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Alloy selection for service in caustic soda

A GUIDE TO THE USE OF
NICKEL-CONTAINING ALLOYS

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Introduction

Caustic soda (i.e., sodium hydroxide, NaOH) and chlorine are co-produced by the electrolysis of a sodium chloride solution. Both chemicals find worldwide application in the chemical and related process industries. Alloy selection for chlorine is discussed in another Nickel Institute publication.¹ Caustic soda ranks third in tonnage production among the inorganic chemicals; worldwide annual consumption is around 65 million tonnes.

Roughly half of all caustic soda produced is used in the manufacture of other chemicals. Another 16% is consumed by the pulp and paper industry. Other important uses are in the production of PVC, rayon, cellulose, textiles, petroleum products, soaps, production of bleach, scrubbing acidic components from industrial off-gases and the refining of bauxite ore in the production of aluminium.

A number of materials of construction may be used to produce and handle caustic solutions. Their suitability for specific applications will depend upon factors associated with the concentration and use of the caustic and the process variables involved. A more detailed discussion of all aspects of materials selection for caustic soda is available elsewhere.²

In general, factors to be considered in materials selection include practicality, safety and health aspects, availability, mechanical properties, corrosion resistance, risk/benefit considerations and economics. Caustic soda is highly toxic by either ingestion or inhalation and is a strong irritant to the eyes, skin, and mucous membranes; that is, it is “corrosive” in the physiological sense as well as being corrosive to materials of construction. Beside potential burns to the eyes or skin, fire may produce irritating or poisonous gases that are harmful if inhaled.

Critical factors in caustic soda service include:

1. The concentration of the caustic solution.
2. The temperatures to be encountered (including possible excursions).
3. The presence of other chemicals in the caustic, as contaminants or additives.
4. Tolerance limits for metallic ion contamination of the caustic itself (or of the process end-product).
5. Residual or applied tensile stresses, which may affect corrosion resistance.
6. The economics of cost/life considerations.

Metals and alloys most frequently considered for use in caustic soda are carbon steel, stainless steels, nickel and high-nickel alloys. Some alloys, with their generic names, common trade names, UNS numbers and nominal compositions are given in *Table 1*.

Table 1 Nominal composition of nickel-containing alloys many are used in Caustic Soda

		Nominal composition, %						ASTM Spec. ^b	
Alloy	UNS Number ^a	Ni	C	Cr	Mo	Cu	Fe	Plate	Seamless tube and pipe
Group I – Commercially pure (C.P.) nickel and nickel-copper alloys									
200	N02200	99.5	0.08	-	-	-	0.2	B162	B161
201	N02201	99.5	0.01	-	-	-	0.2	B162	B161
400	N04400	66.5	0.2	-	-	Bal	1.2	B127	B165
K500	N05500	66.5	0.25	-	-	Bal	1.2	B127	B165
Group II – Chromium-containing nickel alloys									
600	N06600	76	0.08	15.5	-	-	8	B168	B167
601	N06601	60	0.05	23	-	-	Bal	B168	B167
825	N08825	42	0.03	21.5	3	2.25	30	B424	B163
625	N06625	61	0.05	21.5	9	-	2.5	B443	B444
C-22/622	N06022	56	0.01	21.5	13.5	-	4	B575	B622
C-276	N10276	58	0.01	15.5	16	-	5.5	B575	B622
33	R20033	32	0.08	33	1.6	3	32	B625	B622
59	N06059	60	0.01	23	15.5	-	0.7	B575	B622
Group III - Nickel-molybdenum alloys									
B-2	N10665	69	0.01	1	28	-	2	B333	B622
Ni-Resist (castings)									
Type 1	F41000	15	2	2	-	-	Bal	-	-
Type 2	F41002	20	2	2	-	-	Bal	-	-
Type D2	F43000	20	2	2	-	-	Bal	-	-
Ferritic stainless steels									
430	S43000	-	0.05	17	-	-	Bal	A240	A268
444	S44400	-	0.02	18	2	-	Bal	A240	A268
XM-33	S44626	-	0.03	26	1	-	Bal	A240	A268
XM-27	S44627	-	0.005	26	1	-	Bal	A240	A268
29-4	S44700	-	0.005	29	4.0	-	Bal	A240	A268
Austenitic stainless steels									
304	S30400	8	0.04	18	-	-	Bal	A240	A312
304L	S30403	8	0.02	18	-	-	Bal	A240	A312
316	S31600	10	0.04	16.5	2.1	-	Bal	A240	A312
316L	S31603	10	0.02	16.5	2.1	-	Bal	A240	A312
800	N08800	33	0.07	21	-	-	Bal	A240	B407
20	N08020	33	0.02	19.5	2.2	3.2	Bal	A240	B729
28	N08028	32	0.03	27	3.5	1	Bal	B709	B668
6%Mo ^c	S31254	18	0.01	20	6.2	0.7	Bal	A240	A312
6%Mo ^c	N08367	24	0.01	21	6.2	-	Bal	A240	A312

Table 1 Nominal composition of nickel-containing alloys many are used in Caustic Soda cont'd

		Nominal composition, %						ASTM Spec. ^b	
Alloy	UNS Number ^a	Ni	C	Cr	Mo	Cu	Fe	Plate	Seamless tube and pipe
Duplexstainless steel									
2304	S32304	4	0.02	23	0.3	-	Bal	A240	A790
2205	S32205	5	0.02	22	3.2	-	Bal	A240	A790
2507	S32750	7	0.02	25	4	-	Bal	A240	A790
7-Mo Plus	S32950	4	0.03	27.5	2	-	Bal	A240	A790
	S32906	7	0.02	29	2.3	-	Bal	A240	A790
Copper-nickel alloys									
90-10	C70600	10	-	-	-	Bal	1.2	B171	B466
70-30	C71500	31	-	-	-	Bal	0.8	B171	B466

a - UNS numbers beginning with an "N" indicate a nickel alloy, but the definition of a nickel alloy is different than that used by ASTM.

b - in ASTM specifications, most nickel alloys fall into the "B" specifications. However, due to a redefinition of a nickel alloy, a few alloys such as Alloy 20 are being reclassified as stainless steels, and will be included in the "A" specifications. That work is still in progress.

c - the 6% Mo alloys are a series of stainless steels, many of which are proprietary, all with roughly 6%Mo content and roughly equivalent in performance.

CORROSION BEHAVIOUR - CAUSTIC SODA

Corrosion rates in aggressive chemicals usually decrease as the pH increases. In alkaline solutions, the hydrogen ion is present in very low concentrations. Many metals, however, pass through a minimum corrosion rate at some pH, usually basic, and then suffer increased corrosion as pH continues to rise. Quite often, corrosion by alkalis leads to pitting and other localized attack because they tend to form cathodic films, and attack is concentrated at susceptible anodic areas. Carbon and low-alloy steels, austenitic stainless steels, and some nickel alloys may suffer either stress-corrosion cracking or general corrosion in hot, concentrated caustic solutions.

Carbon steels and cast irons

Carbon and low-alloy steels are limited in caustic service by two considerations. Firstly, as the temperature and concentration increase, iron reacts directly with caustic to form sodium salts and liberate hydrogen.



Such reactions limit the use of iron-based alloys when iron contamination is unacceptable or where general corrosion defines the acceptable life (e.g., with steam heating coils to prevent freezing).

Corrosion rates can exceed the following rates under the stated conditions:

- 0.5 mm/y (20 mpy) above 10% NaOH at 100 °C (212 °F)
- 1.3 mm/y (50 mpy) above 40% at 80 °C (175 °F)
- 1.3 mm/y (50 mpy) in 55% caustic, as low as 50 °C (120 °F)

Steels can be subject to a form of stress-corrosion cracking (SCC) to which the misnomer of "caustic embrittlement" has been applied. This environmental cracking occurs well below the critical corrosion parameters. The limiting parameters of temperature and concentration for SCC (determined by a survey of practical experience) are shown in *Figure 1*.

Because of the effect of residual stress in promoting this type of attack, both welded and cold-worked (i.e., flared, bent) fabricated steel equipment must be thermally stress-relieved to extend its life in caustic service. *Figure 2* shows the suggested regions, as defined by temperature and concentration, in which post fabrication thermal stress relief (or an alternative alloy) is recommended to avoid SCC in steels.³

Use of low-alloy steels is inadvisable if they will experience dynamic loading. Under slow-strain rate conditions, the passive film formed by reaction with caustic will rupture and nascent hydrogen is absorbed into the freshly exposed surface, causing embrittlement.

For services where iron pick-up is undesirable, steel tanks are frequently coated with an organic paint system to minimize iron contamination.

Cast iron is not usually used in caustic service, because of the safety problems caused by its inherent brittleness. However, ductile cast iron is sometimes acceptable, and the high-nickel cast irons, such as Ni-Resist® Types 1 (F41000) and 2 (F41002) and the ductile Ni-Resist® Type D2 (F43000), are much more resistant than unalloyed cast iron in caustic solutions up to about 70%.

Austenitic stainless steels

The “18-8”-type stainless steels, exemplified by Types 304 (UNS S30400) and 316 (S31600) and their low carbon equivalents Type 304L (S30403) and Type 316L (S31603), have a useful low corrosion rate in caustic at all concentrations up to about 65 °C (150 °F). Other limits are given in the literature but it is likely that these are influenced by contaminants in the caustic soda.

Types 304 and 316 have low corrosion rates in boiling caustic soda at concentrations up to nearly 20%. An iso-corrosion curve in mpy for these grades is shown in *Figure 3*.⁴

Type 316 has a better resistance to pitting than Type 304 in caustic solutions. The low-carbon grades perform marginally better than the high-carbon grades because of their resistance to sensitization. This means that 316L is a good choice for caustic solutions as long as operating conditions are such that caustic SCC is not a problem.⁵

As indicated in *Figure 3*, 300-series stainless steels are susceptible to SCC in hot caustic, e.g., 15% NaOH at about 150 °C (300 °F). In practice, this is most often encountered in caustic-contaminated steam. Caustic cracking of stainless is characterized by a gun-metal blueing effect, obvious on visual examination.

A NACE task group found little difference between the corrosivity of caustic soda made by the diaphragm cell

Figure 1 Relation of temperature and concentration of sodium hydroxide to cause stress cracking of carbon steel

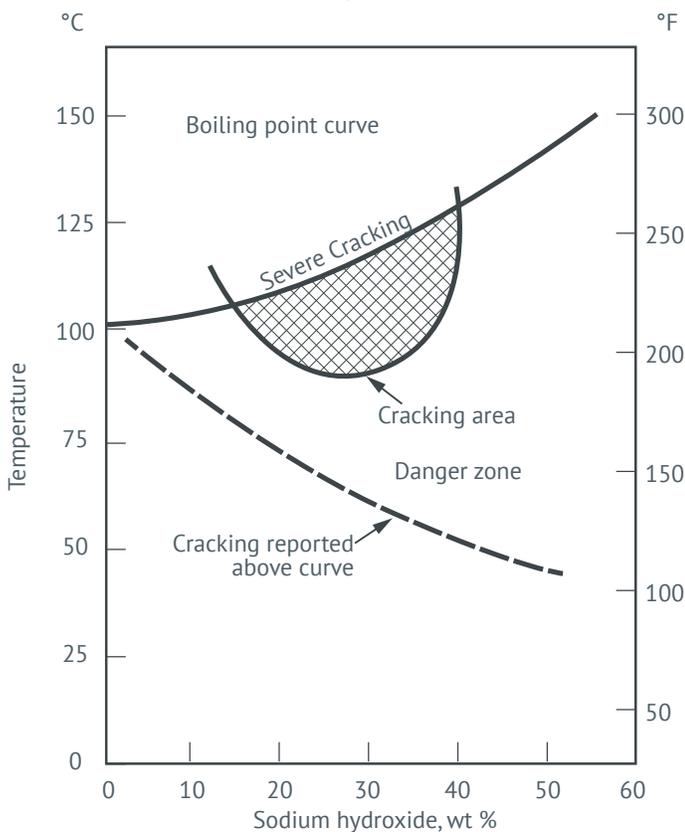
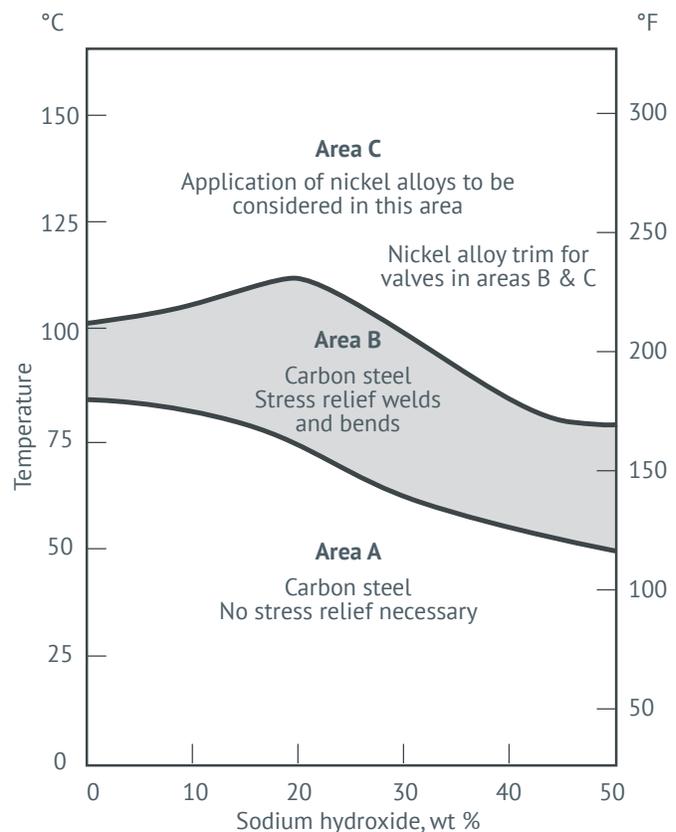


Figure 2 Temperature and concentrations of caustic soda that require stress relief to prevent SCC of carbon steel



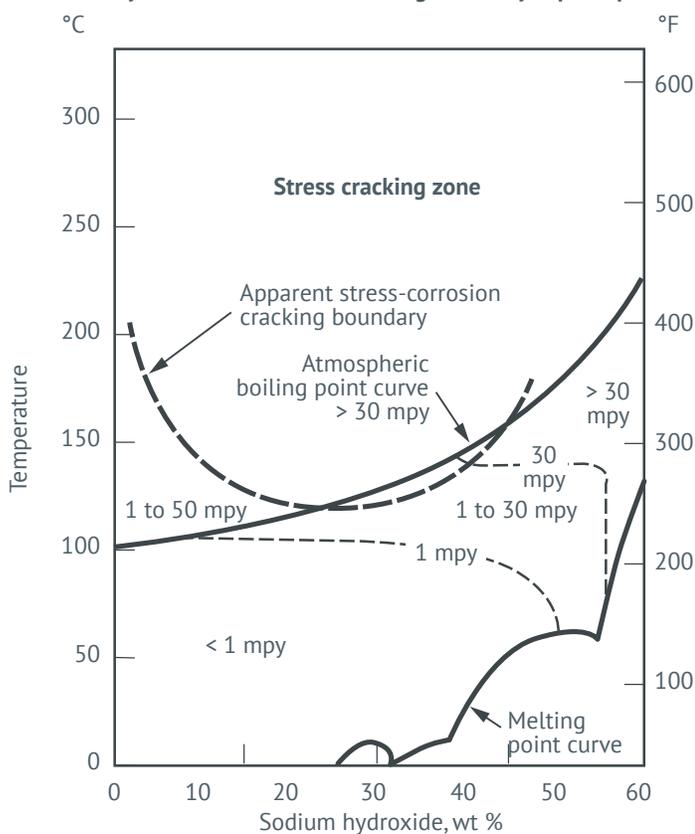
process and that made in mercury cells.⁶ This survey also found little difference in the corrosion resistance of Types 304L and 316L in 50% or 73% caustic solutions, in which both alloys suffered active corrosion as well as some pitting attack. It seems probable that these products contained unknown amounts of chlorates, as produced.

An additional consideration is chloride contamination in the caustic. Mercury cell production yields caustic with low amounts of chloride, typically 20-30 ppm. Diaphragm cell production, on the other hand, yields caustic containing considerable chloride, e.g., up to 1% sodium chloride (6,000 ppm Cl⁻). Membrane cells tend to produce lower chloride caustic with typically <0.01% sodium chloride. Mercury cell caustic production is being phased out throughout the world due to concerns in handling mercury and avoiding pollution.

High-performance austenitic alloys

The original high-performance austenitic alloys were the

Figure 3 Iso-corrosion chart for Type 304 and 316 stainless steels in sodium hydroxide, with stress cracking boundary superimposed



molybdenum-free Alloy 800 (N08800) and the molybdenum-containing Alloy 20 (N08020). Alloy 800 has been used in up to 73% caustic at 120 °C (250 °F) but is susceptible to caustic SCC above 150 °C (300 °F). Alloy 825 (N08825) with 3% Mo, is slightly more resistant than Alloy 800. These nickel-chromium-iron alloys with and without molybdenum have useful resistance up to 73% caustic at temperatures up to about 120 °C (250 °F).

Molybdenum is now a significant alloying element in the group of 6% Mo superaustenitic alloys. The molybdenum in this type of alloy gives resistance to chloride pitting, crevice corrosion, and chloride SCC. However, tests on the corrosion resistance of the 6% Mo (N08367) superaustenitic stainless steel and other alloys in boiling 50% NaOH showed that this type of alloy is not suitable with a corrosion rate of 0.29 mm/y (11.4 mpy) for UNS N08367.⁷

Alloy 28 (N08028) is another iron-nickel-chromium alloy that has useful resistance to caustic solutions, particularly if contaminated, e.g. with chlorides. This alloy has been used for the evaporation of diaphragm cell NaOH. In this application, erosion by sodium chloride crystals can be a problem, and this alloy showed considerably better performance than pure nickel.

At temperatures of the order of 300 °C (575 °F), even 25% caustic will cause SCC of the high performance alloys. It is very important, when both chlorides and caustic are present in an environment causing SCC, to know which is the active species. If it is the chloride, a molybdenum-containing superaustenitic steel will suffice to overcome the problem, whereas if caustic is the cause of the cracking, then a high-nickel alloy will be needed.

Ferritic stainless steels

Traditional ferritic stainless steels, such as Type 430 (S43000), have lower temperature limits in caustic than do the 18-8 austenitic stainless steels and are not generally as resistant in caustic. For example, in 60% NaOH at 212 °F (100 °C), Type 444 (S44400) corroded at 0.61 mm/y (24 mpy), while Type 304 austenitic had a corrosion rate of 0.07 mm/y (3 mpy).⁸ The ferritic grades are also susceptible to caustic cracking.

In recent years, there has been wide-spread application of extra-low interstitial, molybdenum-bearing ferritic stainless steels, such as Alloy XM-33 (S44626), in evaporator tubing.

Performance has ranged from good to poor. Good performance is probably associated with oxidizing contaminants, such as chlorates, which tend to enhance passivity.

Failures, due to either localized or general corrosion, have been associated with one or more of the following factors:

1. Contamination of the tubes with minute amounts of oil, grease or other hydrocarbons in the production, heat-treatment or fabrication. The superferritic grades readily absorb carbon under such conditions, obviating the low-interstitial controls.
2. High temperatures in the first effect evaporator, i.e., in excess of 150 °C (300 °F).
3. Absence of or insufficient chlorate content.
4. Blockage of tubes with insoluble salts, creating locally high skin temperatures.

Typically, the extra-low interstitial (ELI) grades will show <0.025 mm/y (1 mpy) under conditions in which the conventional austenitic grades are attacked at rates >2.5 mm/y (100 mpy).

Duplex stainless steels

Duplex stainless steels usually have a microstructure containing roughly equal amounts of ferrite and austenite. Modern grades typically containing 1-4% Mo as well, and are strengthened and stabilized by 0.10% to 0.35% nitrogen. The result is a family of stainless steels with high strength and outstanding resistance (although not immunity) to chloride pitting and SCC.

Corrosion testing in a range of caustic solutions at the boiling point showed that duplex alloys with and without molybdenum can be used in boiling solutions up to at least 30% with negligible corrosion.⁹ These tests also showed that these duplex alloys were not susceptible to SCC in boiling caustic solutions from 20% to 70%.

The duplex alloy UNS S32950 and the ferritic alloy XM-27 (S44627) stainless steels both showed good resistance to SCC and corrosion in 50% caustic at 135 °C (275 °F).⁵

Corrosion testing of various duplex stainless steels in 30% to 70% NaOH solutions found that their resistance was in the order of:

S32304 < S32205 < S32750 < S32906

The effect of chromium in the austenite phase was investigated in a set of experimental duplex alloys. It was found that corrosion resistance of the duplex steels was directly proportional to their chromium content. The range of chromium contents in the experimental heats was from 26.54% to 29.04% with corrosion rates in boiling 60% NaOH of 0.39 mm/y to 0.05 mm/y (15.6 mpy to 2 mpy), respectively. SCC tests in 50% NaOH at 137 °C (279 °F) showed that S32906 was immune to cracking in this environment.¹⁰

Nickel 200, however, had a lower corrosion rate than any of the duplex alloys in pure caustic solutions at any test temperature.

Because of the uncertainties about the amount of chlorides and oxidizing salts, such as hypochlorites and chlorates, extensive field corrosion tests should be made before selecting duplex stainless steels for caustic soda service.

Commercially Pure (C.P.) Nickel and its alloys

The resistance of nickel and its alloys to general corrosion and SCC increases with increasing nickel content.¹¹

Nickel-based alloys, i.e. having more than 50% nickel, can be conveniently divided into two groups; those that do not contain chromium, and those that do.

Chromium-free nickel alloys

These comprise a group of three generic types, C.P. Nickel itself, nickel-copper (Alloy 400 and variants thereof) and nickel-molybdenum alloys, e.g. Alloy B-2 (N10665). All of these are generally resistant to caustic itself but are attacked stoichiometrically by chlorate or hypochlorite contaminants.

C.P. Nickel – is available in two variants, Nickel 200, and a low-carbon Nickel 201, both of which have excellent resistance to caustic soda, even as the hot anhydrous form, as shown in *Figure 4*. Except for silver, nickel is the most resistant metal for high caustic concentrations at the elevated temperatures which generally prevail. At concentrations up to 73% caustic, the corrosion rate is generally less than 0.025 mm/y (1 mpy). The rates increase slightly above 73%, as shown.

Nickel 200 contains up to 0.10% carbon, which can precipitate as graphitic carbon on heating above 425 °C (800 °F), which reduces the ductility of the alloy. This may also occur upon prolonged heating at temperatures as low

as 315 °C (600 °F). Above 300 °C (570 °F), e.g., in molten anhydrous caustic, the low-carbon Nickel 201 should be used to avoid graphite formation and attendant embrittlement and intergranular attack.¹²

In most caustic applications Nickel 200 and Nickel 201 are very resistant to caustic SCC at all concentrations and temperatures up to about 290 °C (550 °F). Though Nickel 200 or 201 are usually most resistant, Alloy 400 and 600 are often used for higher strength.

Nickel 200 is subject to cracking in mercury and a few cases of cracking have been attributed to mercury contamination of the caustic process feed.⁶

Nickel-copper alloys – Alloy 400 has corrosion resistance similar to C.P. nickel for concentrations up to 73%, although it is susceptible to caustic cracking in severe service. At higher concentrations, the corrosion rate is somewhat greater than C.P. nickel. In lower concentrations, and for service conditions

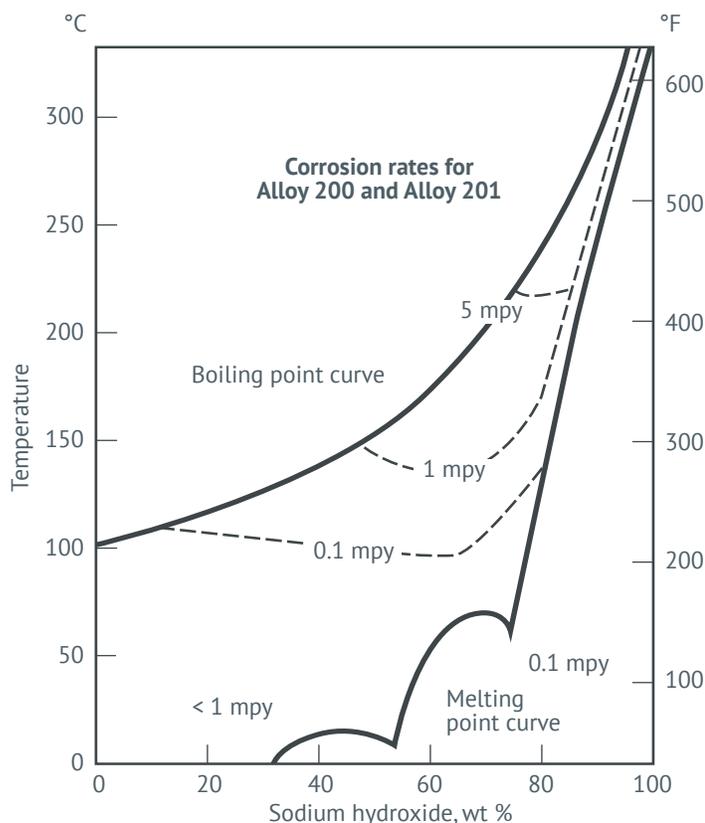
where contamination by small amounts of copper and nickel is not detrimental, Alloy 400 can be useful for caustic service at a lower cost than pure nickel.

Alloy 400 is subject to caustic cracking at elevated temperatures (e.g., in caustic-contaminated 300-400 psi steam) [215-230°C (420-450°F)]. It is also subject to liquid metal embrittlement (LME) by mercury and its salts. There have been instances of LME with Alloy 400 components used in handling mercury-cell caustic prior to final separation of mercury and its salts from the product.

The solution-hardening variants of Alloy 400 (e.g., Alloys 404 and 405) and the age-hardening variants (e.g., Alloy K500 (N05500)) have substantially the same corrosion characteristics.

Nickel-molybdenum alloys – There is little occasion to use Alloy B-2 in caustic service. Published data indicate that it has excellent resistance, at least in lower concentrations in the absence of powerful oxidants, but it finds no application because of the excellent resistance of nickel itself.

Figure 4 Corrosion rates for Nickel 200 and low carbon Nickel 201 in sodium hydroxide



Chromium-bearing alloys

This group comprises Alloy 600 and its variants and the molybdenum-bearing grades, Alloy 625 (N06625) and Alloy C-276 (N010276) and its variants.

Nickel-chromium-iron alloys – Alloy 600 exhibits resistance similar to C.P. nickel up to and including the anhydrous product. It is favoured for heating coils, because of higher strength at temperature than the pure nickel alloys. It may cause a small amount of contamination from Cr (VI) ions, compared to the use of Nickel 200. It is subject to caustic cracking under severe conditions in prolonged exposure, and should be used in the stress-relieved condition.

Alloy 600 offers an advantage, compared to Nickel 201 when a sulphur-bearing contaminant may be present, in being less susceptible to nickel sulphide eutectic formation (a low-melting nickel-nickel sulphide compound which causes intergranular penetration analogous to LME). It has been used for the production of anhydrous caustic where sulphur was present. Alloy 600 has replaced Type 316 stainless heat exchangers in a high-temperature process for the recovery and reuse of chloride-bearing caustic (the stainless having failed by chloride stress-corrosion cracking).

Alloy 600 can offer an advantage over Nickel 200 in caustic

from the diaphragm-cell process, in which chlorates and hypochlorites are present. Being oxidizing in nature, these accelerate corrosion of Nickel 200, whereas the resistance of the chromium-bearing alloy is not greatly affected.

A variant of Alloy 600 is Alloy 601 (N06601) which is a solid-solution strengthened, higher-chromium (23% Cr) alloy. This alloy was developed primarily for high temperature applications but shows excellent corrosion resistance in up to 98% caustic because of the high nickel content.

The other chromium-containing nickel-based alloy that is sometimes used in caustic soda is Alloy 690. The corrosion rate of Nicrofer® 6030 (N06690) in 70% NaOH at 170 °C (338 °F) was 0.03 mm/y (1.18 mpy). In the same tests, Alloy 400 and Alloy 33 (R20033) had the same corrosion rate (i.e. 0.03 mm/y), while Alloy 59 (N06059) corroded at 0.48 mm/y (18.9 mpy) and Alloy C-22 (N06022) at 0.51 mm/y (20.1 mpy).¹⁵

Nickel-chromium-molybdenum alloys – High molybdenum nickel alloys are intended for acid service, little being published about caustic resistance. Their higher cost, as compared with Nickel 200 or Alloy 600, practically excludes them from consideration, except in special applications where higher strength or resistance to other corrodents is needed. These alloys are highly resistant to general corrosion and SCC, compared to lower nickel alloys, however, they can be attacked at high caustic concentrations and temperatures.¹⁴ It should be noted that alloys such as C-276 and its variants, are subject to a dealloying mechanism in boiling 50% NaOH.¹⁵

In a special application, Alloy 625 has become the material of choice for corrugated metal expansion joints in high pressure steam, where environmental cracking of austenitic stainless steels occurs due to caustic carry-over while chloride carry-over may cause pitting of Alloy 600. These alloys are practically unaffected by hot caustic up to at least 320 °C (600 °F).

Copper and its alloys

It is sometimes mistakenly assumed that copper alloys are unsuitable for caustic service. This is probably due to the lack of available data. Copper alloys are not, in fact, used in contact with caustic to be employed in the rayon industry (because of colour problems) or soap industry (because of rancidity).

On the other hand, except for the yellow brasses (which are

susceptible to dezincification), coppers, phosphor (tin) bronzes and cupronickels may be used for up to 70% caustic unless powerful oxidants (e.g., chlorates) are present. A conventional bronze valve or pump is satisfactory to handle 25% caustic, for example, for pH control. Copper alloys have given good life in processes for dehydrating amines with hot 70% caustic, in the total absence of oxygen or oxidizing agents. Aluminium bronzes may be subject to dealuminification, due to the amphoteric nature of the aluminium constituent.

Corrosion resistance increases with nickel content, and the 90-10 (C70600) cupronickel and 70-30 (C71500) grade are sometimes used for caustic service. Because of improved heat transfer properties and strength, the 70-30 grade has been used in evaporators up to 50% concentration in applications in which copper contamination is acceptable.

Copper piping has sometimes been used for caustic soda solutions in situations in which thermal stress relief of steel piping was impractical.¹⁶ In the absence of oxidizing agents (e.g. chlorites, chlorates), copper may be used up to 73% NaOH to 100 °C (212 °F).

ALLOYS IN CAUSTIC SODA PRODUCTION

Caustic soda and its co-product, chlorine, are made by electrolysis of a sodium chloride solution. Sodium hydroxide is produced at the cathode, while chlorine is evolved at the anode.

Mercury cells

Production of chlorine and caustic using mercury cells is rarely used now because of environmental concerns. Rubber-lined carbon steel was the conventional material of construction for mercury-cell caustic. A fresh feed of about 25.5% sodium chloride brine diminishes to about 21% during electrolysis and is recycled to the cell for continued electrolysis. Chlorine is produced at the carbon or titanium anodes while the mercury at the cathode forms an amalgam (Na/Hg). In a separate vessel, the denuder, the amalgam is reacted with demineralized water to obtain 50% NaOH of very high purity.

For the brine heaters, both Alloy 400 and titanium or its variants, have been used. Titanium alloys are preferred, because of the problem of liquid-metal cracking (LME) of the nickel-base alloy by entrained mercury, as well as corrosion by small amounts of chlorine or hypochlorites.

Diaphragm cells

This electrolytic process produces the highest percentage of present-day production of sodium hydroxide. The salt solution, contained in rubber or concrete-lined tanks, is electrolyzed, the carbon anode and steel cathode separated by an asbestos diaphragm. If naturally-occurring brines constitute the feed, they must be treated to remove calcium, iron, manganese and sulphates. The initial product, the cell liquor leaving the electrolysis cell bank, contains only about 10-12% caustic. The other constituents are unreacted sodium chloride (NaCl), sodium chlorate (NaClO₃) plus traces of sodium hypochlorite (NaOCl) and sodium sulphate (Na₂SO₄). Both chlorates and hypochlorites are powerful oxidants.

Impurities must be removed from the cell liquor and it must be concentrated to 50% or 73%, or to the anhydrous grade for commercial use. Multiple-effect evaporators of corrosion-resistant alloy construction are utilized to achieve these higher concentrations.

Membrane cells

The membrane cell is analogous to the diaphragm cell except that the feed brine is more highly purified and the perfluorosulphone membrane has lower permeability than a diaphragm. Consequently, a high-quality concentrated sodium hydroxide is produced. The caustic product from membrane cells is around 30% NaOH and needs to be concentrated for commercial use.

Chlorate removal – Sodium chlorate, being both an oxidizing agent and a source of more sodium chloride upon reduction, is an objectionable constituent. It is removed, either before or during the evaporation step by one of several proprietary processes to alleviate accelerated corrosion, which would otherwise occur at elevated temperatures.

Many plants destroy chlorate, either before or during the evaporation process. The conventional treatment is extraction by ammonia, which also reduces the dissolved salt content. There is a proprietary process that decomposes chlorate with by-product hydrogen in the presence of a catalyst. Nickel 200 and Alloy 400 have been used for the reactor, feed heater and feed/product interchanger in the hot caustic in this process.

Sodium chloride removal – Residual sodium chloride, which concentrates during the evaporation process and crystallizes out, must be removed by settling and filtration. Much of the

crystallized salt is recycled in the cell-feed liquor, the balance being purged by blow-down from the circuit to control build-up of sulphates and other undesirable constituents in the cell liquor.

Specific equipment

50% Caustic – Evaporators

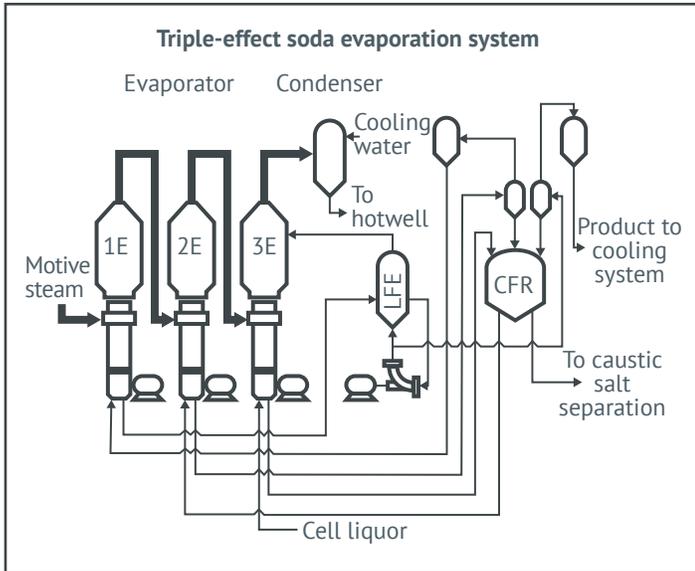
The multiple-effect evaporators required for concentration employ Nickel 200 or Nickel 201 tubing, tube-sheets, circulation piping, and the wetted surfaces of the evaporator bodies. Alloy 600 has been employed where sulphur compounds are present. A triple-effect evaporator for the production of 50% caustic is shown in *Figure 5*, while alloy selection for specific areas is indicated in *Figure 6*. *Table 2* provides information on various applications of nickel-base alloys and nickel cast irons in caustic soda equipment.

The adverse effect of chlorates in a triple-effect evaporator has been reported.¹⁷ Life of the first-effect tubing (the hottest tubes and at the highest caustic concentration, 47-50%) was found to vary from 3 to 12 years. The investigation showed that nickel pick-up in the caustic was directly proportional to the chlorate concentration in the cell liquor, within the 120-200 ppm range encountered. Corrosion of nickel and reduction of chlorate occurs simultaneously across the first-effect heater. Laboratory studies at 148 °C (300 °F), the first-effect temperature, confirmed plant experience. Corrosion rates for Nickel 200 increase dramatically with caustic containing 100 ppm or more of chlorate.

Where chlorate contamination is a problem, some operators have used the XM-33, depending on the chlorates, to maintain passivity. The ferritic alloy XM-27 has been used successfully, but there have been some failures. Failures of XM-33 ferritic alloy in this service has been due to intergranular attack (IGA). Short-term, low-temperature testing does not cause IGA, but such attack becomes more probable as time and temperature increase. Contributory factors include crevices, corrosion products, and perhaps elemental sulphur. This type of alloy is also susceptible to SCC in hot caustic solutions at >30% concentration.

Another superferritic stainless steel, Alloy 29-4 (S44700), has excellent resistance to boiling 50% NaOH, even in the presence of chlorates, and has become a standard material for caustic evaporator steam chests and other associated heat exchangers.¹⁸

Figure 5 Flow diagram of a triple-effect caustic soda evaporation system



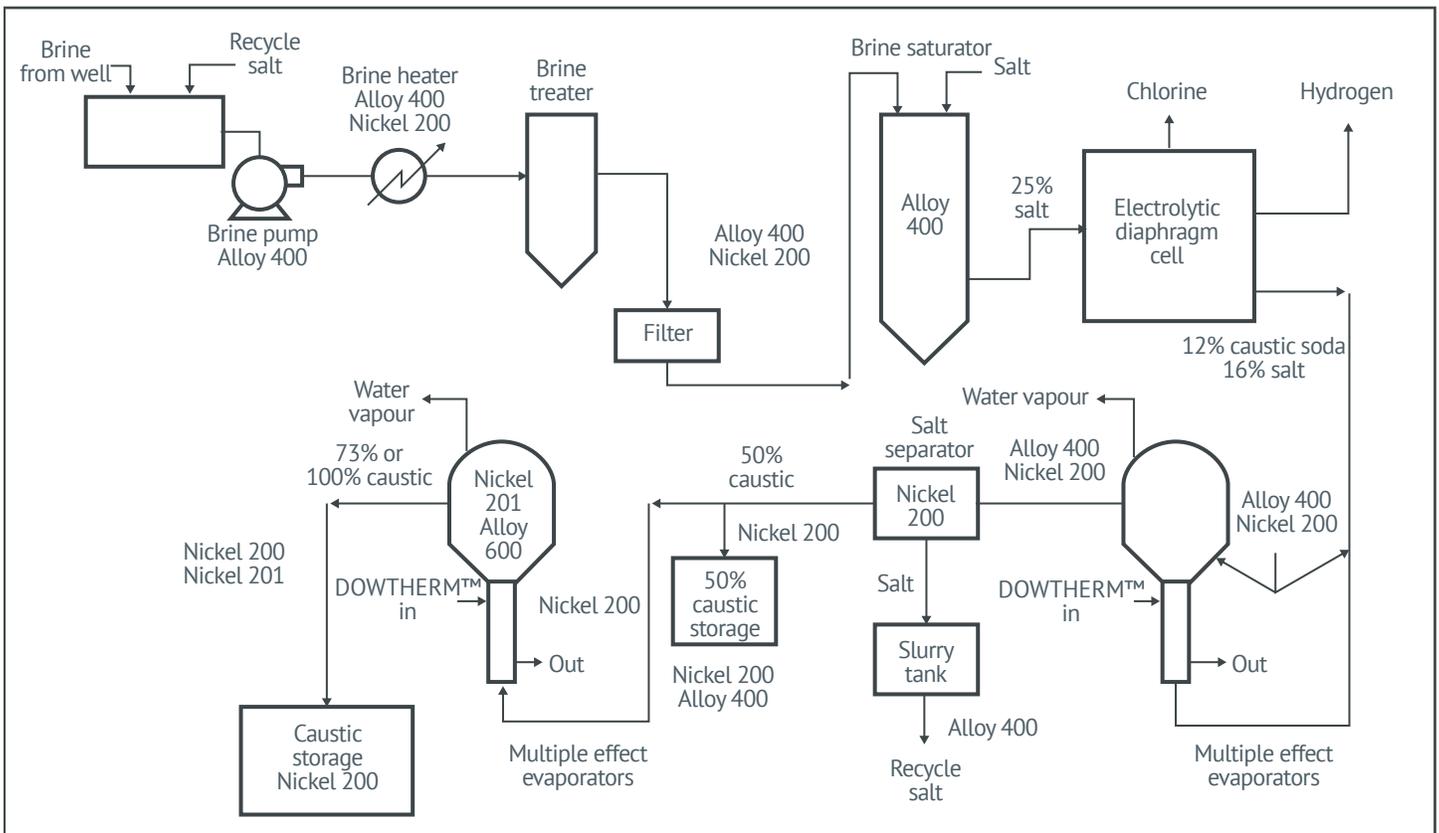
50% Caustic – Salt settlers

The salt settlers (sometimes with filters) are traditionally Nickel 200. When cooling is required, the heat transfer surfaces of the heat exchanger are also C.P. Nickel. Nickel tubes have, however, failed in this application when seawater was used as coolant, and replacement in Alloy 400, welded with Alloy 625 was recommended.¹⁹ The salt-settling tank and slurry-holding tank, prior to recycling of the crystallized salt, are frequently made of Alloy 400.

50% Caustic – Storage tanks and heat exchangers

Stress-relieved carbon steel tanks are employed, with specialty internal organic coatings to minimize iron pick-up. For high purity grades, Nickel 200-clad steel tanks have also been employed. The low-carbon 300-series stainless steels have been used successfully, but they must be protected from external chloride SCC. Ferritic or duplex stainless have also been used because of their superior resistance to chloride SCC.

Figure 6 Flow diagram of a triple-effect caustic soda evaporation system



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To maintain the caustic above its freezing point; internal heating coils (or U-tube bundles) are employed. Tubes and tube sheets are either Nickel 200 or Alloy 400, to have equivalent thermal expansion of both components. Alternatively, external shell and tube heat exchangers can be used to provide the necessary heat to prevent freezing. These are normally made with nickel tubes and steam heating on the shell side. These external heaters have the advantage of ease of inspection and maintenance.

Heat exchangers used for cooling must be resistant not only to caustic but also to the cooling water being used. For example, a 6% molybdenum superaustenitic stainless steel might be used with high-chloride water if the process-side conditions of caustic concentration and temperature permit.

Table 2 Applications of nickel alloys in caustic soda equipment (typical examples, courtesy Special Metals)

Brine Pumps	Ni Resist and Alloy 400
Brine Heaters	Nickel 200 and Alloy 400
Evaporators	
Bodies	Nickel-clad steel or lined with Nickel 200 sheet Nickel 200 or Alloy 400 tube sheets
Steam Chests	Nickel 200, Alloy 400 or nickel-clad steel downtakes Nickel 200 or Alloy 400 tubes
Anhydrous	Nickel 201 or Alloy 600 tubes
Heat Exchangers	Nickel 200 or Alloy 400
Pumps	
Bodies	Nickel 200, Alloy 400 or Ni-Resist
Shafts	Nickel 200 or Alloy 400
Impellers	Nickel 200, Alloy 400 or Ni-Resist
Valves & Fittings	Nickel 200, Alloy 400 or Ni-Resist
Pipe Lines	Nickel 200, Alloy 400 or Ni-Resist
Filters	
Bodies & Drums	Nickel 200 or nickel-clad steel
Filter Cloth	
Backing Wire	Alloy 400 or Nickel 200
Winding Wire	
Piping, Valves and Fittings	Nickel 200, Alloy 400 or Ni-Resist
Settling Tanks	Nickel-clad steel or lined with nickel sheet
Storage Tanks	Nickel-clad steel or lined with nickel sheet
Crystallizers	
Bodies	Nickel-clad steel or lined with nickel sheet
Shafts & Agitators	Nickel 200 or Alloy 400
Centrifugals	Alloy 400 baskets and wire cloth liners
Tank Cars	
Bodies	Nickel-clad steel
Coils	Nickel 200
Transfer Piping	Nickel 200 or Alloy 400

More often, Alloy 400 or Alloy 625 is chosen for brackish or seawater cooling. However, in one caustic membrane heater/cooler handling 33% NaOH, failures were observed as coming from the seawater inside the tube, probably because of marine fouling, microbial corrosion, or the alternating exposure to steam and seawater.

Plate heat exchangers are more often used than shell and tube exchangers for removing heat from caustic dilution operations. Type 304L or 316L are used for low temperatures and concentrations, with Alloy 400 or nickel used at higher temperatures, >60 °C (140 °F). Elastomeric gaskets have been successfully employed with safety screens to avoid caustic spray in case of a gasket failure.

73% and anhydrous caustic – Evaporators

Nickel 200 is the conventional material for caustic evaporation to 73 %, having a low corrosion rate and causing minimal metal ion contamination. For higher concentrations, up to the anhydrous product, high-temperature heat transfer fluids or molten salts are employed at temperatures to 315 °C (600 °F), or higher, and Nickel 201 is required, as previously noted, to avoid graphitic embrittlement. If sulphur compounds are known or anticipated, Alloy 600 is chosen. Because it is susceptible to SCC, thermal stress relief is required. Where this alloy has been employed with this precaution, service performance has been equivalent to Nickel 201.

73% and anhydrous caustic – Tanks and heaters

The same stipulations described for 50% caustic apply, except that resistant internal organic linings or nickel cladding are required to maintain product purity and obtain an economical service life. For storage of 73% NaOH, nickel or nickel clad on carbon steel is commonly used.

ALLOYS FOR PROCESSES USING CAUSTIC SODA

There are a number of commercial processing areas in which corrosion-resistant materials are required to withstand caustic conditions.

Petroleum refining

Mercaptans and other organic sulphur compounds may be removed from refinery streams with either caustic soda or caustic potash (potassium hydroxide - KOH). Since economy

requires regeneration of the caustic, with temperatures and concentrations which exceed the capability of steel, Alloy 400 is frequently used for stripping-tower internals, tubular heaters and reboilers. These handle caustic solutions up to 45% concentration to about 150 °C (300 °F).

When aminodiisopropanol is used for similar sulphur-removal operations, it is recovered by caustic treatment. In such recovery units, steel would be corroded by sulphur-rich oils and austenitic stainless steel, e.g., Type 316L is employed, the temperatures and concentration of caustic not requiring high-nickel alloys.²⁰

Severe caustic corrosion of the crude transfer line immediately downstream of the caustic injection point can occur when 40% caustic is injected into hot desalted crude oil to neutralize remaining HCl. This problem can be controlled by design of the injection point to ensure adequate mixing of the fluids and also is minimized if caustic is diluted to about 3% before injecting. Traces of caustic can become concentrated in boiler feedwater in boiler tubes that alternate between wet and dry conditions because of overheating. This concentrated caustic can cause corrosion, and cracking occurs under the deposits.²⁰

Bauxite refining

In the Bayer Process for treatment to separate alumina (Al_2O_3) from iron oxide in the ore, caustic soda is employed to solubilize the aluminium oxide and remove the insoluble iron component. The alumina is then crystallized out of the cooling caustic solution. While carbon steel is suitable for heating the caustic solution to moderately high temperatures (there are certain inhibiting constituents in the process solution), Alloy 400 tubing is used in the higher-temperature heaters. Either solid Nickel 200 or nickel-lined steel piping transfers the solution from the heaters to the reactors.

A study aimed at finding suitable alloys to replace nickel-lined steel found that the duplex stainless steels 2304 (S32304) and 2205 (S32205) and the austenitic Alloy 28 were much more resistant than the standard 300-series stainless steels. Any of these alloys would be suitable replacement in cases where the nickel-lined steel failed from caustic SCC.²¹

Soap manufacture

Soaps are made by saponifying fatty acids with caustic soda. To minimize iron contamination and extend the useful life

of the process equipment, Alloys 200 and 400 have been commonly used for saponification vessels, replacing the original steel and iron equipment.

Corrosion rates in the top of a soap boiling kettle showed that Nickel 200, Alloy 400 and Alloy 600 were all effectively unattacked (<0.0025 mm/y; <0.1 mpy) while mild steel corroded at 0.08 mm/y (3.2 mpy) and cast iron at 0.28 mm/y (11 mpy).⁶

Sodium hydrosulphide (NaSH)

The reaction of hydrogen sulphide with 50% caustic produces sodium hydrosulphide at about 45-50% concentration. The temperatures involved are at least 107 °C (225 °F). While some producers have obtained reasonable reactor life with the 300-series austenitic stainless steels, Alloy 20 has proven superior in cases where the austenitic steel has suffered general thinning. Field corrosion tests suggest that Alloy 600 should be the preferred alloy for this application.

Caustic fusion reactions

Reactions involving an organic compound and molten caustic soda are referred to as caustic fusions. Because temperatures are usually above 315 °C (600 °F), Nickel 201 is the preferred material of construction, provided no sulphur compounds are present.

When sulphur compounds are present (e.g., in the caustic fusion of benzene metasilphonic acid to produce resorcinol), stress-relieved Alloy 600 is preferred. Nickel 201 would be attacked in an intergranular mode by the nickel sulphide eutectic which would form at the reaction temperature.

Pulp and paper

Pulp and paper operations encounter a wide range of caustic solutions that can cause major corrosion and cracking problems, depending on the process and the conditions encountered.

Austenitic stainless steels are susceptible to caustic SCC above about 121 °C (250 °F) in pure NaOH solutions. When sulphides are present, SCC of austenitic stainless steels can occur at lower temperatures, such as hot sulphide-containing caustic solution (white liquor) which is used in the kraft pulping process. In different process streams of pulp mills, there are different concentrations of sulphide and hydroxide concentrations, along with other chemicals. In some areas, composite tubes with an external layer of 304L on an inner shell of carbon steel are used, such as in the floor and lower

furnace water walls in kraft recovery boilers. SCC occurs during boiler shutdown from exposure to the stagnant floor water that is rich in sulphides and hydroxides. A systematic study of this phenomenon found the following: ²²

SCC did not occur in 304L in pure NaOH <100 °C (<212 °F) in the range of solutions tested (up to saturation; >30 M).

304L stainless steel was not susceptible to SCC in Na₂S solutions at temperatures up to 100 °C (212 °F).

In the presence of sodium sulphide in sodium hydroxide solutions, 304L stainless steel is susceptible to SCC at temperatures as low as 50 °C (122 °F).

Cracking susceptibility and crack velocities increased with an increase in temperature.

In recovery boilers, the solution composition possible at the floor surface can cause SCC during boiler start up at temperatures as low as 75 °C (167 °F).

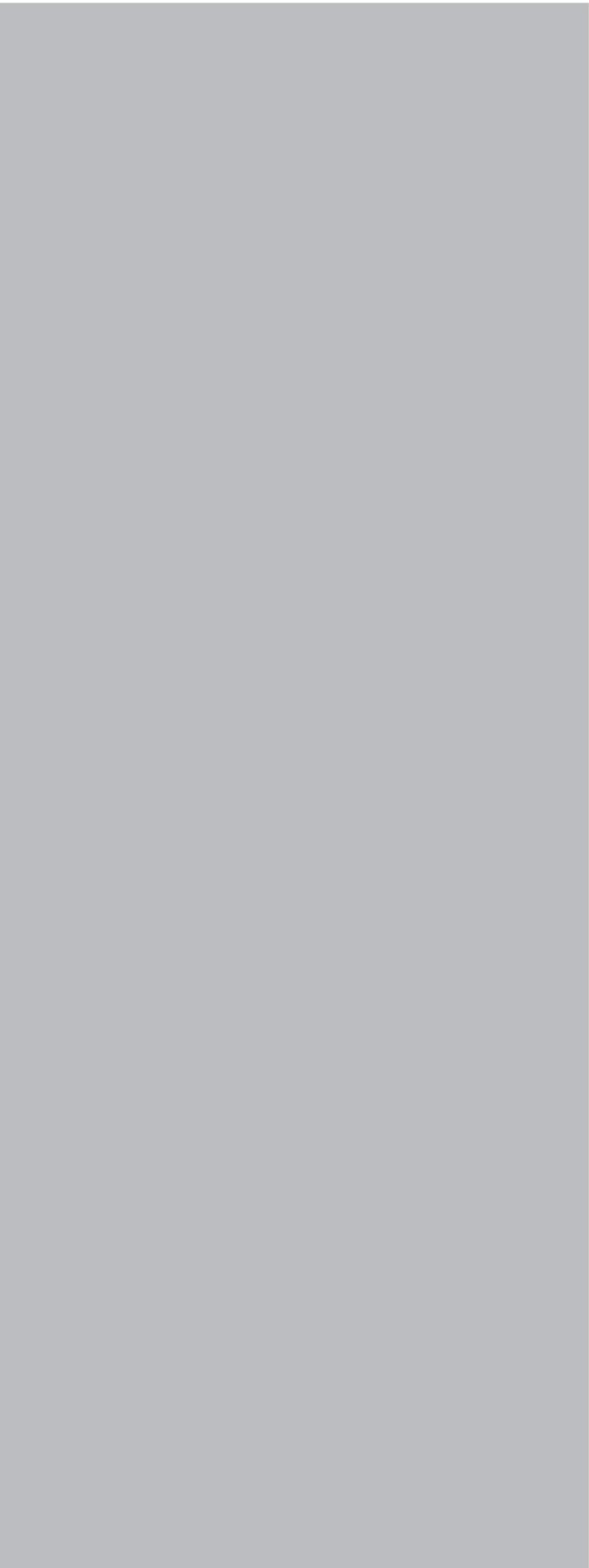
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When molten sodium is used as a carrier (e.g., in certain hydrogenation reactions), traces of water in the reactants may form anhydrous caustic dissolved in the sodium. Austenitic stainless steels and even high-performance nickel-rich alloys can crack very quickly at elevated temperatures. Stress-relieved clad steel vessels are mandatory, using Nickel 200 or, in the case of sulphur contamination, Alloy 600.

References

- ¹Nickel Institute publication No. 10020, 'Alloy Selection for Service in Chlorine, Hydrogen Chloride and Hydrochloric Acid', updated 2013.
- ²MTI Publication MS-6, "Materials Selector for Hazardous Chemicals – Vol. 6: Ammonia and Caustic Soda". Materials Technology Institute of the Chemical Process Industries, Inc., St. Louis, MO (1999).
- ³Anon, Corrosion Data Survey (Houston, TX: NACE International, 1985), p. 176.
- ⁴F.L. LaQue, H.R. Copson (1963), in "Sodium Hydroxide Advisor," ChemCor 6 (MTI/NACE/ NiDI/NIST, 1992).
- ⁵B.D. Craig, D.B. Anderson, eds., Handbook of Corrosion Data (Materials Park, OH: ASM International, 1997), pp. 761–790.
- ⁶"Corrosion Resistance of Nickel and Nickel-Containing Alloys in Caustic Soda and Other Alkalies," Corrosion Engineering Bulletin CEB-2, 1973, International Nickel Company, New York, NY.
- ⁷J.F. Grubb, ed., "AL-6XN Alloy" (Pittsburgh, PA: Allegheny Ludlum Corp., 1995), p. 38.
- ⁸A. Sabata, W.J. Schumacher, "Martensitic and Ferritic Stainless Steels," in CASTI Handbook of Stainless Steels and Nickel Alloys, ed. S. Lamb (Edmonton, AB, Canada: CASTI Publishing Inc., 2000), p. 144.
- ⁹E.-M. Horn et al. (1991), in Corrosion and Environmental Degradation, vol. II, ed. M. Schutze (Weinheim, Germany: Wiley-VCH, 2000), p. 49.
- ¹⁰D. Leander, "Corrosion Characteristics of Different Stainless Steels, Austenitic and Duplex, in NaOH Environment," Stainless Steel World Conference, Maastricht, Netherlands (2003), 9 pp.
- ¹¹J.R. Crum, L.E. Shoemaker, "Corrosion Resistance of Nickel Alloys in Caustic Solutions", NACE CORROSION 2006 Paper No. 06219
- ¹²Anon, "Resistance to Corrosion," publication no. 3M8-88 S-37 (Huntington, WV: Inco Alloys Int., 1985), p. 33.
- ¹³U. Heubner M. Kohler, "High-Alloy Materials for Aggressive Environments," VDM report no. 26 (Werdol, Germany: ThyssenKrupp VDM GmbH, 1998), p. 122.
- ¹⁴Aziz Asphahani, "Corrosion of Nickel-Base Alloy" in Metals Handbook—Corrosion, vol. 13, 9th ed., ed. J.R. Davis (Metals Park, OH: ASM International, 1987), p. 647.
- ¹⁵G. Chambers "Caustic Dealloying Corrosion of High-Performance Alloys", Stainless Steel World Conference, February 12-14, 2002.
- ¹⁶C.P. Dillon, Corrosion Control in the Chemical Process Industries, 2nd ed. (St. Louis, MO: MTI, 1994), 424 pp.
- ¹⁷M. Yasuda, F. Takeya, F. Hine, "Corrosion Behavior of Nickel in Concentrated NaOH Solutions Under Heat Transfer Conditions," Corrosion, Vol 39 (10), October, 1983.
- ¹⁸A. Sabata, W.J. Schumacher, "Martensitic and Ferritic Stainless Steels," in CASTI Handbook of Stainless Steels and Nickel Alloys, ed. S. Lamb (Edmonton, AB, Canada: CASTI Publishing Inc., 2000), p. 149.
- ¹⁹C.M. Schillmoller, "Select the Right Alloys for Caustic Soda Service," Chemical Engineering Progress May (1996): pp. 48–55.
- ²⁰J. Gutzeit, R.E. Merrick, L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," in Metals Handbook—Corrosion, vol. 13, 9th ed., ed. J.R. Davis (Metals Park, OH: ASM International, 1987), p. 1269.
- ²¹A. Cigada, G. Rondelli, B. Vincentini, M.F. Brunella, "Caustic Stress Corrosion Behavior of Some Duplex and Austenitic Stainless Steels," Proc. 3rd Ibero-American Congress of Corrosion and Protection, Brazilian Corrosion Congress, vol. 1 (1989), pp. 223–233.

²²P.M. Singh, O. Ige, J. Mahmood, "Stress Corrosion Cracking of 304L Stainless Steel in Sodium Sulfide-Containing Caustic Solutions," CORROSION/2003, paper no. 03518 (Houston, TX: NACE International), 14 pp.





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