



Subject: Eight Forms of Corrosion

This is the fourth of eight primers which introduce the forms of corrosion likely to be encountered in the petrochemical, refining, fertilizer, and other industries. The eight forms have been used for decades to describe, by appearance, the common degradation mechanisms in metals and alloys.

4. Pitting Corrosion

Pitting corrosion occurs at sites of localized passivity breakdown, material defects, and other locations which become anodic to the surrounding metal surfaces. Pitting is difficult to predict in lab or field studies as it can have an incubation time of months or even years. Once pits form, they can become self-sustaining (autocatalytic) as the environment within the pit trends toward greater acidity. Undercut and cavernous shaped pits are more likely to be self-sustaining as are those which are covered with tubercles, carbuncles, or corrosion caps. Pit growth is generally favored in the direction of gravity though any orientation is possible. Other factors which increase the propensity for pitting include low velocity or stagnant flow, solids deposition, heat tinting from welding, increased surface roughness, cold work, and sensitization.

Chlorides are the most common pitting agent as they can destroy the passive layer on common materials such as stainless steels and high alloys. Oxidizing metal chlorides such as ferric (FeCl_3) or cupric (CuCl_2) chloride are also prolific pitting agents. Recall from the primer on crevice corrosion that an aggressive ferric chloride solution was used in ASTM G48 test methods. Biological activity can also contribute to pitting and is commonly known as Microbiologically Influenced Corrosion (MIC).

The pitting performance of metals and alloys is determined by their chromium (Cr), molybdenum (Mo), tungsten (W), and nitrogen (N) levels. As the percentages of these elements increase in an alloy so does their resistance to pitting corrosion. Based on these elements, alloy manufacturers and owner-operators have developed several formulas for calculating an alloys Pitting Resistance Equivalent Number (PREN). One of the widely used calculation methods is: $\text{PREN} = \% \text{Cr} + 3.3(\% \text{Mo} + 0.5\% \text{W}) + 16(\% \text{N})$ and the value is generally higher for materials with greater pitting resistance. The PREN for Type 316 stainless steel is 25.8, for super austenitic stainless AL-6XN or 254SMO it is 37-45, and for Alloy 625, Alloy C276, and newer generation C-Type alloys such as Alloy 686 it is 41-51.

ASTM G48 provides standardized pitting test method C for nickel-based and chromium-bearing alloys, and method E for iron-based alloys, i.e., various stainless steels. Both methods use an aggressive ferric chloride solution. The G48 tests are repeated at varying temperatures to determine the temperature above which pitting corrosion occurs, i.e., the Critical Pitting Temperature (CPT). NOTE: While knowing the G48 CPT is of value, it may not reflect an alloy's performance in your specific environment.

The CPT values are generally higher for materials with higher levels of those elements known to improve pitting. ASTM G48 also provides a formula for estimating the CPT of both iron-based (stainless) alloys and nickel-based or chromium-bearing alloys. The CPT formula is as follows: $\text{CPT } (^\circ\text{C}) = 2.5(\% \text{Cr}) + 7.6(\% \text{Mo}) + 31.9(\% \text{N}) - 41.0$.

During G48 testing, or through use of the G48 estimating formulas, the CPT for Type 316 stainless steel will be $\sim 2^\circ\text{C}$ ($\sim 36^\circ\text{F}$), for super austenitic stainless AL-6XN or 254SMO it is $70\text{--}75^\circ\text{C}$ ($158\text{--}167^\circ\text{F}$), and for Alloy 625, Alloy C276, and newer generation C-Type alloys such as Alloy 686 it is $>85^\circ\text{C}$ ($>185^\circ\text{F}$), the maximum G48 test temperature. NOTE: The CPT for most alloys is higher than their CCT.

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