates based on measuring through wall hydrogen: pressure, vacuum and electrolytic. NACE [5] has published a comprehensive paper discussing the above techniques and can be referred to for further details.

There are two types of hydrogen pressure probes – insertion and clamp-on. Insertion probes require that the pressure boundary be penetrated to allow for the insertion of a hollow steel tube into the fluid. The tube end inserted into the fluid is plugged and the external end is connected to a pressure gauge and bleeder valve [5]. Corrosion on the exterior of the tube is reflected by an increase in measured pressure. Hydrogen collected within the tube is purged via the bleed valve. Clamp-on pressure probes have the advantage of being installed without interruption to the operating system. Typically the body of clamp-on probes must be machined to fit the pipe or vessel to allow for an adequate seal. O-rings are generally used as the sealing medium and one known disadvantage of the clamp-on style probe is the tendency for seal leakage [5]. To minimize this problem clamp-on probes require an installation surface that is smooth, unpainted and rust free. Clamp-on probes can also be permanently welded to a vessel wall. The volumes of pressure type probes must be minimized to maintain maximum probe sensitivity. Although the response to changes in corrosion rate is slower in clamp-on style probes as compared to the insertion style they are considered to be more accurate [5].

Vacuum type probes can also be categorized as insertion or clamp-on. These probes are accurate and have low response times [5]. Vacuum type probes measure the electrical current drawn while operating a vacuum ion pump which transfers hydrogen from a hollow tube to the surface of a cathode [6]. The instrumentation required for this type of hydrogen measurement includes a strong magnet, ion pump, valve, anode and cathode and instrumentation [6].

The three electrolytic type probes discussed in the NACE report [5] operate on the same basic principle of measuring current change but differ in the methodology and equipment. One type requires the use of a palladium membrane and a plastic chamber containing a solution of sulphuric acid. The second uses complex electronic equipment to measure the current required to ionize H^+ into hydrogen. A third technique uses a nickel dioxide electrode in place of the complex electronics used in the second method. In this case the hydrogen atoms are ionized by the potential generated by the electrode. Electrolytic type probes are considered to be accurate and sensitive with a faster response time then pressure type probes but require more complex equipment.

2. Development of a hydrogen probe by CNER

The development of a hydrogen probe to predict corrosion rate was an initiative of CNER and one of the objectives of the Atlantic Innovation Fund (AIF) Project #181922. This project is jointly funded by Atlantic Canada Opportunities Agency (ACOA), NB Power Nuclear, CANDU Owners Group (COG) and Atomic Energy of Canada Limited (AECL). The objective of this particular project was to design, construct, install and test a probe capable of monitoring the rate of outlet feeder wall thinning at PLGS. On a broader scale it is anticipated that information obtained from this and other feeder installations will help to monitor the integrity of CANDU Primary Heat Transport (PHT) system feeders and optimize the operational life of outlet feeders and potentially reduce the scope and frequency of feeder inspection.

To appreciate the design of the hydrogen probe it is important to understand the inherent restrictions associated with installing a piece of equipment on a PHT feeder pipe in the reactor building of a nuclear generating station. Probe requirements were that it be non-intrusive, intrinsically safe, on-line, capable of remote monitoring, fully automated, require minimum maintenance and be capable of operating at high temperatures (> 310ºC).

The probe designed by CNER and collaborators is referred to as the Hydrogen Effusion Probe or HEP (patent pending). The HEP falls in to the category of clamp-on style pressure probes. The HEP is similar to conventional clamp-on style probes in that it involves sealing the probe to the outside of a pipe and measuring the rate of hydrogen pressure increase within the known probe volume. One unique feature of the HEP is that it seals directly to the pipe wall without the use of an O-Ring or welding. To allow for increased accuracy and sensitivity, the HEP operates under vacuum. The HEP corrosion monitoring system (**HE*Pro***) is fully automated and monitoring is normally done remotely. To minimize the escape of captured hydrogen the probe and attached tubing are constructed of silver. The portion of the probe that attaches to the PHT feeder is metal (silver and carbon steel) allowing for operation well above 310^{o}C. The design allows for the remainder of the system components to be located at a distance from heat and/or radiation environments (in this case the reactor feeder cabinet) while still maintaining a low total volume. No chemicals or electrodes are required and only annual maintenance of the vacuum pump and calibration of the pressure transducer is anticipated. Although the clamp-on style pressure probes have historically suffered some shortcomings compared to the other style probes, the HEP design has minimized many of these limitations allowing for reliable and accurate corrosion rate measurements.

To gain additional confidence that the HEP was quantitatively predicting FAC rates, an on-line ultrasonic monitor was installed adjacent to the HEP. The Feeder On-line Thickness Monitor (FOLTM) is a proven ultrasonic wall thickness monitor constructed and installed at PLGS by the New Brunswick Research and Productivity Council (RPC). The FOLTM requires more data (and thus more time) to trend the thinning rate compared to the HEP. The HEP collects hydrogen effusing through a pipe wall and, provided the chemistry of the fluid is reducing, this can be correlated to the rate of FAC experienced by the pipe wall at that location. This direct measurement of FAC coupled with its high signal-to-noise ratio has allowed changes to be detected by the HEP an order of magnitude sooner than with the FOLTM. Like the FOLTM, the HEP provides an on-line rate of pipe wall thinning. On-line measurement of wall thinning is superior to periodic inspection data because wall thinning predictions based on periodic inspections assume a linear thinning rate between inspections. To more effectively manage PHT feeder integrity it is important to know whether the rate of FAC is constant or whether it increases under transient conditions, such as plant start-up. An on-line HEP measurement is sensitive enough to reveal this.

3. Equipment and methodology

3.1 HEP equipment

The HEP, manufactured by RPC and installed at PLGS, consists of a silver cup, inserted into a 63.5 mm (2 ½”) diameter carbon steel assembly (clamp) (refer to Figure 1), connected via silver and stainless steel tubing to a valve and pressure transducer (Figure 2). A data acquisition and control system is used to control the vacuum pump and valve operation and record readings from the transducer and thermocouples. These components are discussed in further detail below.

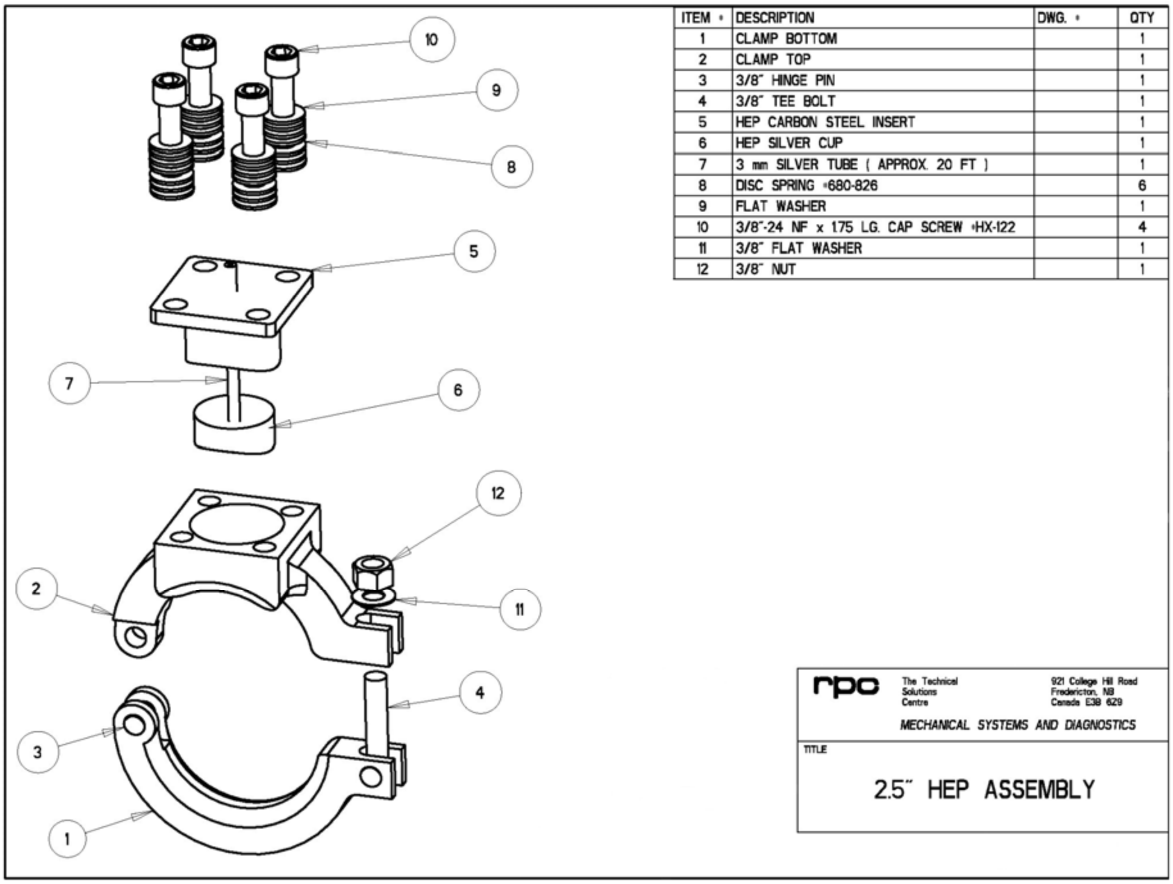

Figure 1 HEP annulus and clamping apparatus

The HEP system operates under vacuum. The HEP, when clamped to the PHT feeder pipe, provides a vacuum tight seal. The pump is used to create a vacuum within the silver cup, tubing and transducer. The valve, when closed, maintains the vacuum. Hydrogen effusing from the pipe (due to FAC) is collected in the HEP and causes the pressure to rise. The transducer measures the hydrogen pressure increase which is then used to calculate wall thinning rates. Four thermocouples provide temperature information that is used to calculate FAC rates. Temperature correction of the measured pressure is necessary to ensure an accurate conversion of the pressure increase into corrosion rates. After a predetermined pressure of 2000 Pa is reached the data acquisition and control system automatically repeats the cycle. The vacuum pump switches on to evacuate the volume and restart the cycle. The computer is used to collect and analyze the data coming from both the FOLTM and the HEP. A telephone line connected to the computer allows for remote data retrieval and monitoring.

To minimize the escape of hydrogen at elevated temperatures small ID (inner diameter) silver tubing is used for the section of tubing routed through the PHT feeder cabinet. Since stainless steel (SS) has an acceptably low diffusion coefficient at boiler room temperature (hydrogen permeability of stainless steel at temperatures of less than 100ºC is similar to that of silver at 300ºC) small ID SS tubing is used for the remainder of the tube run through the boiler room to the isolation valve and for connection between valve and pressure transducer. Constructing the clamp from carbon steel allows for similar thermal expansion characteristics of the pipe and clamp. Compensating washers, positioned under the cap screws securing the probe, were designed to provide dynamic loading capable of ensuring consistent force applied by the clamp to the pipe during temperature fluctuations. The absolute pressure transducer has an accuracy of +/- 0.05% of reading over the full range of 0 to 1000 torr (133 KPa). The vacuum pump is a two stage, oil sealed, sliding vane pump capable of pumping down to an ultimate vacuum of 2.3 x 10^{-3} torr (0.3 Pa). The vacuum pump exhaust is vented to the exterior of the cabinet to prevent the possibility of hydrogen build-up inside the cabinet. The isolation valve is an electromagnetic valve with a low-volume and a known leak rate of 8.6 x 10^{-3} Pa L/day (1 x 10^{-9} mbar L/s). OPTO 22 I/O modules are used for system control and data collection. The control system was designed to operate in either manual or cycle mode. In both modes the data acquisition and control system collects data which can be retrieved and later analyzed off-line. The pressure transducer, valve, vacuum pump and data acquisition system are all housed in an instrumentation cabinet located in the boiler room. Type K thermocouples are used to monitor temperature at four locations: on the feeder pipe, approximately half way along the silver tubing in the feeder cabinet, at the SS to silver tube connection and inside the HEP instrumentation cabinet.

A simplified schematic of the HEP System is shown in Figure 2.

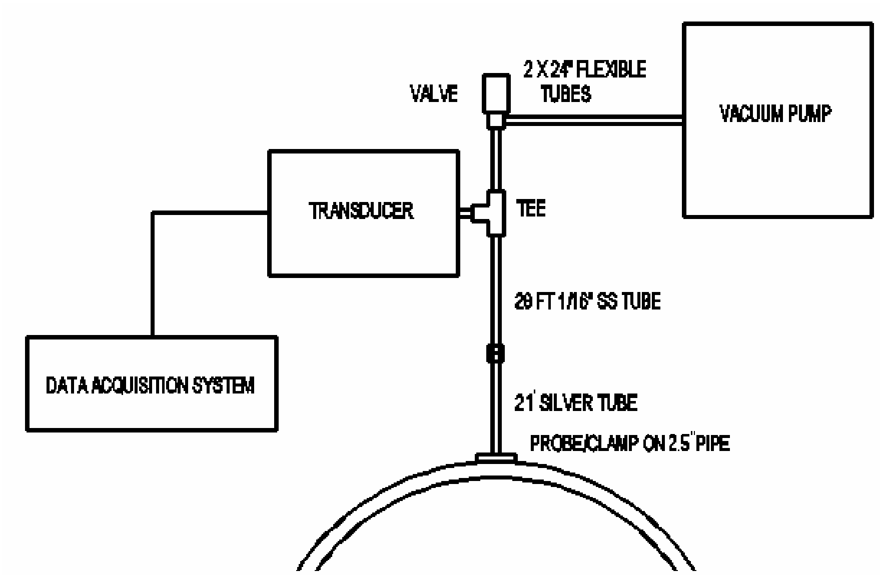

Figure 2 Schematic of HEP components

3.2 Data collection and evaluation method

HEP pressure and temperature data is continuously recorded and time stamped every five seconds by the data acquisition and control system. The following section discusses how this data is used to calculate corrosion rate.

There are a number of assumptions and requirements for an HEP to be used for predicting FAC rates:

a. All the atomic hydrogen produced by the FAC process is absorbed locally by the carbon steel experiencing FAC.
b. All the absorbed hydrogen which diffuses through the wall of the carbon steel pipe recombines to form molecular hydrogen at the external interface.
c. Any molecular hydrogen dissolved in the fluid does not contribute to the hydrogen flux through the wall of the pipe.
d. Very low concentrations of oxidizing species are present in the fluid.
e. Atomic hydrogen does not accumulate at the grain boundaries or at defects.
f. The pipe ID surface under the HEP is assumed to be thinning at a uniform rate.
g. For calculation purposes the molar mass and density of the carbon steel SA-106B pipe is assumed to be equal to that of pure iron.

The rate of FAC can be calculated using Equation 2:

$$C=\frac{a\cdot\frac{\partial n}{\partial t}\cdot MM_{Fe}}{A\cdot\rho_{Fe}} \tag{2}$$

Where C is the rate of FAC in µm/yr and,

$$\frac{\partial n}{\partial t}=\frac{\partial P}{\partial t}\cdot\frac{V}{RT_{eff}} \tag{3}$$

T is the temperature in degrees Kelvin, $\partial n/\partial t$ is the rate of increase in hydrogen expressed in moles/day and $\partial P/\partial t$ is the rate of pressure increase in kPa/day. All other parameters (constants) are identified in Table 2.

Various HEP system components are exposed to different temperatures (ranging from about 300ºC on the pipe to 40ºC in the HEP instrumentation cabinet) and the pressure exerted by the hydrogen molecules within the fixed volume of the system is dependent upon the temperature. The effective temperature (T_{eff}) therefore is based on the volume proportion of the HEP system at known temperatures. The field installation, as previously noted, had four thermocouples located at different points along the length of the system. In addition to the thermocouples, the temperature of the pressure transducer is kept at 45ºC.

Table 2 Constants for determining FAC rate

Parameter	Description	Units	Value
a	conversion of days to year	days/yr	365
A	area under HEP on internal pipe wall	cm^2	3.78
V	total volume of HEP assembly	m^3	13.1×10^{-6}
MM_{Fe}	molar mass of iron	g/mol	55.85
ρ_{Fe}	density of iron	g/cm^3	7.86
R	gas constant	$(m^3)(Pa)/(mol)(K)$	8.314

4. Installation of the HE*Pro* at PLGS

4.1 Installation

The HEP was installed at PLGS during the 2006 maintenance outage. The PHT feeder chosen for the installation of the HEP was an outlet feeder with a flow velocity of approximately 11 m/s which was expected to experience FAC during operation and is located on the outer face of the feeder bank providing for relative ease of access and installation.

In choosing the location for installation it was necessary to consider the distance from the reactor face and the possible presence of deuterium peroxide which is produced by radiolysis in the reactor core. If deuterium peroxide was present at a given location within the feeder pipe it would prevent the reduction of hydrogen, thereby interrupting the diffusion of hydrogen and invalidating the direct relationship between hydrogen pressure and FAC rate. A relatively straight section of PHT feeder pipe was available approximately 150 mm (5.9 in) below the freeze jackets at a distance of 2.4 m (8 ft) from the Grayloc hub that connects to the fuel channel. At this distance no deuterium peroxide was expected to be present in the coolant.

The attachment of the HEP to the PHT feeder pipe required the surface of the pipe be prepared by removing the existing exterior surface oxide layer and polishing an area 6.35 mm (¼”) diameter larger than that required for the silver probe. This was accomplished using successively finer grit polishing discs until finally polishing with diamond paste and cleaning with acetone. The seal between the silver cup and surface of the feeder pipe was obtained through deformation of the edge of the cup which had been machined to match the outside curvature of the pipe.

The freeze jacket of the PHT feeder adjacent to the test feeder had been previously removed but the 12.7 mm (½”) diameter tubing for both the thermocouple and liquid nitrogen supply to the freeze jacket remained. These tubes were used to route the silver tubing and coaxial cabling from the two assemblies located on the feeder through the feeder cabinet to the boiler room. The tubing provided protection for the silver tubing, thermocouple wire and the coaxial cable. The installed HEP and FOLTM are shown in Figure 3. The polished section of feeder pipe is clearly evident between the FOLTM and the HEP.

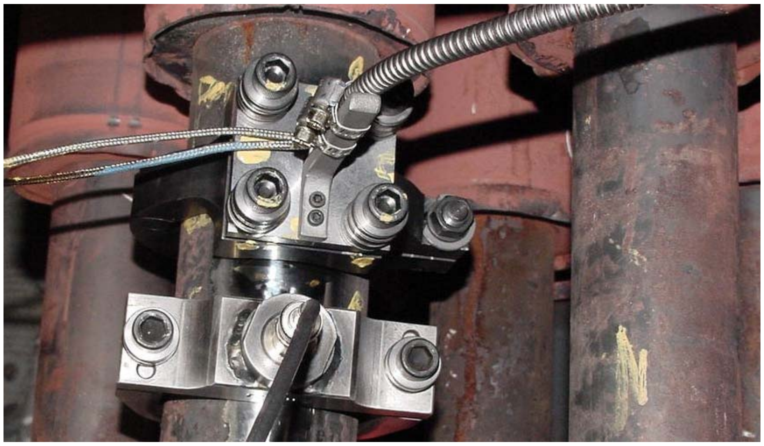

Figure 3 Installed HEP (top) and FOLTM (bottom) on PHT feeder

4.2 Leak testing

The installation of the HEP on the PHT feeder was conducted during the planned station maintenance outage in 2006 when the feeder pipe temperature was below 25ºC. Once the HEP was attached to the test feeder it was necessary to verify the integrity of the seal and determine the air ingress leak rate. Leak testing of the HEP was performed during the period between the HEP installation and plant start-up. At this time the feeder was not experiencing FAC as the flow through the feeders was approximately 5% of the full power flow rate. In addition, oxidizing species were present in the coolant and no hydrogen was being produced at the corroding surface. During this time a leak rate on the order of 5 Pa/day was observed. Given that the expected daily pressure accumulation was approximately 2000 Pa this represents only a 0.25% contribution to the reported pressure due to leakage. During plant start-up, as the temperature rose by over 260ºC, a small increase in pressure, possibly due to minor transient leakage, was observed. This phenomenon was also observed during temperature cycling experiments conducted at RPC. Future evidence (described in Section 4.3) confirmed that this was not a permanent change and that an insignificant leak rate continues to this day.

4.3 HEP operation

The start of HEP corrosion rate monitoring occurred after the first pump down period following station re-start at which time the HEP probe temperature reached 293ºC and the oxygen concentration had fallen below 1 ppb, allowing for the possibility of FAC supported by hydrogen reduction. Figure 4 shows the pressure measurements over the first month of operation.

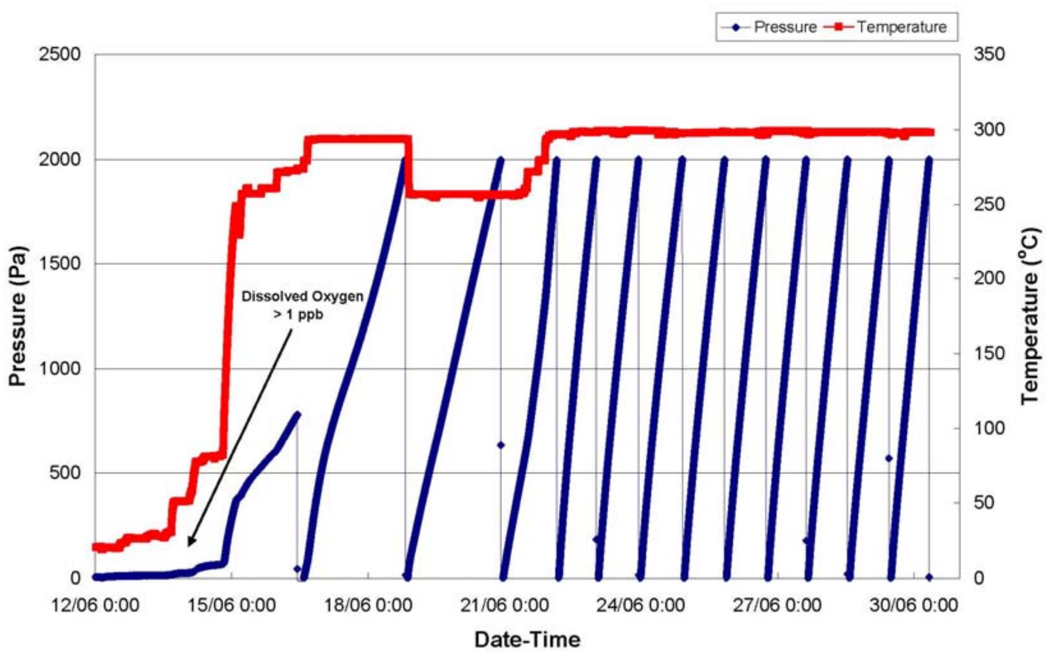

Figure 4 HEP pressure measurements

The results following the first pump-down cycle indicated a pressure accumulation of 816 Pa/day. Further maintenance at PLGS was required and the station temporarily shut-down with the HEP probe temperature falling to 256ºC for approximately 2 days. Once the station returned to full power the HEP probe temperature stabilized at 298ºC and the pressure accumulation rate increased dramatically to 2342 Pa/day. The pressure increase measurements over the period from start-up until the end of August are provided in Figure 5. It can be seen from Figure 5 that the rate of pressure accumulation continued to increase over approximately the first 30 days of measurement to a maximum rate of 3150 Pa/day before gradually decreasing to what appears to be steady state conditions. For a period of three weeks prior to the fuelling of this feeder on August 17th, the average pressure increase was 1890 Pa/day with a standard deviation of 58 Pa/day. Pressure accumulation rates can be directly converted to corrosion rate as discussed in Section 3.2. The aforementioned pressure rise rates correspond to corrosion rates within the expected range of 40 to 140 µm/yr. The FOLTM data are also in this range, agreeing well with **HE*Pro*** predictions.

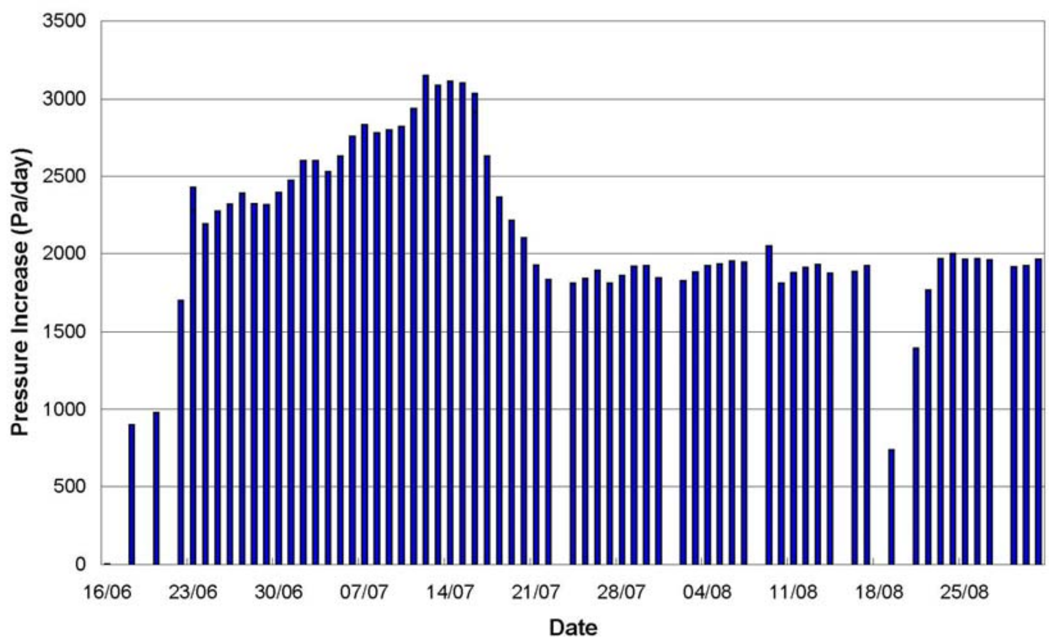

Figure 5 Corrosion rates predicted by HEP

Fuelling of the test feeder occurred on August 17, 2006. During the fuelling process water is taken from the D_2O Storage Tank and enters the fuelling machine before entering the fuel channels and ultimately the outlet feeder pipes. The D_2O Storage Tank has a lower temperature than the outlet feeders and contains significant concentrations of dissolved oxygen. There was virtually no rise in HEP pressure from the time fuelling started until 1.5 hours after fuelling was completed at which time the measured probe temperature increased to 300ºC due to the installation of fresh fuel (Figure 6). The abrupt stop to the pressure rise indicates that hydrogen evolution and/or corrosion had ceased. Whether it was cessation of corrosion or hydrogen evolution, the effect on the HEP measurements would be the same. Even after the pressure increase resumed, the rate of increase was below the pre-fuelling values for a period of six days.

The absence of a rise in HEP pressure coincident with the presence of oxygen during fuelling suggests that the previous increase in pressure experienced by the HEP is in fact through wall hydrogen.

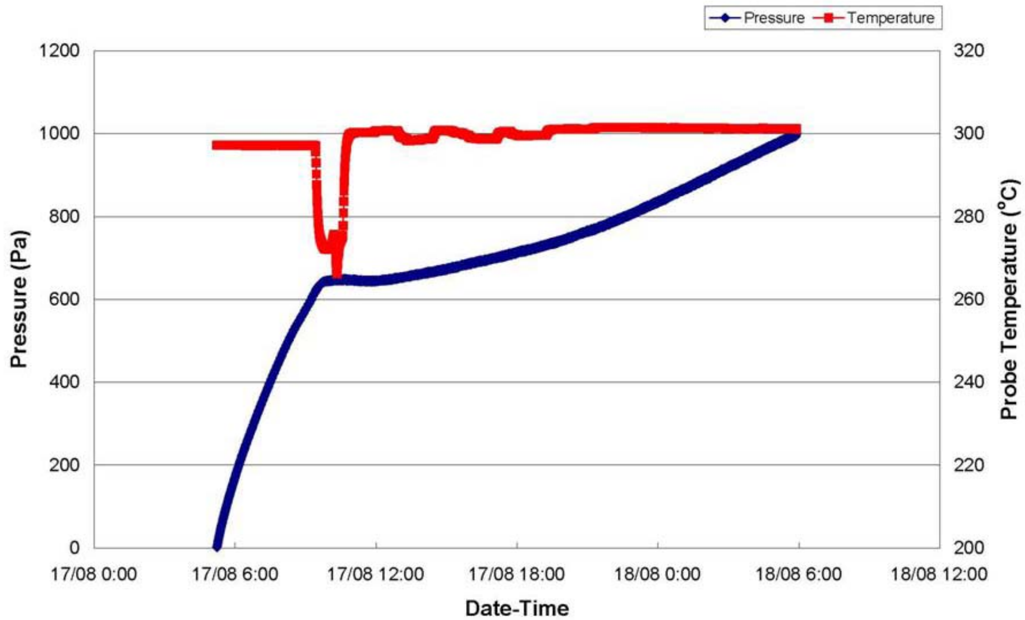

Figure 6 HEP pressure increase during fuelling

The absence of any noticeable change in HEP pressure for more than 1.5 hours after the start of fuelling also indicates that the leak rate for the HEP must be negligible, thereby eliminating any concern that the leak rate may have increased during plant start-up.

5. Conclusion

The ability to monitor flow-assisted corrosion of carbon steel CANDU outlet feeder pipes has been demonstrated by the installation of an **HE*Pro*** at PLGS. The **HE*Pro***, designed and constructed by CNER and its collaborators was successfully installed on an outlet feeder at PLGS during the 2006 maintenance outage. To date, the **HE*Pro*** is operating reliably and continues to provide useful information to the CANDU community.

6. Acknowledgements

CNER would like to acknowledge that the success of this project would not have been possible without the considerable support provided by a number of partner companies and colleagues. AECL contributed the background research and proof-of-principle testing with continued support throughout the design and installation phases. Funding was supplied by ACOA, NB Power, COG and AECL. RPC provided high quality design and manufacturing services. The staff at PLGS provided outstanding design review, field installation and operational support.

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