

# Cracked: The Secrets of Stress Corrosion Cracking

Posted by [Hira Ahluwalia](#) | [2 comments](#)

## Conditions for Stress Corrosion Cracking (SCC)

The conditions necessary for stress corrosion cracking are:

- Suitable environment
- Tensile stress
- Sensitive metal

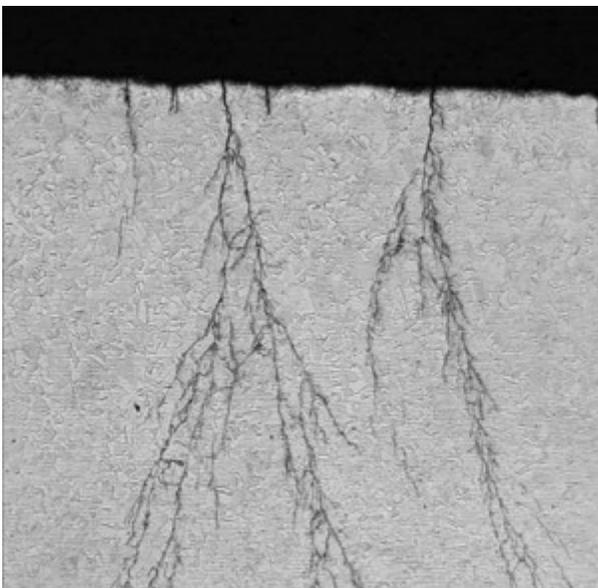
**Suitable Environment:** The most common corrosive species that has caused failures in chemical plant is the chloride ion. Chloride Stress Corrosion Cracking (CSCC) can occur in hot acid chloride solutions, sodium chloride/peroxide solutions, and seawater. Other neutral halides such as bromides, iodides and fluorides can also cause SCC of the 300 series stainless steels.

**Tensile Stress:** The combination of residual stresses from welding, the cold work from fabrication, and the cyclic stress from operating conditions are sources of tensile stress, that when above a certain threshold stress, will make the metal susceptible to stress corrosion cracking.

**Sensitive Material:** The alloy content of stainless steels, particularly nickel, determines the sensitivity of the metal to SCC. The most common grades of stainless steel, 304L, 316L, 321, 347, have nickel in the range 8-10% and are the most susceptible to SCC. Ferritic stainless steels that are nickel free, and the high nickel alloys are not subject to SCC.

## Chlorides

Chlorides, the most common of the family of halides, are the most common agent for stress corrosion cracking of austenitic stainless steels. Chloride SCC has been reported in such diverse media as natural waters, geothermal steam, industrial steam condensate, caustic etc. In most cases, except for caustic (which itself is a SCC agent), the cracking can be traced to inorganic chloride ion, Cl<sup>-</sup>.



## Transgranular chloride SCC in 304L SS

Except for particular cases involving sensitized metallic structure (containing chromium carbide precipitates in the grain boundaries) under particularly aggressive conditions, the morphology of chloride stress corrosion cracking involves multi-branched, transcrystalline cracking (through the grain). Figure 1 shows a photomicrograph of the transgranular lightning strike appearance of CSCC.

### Organic Chlorides

Organic chlorides themselves are not directly harmful to austenitic stainless steels. They will cause SCC only to the extent that they produce inorganic, ionic chlorides, by processes of hydrolysis or thermal decomposition (i.e. pyrolysis) or both.

A careful distinction must be made between organic chlorides that readily form inorganic chloride ions, and those that do not. For example, the symmetrical aliphatic chlorides do not readily hydrolyze. Ethylene dichloride (1,2 dichloroethane) is less readily hydrolyzed than the asymmetric (1,1 dichloro ethane). The chlorinated benzenes (e.g. monochlorobenzene) are less susceptible to hydrolysis than toluyl chlorides, in which the chlorine is attached to a secondary aliphatic group rather than the benzene group itself. Almost all organic chloride streams contain at least trace amounts of homologs and analogs which can contribute parts per million of chloride ions to the environment, often all that is required to initiate SCC. All organic chlorides will pyrolyze to release hydrogen chloride or inorganic chloride if the conditions are severe enough.

### Acidity

It is generally accepted that the effect of acidity or low pH is to aggravate SCC, at least until the degree of acidity needed to initiate general corrosion is attained. It does not follow, however, that raising the pH will necessarily alleviate SCC, because the pH conditions inside an incipient crack or crevice are acidic, and do not necessarily coincide with those of the bulk environment.

### Oxygen

The effect of oxygen on chloride SCC varies with the nature of the solution. It appears to be of fundamental importance in dilute aqueous solutions, like natural waters. Such solutions, if completely free of oxygen, may not cause SCC even at surprisingly high chloride levels. Therefore, effective practical control of chloride SCC has been achieved by eliminating the last vestiges of dissolved oxygen with chemical scavenging using catalyzed sodium sulfite or catalyzed hydrazine. Less thorough removal of dissolved oxygen (to 0.1 or 0.2 ppm) is of dubious value.

In more concentrated solutions of sodium, calcium or magnesium chloride, or in solutions with heavy concentrations of oxidizing ions, the presence of dissolved oxygen does not seem necessary for SCC to occur. Its role in mixed chloride/sulfide SCC varies with the alloy system.

### Temperature

Most austenitic stainless steels vessels and piping plant experience with SCC suggests that incidence of SCC rises dramatically when temperatures exceed 55-60 °C. Stainless steel items operating above these temperatures are definitely candidates for preventative measures. Stainless steel equipment operating below 55-60°C will not be totally immune to SCC. (Occasional failures have been reported on ambient temperature equipment after 10-15 years of service).

An increase in temperature generally aggravates the conditions for SCC, other conditions being equal. Cracking is more likely to occur at 80°C proceeding about four times faster at this higher temperature in “wicking” tests compared with 50°C. In tests lasting 10,000 hours each, the maximum

chloride concentration to initiate SCC was determined to be about 400 ppm at 20°C and 100 ppm at 100°C. These parameters however will vary with the nature of the specific chloride involved. For example, SCC has been reported at temperatures as low as -20°C in methylene chloride, where the aggressive species was almost certainly hydrochloric acid itself, formed by hydrolysis.

## Concentration

It is not possible to state categorically at what levels of concentration chlorides will cause SCC. In laboratory tests, one can study the time to failure in different concentrations (stress, temperature, oxygen concentration, and acidity or pH being held constant) and arrive at some conclusions. However, at low chloride concentrations, the testing time becomes excessively long. SCC must be observed (since one cannot prove a negative premise, i.e. SCC will not occur), and it has been established that very low concentrations of chloride ion (e.g. less than 10 ppm) can cause stress corrosion cracking.

## Surface Films and Deposits

In industrial practice, two other factors complicate the question of critical concentration. One is the possibility of concentrating chlorides (or other corrosive species) in crevices or vapor spaces, where evaporation or consumption of the diluents can occur. The second is that surface films can absorb or occlude chlorides, bringing their concentration to a level several orders of magnitude higher than their concentration in the bulk solution. Calcareous deposits from water, hydrated aluminum or iron oxides from steam, condensate or aqueous/organic mixtures, organic or biological films, each have been reported to cause SCC by adsorption and local enrichment of chloride species on the metal surface. Concentrations as low as 0.02 ppm in the bulk solution have been concentrated to 10,000 ppm on the metal surface by aluminum oxide films.

## Hot-Wall Effects

“Hot-wall” effects aside from deposits of water salts themselves, enter into the corrosion mechanism. It is commonly observed that water-cooled heat exchangers suffer SCC at areas of maximum heat transfer, whereas stainless components subjected to simple immersion under the same conditions do not crack within the periods of observation.

## Sulfide-Chloride Cracking

The simultaneous presence of hydrogen sulfide (or sulfides from other sources) and chlorides has a synergistic effect upon the 18-8 stainless steels. Transgranular SCC may be observed at ambient temperatures, with as little as 2 to 8 ppm chloride in the bulk solution, for 304 stainless steel in the presence of hydrogen sulfide. Apparently, hydrogen sulfide plays a specific role possibly competing with oxygen for film formation.

## 2 comments

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do you have any reference on your statement:

“Cracking is more likely to occur at 80°C proceeding about four times faster at this higher temperature in “wicking” tests compared with 50°C. In tests lasting 10,000 hours each, the maximum chloride concentration to initiate SCC was determined to be about 400 ppm at 20°C and 100 ppm at 100°C. These parameters however will vary with the nature of the specific chloride involved.”

I am writing a research paper regarding this. Any help would be appreciated.

Thanks!

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