A SURVEY ON THE CORROSION SUSCEPTIBILITY OF ALLOY 800 CANDU STEAM GENERATOR TUBING MATERIALS

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Abstract

To provide support for a proactive steam generator (SG) aging management strategy, a survey on the corrosion susceptibility of the archived Alloy 800 tubing from CANDU SGs under plausible crevice chemistry conditions was conducted to assess the potential material degradation issues in CANDU SGs.

Archived Alloy 800 samples were collected from four CANDU utilities. High-temperature electrochemical analysis was carried out to assess the corrosion susceptibility of the archived SG tubing under simulated CANDU crevice chemistry conditions at both 150°C and 300°C. The potentiodynamic polarization results obtained from the archived CANDU SG tubes were compared to the data from ex-service tubes removed from Darlington Nuclear Generating Station (DNGS) SGs and a reference nuclear grade Alloy 800 tubing. It was found that the removed Darlington SG tubes, with signs of in-service degradation, were more susceptible to pitting corrosion than the reference nuclear grade Alloy 800 tubing. At 150°C, under the same neutral crevice chemistry conditions, the potentiodynamic polarization curve of the ex-service Darlington SG tubing has an active peak, which is a sign of propensity to crevice/underdeposit corrosion. This active peak was not observed in any of the potentiodynamic polarization curves of all archived Alloy 800 CANDU SG tubing indicating that archived CANDU SG tubes are less susceptible to the underdeposit corrosion under SG startup conditions. The corrosion behaviour of the archived Alloy 800 tubes from CANDU SG was similar to that of the reference nuclear grade Alloy 800 tubing. The results of this survey suggest that the Alloy 800 tubing materials used in the existing CANDU utilities (other than ex-service DNGS tubing) will continue to have reliable performance under specified CANDU operating conditions.

Ex-service SG tubing from DNGS, although showing lower than average corrosion resistance, still has a wide acceptable operating margin and the in-service degradation issues such as pitting and underdeposit corrosion could be controlled through water chemistry management. The test procedures used here may be considered as an optional examination procedure to qualify SG tubing for new or replaced SGs. It may also provide an assessment of the impact of in-service aging on SG tube performance.

1. INTRODUCTION

A recent examination of steam generator (SG) tubes (D2 SG4 R52C60 and D4 SG1 R49C61) removed from Darlington Nuclear Generating Station (DNGS) found that these SG tubes were more susceptible to pitting corrosion in the ex-service condition than reference new nuclear grade Alloy 800 tubing. There is also evidence that a few Alloy 800 tubes at Biblis A and Borselle have detectable degradation indications, which may be signs of cracking. These findings suggest that Alloy 800 tubing may indeed have some aging degradation susceptibility after many years of service. However, degradation of Alloy 800 SG tubing has only been found in a few nuclear generating stations to date. Whether the degradation of Alloy 800 tubing is due to the imperfections in its compositional or metallurgical properties inherent from manufacturing or from environmental factors, or as a result of in-service aging requires clarification. It was considered useful to survey the corrosion susceptibility of the archived Alloy 800 tubing from CANDU® SGs under plausible crevice chemistry conditions and find out the potential material degradation issues in CANDU SGs. This work could provide important information to support proactive SG aging management. The benefit to the COG community is that potential steam generator tube degradation issues can be identified and this information supports steam generator aging management in a proactive manner.

The corrosion susceptibility of the ex-service DNGS Alloy 800 tube was assessed under simulated CANDU crevice chemistry conditions at 300°C. The experimental results suggested that the ex-service SG tubes are more susceptible to pitting corrosion than a reference nuclear grade Alloy 800 tubing that has not been in-service conditions. The conditions and the root cause leading to the Alloy 800 SG tube degradation at DNGS are under investigation. The work reported here was to determine whether the Alloy 800 SG tubing material at other CANDU NGS will experience the same degradation issue as that found at DNGS.

Archived Alloy 800 CANDU SG tubing samples were collected from Centrale nucleaire Gentilly-2 (CNG2), Point Lepreau Generating Station (PLGS), Bruce Nuclear Generating Station (BNGS), and Third Qinshan Nuclear Power Co., Ltd (TQNPC). The corrosion susceptibility of this available archived Alloy 800 tubing from representative CANDU SGs was evaluated and compared under plausible SG crevice chemistry conditions.

Corrosion-related SG tube degradations including intergranular attack (IGA), pitting, underdeposit corrosion and SCC were normally detected in SG crevices. The chemistry conditions in CANDU SG crevices has been previously reported [1]. The assessments and analysis were performed based on the data from BNGS-A plant operation. Systematic SG hideout return monitoring was performed on all BNGS-A units over several years. The majority of the available information was obtained prior to performing deposit removal activities (chemical cleaning and waterlancing), which commenced in 1993. The results of the hideout return monitoring indicated that large quantities of impurities had accumulated in the fouled SG crevice/underdeposit regions. The predominant inorganic species, based on hideout return cumulative mass amounts, were

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calcium, sulphate, silica, chloride, sodium, potassium, and magnesium. Hideout return of organic species, such as acetate, was also observed. Predictions of crevice chemistry were performed using EPRI's MULTEQ-REDOX computer code. The MULTEQ predictions indicated that the normal BNGS-A SG crevice pH was bounded within a range of pH 4 to 9 (at SG operating temperature) and was not in a strongly acidic or alkaline regime [1]. The majority of the crevice pH predictions were on the weak-alkaline side of neutral pH. The MULTEQ predictions indicated that the crevice solution chemistry during operation consisted of a concentrated salt solution with the dominant species being sodium, chloride, and potassium and, in some cases, acetate. Calcium and sulphate were present in solution at much lower concentrations and were predicted to exist mainly in precipitate form (e.g., $CaSO_4$) during operation along with other calcium-magnesium and silicate precipitates. Electrochemical potentiodynamic polarization curves obtained under specific environments could offer a quick and reliable assessment on the corrosion resistance of SG tube material. A potentiodynamic polarization curve provides information of corrosion rate of an alloy material as a function of ECP under specific environments.

Some background information about the potentiodynamic polarization curves of chromium containing alloys may be useful. Figure 1 shows a typical polarization curve for chromium-containing alloys. In the cathodic potential region, the predominant electrode reaction is the reduction of the oxidant(s) in the system. At the potential E_{Corr} , the total current density contributed by the anodic reactions and cathodic reactions equals zero. Above this potential, the curve reaches an active region where the alloy surface experiences anodic dissolution. The components of the alloy do not dissolve at the same rate and, therefore, surface segregation results. The surface enriches in the beneficial alloying elements such as chromium. The surface films protect the alloy from further dissolution. When the potential reaches a point called the primary passivation potential (E_{pp}), the anodic current density reaches a maximum value ($i_{Critical}$) called the critical current density. After this point, the current density starts to fall and a passive film covers the alloy surface and inhibits the anodic dissolution. The current density at the passive state ($i_{Passive}$) is called the passive current density. When the applied potential reaches a value called the transpassive potential (E_{Trans}), Cr^{3+} in the passive film starts to further oxidize to Cr^{6+} and dissolves [4]. The passive film experiences a restructuring stage and the curve reaches a plateau with a much higher current density than the passive current density. Further anodic polarization will draw the potential of the alloy to a region where oxygen evolution will take place. Aggressive halide anions such as chloride ions can cause the passive films to break down in the passive potential region. The breakdown of the passive film is characterized by a sudden increase in the current density at a potential called the pitting potential E_p. The high current density is due to a very fast anodic dissolution in confined areas. This local dissolution can cause pitting corrosion of the alloy. In a cyclic polarization, when the current density reaches a pre-determined threshold, the applied potential is reversed. Once pits initiate above the pitting potential, they will grow even after the potential decreases to a value below the pitting potential. Only when the potential decreases below a protection potential E_{protec}, the reversing curve crosses the forward scan and the pits cease to develop. This potential under certain circumstances could be used to determine the repassivation ability of an alloy. However, due to the uncertainty of the local chemistry and the huge IR drop inside the pit, using E_{protec} to determine the corrosion resistance of an alloy may be misleading.

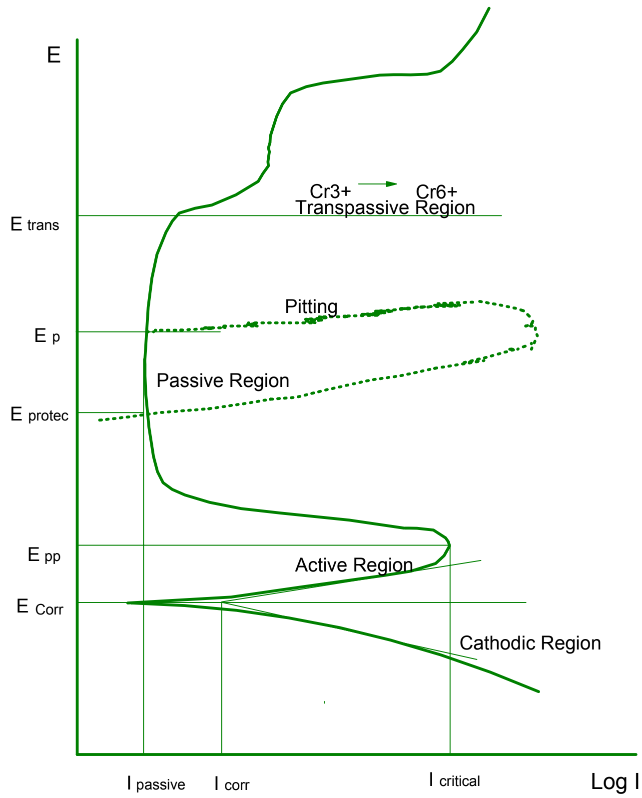

Figure 1 Schematic Plots of Typical Polarization Curves for Chromium Containing Alloys

As described earlier, for the majority of the CANDU SGs, crevice pH was on the weak-alkaline side of neutral pH. This is the basis used to evaluate the archived CANDU SG tubing under neutral crevice chemistry conditions. In addition to this reason, the potentiodynamic polarization curves of Alloy 800 SG tubing obtained previously [2] suggest that acidic crevice chemistry conditions are too aggressive to assess the in-service corrosion susceptibility of SG tubing. On the other hand, alkaline crevice chemistry conditions are too benign for Alloy 800 tubing degradation and also not a good environment to evaluate any in-service corrosion susceptibility. Only the potentiodynamic polarization curves obtained in the neutral crevice chemistry conditions show a distinctive pitting potential and a clear active peak. Therefore the neutral crevice chemistry conditions are selected for performing tests to assess the corrosion susceptibility of the archived Alloy 800 from different CANDU SGs.

2. METHODOLOGY

2.1. Material and Sample Preparations

Archived SG tubes from different CANDU Stations are cut to 10-mm long tube segments for electrochemical testing. The detailed information on the tube material is listed in Table 1 and Table 2. It should be noted that the DNGS tubing (Unit 2 SG 4 R52C60) has the lowest Ti/C ratio and the aluminum concentration is lower that ASTM standard specified value. IGA tests normally used for characterize the corrosion susceptibility of SG alloys are considered not relevant to SG tubing degradation in service and were not selected in this test plan.

Table 1
Chemical Composition of the Alloy 800 Steam Generator Materials
(from mill test certificate if not specified)

Material/Heat Number/Size	Element Concentration (wt %)											
	C	N	Al	Si	S	Ti	Cr	Mn	Fe	Ni	Cu	Ti/C
ASME Standard SB 163 UNS N08800	Max 0.10	-	0.15-0.60	1.0 max	0.015 max	0.15-0.60	19.0-23.0	1.5 max	Bal.	30.0-35.0	0.75 max	>12
Reference Nuclear Grade Alloy 800 HT # 9043A	0.015	0.028	0.41	0.10	0.002	0.42	21.7	0.80	42.4	34.1	0.03	28
DNGS (Darlington) Unit 2 SG 4 R52C60	0.016*	na	0.13	0.61	0.001*	0.22	23.0	0.3	42.0	34.8	na	14
DNGS Unit 4 SG 1D4 R49C61	0.016	na	0.27	0.42	0.001	0.40	21.4	0.57	41.2	32.2	0.012	25
BNGS (Bruce) Tube No. 91708 HT # 507731	0.014	0.013	0.22	0.49	0.001	0.45	21.78	0.57	43.29	33.11	0.034	32
BNGS Tube No. 92603 HT # 507937	0.009	0.010	0.21	0.43	0.001	0.55	21.65	0.49	43.39	33.20	0.032	61
BNGS Tube No. 95091 HT # 507937	0.010	0.011	0.23	0.53	0.001	0.56	21.75	0.50	43.18	33.17	0.034	56.0
PLGS (Point Lepreau) HT # N/A (AECL analysis)	0.024	na	0.25	0.66	N/A	0.55	22	0.57	43.0	34	0.010	23
CNG2 (Gentilly-2) HT # 13350	0.010	0.021	0.41	0.54	N/A	0.41	21	0.62	44	33	0.026	41
Qinshan (TQNPC) HT # RC577	0.009	0.009	0.30	0.49	< 0.0010	0.51	21.60	0.69	43.3	32.79	0.02	57
Qinshan (TQNPC) HT # WL809	0.016	0.010	0.26	0.48	< 0.0005	0.50	21.41	0.66	43.8	32.64	0.02	31

*by combustion; others by ICP; na- not analysed

2.2. Test Environments

The composition of the electrolytes for the simulated neutral crevice environments for evaluating the corrosion susceptibility of the archived Alloy 800 SG tubing is listed in Table 2. It should be noted that the environments listed in Table 2 are overall compositions of the autoclave contents. Under the test conditions precipitations are possible.

Table 2
Summary of the Composition of Model Crevice Environments
(Solution + Precipitations)

ID	Composition	pH_T
NC ("Neutral")	0.15 M* Na_2SO_4 0.30 M NaCl 0.05 M KCl 0.15 M $CaCl_2$	$pH_{300°C}$ = 6.10; $pH_{neutral}$ = 5.16 $pH_{150°C}$ = 6.03; $pH_{neutral}$ = 5.56

2.3. Electrochemical Test Method Used

Potentiodynamic polarization tests were used to determine the corrosion susceptibility of the archived Alloy 800 CANDU SG tubing materials. All electrochemical polarization tests were performed in static autoclaves using a typical three-electrode system. The schematic of the electrochemical cell and sample mounting for high-temperature electrochemical measurements is shown in Figure 2.

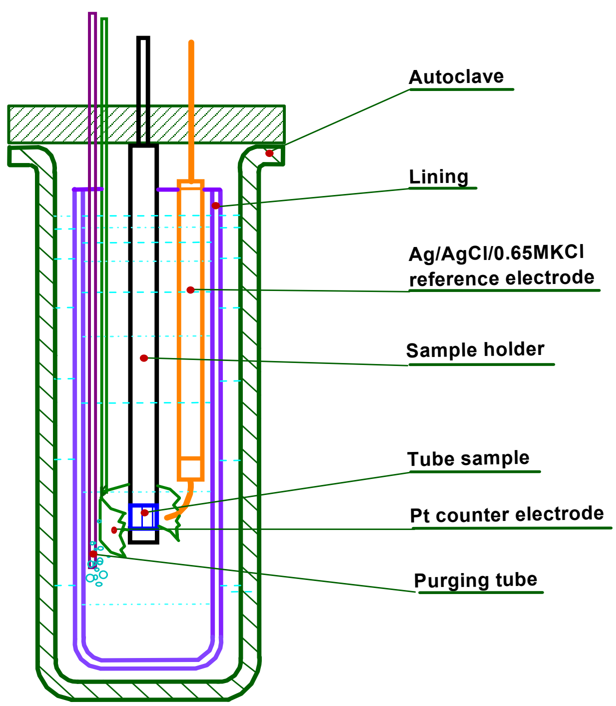

Figure 2 A 3-Electrode System for Electrochemical Measurements in a Static Autoclave

An EG&G Model 263A/99 Potentiostat/Galvanostat with a floating/auxiliary input option was used for the potentiodynamic polarization tests in autoclave systems. The scan rate was fixed at the ASTM standard recommended rate of 0.167 mV/s [5]. All samples were tested under isothermal conditions. Internal Ag/AgCl/0.65 M KCl high-temperature reference electrodes were used to make high-temperature electrochemical measurements. To minimize the solution IR drop (an voltage drop in the electrolyte), the Luggin capillary of the reference electrode was placed close to the sample surface (≤1 mm). All potentials reported were converted to the standard hydrogen electrode scale (SHE) ([6],[7]).

The samples for electrochemical tests were 10 mm-long segments cut from archived Alloy 800 tubing. To minimize the effect of differences in as-received surface conditions on corrosion susceptibility, the external surfaces of all tested tubing were finished by grinding with 600-grit silicon carbide paper and ultrasonically cleaned first with acetone, and then with ethanol before the tests. Tests were repeated until duplicate results were obtained.

3. EXPERIMENTAL RESULTS

3.1. Metallography Examination Results

Data associated with the microstructure, micro hardness measurements, and grain size, an average of a lognormal or normal distribution were collected to assess the tube materials. The results are presented in Table 3 and shown in Figure 3.

Table 3
Vickers Hardness Measurement and Grain Size of the Alloy 800 Tubing Material

Specimen I.D	Direction	Vhn Range	Vhn Average	Grain Size Range (µm)	Grain Size Average (µm)
ASTM B163	-	≤ 95 HRB (≤ 213 Vhn)	-	#5 or finer (≤ 63.5µm)	-
Reference Alloy 800 HT# 9043A	Axial	151 to 163	157	14.8 to 18.4	16.8
	Transverse	143 to 168	156	18.1 to 22.8	19.6
G2 NGS HT # 13350	Axial	144.3 to 153.0	149.3	13.46 to 15.38	14.42
	Transverse	160.3 to 186.6	175.6	8.71 to 11.96	10.33
DNGS D4 SG1 R49C61	Axial	154.3 to 174.7	162.3	7.79 to 9.57	8.77
	Transverse	192.8 to 232.3	213.6	9.75 to 12.05	10.90
PLGS -	Axial	171.0 to 173.0	172.2	5.38 to 7.94	6.66
	Transverse	166.4 to 180.6	172.4	6.38 to 7.36	6.87
TQNPC HT # WL809	Axial	159.0 to 160.8	159.9	8.61 to 11.05	9.83
	Transverse	172.2 to 180.4	177.0	8.64 to 12.76	10.70
BNGS HT # 507937	Axial	140.2 to 149.9	144.8	8.26 to 9.56	8.91
	Transverse	145.2 to 150.7	148.1	9.79 to 12.49	11.14

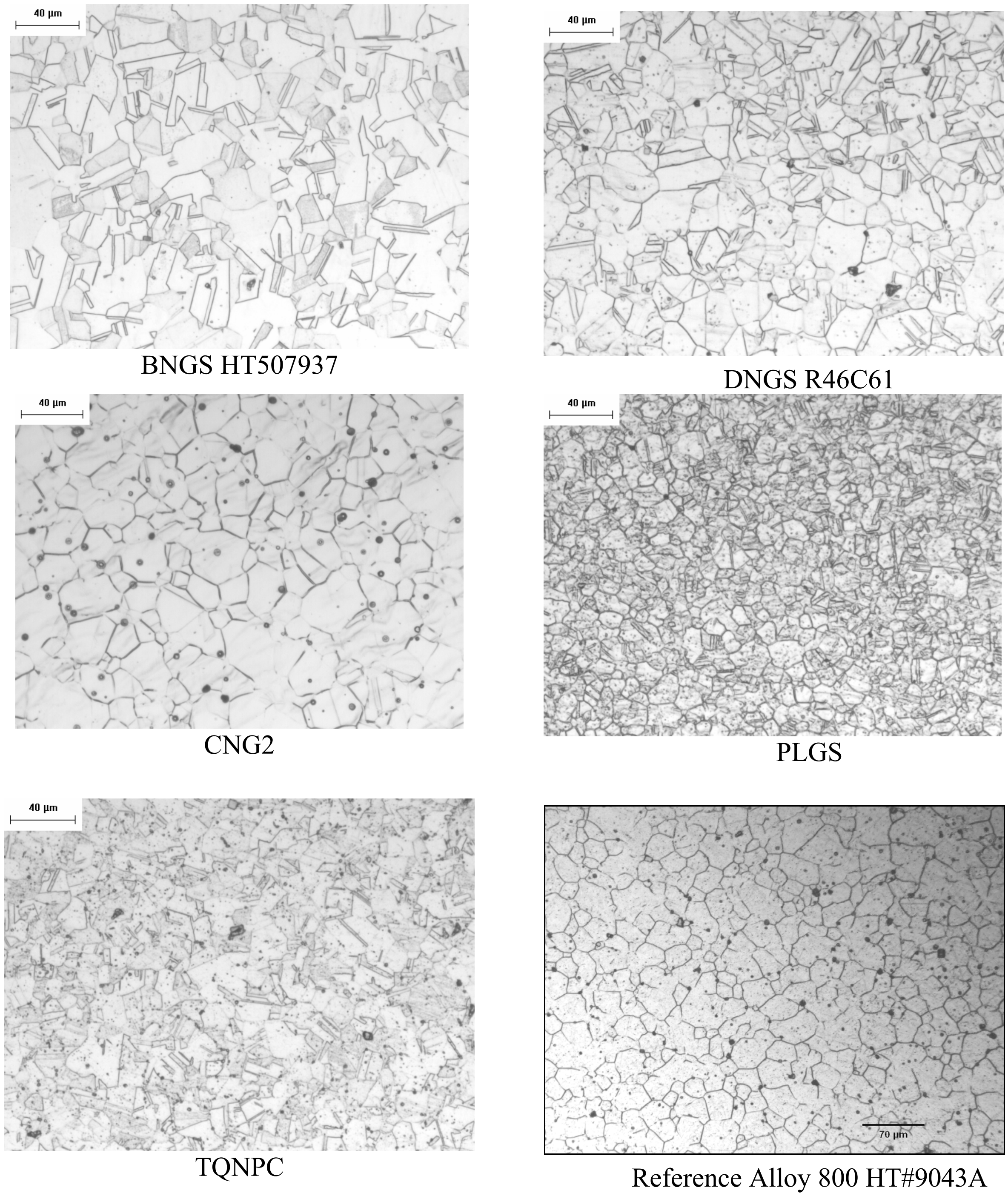

Figure 3 Microstructure of the Materials taken from the Cross-Section of the Alloy 800 Tubes

The microhardness values obtained from the archived SG tubing are within the expected range for this material. The values for the commercial Alloy 800 were slightly lower than for the removed SG tube materials. The hardness value is presented in Table 3. It should be noted that the hardness of the removed DNGS tubing R49C61 is slightly exceeded the standard and the hardness values obtained for the reference nuclear grade

Alloy 800 were slightly below the hardness for most of the SG materials from the CANDU stations. The average grain size, measured for the archived SG tube materials, ranged from 6.7 to 14.4 µm. The grain size of the reference nuclear grade Alloy 800 material ranged from 14.8 to 22.8 µm, notably larger than the archived tubes from the stations.

3.2. Electrochemical Test Results

Electrochemical potentiodynamic polarization tests were performed for all SG tubing materials at 150°C and 300°C in a neutral crevice solution.

Figure 4 shows the experimental results of the reference Alloy 800 tubing and a sample prepared from the removed Darlington tubing D4 SG1 R49C61 that had a 5% through-wall pit. It is seen that the ex-service tubing has a narrow passive range and lower pitting potential. The ex-service tubing also shows an active peak at -540 mV. The passive current density of the Darlington tubing is also higher than the reference tubing.

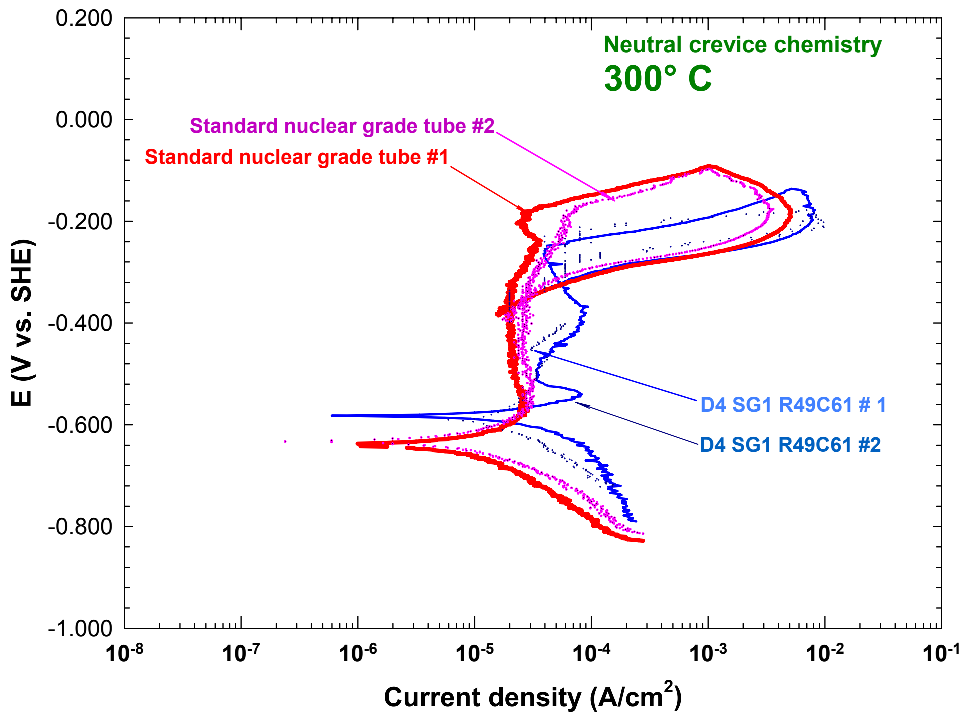

Figure 4 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing and the Darlington Tubing D4 SG1 R49C61 Obtained at 300°C in Neutral Crevice Chemistry

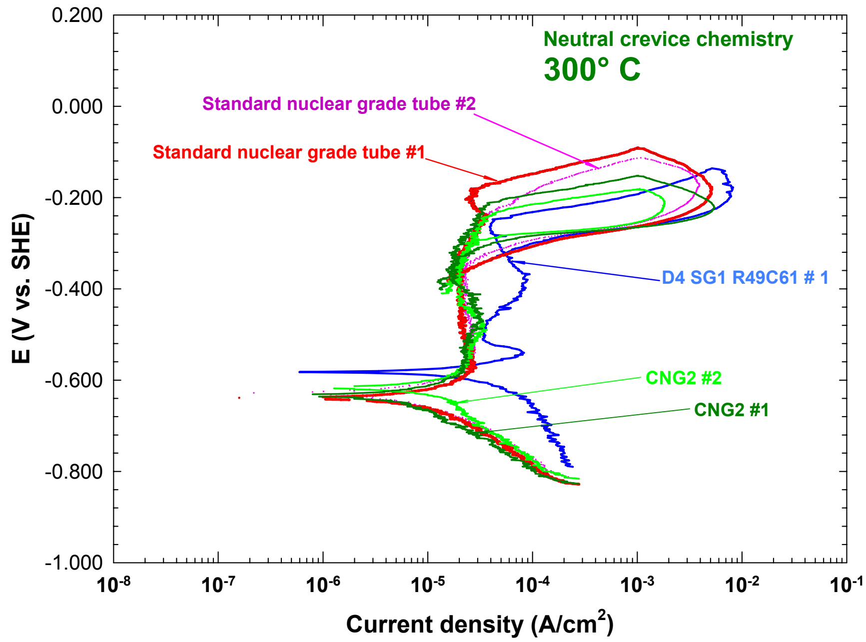

Figure 5 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived G2 NGS Tubing Obtained at 300°C in Neutral Crevice Chemistry

Figure 5 shows the potentiodynamic polarization curves of the archived SG tubing from CNG2 obtained at 300°C in the neutral crevice chemistry compared with the curves of the reference nuclear grade Alloy 800 tubing and the PLGS tubing D4SG1 R49C61 obtained under the same conditions. From the figure, it is seen that the archived CNG2 tubing has higher pitting potential than the Darlington tube D4SG1 R49C61, where the pitting potential is slightly lower than the reference Alloy 800 tubing. It is also very clear that CNG2 archived SG tubing did not show any active peak in the polarization curve. It also has lower passive current density than the Darlington tube D4SG1 R49C61 tube has.

Figure 6 presented the superimposed polarization curves of the archived Alloy 800 tubing from PLGS, the reference Alloy 800 tubing and the Darlington tubing D4 SG1 R49C61 obtained at 300°C in neutral crevice chemistry. From the figure it is seen that the pitting potential of the archived tubing from PLGS is very close to the pitting potential of the reference Alloy 800 tubing. The polarization curves of the archived PLGS tubing also have no active peak and have a lower passive current density than that of Darlington tubing D4 SG1 R49C61.

Figure 7 shows the potentiodynamic polarization curves of the archived SG tubing (HT# 507937) from BNGS obtained at the same test conditions as those shown in the previous figures. The polarization curves are compared with those of the reference nuclear grade Alloy 800 tubing and the PLGS tubing D4SG1 R49C61. The data suggest that the archived BNGS tubing is close to the pitting potential of the reference Alloy 800 tubing and is about 80 mV higher than that of the Darlington tube D4SG1 R49C61. The polarization curves of the BNGS archived SG tubing also have lower passive current density than that of the Darlington D4SG1 R49C61 tubing and show no active peak.

Figure 8 shows the data from another archived SG tubing (HT# 507731) from BNGS obtained at the same test conditions as those shown in the previous Figure 7. The data show that the pitting potential of the archived BNGS tubing (HT# 507731) is also close to the pitting potential of the reference Alloy 800 tubing and is about 50 mV higher than that of the Darlington tube D4SG1 R49C61. Again the polarization curves of the BNGS archived SG tubing (HT# 507731) have lower passive current density than that of the Darlington D4SG1 R49C61 tubing and show no significant active peak.

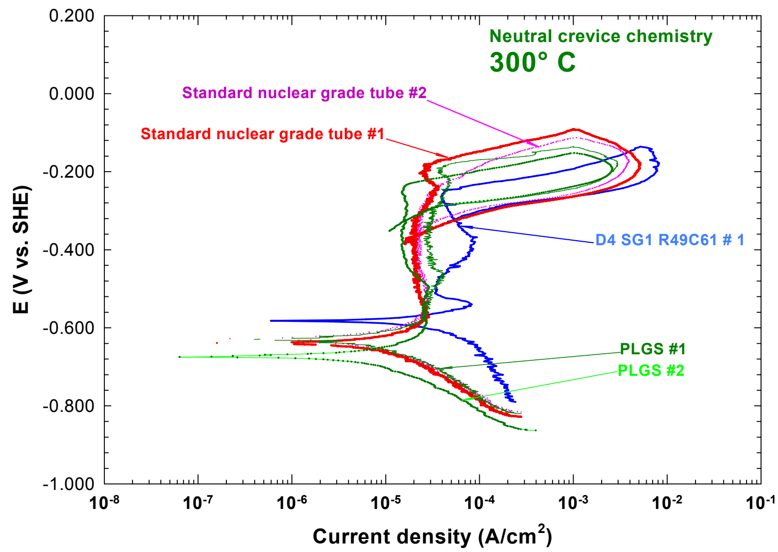

Figure 6 Superimposed Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived Alloy 800 Tubing from PLGS obtained at 300°C in Neutral Crevice Chemistry

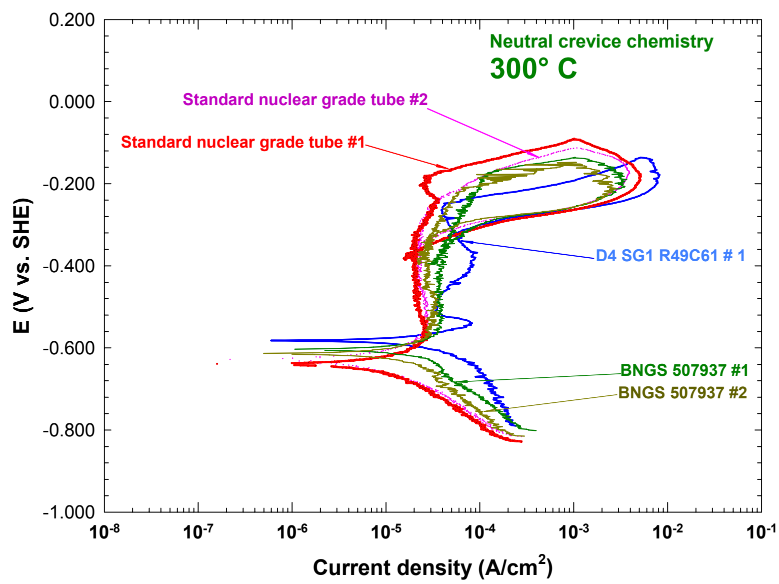

Figure 7 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived BNGS Tubing (HT# 507937) obtained at 300°C in Neutral Crevice Chemistry

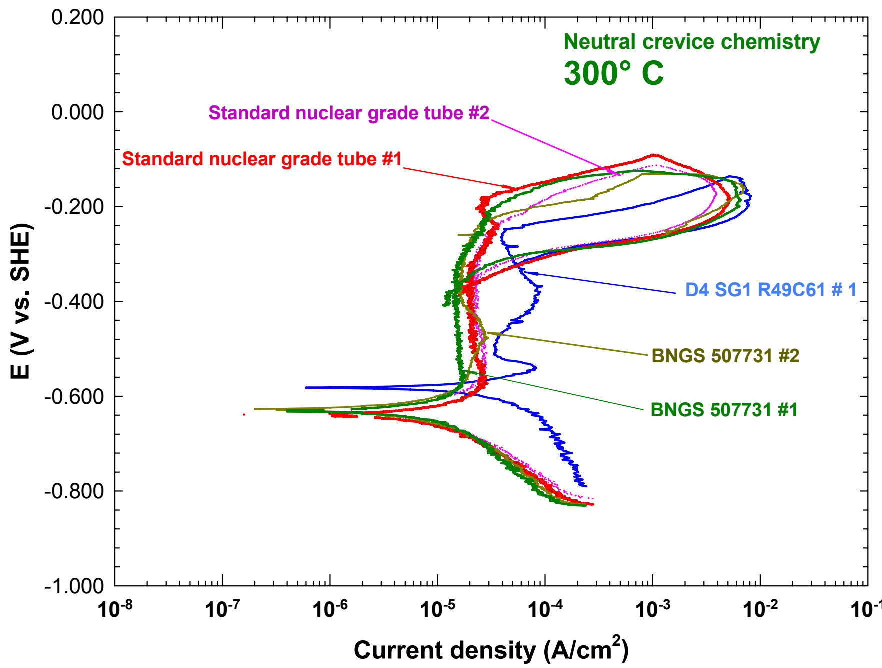

Figure 8 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived BNGS Tubing (HT# 507731) obtained at 300°C in Neutral Crevice Chemistry

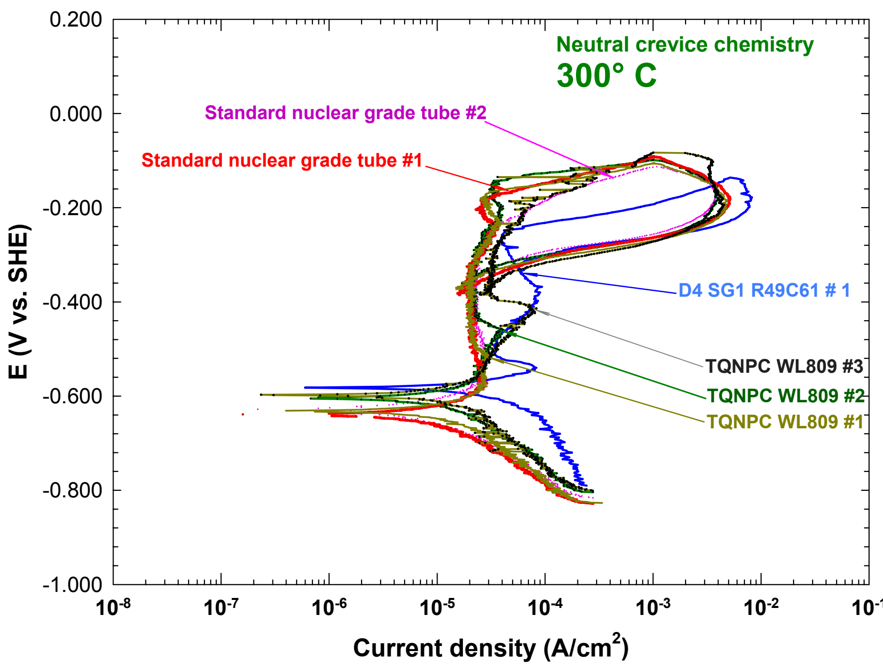

Figure 9 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived TQNPC Tubing (HT# WL 809) obtained At 300°C in Neutral Crevice Chemistry

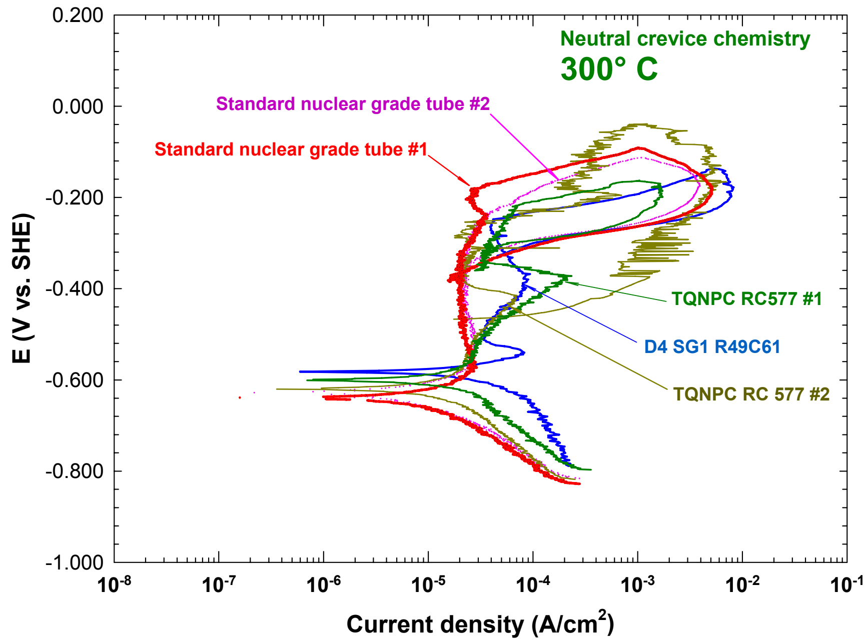

Figure 10 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived TQNPC Tubing (HT# RC577) obtained at 300°C in Neutral Crevice Chemistry

Figure 9 presents the comparisons of the polarization data between the archived TQNPC tubing (HT# WL908), the reference Alloy 800 tubing and the Darlington D4SG1 R49C61 tubing obtained in the neutral crevice chemistry at 300°C. The pitting potential of the archived TQNPC tubing (HT# WL908) is higher than the Darlington removed tubing D4SG1 R49C61. However, there are current peaks observed in some of the polarization curves at about –460 mV and –420 mV.

Figure 10 presents the comparisons of the polarization data between another archived TQNPC tubing (HT# RC577), the reference Alloy 800 tubing and the Darlington D4SG1 R49C61 tubing obtained under the same test conditions. The pitting potential of this archived TQNPC tubing is close to the Darlington removed tubing D4SG1 R49C61 and lower than the reference nuclear grade Alloy 800 tubing. Distinctive current peak is observed in the polarization curves of TQNPC archived tubing between –420 mV and –380 mV.

SG shutdown and startup transients may introduce hazardous conditions for the tube integrity. Therefore, it is important to assess the corrosion susceptibility of the SG tubing materials in crevice chemistry at an intermediate temperature. In previous work to define the safe ECP/pH zone for SG shutdown and startup, 150°C was selected as a representative temperature [3]. In this work, the corrosion susceptibility of the archived CANDU SG tubing was also assessed at 150°C in the neutral crevice chemistry conditions. Figure 11 through Figure 17 compare the potentiodynamic polarization curves between the reference nuclear grade Alloy 800 tubing, the Darlington ex-service D4SG1 R49C61 tubing and the archived CANDU SG tubing, respectively.

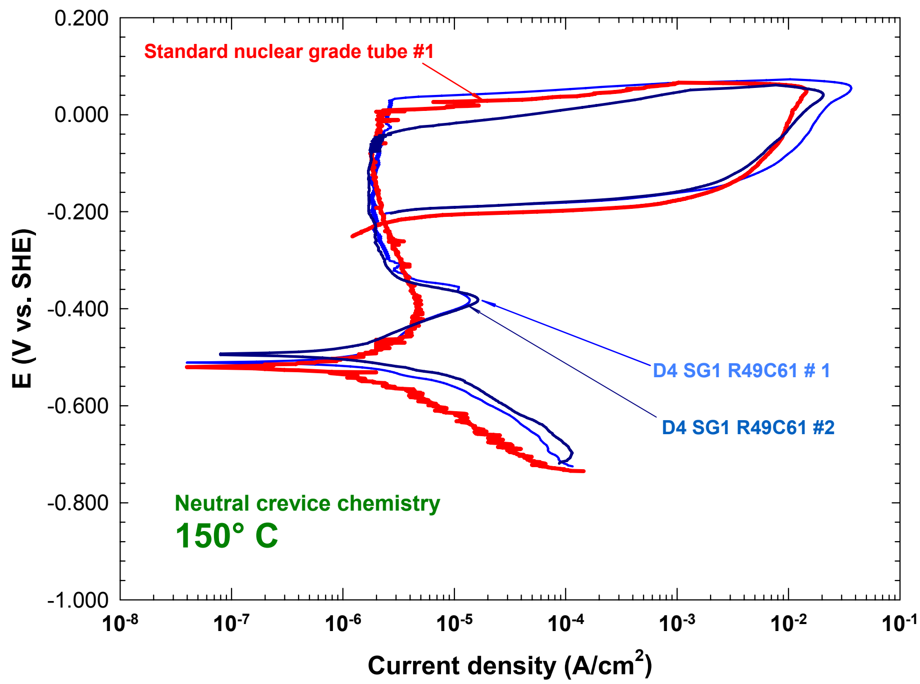

Figure 11 Superimposed Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 obtained at 150°C in Neutral Crevice Chemistry

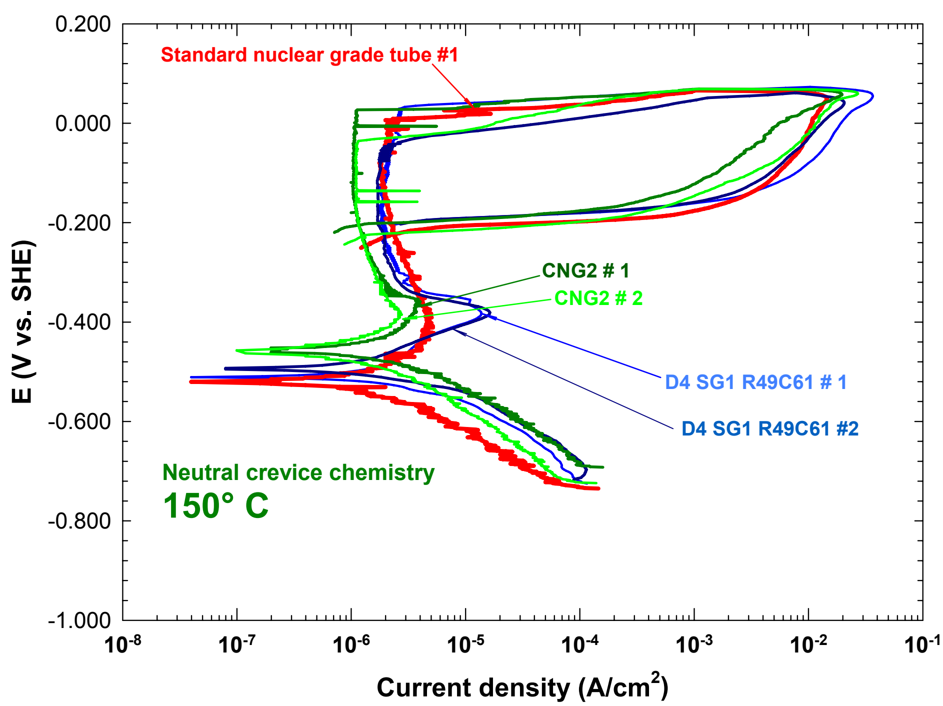

Figure 12 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived G2 NGS Tubing obtained at 150°C in Neutral Crevice Chemistry

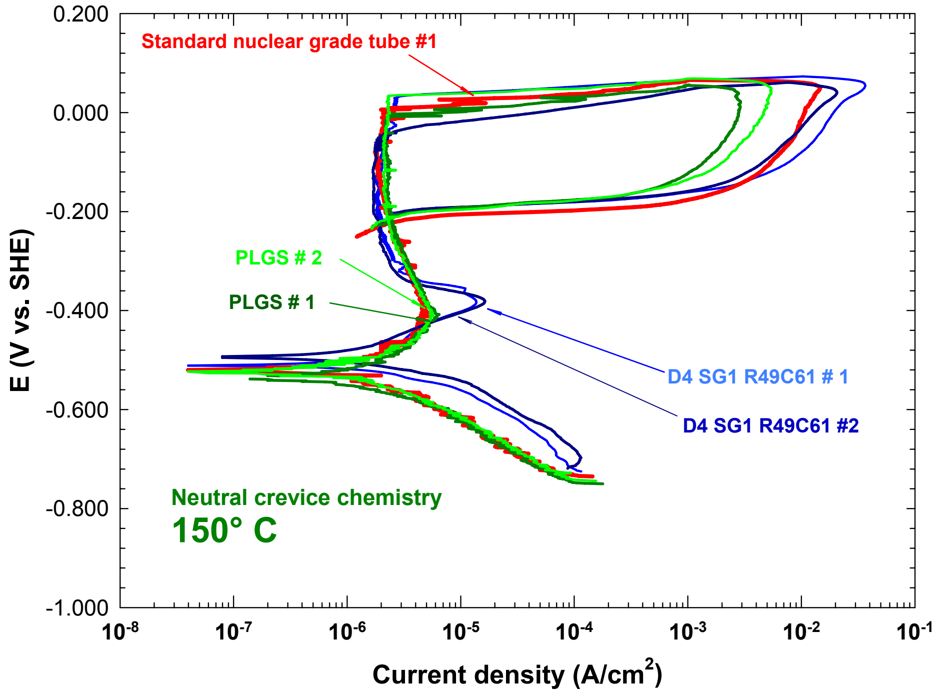

Figure 13 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived PLGS Tubing obtained at 150°C in Neutral Crevice Chemistry

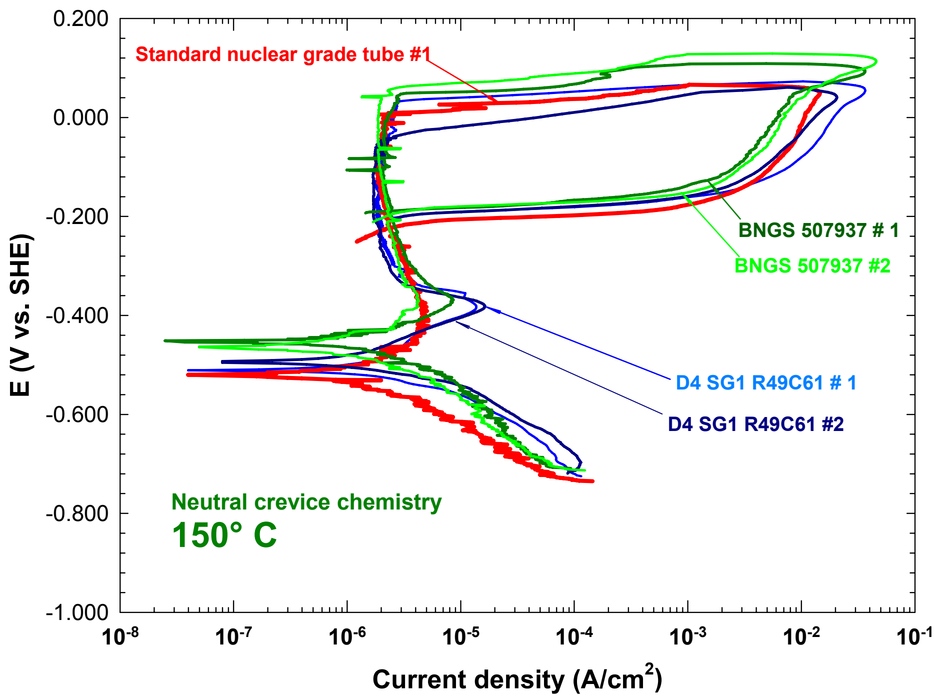

Figure 14 Superimposed Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived BNGS Tubing (HT# 507937) obtained at 150°C in Neutral Crevice Chemistry

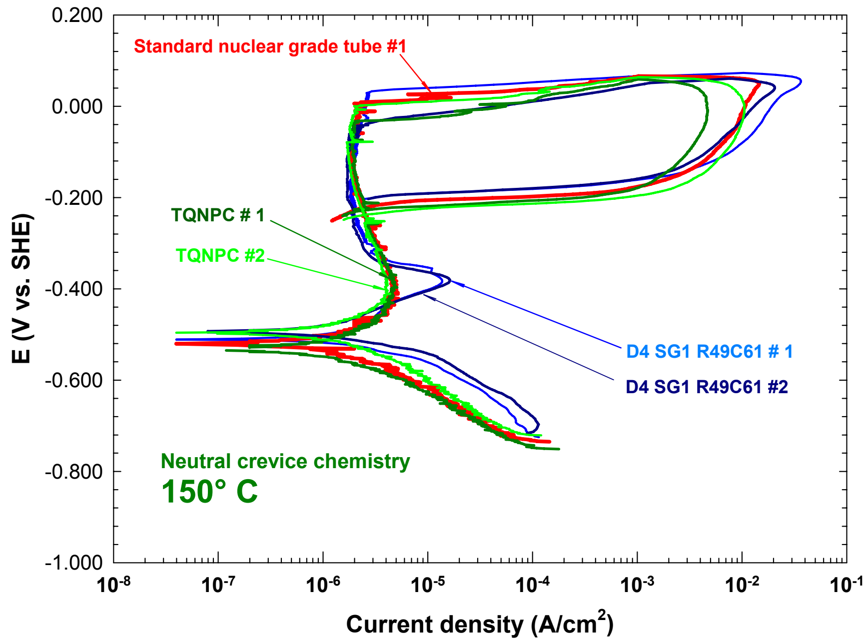

Figure 15 Superimposed Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived BNGS Tubing (HT# 507731) obtained at 150°C in Neutral Crevice Chemistry

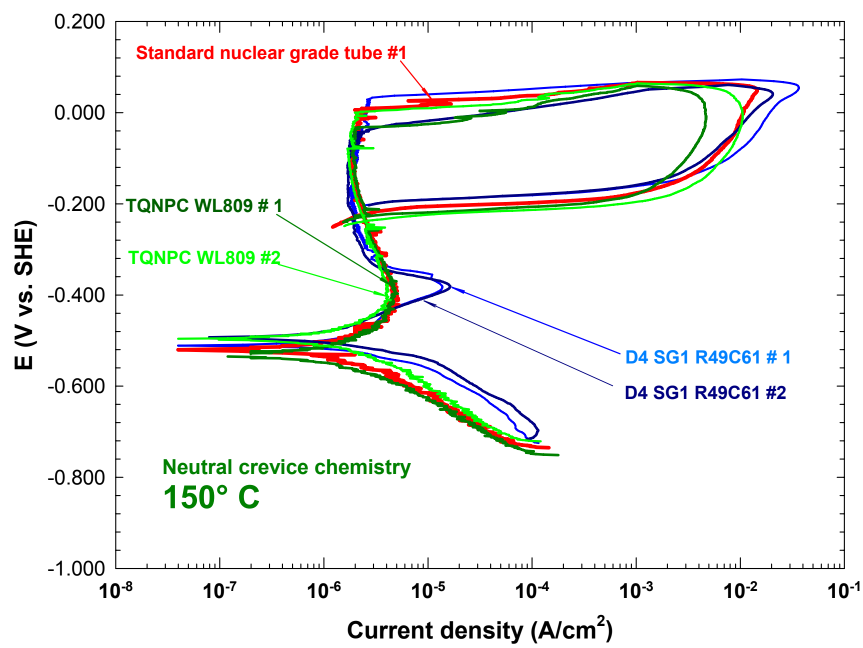

Figure 16 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived TQNPC Tubing (HT# WL809) obtained at 150°C in Neutral Crevice Chemistry

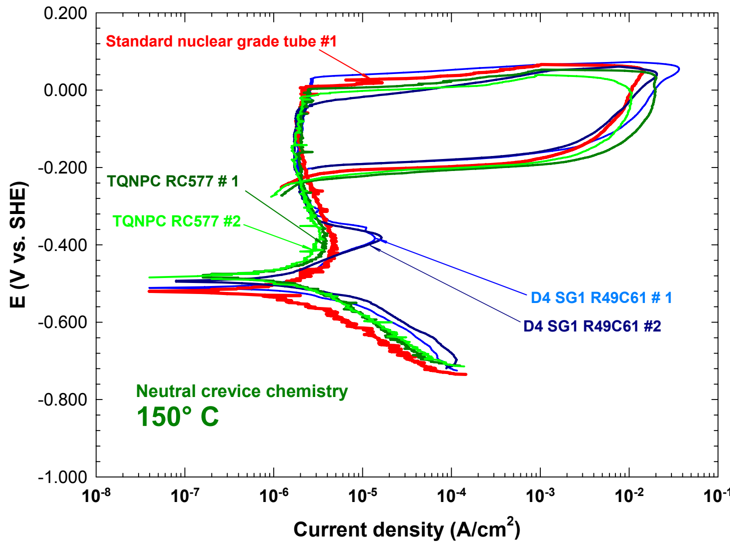

Figure 17 Comparisons between the Potentiodynamic Polarization Curves of the Reference Alloy 800 Tubing, the Darlington Tubing D4 SG1 R49C61 and the Archived TQNPC Tubing (HT# RC577) obtained at 150°C in Neutral Crevice Chemistry

These figures show that there is not a significant difference in pitting potential and passive current densities between these tube alloys at 150°C under the test conditions. Only the Darlington ex-service tubing D4SG1 R49C61 shows a distinctive active peak in the potentiodynamic polarization curve. From the polarization curves of archived tubing, there is little indication of any active peak. The archived SG tubing from CANDU SGs appears to be self-passive at 150°C. The significance of this active peak to the crevice/underdeposit corrosion initiation of the SG tubing will be discussed in the next section. For the convenience of comparisons the amplitude of the active peak is compared in FIGURE 18 and the salient parameters of the potentiodynamic polarization curves obtained at 300°C and 150°C in neutral crevice chemistry are listed in Table 4 and Table 5, respectively.

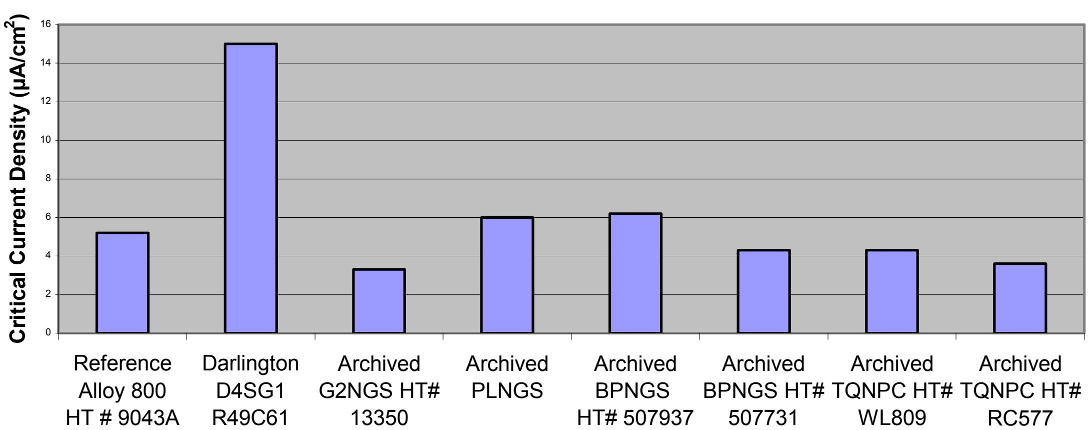

Figure 18 The Amplitude of the Active Peak of the Polarization Curves of different Alloy 800 SG Tubing obtained at 150°C in Neutral Crevice Solution

Table 4
The Average Electrochemical Parameters from the Potentiodynamic Polarization Curves of Alloy 800 SG Tubes obtained at 300°C in Neutral Crevice Chemistry

SG Tubing ID	E_{Corr} (mV vs. SHE)	E_{pp} (mV vs. SHE)	E_p (mV vs. SHE)	E_{Protec} (mV vs. SHE)	$I_{Critical}$ (μA/cm^2)	$I_{Passive}$ (μA/cm^2)
Reference Alloy 800 HT # 9043A	-625	-*	-170	-355	27*	24
Darlington D4SG1 R49C61	-580	-540	-240	-300	83	42
Archived CNG2 HT # 13350	-625	-*	-225	-315	33*	20
Archived PLGS Tubing	-650	-*	-210	-310	36*	23
Archived BNGS HT # 507937	-610	-*	-190	-330	33*	33
Archived BNGS HT # 507731	-630	-*	-190	-370	28*	20
Archived TQNPC HT # WL809	-610	-420 to -520	-170	-360	32 to 78	24
Archived TQNPC HT # RC577	-610	-420 to -380	-220 to -260	-460 to -320	70 to 210	28

* The alloy is self-passive. No significant active peak is observed.

Table 5
The Average Electrochemical Parameters from the Potentiodynamic Polarization Curves of Alloy 800 SG Tubes obtained at 150°C in Neutral Crevice Chemistry

SG Tubing ID	E_{Corr} (mV vs. SHE)	E_{pp} (mV vs. SHE)	E_p (mV vs. SHE)	E_{Protec} (mV vs. SHE)	$I_{Critical}$ (μA/cm^2)	$I_{Passive}$ (μA/cm^2)
Reference Alloy 800 HT # 9043A	-560	-420*	60	-270	5.2*	0.9
Darlington D4SG1 R49C61	-500	-380	-5	-210	15	1.8
Archived CNG2 HT # 13350	-460	-375*	-5	-215	3.3*	1.1
Archived PLGS Tubing	-530	-410*	10	-215	6.0*	2.2
Archived BNGS HT # 507937	-460	-375*	50	-195	6.2*	2.0
Archived BNGS HT # 507731	-490	-400*	10	-210	4.3*	2.0
Archived TQNPC HT # WL809	-515	-400*	-20	-235	4.3*	1.8
Archived TQNPC HT # RC577	-485	-385*	-10	-235	3.6*	1.9

* The alloy is self-passive. No significant active peak could be observed.

The technical terms used in the table are defined as follows:

E_{Corr}: the potential in the polarization curve where the total current density contributed by the anodic reactions and cathodic reactions equals zero, called the corrosion potential. (It is also called the ECP).

E_{pp}: the potential at which the anodic peak reaches its maximum current density ($i_{Critical}$) before decreasing as passive behaviour starts, called the primary passivation potential.

$i_{Critical}$: the amplitude of the active peak, called the critical current density.

$i_{Passive}$: the current density at the passive state, called the passive current density.

E_b : a potential called the pitting potential. Aggressive halide anions such as chloride ions can cause the passive films to breakdown in the passive potential region. The breakdown of the passive film is characterized by a sudden increase in the current density at this potential.

E_{Protec}: the protection potential. In a cyclic polarization, when the current density reaches a pre-determined threshold, the applied potential is reversed. Once pits initiate, they will grow even after the potential decreases to values below the pitting potential. Only when the potential decreases below the protection potential does pitting stop. This change is indicated by the reversing curve crossing the forward scan as it returns to lower potentials. This potential is sometimes used to verify the repassivation ability of an alloy. However, this potential is determined by the local chemistry in a developing pit, which is controlled by many factors, such as the geometry of the pit and whether it is covered or opened, etc. It should be used cautiously to verify the localized corrosion susceptibility of passive metals.

4. DISCUSSION

The potentiodynamic polarization data presented in Section 3 revealed that the electrochemical behaviours of the archived CANDU SG alloys under the test conditions are similar to that of the reference nuclear grade Alloy 800. However, the electrochemical behaviour of the ex-service Darlington tube D4SG1 49C61 in the neutral crevice chemistry differs from other Alloy 800 SG tubing surveyed. At 300°C, the Darlington tubing D4SG1 R49C61 has lower pitting potential and higher passive current density than the other tested tubing. The Darlington tubing D4SG1 R49C61 also has an active peak between the free corrosion potential E_{corr} and the passive region. This trend is even more clear and significant 150°C. An active peak is only seen in the polarization curve of Darlington tubing D4SG1 R49C61 and is not seen in the polarization curves of the other surveyed tubing. The conditions and the root cause leading to the Alloy 800 SG tube degradation at DNGS are under investigation in a separate COG work package (COG 40817). This active peak is a sign that indicates the alloy may be susceptible to crevice/underdeposit corrosion. This can be explained by the IR drop induced crevice corrosion mechanism proposed by H. Pickering ([8],[9],[10],[11]). This mechanism suggests that the IR drop that exists along a geometrically restricted crevice is responsible for crevice corrosion. In contrast to the conventional views of localized corrosion, in which the chemistry compositional change inside the cavity is regarded as the most significant consideration, the IR drop mechanism considers the potential drop between the surface inside the crevice and the surface outside the crevice to be the determining parameter that is responsible for depassivation and accelerated dissolution inside the crevice. This IR drop "shifts" the potential inside the crevice towards the active region, while the surface outside the crevice remains in the passive region.

One of the successes of the IR drop theory is its rationalization for the shape of the attack inside the crevice [11]. Figure 19 schematically illustrates the interpretation of the attack shape, based on the IR drop theory. The IR drop theory also explained vividly that an alloy, which is self-passive (i.e., no active peak), is unlikely to be susceptible to crevice/underdeposit corrosion.

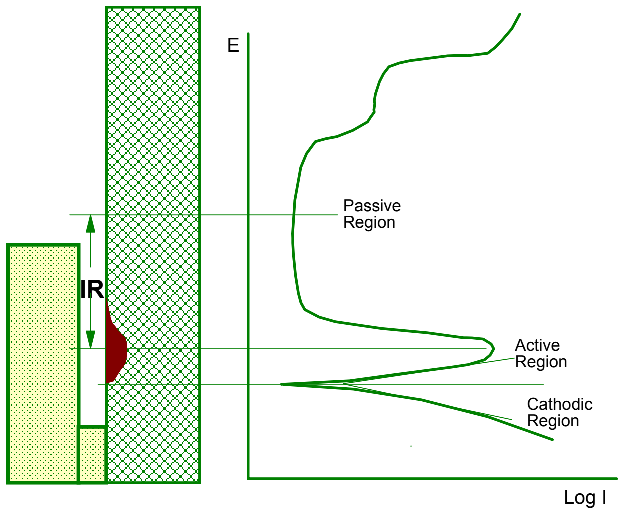

Figure 19 Schematic Illustration of the IR Drop Mechanism of Crevice Corrosion

All Alloy 800 SG tubes studied in this work are qualified nuclear grade SG tubing according to the current nuclear SG tube specifications except the aluminum concentration of the DNGS tubing (Unit 2 SG 4 R52C60) is lower that ASTM standard specified value. So far there is no strong evidence suggesting that the difference between the grain size hardness and elemental composition for any of the SG tubing investigated could affect the corrosion susceptibility of the alloy. However, one fact should be noted that the Alloy 800 tubing removed from Darlington SG had a history of more than a decade of service. Whether the difference in the electrochemical corrosion behaviour between the archived Alloy 800 tubing and the ex-service Darlington Alloy 800 tubing was due to the aging of the materials under the SG operating conditions requires further investigation. The anodic peaks observed in polarization curves obtained from TQNPC archived tubing at 300°C is not resulting from aging. The root cause of these active peaks and their implication to SG tube integrity is unknown.

5. CONCLUSIONS

Based on the survey of the corrosion susceptibility of the archived Alloy 800 SG tubing from different CANDU stations, the following conclusions could be made:

1. All archived CANDU Alloy 800 SG tubing and the reference nuclear grade Alloy 800 tubing, except the TQNPC tubing, show similar electrochemical corrosion behaviour

at 300°C in a neutral crevice chemistry solution, which is the most probable environment SG tubing will encounter during CANDU operation.

2. The electrochemical polarization curve of the Darlington removed tubing D4SG1 C49R61, which had in-service underdeposit corrosion, has a lower pitting potential and a higher passive current density than most of the archived Alloy 800 tubing tested at 300°C under neutral crevice chemistry conditions. The TQNPC archived tubing is an exception among the archived CANDU SG tubes tested. It shows an active peak in the polarization curve. This phenomenon is more apparent for TQNPC tubing heat # RC577, which not only has a distinctive active peak in the polarization curve between – 420 mV and –380 mV but also has a lower pitting potential than most of other archived Alloy 800 tubing.
3. At 150°C under the same neutral crevice chemistry conditions, the potentiodynamic polarization curve of the ex-service tubing shows an active peak, which is a sign of propensity of crevice/underdeposit corrosion. This active peak was not observed in any of the potentiodynamic polarization curves of the archived CANDU Alloy 800 SG tubing, including the TQNPC tubing, indicating that all archived tubing tested were less susceptible to the underdeposit corrosion than the ex-service Darlington tubing under startup conditions.

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