

A review of Chloride Stress Corrosion Cracking factors for Austenitic Stainless Steel

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ABSTRACT

Chloride-Stress Corrosion Cracking (CISCC) of austenitic stainless steels has been one of the biggest challenges in the refining industry and one of the main reasons where upgrading to stainless steel may not be the miracle solution for battling corrosion problems. Even with all that is known about this mechanism, the industry still faces failures, mainly because chlorides show up when they are not expected and accounted for, leading to economic or worse, catastrophic failures.

Factors affecting CISCC like pH, operating temperature and chloride ion concentration are considered in API 581 to designate a Severity Index. Other factors like the number of inspections, the effectiveness of the inspections and time since the last effective inspection etc. are considered to determine the Damage Factor. However, factors like presence of oxygen, effects of extreme pH and temperatures or stress relieving are not considered. A proposed Risk Assessment Tool using a new factor “susceptibility modifier” to API RP 581 Task Group was presented in November 2016 and has been incorporated in the newly released API 581 – Addendum 2 in October 2020.¹

This paper will identify and document how these different factors affect the susceptibility of austenitic stainless steel to Chloride-Stress Corrosion cracking based on a review of currently available literature. A review of current industry best practices and a review of how the Oxygen content, the pH and application of stress relief affects Chloride-Stress Corrosion Cracking will be documented and presented.

Key words: stainless steel, chlorides, stress corrosion cracking, pH, chloride content, temperature, oxygen, stress relief

INTRODUCTION

Chloride promoted stress corrosion cracking (CISCC) is a damage mechanism that can occur in a chloride containing aqueous environment. Damage can occur during in-service or during shutdown, if chloride containing solutions are present, especially at temperatures above 66°C (150°F). Austenitic stainless steels are highly susceptible to CISCC. Damage can occur internally (from process, wash water or firewater etc.) or it can occur externally under insulation. CISCC is typically transgranular and highly branched. Susceptibility to CISCC is usually assessed based on the chloride content, pH and

temperature. The formal risk assessment methodology used in API RP 581 Third Edition ⁽¹⁾ provides a quantitative procedure to establish an inspection program using risk-based methods for pressurized fixed equipment. In API 581, Section 12 “SCC Damage Factor – Chloride Stress Corrosion Cracking,” the basic assumption is that CISC of austenitic stainless steels can occur in a chloride-containing aqueous environment and the susceptibility to CISC is dependent on:

- the concentration of the chloride ions,
- the temperature, and
- pH

These factors are outlined in the API Basic Data Table, 12.1. The susceptibility, characterized as High, Medium, Low, or None, is determined by using Figure 12.1, Table 12.2 (Temperature in °F) and Table 12.3. Table 12.2 and Figure 12.1 determines the base susceptibility to cracking for a range of pH and temperatures. Table 12.3 determines the Susceptibility Modifier for variables like chloride content, oxygen content and the presence of deposits. The CISC susceptibility value is determined by adjusting the base susceptibility with the susceptibility modifiers. Table 12.2, Figure 12.1, and Table 12.3 have been newly incorporated into API in October 2020.

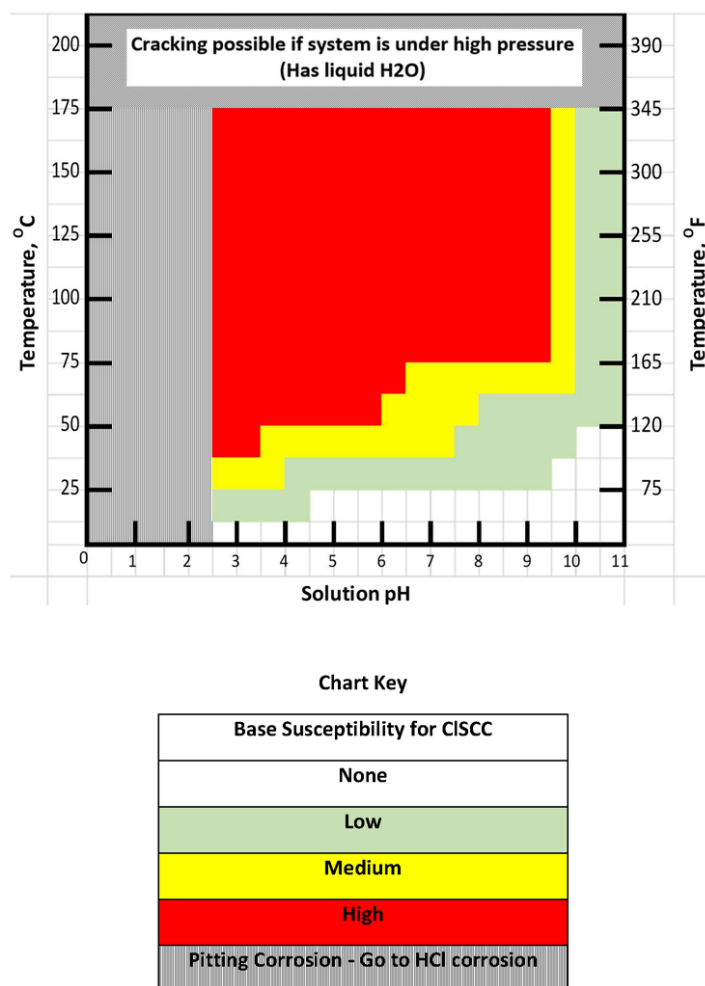


Figure 1: API 581, Figure 12.1 Determination of CISC Susceptibility²

¹ API, American Petroleum Institute, 1220 L Street, NW, Washington, DC 20005 USA

Table 1: API 581, Table 12.3 – Determination of the Susceptibility Modifier for CISCC²

Environmental Variable	Susceptibility Modifier
Cl < 10 ppm	-1
Oxygen < 90 ppb	-1
Cl > 100 ppm	+1
Deposits	+1

The determination of susceptibility using these methods has worked to a good extent in anticipating conditions where susceptibility to CISCSC could be high and in preventing catastrophic failures by controlling those factors. However, relying on these simplistic factors has proven to be insufficient. Additional factors like condition of the steel (sensitized, pitting or crevice corrosion already present), extreme pH, oxygen content and temperature excursions are critical and interconnected. These factors affect cracking susceptibility and should be considered.

OVERVIEW OF TECHNICAL LITERATURE REVIEW

Effect of localized corrosion and pitting

Wrought austenitic stainless steels have high fracture toughness and for pressure vessels and piping “Leak-Before-Break” is the most likely consequence of CISCSC. There is a large amount of published work on various aspects of CISCSC in austenitic stainless steels and it has been established that CISCSC initiates from sites of localized pitting or crevice corrosion and that CISCSC crack growth can be sustained at a chloride concentration and temperature levels significantly below those required to initiate cracking.³

The high corrosion resistance of austenitic stainless steels in most atmospheric and aqueous environments is due to passivation by a thin layer of chromium oxide. Wet and humid environments containing chloride ions can cause pitting corrosion and crevice corrosion of austenitic stainless-steel components. Components under an applied or residual stress can deteriorate further by stress corrosion cracking in these conditions. This demonstrates an essential feature of localized corrosion on stainless steels, i.e. the region inside a pit, a crevice or a crack is an isolated electrochemical cell that contains a much more aggressive environment than the bulk solution. Localized corrosion in an active pit or inside a crevice produces a solution with the following characteristics:³

- Higher chloride level than the bulk solution
- Strongly acidic with a very low pH
- Nearly saturated with complex ions produced from dissolved metal, chloride and water.

The initiation of CISCSC has been shown to involve a competition between localized corrosion, which is strongly dependent on chloride concentration but has a weak dependence on temperature, and crack growth which has a strong dependence on temperature but is relatively unaffected by chloride concentration and pH. CISCSC propagation occurs when cracks grow more quickly from the pit or crevice than the rate of corrosion. It follows that environmental factors, which affect localized corrosion, are also likely to affect the initiation of CISCSC and that more severe conditions will be required to initiate CISCSC than are needed to sustain crack growth. Fracture mechanics tests have shown that CISCSC propagation can begin at low stress intensities and for fabricated structures containing tensile residual stresses, the critical depth of localized corrosion to initiate CISCSC would be <1mm.³

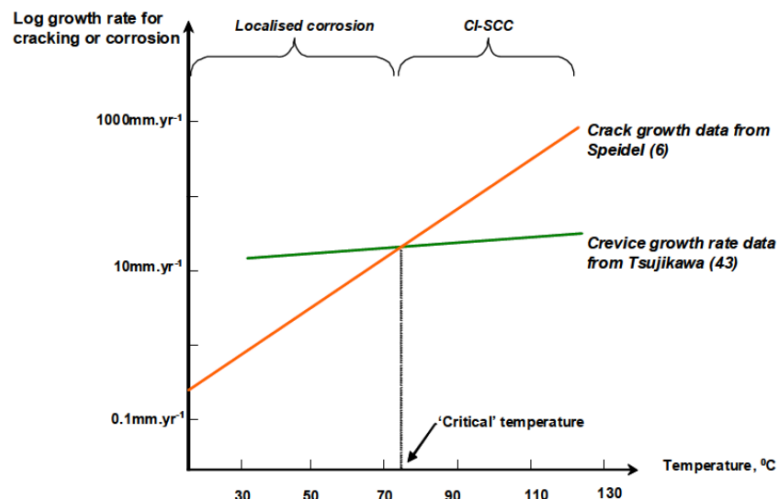


Figure 2: Schematic graph demonstrating how changes in crack growth rate or corrosion rate affects the critical temperature for CISC³

It has been proposed that crack growth is also restricted to a range of electrochemical potential that is defined by an upper limit where dissolution exceeds crack growth and a lower limit set by re-passivation i.e., CISC only occurs when a crack grows more quickly than the rate of metal removal by localized corrosion. Figure 2 is a schematic description of this theory. This demonstrates a temperature dependency of CISC because crack growth increases more rapidly with temperature than the rate of localized corrosion.³

Results of stress corrosion tests carried out and other published data have confirmed that it is very difficult to initiate CISC on bare, smooth specimens under laboratory conditions when there is no localized corrosion of the surface under stress.³

Effect of Oxygen Content

Austenitic stainless steel can suffer SCC even at ambient temperatures in the presence of concentrated chlorides and strong oxidizers. Such conditions can arise in the thin condensed aqueous films which can form in humid seacoast atmospheres. In addition, ferric ions from surface rusts and chlorine compounds from biocides can supply strong oxidizers. Austenitic stainless steels are used extensively in boilers and heat exchangers of nuclear-fueled power plants, and they are generally resistant in such environments. Results of experimental data in Figure 3 shows that careful control must be exercised over chloride and dissolved oxygen.⁴

A lot of studies have been performed to assess the chloride-oxygen stress corrosion cracking mechanisms in austenitic stainless steels in high purity water at temperatures 250°C to 350°C (482°F to 662°F) over a wide level of stress levels. Cracks formed by CISC are usually transgranular with extensive branching and are relatively unaffected by grain boundaries. Oxygen is viewed as a critical component and it has been reported that cracking is transgranular unless the material is sensitized, when mixed or intergranular modes are observed.⁵ IGSCC of sensitized austenitic stainless steel has been a recurring and expensive problem in cooling water piping of boiling-water nuclear power plants.

It has been found that in annealed 304 SS prestressed specimens exposed to oxygen (~8 ppm of O₂) solutions at 260°C (500°F) containing 6 and 30 ppm of chlorides, transgranular stress corrosion cracking occurred in 25 and 5 hours, respectively. If the oxygen content was increased to 158 ppm and chlorides concentrations increased to 600 ppm, then failure occurred in 30 minutes.