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OPERATING EXPERIENCE

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Relationships Between Stress Corrosion Cracking Tests and Utility Operating Experience

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Abstract

Several utility steam generator and stress corrosion cracking databases are synthesized with the view of identifying the crevice chemistry that is most consistent with the plant cracking data. Superheated steam and neutral solution environments are found to be inconsistent with the large variations in the observed SCC between different plants, different support plates within a plant, and different crevice locations. While the eddy current response of laboratory tests performed with caustic chemistries approximates the response of the most extensively affected steam generator tubes, the crack propagation kinetics in these tests differ from plant experience. The observations suggest that there is a gradual conversion of the environment responsible for most steam generator ODSCC from a concentrated, alkaline-forming solution to a progressively more steam-enriched environment.

Introduction

The initial occurrences of steam generator OD-initiated stress corrosion cracking (ODSCC) were attributed to the presence of an alkaline environment (1). These included the ODSCC at the Beznau 1 plant in Switzerland in the early 1970s, followed by the cracking in deep tubesheet crevices in a number of U.S. plants during the late 1970s, and then in tube support plate crevices in three Japanese plants in the early 1980s. During the ensuing years, ODSCC in tube support plate and tubesheet crevices has been identified in many plants, and has become the dominant steam generator corrosion mechanism. During this time, several other environments have been proposed as the primary cause of the observed corrosion. These environments include acid sulfates (2), neutral chemistries (3), aluminosilicates (4), and superheated steam (5). Most recently, neutral environments are believed to be the most likely cause of the majority of the observed ODSCC (6). In some cases, the presence of lead is also believed to contribute to, or perhaps be primarily responsible for, the corrosion (7).

This paper integrates a number of databases to formulate a degradation scenario that appears to be compatible with the observed plant corrosion. Data evaluated include selected utility steam generator eddy current distributions, destructive examination findings from removed tubes and published laboratory tests, and corrosion noise tests.

Plant Eddy Current Distributions

Variations in plant eddy current results can provide insights regarding the likelihood of superheated steam being the environment responsible for the corrosion. As described in Reference (8), estimates of the crevice hideout rate can be combined with typical steam generator bulk water chemistries to show that superheated steam is the predominant constituent of the crevice pore volume. Consequently, if a superheated steam environment were primarily responsible for the observed corrosion, it should be expected to be quite widespread. In fact, however, distributions of plant eddy current measurements suggest the opposite to be true. Figure 1 shows that there are large plant-to-plant differences in the number of tubes being plugged because of ODSCC in tube support plate crevices. The data points represent individual plants having Westinghouse Model D steam generators, so that design differences are relatively small. As indicated, there are more than three orders of magnitude difference in the number of plugged tubes between different plants at a given time in life. Although not all plants utilize the same criterion for plugging a tube, plants typically seek to apply less stringent criteria as the extent

of corrosion increases, so that data based upon a consistent criterion would likely show more variation than is suggested in the figure.

Figure 2 shows an Arrhenius plot of the variation of the percent of tubes having ODSCC indications at successive tube support plates in three Westinghouse-design plants having Model D steam generators and two having Series 51 steam generators (8). The percent of crevices having indications at a given support plate elevation is represented by a point. Although the number of indications is an inexact measure of either crack initiation or crack propagation, it should provide a measure in the variation of the extent of corrosion. As indicated, the inferred activation energies are on the order of 250 kcal/mole. This compares to activation energies on the order of 40 kcal/mole, typically measured in isothermal laboratory tests (9). Since lower support plates typically have slightly higher average voltages than upper support plates, a more direct measure of the extent of corrosion would likely produce an even stronger variation than indicated in the figure. A superheated steam environment, in which solubilities decrease with increasing superheat (and decreasing density), would appear to be unlikely to produce the variation in the extent of corrosion shown in Figure 2. It is also interesting to note that both Westinghouse Model D and Series 51 steam generators produce similar variations, even though the Series 51 temperatures are lower.

Figure 3 shows a representative histogram of the distribution of tube support plate ODSCC indications from an extensively affected plant (as well as a histogram of pulled tube indications, to be discussed below). As indicated, the distribution is quite broad, with only a few large indications, suggesting the presence of a varying environment.

Figures 1, 2, and 3 demonstrate that there are large variations in the extent of ODSCC between plants, between adjacent support plates within individual plants, and between individual crevices. These variations all point to the presence of a variable, highly localized environment as being the primary cause of ODSCC, rather than an omnipresent environment, as would be associated with superheated steam.

A somewhat analogous argument suggests that a neutral environment is unlikely to be responsible for the ODSCC on at least the more extensively affected tubes. Perhaps the main reason for concluding that ODSCC is caused by a neutral environment is that the elemental distribution on the crack face oxide films on removed tubes frequently suggests the presence of a neutral environment. Figure 3 includes a histogram of the eddy current voltages of tubes removed for destructive examination. As indicated, these tubes have higher voltages than do the majority of tubes with indications, also shown on the figure. The cracking rate as a function of pH, based primarily on isothermal laboratory test results, is presented in Figure 4 (10). As indicated, the rate at neutral pHs is several orders of magnitude lower than the rate for more alkaline or acidic chemistries. This variation is inconsistent with the distributions presented in Figure 3. That is, the tubes having the largest eddy current indications in Figure 3 should not experience the lowest corrosion rates as shown in Figure 4. Attributing the corrosion of the most extensively affected tubes to the least aggressive environment is inconsistent with the variations presented in Figures 1 and 2 as well.

If the corrosion of tubes having the highest eddy current voltages were attributed to a neutral environment, other factors, unrelated to the pH, must be responsible for the corrosion of the most extensively affected tubes. Two such factors could be the presence of lead or the presence of local tubing microstructures that are particularly susceptible to ODSCC. Although lead has clearly accelerated ODSCC rates in certain specialized circumstances, a systematic evaluation of deposit lead levels would likely find that there has been less variation in lead concentrations in most steam generators than there is variation in the extent of ODSCC. While it is difficult to establish the degree

to which lead is contributing to the corrosion, its presence is unlikely to account for the variability shown in Figures 1, 2, and 3.

Studies relating ODSCC propensity to tubing chemical and physical property variations have been conducted by Electricité de France (EDF) (11) and Dominion Engineering (12). While the EDF evaluations were able to correlate ODSCC variations between different steam generators to differences in tubing mechanical properties, the Dominion Engineering evaluation was unable to find a correlation with the tubing chemical or mechanical characteristics. Although not formally documented, it is believed that laboratory testing has found less variability between different heats of material in obtaining ODSCC than in obtaining primary water stress corrosion cracking (PWSCC). If so, tubing microstructural differences could likely account for only a small part of the variability found in Figures 1, 2, and 3.

MULTEQ predictions of the crevice chemistry, utilizing steam generator hideout return evaluations provide a second reason for why ODSCC is believed to be caused by a relatively neutral environment. Nevertheless, the MULTEQ predictions must necessarily homogenize the crevice hideout return; that is, assume that the hideout return coming from all crevices and from all locations within a crevice is the same. The very strong axial variation in the number of affected tubes presented in Figure 2 suggests that there may be differences in the local chemistry between adjacent support plates.

Tube Destructive Examination Comparison

The localization evaluations described above suggest that neither superheated steam nor neutral environments are consistent with the variability found in the steam generator ODSCC distributions. A possible means of correlating plant findings with the laboratory data base is to compare eddy current measurements to the extent of corrosion. Destructive examinations of tubes removed from utility steam generators and from tests suggest that there are significant variations in the bobbin probe eddy current voltage corresponding to a given depth of corrosion. It has been conjectured that more aggressive environments produce thicker, more continuous crack face oxide films and fewer connecting ligaments, thereby providing a larger resistance to the currents used to compute the voltages. Less aggressive environments may not fully oxidize the grain boundary, allowing some current to traverse the crack face and reduce the voltage.

A plot relating the bobbin probe voltage to the through-wall crack length determined from destructive examinations of pulled tubes and from two forms of laboratory tests is presented in Figure 5. Laboratory test data include results from Westinghouse Model Boilers and Westinghouse doped steam tests (13). Both test sets were conducted on 2.22 cm (0.875") OD mill annealed Alloy 600 tubing. The model boiler tests were conducted exclusively with caustic-forming chemistries, while the steam tests utilized a mix of alkaline-forming dopants. The pulled tube samples primarily represent 1.91 cm (0.75") OD tubing, because there have been relatively few examinations conducted in the United States of 2.22 cm-OD tubing having throughwall cracks. While more rigorous evaluations have found some variation in bobbin probe measurements corresponding to a given extent of ODSCC with varying tube diameters, these variations are small relative to other uncertainties inherent in this evaluation.

It would be instructive if laboratory samples of throughwall ODSCC produced in acid sulfate environments could be included in Figure 5. However, no such data are available. The most relevant known data are oxide film resistance measurements performed in an equimolar solution of sodium hydroxide and sodium sulfate (14). The film resistance was found to be about two orders of magnitude higher than that produced by a 1 molar sodium hydroxide solution, suggesting that the eddy current voltages of cracks produced in acid sulfate solutions would be higher than those included in Figure 5.

Since the eddy current measurements represent a composite of many variables reflecting the corrosion morphology, including the number, length, and depth of cracks, the uniformity of the crack depth, and the relative fraction of corroded grain boundaries (that is, the extent to which the corrosion represents isolated cracks or more widespread intergranular attack), it is not surprising that the plot contains considerable scatter. Nevertheless, it is clear that the pulled tube measurements approximate the trend of the model boiler tubes much more closely than of the doped steam tubes. It should also be noted that the crack length of the model boiler and steam generator tubes is typically limited by the 1.91 cm thickness of the tube support plates, while the doped steam tubes have no such restriction. The voltages for the doped steam tubes appear to reach an asymptote as the throughwall crack length exceeds approximately 2.2 cm.

It is potentially noteworthy that most of the pulled tube voltages are slightly below the model boiler tube voltages for a given crack length, suggesting that the environment responsible for the corrosion may be somewhat less aggressive. The few data points representing 2.22 cm-OD tubes are noted to be furthest from the model boiler data. These tubes, removed from Series 51 steam generators were in operation considerably longer than the 1.91 cm-OD tubes, removed from Model D steam generators. Consequently, average cracking rates were lower for these tubes, consistent with the lower bobbin probe voltages.

Inferences regarding the environment responsible for ODS-CC may be drawn from the very high activation energies presented in Figure 2. Apart from the direct temperature effect on corrosion rates, other factors which may account for the large variation in the number of affected tubes with successive support plates include a variable heat flux (affecting the rate of solute accumulation), a variable superheat (affecting the equilibrium thermodynamic concentration), and a variable local chemistry. The heat flux and superheat effects may not account for the large differences between the steam generator activation energies and the isothermal laboratory test activation energies (8). Conversely, the local chemistry can vary between support plates by virtue of both the higher temperature and the higher superheat. Volatilities increase with increasing temperature and with increasing concentration factor, which vary directly with the superheat. Less soluble species precipitate with increasing concentration factor. Consequently, acid-forming species (which are more volatile than alkalis) and salts (which typically have limited solubility) are likely to be preferentially absent at the hottest tube support plate locations. Both neutralization and buffering capability are reduced with increasing temperature and superheat. These local chemistry variations are not considered in crevice pH calculations based upon hideout return evaluations, in which the return from all crevice locations is homogenized.

Corrosion Noise Testing

Inferences regarding the crack face oxide film formation kinetics can be drawn from corrosion noise testing (15). The tests were performed on a tube support plate crevice assembly containing prepacked, mechanically consolidated magnetite. A cartridge heater was used to simulate the primary system. Crevice superheats were maintained at a level comparable to those found at the first tube support plate in a Westinghouse steam generator. The only applied stress was due to the primary-to-secondary pressure difference. Crack propagation was typically manifested by simultaneous negative perturbations in both the current and potential noise. Although there is no firm consensus regarding the aspect of the cracking process that is responsible for producing these signals, one hypothesis holds that the perturbations are caused by the oxidation of newly formed crack faces attendant with crack propagation.

A plot showing the current and potential noise perturbations during a test in which throughwall SCC was produced in only 3-1/2 days is presented in Figure 6. The test was conducted in a 43.5-ppm sodium hydroxide solution. As indicated, the potential noise is perturbed for approximately 80 seconds. During this time, the crack face oxide film has formed to the point that it no longer affects local electrochemical measurements. The extent to which either the chemical or the physical characteristics of the crack face oxide film are established during the electrochemical perturbation cannot be determined. Nevertheless, this time period is much shorter than the time between when the crack face is formed and when a tube is removed for destructive examination. Given this difference in time duration, there is reason to question the correlation between the elemental distribution within the oxide film identified during the destructive examination and the environment responsible for its formation. This is likely to be particularly true for cracks which propagate relatively slowly. It is consistent with the evolution in crack face oxide film analysis results, from being suggestive of an alkaline environment to a more neutral environment. Since superheated steam is likely to be the continuous fluid within the crack, the elemental distribution may slowly change following formation of the oxide film.

The corrosion noise test results can also be used to draw inferences regarding the kinetics of crack propagation. Evaluation of the test data found that the integral of a parameter termed the power noise provided the best correlation with post-test eddy current measurements. The power noise is the product of the standard deviations of the current and potential noise. The standard deviations are a representation of the number and frequency of the perturbations presented in Figure 6. The variation in the power noise over the course of a second monitoring test, conducted primarily in a 5.2-ppm sodium hydroxide solution, is presented in Figure 7. As indicated in the figure, there was little evidence of crack propagation until after the initial shutdown for an interim inspection, after which there was a sharp increase in the noise. The noise then decreased slightly prior to a second shutdown. The noise increased again following the return to operation and throughwall cracking occurred shortly thereafter.

The integral of the power noise is presented in Figure 8. As indicated, this measure of the cumulative corrosion suggests that the cracking rate accelerates as cracking progresses. The results are consistent with Westinghouse Single Tube Model Boiler tests performed in a reference cracking chemistry, in which a destructive examination performed after 10 days of operation found no SCC, while throughwall cracking typically occurred after 15 to 19 days (16).

The crack propagation kinetics found in the corrosion noise and model boiler testing are noted to be quite different from field experience. While crack propagation is short compared to the initiation time in the lab studies, the reverse is typical of most plant experience. Plots of the average increase in the eddy current voltage on the same tube over successive operating cycles are presented in Figures 9 and 10 (17). The results are presented in terms of the voltage increase compared to the voltage at the beginning of the cycle. Since tubes having the highest voltages are removed from service, while tubes with reportable indications for the first time typically have smaller voltages, the average voltage typically increases only slightly from cycle to cycle. Although theoretical studies indicate the eddy current voltage does not vary linearly with the extent of corrosion, comparison of Figure 8 to Figures 9 and 10 suggests that there are fairly large differences in the crack propagation kinetics. Indeed, if the majority of plant SCC experience followed the crack propagation kinetics shown in Figure 8, it would be very difficult to justify the continued operation of tubes having measurable eddy current indications.

The key difference between the laboratory observations and the plant experience may be that the environment responsible for crack propagation is continuously being replenished in the laboratory while it is replenished intermittently or not at all in the field. The bulk sodium concentrations used in the lab tests varied between 100 ppb and 25 ppm, while concentrations of all highly soluble, low-

volatility species in the field are typically in the low-ppb range. Further, the porosity of the crevice deposit in the lab tests likely varied between 20 and 60%, while examinations of crevice assemblies removed from operating steam generators find that the porosity is usually well below 20% near the ends of the crevices (18, 19). Consequently, it is likely that the local crevice environment is far more steam-enriched in the field than in the laboratory studies.

The difference between the laboratory and field crack propagation kinetics in Figures 8, 9, and 10 is noted to be considerably larger than the difference between the laboratory and field eddy current voltages of tubes having throughwall cracking noted in Figure 5. The difference between the two data sets could be that the steam generator data included in Figure 5 represent the most extensively affected tubes in the steam generator, while data in Figures 8 and 9 represent the average of all tubes having indications for two successive cycles. The tubes included in Figure 5 may have been exposed to a more aggressive environment than the composite of the tubes in Figures 9 and 10. From this, it may be inferred that with ongoing plant operation, the corroded grain boundary network becomes progressively more steam-enriched, with a consequent reduction in the crack propagation rate. Crack propagation may reflect a continuum of environments depending upon the rate of concentrated solution formation and depletion, and the permeabilities of the deposits, with a long-term conversion to progressively more steam-enriched chemistries. This conversion may be consistent with the difficulty in characterizing the environment in more recent examinations.

Summary and Conclusions

Several operating plant and laboratory test data sets have been synthesized to provide insights regarding the environment that may be responsible for the ODS-CC found in PWR steam generators. The large variations in the extent of ODS-CC between different plants, between successive support plates within individual plants, and between different crevices within individual support plates suggest that the corrosion is unlikely to be caused by a superheated steam environment that is omnipresent within steam generator crevices, or by a neutral solution that has the minimum associated corrosion rate. Rather, the large variations are more consistent with the presence of small quantities of more aggressive solutions, from which the more volatile and less soluble species become progressively excluded with increasing temperature and superheat. The strong correlation between the eddy current voltages of tubes containing throughwall cracks that have been removed from steam generators and that were produced in model boiler testing suggests that an alkaline environment may be responsible for the ODS-CC found on the steam generator tubes having the highest eddy current voltages.

Interpretation of the perturbations in the local current and potential attendant with the crack propagation produced in corrosion noise tests suggests that electrochemical equilibrium of the crack face oxide film is restored shortly after it is formed. Since this time is likely to be very short compared to the time between crack face formation and when the tube is removed for examination, there should be ample opportunity for further changes in the composition of the crack face oxide film. This may account for why analyses of the composition of the oxide film frequently suggest the presence of a neutral environment.

Differences in the crack propagation kinetics between laboratory samples (as in Figure 8) and steam generator experience (Figures 9 and 10), particularly for tubes not having the most degradation, suggest that the local crack network environment becomes more steam-enriched with ongoing operation. Rather than deeming that further crack propagation is caused by either a concentrated solution or doped steam, there would appear to be a continuum of environments which is a function of the rate of concentrated solution formation and the deposit permeability. As bulk-water contaminant

levels are reduced and crevices become less permeable, the doped steam contribution may increase with an associated reduction in the corrosion rate.

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Figure 1. Plant-to-Plant Variation in the Extent of Tube Support Plate ODSCC

Figure 2. Variation in Percent of Affected Tubes at Successive Tube Support Plates

Figure 3. Representative Tube Support Plate and Pulled Tube Eddy Current Distributions

Note: There are not enough data to develop the trend lines for oxidizing conditions. Accordingly, they were drawn parallel to the non-oxidizing condition trend lines.

Figure 4. Variation in ODSCC with pH (Reference 10)

Figure 5. Comparison of Eddy Current Indications from Model Boilers, Doped Steam Tests and Pulled Tubes

Figure 6. Perturbations in Current and Potential Noise During Crack Propagation

Figure 7. Power Noise History from Corrosion Noise Test

Figure 8. Crack Propagation Rate Inferred from Corrosion Noise Test

Figure 9. Relative Change in Eddy Current Voltage for Westinghouse Series 51 Steam Generators (Reference 17)

Figure 10. Relative Change in Eddy Current Voltage for Westinghouse Model D Steam Generators (Reference 17)