




## In situ experimental data on passivation of Alloy 690 in Hot Conditioning water chemistry

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Confidentiality Public

Report's title In situ experimental data on passivation of Alloy 690 in Hot Conditioning water chemistry		
Customer, contact person, address SAFIR2010 / TEM	Order reference	
Project name Vesikemia ja hapettuminen reaktoripiirin olosuhteissa	Project number/Short name 41745 / WATCHEM	
Author(s) Timo Saario	Pages 17	
Keywords Alloy 690, Hot Conditioning, passivation	Report identification code VTT-R-08766-10	
<p>Summary</p> <p>The primary circuit surfaces of a new pressurized water nuclear reactor are passivated before the first fuel loading. This treatment is called Hot Conditioning. The main purpose of the Hot Conditioning is to minimise the rate of generation of soluble and insoluble corrosion products (corrosion rate), and thereby minimize the activity build-up during power operation. There is still no international consensus on optimal passivation water chemistry. Open issues are e.g. the optimal concentration of lithium and the length of the passivation treatment. New issues are the possible benefits of using boron and zinc in the water during the passivation.</p> <p>This report presents the first part of experimental results on Alloy 690 gained by the electrochemical impedance spectroscopy (EIS) in situ technique at <math>T = 292^{\circ}\text{C}</math>. These results indicate that addition of boron is highly beneficial, 1200 ppm B resulting in reduction of the estimated corrosion rate by a factor of about 2. An increase of the lithium concentration from 1 to 2 ppm Li was found to result in an increase of the estimated corrosion rate. The time to form a stable passive layer on Alloy 690 at <math>T = 292^{\circ}\text{C}</math> was found to be about 40 hrs. Thus, the time normally used for passivation, i.e. 300 – 1000 hrs, is certainly long enough. In experiments without boron, the conductivity was found to decrease during the experiment, indicating a possibility of lithium hide-out on the hot part of the test equipment surfaces.</p> <p>There are three lines of further research in optimisation of the Hot Conditioning procedure that require attention. The first one is the lower range of Li concentration, i.e. in situ results need to be gained also for 0.5 ppm Li, in order to quantify the difference between the Japanese and Western approaches. Secondly, the effect of boron concentration should be studied in a more wide range, e.g. duplicating some of the current measurements at a level of 500 ppm B. Thirdly, the mechanism, extent and consequences of possible Li hideout during the passivation treatment should be studied in detail.</p>		
Confidentiality	Public	
Espoo 15.12.2010		
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Distribution (customer and VTT) Customer 1, VTT 1		
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## Preface

This report has been produced as part of the work in project WATCHEM of the SARIF2010 - The Finnish Research Programme on Nuclear Power Plant Safety 2007 – 2010.

Espoo 15.12.2010

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# 1 Introduction

The primary circuit of a new reactor is passivated (preoxidised) before loading in the first fuel. The passivation procedure is called Hot Conditioning which is part of the Hot Functional Testing (HFT). The main purpose of the preoxidation is to minimise the concentration of corrosion products in the coolant during the future power cycles, and thus minimise the activity build-up at the plant. During Hot Conditioning water is heated by the waste heat from the main circulation pumps, resulting in a maximum temperature of slightly less than 300°C. Preoxidation of system and component surfaces may also come into focus when larger system parts have been decontaminated and are possibly preoxidised before taking into use or e.g. in case of replacing the steam generator.

There has been a continuous development in optimisation of the Hot Conditioning procedure during the last 30 years /1/. The aim of water chemistry development is to establish a Cr-rich stable oxide film on the surface of the primary system components, especially on steam generator tubing which represents about 70% of the surface exposed to the coolant. A Cr-rich spinel-type oxide film results in a lower corrosion product release and thus contributes to a lower level of activity build-up during power operation.

Plain deaerated water is not sufficient in establishing a reducing condition (which is needed to form the desired passivating Cr-rich spinel-type oxide film), and thus dissolved hydrogen is added (typically 25 to 35 ccH<sub>2</sub>/kgH<sub>2</sub>O). Adjustment of the high temperature pH to a value close to the solubility minimum of the main elements Fe, Ni and Cr supports formation of a Cr-rich spinel-type oxide and in PWR's is achieved by adding lithium hydroxide, LiOH. For a target pH<sub>T</sub> in the range 7.2...7.4 the concentration of Li is 0.5...1.0 ppm, respectively, in the absence of boric acid. Adding the base, LiOH, without H<sub>2</sub> would result in markedly higher corrosion product release rate, even higher than that in deaerated water /1/.

The Japanese have proposed that a Hot Conditioning chemistry with 0.5 ppm Li + 30 ccH<sub>2</sub>/kgH<sub>2</sub>O is optimal, and showed e.g. at Tomari-1 /2/, Ikata-3 /3/ and Genkai-4 /4/ that this chemistry results in a 10-30% reduction in dose rate during the first outages, when compared to plants passivated with deaerated water. A further 40-60% reduction in dose rate can be gained by introducing Zn-injection (at the level of 5 ppb) during the Hot Conditioning, as shown for the case of Tomari-3 /5/. EDF and AREVA currently promote a Hot Conditioning chemistry with 1-2 ppm Li + 30 ccH<sub>2</sub>/kgH<sub>2</sub>O.

An example of the kinetics of passive film formation on different steam generator tubing materials under typical PWR operational water chemistry conditions is shown in Fig. 1. The film thickness presented in Fig. 1 consists of both the inner (in-grown) layer and the outer (deposited) layer. While the total film thickness for Alloy 690 grows continuously in a near parabolic fashion, it is presumed that the part of the inner layer which is responsible for corrosion resistance, i.e. the barrier layer, actually forms rather rapidly /6,7/.

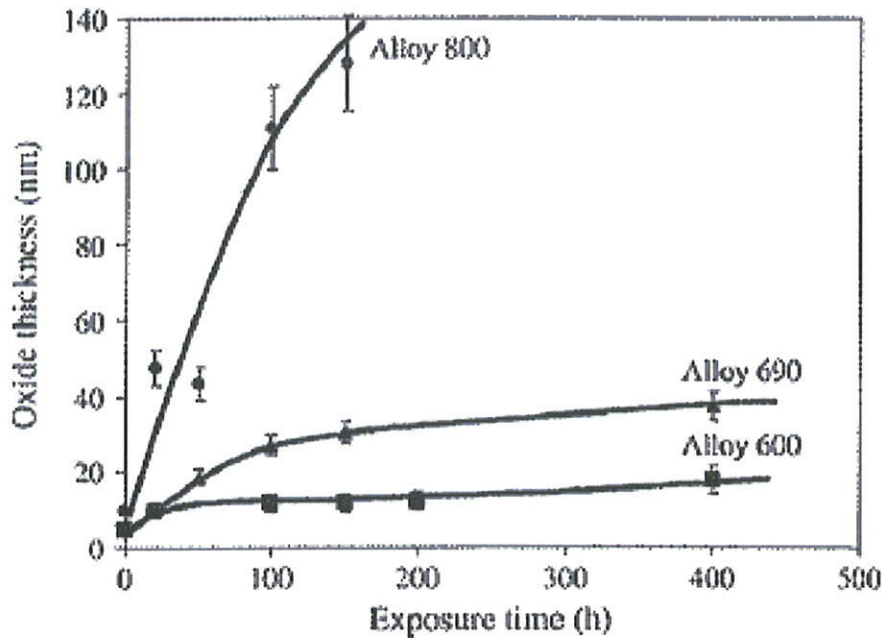


Figure 1. Oxide thickness vs. oxidation time for alloys 600, 690 and 800, oxidised in PWR primary water at  $T = 325^{\circ}\text{C}$  (2 ppm Li, 1200 ppm B, 35 cc/kgH<sub>2</sub>O H<sub>2</sub>) /6/.

Electrochemical impedance spectroscopy (EIS) is a tool that has been earlier shown to be applicable for in situ monitoring of properties of passive films forming under Hot Conditioning water chemistry conditions /8/. Impedance is resistance of a system to alternating current, analogous to the electric resistance of a material. According to Ohm's law voltage ( $V$ ) is resistance ( $R$ ) times the current ( $I$ ),

$$U = R \cdot I \quad (1)$$

Simplifying, in the case of a PWR environment, one may take that the voltage is the redox-potential ( $\sim$ constant), resistance is equal to impedance at low frequencies and current is the corrosion current which is directly proportional to the corrosion rate. Thus, the value of impedance at low frequencies becomes inversely proportional to the corrosion rate. In general, the higher is the value of impedance at low frequency end of the spectrum, the lower is the corrosion rate. The EIS data can be formally interpreted using the Mixed Conduction Model (MCM), as shown later in Chapter 4.1.

There is still no international consensus on the best available procedure for the water chemistry to be used during HFT. Open questions exist on the minimum length of the passivation time, the optimal concentration of Li, and the use of boric acid. In SAFIR2010 –programme, in the project WATCHEM, on-line in situ electrochemical methods have been developed in co-operation with BARC, India, and UCTM, Bulgaria to monitor the passivation process and to determine the degree of success. The methods have been earlier verified for carbon steel /8/. This report contains the first part of verification results for Alloy 690.



## 2 Goal

The main goal of the present report has been to verify the use of in situ electrochemical impedance (EIS) technique for monitoring of the progress and success of passivation of Alloy 690 during exposure to simulated Hot Conditioning water chemistries. A second goal was to perform a preliminary assessment of the main water chemistry parameters, i.e. lithium hydroxide and boric acid concentration, in relation to determining the optimal water chemistry for Hot Conditioning of a PWR plant having Alloy 690 steam generator tubing.

## 3 Experimental

The measurements were performed in an AISI 316 autoclave at temperature of 292°C and pressure of 100 bar. The autoclave was connected to a recirculation loop enabling refreshing of the water in the autoclave about twice in an hour. The electrolyte used was prepared from deionised water. Lithium was added as LiOH and boron as H<sub>3</sub>BO<sub>3</sub>. In the experiments where B was added, a concentration of 1200 ppm B was used, corresponding to 6867 ppm of H<sub>3</sub>BO<sub>3</sub>. Hydrogen overpressure of 1.5 bar was added to the feed water tank corresponding to about 30 cc/kgH<sub>2</sub>O (2.3 ppm) dissolved hydrogen. All potentials were measured vs. an internal reference electrode made of Pd and cathodically polarised to  $i_c = -5 \mu\text{Acm}^{-2}$  to stabilise the potential of the reference electrode at the hydrogen line (i.e. the reversible H<sub>2</sub>/H<sup>+</sup> - redox-potential, RHE). The potential was converted to the SHE scale by the Nernst equation after calculating the solution pH at the temperature. A cylinder made of Pd and placed around the specimen was used as a counter electrode.

Specimens were cut from an Alloy 690 tube (courtesy of EPRI NDE Center). The material was in annealed condition. Measurement wires (0.8 mm Ni-wires) were attached to the specimen mechanically, and the connection point was covered with several layers of PTFE-tape.

Impedance spectra were obtained with a Solartron 1287/1260 system controlled by ZPlot software (Scribner Associates) in a frequency range of 0.001 to 80,000 Hz at an a.c. voltage amplitude of 10 mV (rms). Impedance spectra were measured every ca. three hours till the end of the exposure at open circuit. The validation of the impedance spectra was performed by checking the linearity condition, i.e. measuring spectra at different signal amplitudes, and the causality using a Kramers-Kronig compatibility test. For the simulation and fitting of impedance spectra to the transfer functions derived from the kinetic model, Microcal Origin-based software has been employed.

## 4 Results

### 4.1 Impedance spectra

Several successful experiments were carried out using water with 1200 ppm B as the base electrolyte into which lithium additions were made as LiOH. An example of the inlet conductivity from one of the experiments is shown in Fig. 2. First the loop was cleaned by changing all the water into ion pure water and circulating the ion pure water through the loop until conductivity was less than  $0.2 \mu\text{Scm}^{-1}$ . Then, 1200 ppm boron as  $\text{H}_3\text{BO}_3$  and 1 ppm of Li as LiOH were added, temperature was increased to  $T = 80^\circ\text{C}$  and nitrogen bubbling was continued in the mixing tank until dissolved oxygen level was  $\text{DO}_2 < 5 \text{ ppb}$ . After this, 1.5 bar hydrogen overpressure was introduced into the mixing tank and temperature was increased to  $T = 292^\circ\text{C}$ .

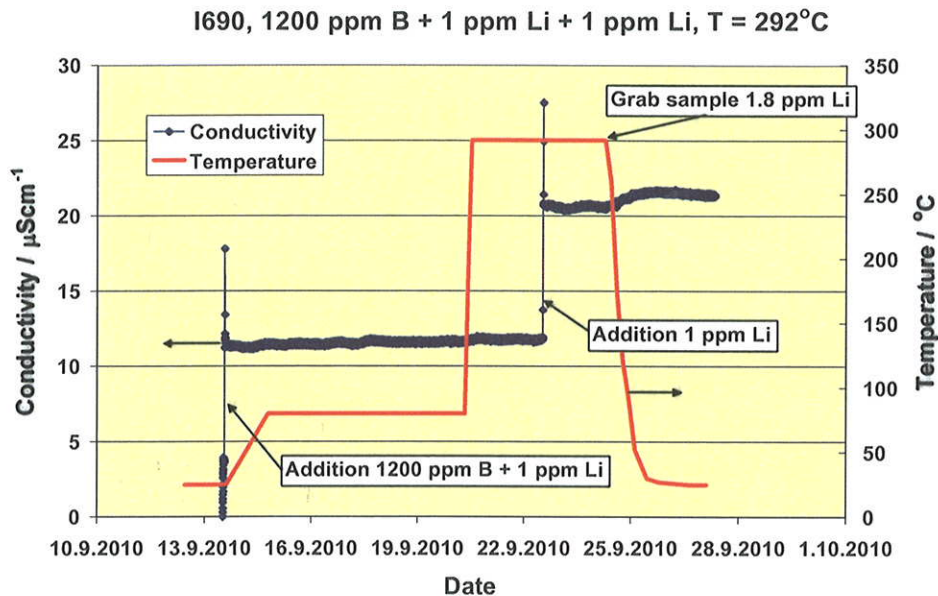


Figure 2. Temperature and inlet conductivity ( $25^\circ\text{C}$ ) as a function of time in a test run where originally 1200 ppm of B and 1 ppm Li, and after stabilization of the in situ impedance spectra of Alloy 690 an additional 1 ppm Li was added as LiOH.  $[\text{H}_2] = 30 \text{ ccH}_2/\text{kgH}_2\text{O}$  from the start.

During the exposure at  $T = 292^\circ\text{C}$  EIS was recorded, one spectra roughly each 3 hrs. After the spectra had stabilized, an additional 1 ppm Li was injected to the mixing tank and the EIS was again recorded until the spectra stabilized, after which the test was ended and the pressure vessel was cooled down. At the end of the test a grab sample analysis for Li showed  $[\text{Li}] = 1.8 \text{ ppm}$ . The high temperature pH would be  $\text{pH}_{292\text{C}} = 6.5$  for a solution with 1200 ppm B + 1 ppm Li and  $\text{pH}_{292\text{C}} = 6.8$  for a solution with 1200 ppm B + 2 ppm Li.

Fig. 3 shows a comparison of the EIS (stabilized values) measured during the experiment. The increase of Li concentration from about 1 ppm to about 2 ppm results in a decrease of the impedance value at low frequencies from about  $|Z| = 1580 \Omega\text{cm}^2$  to roughly  $970 \Omega\text{cm}^2$ . In a straightforward interpretation, this means



that increasing the lithium concentration by about 100% results in an increase of the corrosion rate by roughly 60%. A more accurate interpretation of the results will be given below in Chapter 4.2, involving modeling of the impedance spectra and extraction of relevant parameters thereof describing the different processes responsible for the impedance signal.

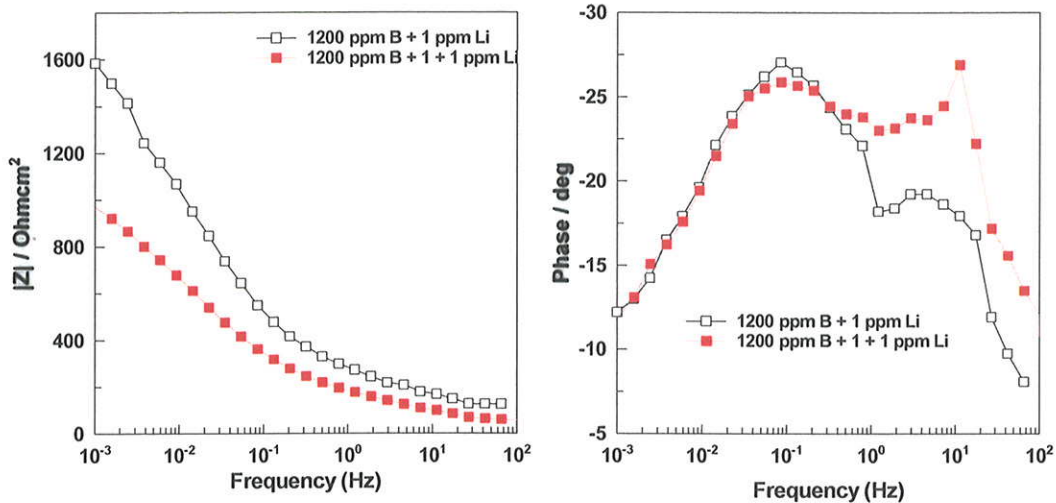


Figure 3. The effect of increasing the lithium concentration during one single experiment from about  $[\text{Li}] = 1$  ppm to  $[\text{Li}] = 2$  ppm on the impedance magnitude (left) and phase angle (right).  $T = 292^\circ\text{C}$ ,  $[\text{B}] = 1200$  ppm.

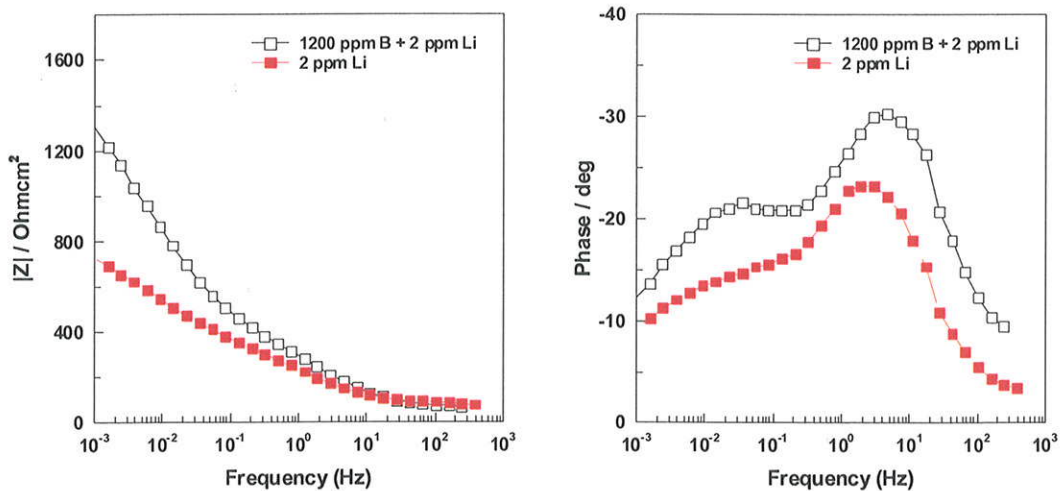


Figure 4. Comparison of results from an experiment with 1200 ppm B + 2 ppm Li and a separate experiment with 2 ppm Li (no B). In these experiments the chemistry was kept constant throughout the duration of each experiment.

Fig. 4 shows a comparison of results from an experiment with 2 ppm Li (without any B) and a separate experiment with 1200 ppm B + 2 ppm Li. The high temperature pH would be  $\text{pH}_{292\text{C}} = 7.8$  for a solution with 2 ppm Li (no B), which is about 1.0 pH-units higher than that for the case with 1200 ppm B + 2 ppm Li. In

case of 1 ppm Li without B, the high temperature pH would be  $\text{pH}_{292\text{C}} = 7.4$ , about 0.9 pH-units higher than for the case with 1200 ppm B + 1 ppm Li. In these experiments the chemistry was kept constant throughout the duration of each experiment.

In Fig. 4, despite the slightly less favourable  $\text{pH}_{292\text{C}}$ , the impedance with 1200 ppm B is clearly higher, at low frequencies by about 70%. Thus, the corrosion rate and rate of generation of soluble and insoluble corrosion products into the primary circuit would be expected to be clearly smaller in the presence of B than without it. Fig. 5 shows a similar comparison with 1 ppm Li concentration. The presence of 1200 ppm B results in roughly twice as high impedance, indicating an even higher reduction in the rate of generation of soluble and insoluble corrosion products than in the case of 2 ppm Li concentration in the solution. In Fig. 6, another comparison is shown, similar to that in Fig. 3, on the effect of increasing the Li concentration from 1 ppm to 2 ppm in a solution with 1200 ppm B. In this case, the comparison is between two separate experiments, so that in both cases the chemistry has been kept constant throughout the experiment. In this case, the reduction in impedance resulting from the increase in Li concentration was roughly 25%.

A comparison of two experiments with no B, one with 1 ppm Li and the other one with 2 ppm Li, is shown in Fig. 7. Here, the decrease in impedance due to the increase of Li concentration was about 8%.

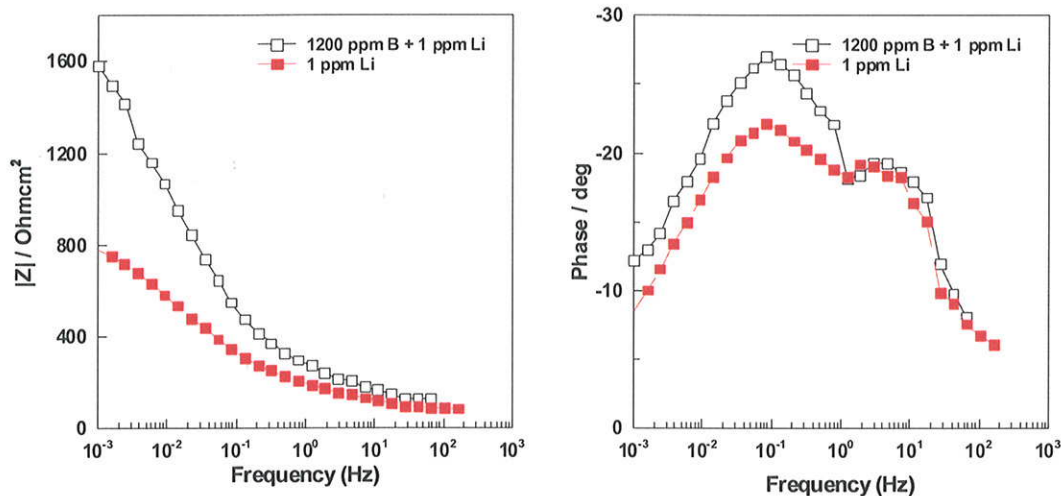


Figure 5. Comparison of results from an experiment with 1200 ppm B + 1 ppm Li and a separate experiment with 1 ppm Li (no B). In these experiments the chemistry was kept constant throughout the duration of each experiment.

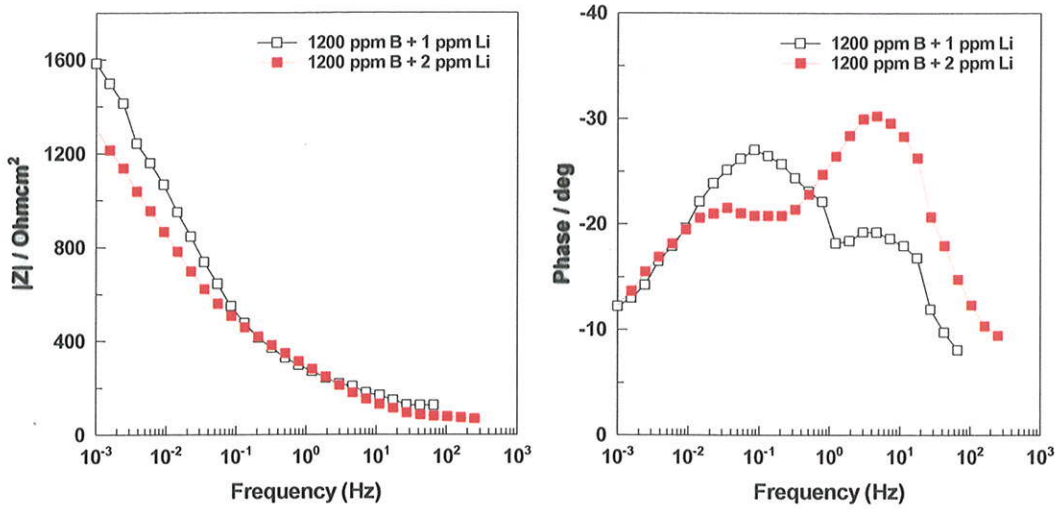


Figure 6. Comparison of two separate experiments. The effect of increasing the lithium concentration from about  $[\text{Li}] = 1 \text{ ppm}$  to  $[\text{Li}] = 2 \text{ ppm}$  on the impedance magnitude (left) and phase angle (right).  $T = 292^\circ\text{C}$ ,  $[\text{B}] = 1200 \text{ ppm}$ .

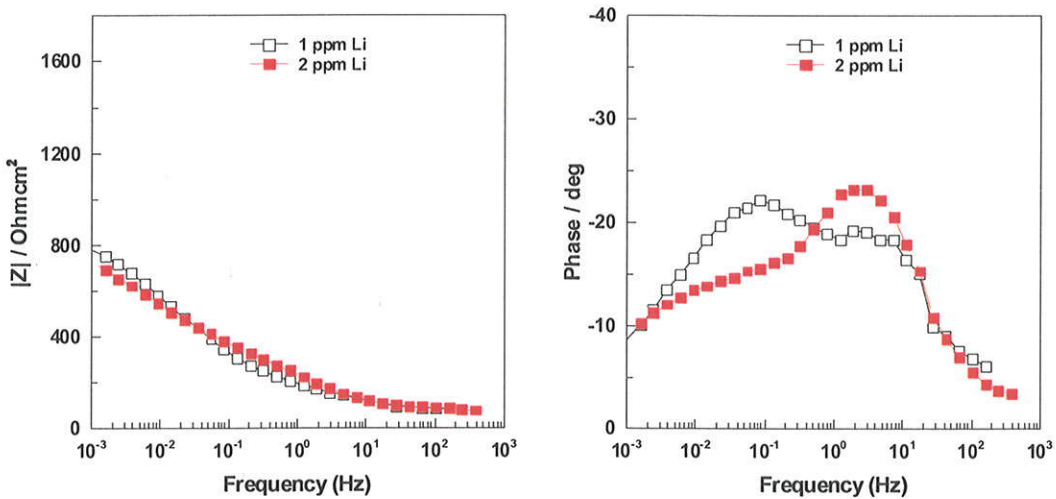


Figure 7. Comparison of two separate experiments, the first one with lithium concentration of about  $[\text{Li}] = 1 \text{ ppm}$  and the second one with about  $[\text{Li}] = 2 \text{ ppm}$ . Impedance magnitude on the left and phase angle on the right.  $T = 292^\circ\text{C}$ ,  $[\text{B}] = 0 \text{ ppm}$ .

The exposure time for stabilization of the impedance spectra may be taken as the minimum time needed to achieve a stable passive layer. In case of carbon steel under PHWR Hot Conditioning conditions stabilization of the impedance spectra occurred within 30-40 hrs /8/, in agreement with the estimates (based on conventional ex situ techniques) for achieving a stable magnetite film on the surface /8/. Figs 8 and 9 show the impedance spectra measured as a function of exposure time for 1200 ppm B + 1 ppm Li and 1.3 ppm Li (no B), respectively. In both cases stabilization of the spectra is evident within about 30 to 40 hrs of exposure. An interesting point is that the impedance is larger in the beginning of



the exposure and decreases until stabilization occurs. This is exactly the opposite to the behaviour of carbon steel /8/. One possible explanation to this phenomena could be that on Alloy 690 under PWR conditions, the first about 3 nm thick layer forming within less than one minute is almost purely  $\text{Cr}_2\text{O}_3$  /7/. Transformation of this layer to the normally observed  $\text{Cr}_2\text{FeO}_4$  spinel oxide could be resulting in the observed behaviour. In the case of carbon steel, the layer is magnetite,  $\text{Fe}_3\text{O}_4$ , and only the thickness of the layer changes as a function of the exposure time without any changes in the layer crystallography.

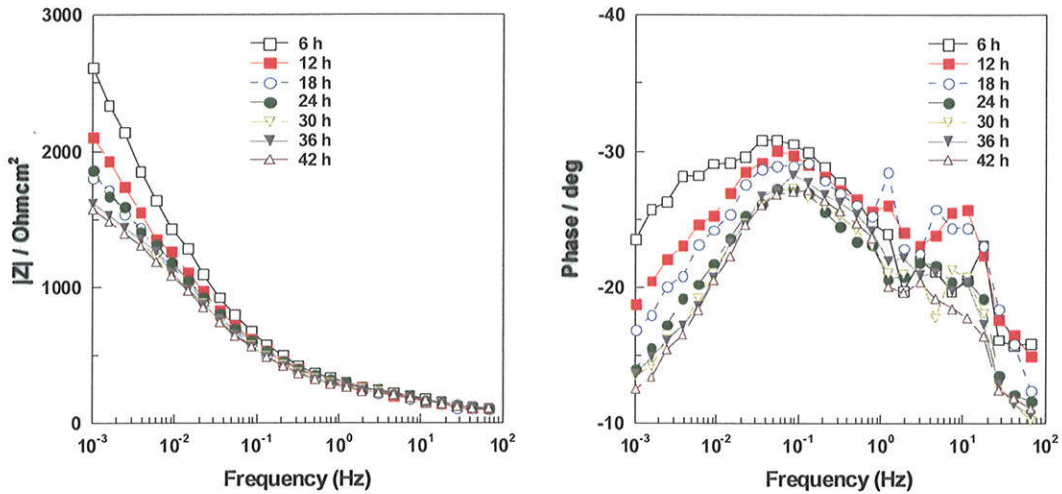


Figure 8. The effect of exposure time on stabilization of EIS. Impedance magnitude (left) and phase angle (right). Lithium concentration  $[\text{Li}] = 1$  ppm,  $[\text{B}] = 1200$  ppm,  $T = 292^\circ\text{C}$ .

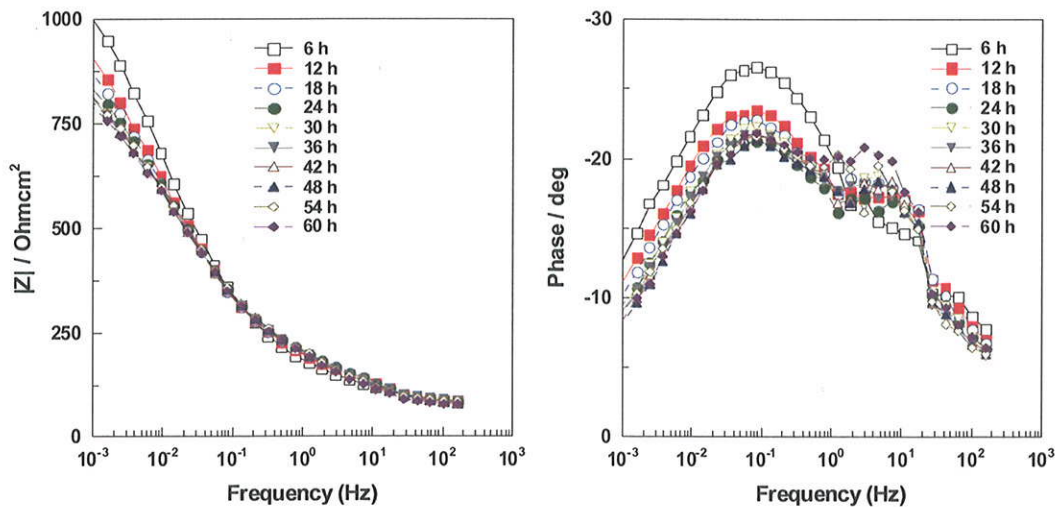


Figure 9. The effect of exposure time on stabilization of EIS. Impedance magnitude (left) and phase angle (right). Lithium concentration  $[\text{Li}] = 1.3$  ppm,  $T = 292^\circ\text{C}$ ,  $[\text{B}] = 0$  ppm.

## 4.2 Modelling the impedance response

Following the line of reasoning in /8/, the overall impedance of the Alloy 690 / oxide / coolant system can be written as being a sum of the resistance of the electrolyte,  $R_{el}$ , and the impedances of the barrier layer and the outer deposited layer,  $Z_b$  and  $Z_{out}$ , respectively,

$$Z = R_{el} + Z_b + Z_{out} \quad (2)$$

For the impedance of the outer layer, trials of different distributed functions demonstrated that the so-called Havriliak-Negami impedance /9/ gave the best fit to the experimental data

$$Z_{out} = \frac{R_{out}}{\left[1 + (j\omega R_{out} C_{out})^u\right]^n} \quad (3)$$

Here  $C_{out}$  and  $R_{out}$  are the capacitance of the outer layer and the apparent resistance of defect migration through that layer, whereas  $u$  and  $n$  are fractional exponents. The Havriliak-Negami response represents a generalisation of the Constant Phase Element (CPE) to account for asymmetric capacitive loops. The Havriliak-Negami element has been proposed originally for polymer dispersions and can be regarded according to the original authors as the impedance of a two phase mixture, which seems to be a good approximation for the outer layer of oxide.

The impedance of the barrier layer is given by the sum of the impedances characterising its electric properties and ionic transport through it in parallel

$$Z_b = \left(Z_e^{-1} + Z_{ion}^{-1}\right)^{-1} \quad (4)$$

The electronic contribution to the impedance,  $Z_e$ , is related to the spatial variation of the steady-state concentration of oxygen vacancies in the oxide, which creates a positive ionic space charge that requires electronic compensation to achieve electroneutrality. The following expression for  $Z_e$  has been derived earlier /9/

$$Z_e = \frac{RT}{2j\omega F \bar{E} \epsilon \epsilon_0} \ln \left[ \frac{1 + j\omega \rho_d \epsilon \epsilon_0 e^{\frac{RT}{2F\bar{E}L_b}}}{1 + j\omega \rho_d \epsilon \epsilon_0} \right] \quad (5)$$

Here  $\rho_d = \frac{RTk_1}{F^2 D_e k_2}$ ,  $\epsilon$  is the dielectric constant of  $\text{Fe}_2\text{CrO}_4$  spinel oxide, assumed to be equal to 25,  $\epsilon_0$  is the dielectric permittivity of free space,  $\omega$  is the angular frequency and  $D_e$  is the diffusion coefficient of the electronic current carriers.

On the other hand, the impedance due to the motion of oxygen vacancies,  $Z_{ion}$ , has been shown /9/ to be well approximated by



$$Z_{ion} = R_t + \frac{RT}{4F^2 k_1 \left[ 1 + \sqrt{1 + \frac{j\omega(RT)^2}{(F\bar{E})^2 D_o}} \right]} \quad (6)$$

The above described model for the transport of electronic and ionic charge carriers through the oxide film is known as the Mixed Conduction Model (MCM). The kinetic and transport parameters, namely, the rate constant of oxidation at the alloy/barrier layer interface,  $k_1$ , the diffusion coefficient of oxygen vacancies,  $D_o$ , the field strength in the barrier layer,  $\bar{E}$ , the charge transfer resistance at the alloy/oxide interface,  $R_t$ , the  $\rho_d \varepsilon$  parameter defined in eqn. (5), as well as the parameters characterizing the outer layer ( $C_{out}$  and  $R_{out}$ ) were estimated using non-linear least square fitting of the experimental spectra to the transfer function derived in the previous paragraph. Statistical weighting was used for the experimental data set and the errors of parameter estimation were multiplied by the square root of the reduced  $\chi^2$ -value resulting from the fit. In spite of the relatively large number of parameters, this resulted in a sufficient number of degrees of freedom in the system in order to obtain statistically reliable values of the kinetic parameters.

Table 1. Impedance model fitting results.

Param	Unit	1 ppm Li	2 ppm Li	1 ppm Li 1200 ppm B	1+1 ppm Li 1200 ppm B	2 ppm Li 1200 ppm B
C	$\mu\text{F cm}^{-2}$	53.8	81	36.5	36	22.5
p	-	0.07	0.0685	0.0736	0.0716	0.0713
$\rho_d \varepsilon$	$\Omega\text{cm}$	4.94E6	5.31E6	1.20E7	6.04E6	4.43E6
$R_t$	$\Omega\text{cm}^2$	76.7	216.9	1.1	27.0	25.0
$k_1$	$\text{mol cm}^{-2}\text{s}^{-1}$	7.57E-12	9.96E-12	2.12E-12	5.16E-12	3.96E-12
$R_{out}$	$\Omega\text{cm}^2$	4.7	13.9	50.3	35.6	127.3
$C_{out}$	$\text{F cm}^{-2}$	1.97E-4	7.4E-5	4.6E-4	1.42E-3	4.5E-4
$D_o$	$\text{cm}^2\text{s}^{-1}$	6.1E-17	5.9E-17	9.8E-18	2.9E-17	2.6E-17
field	$\text{V cm}^{-1}$	86294	99252	92758	88242	90869
thickness	nm	40.3	35.8	35.7	38.5	37.6

In the oxidation of Alloy 690, the possible rate limiting processes can be a) the rate of oxidation at the alloy/barrier layer interface (described by the parameter  $k_1$ ) or b) the transport of oxygen/oxygen vacancies through the existing film (described by the parameter  $D_o$ ). Dissolution of the oxide / hydrolysis of metal cations at the film/electrolyte interface are typically fast in comparison with the two preceding steps and are thus assumed not to be rate limiting.

As shown in Table 1, in the case of 1 ppm Li, the rate constant of oxidation at the alloy/barrier layer interface decreases by roughly a factor of 3.5 due to addition of 1200 ppm B. Simultaneously, the diffusion constant  $D_o$  decreases by roughly a factor of 6. In case of 2 ppm Li, the decrease in the same parameters due to



addition of 1200 ppm B is less, roughly 2.5 and 2.3, respectively. In the case of 2 ppm Li, as the effect on both parameters is almost the same, it is difficult to say which one of the processes is rate determining. However, in the case of 1 ppm Li the effect of B is about twice as strong on the diffusion rate, indicating that at least in this case the rate determining step of oxidation and corrosion is the diffusion of oxygen / oxygen vacancies through the barrier layer. The difference in the parameters for the solution containing only Li (i.e. between 1 and 2 ppm Li) is relatively small.

### 4.3 Conductivity data

The pressure vessel used for the tests was made of AISI316L, and had been cleaned of surface oxides with glass pebble blasting and further passivated for 72 hrs at 292°C in PWR water. The total exposure time of the pressure vessel to high temperature PWR water at the end of the experiments described in this report was not more than 1000 hrs. Thus, the thickness of the oxides on the pressure vessel surfaces was relatively small. During the experiments where only LiOH was added, the conductivity was found to decrease as a function of test duration. Fig. 10 shows an example of a test where, after cleaning the loop with ion exchangers until conductivity was  $\gamma < 0.2 \mu\text{Scm}^{-1}$ , first temperature was increased to  $T = 80^\circ\text{C}$ , then dissolved oxygen was removed by nitrogen bubbling, then 1.5 bar overpressure of hydrogen gas was added to the mixing tank and finally a target concentration of 1.0 mg/l (ppm)  $\text{Li}^+$  was added to the water volume as LiOH. The ion exchanger was accidentally left on for a short period right after the addition of the Li. This is seen as a rapid decrease of conductivity. A second addition of Li was made after shutting off the ion exchanger, resulting in a slight overshoot of the starting Li concentration. Already during the equilibration time at  $T = 80^\circ\text{C}$  before heating up some decrease of conductivity can be noticed, the rate of decrease increasing after heating up to  $T = 292^\circ\text{C}$ . The water grab sample at the end of the test showed 1.3 ppm Li.

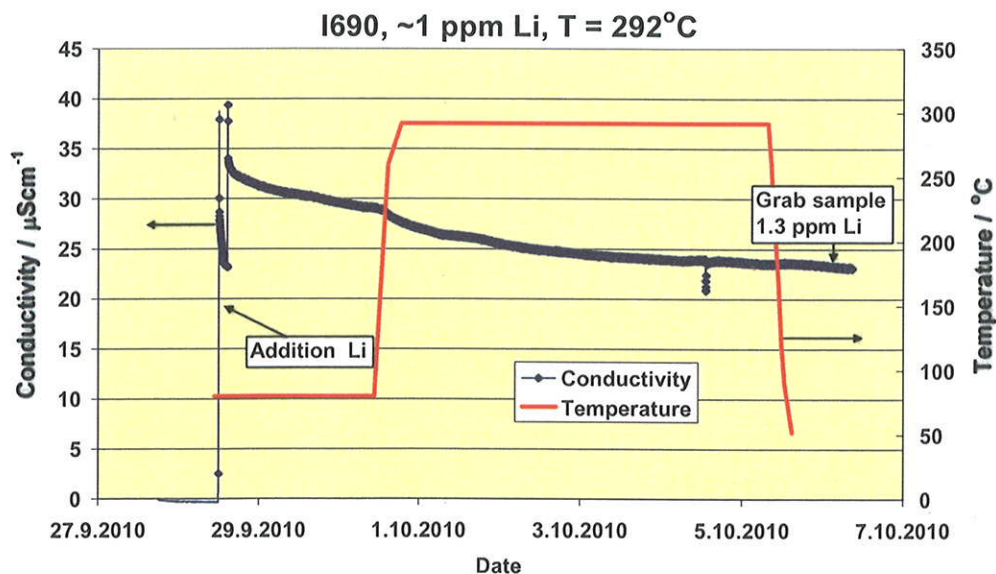


Figure 10. Conductivity (25°C) as a function of time in a test run where originally a target concentration of 1.0 ppm Li was added as LiOH.  $[\text{H}_2] = 30 \text{ ccH}_2/\text{kgH}_2\text{O}$  from the start.

Another example of the conductivity is shown in Fig. 11. In this test run, the target Li-concentration was 2.2 ppm. Similarly to Fig. 10 for water with about 1 ppm Li, the conductivity decreases rather steadily as a function of time. The water grab sample at the end of this test showed 2.2 ppm Li. A check was made on the stability of the conductivity sensors so that water with 2.2 ppm Li (no B) was circulated through them, without passing through the high temperature section of the experimental system. In a one week test no change in the sensor signal was noticed, indicating that the decrease of conductivity is solely due to adsorption of Li on the surfaces within the high temperature section of the system.

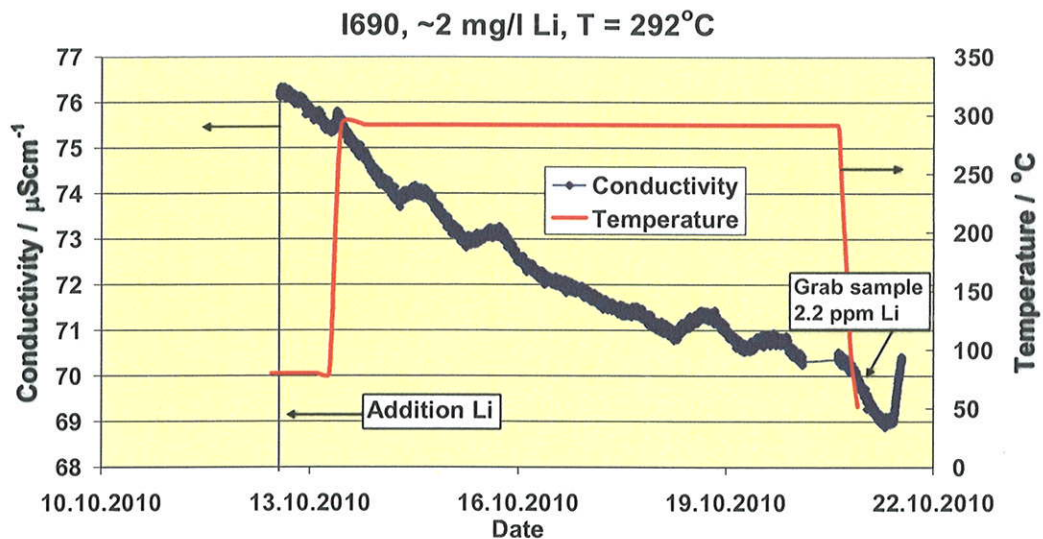


Figure 11. Conductivity ( $25^{\circ}\text{C}$ ) as a function of time in a test run where originally a target concentration of 2.2 ppm Li was added as LiOH.  $[\text{H}_2] = 30 \text{ ccH}_2/\text{kgH}_2\text{O}$  from the start.

## 5 Conclusions

Based on the in situ electrochemical impedance data gained so far it seems evident that the formation and stabilisation of the barrier layer part of the oxide forming on both carbon steel and Alloy 690 in lithiated high temperature water takes place during the first 40 hrs of the exposure. Taking into account that the typically proposed exposure time during Hot Conditioning period is between 300 and 1000 hrs, the passivation time is more than adequate.

At the exposure temperature of  $T = 292^{\circ}\text{C}$ , the impedance magnitude and thereby the rate of generation of soluble and insoluble corrosion products increases only slightly when lithium concentration increases from 1 to 2 ppm, in absence of boron. The introduction of 1200 ppm B into the coolant increases the impedance magnitude by roughly 100% in comparison with the case of 1 ppm Li concentration and slightly more in case of 2 ppm Li concentration. This indicates that addition of boron decreases dramatically the rate of generation of soluble and insoluble corrosion products for Alloy 690.



Through the modeling of the impedance spectra using the Mixed Conduction Model (MCM) approach, parameters relevant to the different processes involved in corrosion of Alloy 690 in simulated Hot Conditioning environment could be derived. The diffusion coefficient of oxygen through the barrier layer part of the oxide is of the order of  $D_{O_2} = 10^{-17} \text{ cm}^2\text{s}^{-1}$ . The diffusion coefficient decreases roughly by a factor of 6 when the boron concentration increases from 0 to 1200 ppm, and by a factor of about 2, for lithium concentrations of 1 and 2 ppm, respectively. Simultaneously the reaction rate constant for the oxidation of Alloy 690 at the alloy / oxide interface decreases by roughly a factor of 2.5. The analysis of the impedance spectra through the MCM thus corroborates the straightforward analysis given above in 4.1, indicating specifically that addition of boron into the coolant is highly beneficial and that increasing the lithium concentration is detrimental to the quality of the passive layer on Alloy 690.

There are three lines of further research in optimisation of the Hot Conditioning procedure that require attention. The first one is the lower range of Li concentration, i.e. in situ results need to be gained also for 0.5 ppm Li, in order to quantify the difference between the Japanese and Western approaches. Secondly, the effect of boron concentration should be studied in a more wide range, e.g. duplicating some of the current measurements at a level of 500 ppm B. Thirdly, the mechanism, extent and consequences of possible Li hideout during the passivation treatment should be studied in detail.

## 6 Summary

The primary circuit surfaces of a new pressurized water nuclear reactor are passivated before the first fuel loading. This treatment is called Hot Conditioning. The main purpose of the Hot Conditioning is to minimise the rate of generation of soluble and insoluble corrosion products (corrosion rate), and thereby minimize the activity build-up during power operation. There is still no international consensus on optimal passivation water chemistry. Open issues are e.g. the optimal concentration of lithium and the length of the passivation treatment. New issues are the possible benefits of using boron and zinc in the water during the passivation.

This report presents the first part of experimental results on Alloy 690 gained by the electrochemical impedance spectroscopy (EIS) in situ technique at  $T = 292^\circ\text{C}$ . These results indicate that addition of boron is highly beneficial, 1200 ppm B resulting in reduction of the estimated corrosion rate by a factor of about 2. An increase of the lithium concentration from 1 to 2 ppm Li was found to result in a higher estimated corrosion rate. The time to form a stable passive layer on Alloy 690 at  $T = 292^\circ\text{C}$  was found to be about 40 hrs. Thus, the time normally used for passivation, i.e. 300 – 1000 hrs, is certainly long enough. In experiments without boron, the conductivity was found to decrease during the experiment, indicating a possibility of lithium hide-out on the hot part of the test equipment surfaces.

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