

Enclosure 2 to SBK-L-11062

Chemistry Control in the Seabrook Thermal Barrier Loop

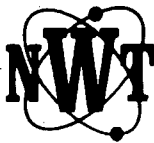
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**Chemistry Control in the Seabrook Thermal
Barrier Loop**

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CONTENTS

Section 1 - Introduction	1-1
Section 2 - Chemistry Guidelines	2-1
2.1 EPRI Closed Cooling Water System Chemistry Guidelines	2-1
2.2 Control Parameter Chemistry	2-1
2.2.1 Hydrazine.....	2-1
2.2.2 pH.....	2-6
2.2.3 Chloride and Fluoride	2-9
2.2.4 Sulfate	2-11
2.2.5 Oxygen.....	2-14
2.3 Diagnostic Parameters	2-16
2.3.1 Iron and Copper	2-16
Section 3 - Impact of Hydrazine/Oxygen Ratio on ECP of Stainless Steel.....	3-1
Section 4 - TB System General Corrosion.....	4-1
Section 5 - Conclusions	5-1
References.....	R-1

Section 1 INTRODUCTION

The Seabrook thermal barrier system (TB) provides cooling to the reactor coolant pump shafts during normal operation. It is a closed loop system. A head tank which is vented to atmosphere provides suction to two parallel pumps which feed two stainless steel tubed heat exchangers which are in series. Associated piping and heater shells are carbon steel. There are no copper alloys in the system. The heat sink for the system is the Primary Component Cooling Water System (CC) which is also a closed loop system. The TB system normal operating temperature is approximately 86°F.

Chemistry control in the TB system has been established to minimize corrosion of ferrous alloys and is based on minimizing the concentrations of contaminants known to accelerate corrosion of such alloys at high concentrations and minimization of oxygen concentrations by addition of hydrazine. The presence of hydrazine and ammonia, a decomposition product of hydrazine, elevate the pH thereby reducing general corrosion of ferrous alloys. This type of chemistry control is employed at several other nuclear stations in closed cooling water systems and in PWR steam generators during wet layup on the secondary side.

Industry Guidelines on closed cooling water (CCW) system chemistry control, which were initially published by EPRI in 1997 [2], provided only limited specific guidance on establishing chemistry limits on oxygen and impurities in these systems. However, it was recognized that minimization of chloride and fluoride concentrations was advisable. Recommendations for sulfate control were not provided in the 1997 Guidelines. Note that the Westinghouse Standard Information Package (SIP) for chemistry control in closed cooling water systems only recommended monitoring for chlorides and fluorides when it was first issued in 1974, and the 1985 version of the SIP retained this position

[1]. In 2004, the EPRI CCW Chemistry Guidelines were revised [3], and detailed chemistry control recommendations for a variety of chemistry control approaches were provided. In Table 5-5 of the 2004 Guidelines, operating ranges and monitoring frequencies for hydrazine-based control programs were established. Minimization of oxygen, chloride, fluoride and sulfate concentrations was recommended, and specific Action Levels were established when concentrations exceeded recommended values.

In general, chemistry control in the TB system at Seabrook has been consistent with the Guideline recommendations for hydrazine based programs. However, sulfate concentrations have exceeded the currently recommended Action Level 1 value of 150 ppb but have not exceeded the Action Level 2 value of 1000 ppb [4]. Concentrations were generally in the range of 200 to 450 ppb from 1999 through 2009. The sulfate concentration was reduced in 2010 by feed and bleed to ~100 ppb where it has remained. Hydrazine also exceeded the EPRI normal operating range maximum of 200 ppm (for all ferrous systems) for several months in 2004 [4]. Note that no upper limit Action Level is established in the Guidelines for hydrazine. Only lower limit values are established [3].

In RAI B.2.1.12-1, the NRC staff requested information on the effect of elevated levels of hydrazine and sulfate in the TB system on corrosion and component degradation in the system [4]. The initial response to the NRC stated that "routine monitoring during operation at the elevated ranges showed no indication of system or component degradation". However, the NRC has indicated that Seabrook did not provide details of its evaluation that determined that operation at the elevated levels of hydrazine and sulfate would not cause any accelerated aging that could affect components during the period of extended operation and did not describe the routine monitoring it had performed during operation at the elevated ranges that could be credited for showing that no system or component degradation had occurred.

To respond to the issues raised by the NRC relative to chemistry control in the TB system and its effect on corrosion of system materials, the basis for the EPRI Guidelines for hydrazine and sulfate were reviewed, and the probable impact of operating above the sulfate Action Level 1 value for several years and above the hydrazine normal operating range upper value for ~ 5 months was assessed.

Section 2

CHEMISTRY GUIDELINES

2.1 EPRI Closed Cooling Water System Chemistry Guidelines

Revision 1 of the closed cooling water system EPRI Guidelines [3], which were published in 2004, provides detailed recommendations for control of chemistry for corrosion minimization for a variety of chemistry control approaches. Recommendations for hydrazine based systems are shown in Table 2-1. This type of control approach is used for the Seabrook TB system.

As shown, Control Parameters are the hydrazine, chloride, fluoride, sulfate and dissolved oxygen concentrations and pH. Control Parameters are known to have a significant effect on corrosion. Thus, Action Level values are established for each of these parameters. The Diagnostic Parameters include cation conductivity, ammonia, iron and copper concentrations and radioactivity. Diagnostic parameters provide additional information that may be of value in monitoring system chemistry and developing corrective actions if necessary. Note that corrosion coupon installation for monitoring general corrosion of carbon and stainless steel or stress corrosion cracking (SCC) of stainless steel is not addressed in Table 2-1.

2.2 Control Parameter Chemistry

2.2.1 Hydrazine

Addition of hydrazine to CCW systems has the goal of reducing and maintaining oxygen concentrations at low values to reduce the electrochemical potential (ECP) of carbon and particularly stainless steels. Hydrazine also leads to an elevation of pH (See Section 2.2.2).

Table 2-1

Operating Ranges and Monitoring Frequencies for Hydrazine-Based Programs [3]

Parameter	Normal Operating Range	Action Levels (AL 1 – 90 days AL 2 – 30 days)	Monitoring Frequency		
			Tier 1 Systems (1)	Tier 2 Systems	Intermittent Systems
Control Parameters					
Hydrazine, mixed metallurgy	5–50 ppm as N ₂ H ₄	AL 1: <5 ppm AL 2: <1 ppm	Weekly	Monthly	Monthly or as operated
Hydrazine, all-ferrous metallurgy	5–200 ppm as N ₂ H ₄	AL 1: <5 ppm AL 2: <1 ppm	Weekly	Monthly	Monthly or as operated
pH, mixed metallurgy	8.5–9.6	AL 2: <8.0 or >10.0	Weekly	Monthly	Monthly or as operated
pH, all-ferrous metallurgy	8.5–10.5	AL 2: <8.0 or >10.5	Weekly	Monthly	Monthly or as operated
Chloride, Fluoride, Sulfate (2)	≤150 ppb as ion (each)	AL 1: >150 ppb AL 2: >1000 ppb	Monthly	Monthly	Monthly or as operated
Dissolved Oxygen	≤100 ppb	AL 1: >100 ppb AL 2: >1000 ppb	Monthly	Monthly	Monthly or as operated
Diagnostic Parameters					
Cation conductivity (3)	Evaluate trend		Weekly	Monthly	Monthly or as operated
Ammonia	Evaluate trend		Monthly	Monthly	Monthly or as operated
Iron and Copper	Evaluate trend		Monthly	Monthly	Monthly or as operated
Radioactivity (4)	Evaluate trend		Quarterly	Quarterly	Quarterly or as operated
(1) The weekly frequency for Tier 1 parameters can be reduced to once per two weeks if steady-state chemical control has been maintained (all control parameters are maintained within the normal operating range) for at least one quarter.					
(2) Weekly cation conductivity can be substituted for Cl, F, and SO ₄ if organic anions are not present. If cation conductivity is <1 μS/cm, Cl, F, and SO ₄ are considered to be within specification.					
(3) See section 7.2.5 for specific effects of some contaminants on cation conductivity.					
(4) Applicable to those systems with the potential to become contaminated.					

At low ECP, the tendency for stress corrosion cracking of stainless steels is greatly reduced. In addition, general corrosion rates of carbon steel and stainless steel are reduced at elevated pH, and the tendency for pitting attack of stainless steel in chloride bearing solutions is reduced.

Variations in the TB system hydrazine concentrations and pH from 1999 through early 2010 are shown in Figure 2-1. Hydrazine exceeded the EPRI normal CCW operating range maximum of 200 ppm (for all ferrous systems) for several months in 2004 [4]. However, it should be noted that no upper limit Action Level is established in the Guidelines for hydrazine [3]. Only lower limit values are established based on the desire

to minimize oxygen concentrations to minimize rates of general corrosion and pitting and reduce the tendency for SCC of stainless steels. No negative effect of operating above the 200 ppm normal operating range limit is expected even at concentrations as high as 500 ppm since there are no copper alloys in the system. Note that Revisions 5 and 6 of the PWR Secondary Water Chemistry Guidelines [5, 6] listed normal wet layup values of > 75 ppm hydrazine for recirculating steam generators (e.g., Table 2-2) and 75 to 500 ppm (Table 2-3) for OTSGs at temperatures <200°F (e.g., Table 2-3). Revision 7 of the Guidelines [7] specifies a minimum level of 25 ppm or 3 times the oxygen concentration in both types of systems (e.g., Table 2-4), but no upper limit was specified since a justification for an upper limit could not be developed. The ratio approach was adopted in Revision 7 based on Reference 8, which clearly showed that the ECP of carbon steel, stainless steel, Alloy 600 and Alloy 690 could be minimized at ratios above three even at elevated oxygen concentrations.

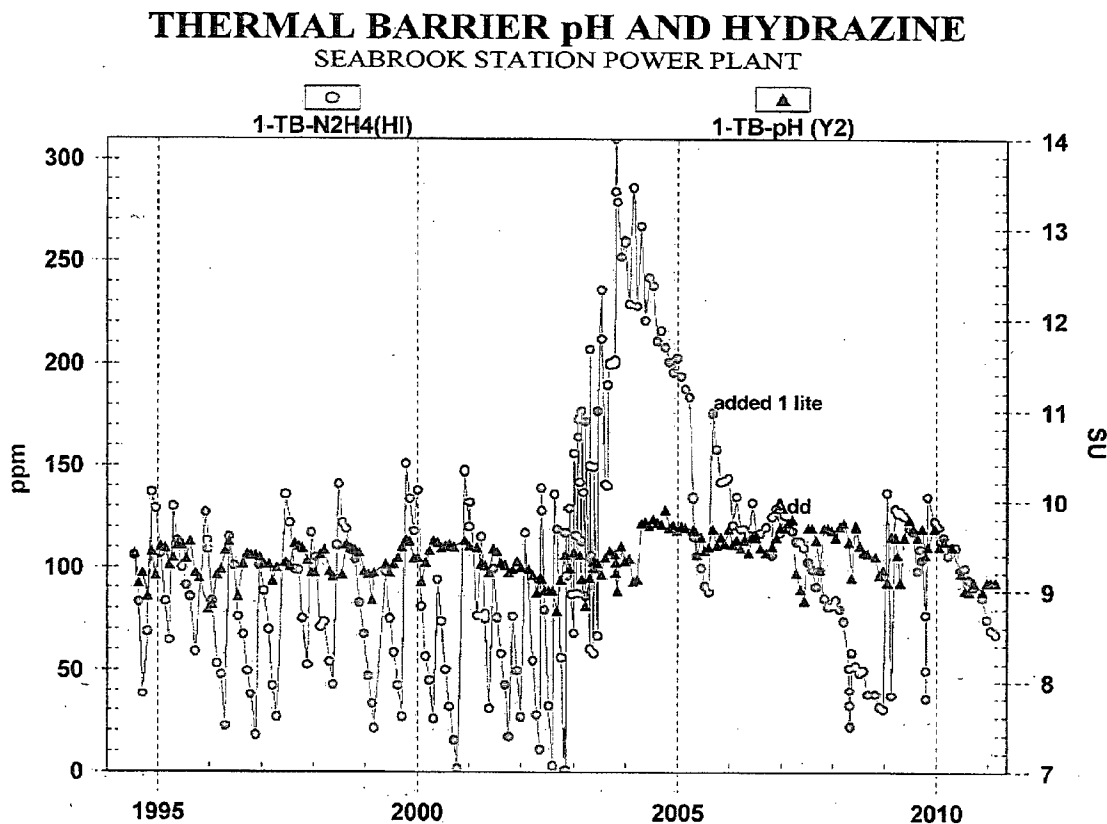


Figure 2-1 TB System Hydrazine and pH Variations [4]

Table 2-2

Full Wet Layup (RCS ≤200°F): Recirculating Steam Generator Sample [6]

CONTROL Parameters for Steam Generator Sample		
Monitor Values Until Stable at a Frequency of Three Times Per Week, Then Weekly Once Values are Stable.		
Parameter	Initiate Action	Value Necessary Prior to Heatup (>200°F)
pH @ 25°C	<9.5	—
Hydrazine, ppm ^a	<75	—
Sodium, ppb	>1000	≤100
Chloride, ppb	>1000	≤100
Sulfate, ppb	>1000	≤100
Diagnostic Parameters for Steam Generator Sample		
Parameter	Consideration	
Boron	Applies only to plants using secondary side boric acid treatment.	
Sludge analysis	When sludge is available as a result of sludge lancing or other maintenance.	
CONTROL Parameters for Steam Generator Fill Source		
Parameter	Frequency	Initiate Action
Dissolved O ₂ , ppb	(b)	>100 ^c

a. Alternatives to hydrazine may be used if qualified by the utility. Appropriate limits for any hydrazine alternative should be substituted.

b. Required prior to and/or during fill for plants with oxygen control of their fill water source.

c. For plants without control of oxygen in their fill source, appropriate compensatory actions shall be taken to minimize steam generator exposure to oxygen, e.g., nitrogen sparging or addition of a reducing agent to the fill source or directly to the steam generators.

Table 2-3

Full Wet Layup (RCS ≤200°F) (Technical Specification Modes 5 and 6) OTSG Sample [6]

CONTROL Parameters		
Monitor all Values Every Other Day Until Stable, Then Weekly or after Significant Water Additions^a		
Parameter	Initiate Action	Value Necessary Prior to Heatup Above >200°F
pH @ 25°C	≤9.5	—
Hydrazine, ppm ^b	<75 or >500	—
Sodium, ppb	>1000	≤100
Chloride, ppb	>1000	≤100
Sulfate, ppb	>1000	≤100
Oxygen, ppb ^c	—	≤100
Diagnostic Parameters		
Parameter	Justification	
Nitrogen Overpressure ^d , psig	Minimization of oxygen ingress to the steam generators during wet layup.	
Hideout Return Database ^e (Na, Cl, SO ₄ , SiO ₂ , K, Mg, Ca, Al)	Assessment of OTSG crevice and superheat region solution chemistry during operation; impurity source term assessment.	

a. Chemical addition and OTSG recirculation should be initiated as soon as possible after entering Mode 5.

b. Alternatives to hydrazine may be used if qualified by the utility. Appropriate limits for any hydrazine alternative should be substituted.

c. Routine monitoring not required prior to initial heatup if hydrazine concentration is within normal range.

d. A nitrogen overpressure should be maintained on the steam generators when personnel safety will not be compromised.

e. Hideout return assessments generally should be based on data collected during fill/drain operations immediately subsequent to shutdown.

Table 2-4

Wet Layup (RCS $\leq 200^{\circ}\text{F}$) Recirculating Steam Generator Sample [7]

CONTROL Parameters		
Monitor Values Until Stable at a Frequency of Three Times per Week after Filling or after Significant Water Additions ^a , Then Weekly Once Values are Stable		
Parameter	Initiate Action	Value Necessary Prior to Heatup Above $>200^{\circ}\text{F}$
pH @ 25°C	<9.8 ^{b, c}	—
Hydrazine ^d , ppm	<25 ^b	$>3\times$ Oxygen (ppm)
Sodium, ppb	>1000	≤ 100
Chloride, ppb	>1000	≤ 100
Sulfate, ppb	>1000	≤ 100
Diagnostic Parameters		
Parameter	Justification	
Nitrogen Overpressure ^e , psig	Minimization of oxygen ingress to the steam generators during wet layup.	
Hideout Return Database ^f (Na, Cl, SO_4 , SiO_2 , K, Mg, Ca, Al)	Assessment of OTSG crevice and superheat region solution chemistry during operation; impurity source term assessment.	

a. Chemical addition and OTSG recirculation should be initiated as soon as possible after cooling down to $<200^{\circ}\text{F}$.

b. When the steam generator has not yet been exposed to oxidizing conditions, the hydrazine concentration shall be $\geq 3\times$ the oxygen concentration and may be < 25 ppm and the pH shall be maintained at or above the normal operating feedwater specification. If the steam generator is drained for maintenance or inspection, it shall be re-filled as soon as possible to maintain pH at ≥ 9.5 and hydrazine/oxygen ratio at ≥ 3 , and shall be returned to meet the requirements in Table 6-1 within 7 days of being re-filled.

c. If hydrazine is maintained at ≥ 75 ppm, then the pH @ 25°C "Initiate Action" value may be < 9.5 instead of < 9.8 .

d. Alternatives to hydrazine may be used if qualified by the utility. Appropriate limits for any hydrazine alternative should be substituted.

e. A nitrogen overpressure should be maintained on the steam generators when personnel safety will not be compromised.

f. Hideout return assessments generally should be based on data collected during fill/drain operations immediately subsequent to shutdown.

Table 2-5

Wet Layup (RCS ≤200°F) Once Through Steam Generator Sample [7]

CONTROL Parameters for Steam Generator Sample		
Monitor Values Until Stable at a Frequency of Three Times Per Week after Filling or after Significant Water Additions, Then Weekly Once Values are Stable.		
Parameter	Initiate Action	Value Necessary Prior to Heatup (>200°F)
pH @ 25°C	<9.8 ^{a, b}	—
Hydrazine ^c , ppm	<25 ^a	>3x Oxygen (ppm)
Sodium, ppb	>1000	≤100
Chloride, ppb	>1000	≤100
Sulfate, ppb	>1000	≤100
Diagnostic Parameters for Steam Generator Sample		
Parameter ^d	Consideration	
Sludge analysis	When sludge is available as a result of sludge lancing or other maintenance.	
Nitrogen Overpressure ^e , psig	Minimization of oxygen ingress to the steam generators during wet layup.	
CONTROL Parameters for Steam Generator Fill Source		
Parameter	Frequency	Initiate Action
Hydrazine ^f , ppm	(g)	<3x Oxygen (ppm) ^h

a. When the steam generator has not yet been exposed to oxidizing conditions, the hydrazine concentration shall be ≥ 3x the oxygen concentration and may be < 25 ppm and the pH shall be maintained at or above the normal operating feedwater specification. If the steam generator is drained for maintenance or inspection, it shall be re-filled as soon as possible to maintain pH at ≥ 9.5 and hydrazine/oxygen ratio at ≥ 3, and shall be returned to meet the requirements in Table 5-1 within 7 days of being re-filled.

b. If hydrazine is maintained at ≥ 75 ppm, then the pH @ 25°C "Initiate Action" value may be < 9.5 instead of < 9.8.

c. Alternatives to hydrazine may be used if qualified by the utility. Appropriate limits for any hydrazine alternative should be substituted.

d. If an optional chemical is being added (e.g., boron, titanium, dispersant, etc.), then the appropriate parameter should be monitored per the site specific chemistry program as described in the Strategic Water Chemistry Plan.

e. A nitrogen overpressure should be maintained on the steam generators when personnel safety will not be compromised.

f. Hydrazine may be added directly to the steam generator.

g. Required prior to and/or during fill.

h. Based on calculation or measurement. Hydrazine addition to the fill water or batch addition to the steam generators can be employed to meet this requirement.

2.2.2 pH

It is well accepted that general corrosion rates of stainless steel and carbon steel decrease as the pH is increased above neutral as a result of the formation of a protective oxide film on the surfaces. In hydrazine chemistry systems, the oxidation potential or electrochemical potential (ECP) is decreased to very low values, i.e., approaching the

hydrogen line, and the stable phase is magnetite (Fe_3O_4) (Reference Figure 2-2) [9]. As shown, the magnetite phase is stable over a very wide pH band, and as a result, corrosion rates of carbon steel and stainless steels will be minimal in the indicated control and normal operating bands of Table 2-1.

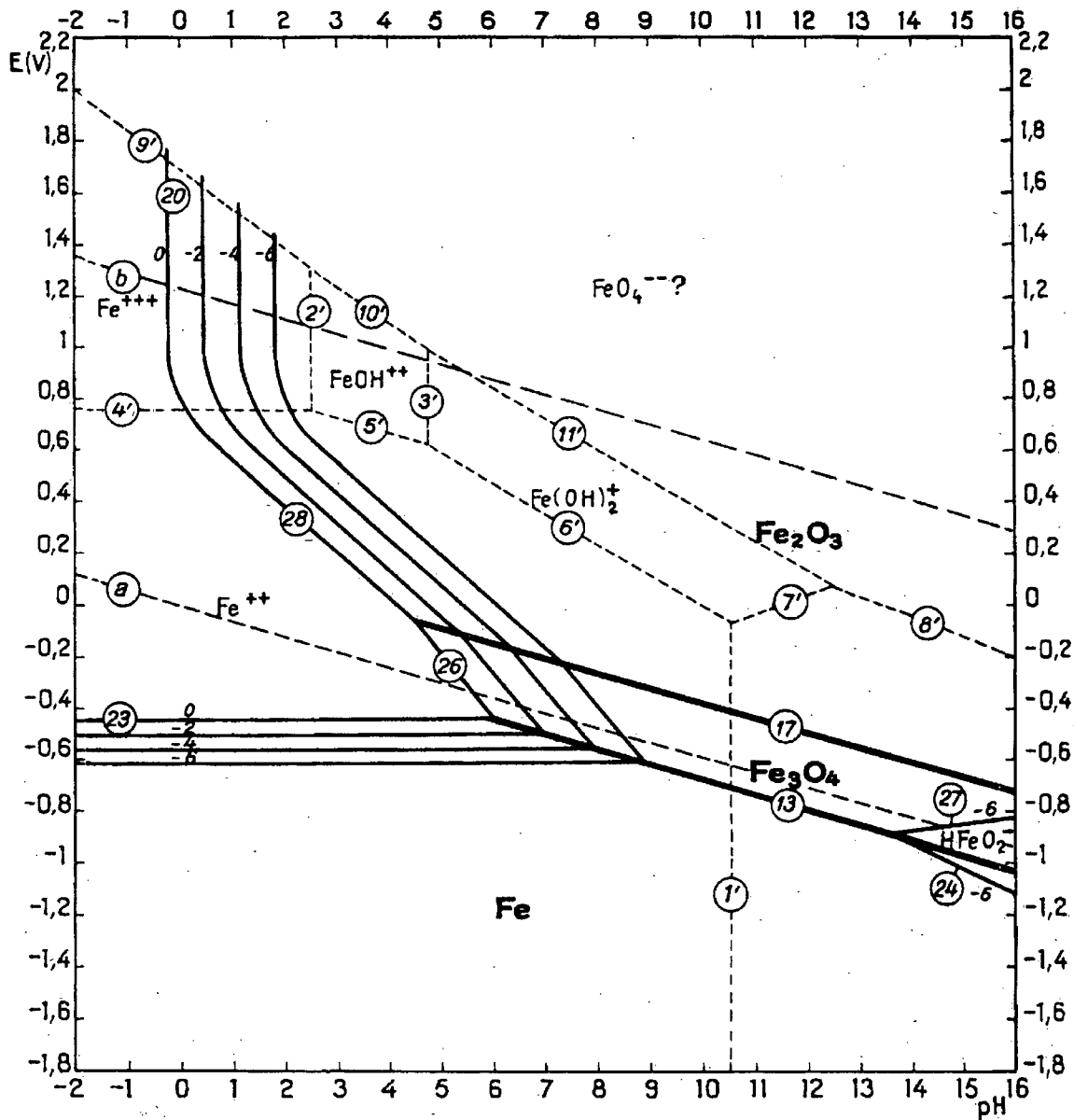


Figure 2-2 Potential-pH equilibrium for the system iron-water, at 25°C
(considering as solid substances only Fe , Fe_3O_4 and Fe_2O_3). [9]

Variations in the pH of the TB system since 1999 are shown in Figure 2-1. pH generally has ranged from ~9 to 9.8 with the upper value being below the Action Level 2 value of 10.0 for all ferrous systems but slightly above the normal operating range upper value of 9.6. Note that the more restrictive pH and hydrazine ranges for mixed alloy systems are due to the presence of copper alloys in these systems. Corrosion rates of such alloys generally are minimal in the normal operating range of Table 2-1 and increase both at reduced and increased pH. The behavior at significantly increased pH is a result of formation of copper/ammonium complexes.

Note that the pH will be ~9.9 in a 200 ppm hydrazine solution in pure water. The pH of such solutions will also increase as a result of ammonia formation due to hydrazine decomposition. (Ammonia ionizes to a greater extent than hydrazine.)

The rate of hydrazine decomposition is system specific since the decomposition reactions are catalyzed by metal surfaces. The stoichiometry of the decomposition reaction can also vary, i.e., different amounts of N_2 , H_2 and NH_3 can be formed in different systems. In the Seabrook TB system, ammonia concentrations varied from ~30 to 60 ppm from 2005 through 2009 but were reduced to 15 to 20 ppm in early 2010 when feed and bleed operations were undertaken (Figure 2-3) [4]. The pH of pure ammonia solutions over this range of ammonia concentrations will vary from ~ 10.1 to 10.4. The EPRI CCW Guidelines [3] note that "Ammonia can be a corrodent to copper and copper alloys under oxidizing conditions" but there is no indication of a negative effect on stainless or carbon steel. In fact, many PWRs, particularly those in Germany, operate with ammonia pH control in the secondary cycle with room temperature pH controlled in the range of 10 to minimize corrosion of ferrous alloys throughout the secondary cycle. This type of approach is also used at one US PWR as a means to reduce feedwater iron concentrations and feedwater system general and flow assisted corrosion.

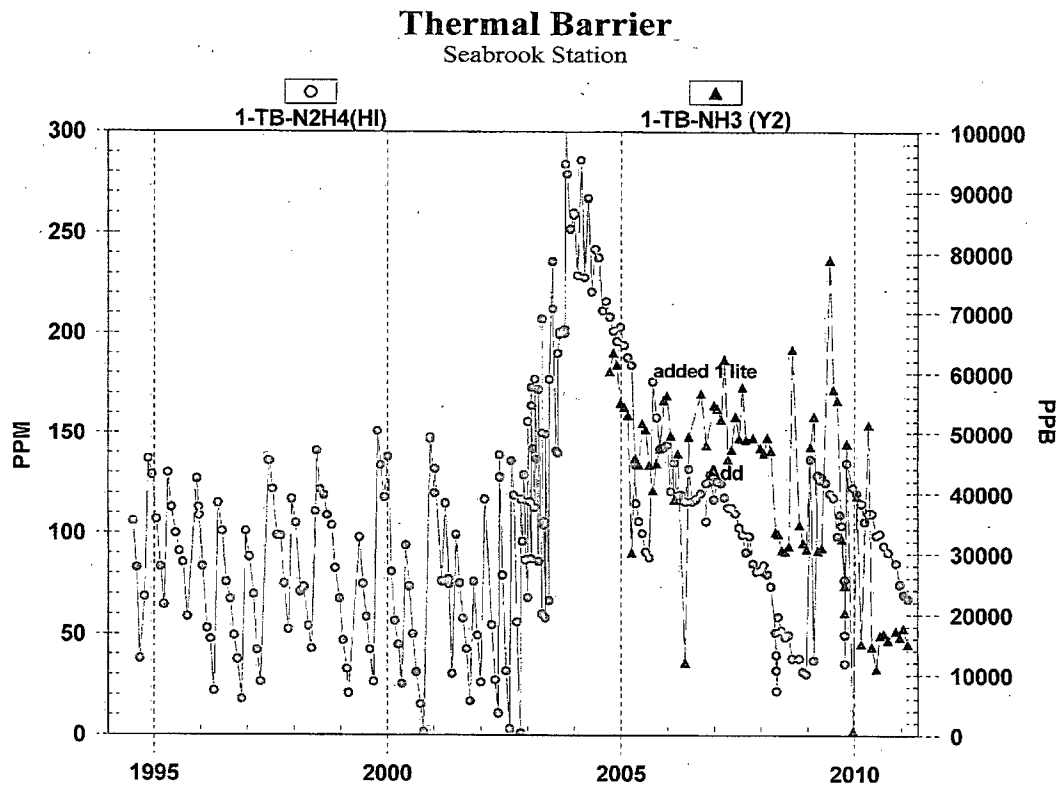


Figure 2-3 TB System Hydrazine and Ammonia Concentration Variations [4]

pH in the TB system generally has been lower than calculated for pure solutions of hydrazine and ammonia. This is probably a result of pickup of CO₂ from the head tank which is vented to the atmosphere. However, the formation of organic acids cannot be eliminated as a possibility without additional analyses. The presence of ppb levels of sulfate and chloride does not significantly impact on the pH of the hydrazine/ammonia TB system solution.

2.2.3 Chloride and Fluoride

The EPRI CCW Chemistry Guidelines [3] provide the following justification for the chloride and fluoride control parameter limits of Table 2-1:

“Chloride can contribute to carbon steel corrosion and chlorides and fluorides can be related to stress corrosion cracking of 300 series austenitic stainless steels. The

chloride and fluoride limit for Hydrazine-treated systems is based on the Westinghouse limit of 150 ppb. The 50 ppb limit for pure water systems is based on consensus of the Closed Cooling Water Chemistry Guideline Task Group. For pure water systems without stainless steel, fluoride would be a diagnostic parameter.”

Chloride, fluoride and sulfate concentration variations in the Seabrook TB system since 1999 are shown in Figure 2-4. With a limited number of exceptions, the chloride and fluoride concentrations have been maintained well below the Table 2-1 Guideline values.

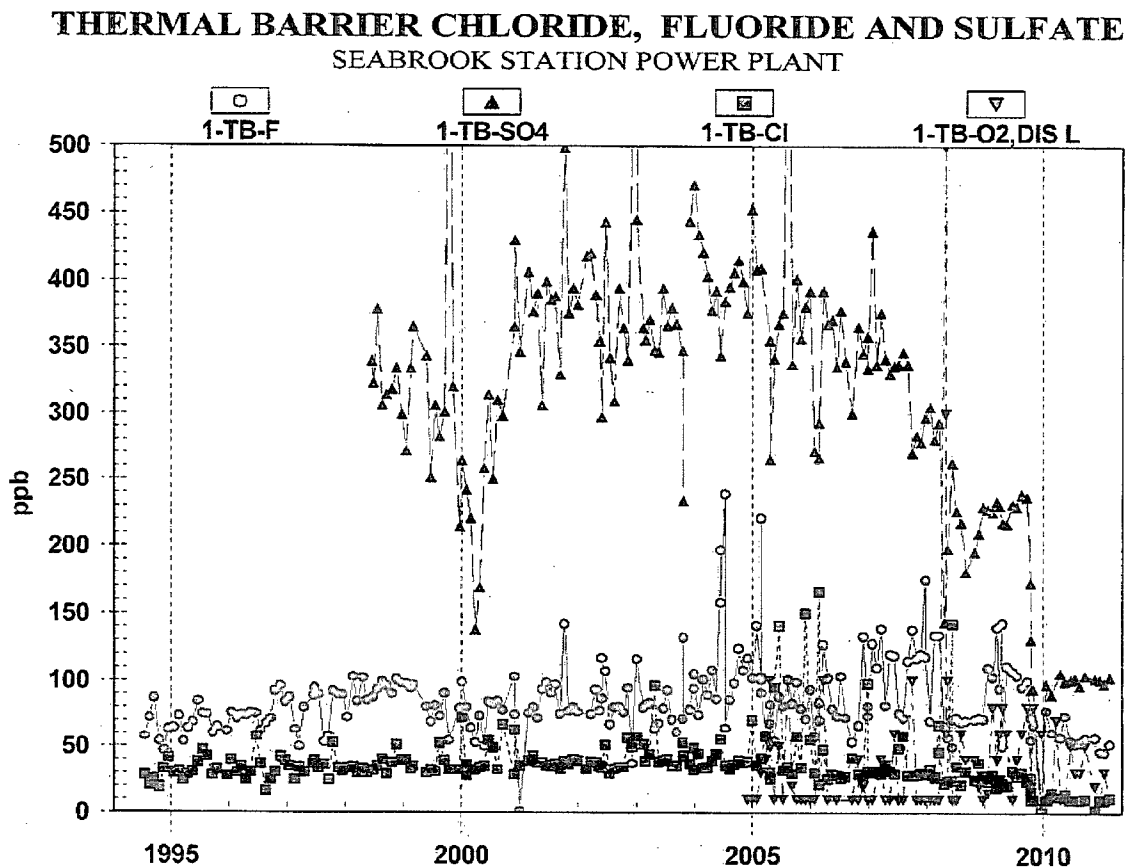


Figure 2-4 TB System Chloride, Fluoride and Sulfate Concentration Variations[4]

2.2.4 Sulfate

The EPRI CCW Chemistry Guidelines [3] gives the following justification for monitoring and controlling sulfate:

“The sulfate ion can contribute to IGSCC in 300 series stainless steels. Sulfate can compete with the corrosion inhibitor in carbon steel. Sulfate contamination can come from poor quality makeup water, service water in-leakage, or biocide additions. Sulfate is a routine Control Parameter in pure water and Hydrazine systems and an Investigative Parameter in other inhibited systems.”

Sulfate concentrations in the Seabrook TB system since 1999 are shown in Figure 2-4. Concentrations were generally in the range of 200 to 450 ppb from 1999 through 2009. These concentrations exceeded the recommended Action Level 1 value of 150 ppb but did not exceed the EPRI CCW Chemistry Guidelines AL 2 value of 1000 ppb [3]. Note that the sulfate concentration was reduced in early 2010 by feed and bleed to ~100 ppb where it has remained.

In Revisions 5, 6, and 7 of the PWR Secondary Water Chemistry Guidelines [5, 6 and 7], the sulfate limit prior to initiation of action at steam generator wet layup conditions is 1000 ppb (Tables 2-2, 2-3 and 2-4). A limit of 100 ppb is established before exceeding 200°F during startup. This difference clearly illustrates the dependence of the tendency for corrosion on temperature. Note that the TB system normally operates at <100°F, well below the temperature where significant acceleration of corrosion of stainless and carbon steel would be expected at the observed TB system sulfate concentrations, particularly since the oxygen concentration is routinely maintained below 100 ppb and normally below 10 ppb and the hydrazine to oxygen ratio is very high.

The Westinghouse Standard Information Package (SIP) for chemistry control in closed cooling water systems only recommended monitoring for chlorides and fluorides when it was first issued in 1974, and the 1985 version of the SIP has retained this position [1].

This again illustrates the industry position that SCC of stainless materials at CCW temperatures is not considered a significant issue.

At low oxygen concentrations, the tendency for stress corrosion cracking of stainless steels is significantly reduced even at elevated concentrations of impurities such as chloride, sulfate and fluoride. For example, consider the results of Cragnolino et al. [10] (Figure 2-5) which were obtained at 100°C (212°F) in a 0.01 molar sodium sulfate solution (960 ppm sulfate).

Figure 2-5 “shows the stress vs. elongation plots obtained at different applied potentials. At all the potentials tested, ranging from -0.26 to 0.40 V_H , the observed elongation to failure was around 60 to 70%. The fracture mode was ductile, as was confirmed by SEM examination. Careful observation of the side surfaces did not reveal the presence of cracks or any other signs of localized attack.” [10]

“Considering that several authors have observed IGSCC at ~100°C on severely sensitized samples at potentials around 0.2 V_H and due to the fact that a significant variability in IGSCC resistance between different heats of Type 304 Stainless Steel in high temperature oxygenated water has been reported, three additional tests were performed with specimens of heat B. In the first test, the sample was sensitized for 12 hours at 650°C, while in the second one, a subsequent low temperature sensitization treatment (24 hours at 500°C) was applied to increase the degree of sensitization. In the third test, the sample was sensitized for 24 hours at 650°C. These tests were carried out at 0.2 V_H and only ductile failure was obtained”. [10]

In reviewing the implications of operating with a sulfate concentration of ~250 to 450 ppb relative to stainless steel SCC in the Seabrook TB system, it should be recognized that 304 stainless steel has for many years been routinely employed for turbine condenser tubing at lake water and river water cooled power stations and has proven to be extremely

resistant to SCC in these environments which routinely have sulfate concentrations in the range of 10 to 40 ppm or almost 100 times the levels observed in the Seabrook TB system from 1999 through 2009. Tubing temperatures in the condenser application frequently exceed 100°F and can be significantly higher during summer months particularly in cooling tower systems.

In reviewing and attempting to apply laboratory test data on cracking of stainless steel and high nickel alloys, it must be recognized that the tendency for cracking of such alloys generally increases with applied stress, temperature, impurity concentrations and the level of sensitization, and increases in these parameters are routinely employed during laboratory studies to accelerate SCC, decrease test time and allow qualitative relations on the impacts of selected variables to be developed. As a result, the applicability of most laboratory test results to the prediction of SCC in dilute solutions at low temperatures must be carefully reviewed before attempting to apply the results to plant materials and systems.

Based on available data, the reviewer would not expect that any significant degradation of the carbon steel and stainless steel materials in the TB system at Seabrook occurred during the 1999 to 2009 period when sulfate concentrations were elevated to ~250 to 450 ppb although the sulfate concentrations exceeded the EPRI Table 2-1 Guideline Action Level 1 value of 150 ppb. Note that the TB system sulfate concentration did not approach or exceed the 1000 ppb Action Level 2 value, oxygen concentrations were generally minimized, and the hydrazine to oxygen ratio was very high thereby reducing the electrochemical potential of the ferrous materials.

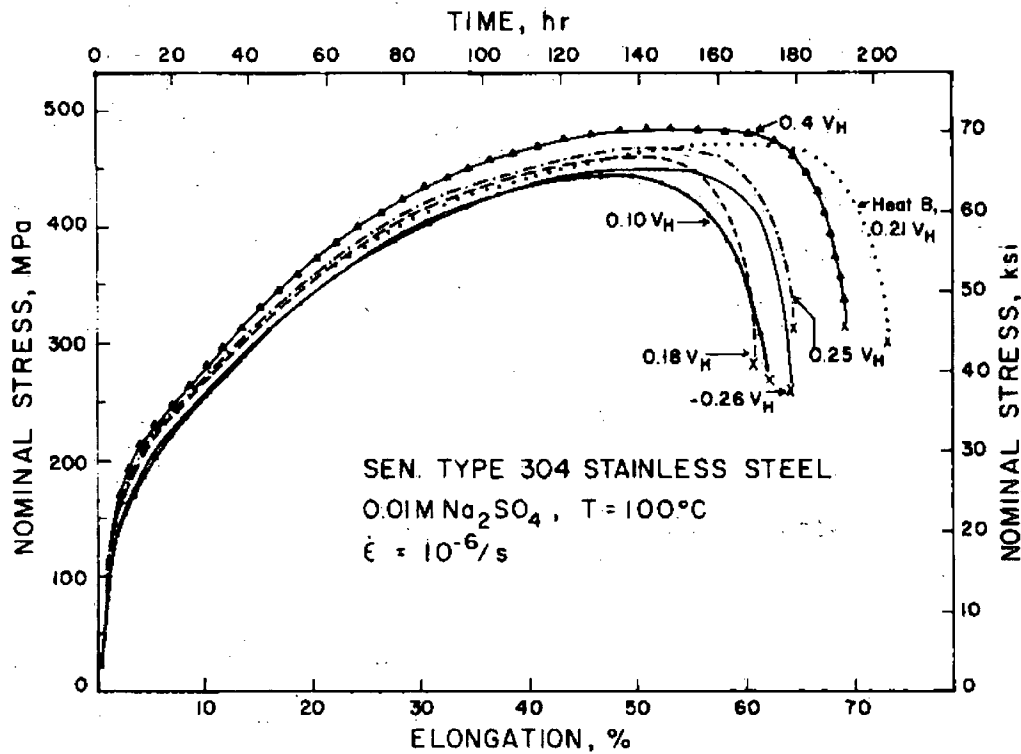


Figure 2-5 Nominal stress vs. elongation curves for sensitized Type 304 Stainless Steel (Heat A, 24 hours at 650°C) in 0.01 M Na₂SO₄ at 100°C, at various potentials [10]

2.2.5 Oxygen

The EPRI CCW Chemistry Guideline provides the following discussion of the impact of oxygen on corrosion in such systems:

“Dissolved oxygen plays a part in the corrosion process. In inhibited CCW systems (nitrite, molybdate, nitrite/molybdate, chromate, silicate), a passive film is established and the presence of dissolved oxygen does not appear to have a significant impact on corrosion rates. In fact, it is commonly believed that some dissolved oxygen is helpful in molybdate-treated systems (see Section 4.3.2). Unless there is significant makeup or the system is designed so that oxygen ingress is normal, dissolved oxygen is rapidly depleted and CCW systems will be

relatively free of dissolved oxygen. In inhibited systems, dissolved oxygen is an Investigative Parameter. There is little value in routine measurement.

“In pure water and hydrazine systems, dissolved oxygen is a Control Parameter. In these systems, oxygen can play a significant role in copper and copper alloy corrosion because most systems do not employ a copper corrosion inhibitor. The limits for hydrazine-treated and pure water systems are based on the Stator Cooling Guidelines [3].”

Oxygen concentration variations in the Seabrook TB system are shown in Figure 2-1. Concentrations did not exceed the Table 2-1 100 ppb Action Level 1 limit and were normally <10 ppb. In addition, it should be noted that the primary concern raised in the EPRI CCW Chemistry Guidelines was corrosion of copper alloys which are not present in the Seabrook TB system. The absence of such alloys is readily confirmed by the absence of detectable copper concentrations in the TB system samples (Figure 2-6).

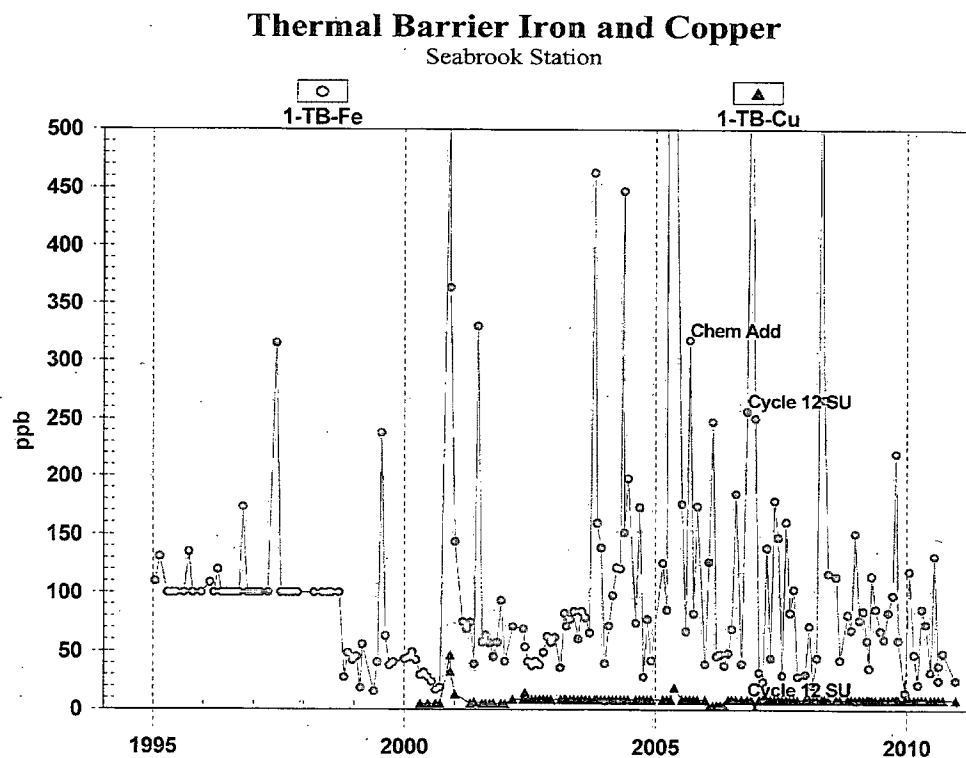


Figure 2-6 TB System Iron and Copper Variations [4]

2.3 Diagnostic Parameters

2.3.1 Iron and Copper

Iron and copper concentration variations in the Seabrook TB system are summarized in Figure 2-6. Iron concentrations generally have varied from 50 to 200 ppb with no clear trend with pH, ammonia or hydrazine. As noted below, a system specific value is generally established, and no limit is set in the CCW Chemistry Guidelines [3]. Since a significant fraction of the iron generally is insoluble, it is difficult to obtain a representative sample during routine monitoring and wide concentration variations are frequently observed. Of particular note is the general absence of a detectable copper concentration since the Seabrook TB system is an all ferrous design. The EPRI CCW Chemistry Guidelines provides the following discussion of these parameters:

“The accumulation of corrosion products (iron, copper, and other metal oxides) in the CCW system is an indirect indication of corrosion. In nitrite-, molybdate-, nitrite/molybdate-, and hydrazine-treated systems, the pH generally favors insoluble iron oxide. However, the pH can vary over a wide range and, thus, the percentage of insoluble iron will vary”.

“Each system establishes a normal concentration of these corrosion products based on the corrosion inhibitor(s) used, the materials of construction of the system, and their respective surface areas. Consequently, a specific number cannot really be assigned as a *not-to-exceed* value.”

“The trends of the total concentration of these metals will provide general information about upsets to the system. Metal concentrations, which trend higher in bulk coolant, might be significant because they can foul heat exchanger tube surfaces, pump seals, and flow-measuring devices. This can result in loss of flow, increased ΔP , loss in efficiency, and increased maintenance for components.

“The values chosen for acceptable ranges or limits for iron and copper should be developed on a plant-specific basis.” [3]

Although iron concentrations have varied widely, such variations are expected and are not directly related to changes in general corrosion rates in the system. However, monitoring is of value for trending purposes. Such concentration data are not related to changes in the sensitivity to SCC of stainless steel alloys.

Section 3

IMPACT OF HYDRAZINE /OXYGEN RATIO ON ECP OF STAINLESS STEEL [7]

Extensive efforts have been performed over the last several years to evaluate the impact of hydrazine and the hydrazine to oxygen ratio in PWR and BWR systems on electrochemical potential (ECP) [e.g., 8, 11]. Such studies have been based on the recognition that the tendency for crack initiation in stainless steels and high nickel alloys such as Alloys 600 and 690 decreases markedly as the oxygen concentration and the ECP decrease. However, even these studies have focused on behavior above ~200°F since the tendency for cracking below this temperature decreases markedly.

To illustrate the dependence of ECP on the hydrazine to oxygen ratio, variations in 304 stainless steel ECP with the hydrazine to oxygen ratio at 250°F are summarized in Figure 3-1 [8]. Results can be summarized as follows:

- ECP decreases monotonically with an increase in hydrazine to oxygen ratio at both 250°F.
- ECP values are similar at a given ratio of hydrazine to oxygen and are relatively independent of the oxygen concentration.
- At hydrazine to oxygen ratios greater than ~2, ECP values for 304 stainless steel are similar to values at 10 ppb oxygen at 250°F.

Based on these results, approaches to control of oxidant concentrations in PWR steam generators was revised in Revision 7 of the PWR Guidelines to establish a minimum hydrazine to oxygen ration of 3 and the lower limit for hydrazine was reduced to 25 ppm. Above this ratio, the ECP is expected to remain at or below that in a solution containing 10 ppb oxygen, and minimum general corrosion and stress corrosion cracking is

expected. Similar observations were made during tests at 200°F simulating BWR startup conditions.

In the Seabrook TB system, the hydrazine/oxygen ratio has varied markedly but values have been much greater than ratios shown to reduce ECP sufficiently to depress rates of IGSCC. For example, at a hydrazine concentration of 20 ppm, the hydrazine /oxygen ratio is 2000 at 10 ppb oxygen and 200 at 100 ppb oxygen. During the period when the hydrazine concentration was in the range of 150 to 300 ppm, the ratio even with 100 ppb oxygen was 1500 to 3000. These values are much greater than that required to suppress the ECP to very low levels and provide protection against stress corrosion cracking.

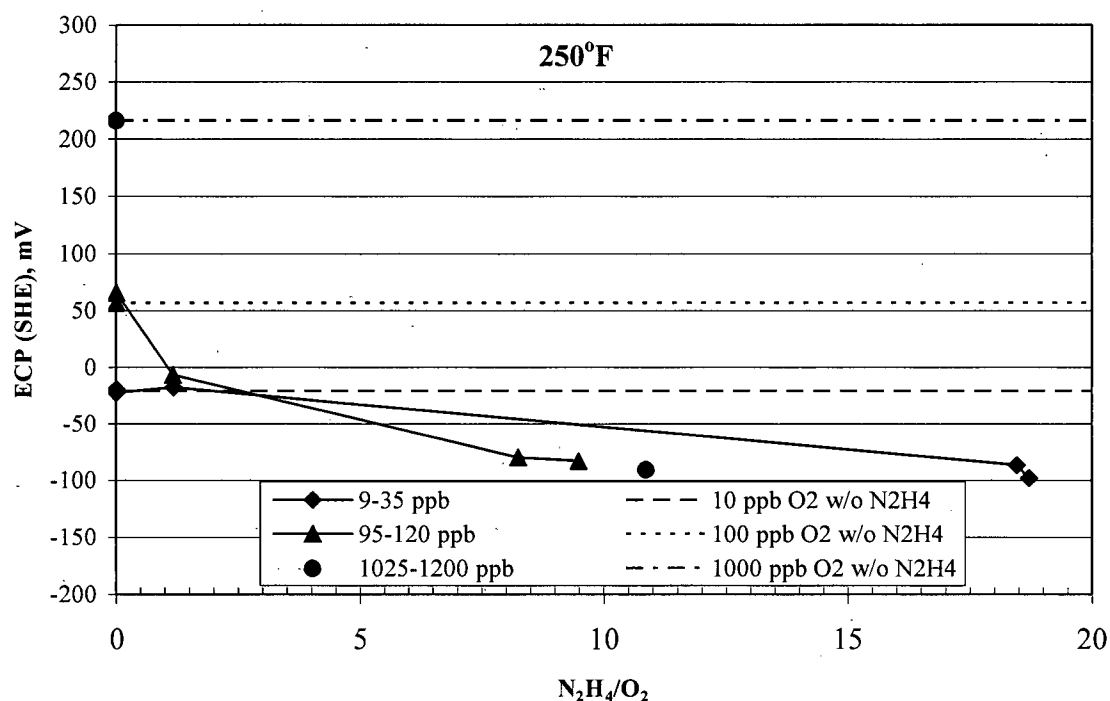


Figure 3-1 Effect of Hydrazine to Oxygen Ratio on 304 SS ECP at 250°F (pH_T Corrected) [8]

Section 4

TB SYSTEM GENERAL CORROSION

To monitor general corrosion rates in the TB system at Seabrook, 304 stainless steel and A515 carbon steel specimens are installed in a coupon section located on the -26' level of the Reactor Containment Building adjacent to heat exchanger 1-CC-E-153B. Coupons are intermittently inspected and analyzed by site personnel. Corrosion rates in mm/year have been as follows [4]:

- Dates: From 12/22/99 to 10/24/01 (672 days in system)
Corrosion rate for SS-304 coupon = $1.61\text{E-}05$
Corrosion rate for SS-304 coupon = $4.31\text{E-}06$
Corrosion rate for CS 7-515 coupon = $3.45\text{E-}04$
Corrosion rate for CS 7-515 coupon = $4.03\text{E-}03$
- Dates: From 10/24/01 to 8/27/03 (672 days in system)
Corrosion rate for SS-304 coupon < $4.03\text{E-}06$
Corrosion rate for CS 7-515 coupon = $1.42\text{E-}04$
Note: Stain spots 25% scattered pitting on CS 7-515
- Dates: From 6/25/05 to 3/4/09 (1347 days in system)
Corrosion rate for SS-304 coupon = $2.01\text{E-}06$
Corrosion rate for CS 7-515 coupon = $2.73\text{E-}05$
Note: Pitting observed on CS 7-515
- Dates: From 5/3/07 to 1/19/11 (1356 days in system)
Corrosion rate for SS-304 coupon = $2.00\text{E-}06$
Corrosion rate for CS 7-515 coupon = $2.66\text{E-}03$
Note: Slight pitting observed on CS 7-515
- Dates: From 3/3/09 to 1/19/11 (687 days in system)
Corrosion rate for SS-304 coupon $\leq 3.94\text{E-}06$
Corrosion rate for CS 7-515 coupon = $1.01\text{E-}04$
Note: Slight pitting observed on CS 7-515

As shown, general corrosion rates of both carbon steel and stainless steel have been minimal. The maximum reported carbon steel corrosion rate was $4\text{E-}3$ mm/year (~ 0.16 mils per year). Corrosion rates of stainless steel were much lower.

Section 5

CONCLUSIONS

There is no reason to expect that increased carbon steel or stainless steel corrosion rates occurred from 1999 to 2009 when hydrazine and sulfate concentrations were elevated in the Seabrook TB system. The elevated hydrazine concentrations would be expected to lead to minimum oxygen concentrations in the bulk water and very low electrochemical potentials of the stainless steel surfaces resulting in a minimum tendency for stress corrosion cracking. Sulfate, in the concentration range that was observed, is not expected to be a significant accelerant of SCC of stainless steel at TB system temperatures particularly at the low electrochemical potential of the stainless steel materials at the high hydrazine to oxygen concentration ratio. The low oxygen levels and the elevated pH due to the presence of ammonia and hydrazine was expected to result in minimal general corrosion rates of both materials, and this was confirmed by analysis of stainless steel and carbon steel coupons exposed over extended periods in the TB system.

Although sensitized specimens with elevated stress levels exposed to 960 ppm sulfate solutions at oxidizing conditions have in some cases exhibited cracking at 100°C in the laboratory, application of these results to the Seabrook case is not considered reasonable due to the severity of the laboratory test conditions compared to those present in the TB system. The Seabrook system normally operates at temperatures well below 100°F in a reducing environment, and the maximum observed sulfate concentration has been ~450 ppb or 2000 times less than the concentration used during the laboratory tests. Note that neither transgranular nor intergranular cracking of Type 304 stainless steel has been observed in other laboratory tests at 960 ppm sulfate over a wide range of applied potential.

In developing these positions, the following additional information was considered:

- Westinghouse CCW recommendations issued in 1974 and 1985 do not list sulfate as a control parameter.
- Revision 5 and 6 of the EPRI PWR Water Chemistry Guidelines recommended >75 ppm hydrazine for wet lay up of PWR recirculating steam generators. No upper limit was recommended. The Guidelines for OTSGs recommended control at >75 to <500 ppm hydrazine. In Revision 7, the recommendations were revised to >25 ppm with no upper limit specified. The hydrazine to oxygen ratio was added as a Control Parameter.
- Revisions 5, 6 and 7 of the EPRI PWR Water Chemistry Guidelines recommended 1000 ppb sulfate as an upper limit during wet lay up of PWR recirculating and once through steam generators. Corrosion risks at this sulfate concentration were considered minimal at layup temperatures. Lower limits were only recommended at elevated temperature, i.e., >200°F.
- Electrochemical potential of the stainless steel surfaces in the TB system has been very low based on the very high hydrazine to oxygen ratio in the system. At low potentials and low temperature, the tendency for SCC of Type 304 stainless steel is minimal.
- Stainless steel has been successfully employed for many years as a condenser tubing material at fossil and nuclear power stations with river water and lake water cooling [12]. To the reviewer's knowledge, observations of SCC have been minimal in such applications even though sulfate concentrations normally are in the range of 10 to 40 ppm.

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