Corrosion Fatigue Crack Initiation of Boiler Tubes:

Effect of Phosphate Boiler Water Treatment

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REPORT SUMMARY

ACKNOWLEDGMENTS

The authors are grateful for the technical support provided by colleagues at the Babcock & Wilcox Research & Development Division. G.R Hoover was principal in running the experiments and in helping in the preparation of this report. R.H. Pelger was responsible for building the reference electrodes and for all of the electrochemical monitoring. The support and advice of Dr. D. Sidey of Ontario Hydro helped in keeping this program focused on the objectives.

SUMMARY

This laboratory study helps to define the environmental variables that influence corrosion fatigue cracking of boiler tubes. Low cycle (strain controlled) fatigue tests were run on segments of SA210-A1 boiler tubing. A main objective of this program was to evaluate what effect pH changes in a phosphate boiler water environment would have on corrosion fatigue.

During boiler start-up and shut down, the pH of the boiler water can be unstable due to phosphate hide-out and return; this in turn can influence corrosion fatigue of boiler tubes. It was demonstrated in this study that pH depressions in phosphate boiler water will cause tubes to be more susceptible to corrosion fatigue, even in deaerated water (< 5ppb dissolved oxygen). The results fully support the new phosphate treatment guidelines from the Electric Power Research Institute (EPRI).

Other results from this study show that a number of variables influence the time to initiate corrosion fatigue cracks. The factors that influence corrosion fatigue include: dissolved oxygen, solution pH, temperature, and the loading frequency (i.e. strain rate). Another new finding in this study is that crack initiation is less sensitive to dissolved oxygen at lower temperatures. This is important in that dissolved oxygen levels in boilers decrease as the boiler becomes hotter. This finding implies that dissolved oxygen may not influence corrosion fatigue in operating plants to the extent that previous work has indicated, although there is still a detrimental effect.

The amount of corrosion that occurs during each loading cycle directly contributes to corrosion fatigue crack initiation. Lowering the pH and/or increasing the dissolved oxygen of the boiler water increase its corrosivity; this in turn reduces the number of cycles to initiate corrosion fatigue cracks. Because corrosion is time dependent, slower loading frequencies (which correspond to slower strain rates) allow more corrosion damage to occur during each loading cycle. Therefore, slower loading frequencies (or slower strain rates) reduce the number of cycles to initiate cracks.

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FIGURES

TABLES

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BACKGROUND

Boiler tube failures due to corrosion fatigue are the leading contributor to unscheduled plant down-time. Corrosion fatigue remains one of the few boiler tube failure mechanisms for which a root cause has not been identified. This lack of understanding is due in large part to the complex nature of corrosion fatigue. There are three principal components that influence corrosion fatigue: stress (or applied strain) factors, environmental factors, and operational factors. The interaction between these factors further complicate the understanding of corrosion fatigue.

This project (1890-10) supplements the initial EPRI-sponsored program investigating corrosion fatigue of boiler tubing (Project 1890-05). The results of the previous work included a field survey[1], laboratory testing[2], field monitoring and stress analysis[3], and a summary report and guidelines document[4]. This work developed an initial "influence diagram" to assess the probability of corrosion fatigue occurring. The influence diagram is shown in Figure 1-1.

The influence diagram uses several factors to evaluate when and at what location corrosion fatigue might occur. Among these factors are a stress rank, equivalent operating hours, and an environmental parameter. The stress rank is based on experience and stress analysis and depends on the local design of the boiler, such as tube bending, attachments, etc. A stress rank of "A" corresponds to a high stress, and a stress rank of "D" corresponds to a low stress. A complete list of the stress rank of specific attachments can be found in EPRI TR-1000455, Volume 4.[4] The equivalent operating hours are based on the number of starts and the total operating hours that the boiler has seen, according to the formula in Equation 1-1.

$$EOH = \left[\frac{H}{1000}\right] + \left[\frac{N_S}{\left[\frac{H}{1000}\right]}\right] \qquad \text{(Eq. 1)}$$

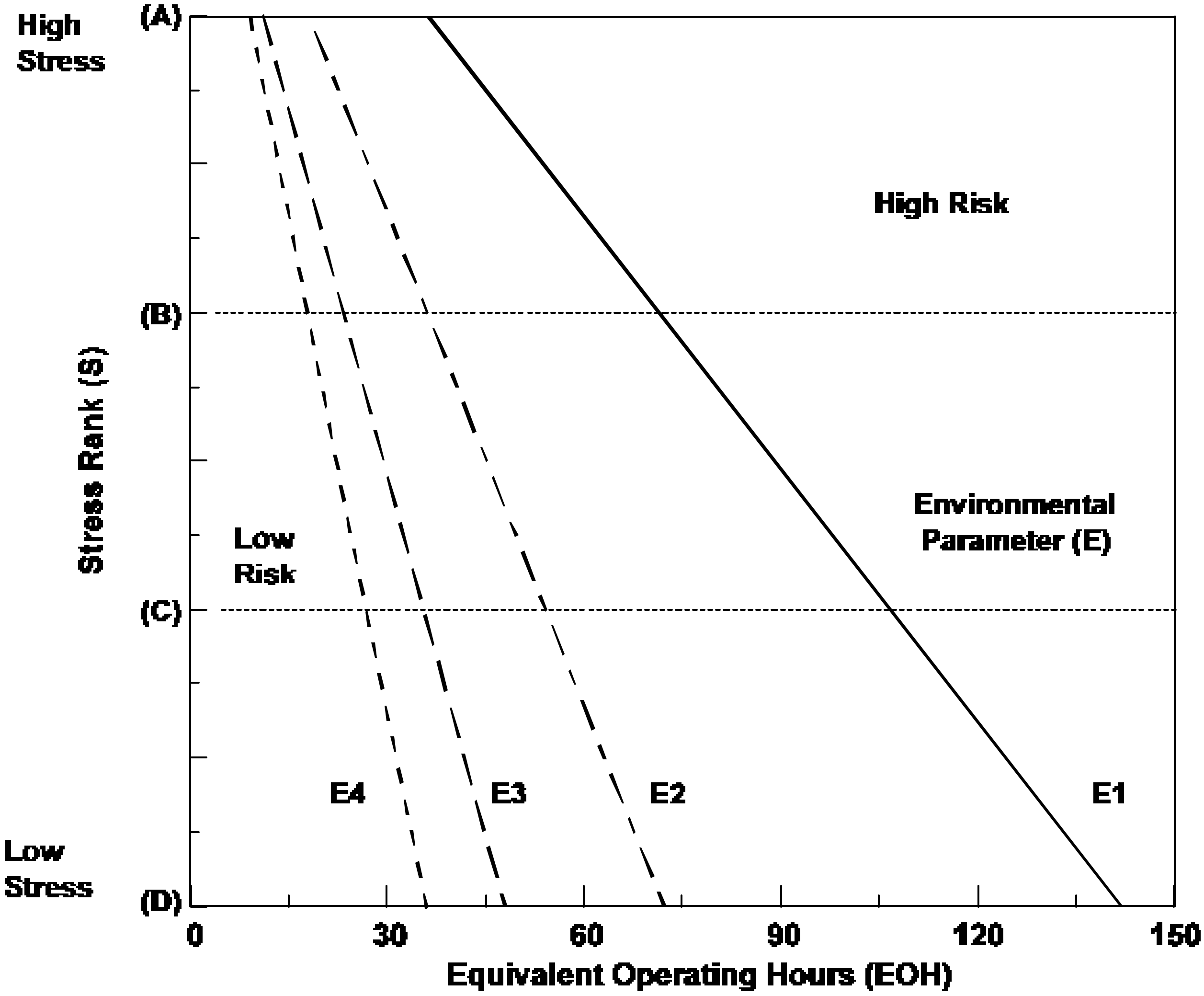
The environmental parameter is based on water chemistry control, chemical cleaning, and lay-up procedures, as described in Table 1-1. The environmental parameter is classified into four categories, designated as E1 through E4. E1 corresponds to good chemistry control consistent with current EPRI guidelines. E2 through E4 correspond to worsening water chemistries, with E4 being the worst.

Of all these, the environmental factors were the least understood. Therefore, this laboratory program had the goal of providing a better understanding and, if possible, a predictive equation to define the environmental factors influencing corrosion fatigue crack initiation.

Table 1-1 Environmental Parameter Evaluation

Value	Evaluation	Score			
3	Phosphate Boiler Alkalinity Control	3	6	9	
	Does the boiler experience phosphate hide-out or phosphate carry-over to the reheater?	No	Irregularly	Regularly	
3	Excursions	3	6	9	
	How many hydrogen damage or caustic gouging events resulting in tube failures have occurs over the life of the boiler?	0	1	>1	
	Typical On-Line Chemical Operating Ranges	1	2	3	
1	(1) Boiler water at blowdown pH	9.0-9.6	8.0-10.0	< 8, >10	
1	Cation conductivity (minus Phosphate correction, 4.1 x ppm PO_4)	≤6	6 - 30	> 30	
1	(2) Feedwater at the economizer inlet Dissolved Oxygen (ppb)	≤5	≤20	> 20	
2	Typical Start-Up Operating Ranges	2	4	6	
	1) Boiler Water-at blowdown pH Cation Conductivity (µS/cm) (minus phosphate correction, 4.1 x ppm PO_4)	9.0-9.6 ≤6	8.0-10.0 6-30	<8, >10 >30	
2	2) Feedwater-at economizer inlet Dissolved Oxygen (ppb)	<50	<200	>200	
1	Chemical Cleans	1	2	3	
	How many chemical cleans using a hydrochloric acid solution has the boiler been exposed to?	0	1	>1	
2	Boiler Shutdown/Lay-Up Procedures	2	4	6	
	What actions are taken for shutdown corrosion protection: a) N2, cap on drum and treat water if boiler not drained. b) Refill drained boiler with chemically treated water to control pH and oxygen. c) Ensure dry storage if drained. d) Monitor and adjust pH and oxygen in boiler during wet lay-up.	Actions a) to d)	actions a) and b)	no action	
	Total Value (Total for Questions Answered)			Total Score	

Environment Parameter (E) = E1, for Total Score/Total Value = 1.0 to 1.5
= E2, for Total Score/Total Value = 1.5 to 2.0
= E3, for Total Score/Total Value = 2.0 to 2.5
= E4, for Total Score/Total Value = 2.5 to 3.0



Water Quality (see Table 1-1 for Details)			
Line	**Designation**	**Desciption**	**Score/Value**
– – – ·	**E4**	**Very Poor**	**2.5 - 3.0**
— —	**E3**	**Poor**	**2.0 - 2.5**
– — –	**E2**	**Marginal**	**1.5 - 2.0**
———	**E1**	**Good**	**1.0 - 1.5**

Figure 1-1. Influence map for corrosion fatigue in Waterwall tubes (based on 15% probability of failure.

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EXPERIMENTAL

Details of the experimental procedures and design have been previously reported[2]. The basic approach was to use high-pressure autoclaves that reproduce pressure and temperature conditions found in operating boilers. Mechanical loading was accomplished through external loading equipment.

Environmental Controls

A schematic of the feedwater delivery systems is shown in Figure 2-1. The autoclave water was refreshed at a rate of 1.89 liters per hour (0.5 gallon per hour) to prevent contaminants from being depleted by corrosion reactions and to prevent build-up of corrosion products (such as hydrogen) in the autoclave. High-purity deaerated water was adjusted with the proper reagents to make up the simulated boiler water.

Boiler water chemistries were achieved by mixing high-purity water with reagent-grade monosodium phosphate, disodium phosphate, trisodium phosphate, sodium sulfate and sodium chloride in a stainless steel reservoir with a cover gas containing a mixture of oxygen and nitrogen. The simulated boiler water was then pressurized and preheated before being injected into the autoclave. A coil of stainless steel tubing was used to equilibrate the inlet water temperature inside the autoclave and to direct the water flow inside the tube specimen.

The chemistry of each batch of water was checked before being used. The phosphate, chloride, and sulfate concentrations were measured along with the conductivity and pH. The dissolved oxygen was controlled by varying the cover gas chemistry and was checked at selected intervals during the test. The environment was controlled to within ±10% of the specification. However, the oxygen content of the effluent from the autoclave was always lower than the influent, a result of oxygen consumption by corrosion reactions on the specimen and autoclave internal fixtures. To minimize the effect of oxygen gradients in the autoclave, the test specimen was pre-oxidized, and the influent water line was directed onto the test specimen.

The major focus of this study was to look at water chemistries corresponding to boilers that experience phosphate hide-out and return when operating on congruent phosphate treatment (CPT). During boiler start-up, the release of acid phosphates from hide-out regions can lower the bulk water pH levels. This is a particular problem when acid phosphates have been added to the boiler during operation to correct for hide-out, which causes the boiler water to be outside the CPT control range. The effect of phosphate hide-out and return upon corrosion fatigue was addressed by using the chemistries shown in Table 2-1.

The conditions in Table 2-1 were selected to correspond to boiler start-up. The dissolved oxygen levels were kept low during all of these tests to allow the effect of pH due to phosphate hide-out return to be clearly identified. The test temperatures are at intermediate levels that occur during start-up. In addition, the strain rates are at low levels (0.0005 hz); this corresponds to the slow strain rates that occur upon boiler heat-up.

In addition, several other test conditions were evaluated to asses other possible influences on corrosion fatigue in phosphate-treated boilers, such as dissolved oxygen, chloride, and strain rates. These additional test conditions are summarized in Table 2-2.

Table 2-1. Primary test matrix used to evaluate the influence of pH depressions, due to phosphate hide-out and return, on corrosion fatigue.

Temperature °F (°C)	Sodium/ Phosphate ratio	Phosphate ppb	pH at 25°C	Chloride ppb	Dissolved Oxygen ppb	Condition Simulated
400 (204)	1	3000	5.9	600	< 5	Hide-out return during start-up
400 (204)	2.6	3000	9	600	< 5	No hide-out return on shut-down
525 (274)	1	3000	5.9	600	< 5	Hide-out return during start-up
525 (274)	2.6	3000	9	600	< 5	No hide-out return on shut-down

Electrochemical Monitoring

A silver chloride electrode (SCE) was installed to monitor the electrochemical potential of the specimen. This reference electrode measured the potential of the outside tube surface, since this electrode could not fit inside the tube specimen due to lack of access imposed by the beam gauge and other hardware. To approximate the potential inside the tube specimen, one bare nickel wire was placed inside the specimen and another wire outside the specimen.

Figure 2-2 shows the placement of the reference electrode and nickel wires. This arrangement allowed the potential difference between the specimen inside and outside surfaces to be measured. This potential difference could be used, along with the Ag/AgCl reference electrode measurement of the outside tube surface, to closely approximate the actual electrochemical potential inside the tube specimen.

Mechanical Controls

A hydraulic loading system was used with a capacity of 250 kN (55,000 lbf). This loading system was interfaced with a computer used for both control and data acquisition. A schematic of the test specimen and loading fixtures is shown in Figure 2-3.

The tubular specimen was held on each end using retaining plates. The upper retaining plate was fixed, while the lower retaining plate was able to move vertically, allowing strains to be applied to the specimen. To electrically isolate the specimen from the load frame, the end plates and split rings were plasma sprayed with a 0.010-inch-thick layer of zirconium oxide. However, uneven wear of this zirconia oxide surface caused concerns regarding alignment and was later abandoned.

A sinusoidal waveform was used throughout the entire test program. The strain range was 1%, with a mean strain of 0. This produces an alternating strain of +/- 0.5%.

A top-mounted beam gauge was used to measure the total deflection of the test system. A clip gauge, directly attached to the specimen gauge section, could not be used on the full tube specimen, because there was not enough room in the autoclave. The deflection measured by the beam gauge includes some contributions from the fixtures and from the specimen outside the gauge length as well as from the specimen gauge length. A stiffness coefficient C for this loading system was experimentally obtained in air at each test temperature at the 1% strain range used in these tests. This stiffness coefficient was determined by comparing the beam gauge reading to clip gauge readings mounted on the specimen gauge area.

Table 2-2 Secondary matrix of environmental variables evaluated for influences on corrosion fatigue in phosphate treated boilers.

Temperature °F (°C)	Sodium/ Phosphate ratio	Phosphate ppb	pH at 25°C	Chloride ppb	Dissolved Oxygen ppb	Condition Simulated
275 (135)	0.6	1960	5	2500	5	Severe pH depression during slow start-up
275 (135)	3	881	9	2500	50	Slight air in-leakage during low start-up with good water
275 (135)	0.6	1960	5	2500	1000	Severe pH depression and severe air in-leakage during slow start-up
275 (135)	3	881	9	2500	5	Good water chemistry control during a fast start-up (0.01 hz)
275 (135)	0.6	1960	5	2500	1000	Severe pH depression and severe air in-leakage during fast start-up (0.01 hz)
275 (135)	0.6	1960	5	2500	1000	Duplicate of above
400 (204)	0.6	1960	5	2500	5	Severe pH depression during slow start-up
525 (274)	0.6	1960	5	2500	300	Significant air in-leakage during slow start-up with good water
525 (274)	0.6	1960	5	2500	300	Duplicate of above
525 (274)	0.6	1960	5	2500	300	Significant air in-leakage during
650 (343)	0.6	1960	5	2500	1000	Approaching full load with severe pH depression and severe air in-leakage
650 (343)	0.6	1960	5	2500	50	Approaching full load with severe pH depression and slight air in-leakage
650 (343)	0.6	1960	5	2500	1000	Approaching full load with severe pH depression and severe air in-leakage

Criteria for Crack Initiation

The environmental influence on corrosion fatigue in phosphate-treated boiler water is measured using the time to initiate a crack. The time to initiate cracks corresponds to a load drop of 25%. The load drops very quickly after a crack is initiated. Figure 2-4 shows a typical load history of a test specimen. Several tests were continued until the specimen cracked in half.

Examining the fracture faces of these test specimens shows several flat “thumb-nail” fatigue cracks initiated on the inside of the tube. The fracture mode changes to a cleavage/tearing mode after the specimen cross section is reduced by about 3% due to the initial fatigue cracks. Once the fracture mode changes to cleavage, the crack grows by 0.1 to 0.2 inches/cycle (2.5 to 5 .1 mm/cycle), so that overload fracture occurs within 30 cycles after the fracture mode changes.

Some of the test specimens exhibited signs of buckling during this test program, particularly those run at 275°F (135°C). When buckling occurred, the test was stopped and repeated with a fresh specimen. Tests at higher temperatures, as well as those from an earlier test program[2] did not exhibit this tendency. The strain aging behavior of the SA210-A1 material is attributed as causing the tendency to buckle at lower temperatures.

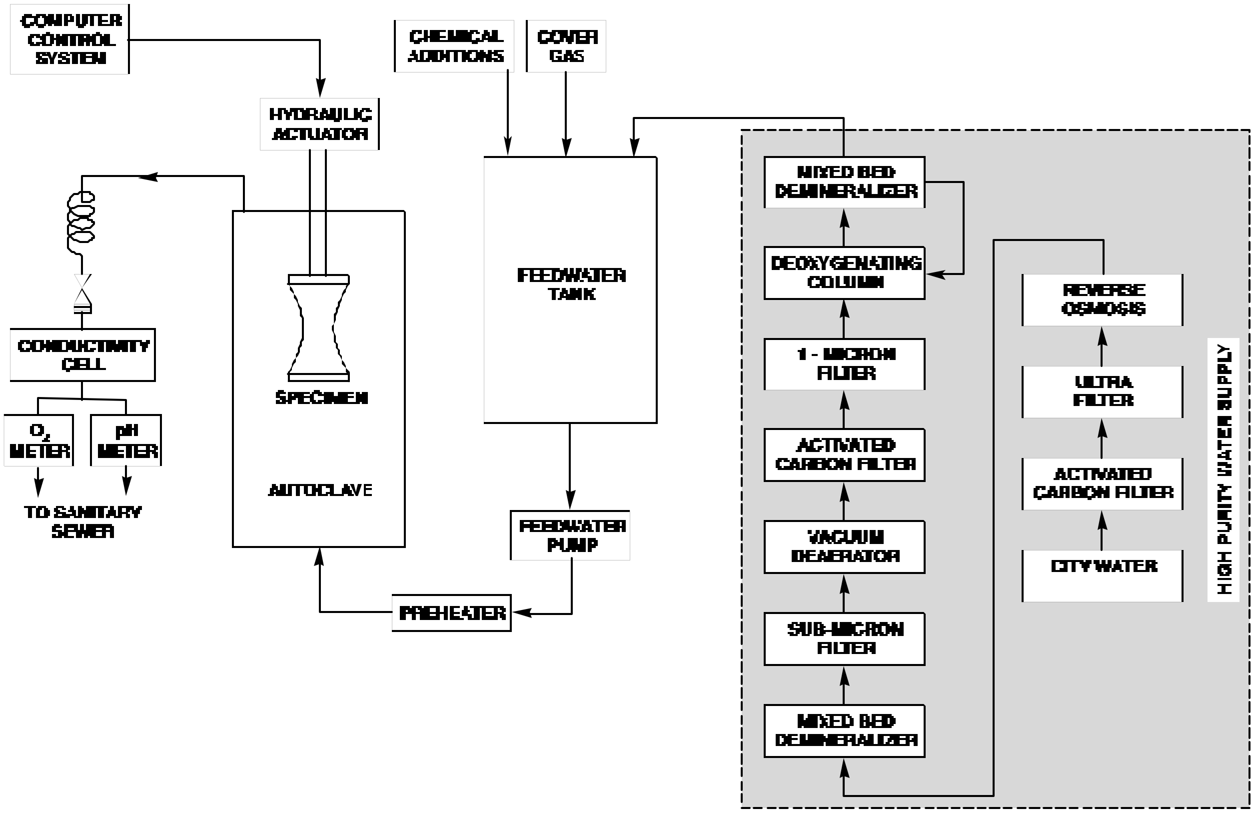

Figure 2-1. Schematic of the feedwater delivery and control system used for corrosion fatigue crack initiation tests.

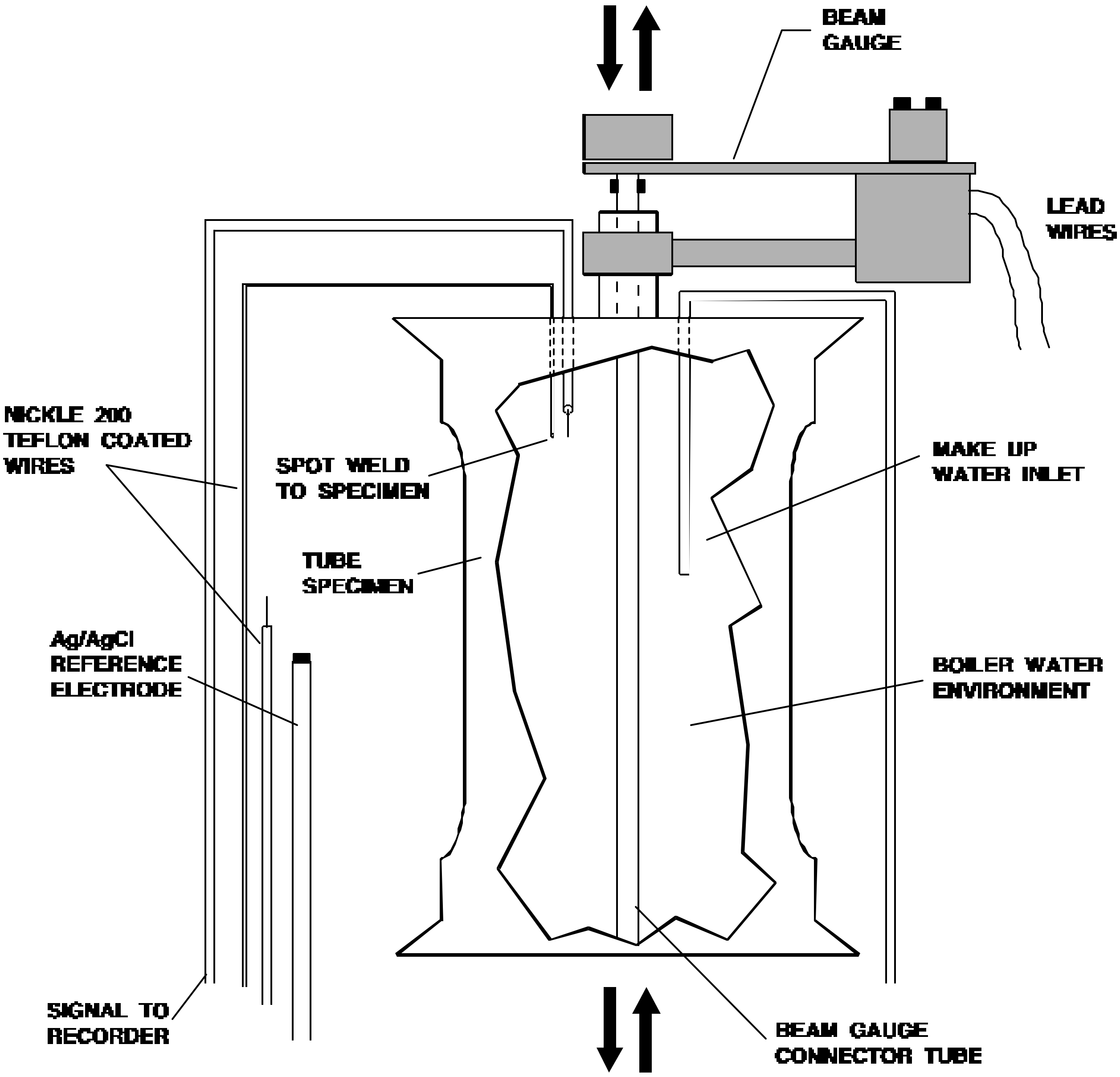

Figure 2-2. Schematic of the reference electrode arrangement used to monitor electrochemical potential of the specimens.

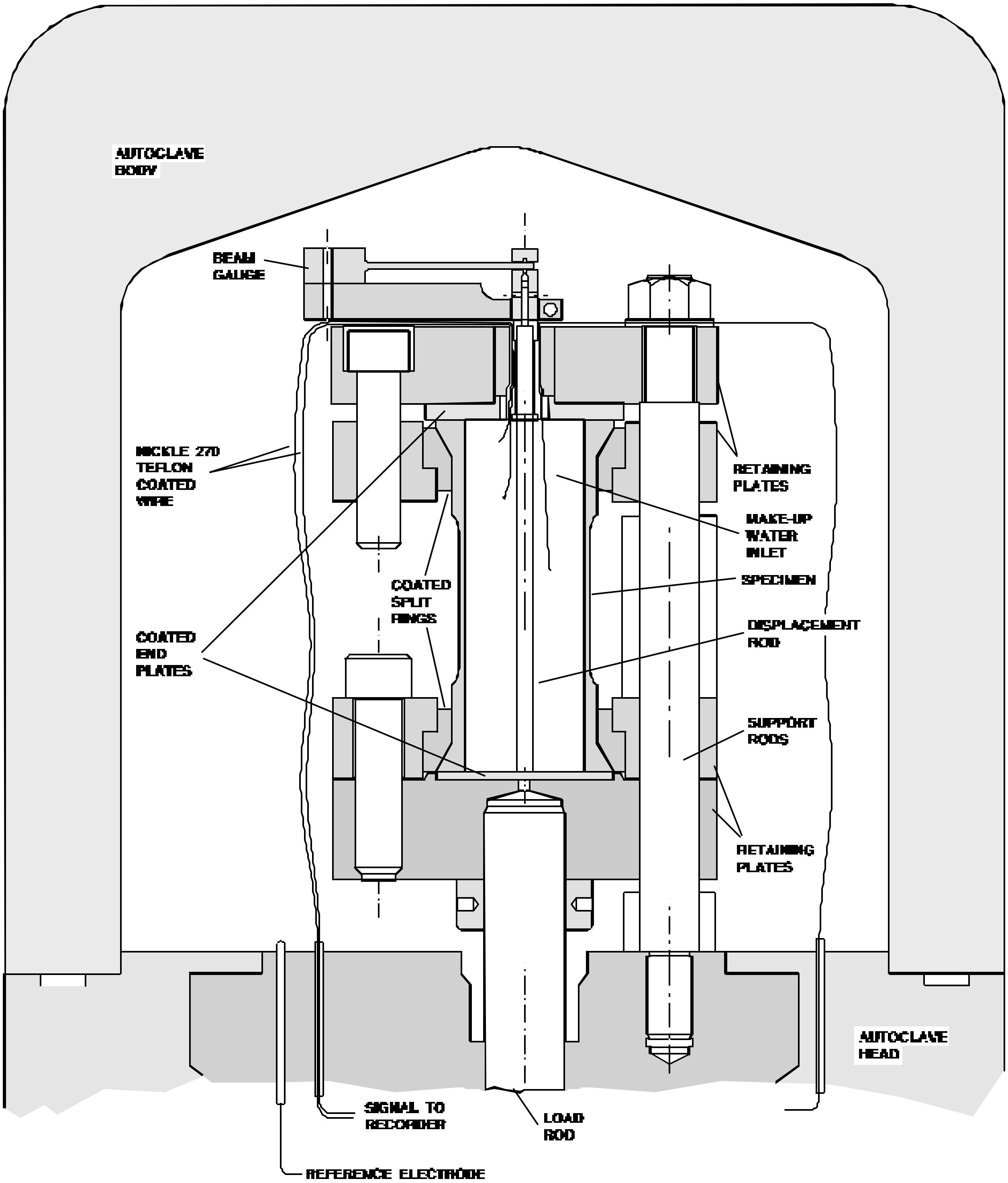

Figure 2-3. Schematic of the mechanical test system arrangement used to apply desired strains to the test specimens.

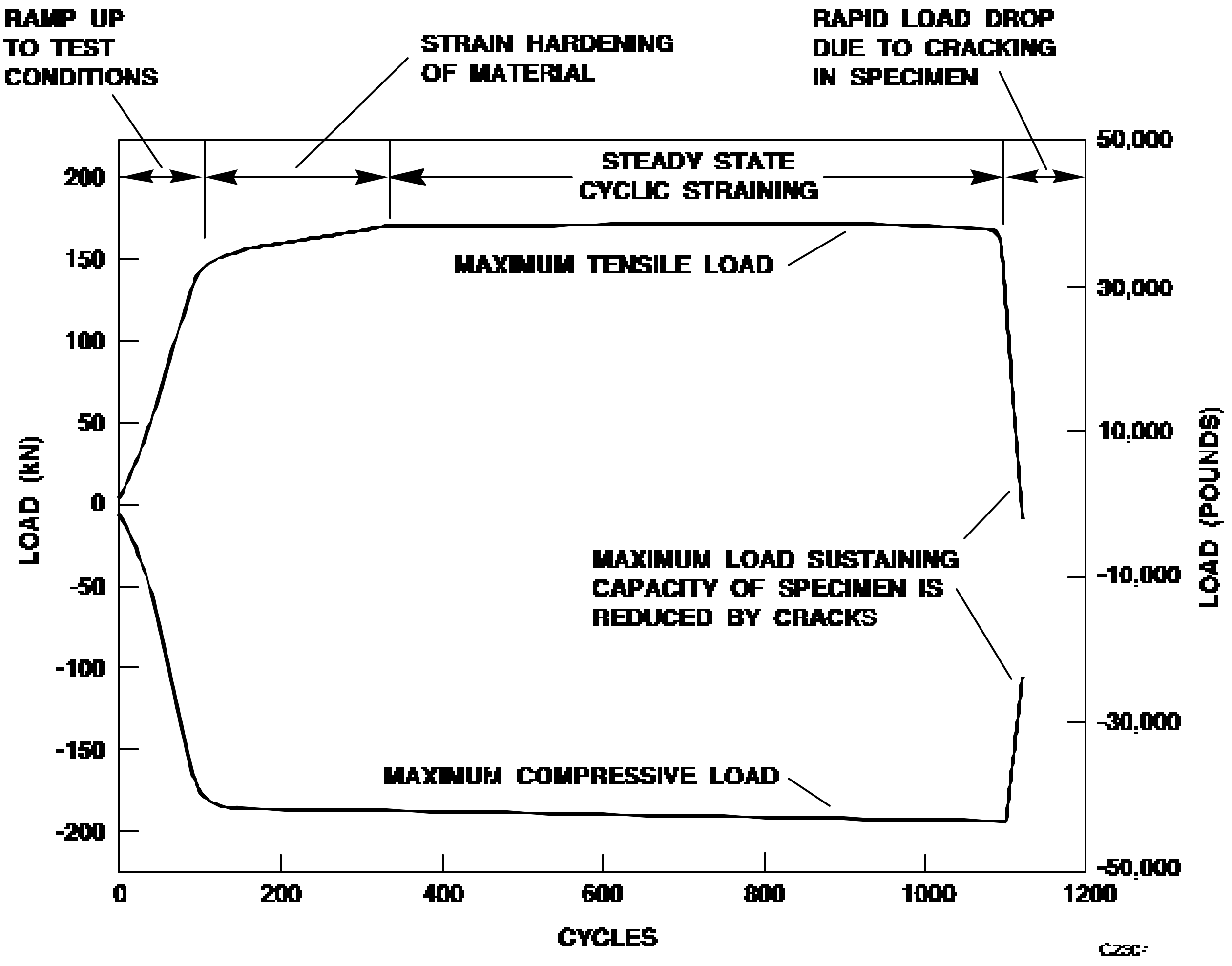

Figure 2-4. Typical Load History of Test Specimens. Note That the Load Drops Dramatically after Cracks are Initiated.

3

RESULTS

Effect of pH Due to Phosphate Return

The effect of phosphate hide-out and return on SA210-A1 boiler tube material is given in Table 3.1. It is clear from these results that lowering the pH reduces the number of cycles to initiate cracks in the SA210-A1 boiler tube material. This suggests that corrosion fatigue may be worse in boilers that exhibit phosphate hide-out and return. During boiler shut-down or pressure reduction, the phosphate that hid out in the boiler during pressure increase is returned to the system. The return of phosphate during reduction in boiler pressure can cause a pH depression of the boiler water; this can reduce the life of a component suffering from corrosion fatigue.

Table 3-1. Summary of the effect of phosphate hide-out and return on the time to initiate cracks in SA210-A1 boiler tubes. All tests were run using a strain amplitude of 0.5% with no mean strain.

Temperature (F/C)	Frequency (hz)	Dissolved Oxygen (ppb)	Chloride (ppb)	pH	Phosphate (ppb)	Sodium (ppb)	Cycles to Initiate Cracks (N)
400/204	0.0005	5	600	5.9	3000	1115	582
400/204	0.0005	5	600	9	3000	2064	772
525/274	0.0005	5	600	5.9	3000	1115	540
525/274	0.0005	5	600	9	3000	2064	857

Figure 3-1 shows how corrosion fatigue is affected by pH depressions in phosphate-treated boiler water. Figure 3-1 also shows selected data from previous corrosion fatigue studies that are consistent with this current study[2]. The pH values used here are all room-temperature values. In deaerated solutions, the time to initiate cracks decreases as the pH is decreased. At 400°F (204°C), the cycles to initiate cracks is described by Equation 3-1

$$\text{Log}(N) = 0.0478(\text{pH}) + 2.462 \qquad \text{Eq. 3-1}$$

At 525°F (274°C) the cycles to initiate cracks is described by Equation 3-2.

$$\text{Log}(N) = 0.0743(pH) + 2.295 \qquad \text{Eq. 3-2}$$

Where N = Number of cycles to initiate a crack

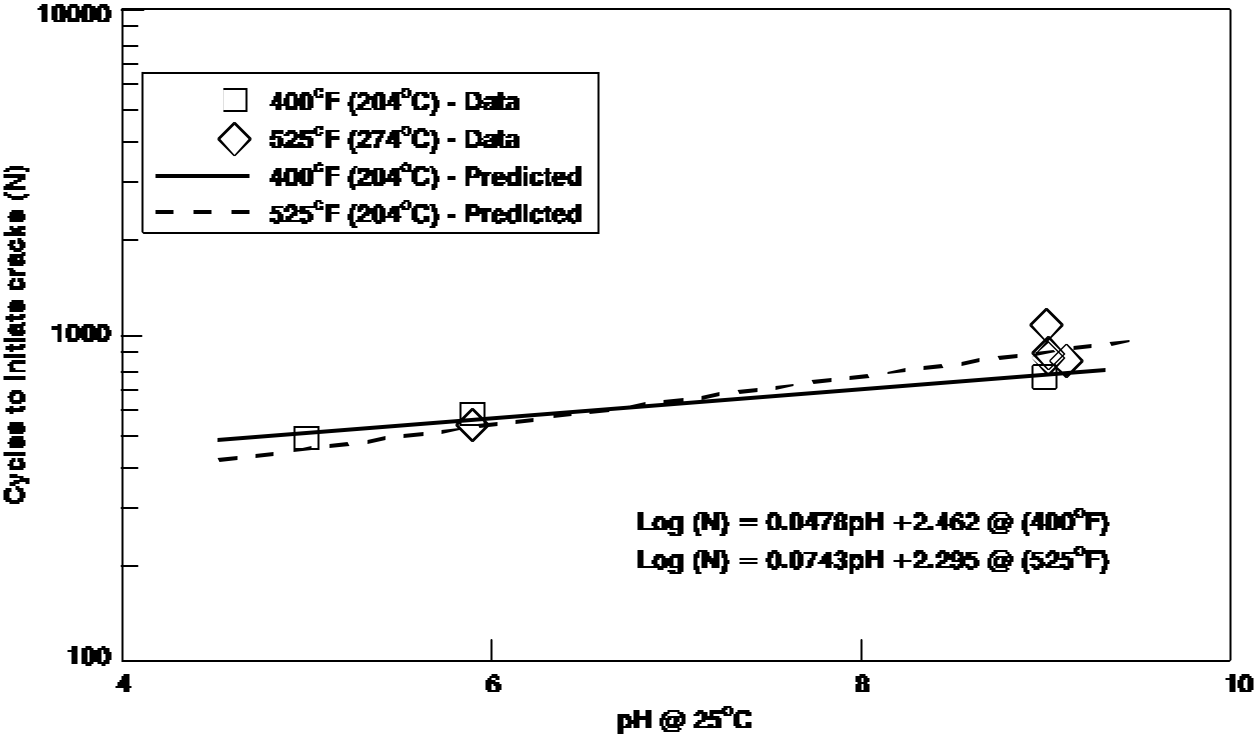

Figure 3-1. The influence of pH on cycles to intiate cracks in phosphate treated deaerated boiler water for SA210-A1 boiler tube material. This data shows that pH depressions resulting from hide-out return during boiler start-up can reduce the life of tubes suffering from corrosion fatigue.

The data in Table 3-1 and Figure 3-1 clearly show that a boiler experiencing phosphate hide-out return and an associated pH depression will also experience accelerated corrosion fatigue. The degree of this effect depends on the degree of phosphate return that occurs during boiler shutdown or pressure reduction. Upon re-starting or increasing pressure, conditions that maximize corrosion fatigue damage occur: high strains, slow strain rates, and intermediate temperatures. Therefore, any upsets in the water chemistry that occur during this time will maximize their influence on corrosion fatigue damage.

Effect of Other Variables in Phosphate Treated Boiler Water

The variables in the secondary matrix of interest in this study were temperature, frequency, and dissolved oxygen. The effect of each of these variables is presented separately.

Temperature. Figure 3-2 shows the influence of temperature on cycles to initiate cracks for deaerated water at pH levels of 5 and 9; all data were generated at 0.0005 hz. There is a general trend for the cycles to initiate cracks to reach a minimum at around 400°F (204°C). This is similar to corrosion fatigue data in other high-temperature water environments, where a maximum in crack growth rates are seen near this same temperature[5,6].

In aerated water, there is a more complex behavior; an interaction between frequency, dissolved oxygen, and other possible variables complicate the effect of temperature. Fatigue crack growth rates vary over two orders of magnitude in the intermediate temperature range of 300° - 600°F (149° - 316°C); these variations in the crack growth rates are attributed to different loading frequencies and dissolved oxygen in the water[5,6]. It is possible that a similar trend is occurring for crack initiation as well: the effects of water chemistry and loading frequency may be maximized at intermediate temperatures for crack initiation.

For both aerated and deaerated water, corrosion fatigue is most pronounced at intermediate temperatures. This suggests that most corrosion fatigue damage does not occur in the early stages of boiler start-up, but rather during later stages when the temperatures rise above 300°F and the boiler begins to build pressure. If water chemistry upsets persist into this stage of start-up and the peak applied strains remain high, then significant corrosion fatigue may occur.

Loading Frequency (Strain Rate)

The effect of loading frequency on crack initiation is shown in Figure 3-3. There is a general trend for slower loading frequencies to reduce the number of cycles to initiate cracks. Furthermore, there is a trend for the effect of slower loading frequencies to be greater as the test environment becomes more corrosive (for example, higher oxygen, higher temperature, etc.).

Lower testing frequencies and more corrosive conditions allow more corrosion damage to occur during each loading cycle. Therefore, there is generally a greater amount of corrosion fatigue for each loading cycle when a boiler experiences slower loading frequencies (slower strain rates) and more corrosive environments. These two factors directly contribute to the corrosion aspect of corrosion fatigue.

It typically takes several hours for boiler start-up, which corresponds to a frequency of less than 0.00005 hz. Because cycling boilers operate at these slower loading frequencies (slower strain rates) that accentuate corrosion fatigue damage, it is particularly important to maintain good quality boiler water during start-up. As shown in Figure 3-3, slower loading frequencies are not as harmful if good quality boiler water is maintained.

At 525°F (274°C) in good quality (5 ppb DO_2 and pH 9) water there is very little effect of test frequency. At lower temperatures (275°F) there is also very little effect of test frequency even for very poor quality water (1000 ppb DO_2 and pH 5); this is consistent with the effect of test temperature noted above. However, the good quality water at 525°F (274°C) still consistently shows less tendency to cause cracks to initiate than the poor quality water at 275°F (135°C). At 525°F (274°C) in poor quality (300 ppb DO2 and pH 7) water, there is a large effect of test frequency.

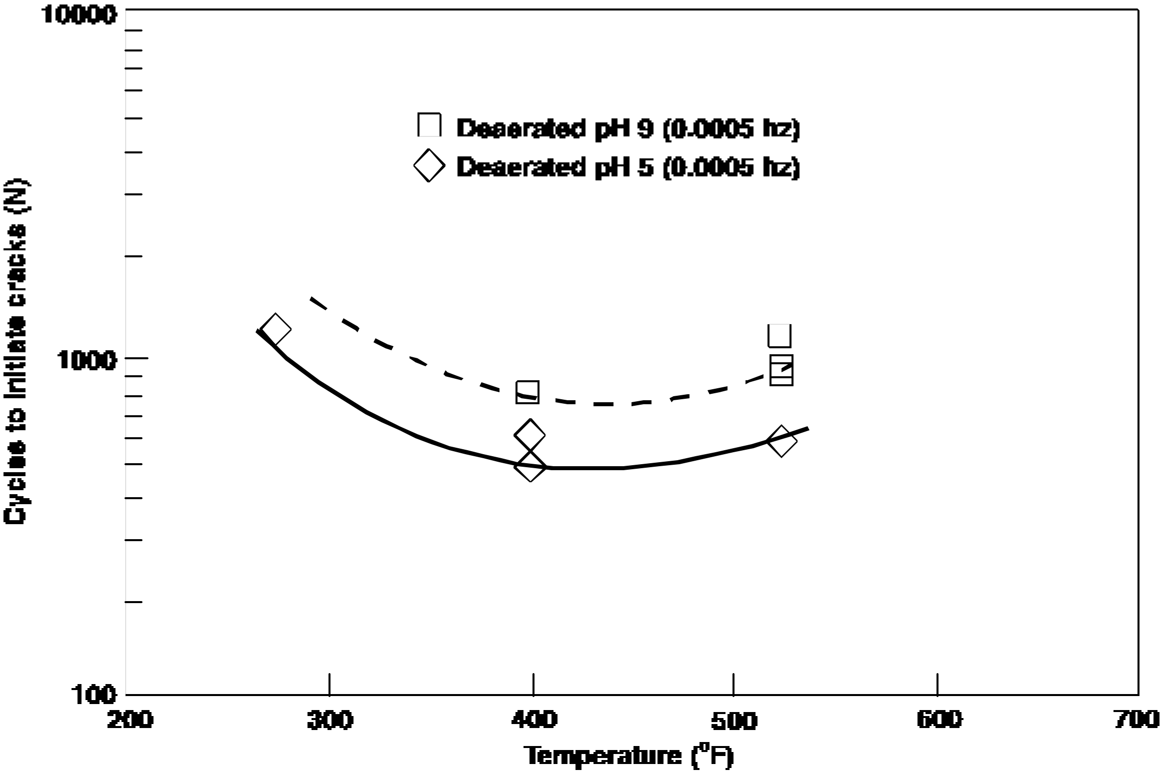

Figure 3-2. The effect of temperature on cycles to initiate cracks for deaerated phosphate treated boier water. All tests were run using +/- 0.5% alternating strain and a frequency of 0.0005 hz.

Table 3-2. Summary of results from the secondary test matrix which evaluates various environmental influences upon the time to initiate cracks on SA210-A1 boiler tubes exposed to phosphate treated boiler water. All tests were run using a strain amplitude of 0.5% with no mean strain.

Temperature (F/C)	Frequency (hz)	Dissolved Oxygen (ppb)	Chloride	pH	Phosphate (ppb)	Sodium (ppb)	Cycles to Initiate Cracks (N)
275/135	0.0005	5	2500	5	1960	1902	1198
275/135	0.0005	50	2500	9	881	2262	905
275/135	0.0005	1000	2500	5	1960	1902	554
275/135	0.01	5	2500	9	881	2262	393
275/135	0.01	1000	2500	5	1960	1902	1584
275/135	0.01	1000	2500	5	1960	1902	481
400/204	0.0005	5	2500	5	1960	1902	484
525/274	0.0005	300	2500	5	1960	1902	552
525/274	0.0005	300	2500	5	1960	1902	210
525/274	0.01	300	2500	5	1960	1902	692
650/343	0.0005	1000	2500	5	1960	1902	60
650/343	0.0005	50	2500	5	1960	1902	559
650/343	0.01	1000	2500	5	1960	1902	405

The trend lines shown in Figure 3-3 follow a power law relationship, as described in Equation 3-3:

$$\log(N) = b \log(n) + c \qquad \text{Eq. 3-3}$$

Where N is the number of cycles to initiate cracking, b is the slope of the line (constant), n is the loading frequency in hz, and c is the intercept of the line (constant). The slope of the line, b, is a direct measure of the influence of loading frequency on corrosion fatigue crack initiation. Table 3-3 summarizes the effect of loading frequency on corrosion fatigue cracking; larger values of b indicate a greater influence of loading frequency.

Dissolved Oxygen

The effect of dissolved oxygen is shown in Figure 3-4. There is a decrease in the cycles to initiate cracks as the dissolved oxygen is increased. The influence of dissolved oxygen at 400°F (204°C), 525°F (274°C), and 650°F (343°C) is significant and generally follows the trend line established previously for 525°F (274°C)[2]. However, the influence of dissolved oxygen appears to be less at 275°F (135°C) than for the higher temperatures.

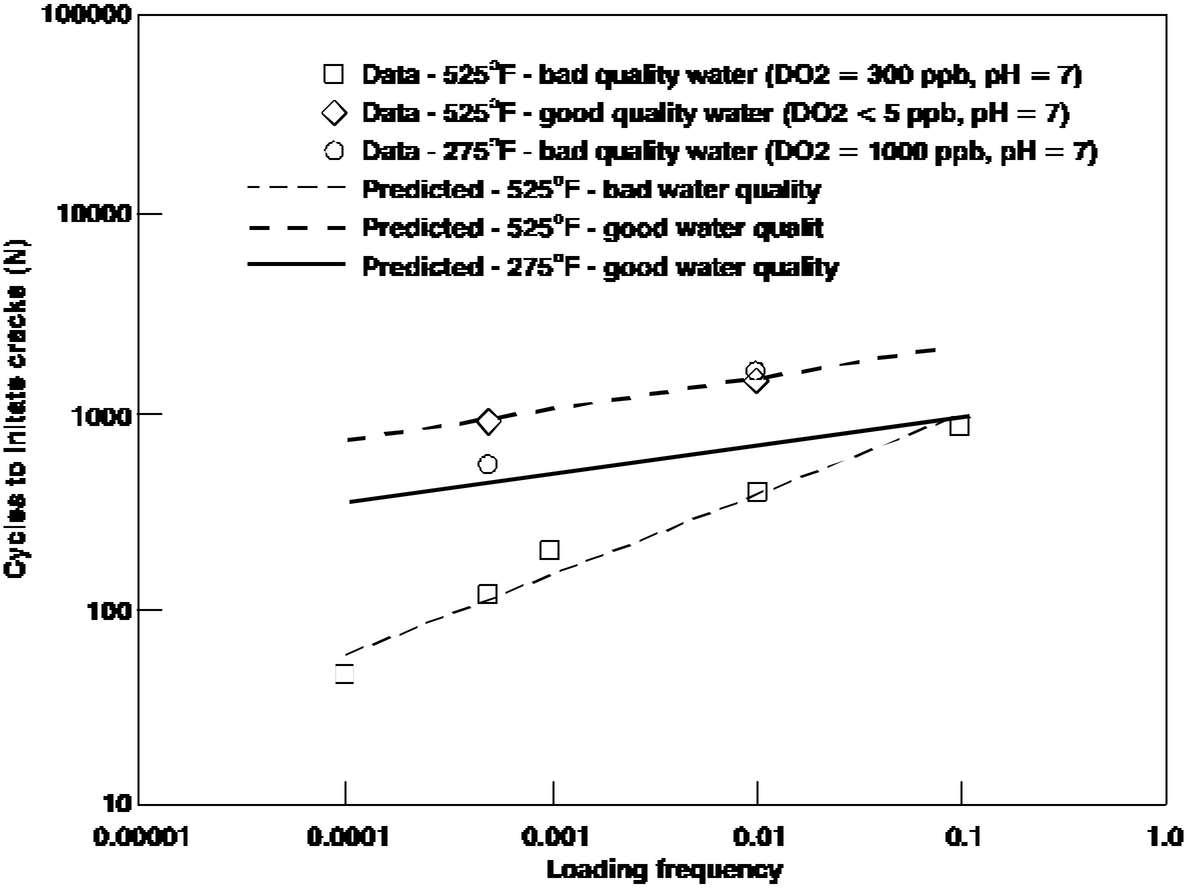

Figure 3-3. The effect of test frequency on cycles to initiate cracks in SA210-A1 tube material.

The predictive equation from previous work[2] for the effect of dissolved oxygen at 525°F (274°C) appears to also be valid for all temperatures between 400°F and 650°F (204°C and 343°C). In addition, the data at 275°F (135°C) appear to follow the same type of relationship. Equation 3-4 gives the general relationship between dissolved oxygen and corrosion fatigue cracking:

$$N = C\,(DO)^{n} \qquad \text{Eq. 3-4}$$

Where N = number of cycles to initiate cracks

DO = dissolved oxygen (ppb)

C = pre-exponential constant

n = oxygen influence exponent

Table 3-3. Influence of loading frequency upon corrosion fatigue crack initiation.

Temperature	Description	Dissolved Oxygen (ppb)	pH	Chloride (ppb)	Influence of Frequency (b)
275°F (135°C)	Poor Quality Water	1000	5	2500	0.1431
525°F (274°C)	Good Quality Water	< 5	9	30	0.1808
525°F (274°C)	Poor Quality Water	300	7	600	0.4093

Table 3-4 gives the values for C and n for the predictive curves at 275°F (135°C) and also for the higher test temperatures.

The smaller influence of dissolved oxygen upon corrosion fatigue cracking at lower temperatures is important. Earlier field monitoring work[3] had shown that a large fraction of corrosion fatigue damage occurs during boiler start-up when the applied strain is the highest and earlier laboratory work had not isolated the effects of temperature. During the shutdown period, the dissolved oxygen can be very high, maybe at saturation levels. But as soon as the unit starts to steam, the dissolved oxygen levels usually quickly reduce to below 100 ppb, and are not excessively high at the time when the strain is the highest. These features combine to indicate that dissolved oxygen is still important but that it lessens at the lower temperatures of start-up.

The dissolved oxygen level influences the electrochemical potential of the carbon steel boiler tube specimen. Figure 3-5 shows the relationship between potential and dissolved oxygen content in the water[8]. Electrochemical potential measurements were made during selected tests and are also shown on Figure 3-5. Higher dissolved oxygen contents correspond to higher potential values. Although there is some deviation between the measured values from this study and the electrochemical behavior for carbon steel reported in the literature, they are in fairly reasonable agreement.

The electrochemical potential of a boiler tube is an indication of the corrosion reaction occurring on its surface. Higher oxidation potentials correspond to higher oxidation states of the metal ion. For the case of corrosion fatigue of carbon steel or iron in water, there are basically two oxidation states: Fe^{2+} and Fe^{3+}.

Table 3-4. Values for the constants in Equation 3-4 for the various test temperatures.

Temperature	Pre-Exponential Constant (C)	Oxygen Influence Exponent (n)
275°F (135°C)	1548	-0.1465
400°F (204°C) 525°F (274°C) 650°F (343°C)	2445	-0.5256

These two oxidation states correspond to the lower and upper plateaus for each curve shown in Figure 3-5. The oxides produced on carbon steel in high-temperature water are Fe_3O_4 and Fe_2O_3; higher oxidizing potentials favor the formation of Fe_2O_3.

Most boiler water chemistries are designed to rely on the formation of an Fe_3O_4 layer on the steel to minimize corrosion of the boiler tubes. Any perturbation of this layer will increase corrosion and can influence corrosion fatigue. Higher oxidizing potentials have consistently been linked to accelerated environmental cracking mechanisms such as corrosion fatigue. Therefore, higher oxidizing potentials, which fall outside the Fe_3O_4 stability range, are expected to lead to accelerated corrosion fatigue damage provided that this occurs when peak strains are high.

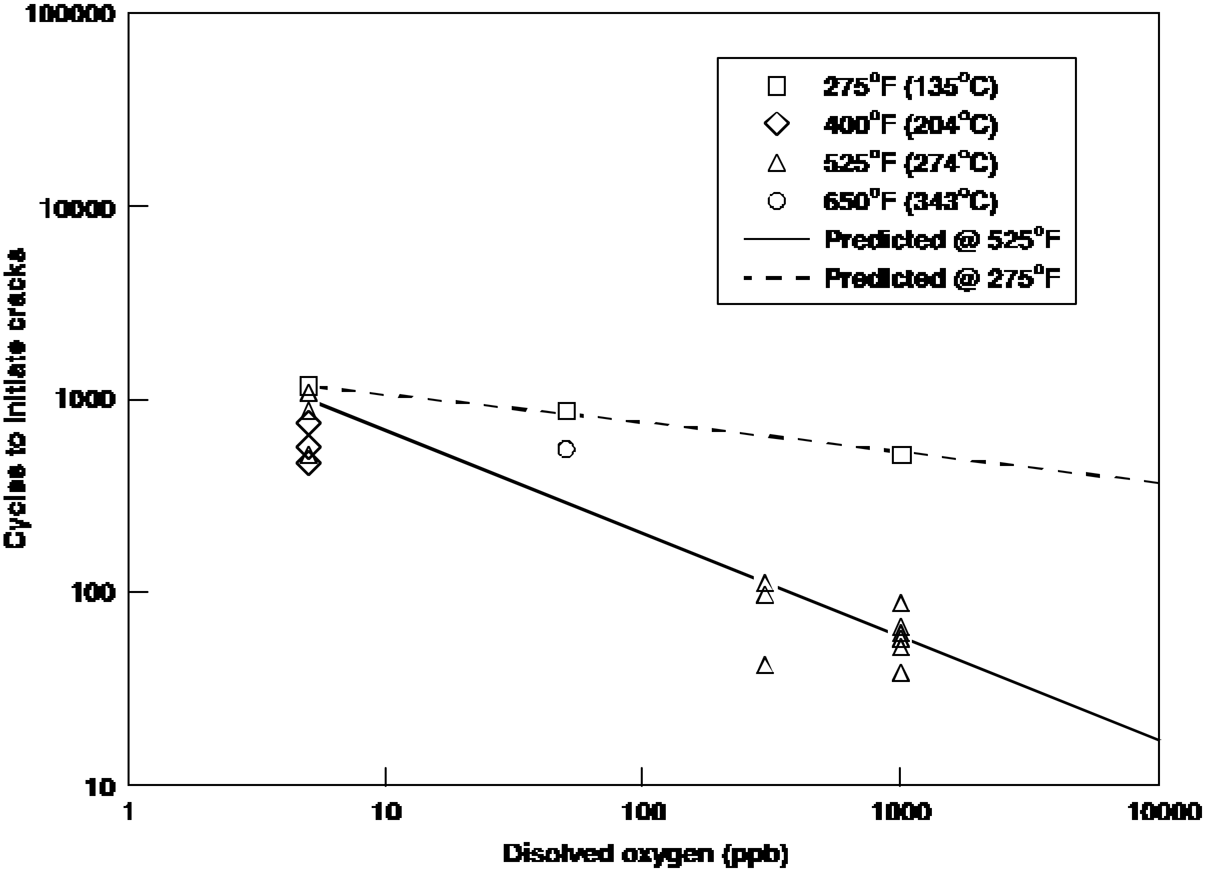

Figure 3-4. The effect of dissolved oxygen on cycles to intitate cracks in SA210-A1 tube material.

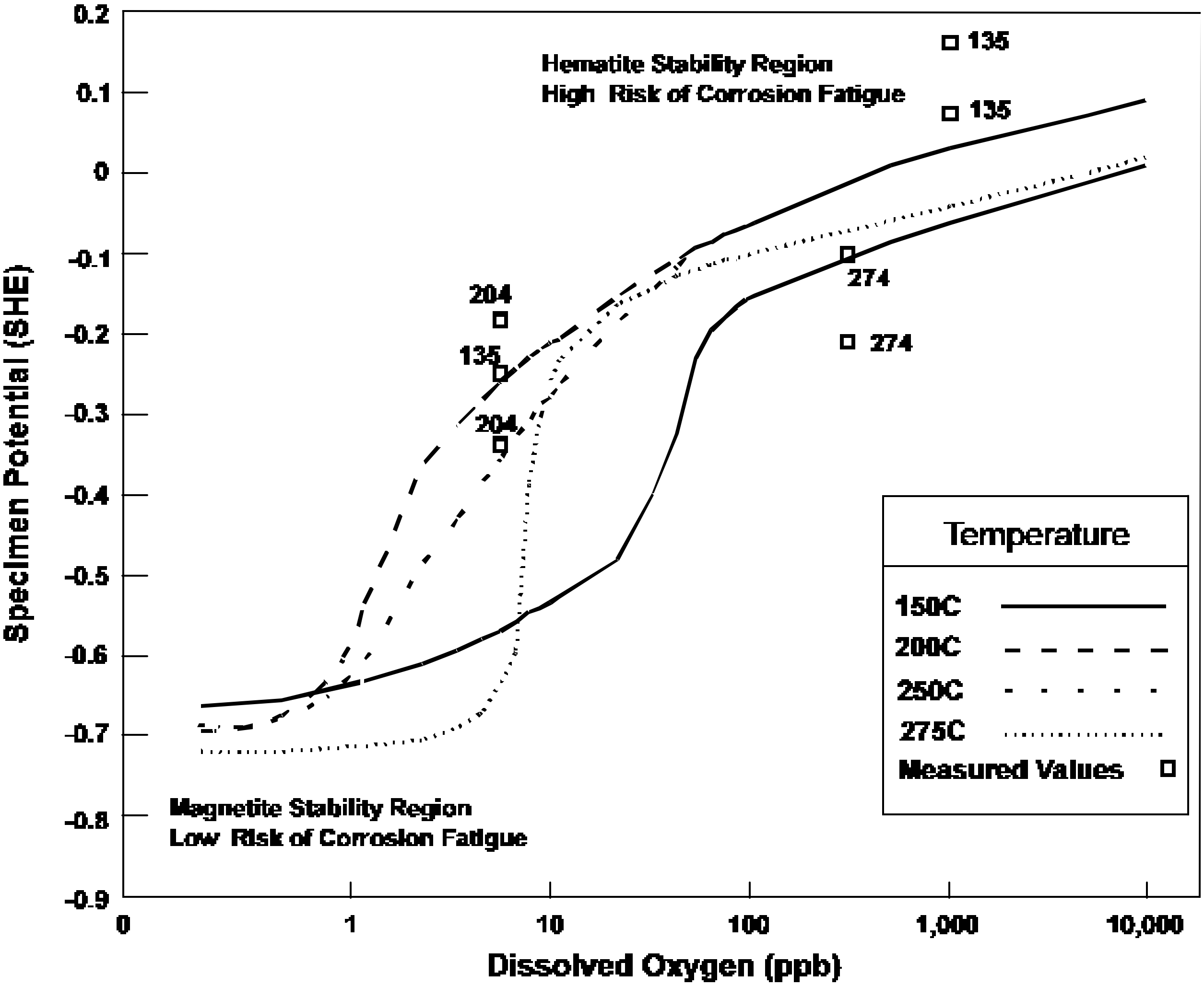

Figure 3-5. The effect of dissolved oxygen on the electrochemical potential of SA210-A1 boiler tube material (after Reference 8)

4

DISCUSSION

The fact that corrosion fatigue resistance of boiler tube material is influenced by the boiler water chemistry has been apparent for a number of years. This program demonstrates how several boiler operating factors can influence corrosion fatigue cracking. While water chemistry and operation variables do influence corrosion fatigue, it should be recognized that strain levels are of primary importance. Corrosion fatigue occurs only at selected locations in a boiler where high local strains can occur (such as adjacent to attachments). However, similar units do not always have similar corrosion fatigue behavior; this indicates that operation and boiler water treatment can indeed play a significant role.

Figure 4-1 shows schematically how several parameters vary with time when starting a boiler. The dissolved oxygen content of the boiler water can initially be at quite high levels, even at saturation. However, the dissolved oxygen levels typically drop to fairly low levels early in the boiler start-up cycle. Dissolved oxygen levels in the boiler typically drop to below 50 ppb before the boiler starts to become pressurized[3].

The pH considered here is for a boiler that experiences phosphate hide-out. During boiler shutdown (or even during pressure reduction), the pH can become depressed to low levels if acidic phosphates are returned into the boiler water. The pH of the boiler water can remain at low levels for a significant period, extending well into the boiler start-up cycle until hide-out starts to recur.

Strain on the boiler tubes will increase during start-up and go through a maximum. There are two sources of strain: pressure-induced strains and thermally induced strains. Pressure-induced strains will continue to increase until steady-state pressure is achieved. On top of these strains are thermally induced strains; the maximum thermal strains will coincide with the time that the largest thermal gradients occur in the boiler, typically near the end of the start-up transient.

As shown in Figure 4-1, the conditions considered the most damaging occur in the middle and later parts of the start-up cycle. Although dissolved oxygen levels are reduced during this time, the strains are at their highest level, the pH may still be considerably depressed, and the temperatures are likely to be near the 400 - 525°F (204 - 274°C) range.

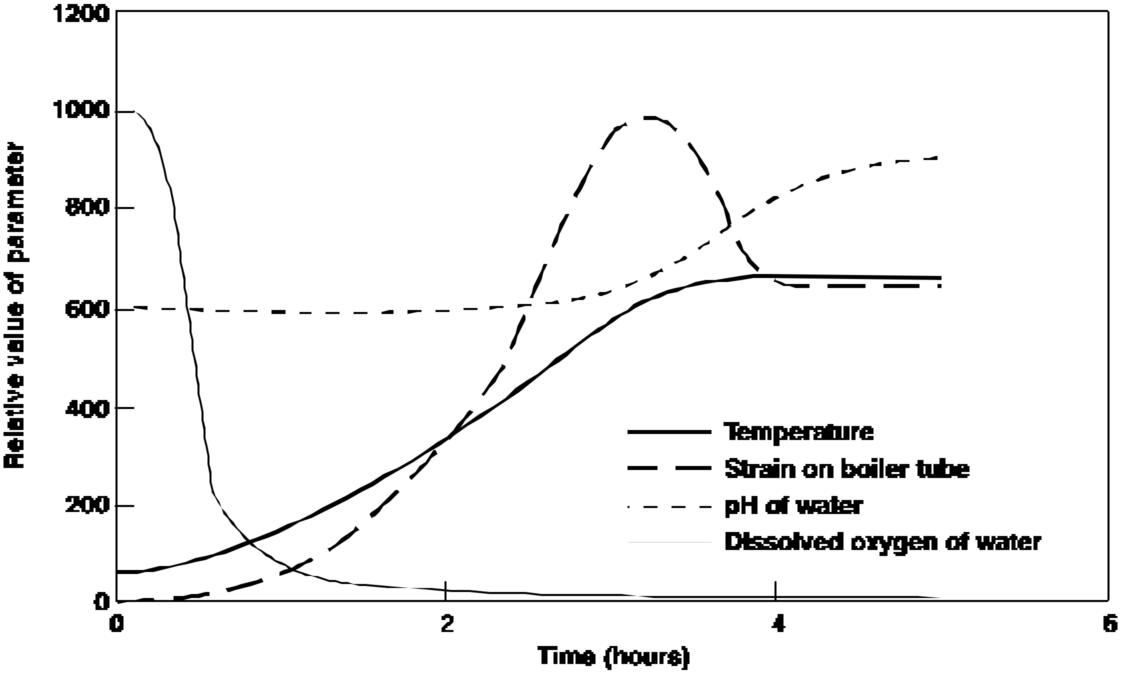

Figure 4-1. Schematic showing how several parameters vary during a boiler start-up.

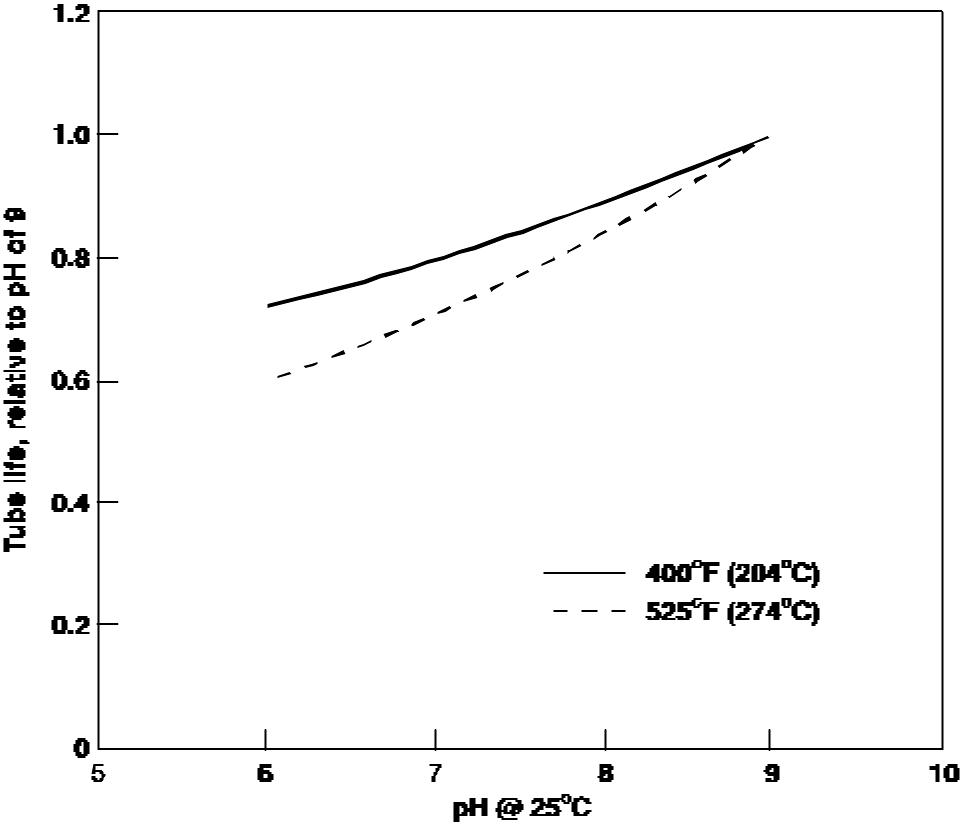

Figure 4-2. Tube life as a function of pH depressions at 400 and 525°F (204 and 274°C).

This program has clearly demonstrated the impact of phosphate hideout return on corrosion fatigue. A depression in the boiler water pH due to phosphate return will increase corrosion fatigue damage. Figure 4-2 shows the loss in tube life due to pH depressions resulting from hideout return. A value of 1 was assigned to a pH level of 9; decreasing the pH level results in tube lives that are some fraction of this value. The more depressed the pH becomes during the hideout return period, the greater the risk for corrosion fatigue damage. For example, Figure 4-2 shows that if the pH is reduced to 8 during shutdown and early boiler start-up, the tube life is reduced 0.90 to 0.84, or a loss of 10% - 16% (corresponding to temperatures of 400 F and 525°F respectively).

Dissolved oxygen has a smaller influence at a temperature of 275°F (135°C) than it does at higher temperatures (see Figure 3-4). When a boiler is shut down, air in-leakage can occur through vents in the steam drum and other locations and by using aerated water as make-up. This gives rise to initially high levels of dissolved oxygen; however, these levels rapidly fall as the boiler heats up. Oxygen is reduced as the boiler water is heated and typically is below 50 ppb by the time steaming first occurs at around 212°F (100°C). Therefore, the occurrence of high oxygen levels will not likely coincide with the damaging temperatures and strain levels. Note that high oxygen levels in the boiler water are undesirable; it aggravates corrosion fatigue and also can influence other forms of corrosion attack, such as pitting and under-deposit corrosion.

An influence diagram, shown in Figure 1-1, is currently being used to assess the potential for corrosion fatigue occurring in a boiler. The data from this study can be used to evaluate the environmental parameter (E) used in the influence diagram for phosphate-treated boilers. The environmental parameter is calculated using the worksheet shown in Table 1-1. This worksheet weights the parameters that influence corrosion fatigue by assigning a value to each parameter; higher values correspond to a greater influence on corrosion fatigue.

Table 1-1 indicates that phosphate hide-out and excursions that cause caustic gouging or hydrogen damage are the most heavily weighted; these events have the highest scores and a value of 3. Since corrosion fatigue is linked to the amount of corrosion damage that occurs, conditions that are most corrosive should receive the greatest weight.

The next most important factors in Table 1-1 are boiler water pH, conductivity, and feedwater dissolved oxygen during start-up as well as good lay-up procedures (low oxygen and controlled pH). These have intermediate scores and a value of 2. The data from this study show that pH excursions can indeed have a pronounced effect on corrosion fatigue for phosphate-treated boilers. It is expected that pH excursions for other water treatment schemes would have a similar effect; this is the subject of an ongoing EPRI-sponsored test program.

The influence of dissolved oxygen has been shown to be most significant at higher temperatures. Dissolved oxygen levels typically drop to low levels before the most damaging temperature regions are reached. The data from this study suggest that dissolved oxygen during start-up is significant, but the most damaging conditions of high strains and temperatures in the 400 - 525°F (204 - 274°C) range do not usually coincide with high oxygen in the boiler water. Therefore, the intermediate ranking appears to be appropriate.

Lay-up procedures are also important because corrosion damage propensity can be influenced. If oxygen levels are high, pitting damage can occur; pits can act as stress concentrators that can initiate corrosion fatigue. In addition, improper lay-up water chemistries (such as high oxygen levels) can lead to crevice corrosion at the tips of existing corrosion fatigue cracks, which further advances the crack tip into the tube wall. Noted that the length of the lay-up period and the level of aeration can influence the amount of corrosion damage and subsequent corrosion fatigue damage. If lay-up periods are particularly long, additional evaluation procedures may be needed.

Chemical cleaning, on-line (at operating conditions) boiler water pH, on-line boiler water conductivity, and on-line feedwater dissolved oxygen are also seen as contributing to corrosion fatigue damage and have a weighted value of 1. Previous work showed that on-line operating hours influence corrosion fatigue and the number of boiler start-ups. Therefore, anything that increases the corrosivity of the boiler water, such as pH depressions or high conductivity excursions, will aggravate corrosion fatigue.

In addition, chemical cleaning removes much of the protective oxide layer on the boiler tubes, putting them into a more active state. Upon re-starting a boiler after a chemical cleaning, there is an increased amount of corrosion (oxidation) of the boiler tubes that will aggravate corrosion fatigue. Chemical cleaning may also cause some pitting damage if not administered correctly, which also aggravates corrosion fatigue.

This study supports the current position on environmental variables that influence corrosion fatigue. There is now additional data that shows in greater detail how some of the environmental factors influence corrosion fatigue. The principal findings from this study are the influence of pH on corrosion fatigue and the synergism between oxygen and temperature. Based on the data from this study, further modifications to the environmental parameters (see score and value in Table 1-1) can be recommended.

The two areas specifically addressed by this study are the on-line operating ranges and start-up ranges for environmental parameters. This study shows that higher dissolved oxygen and lower pH values are more damaging at higher temperatures. To reflect these, the following changes are recommended to the current environmental parameter evaluation shown in Table 1-1.

The principal recommended change to Table 1-1 is to differentiate between early boiler start-up and later start-up. First, emphasis is needed to differentiate between the importance of dissolved oxygen during early and later parts of boiler start-up. Data from this study suggest that operating temperatures of 204°C (400°F) or higher maximize the influence of oxygen on corrosion fatigue.

During early start-up, when temperatures are lower, the influence of dissolved oxygen is minimized. Therefore, two different weighting values should be used for these two temperature regimes. A value of 1 is used during early start-up when temperatures are low, and a value of 2 is used during later start-up when they are higher. It is difficult to assign an exact temperature for the demarcation between early and later start-up. However, operators should understand that peak strains — acting in concert with high oxygen and warmer water temperatures — are the principal damaging conditions.

Secondly, the influence of pH is also greater at higher temperatures. In a similar manner to dissolve oxygen, pH excursions can also be weighted for the two temperature regimes cited for dissolved oxygen. A value of 2 is used is during early start-up when temperatures are lower, and a value of 1 is used during later start-up when temperatures are higher.

It is recognized that higher temperatures generally coincide with higher strain levels. Therefore, any water chemistry upsets that occur in the latter part of the start-up cycle are likely to be more damaging than those that occur early on during boiler start-up.

The greater influence of dissolved oxygen and pH excursions at higher temperatures may be considered also for the typical on-line operating ranges. However, upsets during steady-state operation are not likely to coincide with high-stress gradients found during boiler start-up. These upsets are currently accounted for in Table 1-1; no further modifications are suggested to these values.

The recommended changes to the environmental parameter evaluation are given in Table 4-1. The boiler start-up has now been split into two operating temperature ranges — above and below 204°C (400°F). This is the only change from the previous evaluation parameters shown in Table 1-1.

These environmental parameters provide a good first-order evaluation on their influence on corrosion fatigue. Beyond this, each unit must be considered on an individual basis, since start-up and operational practices vary.

Table 4-1 Modified Environmental Parameter Evaluation, Showing Recommended Changes to Boiler Start-Up.

Value	Evaluation	Score			
3	Phosphate Boiler Alkalinity Control	3	6	9	
	Does the boiler experience phosphate hide-out or phosphate carry-over to the reheater?	No	Irregularly	Regularly	
3	Excursions	3	6	9	
	How many hydrogen damage or caustic gouging events resulting in tube failures have occurs over the life of the boiler?	0	1	>1	
	Typical On-Line Chemical Operating Ranges	1	2	3	
1	(1) Boiler water at blowdown pH	9.0-9.6	8.0-10.0	< 8, >10	
1	Cation conductivity (minus Phosphate correction, 4.1 x ppm PO_4)	≤6	6 - 30	> 30	
1	(2) Feedwater at the economizer inlet Dissolved Oxygen (ppb)	≤5	≤20	> 20	
	Typical Early Start-Up Operating Ranges	1	2	3	
	1) Boiler Water -at blowdown during early start-up				
1	pH	9.0-9.6	8.0-10.0	<8, >10	
1	Cation Conductivity (µS/cm) (minus phosphate correction, 4.1 x ppm PO_4)	≤6	6-30	>30	
1	2) Feedwater - at economizer inlet during early start-up Dissolved Oxygen (ppb)	<50	<200	>200	
	Typical Latter Start-Up Operating Ranges	2	4	6	
	1) Boiler Water -at blowdown during latter start-up				
2	pH	9.0-9.6	8.0-10.0	<8, >10	
2	Cation Conductivity (µS/cm) (minus phosphate correction, 4.1 x ppm PO_4)	≤6	6-30	>30	
2	2) Feedwater - at economizer inlet during latter start-up Dissolved Oxygen (ppb)	<50	<200	>200	
	Chemical Cleans	1	2	3	
1	How many chemical cleans using a hydrochloric acid solution has the boiler been exposed to?	0	1	>1	
	Boiler Shutdown/Lay-Up Procedures	2	4	6	
2	What actions are taken for shutdown corrosion protection: a) N2, cap on drum and treat water if boiler not drained. b) Refill drained boiler with chemically treated water to control pH and oxygen. c) Ensure dry storage if drained. d) Monitor and adjust pH and oxygen in boiler during wet lay-up.	Actions a) to d)	actions a) and b)	no action	
	Total Value (Total for Questions Answered)			Total Score	

Environment Parameter (E) = E1, for Total Score/Total Value = 1.0 to 1.5
= E2, for Total Score/Total Value = 1.5 to 2.0
= E3, for Total Score/Total Value = 2.0 to 2.5
= E4, for Total Score/Total Value = 2.5 to 3.0

5

CONCLUSIONS

Based on this study, the following conclusions are made:

A depression of the pH value during early start-up in a boiler operating on a phosphate water chemistry scheme will reduce the time to initiate corrosion fatigue cracks in boiler tubes. The influence of depressed pH is greater at 274°C (525°F) than at 204°C (400°F).

Boilers that experience phosphate hide-out and return are likely to experience pH depressions upon start-up. Therefore, they are more likely to experience corrosion fatigue than those boilers that do not experience phosphate hide-out.

The implications of these results are that a utility should eliminate boiler water pH instability due to the phosphate treatment. The new EPRI phosphate treatment guidelines[9] have been designed to incorporate this philosophy by using either equilibrium phosphate (EPT) or phosphate treatment (PT) instead of congruent phosphate treatment (CPT), and by removing the need to add acidic phosphates such as mono- and disodium phosphate.

Dissolved oxygen in the boiler water will shorten the time to initiate cracks in boiler tubes. This effect is minimized at temperatures below 150°C (302°F) and increases with temperature to about 204°C (400°F); at temperatures between 204°C (400°F) and 274°C (525°F), this influence of oxygen is fairly constant.

A revised environmental parameter evaluation criteria has been suggested, which accounts for the variable influence of pH and dissolved oxygen with temperature. This criteria emphasizes excursions that occur at later parts of the start-up cycle when temperatures and tube strains are higher.

6

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