ODSCC ALGORITHM SHOWS CORRELATION WITH DEGRADATION

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ABSTRACT

Over the last few years we have attempted to develop an algorithm to evaluate the impact of secondary water chemistry on tube degradation in PWR steam generators. Effects of individual factors were assessed and then consolidated to form an algorithm for ODSCC propensity. The algorithm utilizes secondary water chemistry data to calculate ODSCC propensity as a variable named Mega PHI. Prior attempts to correlate algorithm calculations with actual degradation in operating steam generators have resulted in very disappointing results.

Recent modifications to the algorithm have demonstrated improved correlation between Mega PHI (calculated result from the algorithm) and actual degradation history from operating plants. The recent modifications involve the inclusion of the synergistic effect of boric acid application of secondary water and of high silica concentration in steam generator toward inhibiting ODSCC. Data from several plants with mill annealed alloy 600 tubing in the steam generators and operating with the primary coolant inlet temperature in the range of 608 to 624 °F (320 to 329 °C) were evaluated and the results compared with actual degradation reported from in-service inspections. The population of plants includes those with very few tubes repaired and those with hundreds of tubes repaired due to ODSCC at tube support plates. The observation of substantial correlation between the algorithm calculation and actual degradation signifies the roles of boric acid and silica in inhibiting ODSCC.

It is recommended that further evaluation of the role of these chemical species be performed using more extensive data. The goal is to modify secondary water chemistry guidelines with the ultimate aim of minimizing corrosion of steam generator tubes.

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INTRODUCTION

Outside diameter stress corrosion cracking (ODSCC) is perhaps the dominant cause of steam generator tube repair at present. Tube degradation due to this mechanism is most prevalent in tube support plate (TSP) crevices and at the tubesheet crevices. The local environment plays an important role in the SCC of tubes. The industry has been working hard over the years to improve crevice chemistry by the development and application of improved secondary water chemistry guidelines.

We have concentrated for several years on the development of an algorithm to model the factors affecting ODSCC in steam generators. The objective of the algorithm is to develop the link between plant conditions (primarily, chemistry) and corrosion such that: 1) improvements can be made to operating chemistry control, 2) impact of alternate options can be evaluated and 3) future tube repair estimates can be made for a given operating strategy.

Until recently, attempts to correlate algorithm output with actual degradation in steam generators had been disappointing. The following discussion outlines the recent developments that have significantly improved the correlation of the algorithm output with corrosion history.

ALGORITHM

The ODSCC algorithm is an empirical model developed to evaluate the effect of operating conditions (particularly, water chemistry and temperature) on ODSCC propensity. The mathematical formulation is:

$$\emptyset = \Sigma\,\Sigma \text{ (Blowdown sodium)} \bullet \text{(Inhibitor term)} \bullet \text{(Hideout term)} \bullet \text{(Redox term)} \bullet \text{(Memory term)} \bullet \text{(Temperature term)}$$

$\emptyset$ is the value (arbitrary units) resulting from the above calculation. Since the value calculated for a typical plant with several years of operation is large (tens or hundreds of thousands), it is divided by one million and the result is named Mega PHI.

In the above equation, the blowdown sodium is the concentration of sodium in the steam generator blowdown. The inhibitor term accounts for the effect of inhibitors on corrosion by reducing the contribution from the sodium term. This will be discussed

further. The hideout term represents the factors affecting solute accumulation in the crevices – crevice filling by the ingress of magnetite and other low solubility species in the feed water, crevice porosity, etc. The redox term accounts for the oxidation and reducing agents present in the steam generator and may be looked upon as representing the electrochemical potential. The memory term models the net rate of accumulation of these factors within the local environment. The temperature term normalizes the results for plant to plant variations in operating temperature and allows uniform treatment and comparison of data from different plants.

The calculations are based on daily average inputs, integrated over the entire operating history of the steam generators in a plant. The integration is performed by the double summation. One summation represents the accumulation of the solutes in the crevice, over time and the other represents the resulting crack initiation and propagation (i.e., crack growth over time). The former provides the driving force for corrosion as a function of time. The resulting corrosion during a time interval (day), in concept, is integrated over time by the latter summation.

The most significant of the recent improvements in the algorithm has been in the inhibitor term. The discovery of the significance of silica as an inhibitor based on operating plant data was discussed before.[1] The inclusion of blowdown silica in the algorithm had resulted in a significant improvement in the algorithm in that plants with significant amount of ODSCC (as defined in Reference 1) had higher Ø values than those with low ODSCC. However, a correlation between Ø and degradation was still not apparent.

A second improvement occurred when credit was taken for the inhibiting effect of boric acid. Boric acid as an inhibitor of secondary side corrosion was identified by others.[2,3,4,5,6,7] This had been recognized in some earlier versions of the algorithm. The synergistic effect of boric acid application and high silica concentration was modeled. Incorporation of the resulting inhibitor term into the algorithm resulted in a significant improvement in the correlation of Ø with tube degradation.

CORRELATION

The data from 11 plants were evaluated and algorithm calculations were made for each. These results were correlated with the actual degradation observed in these plants. All the plants in this population contain 0.75 inch (19 mm) diameter mill annealed alloy 600 tubing and have full depth hard rolled tubesheet joints. The primary coolant inlet temperature was in the range of 608 to 624 °F (320 to 329 °C). The population of plants includes those with very few tubes repaired and those with hundreds of tubes repaired due to ODSCC at tube support plates.

The number of tubes repaired for a given degradation mechanism is a simple (and readily available) parameter that can be measured and correlated. Figure 1 is a plot of the cumulative number of tube repairs for TSP ODSCC as a function of Mega PHI. The algorithm calculation is shown in the abscissa and the number of tubes per SG that is repaired for TSP ODSCC in each of the plants is shown in the ordinate. It may be noted that there is a threshold Mega PHI value below which the degradation (number of tubes repaired) is negligible. Above this threshold, there emerges an apparent linear correlation between the number of tube repairs and Mega PHI.

A major concern with the use of the number of tube repairs as a measure of corrosion in a given plant is its strong dependency on the specific tube repair criteria, which had been used. Many plants in the U.S. have implemented voltage based alternate repair criteria (ARC) to disposition ODSCC indications at TSP's. The ARC results in the repair of a much smaller number of tubes than the standard repair criteria. In an attempt to overcome this concern, we defined a voltage-based parameter called "degradation parameter" as a measure of corrosion. This is calculated by summing the bobbin voltage amplitudes of all TSP indications in a plant and dividing by the number of tubes. Hence it is expressed in units of volt/tube. Bobbin voltage of an axial indication is believed to be a good measure of the magnitude of degradation at that location. Hence this parameter meets the three objectives: is a measure of corrosion, is obtained from inspection results, and is independent of repair criteria.

In the calculation of the degradation parameter, two assumptions were made: 1) if TSP ODSCC had been detected in a plant, then ODSCC would have initiated at the 3 hottest TSP's in all tubes in that plant and 2) the bobbin voltage amplitude of a tube-TSP intersection without a detectable indication would be 0.1 volt, i.e., a value below a detection threshold. In retrospect, these arbitrary assumptions were unnecessary and in effect resulted in raising the datum value of the degradation parameter to 0.3 volt/tube (instead of 0). They had no other influence on the results or conclusions.

A plot of the degradation parameter versus Mega PHI is shown in Figure 2. It may be noted that this plot is quite similar in appearance to Figure 1. In both figures, there is one data point that lies far from the apparent correlation. The data were reviewed to assess why it is an outlier. It was observed that that plant had significant quantities of potassium, calcium, and magnesium in prompt hideout return compared to the other plants in the population for which such data was available. The ratios of total cations to sodium and to silica in the prompt hideout return were both high for the outlier plant. Influence of all cations on ODSCC in operating plants was previously reported.[1] The algorithm uses only the blowdown sodium concentration since the concentration of other cations in blowdown are not reported. Hence it was reasonable to expect the subject plant to be an outlier. It was also observed that the pulled tube data from the outlier plant had exhibited high amounts of lead in the

crevices. An area scan of the crevice deposit by energy dispersive spectroscopy (EDS) had revealed up to 6% lead (40% lead had been observed in a spot scan of the crack face in the same crevice). Since lead is known to promote SCC, this may be another reason why that data point was an outlier with excessive corrosion.

DISCUSSION

A correlation between the ODSCC algorithm and actual degradation has been observed. Both the number of tube repairs and the indication voltage based degradation parameter correlate very well with Mega PHI. This fact takes on an added significance to those who have experienced repeated disappointment after having tried very hard to develop a correlating algorithm by experimenting for years with different functional and parametric formulations.

We believe that the success of the algorithm in correlating with tube degradation history is the result of identifying the importance of boric acid and silica in the inhibition of ODSCC. We attribute the prior experience with the algorithm to the lack of proper identification of this factor. Consequently, the most important aspect of the current result is the demonstration of the inhibiting effects of silica and boric acid on ODSCC of alloy 600 tubing in caustic environment.

As pointed out earlier, significant literature exists in support of boric acid as an inhibitor for ODSCC. However, contribution of silica in this context has not been recognized until recently.[1] Possible beneficial effect of silica and inhibiting effect of titania-silica sol gel have been reported[8,9] previously. On the other hand, researchers[10,11,12] have even postulated that alumino-silicate deposits in the crevices may adsorb chemical species, which contribute to corrosion of tubing. However, destructive examination of tubes pulled from Ringhals Unit 3 revealed significant amounts of silica and alumino-silicate deposits in the TSP crevice without any corrosion even after about 10 full power years of operation.[13]

Although much of the data appears to support the effects of silica on ODSCC as beneficial, there is some conflicting data/opinion. Therefore, further investigation is required to better understand the effects of silica. We believe that it will confirm the findings of this paper and could lead to improved secondary water chemistry guidelines and improved corrosion performance.

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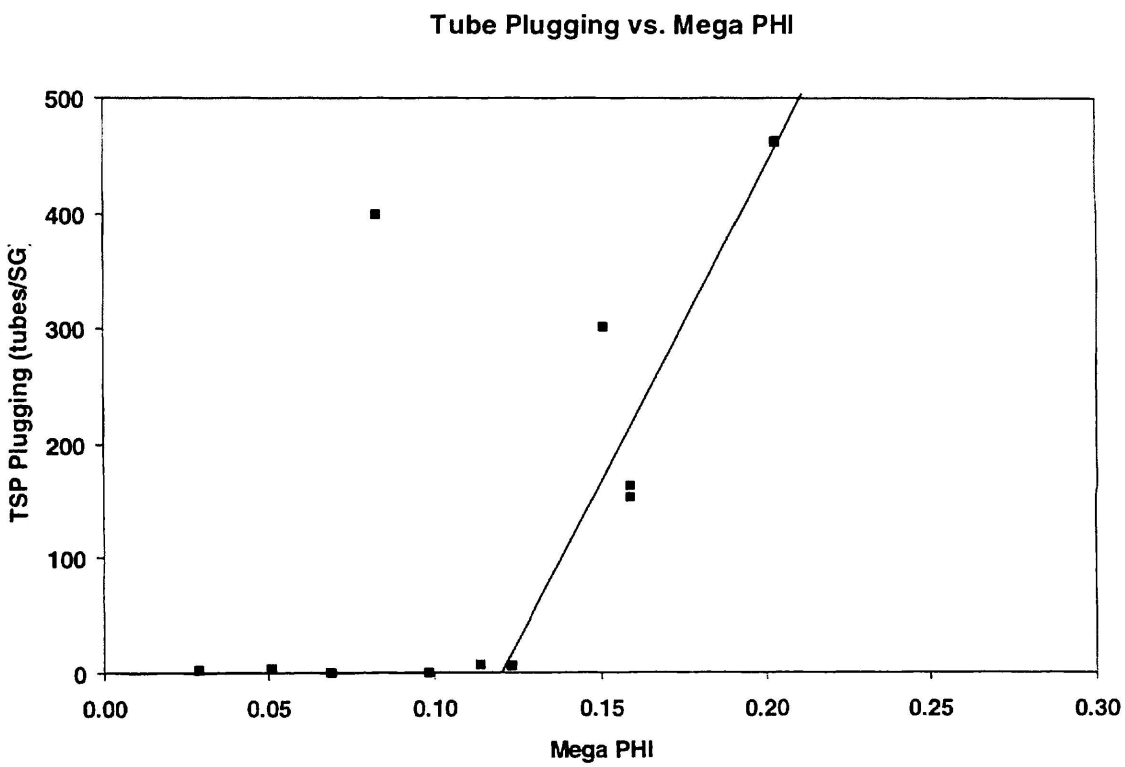

Figure 1. Correlation of algorithm results with number of tube repairs in operating plant steam generators

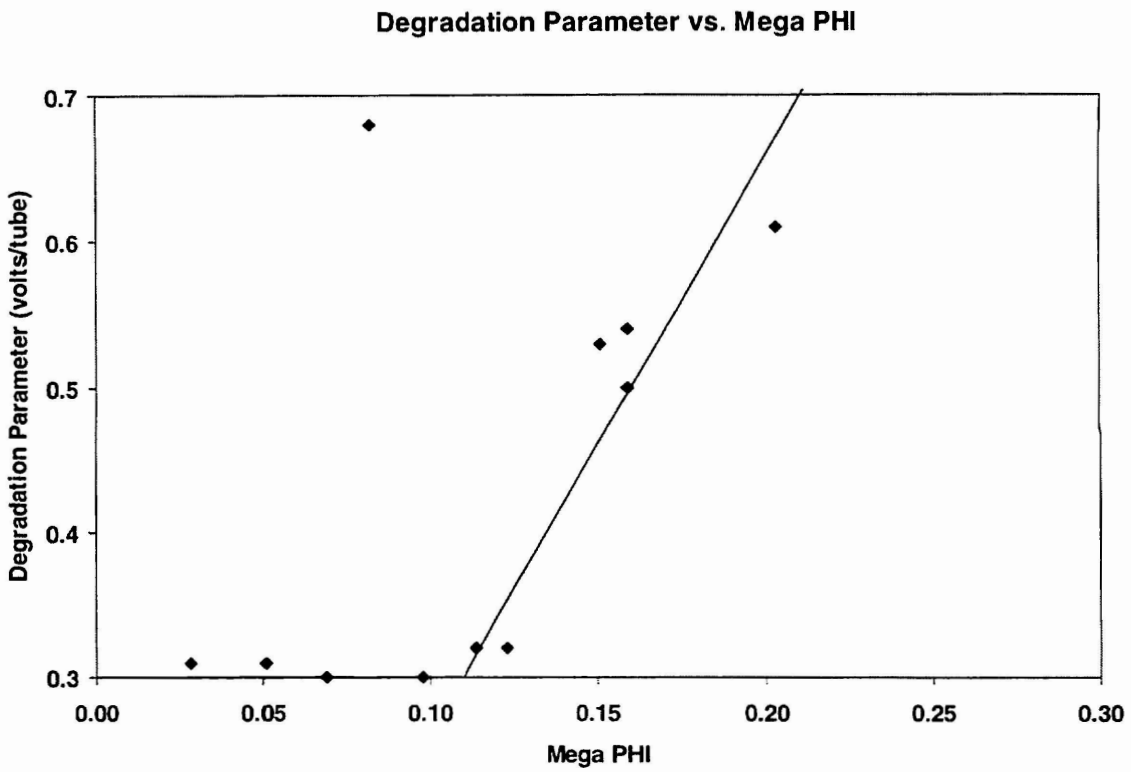

Figure 2. Correlation of algorithm results with degradation parameter in operating plant steam generators