Corrosion by Alkalies

Corrosion rates in chemical processing media usually decrease as the pH increases. In alkaline solutions, the hydrogen ion is present in very low concentrations. However, many metals 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 alkalies leads to pitting and other localized attack because they tend to form cathodic films, and attack is concentrated at susceptible anodic areas. Austenitic stainless steels and other low nickel materials may suffer either stress-corrosion cracking or general corrosion in hot concentrated caustic.

Resistance to attack by alkalies generally improves with increasing nickel content. Results of both plant and laboratory tests, some of which are shown in Tables 15, 16 and 17, show that Nickel 200 and high-nickel alloys are highly satisfactory for handling these materials. The most commonly used nickel alloys in alkali process media are Nickel 200, MONEL alloy 400, and INCONEL alloys 600 and 625.

Nickel 200

The outstanding corrosion characteristic of Nickel 200 is its resistance to caustic soda and other alkalies (ammonium hydroxide is an exception). Nickel 200 is not attacked by anhydrous ammonia or ammonium hydroxide in concentrations of 1%. Stronger concentrations can cause rapid attack in the presence of dissolved oxygen.

Nickel 200 shows excellent resistance to all concentrations of caustic soda (sodium hydroxide) at temperatures up to and including the molten state. Below 50% concentration, corrosion rates are negligible, being usually less than 0.1 mpy (0.003 mm/a) even in boiling solutions. As concentrations and temperatures increase, corrosion rates increase very slowly. The general resistance of Nickel 200 is summarized in the iso-corrosion chart shown in Figure 29.

The chief factor influencing the behavior of nickel in highly concentrated caustic soda is the nature of the film formed during exposure to the caustic. Under most conditions, a protective film of black nickel oxide is formed that results in a marked decrease in corrosion rates over long exposure. For example, specimens of Nickel 201 were exposed to a caustic solution made by adding 500 cc of water to 2 kg of technical grade flake caustic followed by heating in a Nickel 201 pot at a temperature of 790-830˚F (412-443˚C). The corrosion rate during the first 24 hours averaged 21 mpy (0.53 mm/a). The specimens were put back into test without removal of their oxide coating. At the end of a week, the overall corrosion rates had dropped to an average of 2.8 mpy (0.07 mm/a). The test was continued for another week with the same specimens. The average rate of corrosion, 2.8 mpy (0.07 mm/a), was maintained.

The presence of chlorates in caustic soda solutions increases the corrosion rates of Nickel 200 considerably

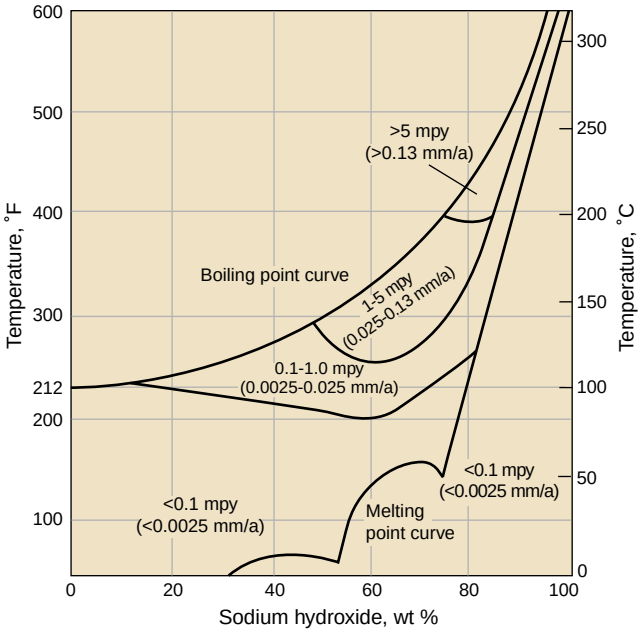

Figure 29 – Iso-corrosion chart for Nickel 200 and 201 in sodium hydroxide.

Table 15 – Plant tests in 23% caustic soda in tank receiving liquor from evaporator. Average temperature, 220°F (104°C)

Material	Corrosion rate, mpy (mm/a)
Nickel 200	0.16 (0.004)
MONEL alloy 400	0.20 (0.005)
INCONEL alloy 600	0.17 (0.004)

(Table 18). In view of these harmful effects, it is advisable to remove chlorates as thoroughly as possible before evaporation in the high-temperature range in the presence of nickel.

It is also known that the presence of oxidizable sulfur compounds tends to increase the corrosiveness of caustic toward nickel. This effect is noted primarily with the sulfides such as hydrogen sulfide, mercaptans, or sodium sulfide and to a much lesser extent with partially oxidized compounds such as thiosulfates and sulfites (Table 19).

It has been found that the effect of oxidizable sulfur compounds can be avoided by the addition to the caustic solution of sufficient sodium peroxide to oxidize them to sulfates. An excess of peroxide does not seem to alter the corrosiveness of caustic soda toward nickel.

As in other environments, when nickel is to be used above 600˚F (315˚C), the preferred material is the low-carbon grade, Nickel 201.

MONEL alloy 400

Because of its high nickel content, MONEL alloy 400 is nearly as resistant as Nickel 200 to caustic soda through most of the concentration range, although subject to stress-corrosion cracking in strong alkalis at elevated temperatures. The corrosion rates of MONEL alloy 400 are higher in highly concentrated caustic soda and caustic potash at high temperatures. MONEL alloy 400 is resistant to anhydrous ammonia and to ammonium hydroxide solutions of up to 3% concentration in the absence of dissolved oxygen.

INCOLOY alloys 800, 825, 020 and 25-6MO

While these alloys have excellent resistance to alkaline solutions, with a corrosion rate of 0.5 mpy (0.01 mm/a) in boiling 50% sodium hydroxide, they are not as resistant as Nickel 200 and are seldom used in alkaline environments unless other corrosives are involved. They also can

Table 16 – Laboratory corrosion tests, mpy (mm/a), in boiling 30 and 47% caustic potash for 26 days

Material	30% KOH saturated with KCl 0.05% $KClO_3$		47% KOH saturated with KCl 0.078% $KClO_3$	
	Liquid	Vapor	Liquid	Vapor
Nickel 200	0.2 (0.005)	0.1 (0.003)	0.1 (0.003)	0.3 (0.008)
INCONEL alloy 600	0.1 (0.003)	0.1 (0.003)	0.4 (0.010)	0.1 (0.003)

Table 17 – Laboratory corrosion tests of Nickel 200 in 75% caustic soda

Caustic concentration, %	Temperature, °F (°C)	Duration of test, h	Corrosion rate, mpy (mm/a)
75	250 (121)	20	1.0 (0.025)
75	400 (204)	48	0.8 (0.020)

Table 18 – Laboratory corrosion tests in evaporation of caustic soda from 73-96%, with and without chlorate

Material	Corrosion rate, mpy (mm/a)	
	Without chlorate	With 0.30% chlorate
Nickel 200	1.5 (0.038)	260 (6.60)
INCONEL alloy 600	2.2 (0.056)	380 (9.65)

Temperatures, 360-840˚F (182-449°C). Duration of tests, 24 hours.

Table 19 – Effect of oxidizable sulfur compounds on corrosion of Nickel 200 in caustic soda

Corrosive	Corrosion rate, mpy (mm/a)
Commercial sodium hydroxide being concentrated from 50 to 75% NaOH (sulfur content at start, calculated as H_2S, 0.009%)	1.7 (0.04)
75% chemically pure sodium hydroxide	0.6 (0.015)
75% chemically pure sodium hydroxide plus 0.75% sodium sulfide	22.8 (0.58)
75% chemically pure sodium hydroxide plus 0.75% sodium thiosulfate	7.9 (0.20)
75% chemically pure sodium hydroxide plus 0.75% sodium sulfite	5.2 (0.13)
75% chemically pure sodium hydroxide plus 0.75% sodium sulfate	0.6 (0.015)

Temperatures, 226 ± 9°F (108 ± 5°C). Duration of tests, 19-22 hours.

suffer stress-corrosion cracking in hot concentrated alkalis. These alloys are resistant to ammonia and ammonium hydroxide solutions under most service conditions.

INCONEL alloy 600

For high-temperature caustic applications in which sulfur is present, INCONEL alloy 600 is preferred to Nickel 201. However, alloy 600 can suffer stress-corrosion cracking in some alkali environments. For this reason, alloy 600 components should be stress relieved prior to use and operating stresses should be kept to a minimum. INCONEL alloy 600 resists sodium hydroxide at boiling temperatures in concentrations through 80%. Test results in sodium hydroxide at 572˚F (300˚C) are shown in Table 20.

As with Nickel 200, the presence of chlorates in caustic soda increases corrosion rates. Because of its chromium content, INCONEL alloy 600 is almost entirely resistant to attack by solutions of ammonia over a complete range of concentrations and temperatures.

INCONEL alloys 622, 625, C-276 and 686

While they offer excellent corrosion resistance, Ni-Cr-Mo alloys are not normally required for service in uncontaminated caustic environments. They can offer some advantages in halide-contaminated environments.

Table 20 – Performance of nickel alloys in boiling caustic solutions (Average of duplicates)

Alloy	NaOH concentration	Test period, h	Corrosion rate, mpy (mm/a)
Nickel 200	50%	720	<1 (<0.025)
MONEL alloy 400	50%	720	<1 (<0.025)
INCONEL alloy 600	50%	720	<1 (<0.025)
INCOLOY alloy 825	50%	720	<1 (<0.025)
INCONEL alloy 625	50%	720	<1 (<0.025)
INCONEL alloy C-276	50%	720	<1 (<0.025)
INCONEL alloy 600	10%	504	Nil
INCONEL alloy 600	20%	504	Nil
INCONEL alloy 600	30%	504	<1 (<0.025)
INCONEL alloy 600	40%	504	<1 (<0.025)
INCONEL alloy 600	50%	504	<1 (<0.025)
INCONEL alloy 600	60%	504	4.1 (0.10)
INCONEL alloy 600	70%	504	2.7 (0.07)
INCONEL alloy 600	80%	504	<1 (<0.025)