Corrosion in Caustic Solutions

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Corrosion by caustic (sodium or potassium hydroxide) at all concentrations is easily handled at room temperature with a variety of metals and alloys, including carbon steels.

It becomes increasingly more corrosive with increasing temperature and concentration. The useful safe limit of carbon steel is approximately 150^{o}F/65^{o}C, both with regard to caustic stress corrosion cracking (CSCC) and corrosion. Stainless steels are more resistant to general corrosion compared with carbon steel; however, they can suffer CSCC at approximately 250^{o}F/121^{o}C.

As a general rule, the resistance to caustic solutions increases with increasing nickel content. Susceptibility to caustic SCC is dependent on several variables, including alloy content, caustic concentration, temperature and stress level. As with other cracking mechanisms, there is a threshold stress level where cracking will not occur; unfortunately, the threshold level for the high nickel alloys in high-temperature caustic has not been determined precisely. Much data has been obtained on alloy 600 in caustic environments because of its extensive use as steam generator tubing in pressure water reactors (PWR). Alloy 200 (pure nickel) is considered to be immune to all but the most severe caustic environments, including molten caustic. Literature corrosion data for other nickel-based alloys is more difficult to find. This is partly due to the fact that many nickel-based alloys, (i.e., alloys 625, C-276, B-2), contain significant quantities of molybdenum for resistance to aggressive acid solutions. As the molybdenum containing nickel-based alloys are more expensive than comparable nickel content alloys without molybdenum (alloy 600), and molybdenum does not significantly contribute to caustic resistance, they have not been studied much. Another difficulty with ranking alloys for caustic service based strictly on nickel content is the dual problem one has with caustic, i.e., it can cause general corrosion and well as SCC. Also, depending on caustic concentration, temperature and other environmental factors, including whether oxygen is present or not, ranking of alloys can change. This is true of alloys 800 and 600. *Table 1* shows alloys with useful resistance to caustic, categorized by resistance limits. The table is based on literature corrosion information and is believed to represent conservative maximum temperature and concentration limits. However, when in determining whether a specific alloy will provide resistance in caustic service, the environment must be known well or testing should be conducted.

Table 1

Alloys for Caustic Soda Service by Corrosion Resistance Category

Composition (wt. %)									
Category	**Alloys**	**UNS Number**	**C**	**Fe**	**Cr**	**Ni**	**Mo**	**Cu**	**Others**
Category A alloys are useful at all concentrations and temperatures									
A.	Alloy 200	NO2200	0.15	0.40	-	99 min.	-	-	-
Category B alloys - useful to 350°F (176°C)and 50% concentration. May show useful resistance up to 600F; however, should be tested first.									
B.	Alloy 690	NO6690	0.03	7-11	27-31	58 min.	-	-	-
B.	Alloy 600	NO6600	0.15	6-10	14-17	72 min.	-	0.5	-
B.	Alloy 400	NO4400	0.30	1.0-2.5	-	63-70	-	28-34	-
B.	Ebrite 26-1*	S44627	0.01	Bal.	25-27	0.50	0.75-1.5	0.2	0.05-0.20 Nb
Category C alloys - Useful to 50% caustic at atmospheric boiling (300F). May exhibit resistance similar to Category B alloys, but based on limited data, should be tested before use									
C.	Alloy 625	NO6625	0.10	5.0	20-23	Bal.	8-10	-	-
C.	Alloy C-276	N10276	0.02	4-7	14-16	Bal.	15-17	-	3-4.5 W
C.	Alloy B-2	N106650	0.02	2.0	1.0	Bal.	26-30	-	-
Category D alloys - useful to 250°F (121°C)and 50% concentration									
D.	Alloy 800	NO8800	0.10	Bal.	19-23	30-35	-	0.75	-
D.	Alloy 20	NO8020	0.07	Bal.	21-23	32-38	2-3	3-4	(4xC) Ti min.
Category E alloys - useful to 200°F (93°C) and 50% concentration									
E.	304SS	S30400	0.03	Bal.	18-20	8-10	-	-	-
E.	316SS	S31600	0.03	Bal.	16-18	10-14	2-3	-	-

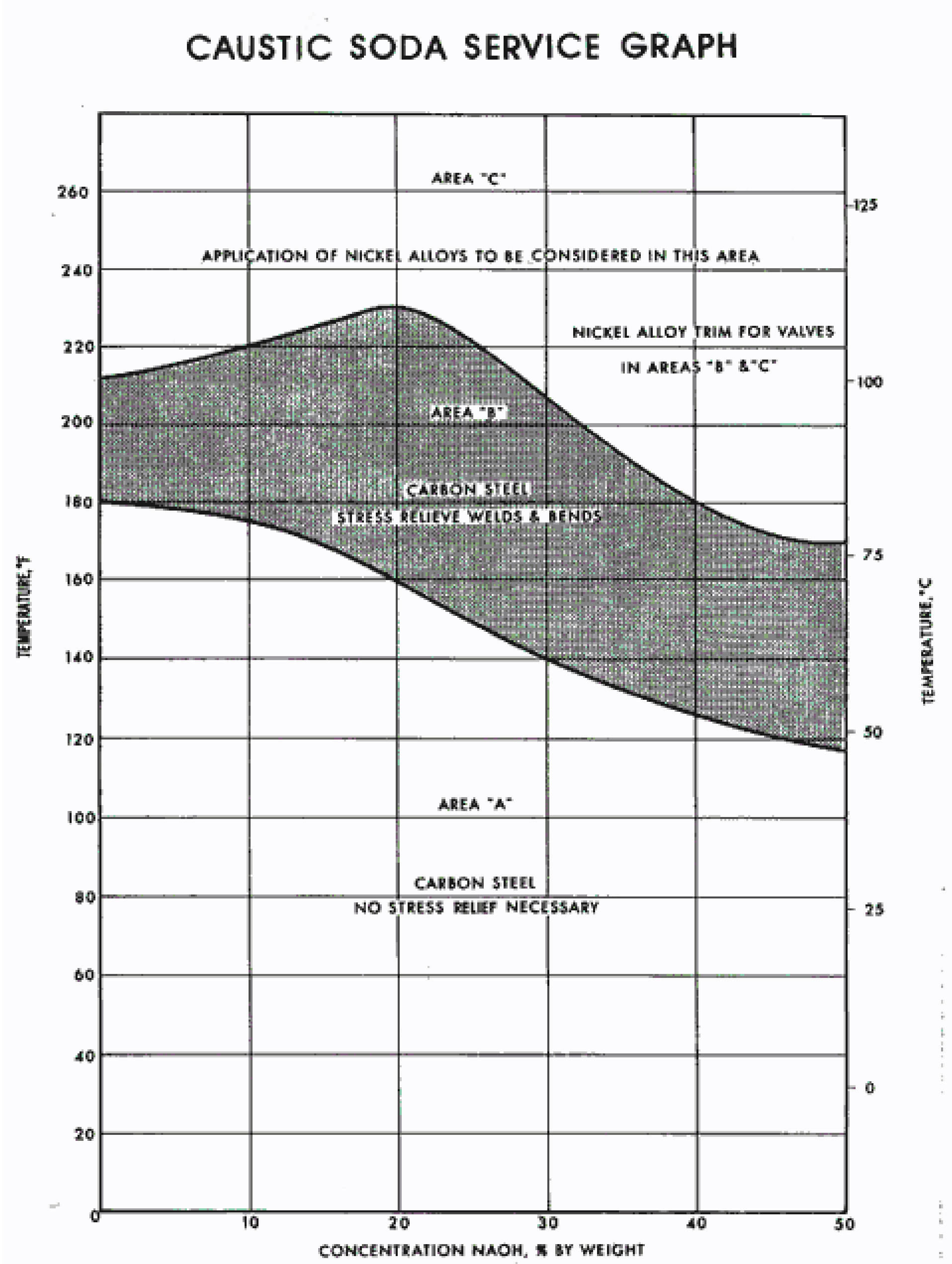
* Tubing and piping only.

Corrosion Resistance of Alloys to Caustic Solutions

Carbon and Low Alloy Steels

Sodium and potassium hydroxides (both hereafter referred to as **caustic**) are commonly handled and stored at ambient temperatures in all concentrations with carbon steel equipment. At temperatures above ambient, corrosion rates of carbon steel become greater and is accompanied by a risk of caustic stress corrosion cracking (CSCC). Low concentrations of caustic can be safely handled by carbon steel up to 180°F/82°C, where CSCC starts to become a risk factor, while the safe upper limit for a 50% solution is approximately 150°F/65°C, although cracking has occurred at temperatures as low as 120°F/48°C. The *Caustic Soda Service Graph* [1] is a widely used guide for determining safe operating temperatures with respect CSCC of carbon steels at various concentrations of caustic.

Corrosion of Carbon Steels in Caustic Soda



Graph showing corrosion resistance of carbon steel, stainless steel and nickel alloys in caustic solutions, based on temperature and concentration.

Ferritic Stainless Steels

The high purity ferritic stainless steels such as E-brite 26-1 (UNS S44627) exhibit excellent resistance to aggressive caustic solutions, with performance far superior to the austenitic stainless steels and, reportedly, at least as good as nickel [2]. This superior resistance in some caustic solutions has been attributed to the presence of hypochlorates or chlorates comtaminants, which are detrimental to nickel alloys [3]. One source reports that 26-1 is useful up to 300°F/148°C to 350°F/177°C [4]. Another reports good resistance at 350°F/177°C - 400°F/204°C and 45% NaOH [5]. Based on their good resistance to caustic, particularly those containing oxidizing contaminants, they see extensive use as caustic evaporator tubes. However, the Achilles heel of the ferritic stainless steels is inherent poor toughness of welded joints and low strength at elevated temperatures; therefore, they are used not normally used for pressure vessel applications.

Austenitic Stainless Steels

Austenitic (300 series) stainless steels possess good resistance to caustic up to approximately 50% and temperatures about 200°F/93°C. At, and above 200°F/93°C, the austenitics exhibit unstable passivity and can suffer severe general corrosion if activated. Above approximately 250°F/121°C they are susceptible to SCC (*see Figure*). No distinction is made between 304SS and 316SS regarding resistance to caustic as their behaviors are similar. They are also susceptible to chloride SCC if substantial chlorides are present in low grade caustic.

Corrosion and CSCC limits of Austenitic Stainless Steels

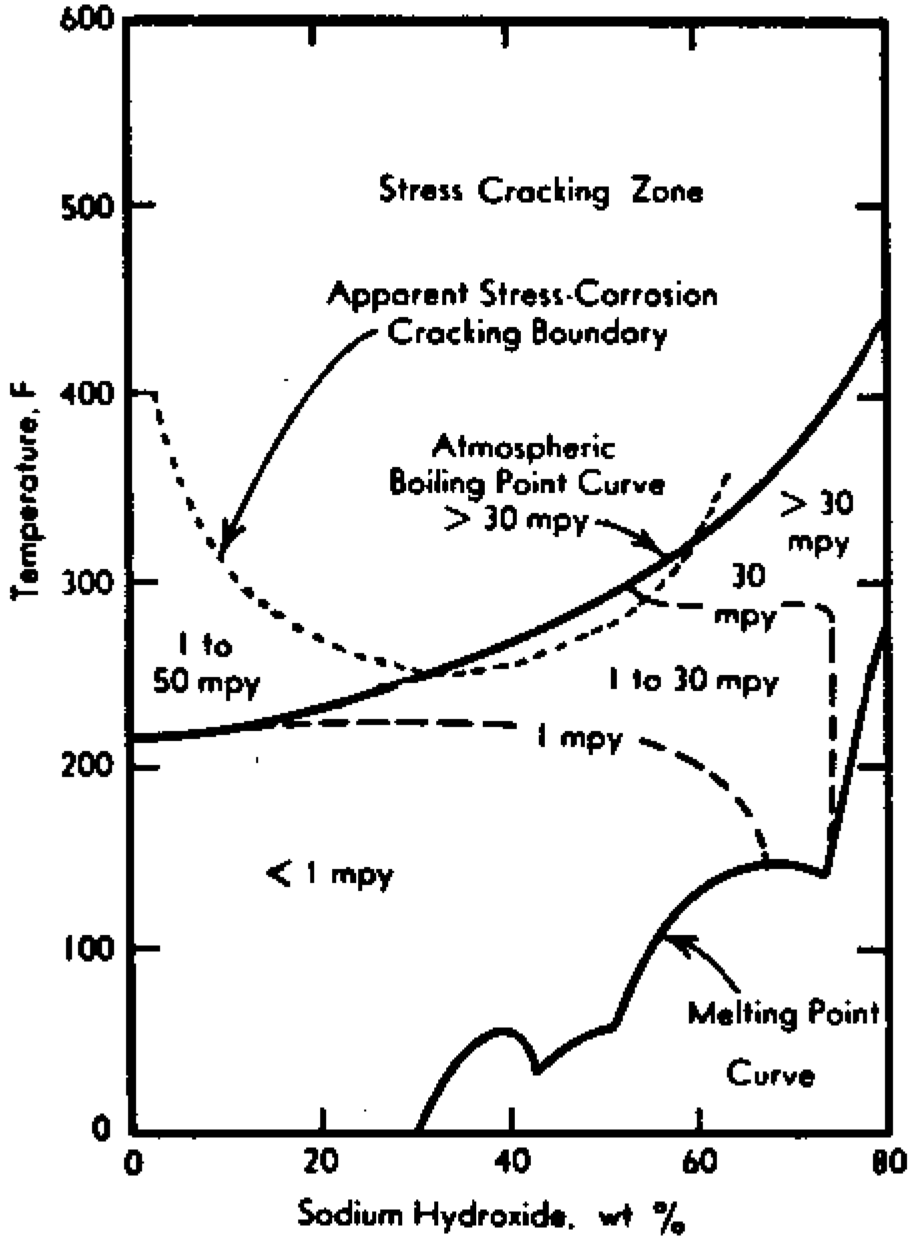


Figure. Caustic corrosion and CSCC of austenitic stainless steels, as depicted by isocorrosion graph

Duplex Stainless Steels

The duplex stainless steels were developed to exhibit comparable general corrosion resistance as 316SS, but with reduced susceptibility to chloride stress corrosion cracking. The higher alloyed duplex stainless steel alloys, ones with significant molybdenum and nitrogen additions, can be superior to 316SS in certain environments.

High Nickel Austenitic Stainless Steels

The high nickel family of stainless steels are those containing approximately 25-35 wt. % nickel, and include such non-patented and proprietary alloys as 904L, Sanicro 28, alloy 20 Cb-3, alloy 800, etc. With these alloys, resistance to aggressive (high temperature) caustic solutions increases significantly compared with the 300-series stainless steels. Meaningful corrosion resistance data is available for alloy 800, much less for the other alloys listed here; therefore, the discussion on the resistance of this family of alloys will concentrate on alloy 800. Although it is not possible to rank the above alloys listed, and resistance will vary between them, based on their similar nickel contents, similar order-of-magnitude resistance between the alloys can be inferred. Most studies of the highly alloyed stainless steels and nickel-based alloys have been based on determining susceptibility to caustic SCC. This would infer that, with these alloys, CSCC is more important as a potential failure mechanism than general corrosion at moderate temperatures. CSCC is also more critical as general corrosion can be observed and monitored, while CSCC is insidious, causing unexpected failures. Based on limited data, alloy 800 should possess satisfactory resistance to caustic solutions of 50% up to 225°F/107°C [6]. It has been made to crack in molten caustic at 600°F/315°C. Between these two temperatures, the data becomes more muddled. According to one source [2], the general corrosion rate of alloy in simulated first-effect caustic liquor (43% caustic) at 300°F/148°C is excessive (>39mpy) [7]. Other, non published data, suggests that alloy 800 may be resistance to SCC at 500°F/260°C in 10% caustic but not in a 50% solution. Another source suggests that the corrosion rate of alloy 800 in boiling 50% caustic (300°F/148°C) is excessive (39 mpy).

Based on the above data, a recommended safe use of alloy 800 is 50% caustic at approximately 250°F/121°C, based on general corrosion. It may exhibit a higher temperature limit, based on CSCC. Its use, predicated on periodic inspection for SCC, is not recommended as are alloys 400, 600 and 690, because when it has cracked the time to cracking was very short (14 days), while the time to cracking of alloys 600 and 690 were much longer.

Nickel-based Alloys

The nickel based alloys under consideration include alloys 400, 600, 200, 625, C-276 and B-2. Alloys 200, 400, 600 and 690 have historically been the materials of choice for aggressive caustic service and possess excellent resistance to caustic over a wide range of temperatures and concentrations. Based on nickel content, all of the listed alloys should possess good resistance to high-temperature, concentrated caustic solutions. However, little data is available for alloys 625, C-276 and B-2. Available data for alloy B-2 suggests that it is resistant to all concentrations of caustic up to 70% at 250°F/121°C, with corrosion rates of less than 2 mpy [8]. In boiling 60% caustic

(328°F/164°C) and boiling 70% caustic (375°F/190°C) the corrosion rate was less than 20 mpy. C-276 suffered CSCC in boiling 50% caustic (300°F/148°C) when cold reduced to 60% and did not crack in the mill annealed condition. In 30% caustic at 550°F/287C, C-276 experienced high corrosion rates (>42 mpy). The same data suggests that alloys C-22, C-276 and B-2 should be resistant to CSCC in boiling 50% caustic. Above 70% caustic at temperatures greater than 300°F/148°C nickel is the preferred choice, as alloys 400, 600, and 690 may experience excessive general corrosion rates.

1. Corrosion Data Survey, Metals Section, NACE Int., Houston, Texas.

2. Kearns, J.R., Johnson, M.J., "The Corrosion of Stainless Steels and Nickel Alloys in Caustic Solutions", Corrosion 84, Paper No. 146, NACE International, Houston, Texas.

3. Process Industries Corrosion - The Theory and Practice, NACE International, Houston, Texas.

4. I.A. Franson, Internal Laboratory Reports, Allegheny Ludlum Steel Corp., Brakenridge, PA 1982.

5. Guidelines For Preventing Stress Corrosion Cracking in the Chemical Process Industries, MTI Publication No. 15, NACE International, Houston, Texas.

6. Inco Alloys, Huntington, W. Virginia.

7. Dechema Corrosion Handbook, Vol. 2, ISBN 3-527-26653-4.

8. Friend, W. Z., Corrosion of Nickel Based Alloys, John Wiley & Sons, New York.