NiDI

Nickel
Development
Institute

Alloy selection for caustic soda service

by C.M. Schillmoller

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Caustic soda (i.e., sodium hydroxide, NaOH) and chlorine are co-produced by the electrolysis of a sodium chloride solution. Both chemicals find world-wide application in the chemical and related process industries. (Alloy selection for Chlorine is discussed in the NiDI publication #10020, "Alloys to Resist Chlorine, Hydrogen Chloride and Hydrochloric Acid.") Caustic soda ranks third in tonnage production among the inorganic chemicals; some 13.2 million tons were used in the USA alone in 1986.

Roughly half of all caustic 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 rayon, cellulose, textiles, petroleum products, soaps and the refining of Bauxite ore in the production of aluminum.

CRITERIA FOR MATERIALS SELECTION

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.

In general, factors to be considered in materials selection include practicality, availability, mechanical properties, corrosion resistance, risk/benefit considerations and economics.

Critical factors in caustic service include:

1. The concentration of the caustic solution.
2. The temperatures to be encountered (including possible excursions).
3. The presence of other chemicals which may be present 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
Alloys commonly used in caustic soda systems

Materials	Reference in text	Nominal Composition, %						ASTM B	U N S Numbers	Most Common Tradenames
		Ni	Cr	Fe	Mo	Cu	Ti			
Nickel										
Nickel	Alloy 200	99.6						161-163	N02200	Nickel 200
Low-carbon Nickel	Alloy 201	99.6						161-163	N02201	Nickel 201
Nickel-Copper Alloys										
Nickel-copper alloy	Alloy 400	67		1.5		31		163-165	N04400	Monel* 400
Nickel-Chromium-Iron Alloys										
Nickel-chromium alloy	Alloy 600	76	15	8				163-168	N06600	Inconel* 600
Nickel-iron-chromium alloy	Alloy 800	32	21	46				163-407	N08800	Incoloy* 800
Nickel-iron-chromium-moly-copper alloy	Alloy 825	42	21	30	3	2.3		163-423	N08825	Incoloy* 825
Nickel-iron-chromium-moly-copper alloy	Alloy 20	34	20	39	2.5	3.3		464-468	N08020	Carpenter** 20 Cb-3**
Stainless Steels										
Chromium-nickel stainless	Type 304	10	18	72					S30400	Type 304
Chromium-nickel-moly stainless	Type 316L	12	18	70					S31603	Type 316L
Chromium stainless	Type 430		17	83					S43000	Type 430
Chromium-moly stainless	26-1		26	73	1					EB 26-1
Titanium										
Titanium, grade 2	Titanium Gr2						99+	338		Titanium Gr2

**Monel, Inconel and Incoloy are tradenames of the International Nickel Co.*
***Carpenter and 20 Cb-3 are tradenames of CARTECH*

*Schillmoller Associates, Houston, TX; Consultant to NiDI

As these represent a considerable variation in first costs, the final choice for a specific service will depend on an analysis of all of the above factors.

MATERIALS OF CONSTRUCTION

Steel and Cast Irons

Carbon steel is useful for handling sodium hydroxide up to about 50% concentration, where iron contamination is not a problem, to moderate temperatures, e.g., 85°C (185°F). However, steels are subject to an anodic form of environmental cracking [i.e., stress-corrosion cracking (SCC)], often called "caustic embrittlement," in hot caustic. The relation of temperature and concentration in promoting cracking is 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.

For services where iron pick-up is undesired, 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 permissible, and the high-nickel cast irons, such as Ni-Resists (UNS* F41NNN and F43NNN series) are even more corrosion-resistant.

Austenitic Stainless Steels

The "18-8"-type stainless steels, exemplified by Types 304 (S30400) and 316 (S31600), have a usefully low corrosion rate in caustic at up to 50% concentration to about 70°C (160°F).

Note that Figure 2, based on Copson's work (5) on SCC of stainless steels, is somewhat more optimistic, showing less than 1 mpy up to about 93°C (200°F). This is probably due to dissolved oxygen or traces of oxidizing species, because it is known that Type 304 can go active in 40% caustic at about 80°C (175°F) and in 50% caustic at 70°C (160°F). In the active state, the 18-8 alloys corrode *faster* than carbon steel.

Table 2 shows the results of a study by NACE Task Group T5A-3D (4) to assess the relative corrosivity of diaphragm-cell caustic vs. mercury-cell caustic. The results indicate no significant difference between Types 304 (S30400) and 316 (S31600) in 50% caustic, nor in 73% concentration in which both materials suffered active corrosion as well as some pitting attack. It seems probable that these products contained unknown amounts of chlorates, as produced.

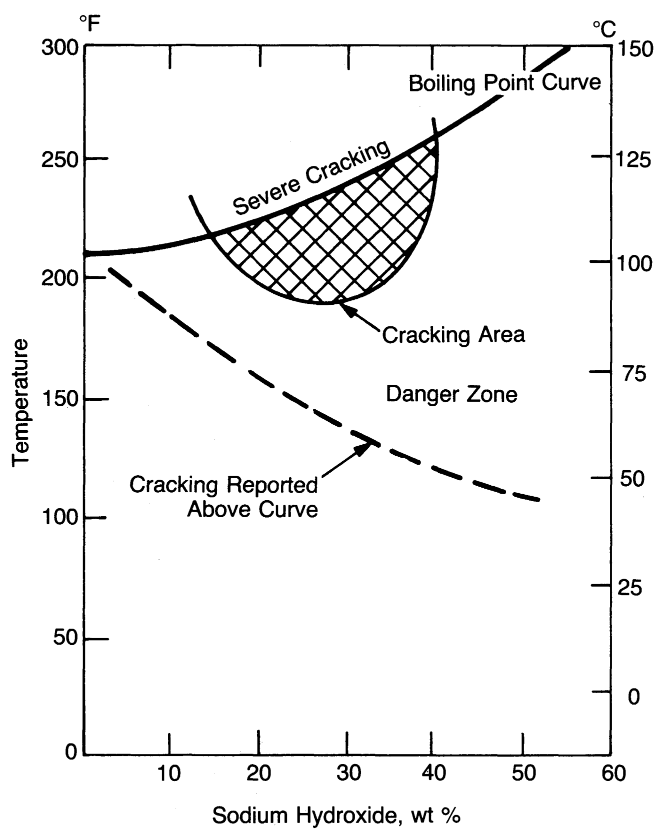

Figure 1
Relation of temperature and concentration of sodium hydroxide to cause stress cracking of carbon steel.

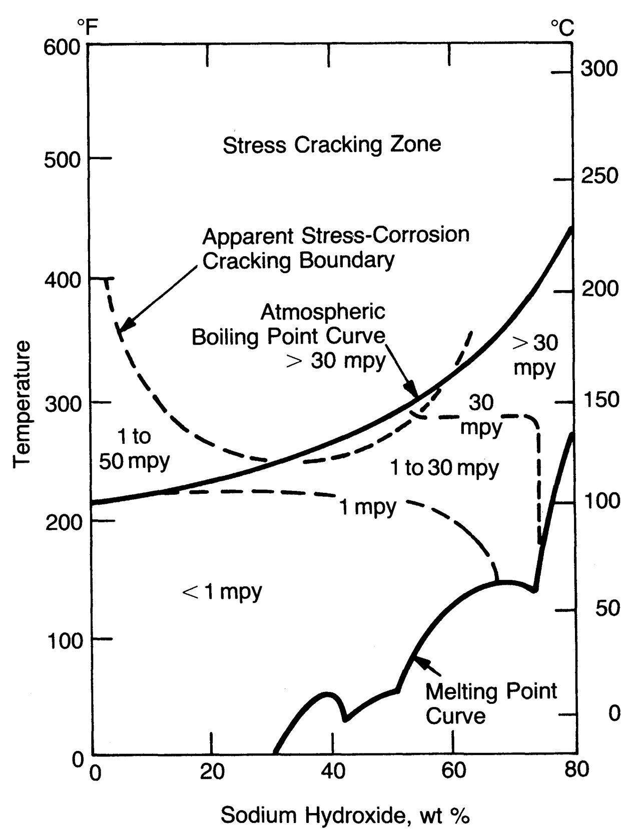

Figure 2
Isocorrosion chart for AISI 304 and 316 stainless steels in sodium hydroxide, with stress cracking boundary superimposed.

*Throughout this publication, Unified Numbering System (UNS) designations have been included for alloy identification.

Table 2

"Round Robin" test program by four caustic soda producers—comparison of corrosiveness of diaphragm cell vs. mercury cell caustic (conducted by NACE Committee T5A-3D)

		Company 1		Company 2		Company 3		Company 4		Company 1	Company 2	Company 3	Company 4
		Average Temperature								Corrosion Rate, mpy			
Material	Corrodent	°C	°F	°C	°F	°C	°F	°C	°F				
Nickel 200	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		<0.1			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	<0.1	1.0	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	<0.1		<0.1
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	<0.1		0.2	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	0.2			
	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	0.3			
Inconel alloy 600	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1 (1)	<0.1	<0.1	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		<0.1			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	<0.1		<0.1
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	<0.1		0.2	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	0.3			
	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	0.2			
Monel alloy 400	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		<0.1			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	0.1	0.2	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	<0.1		<0.1
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	<0.1		0.8	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	0.4			
	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	0.5			
Incoloy alloy 800	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		<0.1			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	<0.1		<0.1
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	0.1		4.1 (2)	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	0.5			
	73% NaOH-Diaphragm Cell	114	236	—	—	—	—	—	—	0.3 (1)			
Carpenter alloy 20 Cb-3	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		<0.1			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	<0.1	<0.1	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	<0.1		<0.1
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	0.4		1.5 (3)	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	0.5			
	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	0.4			
Type 316 Stainless Steel	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	3.3	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		0.2			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	<0.1	0.2	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	0.1		0.3
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	6 (4)		8.7	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	13.1 (5)			
	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	10 (4)			
Type 304 Stainless Steel	50% NaOH-Diaphragm Cell	35	95	29	85	88	190	54	130	<0.1	<0.1	1.1	<0.1
	50% NaOH-Diaphragm Cell	40	104	—	—	—	—	Ambient		<0.1			<0.1
	50% NaOH-Mercury Cell	38	100	105	221	82	180	60	140	<0.1	0.1 (1,6) 11.0	0.3	<0.1
	50% NaOH-Mercury Cell	37	98	45	113	—	—	Ambient		<0.1	<0.1		0.4
	50% NaOH-Mercury Cell	—	—	Ambient		—	—	Ambient			<0.1		<0.1
	73% NaOH-Diaphragm Cell	119	246	—	—	99	210	—	—	15 (4)		13 (7)	
	73% NaOH-Diaphragm Cell	125	257	—	—	—	—	—	—	19.4 (5)			
	73% NaOH-Mercury Cell	114	236	—	—	—	—	—	—	15 (4)			

(1) Pitted to a maximum depth of 1 mil.
(2) Pitted to a maximum depth of 4 mils.
(3) Pitted to a maximum depth of 5 mils.
(4) Stress corrosion crack through one of the identifying punch marks.
(5) Pitted to a maximum depth of 3 mils.
(6) Mercury droplets in tank 2 rates shown are for the duplicate specimens (not averaged). Specimen with high rate showed stress-accelerated local attack.
(7) Pitted to a maximum depth of 8 mils.

As indicated in Figure 2, 18-8 stainless is 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 (e.g., Oxycat units, expansion joints in 400 psi steam). Caustic cracking of stainless is characterized by a gun-metal bluing effect, quite striking on visual examination.

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 of considerable chloride, e.g., up to 1% sodium chloride (6000 ppm Cl^-).

The effect of chloride in caustic is moot (some Russian researchers have claimed it inhibits caustic SCC of 18-8). However, if the sodium hydroxide is used in a process in which it is consumed or otherwise converted to a different compound, its chloride content remains as a potential hazard for chloride SCC. Use of mercury-cell caustic diminishes this risk (6).

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. They are considered susceptible to caustic cracking, as well.

In recent years, there has been wide-spread application of extra-low interstitial, molybdenum-bearing ferritics, such as Alloy 26-1 (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. Blockage of tubes with insoluble salts, creating locally high skin temperatures.

Copper Alloys

It is sometimes mistakenly assumed that copper alloys are unsuitable for caustic service. This is probably due to the dearth of data available. Copper alloys are not, in fact, used in contact with caustic to be employed in the rayon industry (because of color 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 eminently 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.

Aluminum bronzes may be subject to dealuminification, due to the amphoteric nature of the aluminum constituent.

High-Nickel Alloys

The nickel-chromium-iron alloys, with and without molybdenum, e.g., Alloy 800 (N08800), Alloy 825 (N08825), Alloy 20 Cb-3 (N08020) have useful resistance to caustic soda solutions at concentrations up to 73%, as shown in Table 2, up to approximately 120°C (250°F).

Unfortunately, they are susceptible to caustic cracking, certainly around 150°C (300°F). In materials selection to prevent stress-corrosion cracking, it is therefore essential to determine whether the responsible species are chlorides, in which case these are acceptable alternative alloys, or caustic, which calls for nickel-base alloy replacement.

Nickel-Base Alloys

These are the alloys having more than 50% nickel, and can be conveniently divided into two groups; those that do *not* contain chromium, and those that do.

CHROMIUM-FREE ALLOYS

These comprise a group of three generic types, nickel itself, nickel-copper and nickel-molybdenum alloys.

Nickel

Nickel is available in two alloys, Alloy 200 (N02200), and a low-carbon variant Alloy 201 (N02201), both of which have excellent resistance to caustic, even as the hot anhydrous form, as shown in Figure 3. 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 1 mpy (.025 mm/yr.). 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 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 Alloy 201 (N02201) is preferred.

Behavior of these nickel alloys in caustic solutions is apparently unaffected by stress. Prior to development of the low-carbon variant, a few failures of nickel were reported in high-temperature service in concentrated caustic, with an intergranular mode of attack thought to be caustic cracking. These are now believed to have been cases of embrittlement due to graphite precipitation.

Nickel-Copper Alloys

Alloy 400 (N04400) has corrosion resistance quite similar to 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 nickel. In lower concentrations, and for service conditions where contamination by small amounts of copper and

nickel is not detrimental, Alloy 400 (N04400) can be useful for caustic service at a somewhat lower cost than pure nickel.

Alloy 400 (N04400) is subject to caustic cracking at elevated temperatures (e.g., in caustic-contaminated 300-400 psi steam). It is also subject to liquid metal cracking (LMC) by mercury and its salts. There have been instances of LMC with Alloy 400 (N04400) 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., N04404 and N04405) and the age-hardening variants (e.g., Alloy K500 or N05500 and N05502) have substantially the same corrosion characteristics.

Nickel-Molybdenum Alloys

There is little occasion to use Alloy B-2 (N10665) in caustic service. Published data indicate that it has excellent resistance, at least in lower concentrations in the absence of powerful oxidants. Individual applications would have to be explored.

CHROMIUM-BEARING ALLOYS

This group comprises Alloy 600 (N06600) and its variants and the molybdenum-bearing grades, Alloy 625 (N06625) and Alloy C276 (N10276) and its variants.

Nickel-Chromium-Iron Alloys

Alloy 600 (N06600) exhibits resistance similar to nickel up to and including the anhydrous product. It is favored 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.

It is subject to caustic cracking under severe conditions in prolonged exposure, and should be used in the stress-relieved condition.

Alloy 600 (N06600) offers an advantage, compared to Alloy 201 (N02201) when a sulfur-bearing contaminant may be present, in being less susceptible to nickel sulfide eutectic formation (a low-melting nickel-nickel sulfide compound causes intergranular penetration analogous to LMC). It has been used for the production of anhydrous caustic where a sulfur-containing chemical must be tolerated as a contaminant in the heating medium. It has also been used where sulfur has been present in one of the process reactants.

Alloy 600 (N06600) has also replaced Type 316 (S31600) 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 (N06600) can also offer an advantage over Alloy 200 (N02200) in caustic from the diaphragm-cell process, in which chlorates and hypochlorites are present. Being oxidizing in nature, these accelerate corrosion of Alloy 200 (N02200), as shown in Figure 4, whereas the

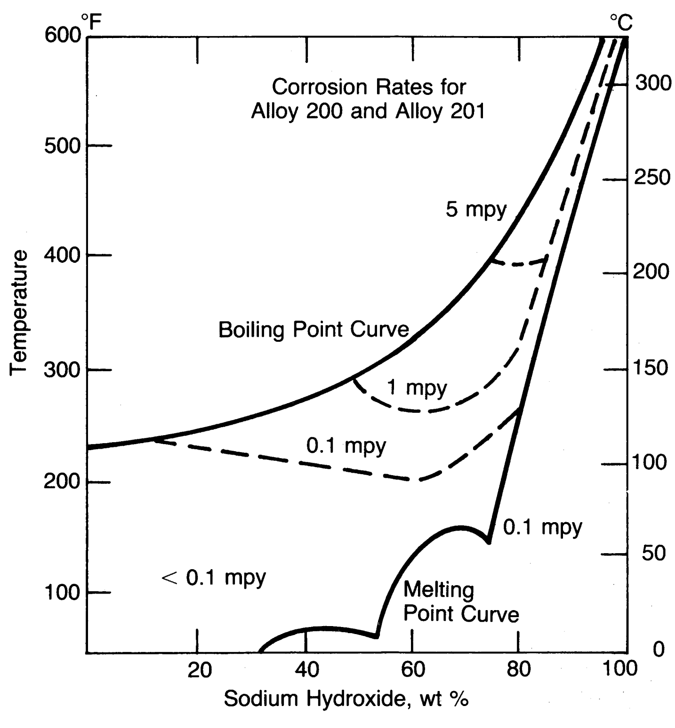

Figure 3
Corrosion rates for Nickel Alloy 200 and low carbon Nickel Alloy 201 in sodium hydroxide.

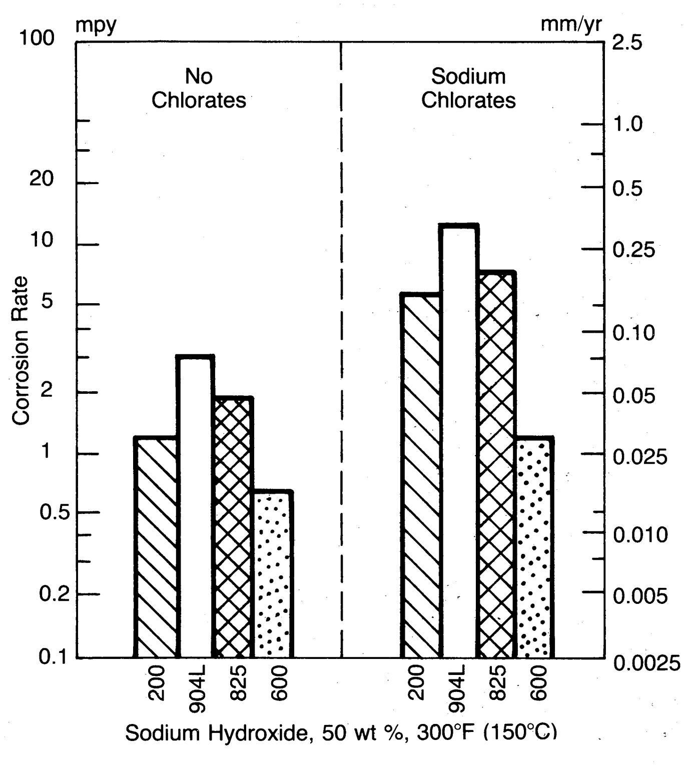

Figure 4
Typical comparative corrosion rates for several alloys in sodium hydroxide in the presence of sodium chlorates.

resistance of the chromium-bearing alloy is not greatly affected.

Nickel-Chromium-Molybdenum Alloys

Such alloys, exemplified by Alloy 625 (N06625) and Alloy C276 (N10276) and its variants, are intended for acid service, little being published about caustic resistance. Of course, their higher cost, as compared with Alloys 200 or 600, practically excludes them from consideration.

There is one notable exception. Alloy 625 (N06625) 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 (N06600), for example. These alloys are practically unaffected by hot caustic up to at least 320°C (600°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 Cell Caustic

Carbon steel has been the conventional material of construction for mercury-cell caustic, resisting caustic up to 70% to about 93°C (200°F). Small amounts of other alloys are used for specific areas in the process.

Subterranean brines used as feedstock for electrolytic processes must be heated and chemically treated to remove calcium, iron, manganese and sulfates. A simplified process flow diagram of the brine processing and chlorine handling in an electrolytic brine-processing circuit is shown in Figure 5.

For the brine heaters, both Alloy 400 (N04400) and titanium (R50400) or its variants) have been used. Titanium alloys are preferred, because of the problem of LMC of the nickel-base alloy by entrained mercury, as well as corrosion by small amounts of chlorine or hypochlorites.

Diaphragm Cell Caustic

This electrolytic process produces about 75% of present-day production of sodium hydroxide. The initial product, the cell liquor leaving the electrolysis cell bank, contains only about 10-12% caustic. The other constituents are unreacted sodium chloride, sodium chlorate plus traces of dissolved chlorine (both powerful oxidants) and sodium sulfate.

This cell liquor must be concentrated to 50% or 73%, or to the anhydrous grade for commercial use. Multiple-effect evaporators are utilized to achieve these higher concentrations.

CHLORATE REMOVAL

Sodium chlorate, being both an oxidizing agent and a source of more chloride upon decomposition, 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.

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 sulfates and other undesirable constituents in the cell liquor.

SPECIFIC EQUIPMENT

50% Caustic

Evaporators

The multiple-effect evaporators required for concentration employ Alloy 200 (N02200) tubing, tube-sheets, circulation piping, and the wetted surfaces of the evaporator bodies. A triple-effect evaporator for the production of 50% caustic is shown in Figure 6, while alloy selection for specific areas is indicated in Figure 7. Also, Table 3 provides information on various applications of nickel-base alloys and nickel cast irons in caustic soda equipment.

Table 3
Applications of nickel alloys in caustic soda equipment
(typical examples, courtesy INCO Alloys International)

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
Steam Chests	Nickel 200 *or* alloy 400 tube sheets 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 Winding Wire	Alloy 400 *or* Nickel 200
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

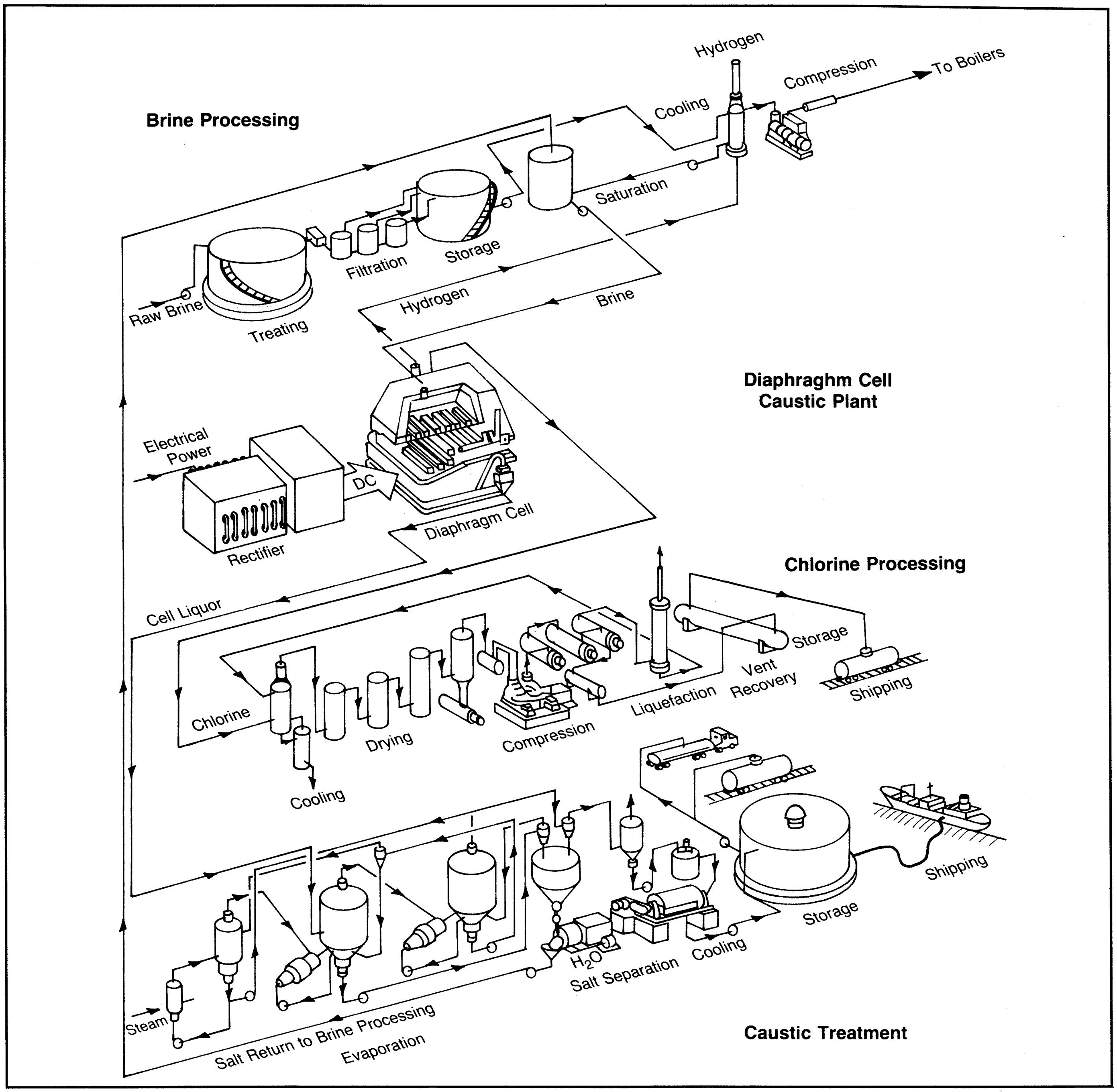

Figure 5
Flow diagram of a diaphragm-cell caustic plant showing the brine processing circuit to the electrolytic cells, the chlorine handling and caustic treatment. (Courtesy Occidental Chemical Corp., Ref. 11.)

The adverse effect of chlorates in a triple-effect evaporator has been reported (Reference 14). 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 Alloy 200 (N02200) increase dramatically with caustic containing 100 ppm or more of chlorate.

Because of this adverse effect, 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. Recently, a proprietary process has been commercialized which decomposes chlorate with by-product hydrogen in the presence of a catalyst. Alloys 200 (N02200) and 400 (N04400) have been used for the reactor, feed heater and feed/product interchanger in the hot caustic in this process.

Salt Settlers

The salt settlers (sometimes with filters) are traditionally Alloy 200 (N02200). When cooling is required, the heat transfer surfaces of the heat exchanger are also nickel.

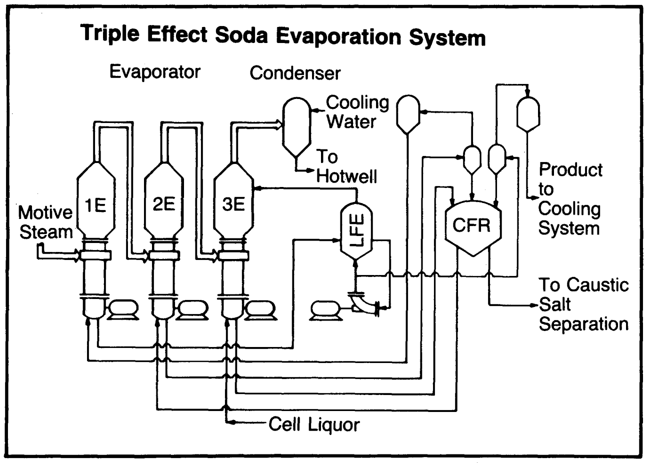

Figure 6
Flow diagram of a triple effect caustic soda evaporation system.

However, nickel tubes recently failed in this application when seawater was used as coolant, and replacement in Alloy 400 (N04400), welded with Alloy 625 (N06625) was recommended. The salt-settling tank and slurry-holding tank, prior to recycling of the crystallized salt, are frequently made of Alloy 400 (N04400).

Storage Tanks and Heaters

Stress-relieved carbon steel tanks are employed, with specialty internal organic coatings to minimize iron pick-up. For high purity grades, Alloy 200 (N02200)-clad steel tanks have also been employed. To maintain the caustic above its freezing point, internal heating coils (or U-tube bundles) are employed. Tubes and tubesheets are either Alloy 200 (N02200) or Alloy 400 (N04400), to have equivalent thermal expansion of both components.

73% and Anhydrous Caustic

Evaporators

Alloy 200 (N02200) 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 Alloy 201 (N02201) is required, as previously noted, to void graphitic embrittlement.

If sulfur compounds are known or anticipated, Alloy 600 (N06600) is required. Because it is susceptible to stress-corrosion cracking, thermal stress relief is required. Where this alloy has been employed with this precaution, service performance has been equivalent to Alloy 201 (N02201).

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.

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 sulfur compounds may be removed from refinery streams with either caustic soda or caustic potash (KOH). Since economy requires regeneration of the caustic, with temperatures and concentrations which exceed the capability of steel, Alloy 400 (N04400) 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 sulfur-removal operations, it is recovered by caustic treatment. In such recovery units, steel would be corroded by sulfur-rich oils and austenitic stainless steel, e.g., Type 316L (S31603) is employed, the temperatures and concentration of caustic not requiring high-nickel alloys.

Bauxite Refining

In the Bayer Process for separation of alumina from iron oxide in the ore, caustic soda is employed to solubilize the aluminum 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 (N04400) tubing is used in the higher-temperature heaters. Either solid Alloy 200 (N02200) or nickel-lined steel piping transfers the solution from the heaters to the reactors.

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 (N02200) and 400 (N04400) have been commonly used for saponification vessels, replacing the original steel and iron equipment.

Sodium Hydrosulfide (NaSH)

The reaction of hydrogen sulfide with 50% caustic produces sodium hydrosulfide 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 18-8 austenitic stainless steels, Alloy 20Cb3 (N08020) has proven superior in cases where the 18-8 has suffered general thinning. Field corrosion tests suggest that Alloy 600 (N06600) 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 tem-

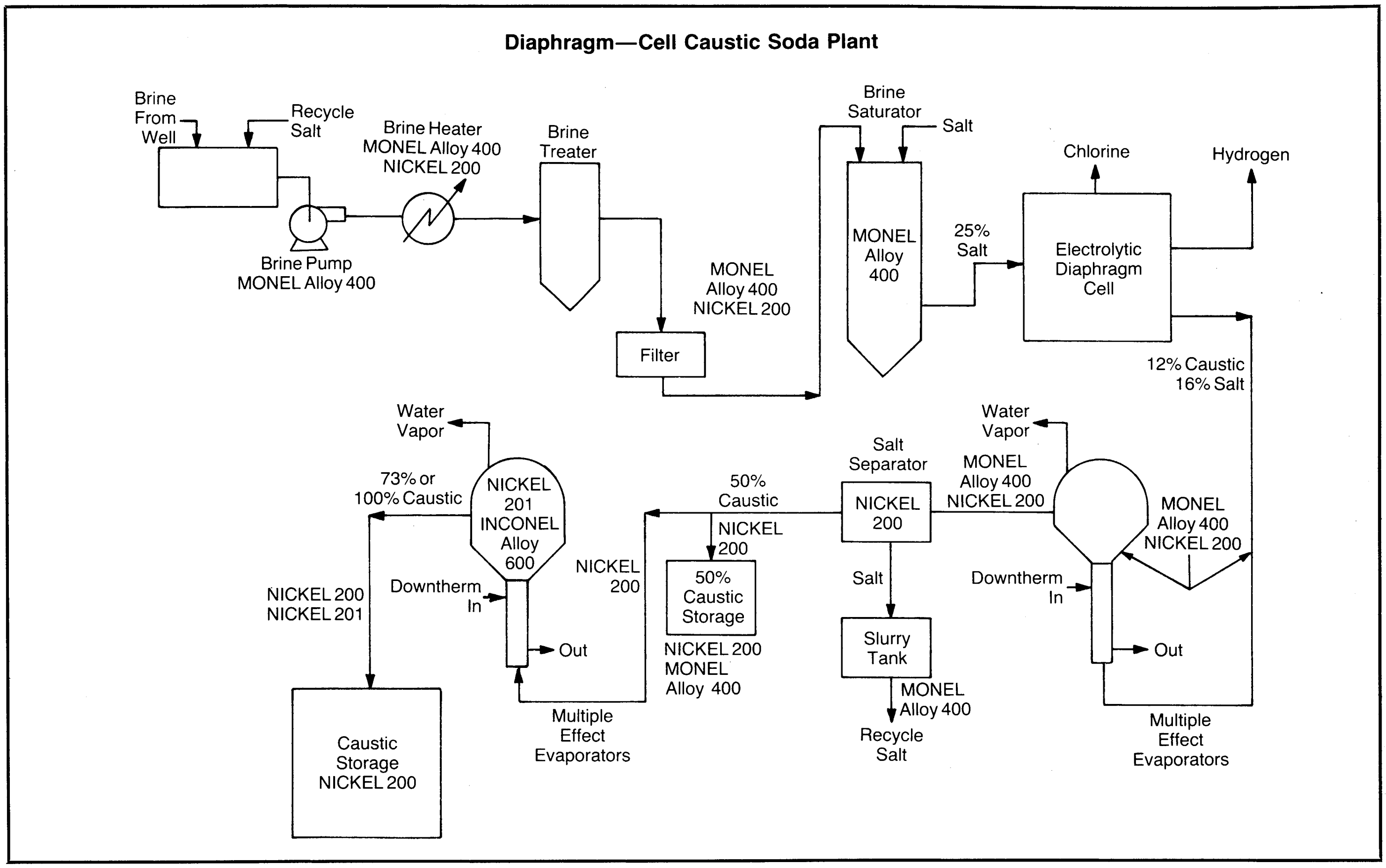

Figure 7
Schematic flow sheet of diaphragm-cell caustic soda plant, showing typical alloy selections. (Courtesy INCO Alloys International)

peratures are usually above 315°C (600°F), Alloy 201 (N02201) is the preferred material of construction, provided no sulfur compounds are present.

When sulfur compounds are present (e.g., in the caustic fusion of benzene metasulfonic acid to produce resorcinol), stress-relieved Alloy 600 (N06600) is preferred. Alloy 201 (N02201) would be attacked in an intergranular mode by the nickel sulfide eutectic which would form at the reaction temperature.

Miscellany

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. Alloy 200 (N02200) or Alloy 600 (N06600) stress-relieved clad steel vessels are mandatory.

REFERENCES

1. P. J. Gegner, "Corrosion Resistance of Materials in Alkalies and Hypochlorites," Process Industries Corrosion Short Course, Paper No. 27, National Association of Corrosion Engineers, Houston, TX, 1974.
2. H. W. Schmidt, P. J. Gegner, G. Heinemann, C. F. Pogacar, and E. H. Wyche, *Corrosion*, Vol 7, p 295, 1951.
3. A. A. Berk and W. F. Waldeck, *Chemical Engineering*, Vol 57 (6), p 235, 1950.
4. "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.
5. F. L. LaQue and H. R. Copson, "Corrosion Resistance of Metals and Alloys," Reinhold Publishing Corporation, New York, NY, 1963.
6. C. W. Funk and G. B. Barton, "Caustic Stress Corrosion Cracking," CORROSION/77, Paper No. 54, National Association of Corrosion Engineers, Houston, TX, 1977.
7. E. C. Hoxie, "Some Considerations in the Selection of Stainless Steel for Pres- sure Vessels and Piping," International Nickel Co., New York, NY, 1975.
8. R. P. Tracy and B. R. Chuba, "Corrosion Resistance, Application, and Economics of Electroless Nickel Coatings inNaOH Production," NACE Corrosion 87, Paper No 462.
9. C. M. Schillmoller, "Amine Stress Cracking: Causes and Cures," *Hydrocarbon Processing*, June 1986, pp 37-39.
10. P. J. Gegner, *Corrosion*, Vol 12, p 261, June 1956.
11. B. M. Barkel, "Accelerated Corrosion of Nickel Tubes in Caustic Evaporation Service," CORROSION/79, Paper No 13, National Association of Corrosion Engineers, Houston, TX, 1979.
12. J. K. Nelson, "Materials of Construction for Alkalies and Hypochlorites," Process Industries Corrosion, NACE 1986, pp 297-310.
13. J. R. Crum and W. G. Lipscomb, "Correlation Between Laboratory Tests and Field Experience for Nickel 200 and 26-1 Stainless Steel in Caustic Service," CORROSION/83, Paper No 23, National Association of Corrosion Engineers, Houston, TX, 1983.
14. M. Yasuda, F. Takeya, F. Hine, "Corrosion Behavior of Nickel in Concentrated NaOH Solutions Under Heat Transfer Conditions," *Corrosion*, Vol 39 (10), October, 1983.

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