MINIMIZE CORROSION DEGRADATION OF STEAM GENERATOR TUBE MATERIALS

-Updated ECP/pH Zone for Alloy 800 SG Tubing-

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ABSTRACT

As part of a coordinated program, AECL is developing a set of tools to aid with the prediction and management of steam generator performance. Although stress corrosion cracking (of Alloy 800) has not been detected in any operating steam generator, for life management it is necessary to develop mechanistic models to predict the conditions under which stress corrosion cracking is plausible. Experimental data suggest that all steam generator tube materials are susceptible to corrosion degradation under some specific off-specification conditions. The tolerance to the chemistry upset for each steam generator tube alloy is different.

Electrochemical corrosion behaviors of major steam generator tube alloys were studied under plausible aggressive crevice chemistry conditions. The potential hazardous conditions leading to steam generator tube degradation and the conditions which can minimize steam generator tube degradation have been determined. Recommended electrochemical corrosion potential/pH zones were defined for all major steam generator tube materials, including Alloys 600, 800, 690 and 400, under CANDU steam generator operating and startup conditions. Stress corrosion cracking tests and accelerated corrosion tests were carried out to verify and revise the recommended electrochemical corrosion potential/pH zones. Based on this information, utilities can prevent steam generator material degradation surprises by appropriate steam generator water chemistry management and increase the reliability of nuclear power generating stations.

1. INTRODUCTION

Experimental data suggest that all SG tube materials can be susceptible to corrosion degradation under some specific off-specification chemistry conditions. The tolerance to the chemistry upset for each SG tube alloy is different. In recent years AECL has been working proactively to deal with the SG degradation issues. An effective way to minimize the SG material degradation is plant life management through effective water chemistry control. To support the proactive materials degradation management (PMDM) of SG materials, high-temperature electrochemical tests were performed under plausible SG crevice chemistry conditions for all SG tube alloys and sufficient corrosion knowledge was accumulated to alert operators to the risk of corrosion degradation under several operating conditions, including off-power operation. This knowledge has now been documented in a form of recommended ECP/pH zone that can be incorporated into ChemAND for SG system monitoring and diagnosis. Tests, especially accelerated corrosion tests and stress corrosion cracking (SCC) tests, have been performed to verify the tube behaviour in transient, off-specification, lay-up and shutdown chemistries. The recommended ECP/pH zones have been documented in the form of a “living” document that is revised and updated periodically as part of SG life management program. ECP and SG crevice chemistry conditions that can lead to the SG degradation have been defined in the ECP/pH map. The recommended ECP/pH zone could be used as a tool for safeguarding the integrity of SG tubing, with the expectation that operation in these “safe” zones will assure at least 60 years of service. This information will also be incorporated into ChemAND and co-ordinated with the crevice/SG chemistry model to provide a guide for online monitoring and diagnosis. The objective of this work is to provide technical support and assessment of SG tubing corrosion susceptibility for CANDU SG life cycle management. The recommended ECP/pH zones for Alloy 800 SG tubing are presented in this paper in their updated version.

2. CORROSION SUSCEPTIBILITY OF SG TUBE ALLOYS

The corrosion susceptibility of SG alloys, including Alloy 800, Alloy 600, Alloy 690 and Alloy 400, has been evaluated by performing a series of electrochemical measurements under plausible SG crevice conditions. The establishment of an electrochemical database provides necessary information for defining recommended ECP/pH zones for different SG alloys to minimize corrosion degradation. Based on the electrochemical data, recommended zones for minimizing the corrosion degradation of SG alloys have been defined [1].

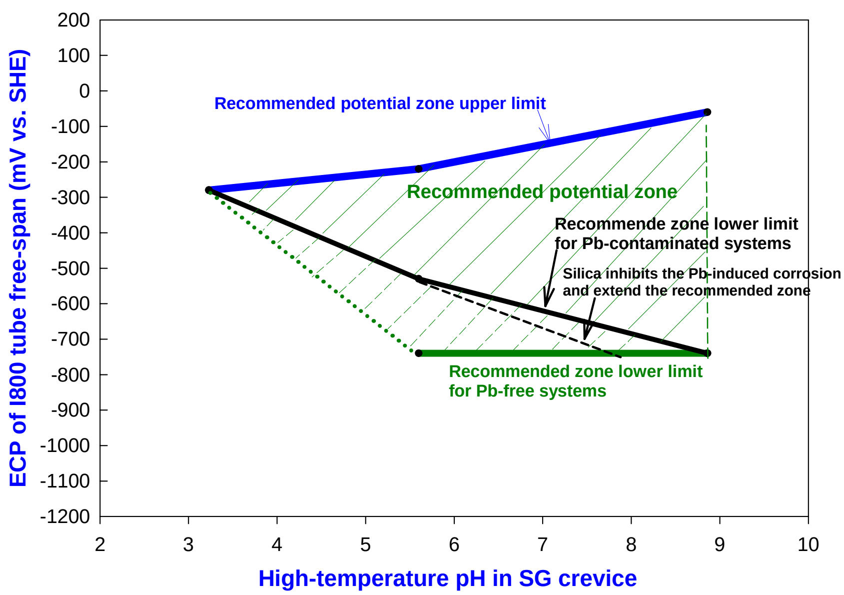

Figure 1: Recommended ECP/pH zone defined by COG-01-052 for Alloy 800 under CANDU SG operating conditions.

3. UPDATED ECP/PH ZONE FOR ALLOY 800 SG TUBING

The recommended ECP/pH zones proposed for Alloy 800 in 2000 [1] were based on tests performed under simulated SG crevice chemistry conditions at three pH levels. Tests performed at 300°C were carried out in chemistry solutions with $pH_{300°C}$ = 9.3, 6.1 and 3.2 respectively. Tests performed at 150°C were done in solutions with $pH_{150°C}$ = 10.1, 6.0 and 2.3 respectively. There is a relatively large gap between the acidic and the neutral chemistry conditions, within which the boundaries are not clear due to the lack of experimental data. Because this pH range is of great interest to the SG chemistry management for minimizing the tubing degradation during SG operation and startup, the existing ECP/pH zones require updating to fill this gap. In addition, constant extension rate tests (CERT) performed recently to evaluate the SCC susceptibility of Alloy 800 allowed the boundary conditions to minimize SCC of Alloy 800 to be revised [2]. The updated ECP/pH zones for Alloy 800 tubing presented in this document have considered the new electrochemical data obtained in crevice chemistries with pH 4.6 and pH 5 (at temperature) and the recommendations made in Reference [2].

3.1 Experimental conditions

Cyclic electrochemical polarization tests were performed in simulated crevice chemistries with pH of 4.6 or 5.0 at temperature shown in Table 1a and 1b. Based on the electrochemical data, revisions have been made to the recommended ECP/pH zones for Alloy 800 tubing.

Table 1a
Simulated CANDU SG crevice chemistries without lead oxide and silica addition.

Crevice Environment Simulated	Test Solution Composition
"Neutral" crevice environment	0.15M Na_2SO_4 0.3M NaCl 0.05M KCl 0.15M $CaCl_2$ (reference solution #1) $pH_{300°C}$ = 6.1; $pH_{neutral}$ = 5.16 $pH_{150°C}$ = 6.0; $pH_{neutral}$ = 5.56
Alkaline crevice environment. Deviation from "neutral" electrolyte	Add 0.4 M NaOH to "reference solution #1" $pH_{300°C}$ = 9.3; $pH_{neutral}$ = 5.14 $pH_{150°C}$ = 10.1; $pH_{neutral}$ = 5.55
pH 4.6 crevice environment. Deviation from "neutral" * electrolyte	**Add 0.0025M $NaHSO_4$ to "reference solution #1"** **$pH_{300°C}$ = 4.6; pHneutral = 5.16** **Add 0.0.00015M $NaHSO_4$ to "reference solution #1"** **$pH_{150°C}$ = 4.6; $pH_{neutral}$ = 5.56**
Acidic crevice environment. Deviation from "neutral" electrolyte	Add 0.05M $NaHSO_4$ to "reference solution #1" $pH_{300°C}$ = 3.2; $pH_{neutral}$ = 5.16 $pH_{150°C}$ = 2.3; $pH_{neutral}$ = 5.56

***** Crevice chemistries at pH 4.6 were calculated by G. Strati using ChemSolv code.

Table 1b
Simulated CANDU SG crevice chemistries without silica addition.

Crevice Environment Simulated	Test Solution Composition
"Neutral" crevice environment	0.15M Na_2SO_4 0.3M NaCl 0.05M KCl 0.15M $CaCl_2$ (reference solution #1) plus: ~500 mg/kg PbO pH_{300C} = 6.9; $pH_{neutral}$ = 5.16 $pH_{150°C}$ = 7.5; $pH_{neutral}$ = 5.56
Alkaline crevice environment. Deviation from "neutral" electrolyte	Add 0.4 M NaOH to "reference solution #1" plus: ~500 mg/kg PbO $pH_{300°C}$ = 9.3; $pH_{neutral}$ = 5.15 $pH_{150°C}$ =10.1; $pH_{neutral}$ = 5.55
pH 5 crevice environment. Deviation from "neutral" electrolyte	**Add 0.0054 M $NaHSO_4$ to "reference solution #1" plus: ~500 mg/kg PbO** **$pH_{300°C}$ = 5.0; $pH_{neutral}$ = 5.16** **Add 0.00457 M $NaHSO_4$ to "reference solution #1" plus: ~500 mg/kg PbO** **$pH_{150°C}$ = 5.0; $pH_{neutral}$ = 5.56**
Acidic crevice environment. Deviation from "neutral" electrolyte	Add 0.05M $NaHSO_4$ to "reference solution #1" plus: ~500 mg/kg PbO $pH_{300°C}$ = 3.4; $pH_{neutral}$ = 5.16 $pH_{150°C}$ = 2.4; $pH_{neutral}$ = 5.56

*High-temperature pH values are based on multi-equilibria calculations.

3.2 Electrochemical Results Obtained in Crevice Chemistries with pH 4.6 and 5 at Temperature.

Cyclic potentiodynamic polarization tests were performed at 150°C and 300°C in the solutions (shown in bold) in Tables 1a and 1b. The experimental details including the test set up, materials and procedures are described in previous publications [1], [3].

The potentiodynamic polarization curves obtained in SG bulk water and in pH 4.6 lead-free crevice solutions and in pH 5.0 lead-contaminated crevice solutions at 300°C are presented in Figures 2 and 3, respectively.

The potentiodynamic polarization curves obtained in SG bulk water and in pH 4.6 lead-free crevice solutions and in pH 5.0 lead-contaminated crevice solutions at 150°C are presented in Figures 4 and 5, respectively.

In each of the figures the recommended ECP zone, within which the corrosion susceptibility of Alloy 800 tubing is minimized, is marked following the guidelines described in a previous publication [1] except for the ECP/pH zone upper limit at 300°C, which was determined by the CERT tests to minimize the SCC susceptibility of Alloy 800 tubing material [2].

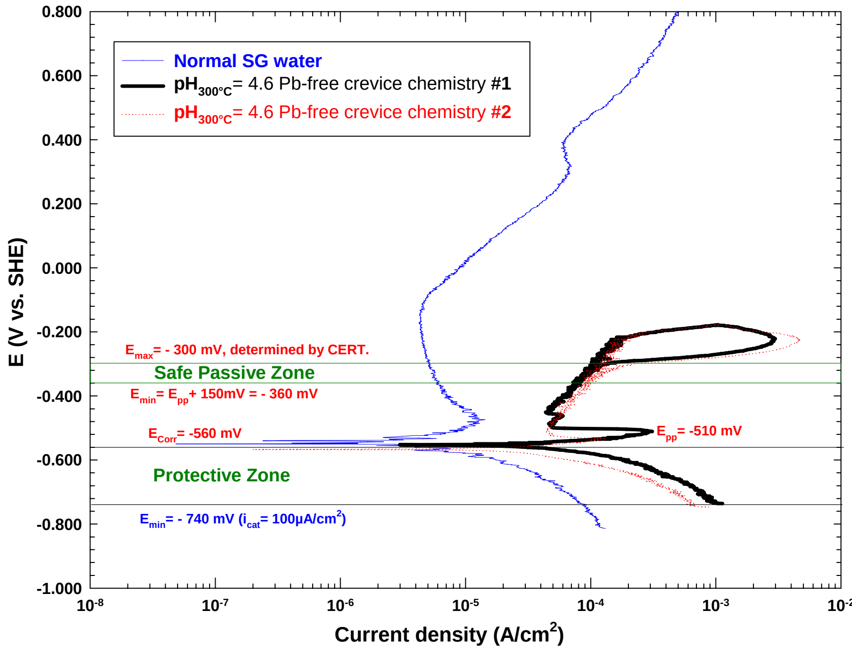

Figure 2: Cyclic potentiodynamic polarization curves of Alloy 800 SG tubing obtained at 300°C in a $pH_{300°C}$ = 4.6 lead-free crevice solutions.

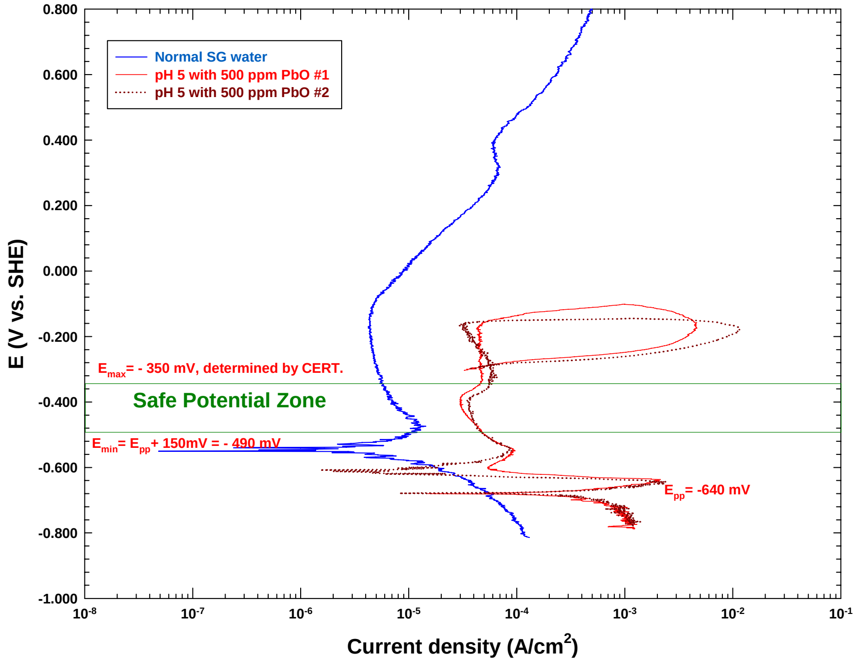

Figure 3: Cyclic potentiodynamic polarization curves of Alloy 800 SG tubing obtained at 300°C in a $pH_{300°C}$ = 5.0 crevice solutions containing 500 ppm of PbO.

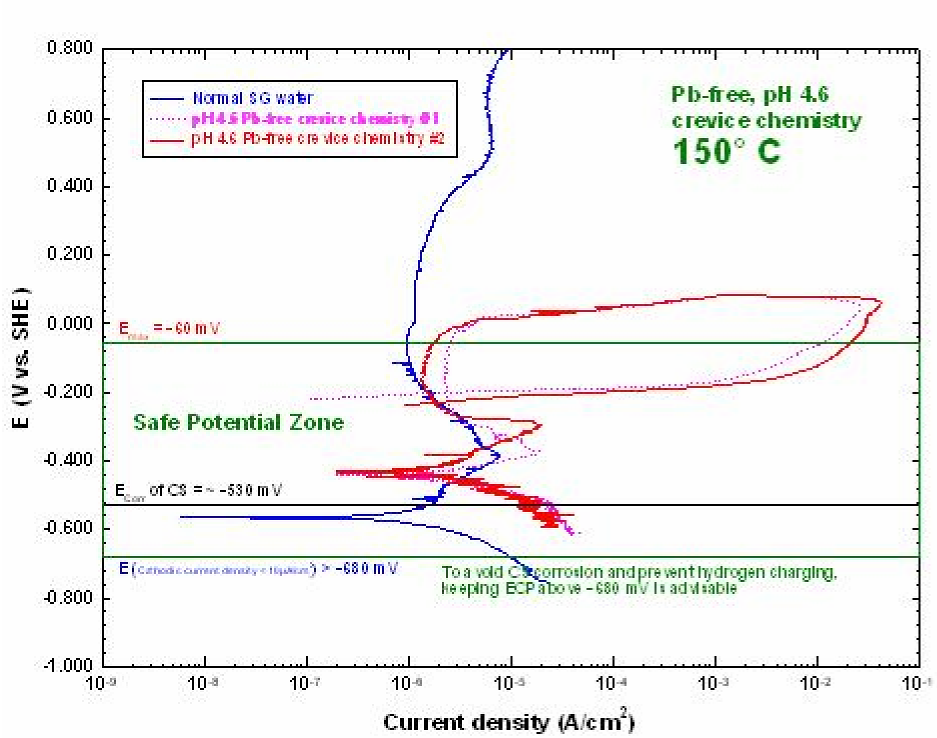

Figure 4: Cyclic potentiodynamic polarization curves of Alloy 800 SG tubing obtained at 150°C in a pH300°C = 4.6 lead-free crevice solutions.

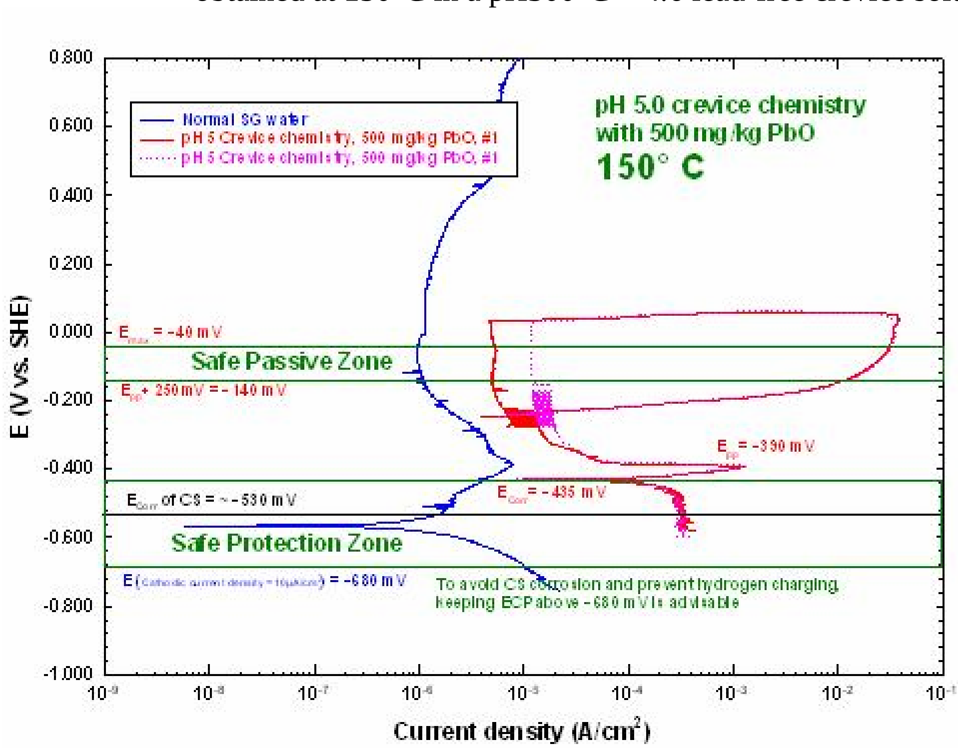

Figure 5: Cyclic potentiodynamic polarization curves of Alloy 800 SG tubing obtained at 150°C in a pH300°C = 5.0 crevice chemistry containing 500 mg/kg.

3.3 Undated ECP/pH Zones for Alloy 800

Based on the CERT data for Alloy 800 obtained under plausible simulated SG crevice chemistry conditions at applied potentials, the SCC susceptibility of Alloy 800 SG tubing was evaluated over the recommended electrochemical corrosion potential (ECP)/pH zones under CANDU SG operating conditions [2]. The effects of lead contamination on the SCC susceptibility of Alloy 800 tubing were also evaluated. The work suggests the ECP zone should be revised to lower the ECP upper limit under both the lead-free near-neutral SG crevice conditions and the lead-contaminated neutral crevice chemistry conditions to minimize SCC. The revised ECP/pH zone recommended to minimize SCC of Alloy 800 SG tubing is shown in Figure 6.

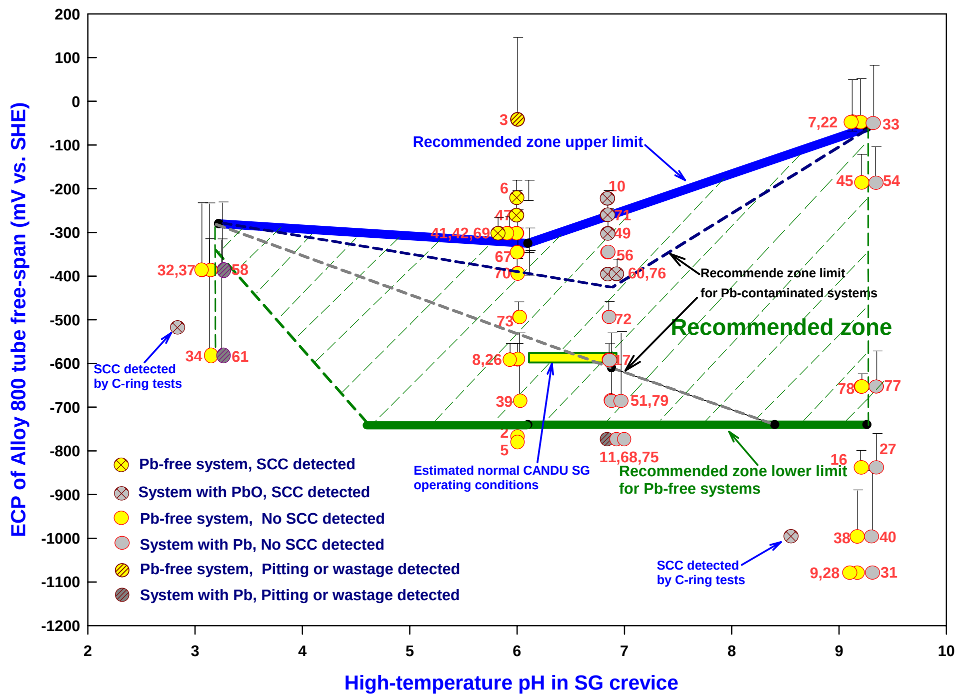

Figure 6: Revised recommended ECP/pH zone for Alloy 800 under CANDU SG operating conditions to minimize SCC [2].

The updated ECP/pH zone for Alloy 800 SG tubing under CANDU SG operating conditions is shown in Figure 7. This updated zone has included the following revisions:

(1) The upper ECP limit of the recommended zone is revised according the CERT test results to minimize SCC of Alloy 800 SG tubing [2].

(2) New data obtained from electrochemical tests performed at pH 4.6 (lead-free solution) and pH 5.0 (lead-contaminated solution) were added.

(3) The pH values of the test solutions were revised according to multi-equilibria calculations.

(4) Areas that could have a high rate of traspassive dissolution, which may lead to the depletion of chromium in the passive film, are marked.

(5) The polarization curve of Alloy 800 obtained in $pH_{300°C}$ 4.6 lead –free crevice solution shows a relatively high active peak indicating the possibility of crevice/underdeposit corrosion. The relevant risk area for crevice/underdeposit corrosion is marked.

With lead contamination, the "safe" ECP/pH zone is significantly reduced and is shown in Figure 8.

The combined ECP/pH zone for Alloy 800 at CANDU SG operating temperature is shown in Figure 9.

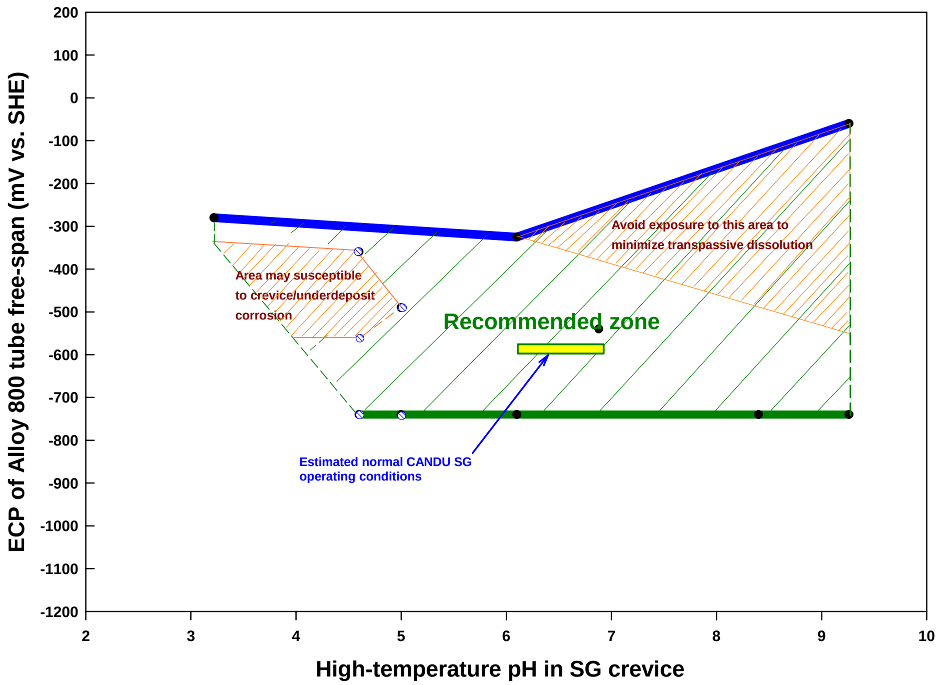

Figure 7: Updated ECP/pH zone for Alloy 800 for lead-free systems under CANDU SG operating conditions.

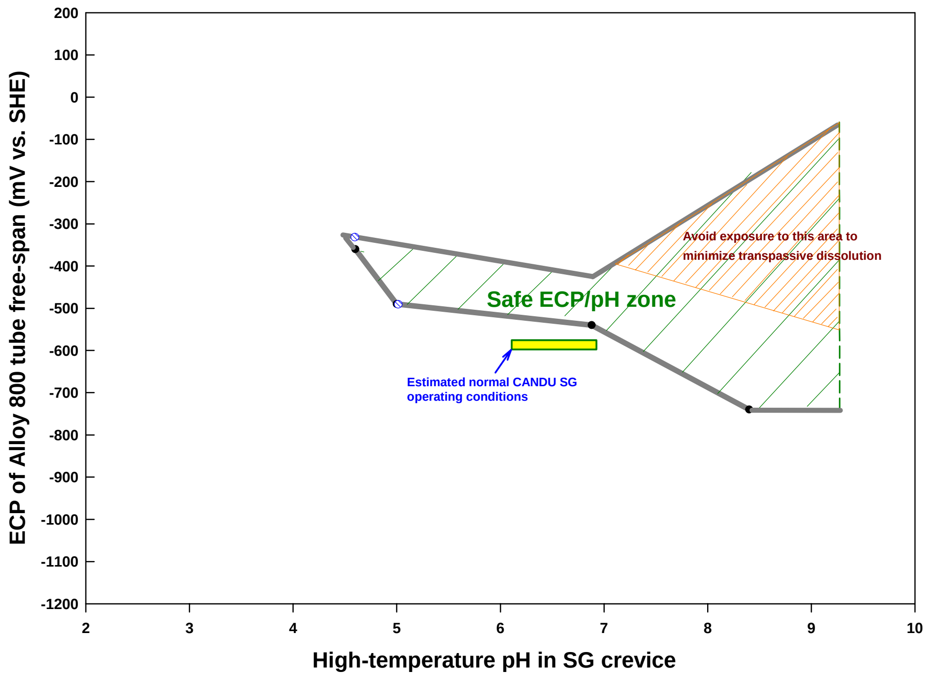

Figure 8: **Updated ECP/pH zone of Alloy 800 for lead-contaminated systems under CANDU SG operating conditions.**

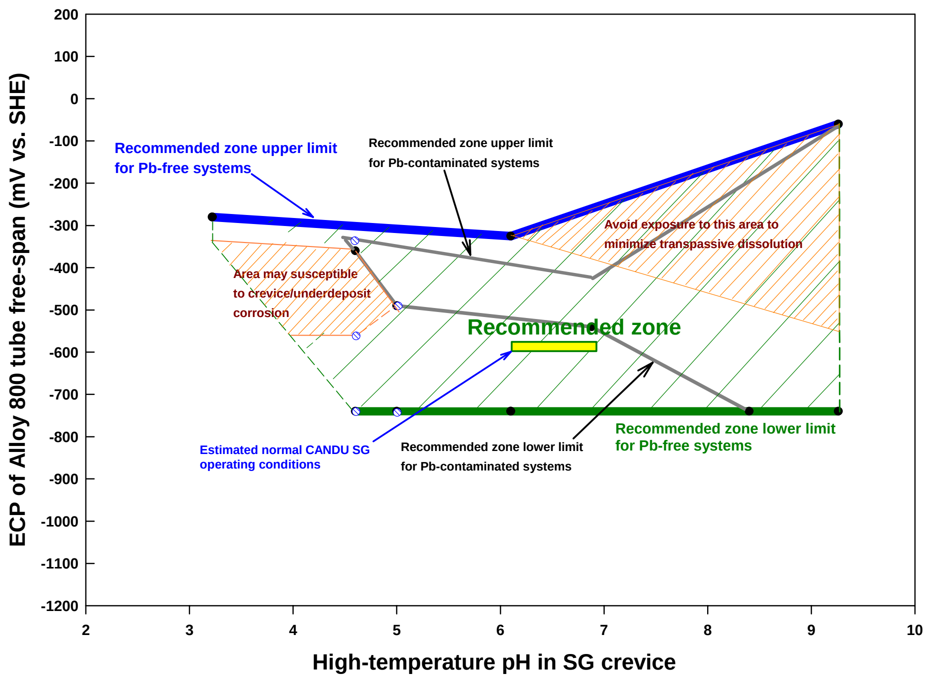

Figure 9: **Updated ECP/pH zone for Alloy 800 under CANDU SG operating conditions. (Superimposed zones for lead-free and lead-contaminated systems).**

The recommended ECP/pH zone for Alloy 800 at 150° is shown in Figures 10 and 11 for the lead-free systems and lead contaminated systems respectively. The recommended ECP/pH zone for Alloy 800 at 150°C shown in this document are merely based on the electrochemical data. No CERT tests were performed to evaluate the SCC susceptibility at 150°C so far.

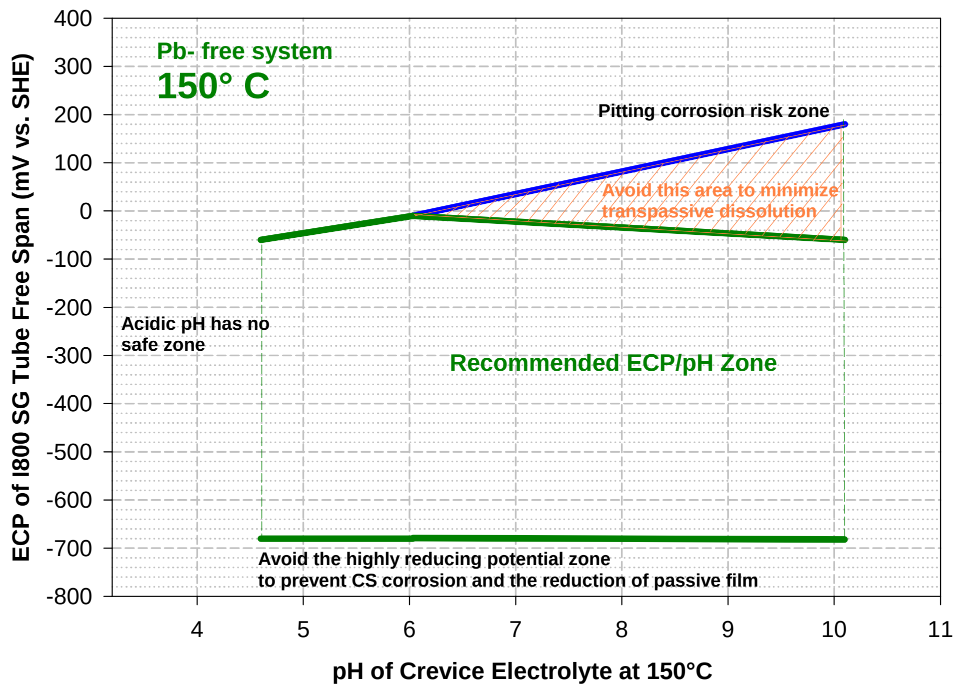

Figure 10: Updated ECP/pH zone for Alloy 800 under CANDU SG startup conditions for lead-free systems.

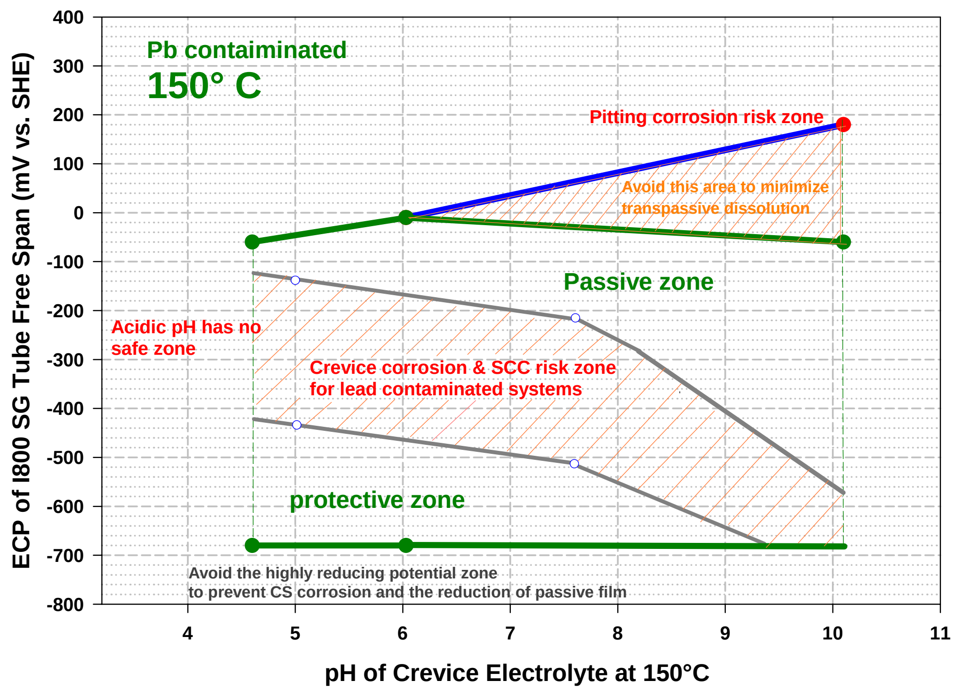

Figure 11: **Updated ECP/pH zone for Alloy 800 under CANDU SG startup conditions for lead-contaminated systems.**

4. THE APPLICATION OF RECOMMENDED ECP/PH ZONE FOR SG TUBING MATERIAL DEGRADATION MANAGEMENT

The recommended ECP/pH zone established under some potentially corrosive environments in CANDU SGs could be used as a tool for safeguarding the integrity of SG tubing, with the expectation that operation in these “safe” zones will assure at least 60 years of service. This information will also be incorporated into ChemAND and co-ordinated with the crevice/SG chemistry model to provide a guide for online monitoring and diagnosis. As shown in the flow chart in Figure 12, the plant operator first gathers water chemistry information from online monitoring systems. Then the information on the SG water chemistry is correlated to the ECP of the tubing free span. The possible crevice chemistry conditions can also be determined by using ChemSolv™, which is a kinetics-based code within ChemAND for modeling SG crevice and feedwater chemistry. Based on the ECP of the free span tubing and the crevice chemistry information, the operator can quickly determine whether hazardous conditions have developed or will develop in the SG crevice and what preventive measures should be taken, and how quickly.

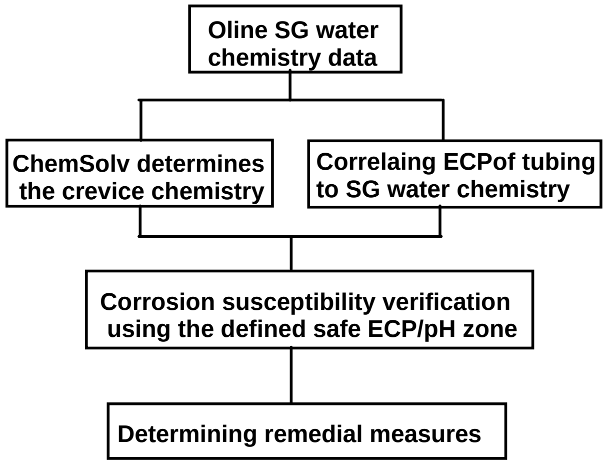

Figure 12: Safe guarding SG tubing through SG water chemistry management.

5. SUMMARY

1. Electrochemical measurements were chosen as a screening method to establish safe ECP/pH zones of operation for SG tubing by carrying out tests under plausible off-specification chemistry conditions. SCC and accelerated corrosion tests are performed to verify the recommended ECP/pH zone defined by the electrochemical data. Data from the field, if available in the future, will also be used to validate the recommended ECP/pH zones.
2. The recommended ECP/pH zone for Alloy 800 SG tubing is documented in the form of a “living” document that is revised and updated periodically as part of SG life management program and will be incorporated into ChemAND for online monitoring and diagnosis.
3. Water chemistry data from an online monitoring system can be correlated with the ECP of the free span SG tubing. The crevice chemistry conditions can be determined from the bulk water chemistry using ChemSolv code.
4. Based on the above considerations, corrosion degradation of Alloy 800 SG tubing in the secondary side crevices can be minimized for an extended service life by operating within the safe ECP zone.

6. ACKNOWLEDGEMENTS

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7. References

[1] Y.C. Lu, "Electrochemical Aspects of Defining the Safe Potential/pH Zone for Corrosion Prevention of Alloy 800 Steam Generator Tubing", in Proc. of the 4^{TH} CNS International Steam Generator Conference. Paper number 3-18, 2002.

[2] S. Liu and Y. C. Lu, "SCC Susceptibility of Alloy 800 under CANDU SG Conditions", Proceedings of this conference, 2006.

[3] Y.C. Lu, R.D. Cleland and M.D.Wright, "Effect of Lead and Silicon on Localized Corrosion of Alloy 800 in Steam Generator Crevice Environments", Proceedings of 10th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Lake Tahoe, Nevada, Paper Number 0028, 2001 August 5-9.