THE EFFECT OF HYDRAZINE ON THE ELECTROCHEMICAL CORROSION POTENTIAL OF STEAM GENERATOR TUBING IN THE PRESENCE OF OXYGEN

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Abstract

The electrochemical corrosion potential (ECP) of steam generator (SG) tubing is governed by plant chemistry during operation. SG tubing is occasionally exposed to dissolved oxygen and CANDU stations rely on hydrazine to lower the feed water oxygen concentration. This lowers the ECP and protects tubing from localized corrosion known to occur under oxidizing conditions. In this examination, CANDU SG tubing materials, Alloys 800 and 600, were exposed to water containing dissolved oxygen and the resulting ECP shift measured. Subsequently, hydrazine additions were made. The ECP was monitored continuously and the effectiveness of different feed water hydrazine concentrations in restoring the ECP to its original value after initial displacement due to dissolved oxygen exposure was determined.

1. Introduction

Minimizing the degradation of steam generator (SG) components in CANDU systems is necessary to ensure the efficient operation of plants over their specified lifetime [1]. In recent years, there has been an incentive to optimize the hydrazine concentration employed during the layup of SGs in order to provide adequate corrosion protection while minimizing the environmental release. Both hydrazine and ammonia, a product of hydrazine decomposition, are reportable substances under Canada's National Pollutant Release Inventory (NPRI). In Ontario, where there are several CANDU units, the Ontario Ministry of the Environment is in the process of establishing a Provincial Water Quality Objective for hydrazine with significantly lower limits than are currently in place. As such, studies focused on hydrazine optimization and, ultimately, lowering concentrations used during layup and startup of SGs are ongoing.

Alloys such as 800 and 600 are passive materials used for SG tubing in some CANDU reactors and rely on the stability of oxide surface films to impart protection. The susceptibility of these materials to different forms of corrosion is influenced by the compositional and electrochemical properties of these surface films, which are, in turn, dependent on the operating water chemistry. Water chemistry is the primary control parameter used for minimizing the impact of various corrosion phenomena in CANDU plants.

One of the most common indexes of corrosive conditions is the electrochemical corrosion potential (ECP). The ECP is a mixed potential parameter which results from a kinetic balance between the sum of all anodic reactions and the sum of all cathodic reactions. Several studies have indicated that intergranular attack and stress corrosion cracking of BWR and PWR reactor materials, such as 304 stainless steel, can be prevented by ensuring the ECP of the steel is maintained below a certain critical value [2, 3]. It follows that the susceptibility of Ni-based passive alloys such as 800 and 600 may also be predicted by ECP monitoring and control. Recommended ECP/pH zones have been defined for Alloy 800 [4, 5] and Alloy 600 [6] under conditions relevant to CANDU SGs.

It is known that dissolved oxygen will ennoble the ECP of passive materials, such as Ni-based alloys, to more positive values and that high potentials can have implications regarding the susceptibility to localized corrosion [7, 8]. In real applications, various types of localized corrosion such as IGA or pitting are often initiated when the potential is shifted in a positive direction. Plants have little control over dissolved oxygen concentration during reactor startup and operation and rely on the addition of hydrazine, an aggressive oxygen scavenger, in the steam cycle to minimize the dissolved oxygen concentration and to maintain reducing conditions.

The objective of the present study is to, first; determine the positive ECP shift experienced by Alloys 800 and 600 at various dissolved oxygen concentrations, and second; evaluate the effectiveness of hydrazine at restoring the ECP and reversing the effects of oxygen exposure to the sample.

2. Experimental Details

2.1 Test Materials

Tests were performed on Alloy 800 (UNS N08800) and Alloy 600 (UNS N06600) to represent SG tubing materials found at Darlington and Bruce nuclear generating stations, respectively. Sample compositions are listed in Table 1.

Table 1: Chemical Composition of Alloys

Alloy	Element (weight %)									
	C	Mn	Fe	S	Si	Cu	Ni	Cr	Al	Ti
UNS N08800	0.08	0.82	46.99	0.001	0.14	0.19	30.78	19.90	0.58	0.52
UNS N06600	0.069	0.36	6.88	0.001	0.36	0.03	76.96	14.63	-	-

2.2 Test Assembly and Specimen Design

The experimental assembly was an autoclave format with the specimen holder designed to rotate within the autoclave to incorporate hydrodynamic functionality at high temperature and pressure. The stainless steel autoclave was pressurized to the expected saturation pressure and experiments were carried out at 100 and 200°C, representative of SG temperatures at startup and full power operation, respectively. A rotating cylinder electrode (RCE) design was employed for alloy test specimens and was accommodated within the autoclave. A RCE design allowed for strict control of hydrodynamic conditions at the electrode surface, simulating low flow conditions. Tests were conducted at a constant rotation rate of 500 rpm. The merits of using this geometry have been demonstrated previously [9].

2.3 Water Chemistry and Control

Solution from a 300 L feed tank was circulated through the autoclave. The feed tank was equipped for chemistry adjustments in the form of direct hydrazine addition or N_2/O_2 purging. Orbisphere sensors were installed at the feed tank and the return line from the autoclave to monitor the dissolved oxygen concentration in solution before and after introduction to the autoclave. A stock hydrazine solution was added to the feed tank. The feed tank solution was sampled and hydrazine concentrations were determined by UV/Vis spectroscopy. Hydrazine content was monitored, and actively controlled, on a daily basis to maintain the desired feed tank concentration. Oxygen and hydrazine concentrations were also measured at the return line from the autoclave. In this study, oxygen concentrations defined as “low” were those measured from the return line and less than 100 ppb. Oxygen concentrations referred to as “moderate” were near 500 ppb and those referred to as “high” were ~2 ppm or greater.

2.4 Electrochemical Measurements and Procedure

The ECP of alloy samples was monitored using a Solartron SI 1286 potentiostat. Potential measurements were made between a working electrode (Alloy sample, RCE) and a Ag/AgCl reference electrode. The reference electrode was designed for use in boiling water reactors and is a pressure balanced external reference that operates at temperatures as high as 290^{o}C and pressures as high as 1150 psig. To facilitate data comparison, all potential values reported have been converted to the standard hydrogen electrode (SHE) scale at 25^{o}C.

The ECP of alloy 800 and 600 RCE electrodes were monitored as various concentrations of dissolved oxygen were introduced. At each dissolved oxygen concentration, the ECP was allowed to reach a steady-state, at which point hydrazine additions were made. The test matrix was designed in such a way as to examine the effect of various concentrations of hydrazine on the alloy ECP in the presence of low, moderate, and high concentrations of oxygen. Tests were performed in series on each alloy sample at 100 and 200^{o}C.

3. Results and Discussion

3.1 Alloy 800

3.1.1 The Effect of Oxygen Concentration on ECP

ECP values for Alloy 800 at 100 and 200^{o}C were recorded as a function of oxygen concentration and are shown in Figure 1. The ECP increases initially in the noble direction but approaches a steady-state value of ~150 mV (at 100^{o}C) and ~75 mV (at 200^{o}C) as the oxygen concentration exceeds 1 ppm. As the oxygen concentration is increased, the equilibrium potential for the cathodic reaction (oxygen reduction) is displaced in a positive direction. This further polarizes the anodic reaction (metal oxidation) and yields a positive ECP shift. To compensate for the increase in potential at the alloy surface, a thickening of the passive film likely occurs [10]. This process continues until the film is sufficiently thick and compositionally stable, and the charge transfer rates at the surface are significantly limited by the resistance of the film [10-12]. When this occurs, the ECP becomes independent of oxygen concentration. Values in Figure 1 that designated steady-state were recorded after at least 24 hours of exposure to a constant oxygen concentration. Superimposed on those, are ECP values at 100°C that resulted from short term fluctuations in oxygen concentration. These short term values agree with the steady-state trend very well, suggesting that the system responds rapidly to short term changes in oxygen concentration and adopts a value near steady-state in a matter of hours. ECP values in the plateau region, when independent of oxygen concentration, are approximately 75 mV more active at 200°C than those measured at 100°C.

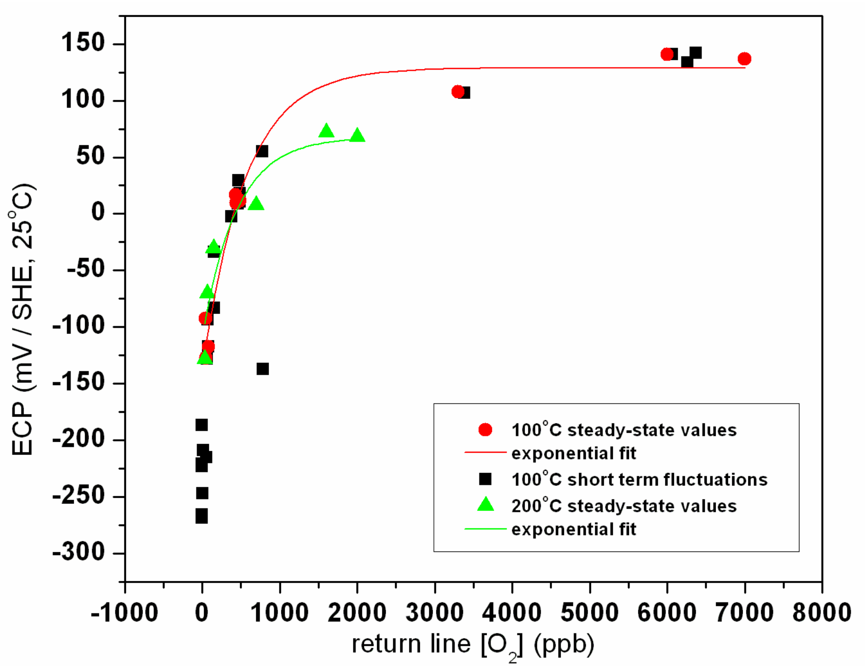

Figure 1: ECP values recorded on Alloy 800 at 100 and 200°C as a function of oxygen concentration. Exponential fits to the steady-state data are included.

3.1.2 The Effect of Hydrazine on the ECP

Once a steady-state ECP value was obtained in the presence of a low, moderate, or high oxygen concentration, hydrazine additions were made to the feed tank. A test matrix involving the combination of various hydrazine additions with low, moderate, and high oxygen levels was carried out. An example of the ECP response of Alloy 800 at 100°C when first exposed to a high concentration of oxygen (3.3 ppm) and, subsequently, a hydrazine feed water concentration of 42 ppm, is shown in Figure 2. The ECP increased slowly at first but rapidly once oxygen began to reach ppm levels. A steady-state ECP of ~ 125 mV was maintained for 300 hrs prior to hydrazine addition. Upon introduction of hydrazine, the return line oxygen concentration (a value representative of the autoclave environment) decreased rapidly to a negligible level and a corresponding sharp decrease in the ECP was observed.

An example of the ECP response of Alloy 800 at 200°C, when first exposed to a high concentration of oxygen (1.8 ppm), and then a feed water hydrazine concentration of 35 ppm, is shown in Figure 3. The ECP response to the increase in oxygen concentration was very rapid and began to level off at approximately 75 mV. Upon exposure to 35 ppm hydrazine from the feed tank, the oxygen in the autoclave dropped rapidly to a level below detection. A rapid exponential decay of the ECP to a value lower than that measured prior to oxygen addition was observed.

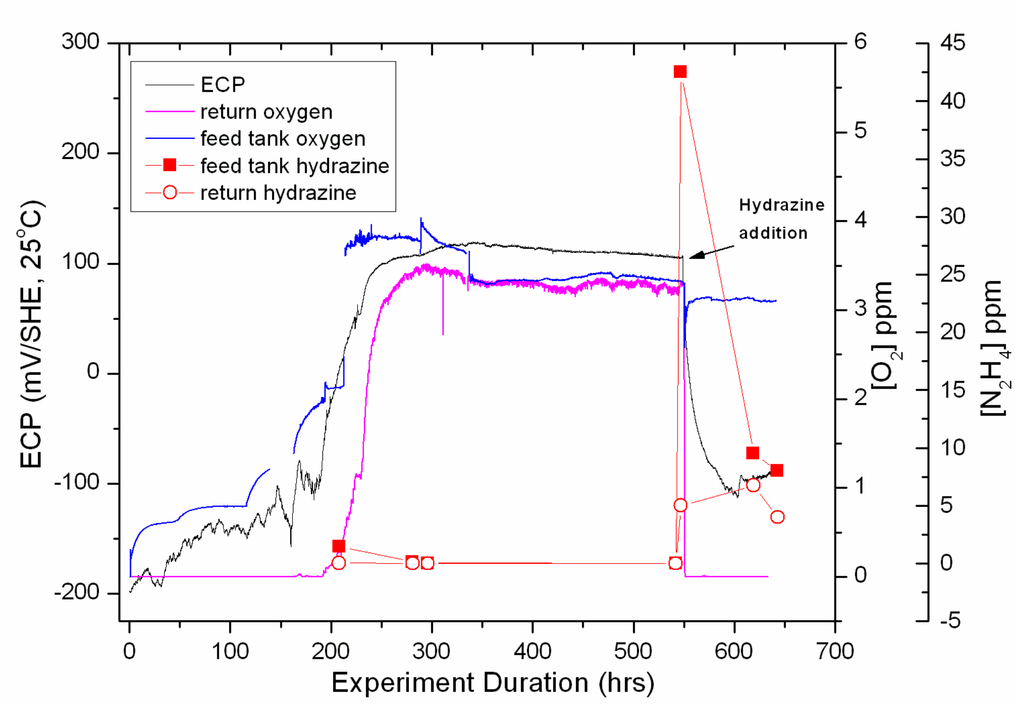

Figure 2: ECP response of Alloy 800 at 100°C during a test in which a feed water hydrazine content of 42 ppm was introduced after exposure to 3.3 ppm of dissolved oxygen.

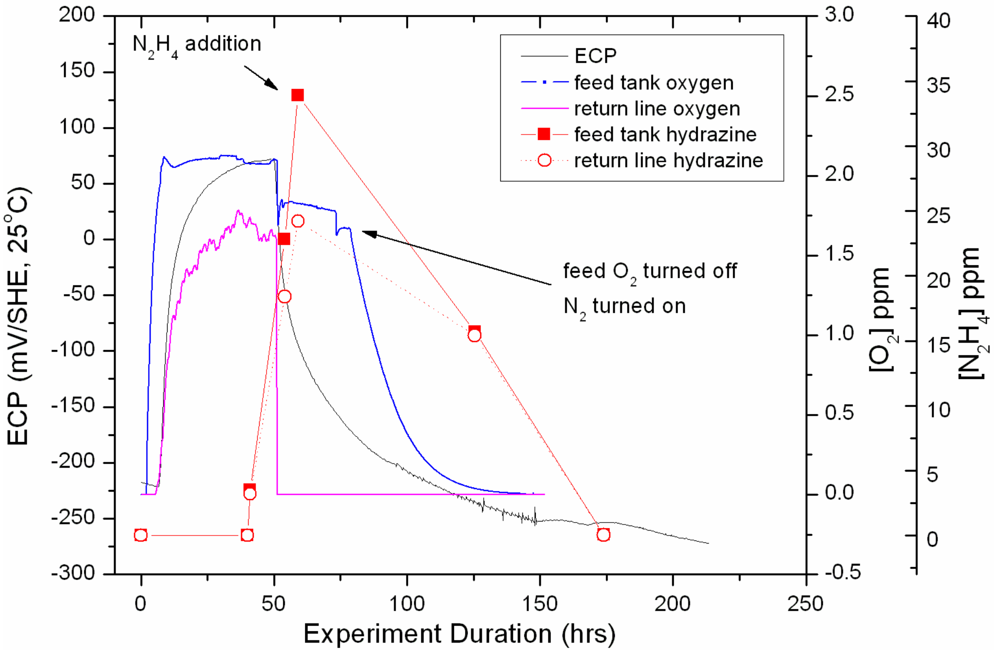

Figure 3: ECP response of Alloy 800 at 200°C during a test in which a feed water hydrazine content of 35 ppm was introduced after exposure to 1.8 ppm of dissolved oxygen.

Of particular interest is the ability of hydrazine to restore the ECP to its initial value prior to the introduction of oxygen. Figure 4 illustrates the effectiveness of hydrazine at countering the influence of oxygen on the ECP of Alloy 800 for a series of tests performed at 100°C. Since the required concentration of hydrazine is a function of the amount of oxygen to be scavenged, data is presented in terms of hydrazine:oxygen concentration ratios produced by the test matrix. The values used to calculate these ratios were the concentration of hydrazine measured in the feed tank (i.e., feed water) and the concentration of dissolved oxygen in the autoclave (as measured at the return line). In Figure 4, ECP_{final} is the value recorded after the addition of hydrazine (e.g., Figure 2, t > 600 hrs) and $ECP_{initial}$ is the value recorded prior to the addition of oxygen in that particular test (e.g., Figure 2, t = 25 hrs). If hydrazine is completely successful at negating the effects of oxygen, a value of zero (or less) in Figure 4 would be expected. A hydrazine to oxygen ratio of approximately 13 is required to reduce the ECP to acceptable levels regardless of oxygen concentration. However, one data point (for the low level oxygen concentration) obtained at a ratio of 3 was successful at restoring the ECP. This suggests that lower ratios (i.e., less hydrazine) may also be sufficient.

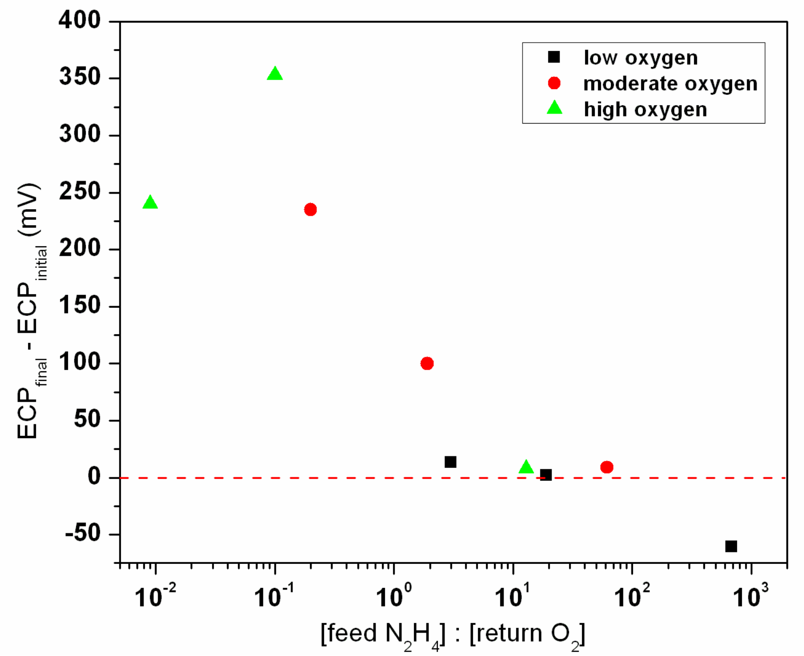

Figure 4: The difference in ECP measured on Alloy 800 at 100°C prior to the addition of oxygen ($E_{initial}$) and after the addition of hydrazine (E_{final}) as a function of the hydrazine to oxygen ratio for low, moderate, and high oxygen concentrations.

The ECP difference, prior to, and after each oxygen/hydrazine cycle of the test matrix is plotted as a function of hydrazine to oxygen ratio for Alloy 800 at 200°C in Figure 5. The data suggests that the hydrazine to oxygen ratio that must be employed to restore the ECP to its value prior to oxygen exposure is 16 or greater. It is interesting to note that, in this case, the required hydrazine to oxygen ratio appears independent of the level of oxygen when it was previously observed that a smaller ratio was sufficient for low levels of oxygen.

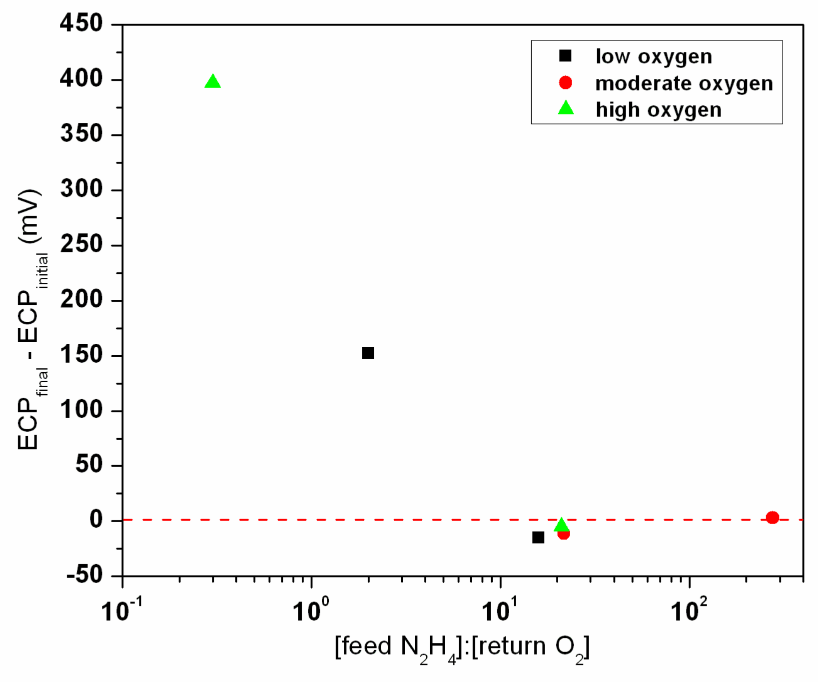

Figure 5: The difference in ECP measured on Alloy 800 at 200°C prior to the addition of oxygen ($E_{initial}$) and after the addition of hydrazine (E_{final}) as a function of the hydrazine to oxygen ratio for low, moderate, and high oxygen concentrations.

3.2 Alloy 600

3.2.1 The Effect of Oxygen Concentration on ECP

ECP values for Alloy 600 at 100 and 200°C recorded as a function of oxygen concentration are presented in Figure 6. Under de-aerated conditions, the ECP of Alloy 600 at 100°C varied by approximately 70 mV, which is possibly a reflection of changes to the passive film that occurred during prior tests. As observed on Alloy 800, the ECP of Alloy 600 increased initially in the noble direction but approached a steady-state, independent of oxygen concentration, at concentrations of ~1 ppm or greater. Although the composition of Alloy 600 is different than that of Alloy 800, the material is also passive and is expected to behave similarly with respect to certain aspects of corrosion. The cathodic reaction is attenuated by the local supply of oxygen when concentrations are relatively small and this is reflected by a positive ECP shift with increasing oxygen concentration. At low oxygen concentrations, Alloy 600 was particularly sensitive to changes in oxygen content and the ECP varied significantly. However, in the presence of increasingly higher oxygen concentrations, a thicker, stable oxide film was likely established [10] allowing the ECP to become independent of oxygen concentration as the rate of film formation and/or compositional adjustments slowed to negligible levels. In general, ECP values recorded at 200°C are approximately 100 mV more active than those measured at 100°C.

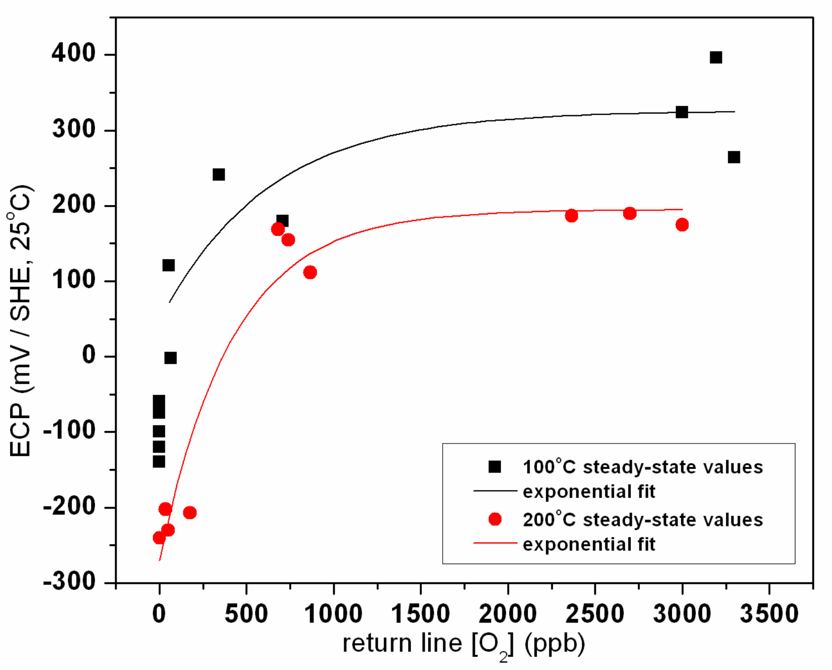

Figure 6: ECP values recorded on Alloy 600 at 100 and 200°C as a function of oxygen concentration. Exponential fits to the data are included.

3.2.2 The Effect of Hydrazine on the ECP

Once steady-state ECP values were obtained in the presence of low, moderate, and high levels of oxygen, a test matrix similar to that employed on the previous alloy was examined. An example of the ECP response of Alloy 600 at 100°C, in the presence of a low concentration of oxygen (70 ppb), when feed water containing 1800 ppb hydrazine was introduced to the autoclave, is shown in Figure 7. Over the initial 50 hours, the oxygen level in the autoclave was maintained at ~70 ppb. The ECP over this time showed a steady increase and could be a result of the small but steady increase in oxygen level. This observation further highlights the sensitivity of Alloy 600 to small changes in oxygen concentrations below 100 ppb and inspection of Figure 6 suggests that an ECP shift of 60 mV induced by an oxygen change of 30 ppb, as observed in Figure 7, is not unreasonable. At ~50 hours, the first hydrazine addition was made. Although this addition was sufficient to reduce the autoclave oxygen content to a value below detection, two subsequent additions were made to achieve the hydrazine to oxygen ratio specified by the matrix for this particular test. As the concentration of dissolved oxygen in the autoclave dropped to a negligible level, the ECP showed a slower, exponential decrease and eventually attained a value negative to that recorded at the beginning of the test. The reason for the relatively noble ECP value measured at t = 0 is not immediately apparent; however, it is possibly associated with the large variability observed at extremely small oxygen concentrations (as demonstrated by the initial 4 data points in Figure 6). At 72 hours into the test, a N_2 purge was introduced to lower the feed tank oxygen level. When the oxygen supply to the feed tank was turned back on, no change in the oxygen concentration within the autoclave was detected and no change in the ECP profile was observed. This indicates that the excess of hydrazine present in the autoclave was sufficient to maintain an oxygen free environment within the autoclave despite a possible ingress of dissolved oxygen from the feed water.

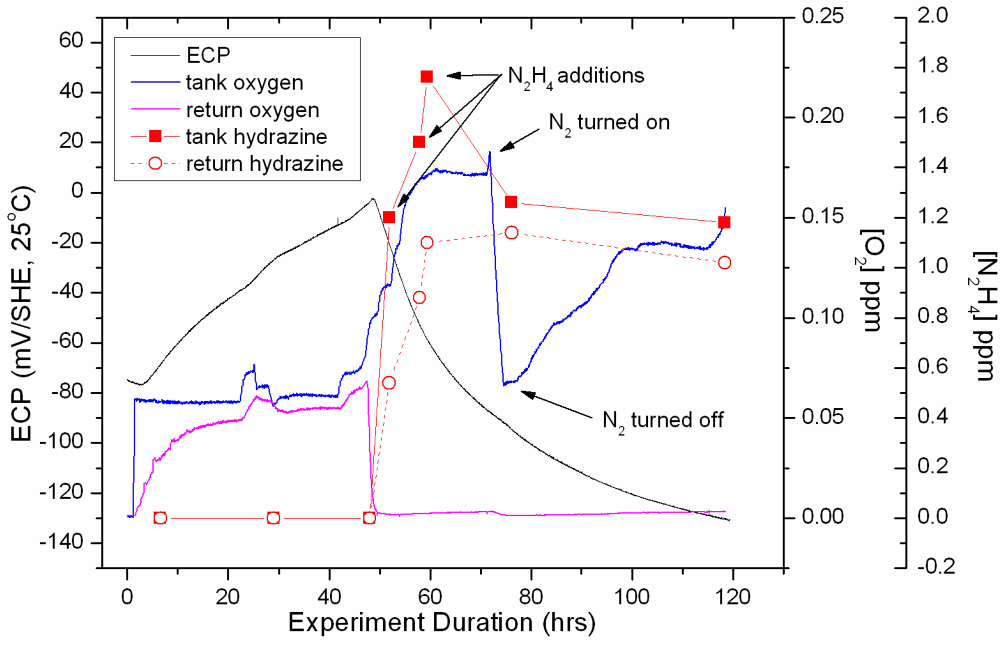

Figure 7: ECP response of Alloy 600 at 100°C during a test in which a feed water hydrazine concentration of 1.8 ppm was introduced after exposure to 70 ppb of dissolved oxygen.

An example of the ECP response of Alloy 600 at 200°C in the presence of a large concentration of oxygen (3 ppm) when 38 ppm of hydrazine was introduced to the system is shown in Figure 8.

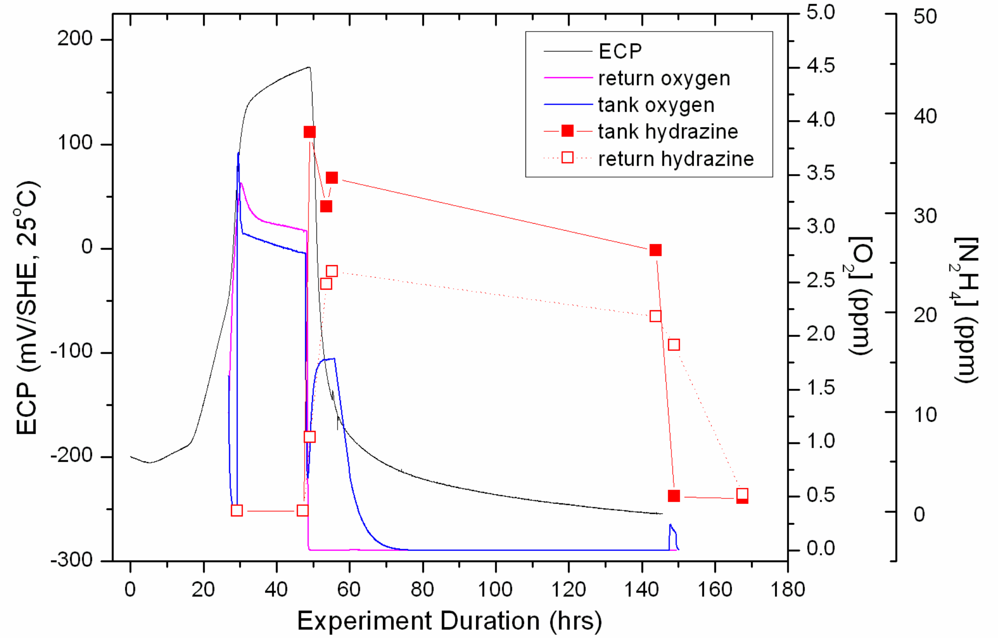

Figure 8: ECP response of Alloy 600 at 200°C during a test in which a feed water hydrazine concentration of 38 ppm was introduced after exposure to 3 ppm dissolved oxygen.

As the autoclave oxygen concentration was adjusted to the desired level (~3 ppm, t = 40 hrs), the ECP experienced a significant noble shift, ultimately approaching a steady-state of ~175 mV. Upon hydrazine addition, the autoclave oxygen level decreased immediately to a value below detection. Correspondingly, a very rapid exponential decay of the ECP was observed to a value more negative than that initially measured prior to oxygen addition.

The ECP difference, prior to, and after each oxygen/hydrazine cycle is plotted as a function of hydrazine to oxygen ratio for Alloy 600 at 100°C and is presented in Figure 9. The results suggest that the hydrazine to oxygen ratio that must be employed to restore the ECP to its value prior to oxygen exposure is 16 or greater, regardless of the level of oxygen which was initially present.

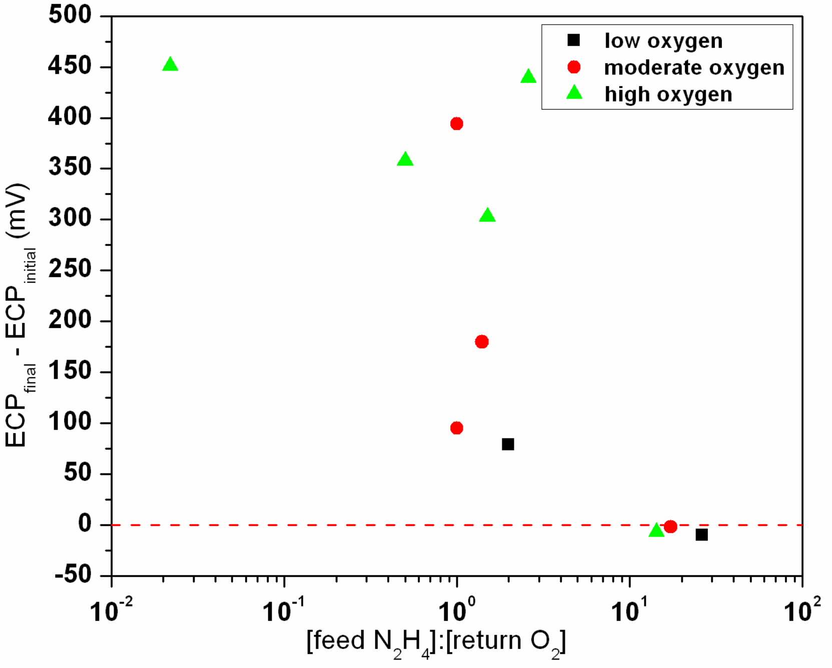

Figure 9: The difference in ECP measured on Alloy 600 at 100°C prior to the addition of oxygen ($E_{initial}$) and after the addition of hydrazine (E_{final}) as a function of the hydrazine to oxygen ratio for low, moderate, and high oxygen concentrations.

An identical plot was made for Alloy 600 at 200°C and is shown in Figure 10. Inspection of Figure 10 shows that, in this case, the hydrazine to oxygen ratio that must be employed to counter the effects of oxygen on the ECP is dependent on the level of oxygen initially present. It may not be necessary in all cases to completely restore the ECP, and further corrosion may be inhibited by reducing the ECP to sufficiently negative values. The dashed blue box encircles a range of values which are likely sufficiently negative. It is suggested that a hydrazine to oxygen ratio of 10 or more is acceptable, regardless of oxygen concentration.

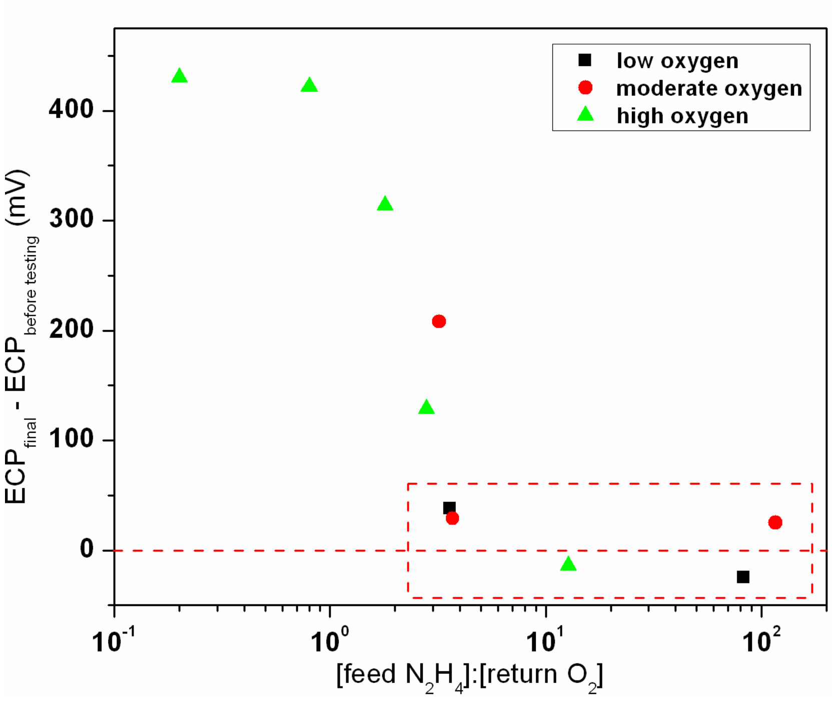

Figure 10: The difference in ECP measured on Alloy 600 at 200°C before the addition of oxygen ($E_{initial}$) and after the addition of hydrazine (E_{final}) as a function of the hydrazine to oxygen ratio for low, moderate, and high oxygen concentrations.

4. Conclusions

The ECP of Alloys 600 and 800 shifts in a noble direction as the concentration of oxygen is increased. The ECP of both alloys was sensitive to changes in dissolved oxygen concentration when present at low levels (<100 ppb) and changes in oxygen content as small as 30 ppb were observed to shift the ECP by 50-100 mV in the noble direction.

For both alloys, when sufficient hydrazine was added, the autoclave oxygen concentration decreased very rapidly to levels below detection. A corresponding exponential decrease in the ECP to final steady-state values equal to, or more negative than, the original ECP measured prior to oxygen addition was observed.

The effectiveness of hydrazine at countering the effects of oxygen on the ECP was most simply viewed by analysis of feed water hydrazine to dissolved oxygen ratios required to restore the ECP to values measured prior to oxygen exposure for each particular test. In some tests, the necessary ratio was a function of the amount of oxygen present. However, it is more practical to specify a single value for each alloy at temperatures representative of startup and full power operation of steam generators. The hydrazine to oxygen ratios that were successful in negating the effects of oxygen on the ECP were 13 (at 100°C) and 16 (at 200°C) for Alloy 800 and 16 (at 100°C) and 10 (at 200°C) for Alloy 600. These are very conservative values since they assume that large concentrations of oxygen exist within the steam generator. A few data points suggest that lower hydrazine:oxygen ratios (between 5 and 10) may be sufficient for restoring the ECP.

This range should be investigated in more detail to determine if lower feed water hydrazine concentrations would be acceptable for ECP control, especially given the desire for limiting the use of agents that are hazardous to the environment.

5. Acknowledgements

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