Electrochemical Potential Monitoring At The Point Lepreau Generating Station During The 2006 Maintenance Outage

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Abstract

Electrochemical corrosion potential (ECP) probes were installed by the Centre for Nuclear Energy Research in the primary heat transport system sample line of the Point Lepreau Generating Station. The probes provided a realistic estimate of the ECP experienced by the outlet feeder pipes during the 2006 maintenance outage and into the start-up.

The results from the installation of the probes indicate that the corrosion potential of the probes, and by extension the feeders, is influenced by temperature, flow velocity and the presence of oxidizing species. Changes in the concentration of oxidizing species were shown to significantly alter the measured potential.

1. Introduction

The Point Lepreau Generating Station (PLGS), located in New Brunswick, Canada, is a 680 MWe CANadian Deuterium Uranium (CANDU®) reactor commissioned in 1982 [1,2]. The reactor contains 380 fuel channels which run horizontally through the reactor core [2]. Feeder pipes, which either supply or remove primary heat transport (PHT) coolant, are attached to either end of each fuel channel. The feeder pipes were originally designed for a 30 year service life at an operating capacity of 80%.

The discovery of through wall cracking of an outlet feeder pipe in 1997 caused considerable concern as to the longevity of the feeders and operation of the plant. Since 1997 cracks have been found through either leakage or inspection in a total of nine bends of outlet feeder pipes [2]. Cracks have occurred on both the inner and outer surface of the pipe. In all cases the cracking was found to be intergranular and at locations of high residual tensile stress [2]. Two mechanisms have been identified to explain the nature of the cracking: stress corrosion cracking (SCC) caused by exposure to mildly oxidizing hot coolant on the inner surface of the pipe and creep cracking on the exterior of the pipe enhanced by atomic hydrogen from flow assisted corrosion (FAC) [1].

The PLGS feeder pipes were constructed of ASME SA 106 Grade B carbon steel, the composition details of which are summarized in Table 1. PLGS bends were produced by cold draw bending of the feeder pipes without stress relief. Straining of the material was estimated at approximately 35% resulting in sustained high residual stresses [2].

Table 1 Chemical composition of feeder pipe material [2]

Element	**Percentage**	**Element**	**Percentage**
C	0.170	Mo	0.002
S	0.013	V	<0.002
P	<0.020	Cu	0.008
Mn	0.570	Si	0.330 Mill Certificate
Ni	0.011	Co	0.003
Cr	0.022	Sb	0.0005
Free-N_2	15 to 65 ($mg.kg^{-1}$)		

The three major factors required for SCC are a susceptible material, stress and strain, and environmental conditions [3]. One of the most significant environmental factors affecting the susceptibility of a metal to SCC is the electrochemical corrosion potential (ECP). Humphries and Parkins [4] have demonstrated the dependence of SCC on the ECP for both aerated and de-aerated solutions under potentiostatic control. It should be noted that the environments used in the work of Humphries and Parkins were significantly more alkaline than that experienced in the PHT system of CANDU reactors so a direct comparison is not possible, but the importance of the ECP in determining susceptibility to SCC is clearly emphasized. Slow strain rate stress corrosion testing of A533B steel in de-ionized water between 150 and 288°C showed the cracking potentials agreed well with the Fe_3O_4-Fe_2O_3 boundary [5]. If the threshold for SCC is correlated with the potential of the Fe_3O_4-Fe_2O_3 boundary over a range of pH and temperature, including CANDU outlet feeder conditions, the measured ECP can provide an estimate of the possibility of cracking under those conditions. The potential of the Fe_3O_4-Fe_2O_3 boundary, under outlet feeder CANDU operating conditions of pH_a 10.3 and 310°C, is approximately - 650 mV_{SHE}.

Knowledge of the ECP of a metal can be used not only to assess the possibility of SCC but also more generally to provide insight into the environment to which the metal is exposed and the resulting form of the oxide. The relationship between ECP and oxygen for stainless steel for instance is shown in Figure 1. The change in potential does not follow a uniform linear relationship with oxygen concentration but rather shows an ‘S-curve’ relationship with a fairly sudden transition from low potentials to more positive potentials. In addition to concentration and nature of the oxidizing species the temperature and type of metal will also affect the measured potential [6].

It is not feasible to measure the ECP of a feeder directly but a measurement of a representative sample subject to similar operating conditions can at least provide some insight into its operation and possible means of degradation. The ECP probe, initially designed by the University of New Brunswick Nuclear, is essentially a small diameter tube made from the same material as that used in the equipment under investigation. In the case of PLGS a section of carbon steel feeder pipe provided the stock material from which the probes were manufactured.

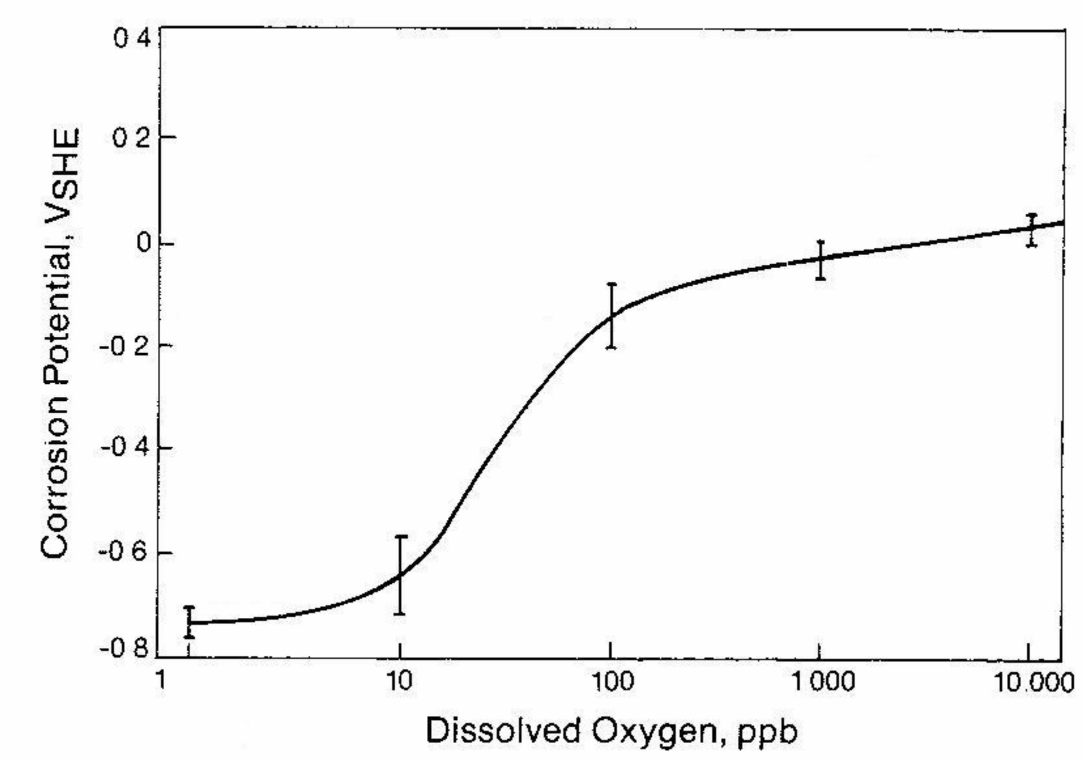


Figure 1 Relationship between potential and dissolved oxygen on stainless steel at 274°C [3].

During maintenance outages significant concentrations of dissolved oxygen and hydrogen peroxide can accumulate in the PHT system leading to elevated potentials of the steel. There is a shift from reducing conditions where magnetite is stable to more oxidizing conditions where maghemite is stable at lower temperatures and hematite at temperatures above approximately 200°C. Slade and Gendron [2] suggest that the conditions most likely to initiate cracking occur during reactor start-up after a maintenance period that allows substantial air ingress into the reactor coolant. It is this start-up period that is of most concern and when ECP measurements would be of greatest value.

The principle objectives of this investigation were to install an ECP assembly in PLGS during the 2006 maintenance outage and to measure the potential of the ECP probes, and by association that of the outlet feeders, during the outage period and into the start-up of the station.

2. ECP probe installation and investigation

Two probes were used to provide duplicate ECP measurements for comparison. The probes used in this investigation were machined from ASME SA 106 Grade B carbon steel PLGS feeder pipe stock having a chemical composition as outlined in Table 1. The ECP probes have an outside diameter of 6.35 mm which was reduced to 4 mm at the centre to facilitate electrical measurements in other applications. The 2 mm inside diameter was produced by electrical discharge machining instead of drilling to avoid excess work hardening. It should be noted however that the final step in the production process involves reaming the bore which may produce some degree of work hardening. The small inner diameter allows the probes to experience fluid velocities similar to those of the feeder pipes but at greatly reduced volumetric flows. The over all length of the probes was 152 mm.

The probes were electrically isolated from the ECP probe assembly by means of Teflon sheaths at either end of the probe. Two silver wires were soldered to the exterior of the probe to provide an electrical connection for ECP measurements. The ECP probe assembly for a single probe is shown in Figure 2.

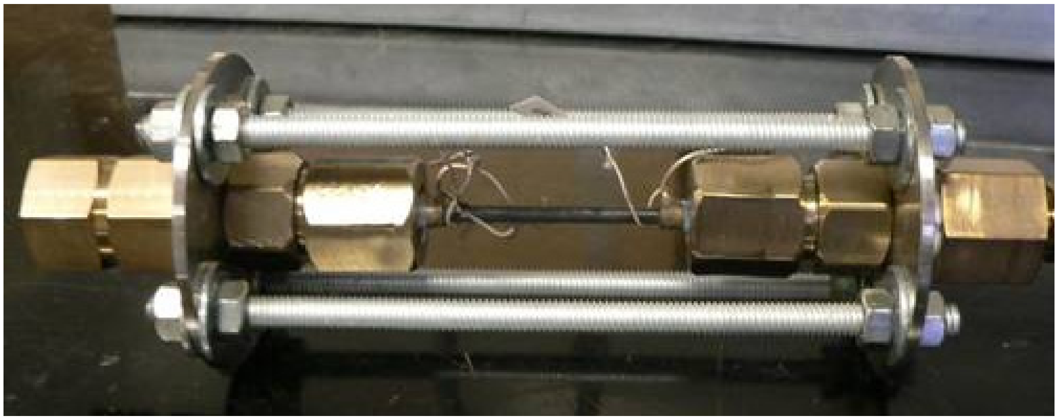


Figure 2 ECP probe assembly

Prior to installation at PLGS two probes were conditioned at the University of New Brunswick (UNB) in a research loop designed to mimic PHT conditions for a period of 30 days. The objective of the conditioning was to form an oxide layer representative of that commonly found on outlet feeder pipes. The filming conditions are outlined in Table 2. Once filming was completed the probes were dried with nitrogen gas and stored in a desiccator until installed at PLGS.

Table 2 UNB probe filming conditions

Parameter	**Value**	**Allowable Deviation**
Oxygen	<1 ppb	<1 ppb
Hydrogen	3 –10 mL/kg	6.5 ± 3.5 mL/kg
pH	9.9	± 0.15
Flow Velocity	10 m/s	± 0.5 m/s
Temperature	310°C	+5°C, -10^{o}C
Pressure	>10 MPa	-

Primary coolant was supplied to the ECP probes by two different sample lines. The ECP test assembly consisted of 316 stainless steel tubing, a pressure reducing coil, isolation valves, flow control valve and a 0.01M Ag/AgCl reference electrode. A schematic of the ECP assembly is provided in Figure 3. In addition to the ECP measurements, flow through the assembly was monitored with an ultrasonic flow meter and temperature by means of thermocouples attached to the exterior of the stainless steel tubing. The data acquisition system allowed for remote monitoring of events and values were recorded every five seconds. The installation of the ECP assembly at PLGS was treated as a permanent modification of the PHT sampling system. Tie-ins were provided from both the shut down cooling (SDC) sample line and the boiler #4 sample line and to the PHT sampling system discharge. These sample lines were chosen as they could provide the ECP assembly with the flow requirement necessary to replicate feeder flow velocities.

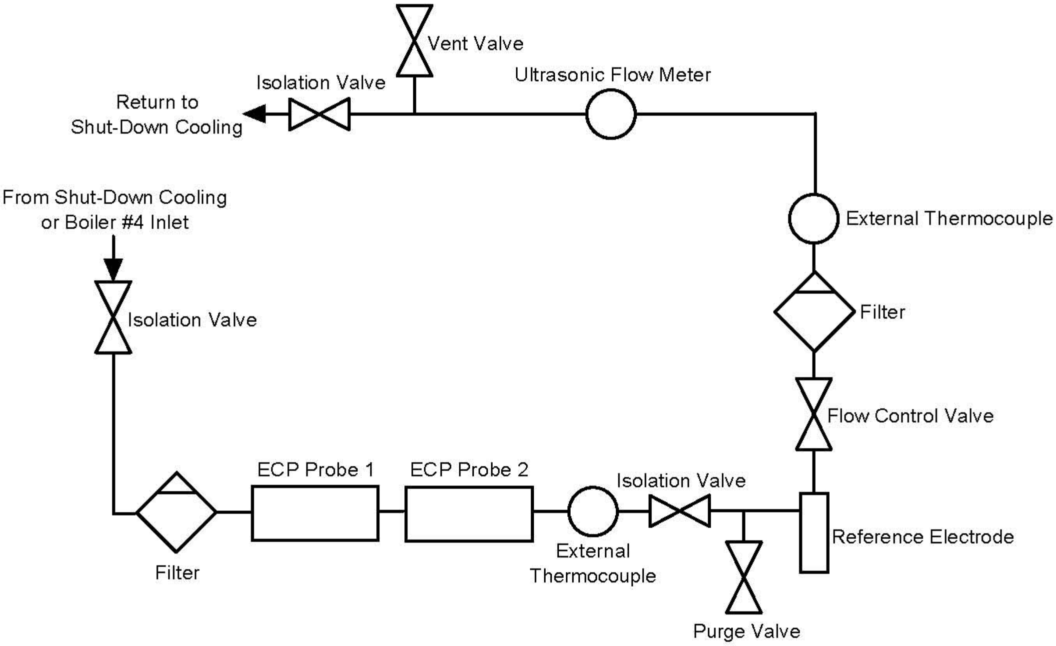
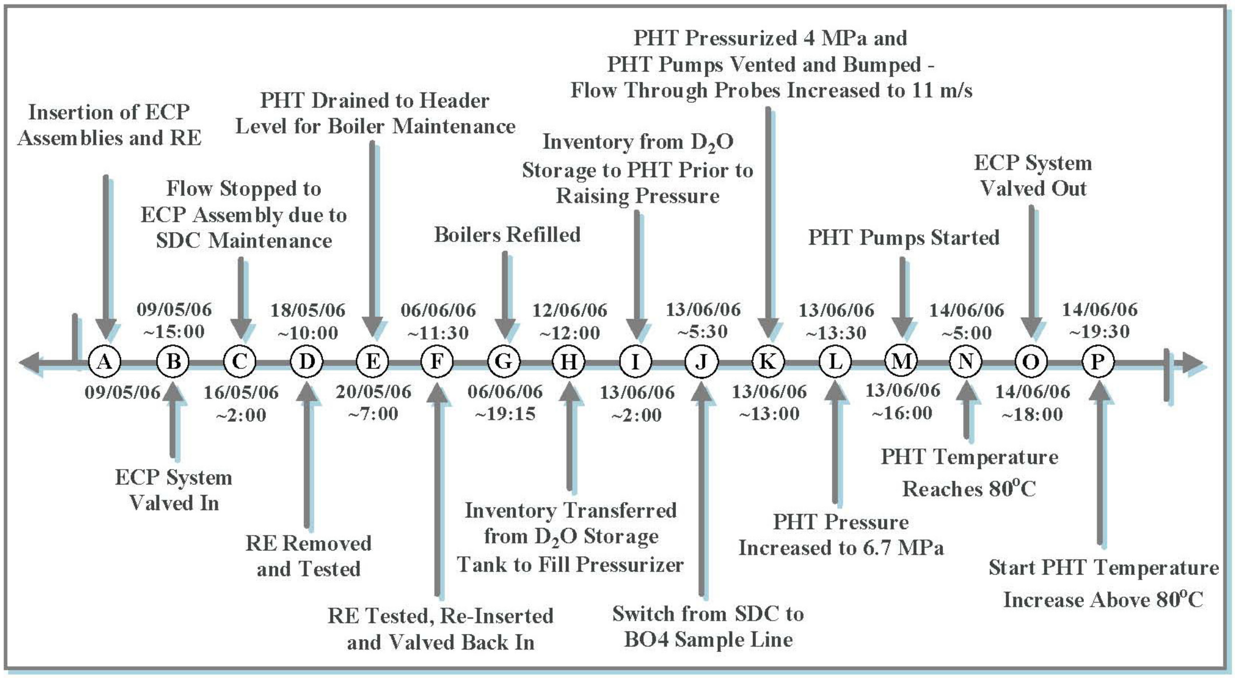


Figure 3 Schematic of ECP assembly

There were two distinct periods of operation during the 2006 maintenance outage at PLGS which can be categorized according to the source of primary coolant, the SDC sample line or the Boiler #4 sample line. During the period when flow through the PHT system was provided by the SDC pumps, flow to the ECP assembly was supplied by the tie-in to the SDC sample line. The ECP assembly was valved-in approximately 40 hours after the start of the outage, once the temperature of the primary coolant had fallen below 40°C. The velocity through the probes was less than 1 m/s, similar to the outlet feeders. The transit time of fluid from the junction of the PHT system with the sample line to the ECP assembly was estimated to be 1-2 hours under these flow conditions. Prior to boiler maintenance, the PHT system was drained to header level resulting in a loss of flow to the PHT sampling system and by extension the ECP assembly. During this period the valve between the reference electrode and the probes was closed, isolating the probes in the wet state and preventing oxygen ingress. The reference electrode was removed to prevent possible chloride contamination and to check its calibration. Once the boiler maintenance was completed the PHT system was refilled, the reference electrode was reinserted and the ECP assembly returned to service.

The source of primary coolant to the assembly was switched from the SDC sample to the boiler #4 sample line just prior to pressurization of the PHT system. After the PHT pumps were vented and started, the pressure increased and the temperature of the PHT coolant stabilized at 80°C. At this time the flow velocity through the ECP probes was set at approximately 11 m/s and the assembly remained in service until the temperature of the PHT coolant was increased above 80°C. A time-line of events relevant to the measurement of ECP and station operations is provided in Figure 4.



BO4 = Boiler #4
D_20 = Heavy Water
ECP = Electrochemical Potential
PHT = Primary Heat Transport
RE = Reference Electrode
SDC = Shut Down Cooling

Figure 4 Time-line of events during the PLGS 2006 maintenance outage

During the 2006 maintenance outage PHT system chemistry conditions were monitored routinely for deuterium and oxygen concentrations in addition to a number of individual grab samples for deuterium peroxide measurements. The impact of maintenance outage chemistry conditions on the potential of the ECP probes, and by extension the outlet feeders, will be discussed in the following section.

3. Results and discussion

There were at least two distinct ECP probe exposure periods during this investigation, which can be designated according to pre and post boiler maintenance. The first of these occurred from the time the ECP assembly was valved-in to the SDC sample line on May 9 until it was valved-out on May 16. The second period was from the time the ECP assembly was valved back in on June 6, after the completion of the boiler maintenance, until the investigation was stopped on June 14 when the temperature was increased above 80°C.

3.1 Pre-boiler work period

A continuous supply of PHT coolant was provided to the ECP probes during the pre-boiler work period at a flow velocity of less than 1 m/s, which was in the same order of magnitude as that experienced by the feeder pipes. The initial potential measurement of the two ECP probes, immediately after they were valved-in, was approximately +250 mV_{SHE} which was significantly higher than the Fe_3O_4-Fe_2O_3 equilibrium potential of -373 mV_{SHE} at 26°C and pH 9.9. The elevated potential indicates that either the PHT coolant contained appreciable concentrations of oxygen or some ferric oxide may have been present on the inner surface of the ECP probes. Deuterium peroxide measurements indicated that low (0.02 to 0.06 ppm) or non-detectable levels were found prior to commencement of primary side boiler work. Due to the limits of the detection equipment, low concentrations (10's of ppb) of deuterium peroxide may have existed in PHT coolant which could also have impacted the ECP of the probes. Potentials for the two ECP probes and the oxygen concentration of the pre-boiler work period are provided in Figure 5.

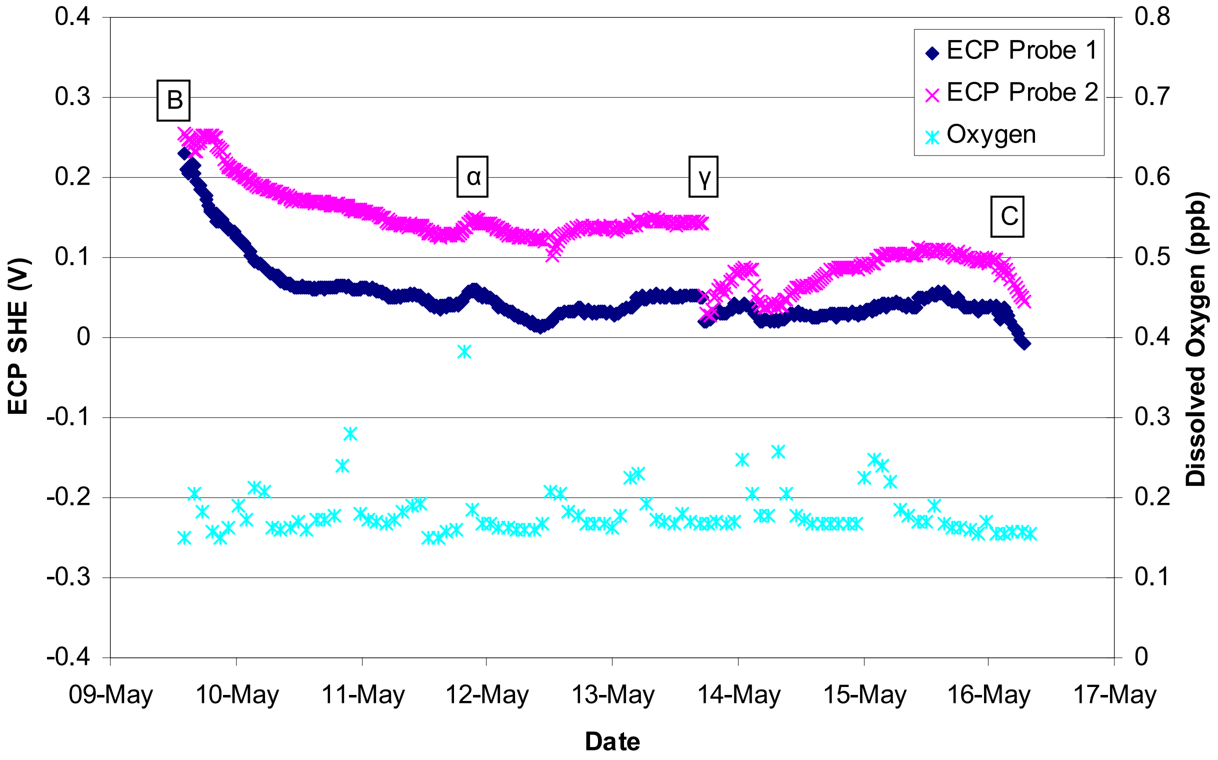


Figure 5 Oxygen concentration and ECP

The oxygen concentration of the PHT coolant was quite low with very little change from the average measured concentration of 0.19 ppb during the pre-boiler work period. The ECP measurements showed a gradual decrease in potential from +250 mV_{SHE} on May 9, point B (Figure 5), to +60 mV_{SHE} prior to flow stoppage of the SDC sample line on May 16, point C. The potentials of the probes, even towards the end of the pre-boiler work period, are higher than would be expected for the measured oxygen concentration. The probes may have experienced some oxidation of the pre-filmed magnetite layer prior to installation or during the valving-in sequence due to entrapped air in the ECP assembly. The valving-in sequence however was done rapidly and in such a manner so as to minimize the contact time of the potentially oxygenated coolant with the ECP probes. It is possible that the ECP probes were not an accurate estimate of the true potential of the feeders during the pre-boiler work period, though further investigation of the influence of low levels of deuterium peroxide on the ECP and more deuterium peroxide measurements during plant shut down are required before a definitive statement can be made.

It can be seen from Figure 4 that there was a deviation in the measured potential between the two probes. Both probes showed the same response to environmental changes as is evident from points α where a short term increase in oxygen concentration to 0.5 ppb and temperature transient resulted in a noticeable increase both ECPs of 15 mV despite having an off-set of approximately 100 mV between the two probes. The greatest variation in response of the two probes occurred at point γ where the potential of Probe 2 decreased by 112 mV over a period of 40 minutes while the potential of Probe 1 decreased by a much smaller amount. The substantial drop in ECP of Probe 2 is more characteristic of a change in oxide condition than an instrumentation fault which would have occurred over a much shorter time period. Manual measurements taken with a digital multi meter during the outage further confirmed the accuracy of the instrumentation. The cause of the sudden decrease in potential did not appear to be correlated with any changes in coolant chemistry, flow or temperature and may have been associated with the spalling of a discrete portion of the oxide surface though verification of this was not possible. A longer study period may have shown a convergence of the two probe values as they were exposed to identical operating environments.

Under ideal conditions, the ECP probes would be exposed to the primary coolant at higher temperatures for an extended period of time prior to the outage to ensure similarity of the ECP probes with feeder pipes. Probe filming was designed to simulate such exposure. Any slight differences that may have existed between the oxide of the filmed probes and the feeder pipes would be eliminated quickly at these elevated temperatures. However, it is important to note that one of the objectives of this investigation was the examination of ECP immediately prior to station start-up. The influence of high oxygen concentration later in the study period, as will be discussed, would ensure that the ECP probes and feeder pipes had similar potentials when the station proceeded beyond the 80^{o}C hold.

3.2 Post-boiler work period

Following the completion of the boiler work on June 6, there was a significant increase in the concentration of oxygen to 6 ppm compared to the 0.19 ppb value prior to May 16. The increase in oxygen was associated with an increase in the ECP from approximately +60 mV_{SHE} on May 16 to +330 mV_{SHE} once the ECP probes were valved back into the PHT system on June 6. Due to radiolysis of the abundant dissolved oxygen, deuterium peroxide concentrations between 3 and 5 ppm were measured after the completion of boiler maintenance. Elevated concentrations of deuterium peroxide would also contribute to the positive shift in the measured ECP values. No deuterium peroxide data are available after June 8.

The post-boiler work period saw the disappearance of the differences in ECP between Probe 1 and Probe 2. The increased oxygen concentration would likely have resulted in the formation of a ferric oxide layer on the inner surface of both probes resulting in the same measured ECP. As the feeder pipes would also have experienced similar oxygen concentrations to the probes, the ECP of the probes and the feeders are thought to have been similar at this point of the investigation. Following the boiler work, the probes provided a reasonable estimate of any further changes in ECP that would be observed by the feeders. The ECP of the probes and oxygen concentration after the completion of boiler work is provided in Figure 6.

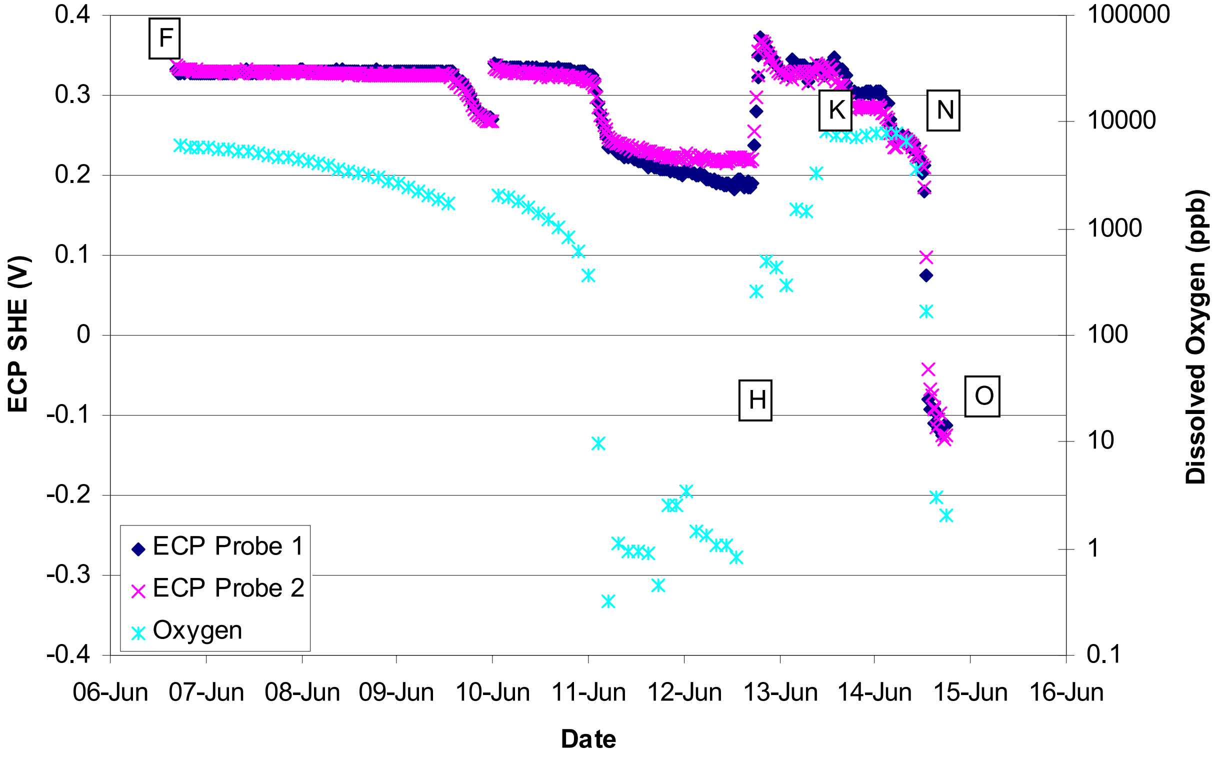


Figure 6 Oxygen concentration and ECP

The ECP measurements remained between +320 mV_{SHE} and +340 mV_{SHE} from the time the probes were valved back into the system until June 11, with the exception of a potential transient on June 9. The brief change in ECP of both probes was a result of a flow disruption and the potentials returned to their previous values when flow resumed. The first major change in potential occurred on June 11. From the time the PHT system was refilled, the oxygen concentration decreased steadily from over 6 ppm until it was less than 10 ppb on June 11. The decrease in oxygen concentration had little effect on the ECP until the concentration fell below a few hundred ppb, which is consistent with the S-shaped oxygen-potential curve as shown in Figure 1.

The reduction in oxygen concentration resulted in the probes being exposed to more reducing conditions and the ECP decreasing rapidly by 60 mV over a four hour period at 26^{o}C. The initial rapid decrease in ECP was followed by a further gradual reduction until the pressurizer and degasser condenser were refilled with PHT coolant from the D_2O storage tank on June 12. The coolant from the D_2O storage tank had appreciable concentrations of oxygen and likely resulted in a substantial jump in the ECP to +370 mV_{SHE} (point H). During the pressurization of the PHT system, additional coolant was drawn from the storage tank and the concentration of dissolved oxygen reached 2 ppm. The flow to the ECP probes was switched from the SDC sample line to the Boiler #4 sample line and the velocity increased from less than 1 m/s to approximately 11 m/s, which was considered representative of average feeder conditions under normal operating conditions. Bumping of the PHT pumps displaced the air trapped in the boiler tubes and lead to a further increase in dissolved oxygen to 8 ppm with little additional increase in measured ECP.

As the temperature of the ECP assembly increased from 26 to 49^{o}C, point H to M, a 40 mV decrease in the ECP was observed as seen in Figure 6. A subsequent increase in the temperature of the ECP assembly to 74°C was associated with a further 40 mV decrease in potential. Once deuterium was introduced on June 14 the oxygen concentration fell from 8 ppm to less than 10 ppb in 12 hours. The resulting decrease in ECP from +240 mV_{SHE} to -110 mV_{SHE} was more significant than the combined effects of the temperature increases until this point. The decrease in ECP by over 300 mV is clearly a result of de-oxidation of the PHT coolant as no significant changes in temperature occurred over this period. It is also evident from the trend in Figure 7 that ECP of the probes, and by extension that of the feeders, did not fall below the Fe_3O_4-Fe_2O_3 equilibrium potential of approximately -450 mV_{SHE} (at 80°C) prior to a further increase in temperature.

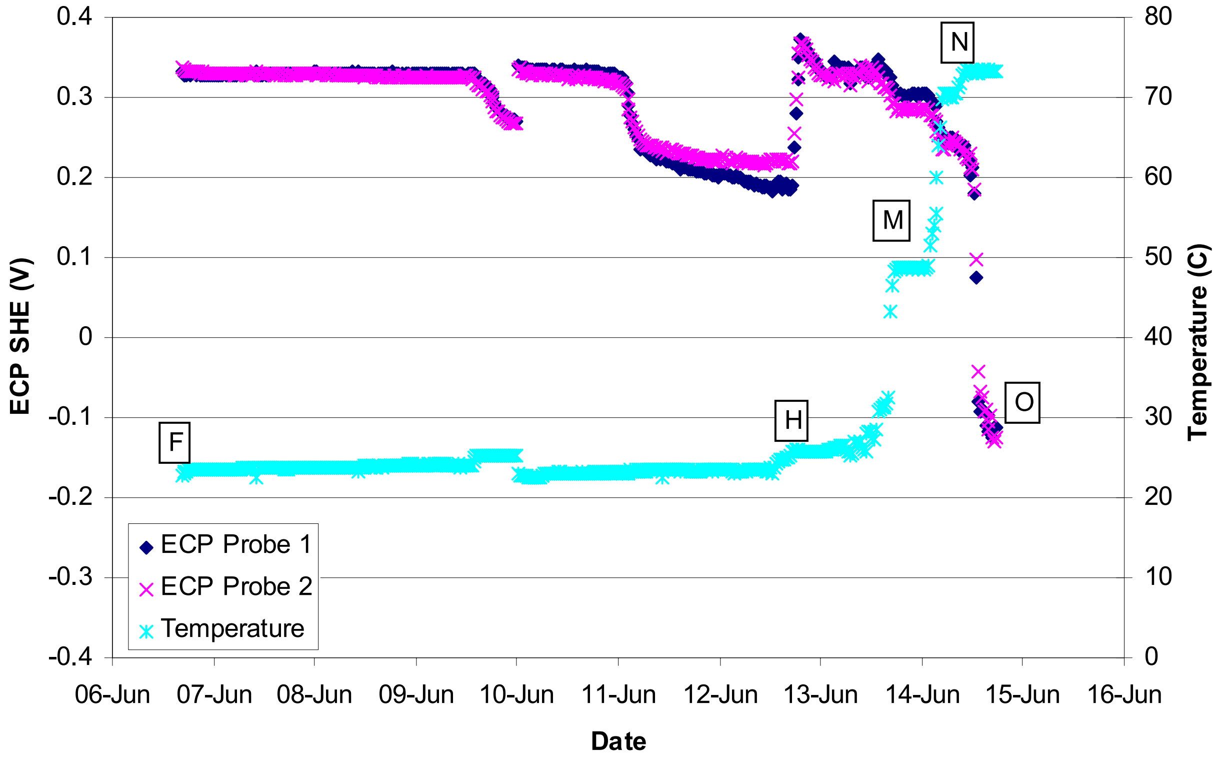


Figure 7 Temperature and ECP

The ECP appears to lag behind changes in coolant chemistry, as was observed when the oxygen was reduced below 10 ppb on June 11. The ECP initially decreased by 60 mV over the first few hours but subsequently decreased by only 30 mV over the next day and a half while exposed to low oxygen levels. The ECP therefore responded partially to the changes in the oxidizing conditions of the coolant but at temperatures below 80°C remained well above the Fe_3O_4-Fe_2O_3 equilibrium potential for SCC susceptibility. It is uncertain at this point how much time would be required for the ECP to decrease to non-critical values and further laboratory investigation into the relationship between temperature, potential and oxidizing conditions could provide valuable insight into the mechanisms at work. It is important to note that even though the potential values may promote SCC, further conditions such as sufficient stress/strain are also required.

4. Conclusion

It has been demonstrated in the course of this investigation that an ECP assembly can be installed and operated in a CANDU generating station. The ECP probes were shown to respond well to changes in PHT coolant conditions, particularly with respect to dissolved oxygen concentration. The initial ECP measurements of the probes were higher than would have been expected for the low levels of dissolved oxygen in the PHT coolant. The elevated potentials may have been a function of partial oxidation of the magnetite oxide film on the interior of the probes during the valving-in process and prior to their installation or due to low levels of deuterium peroxide present during the pre-boiler work period. The gradual decrease in measured potential over time, however tends to favour the former explanation.

Following the boiler maintenance, significant concentrations of oxygen were introduced into the system and the ECP of the two probes was found to be considerably higher than the pre-boiler work period. Furthermore, the difference in potential between the two probes had disappeared after exposure to more oxidizing conditions. The decrease in oxygen concentration to less than 10 ppb after the completion of the boiler work and the associated small ECP change demonstrated the importance of potential measurements compared to purely solution chemistry measurements. The ECP certainly responded to the reduction in oxygen concentration but remained elevated above the Fe_3O_4-Fe_2O_3 equilibrium potential despite the reducing conditions of the coolant. As ECP, rather than oxidizing conditions, controls the possibility of SCC, any attempt to mitigate SCC requires knowledge of the ECP and not simply solution chemistry.

The start-up period is considered one of the most critical periods with respect to the possibility of SCC due to the associated stresses. After the PHT system was pressurized and the temperature increased to 80^{o}C, oxygen in the coolant was quickly removed, falling from 8 ppm to less than 10 ppb in 12 hours. The potentials of the ECP probes also fell during this period but as with the previous decrease in oxygen on June 11 the potential remained elevated by several hundred millivolts above the Fe_3O_4-Fe_2O_3 equilibrium potential prior to any subsequent temperature increases. The ECP probe assembly provided valuable information about not only the probable response of the feeder ECP to changes in PHT system conditions but also the residual effects of chemistry transients on the feeder pipes themselves.

5. Acknowledgments

The authors acknowledge the assistance provided by the Research & Productivity Council, UNB Nuclear, Comstock and Atomic Energy of Canada Ltd. (AECL) in the design and installation of the ECP assembly. PLGS staff provided exceptional support to ensure the successful installation of the ECP probe. Financial contributions were provided by Atlantic Canada Opportunities Agency, NB Power Nuclear, CANDU Owners Group and AECL.

6. References

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