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Chloride pitting and the limits of PREN

Nordoxa — Materials & Corrosion Engineering, Rotterdam

Pitting is the most common reason stainless steel is taken out of service, and chloride is almost always the agent. It is a localised breakdown of the passive film that becomes self-sustaining once it starts.

Chloride ions adsorb at a weak point in the passive film and break it down locally. Metal dissolves at the exposed site. The dissolved metal ions hydrolyse, which lowers the pH inside the pit. Chloride migrates in to balance the charge. The result is a small volume of concentrated, acidified chloride solution that prevents the film from reforming, sitting inside a component whose entire outer surface is available to act as a cathode.

What PREN is

The pitting resistance equivalent number is an empirical weighting of the three alloying elements that most affect resistance to chloride pitting: PREN = %Cr + 3.3 x %Mo + 16 x %N. Some duplex-specific versions use a factor of 30 for nitrogen. Which variant is used matters when comparing published figures, and the variant is often not stated.

Grade	Typical composition	PREN	Common judgement
304 / 1.4301	18Cr, 8Ni	18-19	Indoor and mild atmospheres
316L / 1.4404	17Cr, 10Ni, 2.1Mo	24-26	Marine atmosphere, not immersion
2205 / 1.4462	22Cr, 5Ni, 3.1Mo, 0.17N	34-36	Chloride process service
904L / 1.4539	20Cr, 25Ni, 4.3Mo	34-36	Acid and chloride service
254 SMO / 1.4547	20Cr, 18Ni, 6.1Mo, 0.2N	43-45	Seawater, with limits
Alloy 625	21Cr, 9Mo, 3.6Nb	50+	Severe service

What PREN is not

PREN ranks alloys. It does not predict behaviour, and it carries no units of anything physical. Four things it cannot capture matter more than the number itself.

Temperature. Pitting resistance falls sharply with temperature, and each alloy has a critical pitting temperature below which pits do not initiate in a given solution. Measured to ASTM G48 Method E, 316L typically sits around 15 C, 2205 around 35 C and 6 percent molybdenum grades around 70 C in the standard ferric chloride test.

Surface condition. A ground or pickled surface resists pitting substantially better than an as-welded one. Weld heat tint sits over a chromium-depleted layer and is a preferential initiation site.

Crevices. Crevice corrosion follows the same mechanism as pitting but initiates far more readily, because the occluded geometry is supplied by the design. Critical crevice temperatures typically run 15 to 25 C below the critical pitting temperature for the same alloy.

Stagnation. Stagnant chloride water is much more aggressive than flowing water, because deposits settle and the local chemistry is never refreshed. Hydrotesting seawater left in a system over a shutdown has ruined a great deal of correctly specified stainless steel.

> *316 is not a seawater material. It performs acceptably in marine atmosphere and poorly in continuous immersion, particularly where there are crevices or stagnant periods.*

Standards and further reading

1. ASTM G48 — Pitting and crevice corrosion resistance using ferric chloride solution.
2. ASTM G150 — Electrochemical critical pitting temperature testing of stainless steels.
3. EN 10088-1 — Stainless steels: list of grades and compositions.