

Stress Corrosion Cracking in Steam Systems: Characteristics, Susceptibility, and Prevention

Technical Brief — Steam Turbines—Generators and Auxiliary Systems

Abstract

Stress corrosion cracking (SCC) is a form of environment-assisted cracking occurring in specific environment-alloy combinations in the presence of steady tensile stresses. Due to its complexity, SCC remains one of the most widely studied topics of corrosion. However, years of experience and research have provided a level of understanding sufficient to control this mode of damage. This technical brief covers the major aspects of SCC, with a focus on boilers, heat recovery steam generators (HRSGs), and steam turbines.

Introduction

Environment-assisted cracking (EAC) is a general term for brittle mechanical failure that results from the synergistic effect of stress and environment. EAC generally encompasses three modes of damage—stress corrosion cracking, corrosion fatigue, and hydrogen embrittlement. This technical brief will deal specifically with the first of these—stress corrosion cracking—but the other two forms of EAC are also defined here to illustrate the contrast between these modes of damage:

- **Stress corrosion cracking (SCC)** refers to a form of brittle failure of a ductile alloy exposed to a corrosive environment and constant tensile stress.
- **Corrosion fatigue (CF)** describes the synergistic effect of an aggressive environment and fluctuating loads.
- **Hydrogen embrittlement (HE)** results in brittle fracture caused by penetration and diffusion of atomic hydrogen into the crystal structure of an alloy.

A key defining characteristic of stress corrosion cracking is that it requires the simultaneous occurrence of three conditions—a tensile stress, a corrosive environment, and a material that is susceptible to SCC under these circumstances. The relationship is often depicted by the Venn diagram shown in Figure 1.

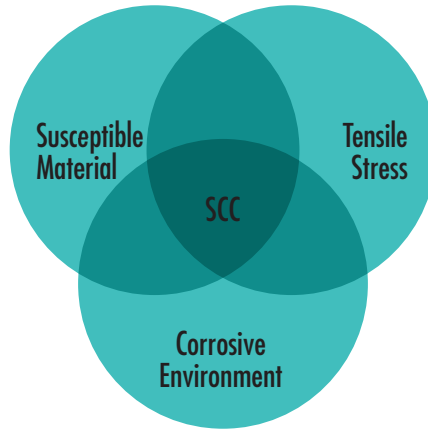


Figure 1: Classical conception of the three required conditions for SCC

Stress corrosion cracking is observed in specific alloy-environment combinations. For example, the SCC of copper alloys (first experienced by British soldiers in India who found that their brass cartridges were cracking), is virtually always due to the presence of ammonia, while stainless steels are susceptible to SCC in an environment where chloride ions are present [1].

In power plant systems, stress corrosion cracking has led to numerous failures of boiler and turbine components. This technical brief will first cover the basic characteristics of SCC and provide an overview of the fundamental scientific understanding of the subject. The latter part of the brief will then focus on some specific aspects of SCC in boilers and turbines, as well as approaches to SCC prevention in these systems.

Characteristics of SCC

In this section, the characteristics of SCC will first be discussed from the point of view of the progression of damage. The necessary synergy between material, stress, and environment will then be revisited in more detail. Finally, the resulting physical appearance of SCC damage will be illustrated.

Progression of Damage

Stress corrosion cracking involves a period of crack initiation, followed by slow propagation, up to the point that the remaining section fails by overload or another damage mode takes over (such as fatigue). Crack initiation can occur at preexisting surface defects, at corrosion pits, or due to intergranular corrosion (when local grain boundary chemistry differs from the bulk material). When the stress intensity factor, K , reaches a certain threshold value, K_{ISCC} , the crack will begin to propagate by SCC. Note that K_{ISCC} is significantly lower than the critical stress intensity factor for purely mechanical crack propagation—the fracture toughness of the material, K_{IC} . As illustrated by Figure 2, the crack growth rate quickly plateaus to a relatively constant value independent of stress intensity factor. This crack growth rate is relatively slow, on the order of 10^{-3} mm/hr (it should be noted that published values often average across the initiation and propagation phase, which is not conservative). Finally, crack growth rates increase as the fracture toughness of the material, K_{IC} , is approached. Sudden failure due to purely mechanical, uncontrollable rapid crack propagation occurs when $K = K_{IC}$.

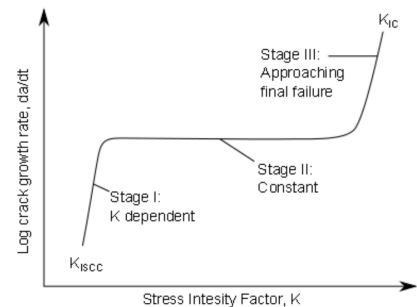


Figure 2: Schematic of the relationship between stress intensity factor and SCC crack growth rate [2]

Conditions for Damage

As already mentioned in the introductory remarks, a primary characteristic of SCC is the synergistic interaction between three necessary conditions: a susceptible material, a corrosive environment, and a tensile stress. Only the most basic requirements for SCC are discussed here; other factors that may accelerate or increase susceptibility to SCC will be addressed in the section “Factors Affecting SCC.”

- Material:** Although recent findings indicate that pure metals can also succumb to stress corrosion cracking, SCC is of most concern in normally low-temperature turbine alloys. Such alloys exhibit the classical active-passive behavior illustrated in Figure 3, whereby as the electrode potential (i.e., the driving force for corrosion) is increased, the rate of general corrosion only increases to a point, beyond which the corrosion rate suddenly drops off. This occurs because of the formation of a passive film (hydrated oxide) that isolates the bulk material from the corrosive environment. At very high potentials there is the danger of pitting, as a breach of the protective film leads to accelerated local corrosion. Stress corrosion cracking occurs in the regimes where the passive film is unstable, as illustrated in Figure 3. In these regions, the passive film is vulnerable but sufficient to prevent general corrosion, thereby allowing concentrated crack growth. Other material factors influencing SCC susceptibility, such as material yield stress, will be discussed in the section “Factors Affecting SCC.”

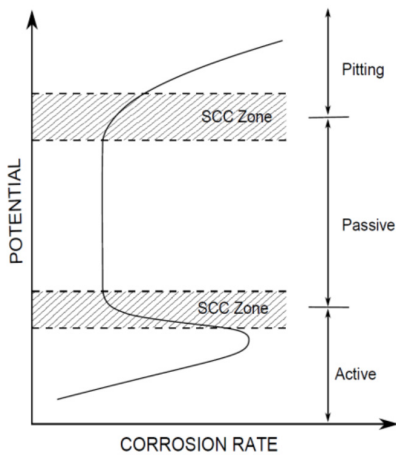


Figure 3: Schematic anodic polarization curve showing zones of susceptibility to SCC [3]

- Environment:** Environments that cause SCC are typically aqueous and can be condensed layers of moisture or bulk solution. The solute species that lead to SCC are particular to each material, and conditions that cause SCC in one alloy may have no effect on another. Some combinations of alloys and environments are listed in Table 1.

Table 1 is by no means comprehensive, and no particular effort has been made here to compile a more exhaustive list, because such lists can be misleading. Although specific alloy-environment combinations are a prerequisite for SCC, new combinations are continually being identified. Furthermore, the bulk environment may not necessarily reflect local surface conditions. For example, the local chemistry in crevices or corrosion pits may be quite different than in the bulk solution.

Table 1: SCC-conducive environments for typical steam turbine materials [1, 3, 4]

Alloy	Environment
Carbon steel	Nitrate Hydroxide Carbonate/bicarbonate
Low-alloy steel (e.g., Cr-MO, Ni-Cr-Mo-V)	High-temperature water Chloride solution/steam
Austenitic stainless steel	Chloride solution/steam
Martensitic stainless steel	Caustic NaOH solution
Brass	Ammonia Nitrites/nitrates
Aluminum alloys	Aqueous electrolytes
Titanium alloys	Aqueous electrolytes

In addition to appropriate solute species, the environmental factors affecting SCC include temperature, pressure, pH, and aeration. These will be discussed in more detail in the section “Factors Affecting SCC.”

- Stress:** The stresses necessary for SCC must be tensile and sufficient in magnitude. For example, low-alloy steel will crack in high-purity water, provided the applied stress is greater than about 70% of yield [4]. Sources of tensile stress include applied primary stress (such as the centrifugal load on a turbine disk), fabrication stresses (including residual stresses from welding, machining, and forming operations) and thermal stresses. These stresses are further amplified by local geometry and surface defects. It is

important to distinguish between the stress intensity factor required for stress corrosion crack propagation, K_{ISCC} , and the fracture toughness of the material, K_{IC} . Since the K_{ISCC} threshold is lower than the K_{IC} , significantly lower stress intensity factors are required for propagation of stress corrosion cracks vs. pure mechanical cracks.

Appearance of Damage

Stress corrosion cracking has a number of identifying features, which can be summarized as follows:

- SCC is surface initiated, usually at a stress concentrator or surface flaw.
- Damage is local—except for the cracking region, the rest of the metal appears normal.
- The fracture surface appears brittle, despite the ductile nature of the bulk material.
- Crack morphology can be intergranular (Figure 4) or transgranular (Figure 5). In some cases both types can be observed at a single site.
- Pitting or crevice corrosion often (but not always) precedes SCC.
- Intergranular attack is apparent for the case of intergranular SCC, and grains may fall out during polishing of material.
- The crack usually appears branched, but can also be straight.

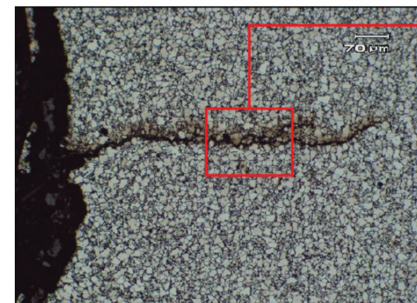
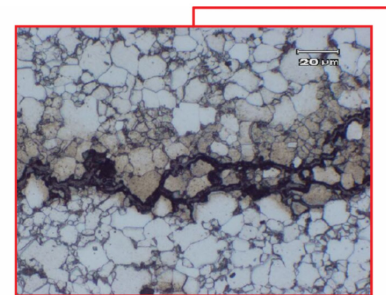


Figure 4: Microscopic appearance of typical intergranular stress corrosion crack propagation [5]

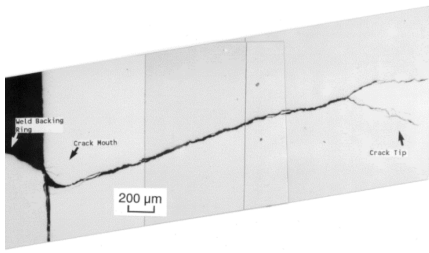


Figure 5: Example of transgranular SCC in SA-213 Type 304H base material near a dissimilar metal weld joint [5]

- Crack orientation is normal to the highest stress.
- Crack opening and deformation are small, and cracks are only detectable using non-destructive evaluation unless close to failure.
- Deposits (Na_2CO_3 , NaOH , and sulfides) are sometimes found on cracked disks, but never near the crack tip.

Mechanisms of SCC

Many mechanisms have been proposed to explain the synergistic effect of load and environment on stress corrosion crack growth, and research is ongoing. A successful theory needs to account for most of the characteristics of SCC, such as the requirement for specific combinations of environments and alloys, the relative immunity of material alloy constituents, and the brittle nature of the damage. Since this has proven to be a difficult challenge, it is likely that more than one of these mechanisms contribute to SCC simultaneously. Some of the most prominent theories are outlined below [3]:

- **Film rupture:** Most investigators now agree that local rupture of the passive surface film by elastic strain is essential to initiate cracking, but considerable controversy persists as to how a stress corrosion crack grows thereafter.
- **Hydrogen embrittlement:** Although hydrogen embrittlement is considered to be a distinct form of environment-assisted cracking, it is generally assumed that hydrogen evolution at the crack tip weakens the local crystal structure, assisting crack growth.
- **Adsorption-induced cleavage:** It has been suggested that metal bonds at the crack tip are weakened by adsorption of specific anions from solution, in a manner similar to hydrogen embrittlement.

- **Film-induced cleavage:** A brittle surface film of corrosion product is postulated, and a crack growing in that surface film is allowed to propagate some distance into the bulk material. The role of the environment in this case is purely to allow the continual formation of the brittle surface film.
- **Localized surface plasticity:** This theory explains many of the metallurgy-related effects of SCC. It suggests that local corrosion due to the ruptured surface film softens the material at the crack tip. The stronger bulk material surrounding the site constrains normal plastic slip and forces crack growth.

Note that all of these proposed mechanisms require a sequence of processes, such as surface reactions, mass transport of corrosive species into the crack, surface adsorption, and bulk diffusion. Any one of these processes can be the limiting factor that sets the rate of crack growth in the plateau region of Figure 2 [1].

Factors Affecting SCC

The key role of specific combinations of material, environment, and stress in causing SCC has already been emphasized numerous times. With the assumption that these necessary conditions for SCC are present, this section will look at specific material, environmental, and stress factors that may trigger or particularly exacerbate SCC.

Material

The material property that has an overwhelming effect on susceptibility to SCC is yield strength. As illustrated by Figures 6 and 7, higher-strength materials have significantly shorter initiation times and higher rates of crack growth.

Some austenitic stainless steels and alloys are more prone to a phenomenon called sensitization, making them particularly susceptible to intergranular SCC. Sensitization refers to the precipitation of chromium carbides at grain boundaries, which depletes the local region of the corrosion-inhibiting chromium, thereby increasing susceptibility to intergranular attack [3]. The process occurs due to particular heat treatment or due to welding. For example, many austenitic stainless steels become sensitized when heated in a temperature range of 1000–1550°F (538–843°C) [1]. Note also that intergranular SCC can occur over a broader

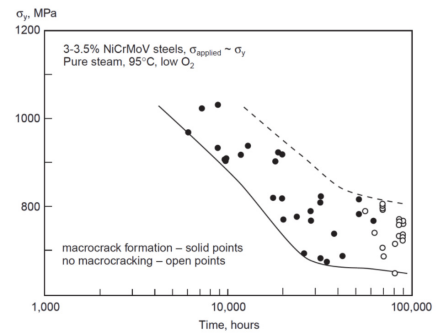


Figure 6: The effect of strength on SCC initiation for 3–3.5% NiCrMoV steels in pure low-oxygen condensing steam at 95°C [6]

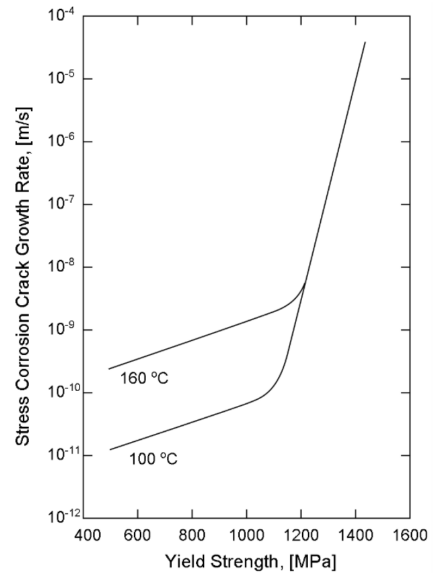


Figure 7: SCC crack growth rate dependence on yield strength for turbine rotor disk steels [7]

range of potentials than the two zones illustrated in Figure 3, due to the different response of sensitized grain boundaries relative to the bulk material.

The effect of impurities (such as MnS and P inclusion) has been investigated by many researchers, with some spread in results. However, impurity segregation at grain boundaries has been found to have an effect similar to sensitization in promoting intergranular SCC [1]. The occurrence of pitting corrosion (a common initiation site for SCC) has also been observed to be reduced with increased metallurgical cleanliness. Cleanliness also has an effect on fracture toughness, and hence the maximum size of crack allowed to propagate before failure [8].

Dissimilar metal joints, such as at welds and turbine rotor blade attachments, may also exacerbate SCC by creating an electric potential that accelerates the corrosion process [9].

Environment

As already emphasized, a particular combination of material and environment is necessary for SCC (see Table 1 for examples). However, in addition to the presence of appropriate solute species and concentration, temperature, oxygen levels, and pH must be within certain levels to allow SCC to be thermodynamically feasible (i.e., to occur at all), and kinetically significant (i.e., to occur at a noteworthy rate).

One of the leading environmental factors affecting SCC is temperature. As Figure 7 illustrates, elevated temperature exacerbates the growth rate of SCC, except for very high strength materials where the effect of yield strength is dominant.

Changes in oxygen concentration alter the electrode potential, with increasing oxygen leading to more oxidizing conditions. Figure 3 indicates schematically the potentials at which SCC is considered to be an issue (though it should be kept in mind that material inhomogeneity at grain boundaries allows SCC to occur over a wider range of potentials). In-service experience clearly shows evidence of a positive correlation between ingress of oxygen and stress corrosion cracking. Experimental data suggest that oxygen plays a role in pitting and crack initiation, but its effect on the growth of long cracks is unclear [8, 10].

The role of pH, in conjunction with electrode potential, is to determine the thermodynamic stability of the passive film. The relationship between these environmental factors is obscured and complicated by the lack of clear knowledge about the specific conditions at the crack tip.

Stress

The stress intensity is a function of uniform stress and crack size. As illustrated in Figure 2, during the propagation phase of SCC, crack growth rates are independent of stress intensity and applied stress.

However, the applied stress does have a very strong effect on initiation time. Constant-load tests have shown that a threshold value exists for the applied stress (usually $> 0.5\sigma_{y}$ and often as high as $0.8\sigma_{y}$ [1]), below which initiation will

not take place (See Figure 6). Above the threshold value, initiation time decreases rapidly with higher applied stress. There is a significant trade-off between environment and applied stress, with lower threshold values for more aggressive environments. Also, although SCC is driven by steady stresses, dynamic stresses can shorten initiation times [9].

Susceptible Boiler and Turbine Locations

This technical brief is primarily intended for an audience dealing with steam equipment at power plants. Accordingly, the most problematic locations within boilers and steam turbines, respectively, are described in this section. A brief discussion of the specific conditions that make these components susceptible to SCC is also included.

Susceptibility in Boiler/HRSG Tubes

In general, any location with potential for high concentration of contaminants and high stresses is more susceptible. This includes bends, low spots, and vertical pendants, where condensate can form during shutdown, and high-stress areas, such as at bends, welds, thickness changes, tube attachments, and support spacers. The heat-affected zone (HAZ) at welds is also a potential site for sensitization and intergranular SCC.

Damage can initiate from the ID or the OD of the steam-touched tubes or water-touched tubes (damage to water-touched tubes being specific to HRSGs). Figure 8 illustrates a typical web of stress corrosion cracks found on an economizer hairpin bend.

Ferritic materials are susceptible to NaOH. Indeed, historically the main cause of SCC in boilers was caustic contamination and buildup in crevices and riveted or welded joints, resulting in intergranular cracks originating on the outside surface of the tubes. Typically the caustic is introduced through the attemperator spray, but it can also be carried over from the boiler. This is a particular consideration for units considering a change-over to NaOH treatment or those operating without phosphate treatment in the free hydroxide zone [5].

Components constructed of austenitic stainless steel and operating at high temperatures, such as superheater and reheater sections in conventional units, are susceptible to sensi-

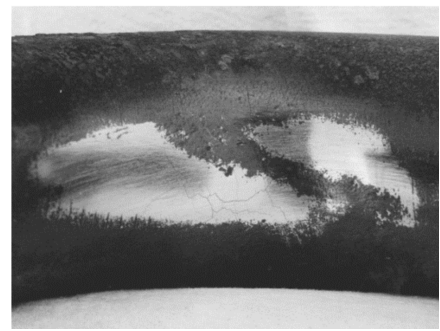


Figure 8: Fine cracks on the OD of an HRSG economizer hairpin bend intrados, apparent after removal of surface oxide by light grinding [5]

zation and intergranular SCC. HRSGs typically have lower operating temperatures, but can still sensitize in the long run [5]. Nuclear units, BWRs in particular, have experienced extensive sensitization problems in the HAZ near welds [1]. NaOH, chlorides, sulfates, and sulfate compounds are all contaminants that can cause SCC in stainless steels. These can be introduced from chemical cleaning, boiler carryover, or leakage from condensate polisher. Polythionic acids that form on the fire/gas-side of boiler tubes can also form in the moist oxygenated environment occurring during shutdown, and subsequently attack sensitized steels [5].

Susceptibility in Steam Turbines

The basic load in a steam turbine is the centrifugal tensile stress in rotating components, amplified by stress concentrations. Although SCC can occur in the longer low-pressure (LP) blades, it is more typically manifested in turbine rotors and disks. Typical locations of SCC cracking in discs are shown in Figure 9, with much of the damage these days focused in the disk rim blade attachment area. LP blade damage has been found at the root, at erosion shields, at brazed tie wire holes, and at welded or brazed covers/shrouds.

Rotors in U.S. plants are made of high-strength low-alloy steels, such as 1CrMoV, 12CrMoV, and 2-3.5NiCrMoV. Blades are typically made of martensitic stainless steel. These are all susceptible to SCC, even in “pure” water and wet steam. However, excessive levels of oxygen and moisture during shutdown, interacting with the deposits accumulated during operation, create an environment that is most damaging:

- The dynamic operating environment leads to the formation of fluid films in the phase

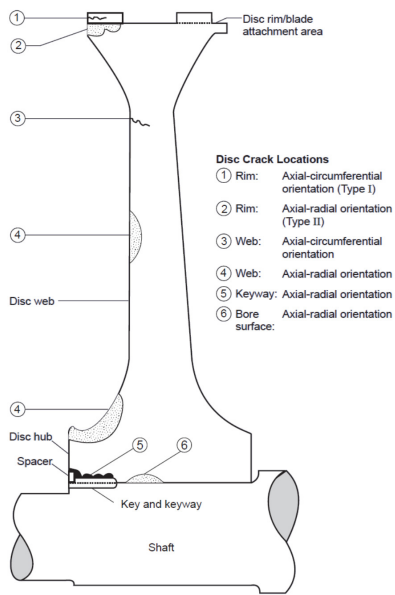


Figure 9: Typical locations of cracks found on LP turbine disks [9]

transition zone (PTZ) that concentrates steam-borne impurities (such as chlorides and sulfate) and reduces the pH. Higher impurity levels, caused by condenser leaks or improperly operated condensate polisher, will exacerbate the problem.

- Moist, oxygenated environments can occur on discs and blades during shutdown, as a result of poor practices. It has been found that oxygen levels can remain high for ~1000 h after the casing has been opened, and up to 48 h following minor air leaks [8].

SCC of turbine rotors is more prevalent in nuclear units. A survey found that 35% of BWR units and 39% of PWR units have experienced disc rim attachment cracking, compared to 26% of supercritical fossil units and only 3% of subcritical fossil units [2]. Similarly, keyway/bore cracking is much less prevalent in fossil units compared to nuclear units. The lower incidence of SCC in fossil units has been attributed to the fact that in general the dry-wet transition (PTZ) occurs at a lower temperature [8].

Preventing and Controlling SCC

As continually emphasized, SCC requires a susceptible material, an appropriate environment, and a tensile stress. Therefore, SCC can be mitigated by eliminating any of these

three necessary requirements. Below are some specific measures that can be taken to control SCC in boilers and steam turbines.

- Cation conductivity is a reliable indicator of the presence of contamination from inorganic species such as chlorides and sulfates, and from organic anions such as acetates and formates. It is commonly used to monitor and control steam and feedwater purity in power plant systems. However, one should be aware that condensation and evaporation experienced by steam-touched equipment can lead to concentration of such contaminants.
- Minimizing oxygen levels, for example through specific water chemistry (such as hydrogen water chemistry, which is suggested for BWRs experiencing intergranular SCC of sensitized steel [1]).
- Minimizing stress concentrations. For example, keyways in disks have largely been eliminated in favor of other designs, and disk rim blade attachments can be modified to incorporate larger hook radii. Hairpin bends in boilers and HRSGs can be replaced with thicker, stress-relieved bends.
- Introducing residual surface compressive stress, such as by heat treatment, rolling, and shot-peening, is an essential ingredient in preventing SCC initiation on turbine disks [9].
- The most common methods of reducing the possibility of developing sensitized microstructure are to reduce the carbon content or use “stabilized” grades of steel [5]. With lower-carbon grades of steel the objective is to have insufficient carbon to precipitate chromium carbides (however there is a tradeoff with creep strength). With stabilized steels, elements that are stronger carbide formers than chromium (such as niobium and titanium) are added to preferentially form carbides other than chromium carbide.
- Proper shutdown and layup practices will also improve the environmental component contributing to SCC. Maintaining low humidity in the turbine will reduce the formation of corrosive products.

Note that in many cases some SCC can be tolerated, as long as it is monitored through regular inspection. Liquid penetrant, eddy current, and magnetic particle inspection

methods can be used to detect indications of SCC on exposed surfaces. Ultrasonic testing is used for inspection of unexposed surfaces at turbine disk rim attachments, but it comes with many challenges and mixed results. Some designs can be inspected without blade removal by application of nondestructive volumetric inspection methods. However, some designs may require that blades are removed to inspect susceptible features using conventional surface inspection methods.

Summary

Stress corrosion cracking is a form of environment-assisted cracking caused by the synergistic effects of a susceptible material, a particular environment, and a steady tensile load. It has been found in boiler and HRSG tubes exposed to condensation and high stresses, and in turbine rotor disks and LP blades. Although ongoing research continues to shed light on this complex problem, some general statements can be made regarding this mode of damage:

- Specific combinations of material and environment must exist in order for damage to occur.
- Damage is surface initiated, usually at stress concentrators and surface defects.
- Following crack initiation, upon which a stress intensity for SCC is reached ($K_{I,SCC} < K_{I,C}$), cracks propagate at a constant rate. When the fracture toughness of the material ($K_{I,C}$) is exceeded, rapid failure ensues.
- The material properties that have the largest effect on SCC are yield strength and susceptibility to sensitization.
- The environmental factors affecting SCC include contaminant concentration, temperature, oxygen level, and pH.
- Eliminating any of the three necessary requirements for SCC can discontinue damage progression. Good water chemistry control, proper shutdown procedures, and an attention to stress levels can prevent or reduce SCC damage.

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Boiler and Turbine Damage Resources

For users interested in further information on SCC and other damage mechanisms in steam turbines and boilers, EPRI has prepared comprehensive technical reports, titled *Turbine Steam Path Damage: Theory and Practice* [9] and *Boiler and Heat Recovery Steam Generator Tube Failures: Theory and Practice* [5], respectively. These multi-volume technical reports contain detailed information and multiple photographs on a range of damage mechanisms. This information will improve plant engineers' understanding of the potential for boiler and turbine problems, condition assessment, and mitigation options. In addition, concise field guide versions, illustrated with dozens of color photos, and a poster version of this information are also available. For more information, or to obtain a copy of these resources, contact Grant Lanthorn, glanthorn@epri.com.

Electric Power Research Institute

3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
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