

DEAERATOR CORROSION

AN OVERVIEW OF DESIGN, OPERATION, EXPERIENCE, AND R & D

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ABSTRACT

An industry-wide deaerator and storage tank weld corrosion cracking problem is currently among the most extensive and expensive problems associated with fossil steam generation (utility and industrial). Over 30% of deaerators contain cracks which have been assessed as corrosion fatigue and/or stress corrosion.

Causes of this problem have not been found yet. Effects of material-fabrication-design-operation and water chemistry need to be investigated. The only correlation we have found so far is that of the crack growth rate vs. time in service: newer deaerators crack faster than the old ones, up to 15% of wall thickness/year.

An overview of deaerator design, operation, and corrosion problems and a brief description of R&D activities are given. Possible material, fabrication, design, operation and water chemistry effects and stress sources are discussed. Conclusions and recommendations are made which include the need for an expanded effort to determine the causes and develop preventive measures for the alleviation of the deaerator cracking problem.

INTRODUCTION

Deaerators (direct contact deaerating heaters) are used in fossil and some nuclear power plants, industrial steam plants, and ship propulsion. They remove dissolved gases (mostly oxygen and nitrogen) by mechanical deaeration and provide water storage capacity to give a residence time at appropriate elevated temperatures for chemical oxygen scavenging. In addition, deaerator storage capacity and hydrostatic head provide flow conditions for the boiler feed pump. The operating temperature range is 103 to over 180°C (215 to over 350°F) with the corresponding saturation pressure up to over 0.96 MPa (140 psia).

Another type of oxygen removal equipment is the deaerating heater. It reduces oxygen to about 0.04 µg/l (40 ppb). The differences between deaerators and deaerating heaters are the degree of refinement used in water atomization, steam scrubbing action, and venting of gases. Open feedwater heaters, with a typical temperature range (70 to 100°C) (160 to 210°F), are also used for deaeration. They remove oxygen only down to 0.5 - 1.0 mg/l.

A typical location of a deaerator in utility drum boiler and once-through fossil cycles is between the low pressure and high pressure feedwater heaters before the boiler feed pump (1, 2). Steam which drives the deaeration is usually supplied from the IP turbine exhaust, the first LP extraction, or from the boiler feed pump turbine exhaust (during high load operation) and from auxiliary sources during startup, shutdown, and hot standby.

In many industrial plant systems, the deaerator is the only feedwater heater and feedwater is pumped from the storage section of the deaerator directly through the economizer into the boiler drum. Frequently, low pressure exhaust, low pressure flash tank, or blowdown flash tank steam is used for deaeration. Also condensate (usually 40-60% of the feedwater) is normally mixed with makeup at the deaerator in systems with condensate return.

There are many deaerator design configurations, horizontal and vertical, with different internals where the feedwater and steam interact. Typical designs incorporate spray, tray, and combination spray/tray heating sections. Figure 1 shows a two vessel horizontal tray deaerator used in most larger industrial and utility systems.

Most deaerator vessels are fabricated from carbon steel. Some, particularly marine steam propulsion deaerators, are made of copper alloys. Some deaerator vessels in industrial applications are glass lined. Attempts to epoxy coat the vessel ID surfaces have not been successful. The coating peels off and there could be corrosion under the coating.

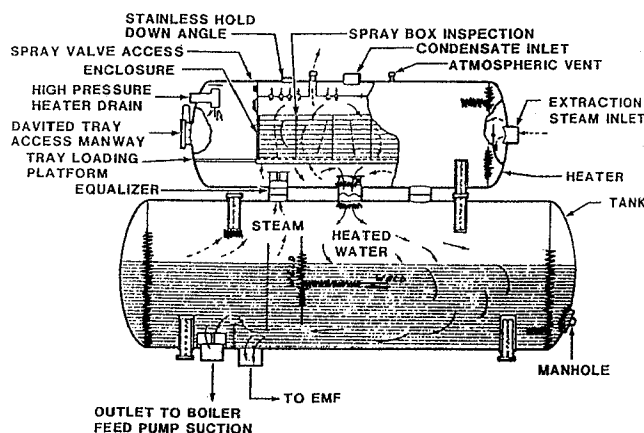


Figure 1 -- Utility tray deaerator with typical corrosion crack locations.

DEAERATION & OXYGEN SCAVENGING

The mechanical deaerating action usually combines removal of gases from the water surfaces and steam stripping. Due to the gas volatilities, the gases dissolved in water are rapidly trying to establish an equilibrium with the vapor-gas mixture in contact. Equilibrium gas concentration in water c_w is according to Henry's law: $c_w = p/k_H$ where p is the partial pressure of gas and k_H is Henry's constant (temperature dependent) (2).

Since the gas concentration in water is proportional to the partial pressure of the gas around the liquid and the deaerating steam has very low contents of gases, gas concentration in water becomes very low, a few ppb. Under typical deaerator operating conditions, 7 ppb of dissolved oxygen is achievable and is guaranteed by the equipment vendors. During deaeration, 90 - 95% of dissolved oxygen is easily removed by mechanical separation; the remaining 5-10% of oxygen must be removed by molecular diffusion.

Heating -- Water in the deaerator must be heated to full saturation temperature corresponding to steam pressure in the unit. Complete gas removal is not possible unless the liquid is kept at boiling temperature.

Agitation -- Heated water must be mechanically agitated by spraying, cascading over trays, or atomizing to expose maximum surface to the scrubbing steam, permitting complete release and removal of gases. Thorough agitation overcomes tendency for surface tension and viscosity to retain gas bubbles and increases the rate of gas diffusion from the liquid to the surrounding steam. Intimate mixing of steam and water is essential - a design requirement.

Gas Removal -- Enough steam must pass through the water to raise it to the boiling point and scrub out and carry away non-condensable gases after their release. Proper venting is required. To reduce steam loss by vents, many deaerators are equipped with vent condensers to conserve energy and water.

Both spray and tray deaerators should be able to remove oxygen to less than 7 ppb and the deaeration efficiency should be good even at low loads (see Figure 2).

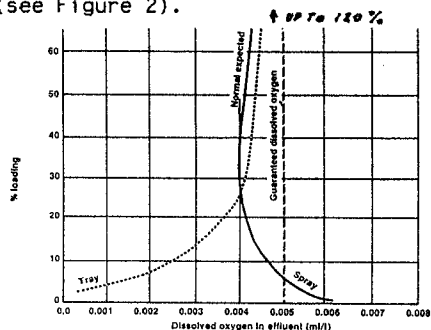


Figure 2 -- Expected dissolved oxygen at the deaerator outlet vs. load for tray and spray deaerators.

Chemical Oxygen Scavenging -- which takes place in the deaerator storage tank depends on temperature, residence time, pH, and scavenger concentration. At temperatures above 200°C (400°F), hydrazine (which is the most common oxygen scavenger in utility applications) thermally decomposes ($2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3$) and a portion of it is, therefore, not available for the reaction with oxygen ($N_2H_4 + O_2 \rightarrow 2H_2O + N_2$) (see Figure 3). Most deaerators operate below 200°C (400°F).

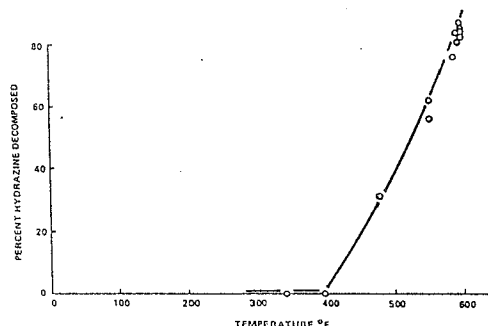
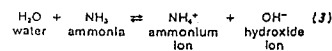
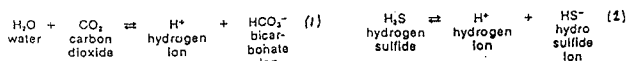


Figure 3--Effect of temperature on the decomposition of hydrazine. Source: Babcock & Wilcox.

Dependence of oxygen scavenging on the residence time, temperature, the hydrazine to oxygen ratio and pH has been reported elsewhere (2, 4). Typical deaerator residence time is 3 to 10 minutes which is sufficient for the oxygen scavenging reaction to proceed. However, in some designs, water from the deaerating vessel may channel through the storage tank into the outlet pipe and the actual residence time may be very short and the scavenging poor.

Deaerators also remove other gases which enter the cycle with air inleakage and some volatile chemicals dissolved in feedwater. Deaerator effectiveness in removing carbon dioxide (a major impurity which can cause corrosion) is limited and depends on pH, temperature, and deaerator and cycle design. At alkaline pH, lower volatility carbonates, such as ammonium carbonate, form. These are not "deaerated" (see Figure 4 for percentages of CO₂ gas removal vs pH). NH₃ is removed only in the form of NH₄OH. Like CO₂, it is very soluble and requires a diffusion process. The removal of ammonia occurs at more alkaline pH levels (see Figure 5). Ammonia, CO₂, and other gases frequently found in water do not follow Henry's law because when dissolved in water, they ionize.

For example:



CORROSION PROBLEMS

The chemical species present in the solution depend strongly on pH.

As equations 1, 2, and 3 show, the solution of the gases in water is a reversible reaction. To obtain almost complete removal of these gases, advantage may be taken of the common ion effect. That is, if the concentration of one of the ions on the right side of the equation is increased, the reaction is driven to the left, resulting in dissolution of the gas. In the case of carbon dioxide and hydrogen sulfide, hydrogen ion may be increased by adding an acid. Any bicarbonate or carbonate in the water will be neutralized and the carbon dioxide formed can be removed by deaeration.

In a similar manner, ammonia removal can be improved by increasing hydroxyl ion concentration through the addition of caustic soda or phosphates.

Properly operated deaerators have beneficial effects on water and steam chemistry and cycle component corrosion control because they help to reduce oxygen in feedwater and, therefore, the pre-boiler system and boiler corrosion. It should be noted that the cycle corrosion depends on many other factors besides the oxygen concentration, such as pH, other impurities, materials, and flow velocity and turbulence (erosion-corrosion).

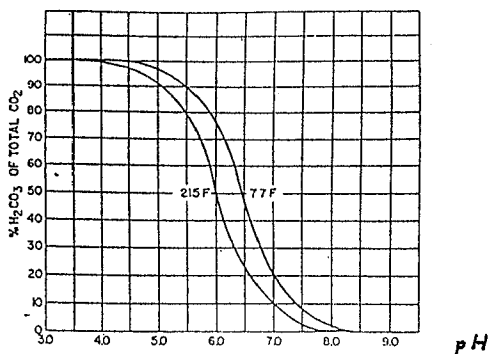


Figure 4--Percent CO₂ available for removal (5).

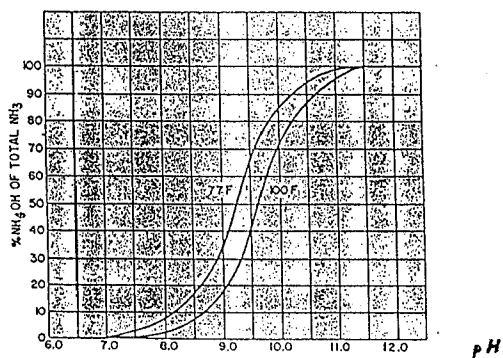


Figure 5--Percent NH₃ available for removal (5).

An industry-wide deaerator vessel and storage tank weld corrosion cracking problem has been discovered after the 1983 deaerator rupture in a paper mill (6, 7). Over 30% of utility and industrial deaerators (out of over two thousand inspected) have been found to experience this type of corrosion. In one utility, 90% of inspected deaerators have cracks, in others, only a few. There have been at least five catastrophic deaerator and other carbon steel pressure vessel failures. Similar problems have been experienced in West Germany over ten years ago (8, 9) and are just being discovered in the CEGB utility units in England and in KEMA units in Holland (26 inspected, 17 cracked). The fracture characteristics are those of corrosion fatigue in hot water, in some cases of stress corrosion. Pitting and heavy oxide often accompany the cracking. Cracking is more frequent below the water line and in the head to shell welds (see Figure 1). Crack penetration through the wall was found in several deaerators.

Causes of this problem have not been discovered yet, but most likely there is a combination of water chemistry, residual welding stress, and cycling service stress factors. Hydrogen cracking due to hydrogen generated by general corrosion and its diffusion into the higher strength heat affected zone is also a possibility.

MATERIALS

Most deaerators are fabricated from carbon steels (ASTM A 212 Gr. C and ASTM A 515 Gr. 70) with some stainless steel or cast iron (trays) internals. Although much is known about carbon steel, there are significant gaps in the knowledge related to deaerator cracking.

There is not a good explanation of the catastrophic failures where the expected "leak before break" did not occur. This shows the need for knowledge of fracture properties and ductility of carbon steel weldments after long time elevated temperature exposure to hot water. Impact energy, FATT, and fracture toughness data need to be developed to improve the knowledge of fast fracture. Fracture toughness may be as low as 50 KSI $\sqrt{\text{in}}$.

Equally important are corrosion properties in relevant environments, such as threshold stress σ_{SCC} , threshold stress intensity K_{ISCC} , corrosion fatigue limits, ΔK_{th} , and crack propagation rates under corrosion fatigue and stress corrosion conditions. Also needed is information on the effects of pitting on the above properties.

Knowledge of these properties would allow the use of a more rational approach in evaluation of NDT results and better prediction of service life and determination of inspection intervals.

Carbon and low alloy steels are susceptible

to corrosion cracking in several environments, including:

- o sodium hydroxide
- o carbonate - bicarbonate
- o carbonate - carbon dioxide
- o nitrate
- o hydrogen producing

All these environments can exist in deaerators under certain feedwater chemistry and operating conditions. At high enough yield strength (hard welds) or under high tensile stresses, even pure water and steam can cause stress corrosion and corrosion fatigue cracking.

WATER CHEMISTRY

The water chemistry and environmental factors which can lead to deaerator corrosion include high levels of oxygen and CO₂, low pH, accumulation of corrosion products on surfaces and of ionic impurities within these oxides, and moisture and air or aerated water exposure during unprotected layup (common U. S. practice).

One design aspect which can influence feedwater chemistry is the enormous length of some deaerator storage tanks in large units (up to 200 ft.) with the storage tank inlet and outlet in the middle. When water purity in the tank is allowed to deteriorate, such as during an unprotected layup (water saturated with air), the deaerator tank water can contain impurities for a long time. Flow channeling can occur in two vessel units when a stream of water flows from the deaerator vessel directly into the storage tank outlet and the impure water stays in the end sections of the storage tank. This can also contribute to weld corrosion which is prevalent in the head to shell welds. In some deaerator storage tanks, high pH deposits were found during failure analysis and sodium and silica were identified by EDAX.

Salts and caustic can concentrate on deaerator storage tank surfaces by several mechanisms. When water flashes into steam during even minor pressure drops, dissolved impurities distribute between the liquid and vapor according to their distribution coefficients (for molecular species) (1, 2). The distribution depends on the volume ratio (or pressure). When the metal surface temperature is higher than the saturation temperature (even by a few degrees) dissolved impurities can concentrate from any low concentration (ppm or ppb) to percent. Iron oxides which are allowed to accumulate can also concentrate corrosive impurities.

STRESSES

The influence of design, residual, and operating stresses and fabrication/welding practices on the storage tank cracking is not known yet. Operating stress levels and the frequency of the fatigue-causing variable stresses and their origins need yet to be determined. During observations of deaerators

during startup, it was found that vigorous boiling and vibrations occur when the load and feedwater demand increase rapidly and the deaerator pressure drops. Violent boiling and storage tank vibration can also be observed during and after the shutdown depressurization and particularly after a turbine trip. In one U.S. utility, a horizontal deaerator was found "jumped off" its foundation, which certainly indicates significant forces.

The basic deaerator design feature i.e. keeping large volume of water exactly at saturation, makes it very sensitive to even small pressure changes. While pressure can change rapidly, temperature and heat energy of the stored water vary slowly. This can and does result in a mismatch and rapid boiling and condensation.

One source of variable stress is the "water-piston" instability, also known as the Kelvin-Helmholtz instability (10). Under certain conditions of the storage tank water level and Froude number, repeated movement of the "water-piston" occurs (see Figure 6). The "water-piston" is propelled along the tank and impacts the tank head. As it travels, it pushes water into the steam transfer pipes and drains causing damage of the deaerator internals. Water-piston and its effects are more pronounced in longer deaerators.

Residual welding stresses are highest in the weld direction and can be as high as the weld yield strength. Complete stress relief of a large vessel is difficult and some residual tensile stresses remain.

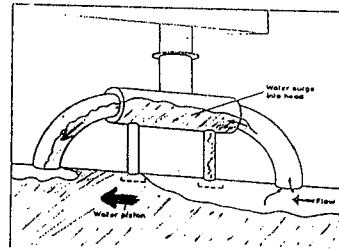


Figure 6--"Water piston" instability in a deaerator storage tank.

CORRELATIONS

In the attempt to correlate NDT data with a few design and operational parameters, the only correlation we have found so far is that of the corrosion crack growth rate vs. time in service (see Figure 7). This correlation for the cracked deaerator storage tanks shows that in the old ones, the crack growth rate is typically about 1% wall thickness per year, while in the deaerators of the built 3 to 10 years ago, it is 6 to 16% per year. There is no correlation at this time of cracking vs pressure (see Figure 8) and cracking vs design to operating pressure ratio (see Figure 9). Most of the above data are for industrial deaerators and include results of the inspections performed by the Industrial NDT Co. and results of the American Petroleum Institute Survey.

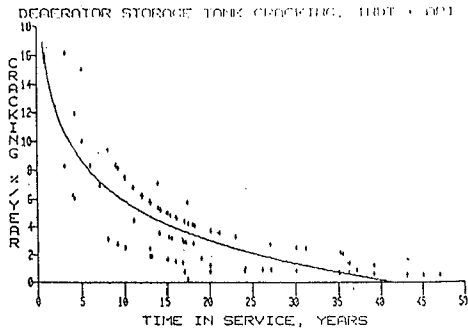


Figure 7--Deaerator storage tank weld cracking: crack propagation rate, % of wall thickness per year vs. time in service.

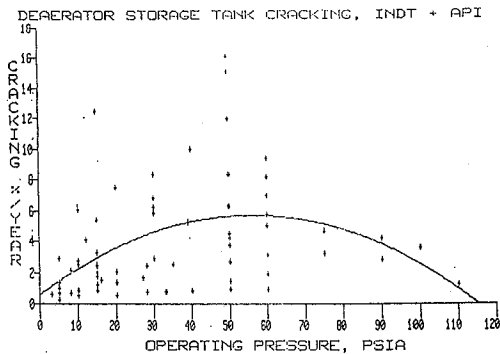


Figure 8--Deaerator storage tank weld cracking: crack propagation rate, % of wall thickness per year vs. pressure.

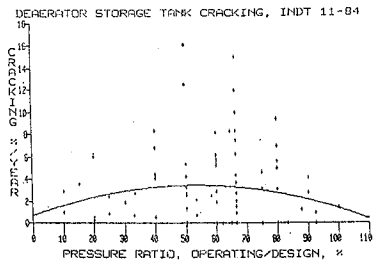


Figure 9--Deaerator storage tank weld cracking: crack propagation rate, % wall thickness per year vs. design to operation pressure ratio.

There is also no significant difference between cracking of stress relieved and not stress relieved deaerators. The survey (11) of a small number of deaerators identified possible correlation of cracking with reported "water hammer" conditions.

OTHER PROBLEMS

Other deaerator corrosion problems include corrosion-erosion of vertical deaerators and general corrosion when oxygen concentration is high (up to 1000 ppb observed).

Corrosion cracking of carbon steel hot water vessels is not confined to deaerator storage

tanks. Deaerator vessels, steam accumulators, PWR steam generators, CANDU feedwater pipe, and cascade heaters experienced similar cracking.

SAFE OPERATION AND INSPECTION INTERVALS

Safe operation can be assured by NDT at proper inspection intervals and repairs as needed. There are no standards or codes which provide guidelines for interpretation of the NDT data. Some are using the ASME Pressure Vessel Code addition for general corrosion as a criteria for repair of cracks. This is not a very rational approach since localized corrosion cracking and fracture are not governed by general corrosion. It may be both conservative or non-conservative, depending on stress, environment, rate of crack propagation, and fracture properties of the material.

We have developed a calculation procedure which takes all the above effects into account and considers both stress corrosion and corrosion fatigue as crack propagation mechanisms. The approach is schematically shown in Figure 10 (12). Use of this procedure may lead to identification of root causes of deaerator cracking.

LIFE ASSESSMENT OF DEAERATORS

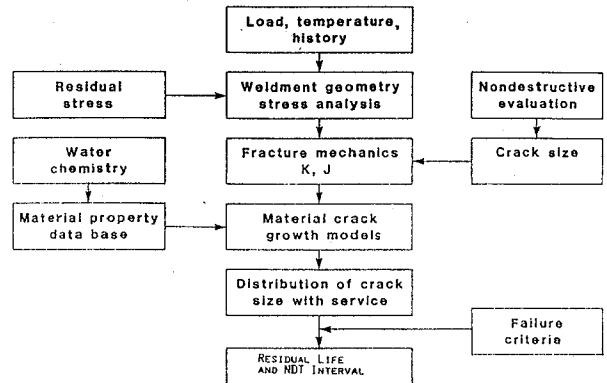


Figure 10--Procedure for life and NDT interval determination.

RESEARCH ACTIVITIES

We don't know about any coordinated industry-wide R&D project (worldwide) which is addressing the various aspects of deaerator corrosion cracking and problems with distress of deaerator internals. Major efforts by individual companies are aimed at NDT and repair. We know of two companies, one utility and one oil company, who have broader experimental programs aimed at resolving the storage tank cracking problem. Most major companies and some company groups (American Petroleum Institute) compiled statistics.

The National Association of Corrosion Engineers (NACE) formed a Deaerator Corrosion Task Group, T-7H-7 in the Spring of 1984. The objectives of the Task Group were to:

- o Coordinate investigation and R&D
- o Collect and disseminate information (experience, corrosion,...)
- o Provide guidelines
- o Collect materials - design - operation - NDT - failure analysis data for statistical analysis of causes of cracking

The Task Group started with five Work Groups:

- WGa Non-Destructive Testing
- WGb Operation & Water Chemistry
- WGC Design, Materials, Fabrication, and Repair
- WGD Failure Analysis
- WGe Failure Mechanisms & Corrosion Data

Work Group "a" promptly published Proposed Guidelines on NDT and Work Group "c" Proposed Guidelines on Deaerator Design, Materials, Fabrication, and Repair (13). The NDT guidelines reflect experience with the wet fluorescent and magnetic particle inspection and surface preparation which are most widely used today. They do not describe other techniques which have also been successfully used, such as wet magnetic inspection with white paint and black magnetic ink, ultrasonics, eddy current, and acoustic emission.

The Proposed Guidelines on Deaerator Design, Materials, Fabrication, and Repair give general recommendations including lowering of the residual welding stresses (stress relief), and limit of tensile strength of weld and base metal to 70 KSI. According to this document, cracks violating minimum design wall thickness should be repaired. (usually cracks 1/16 in. deep). A recommendation for the design shell stress not to exceed 50% of the plate yield strength was considered but it was not included in the document because supporting experimental data are needed.

Issuance of a good design standard supported by material and corrosion data will not be an easy job. It should be coordinated with the ASME (Pressure Vessel Code), Heat Exchange Institute, and other organizations, none of which considers localized corrosion in their current practices (with the exception of corrosion fatigue considerations in the ASME Pressure Vessel Code, Section XI, Reactor Vessels).

Associated with the localized corrosion cracking considerations should be appropriate fracture criteria, knowledge of stress fluctuations, local stresses, and characterization of the chemical environment. The leak-before-break failure mode of ductile materials does not always occur in pressure vessels for hot water and steam service.

The state of the problem and level of the collective knowledge were well summarized during the 1986 NACE Symposium (14). Additional papers were presented at the 1987 NACE Symposium (15).

CONCLUSIONS AND RECOMMENDATIONS

1. Deaerators are beneficial for oxygen control and can be marginally effective in removing CO₂. Deaerators themselves need to be protected against corrosion (general, stress corrosion, corrosion fatigue, and corrosion-erosion) by feedwater chemistry and impurity concentration control during operation and layup, and by control of operating and design stresses.
2. Deaerator vessel and storage tank corrosion cracking is among the most extensive and expensive U. S. corrosion problems associated with steam generation. This type of cracking is not however, limited to deaerators and many types of carbon steel welded vessels and piping for hot water and steam service are susceptible to it.
3. The fracture mechanisms appear to be corrosion fatigue and stress corrosion cracking.
4. So far, there is limited knowledge on actual stress levels and stress variations, composition of service and layup environments, and fracture properties of the carbon steel weldments after short and long-time service. Residual welding stresses (as high as yield strength), vibratory stresses caused by "water piston", water hammer, and routine pressure changes, and corrosive impurities dissolved in feedwater or concentrated on deaerator surfaces are all likely contributors to the corrosion cracking problem.
5. An industry-wide effort beyond the NACE volunteer activity is needed to resolve the multi-faceted problem of deaerator cracking.
 - 5.1 As a first step in the investigation of causes, design-operation-material data should be collected and correlated with crack growth found by NDT.
 - 5.2 Corrosion fatigue and stress corrosion properties need to be compiled and/or developed for appropriate material-environment-stress conditions.
 - 5.3 Fracture properties such as K_{Ic} and J_{Ic} should be tested for new and aged welds and HAZ.
 - 5.4 Ultimately, localized corrosion considerations should be included in design and operating practices.
6. NDT practices are adequate with the wet fluorescent magnetic particle inspection being used most often. All deaerating section vessels and storage tanks should be periodically inspected or proof tested.

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