Corrosion of stainless steel by hot caustic

Research using solutions of chemically pure caustic (sodium hydroxide [NaOH]) led to the development of a diagram that attempts to delineate the parameters of concentration and temperature governing stress corrosion cracking (SCC) of type 300 series austenitic stainless steels (SS), such as types 304 (UNS S30400), 316 (S31600), and their low-carbon forms, types 304L (S30403) and 316L (S31603). This diagram (Figure 1) is analogous to a similar diagram for caustic embrittlement of carbon steel under stress from welding or cold-forming. The term caustic embrittlement is a misnomer because the phenomenon is simply SCC of steel in the alkaline solution.

The 1 mpy (0.0254 mm/y) isocorrosion line in Figure 1 is nearly constant at 100°C (212°F) from -20% to 50% caustic. The dashed line delineating SCC (labeled Apparent SCC boundary) is U-shaped, with the minimum at ~40% caustic and ~240°F (115°C).

In actuality, there is a real possibility that type 300 series SS may lose passivity and undergo rapid general corrosion in hot 40% to 50% caustic. Probable safe limits are well below those indicated by the diagram, perhaps 70°C (158°F) for 50% caustic and 80°C (177°F) for 40% solution. However, oxidizing contaminants can maintain passivity. Extra-low interstitial ferritic SS grades, such as alloy 26-1 (S44627), have been used instead of Ni (UNS N02200) in caustic evaporators provided the chloride content is sufficiently high.

Above 300°C (570°F), the danger of caustic SCC is very great. Bellows-type piping expansion joints made of type 321 (S32100, Fe-18% Cr-10% Ni-Ti stabilized) in 300-lb to 400-lb steam (~215°C to 230°C [420°F to 445°F]) are prone to rapid SCC if there is entrainment of caustic from boiler treatment. When high-temperature caustic SCC of SS is encountered, there is a characteristic gunmetal blueing of the surface.

The role of chlorides in caustic cracking is often misunderstood. Chlorides, if present, are not a factor. There have been failures of alloys 800 (N08800, Fe-30% Ni-20%

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Cr) and 825 (N08825, Fe=40%, Ni-20% Cr-3% Mo-2% Cu), high-Ni alloys that are very resistant to chloride SCC, used as replacements for type 300 series SS. Russian investigators reported that chlorides, a common contaminant in concentrated caustic, do not aggravate SCC and may even play an inhibitive role.

Alloy 600 (N06600, Ni-15% Cr-8% Fe) is satisfactory in hot caustic service. For bellows, alloy 625 (N06625, Ni-20% Cr-8% Mo-Cb stabilized) is currently used almost exclusively.

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Reference

Corrosion Scientists,
Engineers, Practitioners...
Share your “Phorgotten Phenomena” items with your colleagues. Articles should be 1,000 words or less; photos and drawings are appreciated. Send submissions to Warren I. Pollock, MP Technical Editor, NACE, P.O. Box 218340, Houston, TX 77218-8340.

C.P. Dillon is the 1998 NACE International T.I. Hull Award recipient for his outstanding contributions in the field of publications. He is the author of Corrosion Control in the Chemical Process Industries, 2nd Edition (St. Louis, MO: MTI, 1997), now in its second printing. This book is available from NACE.

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