Kirk-Othmer Encyclopedia of Chemical Technology.

SODIUM HYDROXIDE

Alkali and chlorine products are a group of commodity chemicals which include chlorine [7782-50-5], Cl_2; sodium hydroxide (caustic soda) [1310-73-2], NaOH; sodium carbonate (soda ash) [497-19-8], Na_2CO_3; potassium hydroxide (caustic potash) [1310-58-3], KOH; and hydrochloric acid (qv) (muriatic acid or anhydrous) [7647-01-0], HCl. Chlorine and caustic soda are the two most important products in this group, ranking among the top ten chemicals in the United States.

1. Physical Properties

Sodium hydroxide, NaOH, mol wt 39.998, is a brittle, white, translucent crystalline solid. Because of its corrosive action on all human body tissue, it is also known as caustic soda. Physical properties of the pure material are noted in Table 1. Sodium hydroxide is produced and shipped in the anhydrous state in the form of solid cakes, flakes, or beads, but is used in solution (1). Properties of aqueous sodium hydroxide solutions relevant to industrial operations are available from manufacturers and in handbooks (2).

Sodium hydroxide deliquesces on exposure to air, resolidifying because of sodium carbonate formation upon absorbing carbon dioxide. It is very soluble in water and forms hydrates containing 1, 2, 3, 5, and 7 molecule of H_2O, depending on the concentration. Heat is generated during the dilution of concentrated caustic solution, or when solid NaOH is dissolved in water. Figures 1 and 2 illustrate solution freezing point and enthalpy data. Because the heat can be excessive to the extent that the temperature of a solution can increase above the boiling point, caution should be exercised during the dilution of caustic from concentrations of $>25\%$ by providing proper cooling (5, 6).

2. Chemical Properties

Aqueous solutions of caustic soda are highly alkaline. Hence caustic soda is primarily used in neutralization reactions to form sodium salts (2). Sodium hydroxide reacts with amphoteric metals (Al, Zn, Sn) and their oxides to form complex anions such as $AlO^{-}{}_2$, $ZnO^{2-}{}_2$, $SnO^{2-}{}_3$, and H_2 (or H_2O with oxides). Reaction of Al_2O_3 with NaOH is the primary step during the extraction of alumina from bauxite (see Aluminum compounds):

$$Al\,(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2\,H_2O \qquad (1)$$

Table 1. Physical Constants of Pure Sodium Hydroxide

Property	Value
CAS Registry Number	[1310-73-2]
molecular weight	39.998
specific gravity at 20°C	2.130
melting point, °C	318
boiling point, °C at 101.3 kPa[a]	1388
specific heat, J/g·°C[b] at 20°C	1.48
refractive index at 589.4 nm	
320°C	1.433
420°C	1.421
latent heat of fusion, J/g[b,c]	167.4
lattice energy, kJ/mol[d]	737.2
entropy, J/(mol·K)[b] at 25°C and 101.3 kPa[a]	64.45[e]
heat of information ΔH_f, kJ/mol[a]	
α form	422.46
β form	426.60
heat of transition from α to β form, J/g[b]	103.3
transition temperature, °C	299.6
free energy of formation ΔG_f, kJ/mol[d,e] at 25°C and 101.3 kPa[a]	−379.5[e]

[a]To convert kPa to mm Hg, multiply by 7.5.
[b]To convert J to cal, divide by 4.184.
[c]To convert J/g to Btu/lb, multiply by 0.4302.
[d]To convert kJ to kcal, divide by 4.184.
[e]Values from ref. 3.

Table 2. Typical Specifications for Feed Brine to Electrolyzers

	Membrane cell process[a]	Diaphragm cell process[a]
sodium chloride	280–305 g/L	320 g/L[b]
calcium and magnesium	20 ppb	5 ppm
sodium sulfate	7 ppm	5 ppm
silicon dioxide	5 ppm	0.5 ppm
aluminum	50 ppb	0.5 ppm
iron	0.5 ppm	0.3 ppm
mercury	0.04 ppm	1 ppm
heavy metals	0.05 ppm	0.05 ppm
fluoride	1 ppm	1 ppm
iodine	0.4 ppm	
strontium	0.5 ppm	[c]
barium	0.4 ppm	[c]
total organic carbon	1 ppm	1 ppm
pH	2–11	2.5–3.5

[a]All ppb and ppm values represent maximum concentration allowed.
[b]Minimum concentration allowed.
[c]Included with calcium.

Caustic soda reacts with weak-acid gases such as H_2S, SO_2, and CO_2.

$$H_2S + 2\,NaOH \longrightarrow Na_2S + 2\,H_2O \qquad (2)$$

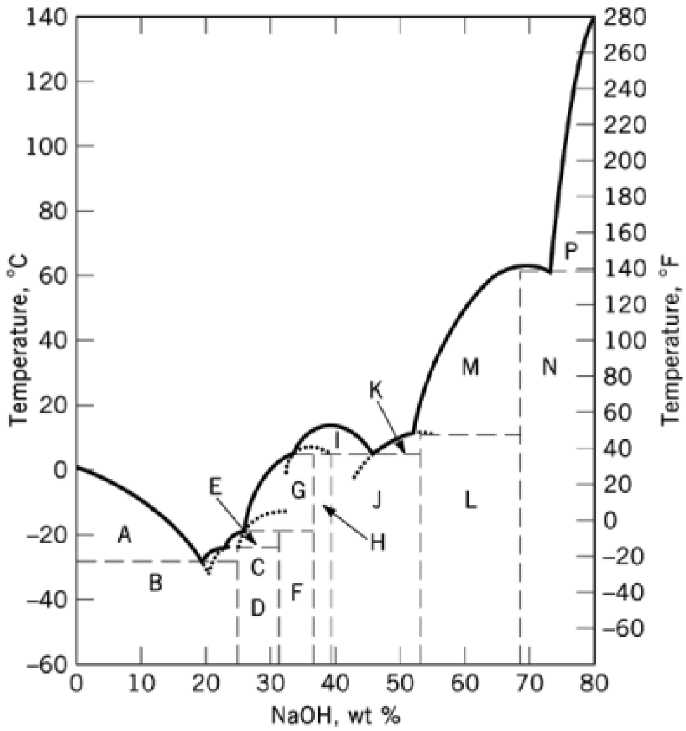

Fig. 1. Freezing points of caustic soda solutions (4): A, ice; B, ice+$NaOH{\cdot}7H_2O$; C, $NaOH{\cdot}7H_2O$; D, $NaOH{\cdot}7H_2O$+$NaOH{\cdot}5H_2O$; E, $NaOH{\cdot}5H_2O$; F, $NaOH{\cdot}5H_2O$+$NaOH{\cdot}4H_2O$; G, $NaOH{\cdot}4H_2O$; H, $NaOH{\cdot}4H_2O$+$NaOH{\cdot}3/\frac{1}{2}H_2O$; I, $NaOH{\cdot}3/\frac{1}{2}H_2O$; J, $NaOH{\cdot}3/\frac{1}{2}H_2O$+$NaOH{\cdot}2H_2O$; K, $NaOH{\cdot}2H_2O$; L, $NaOH{\cdot}2H_2O$+$NaOH{\cdot}H_2O$; M, $NaOH{\cdot}H_2O$; N, $NaOH{\cdot}H_2O$+NaOH; and P, NaOH.(Courtesy of the Chlorine Institute, Inc.)

$$SO_2 + 2\,NaOH \longrightarrow Na_2SO_3 + H_2O \qquad (3)$$

$$CO_2 + 2\,NaOH \longrightarrow Na_2CO_3 + H_2O \qquad (4)$$

These reactions are used industrially for scrubbing operations and for selective removal of H_2S from natural gas containing CO_2.

Metallic ions are precipitated as their hydroxides from aqueous caustic solutions. The reactions of importance in chlor–alkali operations are removal of magnesium as $Mg(OH)_2$ during primary purification and of other impurities for pollution control. Organic acids react with NaOH to form soluble salts. Saponification of esters to form the organic acid salt and an alcohol and internal coupling reactions involve NaOH, as exemplified by reaction with triglycerides to form soap and glycerol,

$$C_3H_5\,(COOR)_3 + 3\,NaOH \longrightarrow C_3H_5\,(OH)_3 + 3\,NaCOOR \qquad (5)$$

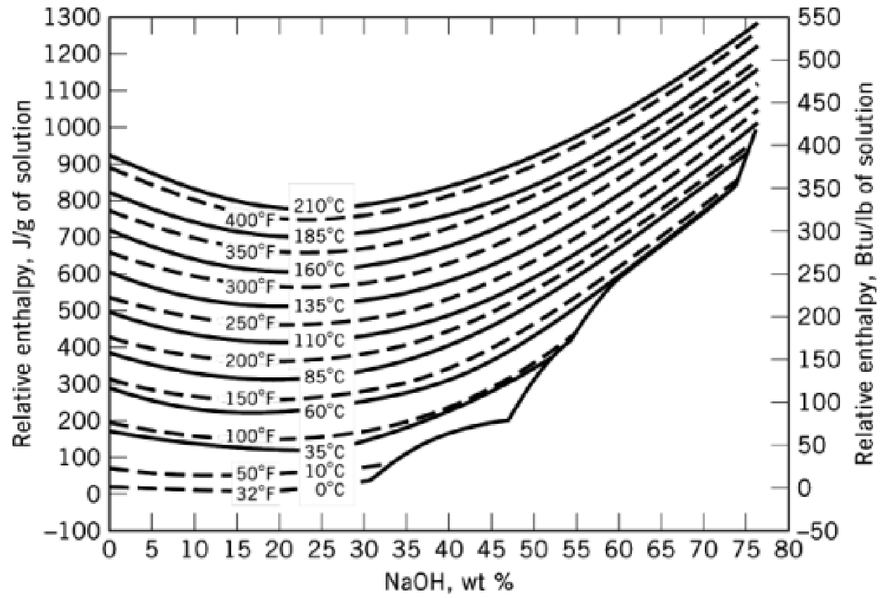

Fig. 2. Enthalpy vs concentration of caustic soda solutions.

Table 3. Components of Diaphragm, Membrane, and Mercury Cells

Component	Mercury cell	Diaphragm cell	Membrane cell
anode	$RuO_2 + TiO_2$ coating on Ti substrate	RuO_2-based coating on Ti substrate	RuO_2 based coating on Ti substrate
cathode	mercury on steel	steel or steel coated with activated nickel	steel or Ni based catalytic coating on nickel
diaphragm	none	asbestos, polymer-modified asbestos, or Polyramix (nonasbestos)	ion-exchange membrane
cathode product	sodium amalgam	10 – 12% NaOH + 15 – 17% NaCl and H_2	30 – 33% NaOH + $<$0.01% NaOH and H_2
decomposer product	50% NaOH and H_2	none	none
evaporator product	none	50% NaOH with ~1.1% salt and solid salt	50% NaOH with ~0.01% salt
steam consumption	none	1500–2300 kg/t NaOH	450–550 kg/t NaOH
cell voltage, V	4–5	3–4	2.8–3.3
current density, kA/m^2	7–10	0.5–3	2–5

and with propylene chlorohydrin to form propylene oxide,

$$ClC_3H_6OH + NaOH \longrightarrow C_3H_6O + NaCl + H_2O \qquad (6)$$

Reactions of NaOH with natural products are complex. They include solubilization of cotton in rubber reclaiming, starch dextrination, cotton scouring, refining of vegetable oils, and removal of lignin and hemicellulose in the Kraft pulping process. The primary step during the reaction of cellulose, caustic soda, and monochloroacetic acid to form the sodium salt of carboxymethylcellulose is similar to that used in

Table 4. World Caustic Soda Capacity[a]

Region	Capacity, $\times 10^3$ t, yr
North America	16,127
South America	1,931
Western Europe	10,716
Middle East	677
Asia	15,882
other	5,000
Total	*50,333*

[a]Ref. 8.

Table 5. U.S. Caustic Soda Producers[a]

Company	Locations	Technology	Capacity, $\times 10^3$ t/yr
Dow	Freeport, TX; Plaquemine, LA	electrolysis	4,091
Elf Atochem	Portland, OR	electrolysis	209
FMC	Green River, WY; Granger, WY	lime soda	150
Formosa	Baton Rouge, LA; Point Comfort, TX	electrolysis	895
Fort Howard	Green Bay, WI; Muskogee, OK, Rincon, GA	electrolysis	23
GE Plastics	Burkville, AL; Mount Vernon, IN	electrolysis	136
Georgia Gulf	Plaquemine, LA	electrolysis	455
Georgia-Pacific	Bellingham, WA	electrolysis	91
HoltraChem	Acme, NC; Orrington, ME	electrolysis	132
LaRoche	Gramercy, LA	electrolysis	200
Olin	Augusta, GA; Charleston, TN; McIntosh, AL; Niagra Falls, NY	electrolysis	1,014
OxyChem	Convent, LA; Corpus Christi, TX; Deer Park, TX; Delaware City, DE; LaPorte, TX; Mobile, AL; Muscle Shoals, AL; Niagra Falls, NY; Taft, LA	electrolysis	2,893
Pioneer	Henderson, NV; St. Gabriel, LA; Tacoma, WA	electrolysis	586
PPG	Lake Charles, LA; Natrium, VW	electrolysis	1,694
Solvay	Green River, WY	lime soda	68
Sunbelt	Mintosh, AL	electrolysis	225
Vulcan	Geismar, LA; Port Edwards, WI; Wichita, KS	electrolysis	541
Westlake	Calvert City, KY	electrolysis	118
Weyerhaeuser	Longview, WA	electrolysis	159
Total			*13,679*

[a]Ref. 9.

mercerizing cotton and in the preparation of rayon from cellulose xanthate (see Cellulose ethers; Fibers, regenerated cellulosics).

3. Manufacture

Electrolysis of sodium chloride accounts for nearly all of today's installed capacity for sodium hydroxide.

$$2\,NaCl + 2\,H_2O \longrightarrow 2\,NaOH + Cl_2 + H_2 \qquad (7)$$

As shown, chlorine is coproduced, so companies that are in the sodium hydroxide business are also usually involved in the chlorine business.

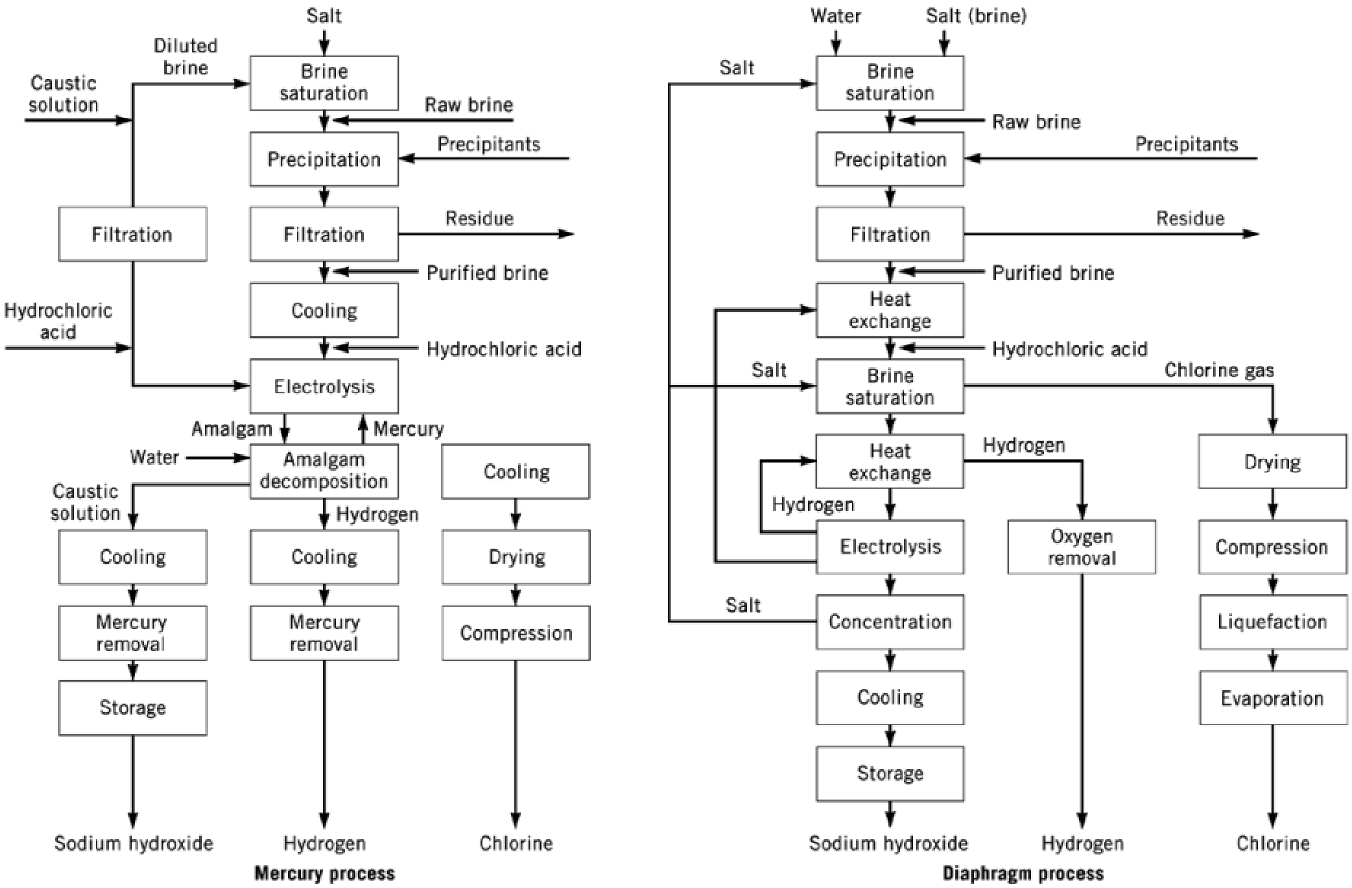

Fig. 3. Flow diagrams of the Mercury and Diaphragm chlor-alkali processes.

The electrolysis is done in one of three types of cells: the mercury cell, the diaphragm cell and the membrane cell. Flow diagrams for processes using each type of cell are given in Figures 3 and 4.

The first step in all three processes is to purify the feed salt brine. Brines contain many contaminants such as calcium, magnesium, barium, and sulfate ions which are detrimental to the electrolytic process. Removal of brine contaminants accounts for a significant portion of overall chlor–alkali production cost, especially for the membrane process since it requires a higher degree of brine purity.

Brines are treated with sodium carbonate to precipitate calcium carbonate, followed by treatment with sodium hydroxide to precipitate magnesium hydroxide (7). Most trace metal impurities are also precipitated during the process. The precipitates are allowed to settle in a clarifier where most of the solids are removed as a mud. The brine is then filtered by sand filters and precoat polishing filters. At this point the brine contains less that 4 ppm calcium and 0.5 ppm magnesium ions, which is satisfactory for the mercury and diaphragm processes. The membrane process however requires additional ion exchange to reach hardness levels below 20 ppb. The treated brine feed is also usually acidified with hydrochloric acid to reduce oxygen and chlorate formation in the anolyte. Table 2 lists typical specifications for purified brine.

After treatment, the brine is sent to the electrochemical cell. The anode reaction:

$$2\,Cl^- \longrightarrow Cl_2 + 2e^- \qquad (8)$$

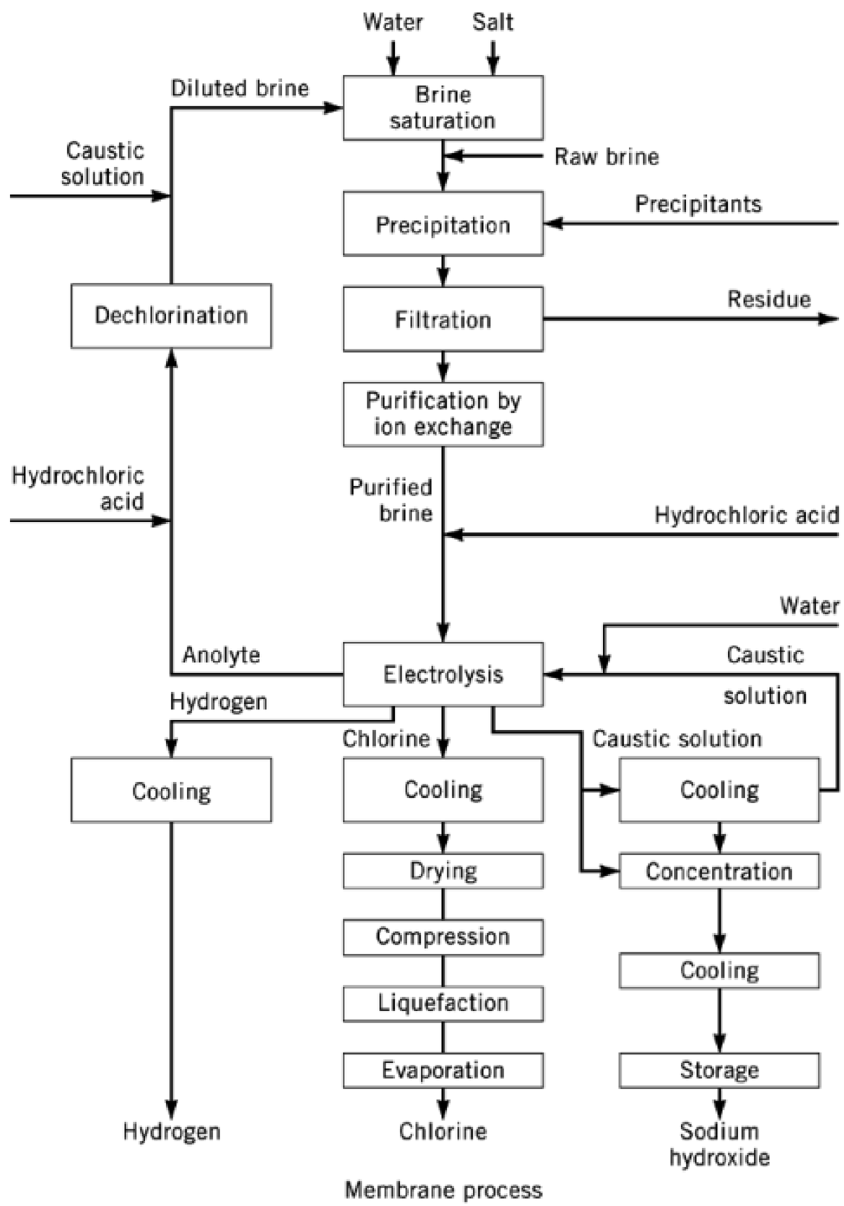

Fig. 4. Flow diagram of the membrane chlor-alkali process.

is the same for all three types of cells. For the diaphragm and membrane cells, the cathode reaction is

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^- \qquad (9)$$

For mercury cells, the cathode reaction is

$$2\,Na^+ + 2\,Hg + 2e^- \longrightarrow 2\,NaHg \qquad (10)$$

Table 6. Analytical Methods for Caustic Soda

Parameter	Method
total alkalinity and NaOH	titration with standard acid
Na_2CO_3	gas-volumetric or gravimetric after decomposing carbonate to CO_2
NaCl	titration with $AgNO_3$ using Volhard method
Na_2SO_4	gravimetric by removing sulfate as $BaSO_4$
$NaClO_3$	volumetric by reaction of the chlorate with $FeSO_4$ in acid solution and titrating the excess $FeSO_4$ with potassium dichromate using diphenylamine sulfonic acid indicator
Fe, Ni	spectrophotometric or atomic absorption spectroscopy

Table 7. Caustic Soda Use[a]

Category	Subcategory	U.S. consumption,%
direct application	pulp and paper	13.2
	soaps and detergents	5.5
	alumina	3.3
	petroleum	3.9
	textiles	2.8
	water treatment	2.8
	miscellaneous	23.7
Subtotal		*55.0*
organic chemicals	propylene oxide	8.3
	polycarbonate	1.8
	ethyleneamines	1.1
	epoxy resins	1.1
	miscellaneous	23.8
Subtotal		*36.0*
inorganic chemical	sodium/calcium hypochlorite	2.2
	sulfur-containing compounds	1.3
	sodium cyanide	0.9
	miscellaneous	4.7
Subtotal		9.0
Total		100.0

[a]Ref. 9.

The amalgam then reacts separately with H_2O in denuders or decomposers as follows:

$$2\,NaHg + 2\,H_2O \longrightarrow 2\,NaOH + 2\,Hg + H_2 \qquad (11)$$

The catholyte from diaphragm cells is typically 10–12% NaOH and 15–17% NaCl. This liquor is concentrated to 50% NaOH in a series of evaporative crystallizers. The crystallized salt is recovered and recycled. Sodium hydroxide remains in the liquid phase. Membrane cells produce 30–35% NaOH solutions which are evaporated to 50% in a single evaporation step. Seventy three percent caustic containing very little salt is made in the mercury cell denuders. The product is filtered to remove entrained mercury and further processing to meet final product specification on concentration are done as needed.

Table 3 summarizes the three electrolysis cell designs. Considerable amounts of power and steam are required, as illustrated by the energy diagram for the diaphragm process in Figure 5. For this reason, cogeneration power plants are often sited with chloralkali units.

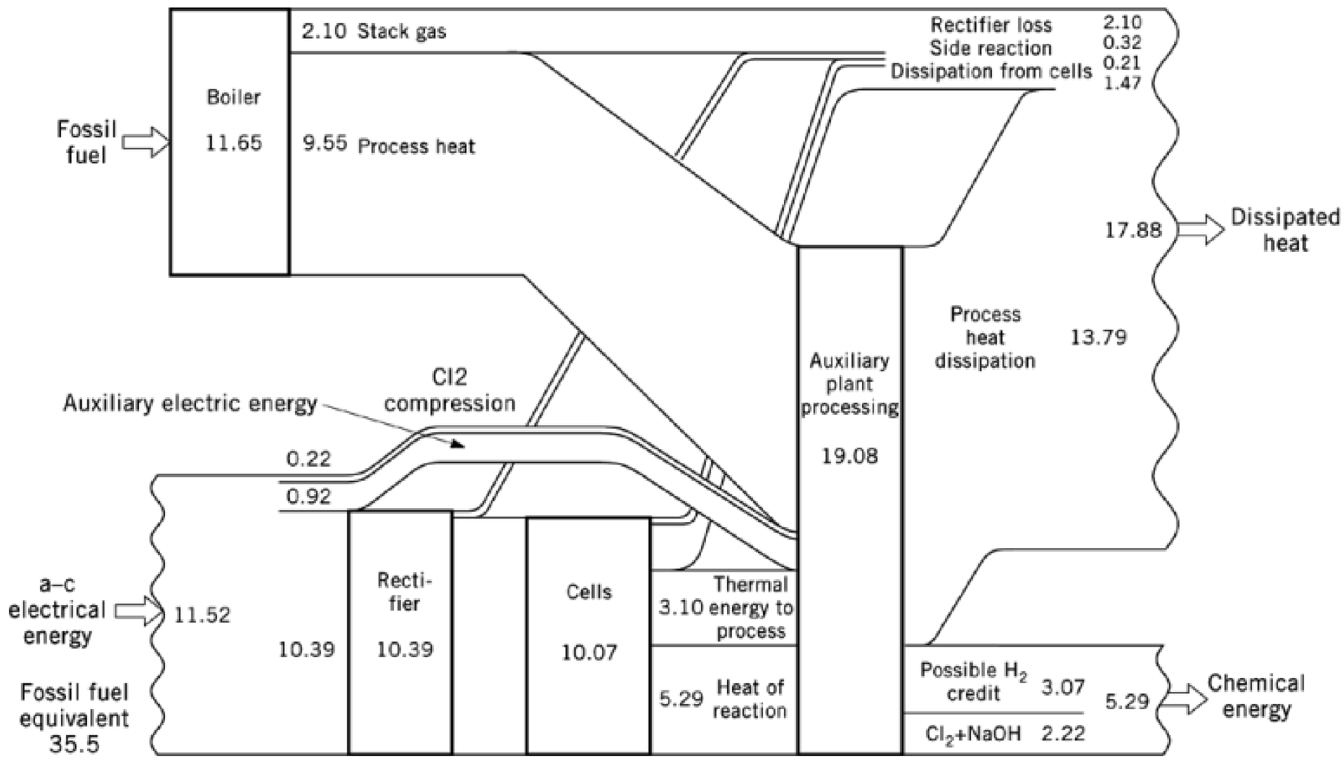

Fig. 5. Energy flow diagram of a typical diaphragm cell operation where numbers represent energy in millions of kilojoules per ton of chlorine. To convert kJ to Btu, multiply by 0.949.

The trend for new installations is to use membrane cells since they give good performance with low energy requirements. Environmental, health and safety issues have led to a long term move away from mercury cells.

The chlorine coproduct from electrolysis is dried in a packed tower using concentrated sulfuric acid (96–98 wt%) to absorb water vapor. After drying, the chlorine is compressed. The operating conditions for compression depend on whether the chlorine is be shipped as a vapor by pipeline or liquefied and transferred as a liquid product.

The hydrogen coproduct from electrolysis is relatively pure and can be used for a wide variety of chemical uses with only minimal additional processing. However, hydrogen is often burned for fuel if there are no nearby markets.

Owing to imbalances in the chlorine and caustic markets, commercial interest in production of sodium hydroxide by the lime soda process:

$$Na_2CO_3 + CaO + H_2O \longrightarrow 2\,NaOH + CaCO_3 \qquad (12)$$

has been revived. FMC and Solvay have about 218,000 t/yr of installed capacity in Wyoming.

4. Shipment

Caustic soda is classified as a corrosive material by U.S. Department of Transportation (U.S. DOT) and their regulations must be followed during transportation. The DOT identification number is UN1824 for 50% or 73% liquid and UN1823 for anhydrous caustic.

Liquid caustic is shipped in tank trucks, tank cars, and barges. Typical tank trucks, constructed from stainless steel without insulation or heating coils, carry 150,000 L or 11.3 ton of caustic soda. Tank cars, usually insulated and equipped with heating coils, are made of nickel clad steel or lined steel. Barges carrying 50% caustic have capacities ranging from 1100 to 2200 t; 25% of the caustic produced in the United States is shipped by barges. Anhydrous caustic marketed as beads or flakes is transported in bulk hopper cars or in drums of 204 kg capacity. They are also packaged in 22.7 kg multiwalled polyethylene-lined paper bags.

5. Economic Aspects

Table 4 is a breakdown of world caustic soda capacity by region. Table 5 lists United States producers as of 1998. There has been much merger and acquisition activity in the industry. The Chlorine Institute (www.cl2.com) keeps up to date records on the industry.

Historical list prices for 50% solution FOB U.S. Gulf Coast have ranged from $150–335 per ton. Current list price is at the upper end of this range.

6. Grades and Specifications

Regular 50% caustic is suitable for most applications. Three special grades are also available: 50% rayon grade, 73% caustic and anhydrous caustic.

The 50% rayon grade is a high purity (ie, low salt and low metals content) grade which is made directly in the mercury and membrane routes. Additional purification using liquid–liquid extraction with ammonia (10) is required to upgrade caustic made from diaphragm cells to rayon grade standards.

The 73% caustic grade is produced for customers who want a liquid product but are sensitive to transportation costs. The product has to be kept above 62°C to prevent freezing during shipping and storage.

Anhydrous caustic is produced by evaporation followed by formation of a solid in the form of a flake, prill, tablet, pastille, or cast block.

7. Analytical Methods

Caustic soda solutions are normally tested for general alkalinity and percentages of NaCl, Na_2SO_4, and $NaClO_3$ as well as for Fe and Ni levels. The general methods are outlined in Table 6. Detailed analytical methodologies are available from the major caustic soda suppliers.

8. Environmental Concerns, Health, and Safety Factors

The main environmental concern for production methods centers around the use, storage, and handling of mercury in facilities that use mercury cells. Although the industry has a good track record, most new facilities are based on membrane cells to avoid the mercury issue. Use of asbestos diaphragms in the diaphragm process has been addressed by improved procedures and introduction of nonasbestos-based diaphragms.

Table 8. Sodium Hydroxide Derivatives

Sodium hydroxide → (brine electrolysis; lime-sodium carbonate reaction (not presently used))

- chemicals →
  - sodium phosphate tribasic
  - sodium chlorite →
    - oxidizing agent for improvement of potable water
    - bleach for textiles, paper pulp, edible oils, straw products
    - oxidizing agent for vat dyes
  - sodium chloroacetate →
    - 2,4-dichlorophenoxyacetic acid (2,3-D)
    - 2,4,5-trichlorophenoxyacetic acid (2,4,5-T)
    - dyes
    - vitamins
    - defoliants
    - sodium carboxymethylcellulose
  - sodium cyanide →
    - adipontrile
    - ethylenediaminetetraacetic acid (EDTA)
    - case hardening and heat treating agent for steel
    - sodium thiocyanate
    - extraction agent for gold and silver production from ores
    - electroplating agent for copper, zinc, brass, and cadmium
    - ore flotation (sulfide ore depressant)
    - dyes
    - pharmaceuticals
    - plastics
    - hydrogen cyanide (for specialty chemicals)
  - sodium formate
- refining of kraft (sulfate) process pulp to higher α-cellulose content (chemical cellulose) →
  - rayon via cuprammonium process
  - sodium cellulose →
    - cellulose xanthate → viscose rayon
    - other cellulose derivatives
- petroleum refining
- wood pulp (sulfate process)
- manufacture of detergents:
  - sodium salt, linear alkylate sulfonate → surface-active agent
  - sodium lauryl sulfate → wetting agent for textiles, surface-active agent, food additive
  - sodium salt, benzenesulfonic acid → phenol
  - sodium salt, toluenesulfonic acid; sodium salt, xylenesulfonic acid →
    - dyes
    - synthetic detergents
    - catalysts
- manufacture of soaps:
  - sodium salt, stearic acid (sodium stearate) →
    - soaps and greases
    - pharmaceuticals
    - waterproofing
    - gelling agent
    - plastics stabilizer
    - aluminum stearate
    - calcium and zinc stearate
  - sodium salt, oleic acid (sodium oleate) →
    - ore flotation, waterproofing textiles
    - emulsifier and soaps
- sodium naphthenate →
  - surface-active agent emulsifier, disinfectant, and driers
  - sodium abietate; glycerin (by-product) →
    - pharmaceuticals
    - soap
    - paper coating
- textile processing: crepeing agent for textiles, mercerizing and scouring cotton, vat dyeing
- refining vegetable oils
- rubber reclamation agent
- metal processing: ore flotation, metal degreasing, and aluminum ore (bauxite)
- water and acid waste stream treatment
- pH control
- wood pulp (soda process)
- wallboard made from agricultural residues
- groundwood pulp bleaching, paint remover, disinfectant, washing naphthalene
- alkaline bottle washing formulations
- rubber latex stabalizer
- stabilization of sodium hypochlorite

Table 8. Continue

→ herbicide
→ herbicide

→ hexamethylenediamine → nylon-6,6 → films, fibers, resins; nylon-6,10 → monofilaments
→ chelating agent

dyeing
→ pharmaceuticals
aritficial mustard oil
rubber treatment
black nickel plating
polyacrylate solvent

→ reducing agent
pharmaceuticals
formic acid
oxalic acid
mordant
nickel formate
leather tanning agent
wallpaper printing
plating
catalyst

sodium propionate → pesticides; mold preventative for food
sodium phenolate → antiseptic; salicylic acid
sodium metasilicate
sodium orthosilicate
sodium picramate → dye intermediate
sodium stannate → tin, metal (electrolytic process); blueprint papers; dye mordant; ceramics and glass; tin electroplating; textile fireproofing; stabilizer for hydrogen peroxide; alkaline electroplating of tin; immersion tinning of aluminum alloys
sodium polysulfides → sulfur dyes; insecticides; synthetic rubber; petroleum additives; electroplating
sodium sulfite (from sodium benzene sulfonate)
sodium arsenite
sodium bromite → textile desizer
sodium dimethyldithiocarbamate → zinc dimethyldithiocarbamate → fungicide; activator for rubber vulcanization

sodium dinitro-o-cresylate → herbicide; control agent for fruit setting; fungicide
sodium diuranate
sodium tungstate

sodium fluoroacetate → rodenticide
sodium formaldehyde sulfoxylate → textile stripping; bleaching agent for molasses and soap
monosodium glutamate → flavor enhancer
sodium molybdate
cupric hydroxide
manganous hydroxide
nickel hydroxide
beryllium hydroxide
barium hydroxide
cadmium hydroxide
cobalt hydroxide
lead hydroxide
amyl alcohol
ethylene oxide
hydrazine (Raschig process)
1-naphthol
2-naphthol
phenol (chlorobenzene process)
resorcinol
vanillin (from waste sulfite pulping liquor) → flavors; perfumes
vinyl chloride (from ethylene dichloride)
sodium salt, oil-soluble petroleum sulfonate → lubricating oil additives
rosin size → paper
cryolite, synthetic (sodium aluminum fluoride)

Caustic soda is corrosive to all body tissue. Even dilute solutions have a deleterious effect after prolonged contact. Inhalation of dust or mist can cause damage to the upper respiratory tract; ingestion causes damage to the mucous membrane. During handling, all persons should wear proper protective clothing: safety goggles or full-face shield, rubber gloves, boots, and a caustic resistant apron or suit.

9. Uses

Table 7 gives a breakdown of uses for caustic soda. Table 8 presents more detail concerning the various applications.

The caustic soda and chlorine markets are separate, however, production of caustic soda and chlorine are tied together by chemistry. Chlorine markets are predicted to grow at about 1.5% per year while caustic soda markets are predicted to grow at about 2% per year (9, 11), thus creating short term imbalances between supply and demand for caustic soda.

When supply is unable to match demand, some consumers switch to other base sources (eg, sodium carbonate, ammonia, etc.) for their needs. This imbalance has also been the motivating factor behind the revival in sodium hydroxide production from the lime soda process, thus breaking the connection between chlorine and sodium hydroxide production.

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