Thomas F. O'Brien

## Sodium Chloride

There are very many inorganic salts, but only one of them, sodium chloride, is commonly referred to by the simple name "salt." Sodium chloride is ubiquitous, and more than 14,000 uses have been tabulated [1]. It is a raw material in the production of many chemicals, including chlorine, caustic soda (sodium hydroxide), synthetic soda ash (sodium carbonate), sodium chlorate, sodium sulfate, and metallic sodium. Indirectly, it is also used to produce many other sodium salts and the very useful hydrochloric acid.

Pure sodium chloride crystals (halite) are colorless to white and contain 39.34% Na and 60.66% Cl. NaCl is rather soluble in water, and temperature has little effect on its solubility. A saturated solution holds 26.3% (w/w) NaCl at 0°C and 28.1% at 100°C.

Salt is a nutrient essential to both humans and animals. It has been a vital commodity throughout human history. Wars have been fought over its supply, words derived from "salt" appear in all languages and a vast number of place names, and the very spread of civilization depended on its availability.

Besides serving as a chemical feedstock, sodium chloride is used in food processing to add flavor and palatability and as a texturizing agent in bread and other baked goods. Salt also is used as a fermentation controller in dairy products, a bactericide in preserved foods, and a color developer in processed meats. A few of its other applications are hide-processing, leather tanning, fabric dyeing, and water softening. China and the United States are the leading producers of salt (Table 26.1). Between them, they account for more than 40% of the world's supply. Germany, India, Canada, and Australia form the next tier, producing more that 20% of the total. One of the largest uses in the United States is as a

highway de-icing and anti-icing chemical [2]. Table 26.2 summarizes US consumption of salt by its principal uses. Annual consumption can fluctuate widely, as shown by the first column of Table 26.3. This is almost entirely due to variations in highway salt usage (column 2).

There are underground deposits of salt ("rock salt") throughout the world. NaCl also makes up about 3% of seawater [3]. The latter is an inexhaustible supply, used in many parts of the world to produce solid salt ("solar salt") by evaporation. In the United States, rock salt predominates. There are mines in Kansas, Louisiana, Michigan, New Mexico, New York, North Dakota, Ohio, Oklahoma, and Texas. Some Canadian provinces also mine salt deposits.

There are two distinct types of rock salt deposit, stratified beds and domes. In the first of these, the salt is in relatively shallow layers that often cover great areas. They may be roughly horizontal or disturbed by tectonic movements. Depths below the surface may range from 100 m to more than a kilometer. Shafts from the surface to the deposit typically are 6 m in diameter. Usually, the salt is in a number of strata, interspersed for the most part with shale or anhydrite. Total thickness of the deposit may be several hundred meters. Each stratum may be mined separately by drilling and blasting or by using a continuous machine. Mining is by the room-and-pillar method, with frequent crosscuts between rooms. A typical room may be 15 m wide and 8 m high.

The configuration of salt domes is very different. A dome forms when deep-lying salt is forced into plastic flow through faults in its overburden. The dimensions of a dome may be measured in kilometers, and it may contain many billions of tons of salt. In the United States, domes are found on or near the Gulf Coast. Mining is similar in principle to that practiced in bedded deposits, but individual blasts may be on a much larger scale.

Salt can also be extracted from underground deposits by solution mining. In this process, a small-bored shaft is drilled into the cavity or deposit. It is then fitted with concentric pipes, one to pump water into the deposit and the other to

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**Table 26.1** Estimated salt production, 2010

| Country | Production[a] |
| --- | --- |
| China | 60 |
| United States | 45 |
| Germany | 16.5 |
| India | 15.8 |
| Canada | 14 |
| Australia | 11.5 |
| Mexico | 8.8 |
| Brazil | 7 |
| World total | 270 |

[a]Millions of metric tons
*Source*: United States Geological Survey, Mineral Commodity Summary, *Salt*, 2011

**Table 26.2** Salt consumption in United States, 2010

| Market | % of total |
| --- | --- |
| Chemical industry | 40 |
| Highway de-icing | 38 |
| Distributors | 8 |
| Agricultural | 4 |
| Food | 4 |
| General industry | 2 |
| Water treatment | 2 |
| Others (incl. exports) | 2 |

*Source*: United States Geological Survey, Mineral Commodity Summary, *Salt*, 2011

**Table 26.3** US dry salt sales[a]

| Year | Total | Highway | Non-highway |
| --- | --- | --- | --- |
| 2005 | 32.0 | 20.5 | 11.6 |
| 2006 | 23.1 | 12.1 | 11.0 |
| 2007 | 31.7 | 20.3 | 11.5 |
| 2008 | 34.2 | 22.2 | 12.0 |
| 2009 | 27.3 | 16.5 | 10.8 |

[a]Millions of metric tons
*Source*: www.saltinstitute.org/Uses-benefits/Salt-in-industry, 2011-08-12

bring saturated brine back to the surface. The purity of the brine is enhanced because insoluble and very slowly soluble impurities, notably anhydrite (calcium sulfate), remain in the cavity as settled residue. The geometry of a bedded salt deposit (large area, small thickness) does not favor injection and withdrawal at essentially the same point. Instead, it is normal practice to operate galleries that contain numbers of pipes placed at horizontal intervals along the deposit. The dissolving fluid goes down one pipe, and the saturated brine rises through another some distance away. The cavity naturally formed as salt dissolves then takes the shape of the deposit much more efficiently.

Many processors mine their own deposits this way and feed the salt solution (brine) directly into their processes.

Other companies specialize in large-scale solution mining and serve the processing industry as brine merchants. When it is not necessary to evaporate the brine down to solid salt, this is normally the cheapest form of supply.

The saturated raw brine can be handled in several ways. Evaporation in vacuum pans without chemical treatment produces evaporated granular salt, which usually assays more than 99% NaCl. The evaporation always is in multiple-effect systems, in which the vapor produced in one effect becomes the heating medium in another, or in vapor-recompression systems. The steam economy achieved in either case can be quite high. Evaporator condensate can be used as process water or as a source of steam.

Chemical treatment of raw brine before evaporation enhances the purity of the final product salt. For the most part, this involves the precipitation of calcium and magnesium by adding, respectively, soda ash and caustic soda:

$$Ca^{2+} + Na_2CO_3 \rightarrow 2Na^+ + CaCO_3$$

$$Mg^{2+} + 2NaOH \rightarrow 2Na^+ + Mg(OH)_2$$
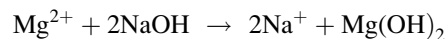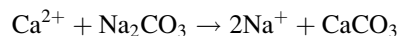
After clarification of the brine to remove the precipitated mud, evaporation produces a salt that is more than 99.95% NaCl, often 99.99%. The higher purity is advantageous in all processes and allows the use of salt in new applications. Examples are food (human and animal), raw material for certain chemical reactions, and polishing pharmaceutical tablets. Purified salt can also be used in the pharmaceutical industry to make hemodialysis and intravenous fluids [4].

Sea salt, or solar salt, is harvested in many countries. Flat coastlines, warm breezes, plentiful sunlight, and little rainfall are all desirable, and operation may be seasonal. Solar salt works naturally are most common in low-latitude countries. Production also is favored in inland locations where brines more concentrated than seawater are available. The process is passive; salt water from lake or ocean is trapped into shallow ponds and allowed to concentrate under the influence of solar energy. In the case of seawater, about 90% of the volume must evaporate before salt begins to precipitate.

The salinity of seawater varies with its location, but a global average is about 3.5 wt.% total dissolved solids. Reported compositions frequently are normalized to this basis. The composition of seawater is complex, and total evaporation would produce solids that are only about 78% NaCl (anhydrous basis). Production of salt therefore involves a series of fractional crystallizations, and a solar salt plant will include a large number of separate ponds with different functions. These include (a) concentrating ponds, which allow suspended solids to settle and bring the brine close to saturation, (b) lime ponds, which allow species less soluble than NaCl (principally calcium compounds) to

**Table 26.4** Purity of various types of salt (wt%, dry basis)

| Component | Rock salt | Washed solar salt[a] | Purified vacuum salt |
|---|---|---|---|
| NaCl | 93–99 | 99 | 99.95 |
| Sulfate | 0.2–1 | 0.2 | 0.04 |
| Calcium | 0.05–0.4 | 0.04 | 0.0012 |
| Magnesium | 0.01–0.1 | 0.01 | 0.0001 |
| Iron | 0.05–0.5 | 0.03 | 0.0001 |

*Source:* Akzo Zout Chemie brochure, *Electrolysis Salt* (*Sodium Chloride*)
[a]See refs. [3, 5] for recent improvements

**Table 26.5** Salt usage by type, USA in 2009

| Type of salt | % of total, 2009 | Average price, 2010, \$/ton[b] |
|---|---|---|
| Rock salt | 45 | 35 |
| Salt in brine[a] | 38 | 8 |
| Vacuum pan salt | 10 | 170 |
| Solar salt | 8 | 70 |

[a]Predominantly for chlor-alkali manufacture
[b]Average for all forms and quantities; bulk costs of solid salt will be lower
*Source*: United States Geological Survey, Mineral Commodity Summary, *Salt*, 2011

precipitate, (c) crystallizers, which produce salt crystals, and (d) bitterns ponds, which hold concentrated solutions rich in magnesium salts. Proper management of the process requires transfer of brine from pond to pond at the proper time, and it is not uncommon for seawater to require 2 years or more in process. Division of the stages of precipitation is not clear cut; thus, magnesium precipitation begins before sodium precipitation is complete. The cutoff point is a compromise between yield and quality. Typically, NaCl is collected until the liquor reaches a certain specific gravity, at which point the brine is transferred to the bitterns ponds. Recovery of the NaCl originally present in seawater generally is 70–80%.

The quality of solar salt is determined primarily by the care taken in separating the various products of crystallization and in harvesting salt from the bottom of the crystallizing ponds. Attempts to increase the size of the NaCl cut necessarily increase the level of contamination. Washing of the recovered salt in any case can improve its quality [5]. Magnesium deposited on the crystals and held in occluded bitterns is most easily removed. More vigorous processing can also remove inclusions of calcium, and as a result washed salts may contain more 99% NaCl. Table 26.4 compares this to typical rock and purified vacuum salts. Table 26.5 then breaks down US consumption by type of salt. It reflects the widespread use of on- or near-site solution mining by the chemical industry, followed by direct use of brine.

Particularly when salt is recovered from inland brines, the bitterns may contain valuable minerals and justify further processing. To take a single example, Dead Sea water is rich in bromine and is one of the world's major sources of the element (*infra*).

Sodium chloride is the ultimate source of many industrial chemicals, and this chapter treats a number of them. Sodium phosphates and phosphoric acid are important examples. They do not appear here but rather are covered in Chap. 23.

It is also worth noting that potassium chemicals have similar chemistry and that many of them are produced simply by replacing Na in the raw material with the scarcer and more expensive K.

## Sodium Carbonate (Soda Ash)

Soda ash, or sodium carbonate, is derived commercially from three sources: trona/nahcolite ores, naturally occurring alkaline brines, and synthetic processes. Most common in the last category is the Solvay ammonia-soda process. Variations of this process operate in many parts of the world. The United States has 95% of all known deposits of trona. Since natural production has significant cost advantages, the United States no longer produces synthetic soda ash. Because natural reserves are limited elsewhere, synthetic processes still provide about three-quarters of the world's supply of $Na_2CO_3$. China is the leading producer, with about 40% of the total. The United States produces about 22% of all soda ash. Data on natural soda ash production and reserves are in Table 26.6. Market distribution in the United States is shown in Table 26.7.

The area near Green River, Wyoming, is the primary source of natural ash. The deposit contains over $10^{11}$ metric tons of trona, enough to satisfy global demand for over 2,000 years [6]. Significant amounts are also recovered from the alkaline brines of Searles Lake in California.

"Trona" is the dihydrate of sodium sesquicarbonate, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$. Processing is required to purify it and to calcine the bicarbonate portion. There are two approaches to this task. Purification may either precede or follow calcination. The older (sesquicarbonate) process first hot-leaches the crushed ore to extract the mineral. Purification involves clarification, filtration, and crystallization by cooling. The refined trona then is calcined to form soda ash. The newer (monohydrate) process first calcines the crushed ore to form a crude carbonate. This is dissolved and the solution evaporated to crystallize the monohydrate, $Na_2CO_3 \cdot H_2O$. Mild calcination then yields the anhydrous soda ash. The monohydrate process is normally more energy efficient. Because trona has low solubility, the dissolving and separation steps in the sesquicarbonate process are at high temperature. The higher temperature and $CO_2$ concentration make the process fluids more corrosive. The disadvantage of the monohydrate process is contamination of the carbonate solution with organics and minerals. A purge of the crystallizer mother liquor is necessary, its size dependent on the extent of contamination.

**Table 26.6** World production and reserves of natural soda ash in 2010[a]

| Country | Production[b] | Reserves[c] |
|---|---|---|
| United States | 10,000 | 23,000,000 |
| Turkey | 1,000 | 200,000 |
| Botswana | 250 | 400,000 |
| Kenya | 450 | 7,000 |
| Mexico | – | 200,000 |
| Others | – | 280,000 |
| World total (rounded) | 11,700 | 24,000,000 |

[a]Quantities are estimates in thousands of metric tons
[b]World production of synthetic soda ash was 34,300,000 metric tons
[c]Sodium carbonate basis; about 1.8 t of trona yield 1 t of $Na_2CO_3$
*Source*: United States Geological Survey, Mineral Commodity Summary, *Soda Ash*, 2011

**Table 26.7** Soda ash market distribution—USA in 2010

| Segment | % of total |
|---|---|
| Glass | 46 |
| Chemicals | 29 |
| Soap and Detergents | 10 |
| Distributors | 6 |
| Flue gas desulfurization | 3 |
| Pulp and paper | 2 |
| Water treatment | 1 |
| Miscellaneous | 3 |

*Source*: United States Geological Survey, Mineral Commodity Summary, *Soda Ash*, 2011.

Mechanical mining of trona resembles that of coal or salt. The ore is disposed in nearly horizontal beds 2.5–5 m thick and found at depths of 250 to more than 1,000 m [7]. Solution mining is an alternative. The solubility of the bicarbonate can be enhanced by using a dilute solution of NaOH. This converts the bicarbonate portion of trona into the more soluble carbonate. Production of a 30% solution of $Na_2CO_3$ theoretically requires about a 6% solution of NaOH [9].

Figure 26.1 is a block flow sheet of the ammonia-soda process. The description that follows is keyed to the numbered blocks. NaCl enters the process as a solution, or brine. It must first have been purified to remove calcium and magnesium ions, so that they will not precipitate within the process, contaminating the product and fouling the equipment. Solutions of soda ash and caustic soda are added to the brine, precipitating $CaCO_3$ and $Mg(OH)_2$ according to the equations noted in the preceding section. The solids are flocculated, removed in a clarifier, and discarded. The purified brine goes to the ammonia absorber (1) in the main process.

The other major raw material is limestone. Normally, the best available limestone is calcined in vertical-shaft kilns (2) at high temperature to produce lime and carbon dioxide. Kilns typically are fired with foundry coke. Their design is highly efficient and produces a gas containing very little oxygen and more than 40% $CO_2$. Lime from the kiln is cooled by the entering combustion air, which is thereby preheated. Similarly, gas leaving the kiln preheats incoming limestone and fuel, again promoting energy economy. Economizing steps such as these are frequent in the Solvay process because of its normally large scale and high utility demands. The dry lime is slaked (3) before use in the process.
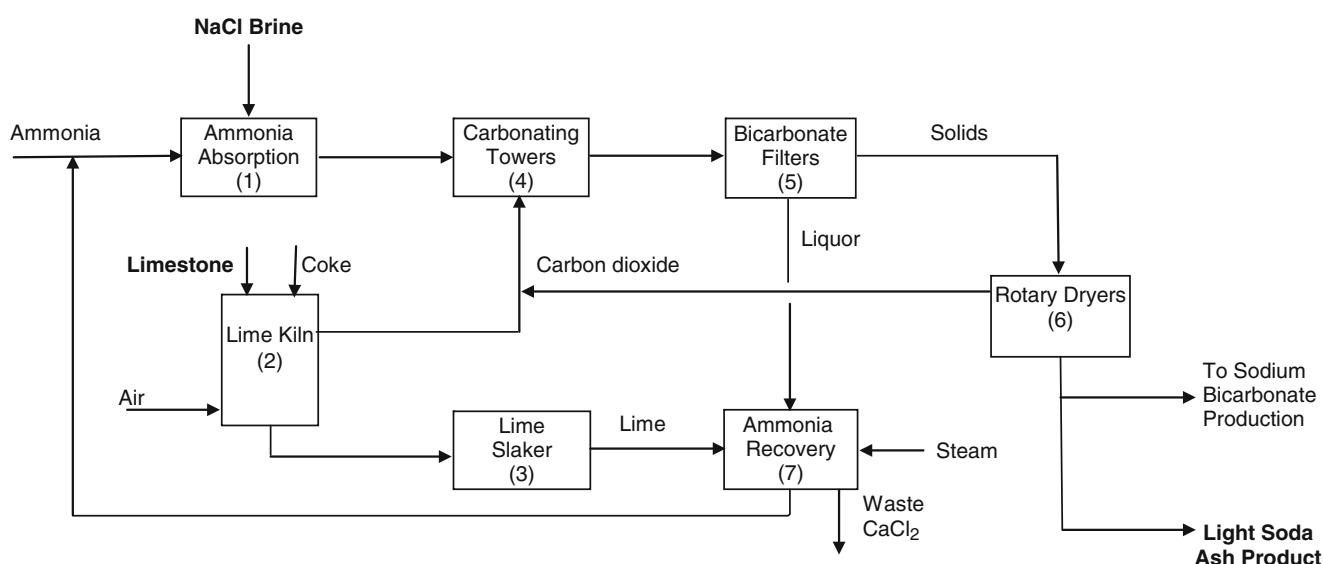


**Fig. 26.1** Block flow sheet for Solvay ammonia-soda process for production of soda ash

The overall stoichiometry of the Solvay process is quite simple and involves only salt and limestone:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$
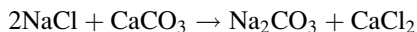
However, direct carbonation of NaCl solution is not feasible because of the acidity due to the implied formation of HCl from NaCl and carbonic acid. The ammoniation of the brine in step (1) creates an alkaline solution of $NH_4Cl$ and allows the carbonation to proceed. Ammoniated brine then enters near the top of a carbonating tower (4) and cascades down over a set of disc-and-donut baffles. Carbon dioxide enters both at the bottom of the column and approximately at the midpoint. Off-gases vent from the top, and bicarbonate slurry leaves the bottom.

The carbonation area includes groups of identical towers. The alternating discs and rings promote mixing of the falling liquor with the rising gas stream and resist plugging by the crystallizing solid phase. The lower parts of the towers also include series of heat-exchange bundles. Still, several days' operation as a crystallizing unit tends to plug the internals with sodium bicarbonate. Then, ammoniated brine is passed downward through the column while gas from the kilns provides agitation and heat to dissolve the scale and bring the liquor close to saturation. After adjustment to the desired temperature, this liquor passes to the tops of the other towers in the equipment group.

Mixing 40% $CO_2$ gas from the kilns with 90% gas from the calcination of bicarbonate gives 60–75% $CO_2$ as feed to the crystallizing units. The heat evolved from absorption and neutralization of carbonic acid gas and the crystallization of bicarbonate tend to raise the temperature of the liquid in the column by about 25°C. In normal operation, the temperature of the discharged slurry is held at about 27°C by flow of water through cooling tubes. The heat removed from the carbonator is about 75,000 kcal/net metric ton of ash produced, whereas that removed from the crystallizing units is 350,000 kcal/t (all "tons" in this chapter are metric).

Washed bicarbonate is recovered from reactor slurry on rotary vacuum filters (5). The filtrate and wash liquor flow to the distillation unit for recovery of ammonia. The crude solid contains 3–4% $NH_4HCO_3$ (dry basis) and so is not an item of commerce. It will assay about 80% $NaHCO_3$ and have a water content of 12–15% $NaHCO_3$. Its calcination produces the carbonate while releasing half of the $CO_2$ content:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$
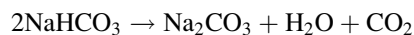
This is achieved in rotary dryers (6) with rotating seals and gas-tight feed and discharge mechanisms. The design excludes air and keeps the concentration of $CO_2$ in the gas as high as 90%. The product of the reaction is about 99.7%

$Na_2CO_3$, containing 0.1–0.15% each of NaCl and water, along with small concentrations of metallic impurities. The heat consumed in the process is about 560,000 kcal/t of soda ash produced.

The second major product of the carbonation of ammoniated brine is ammonium chloride, $NH_4Cl$. It collects in the liquor from the bicarbonate filters. Ammonia is regenerated (7) by reacting filtrate with milk of lime. The reaction is

$$Ca(OH)_2 + 2NH_4Cl \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$
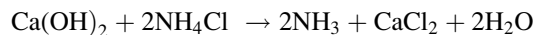
The resulting solution goes to the top of a distillation column, with steam injected at the bottom. The stripped ammonia is ready for recycle to the process, and the residual calcium chloride liquor normally contains less than 10 ppm $NH_3$.

The amount of ammonia in circulation is large, and there are a number of gas streams that contain $NH_3$. Several of these are scrubbed to prevent losses. Thus, the incoming purified brine first washes the ammonia-bearing air pulled through the bicarbonate cake on the vacuum filters. This is accomplished in a packed absorber. The brine then passes through a second packed section, where it absorbs the $NH_3$ in the gases from the carbonating towers, and finally flows to the main $NH_3$ absorber. A small amount of makeup ammonia enters the process here, and the absorber also picks up $CO_2$ and traces of $H_2S$ from the carbonators. Heat released in the absorption process is about 345,000 kcal/t of soda ash produced. It is removed by circulating brine through water-cooled heat exchangers. The ammoniated brine typically is at a temperature of 38°C and contains 260 g/L NaCl, 90 g/L $NH_3$, 40 g/L $CO_2$, and 0.1 g/L $H_2S$.

It is worthy of note that sulfide will maintain a protective film of iron sulfide on the cast iron equipment and minimize contamination of the crystals by iron corrosion products. A solution containing sulfide ion therefore is usually added to the liquor before the ammonia distillation pre-heater. After preheating, the process stream enters a stripper where excess $CO_2$ is removed.

Byproduct $CaCl_2$ may be recovered from process waste liquor by evaporation. Most often, the solution is clarified and pumped into watercourses whose natural flow is sufficient to provide the dilution needed for disposal.

The normal product is "light" soda ash. This can be reprocessed to give higher bulk density, less tendency to dust, and better flow properties. The latter product is preferred in some applications (e.g., glassmaking). Some soda ash also is used to produce sodium bicarbonate (*infra*) and, by causticization with lime, caustic soda without chlorine as a co-product.

The natural alkaline brines referred to at the beginning of this section are a relatively small source of $Na_2CO_3$. It is

recovered by a process of fractional crystallization that also produces other sodium and potassium salts. Formation of $Na_2CO_3$ may be promoted by carbonation of the brine.

## Sodium Bicarbonate

Further carbonation of a saturated solution of sodium carbonate produces the bicarbonate:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3$$
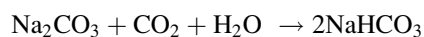
The $Na_2CO_3$ may be produced synthetically or mined as a natural ore (*supra*). The relatively insoluble bicarbonate crystals precipitate from solution and are centrifuged and then dried. Drying temperatures below 50°C prevent reversion to carbonate.

Sodium bicarbonate also can be obtained by solution mining of the mineral nahcolite. Wells are drilled in groups or in pairs. Steam or hot water (175–215°C) is pumped down one well to dissolve the ore, and the resulting solution is pumped up from another. The solid product may be obtained by crystallization. In some circumstances, such as those in which the mined solution must be transferred a long distance for processing, direct recovery may not be feasible. The positive temperature coefficient of solubility of $NaHCO_3$ would allow plugging of piping or equipment. In such cases, the bicarbonate first is converted to carbonate, which is reprocessed at the destination.

Nahcolite is often associated with oil shale or with deposits of salt or trona [9]. Reserves in the Piceance Creek basin in northwestern Colorado alone amount to nearly 30 billion tons [10]. This amount would supply the world for about 20,000 years. Total US capacity for $NaHCO_3$ is about 780,000 t/year, two-thirds of it in Wyoming and Colorado. Current production is about 600,000 t/year, with a long-term growth rate of 2–3%/year [11].

As the common name "baking soda" implies, most applications of $NaHCO_3$ (~60%) are in the food industry. The product must be purified as necessary and handled in accordance with all food-grade rules. Refined product accordingly has some use in pharmaceuticals. Sodium bicarbonate's use as a rising agent in baked goods derives from its alkalinity and the fact that $CO_2$ evolves at the convenient temperature of 70°C. It is also used as a buffer, an antacid, and a cattle feed supplement/rumen pH regulator. A very successful application in the household market is as a deodorizer and air freshener. It has also established a market as a paint remover, replacing the environmentally unacceptable methylene chloride. Some traditional applications now are shared with the sesquicarbonate, and this change should perhaps not be viewed as a true loss of market.

## Sodium Sulfate

Sodium sulfate classically was a co-product (with HCl) of the reaction of salt with sulfuric acid (Mannheim process) or $SO_2$ and air (Hargreaves process). While these processes may survive elsewhere, they are no longer in use in the United States. Instead, all production is by recovery from natural sources or as a byproduct of other operations. US production is approximately evenly split between these two categories [12]. Estimates of worldwide production in 2010 are six million tons from natural sources and 1.5–2 million tons as byproduct. Known reserves, shown in Table 26.8, are widespread and would last hundreds of years at the present rate of consumption. Reserves in China are extensive. Production is concentrated in Jiangsu Province, where annual production of 4.8 million tons is anticipated by 2013 [12].

There are two producers of natural sodium sulfate in the United States, one in Texas and one in California. The former location has the advantage that the brine is located near salt domes and natural gas wells. Byproduct $Na_2SO_4$ is recovered in 11 plants in 9 states. Sources include battery reclamation and the production of ascorbic acid, cellulose, chromium chemicals, rayon, resorcinol, and silica pigments. Approximate consumption by end use is summarized in Table 26.9.

**Table 26.8** World reserves of sodium sulfate

| Country | Reserves[a] |
|---|---|
| United States | 860 |
| Spain | 180 |
| Mexico | 170 |
| Turkey | 100 |
| Canada | 84 |
| Others[b] | 1900 |
| World total | 3300 |

[a]Millions of metric tons
[b]Principally Botswana, China, Egypt, Italy, Mongolia, Romania, and South Africa
*Source*: US Geological Survey, Mineral Commodity Summary, *Sodium Sulfate*, 2011

**Table 26.9** Sodium sulfate market distribution—USA in 2010

| Market sector | % of total |
|---|---|
| Soap and detergents | 35 |
| Glass | 18 |
| Pulp and paper | 15 |
| Textiles | 4 |
| Carpet fresheners | 4 |
| Others | 24 |

*Source*: US Geological Survey, Mineral Commodity Summary, *Sodium Sulfate*, 2011.

A frequent advantage of natural products over synthetic and byproduct materials is their higher purity. In one process, natural brine containing about 10% $Na_2SO_4$ is saturated with NaCl by pumping it through a salt deposit. Cooling the concentrated brine to about $-10°C$ produces quite pure crystals of Glauber's salt ($Na_2SO_4 \cdot 10H_2O$). This is then melted and the water of hydration removed by evaporation driven by a submerged burner. The wet $Na_2SO_4$ is dried in a rotary kiln until anhydrous. More than 10 t of natural brine and 450,000 kcal are required per ton of product. In a similar process, a different brine is first carbonated and chilled to remove sodium carbonate and borax. Further chilling crystallizes Glauber's salt and some residual borax. After recovery by hydraulic classification, the sulfate fraction is handled as described above to recover the anhydrous salt.

An alternative process when carbonate is also present in a brine (e.g., Searles Lake) is evaporation to produce NaCl and a double salt of $Na_2CO_3$ and $Na_2SO_4$. The two solids are separated in a hydraulic classifier, and the sulfate fraction is re-dissolved and re-crystallized as Glauber's salt. Anhydrous $Na_2SO_4$ can be recovered without the need for thermal decomposition by adding the Glauber's salt to concentrated NaCl brine. The altered solubility characteristic forces the unhydrated sulfate to precipitate. In the first process mentioned above, it was Glauber's salt that precipitated from solution; in the final step here, it is anhydrous $Na_2SO_4$. The difference is explained by different positions on the graph of mutual solubilities of NaCl and $Na_2SO_4$. The first process takes place in the low-chloride region, and the process follows a Glauber's salt isotherm. Addition of small amounts of water or salt may be necessary to the material balance in a continuous crystallization process.

Sodium sulfate often is a byproduct of the reaction of sulfuric acid with a sodium salt or of the neutralization of caustic soda. An example is the viscose rayon process, in which cellulose xanthate reacts with $H_2SO_4$, which also neutralizes free NaOH in the fiber spinning bath. Evaporation of spin-bath liquor produces crystals of Glauber's salt, which are centrifuged off, melted and evaporated to produce anhydrous $Na_2SO_4$. The sulfate produced actually outweighs the rayon product by 10%.

Changes in markets or regulation can affect the available supply of byproduct $Na_2SO_4$. Thus, for example, increased on-site generation of chlorine dioxide for bleaching itself produces more $Na_2SO_4$ byproduct. Opposing this change, the production of sodium dichromate and its byproduct sulfate has declined with mandated recycling of electroplating wastes. Other changes affect demand. The kraft pulping process formerly consumed huge quantities of $Na_2SO_4$. Changes in the process and tightening of the sulfur balance have caused a major reduction in its use. Next, the use of $Na_2SO_4$ as an inert filler in detergent formulations

**Table 26.10** US production and consumption of sodium sulfate (natural and synthetic)

|                              | 2007 | 2008 | 2009 | 2010(est.) |
|------------------------------|------|------|------|------------|
| Production                   | 312  | 319  | 292  | 300        |
| Imports for consumption      | 43   | 69   | 77   | 60         |
| Exports                      | 101  | 107  | 140  | 190        |
| Apparent consumption[a]      | 254  | 281  | 229  | 170        |

All data in thousands of metric tons
[a]Production plus imports minus exports
*Source*: US Geological Survey, Mineral Commodity Summary, *Sodium Sulfate*, 2011

has decreased as liquid detergents have become more common and dry products have become more concentrated. Finally, sulfate also is gradually disappearing from glass manufacture, where it has been used as a fluxing and fining agent. The consumption of $Na_2SO_4$ in the United States therefore is much lower than it was in previous decades. As Table 26.10 shows, it has been dropping irregularly in recent years. Variations have been much smaller in production than in consumption, the difference being picked up by a shifting trade balance. Worldwide production of sodium sulfate continued to increase into the 1990s before similar trends prevailed and total consumption became stagnant [13].

## Sodium Sulfides

Sodium sulfide, $Na_2S$, and sodium hydrosulfide or sulfhydrate, NaHS (often written as NaSH), both are derived from caustic soda and $H_2S$. Controlled caustic scrubbing of $H_2S$ forms a solution of the half-neutralized NaHS:

$$NaOH + H_2S \; \rightarrow \; NaHS + H_2O$$
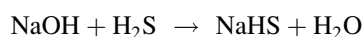
The NaHS solution is filtered to remove heavy metal sulfides. The clear filtrate may be sold as a 44–46% solution or evaporated in stainless steel equipment to produce a flaked product containing 70–72% NaHS. There is ample capacity for generation of NaHS from waste gases. Approximate capacity in the United States in 2006 was 240,000 t/year, but production was only about 77,000 t [14].

Treating NaHS solution of the proper concentration with solid caustic soda yields a hydrated product of 60–62% $Na_2S$:

$$NaHS + NaOH \; \rightarrow \; Na_2S + H_2O$$
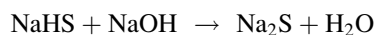
This is sold as flakes or cast solid in drums. High-quality raw materials produce $Na_2S$ suitable for use in dyes, photography, rayon, and leather manufacture. Lower-quality sulfides are obtained by using $H_2S$ byproduct from the

manufacture of $CS_2$ from methane (or other low molecular weight hydrocarbons) and sulfur:

$$CH_4 + 4S \rightarrow CS_2 + 2H_2S$$
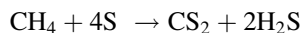
The gas from this catalytic reaction is cooled and then scrubbed with caustic soda. The sulfide produced contains small amounts of mercaptans (e.g., $CH_3SH$), and thus has a very objectionable odor.

The manufacture of $BaCO_3$ from barite ore also yields a sodium sulfide byproduct. The process involves roasting with coal, leaching with water, and treatment with soda ash:

$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

$$BaS + Na_2CO_3 \rightarrow Na_2S + BaCO_3$$
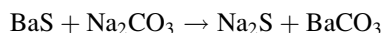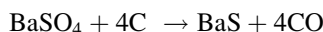
The principal use for sodium sulfide in the United States is de-hairing leather before tanning. In Western Europe it is further used in tanning and in Japan more extensively in synthetic chemistry. Most NaHS in the United States is used in the pulp and paper industry (42%). The market has grown at the expense of the more expensive sodium sulfate [14]. Other uses are in metals and minerals, most especially as a copper mineral flotation agent (30%), and in chemicals and dyes (13%). Leather processing (10%) is a declining market. Again in Japan, NaHS historically has found more downstream uses in chemicals, dyes, wastewater treatment, and leather tanning [15].

A solution of sodium sulfide can dissolve elemental sulfur, which then forms covalently linked chains of sulfur atoms and polysulfide ions $S_n^{2-}$. Chain lengths vary from three to more than ten [16]. One of the uses of sodium polysulfide is the production of polymers that are insoluble in water, oils, and most organic solvents. The polymers are used widely as sealants. They form by condensation with bifunctional derivatives of hydrocarbons. Ethylene dichloride (EDC) is an example:

$$Na_2S_n + ClCH_2CH_2Cl \rightarrow (CH_2CH_2S_n) + 2NaCl$$
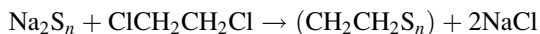
## Sodium Thiosulfate

Most sodium thiosulfate, $Na_2S_2O_3$, is obtained as a byproduct in the manufacture of sulfur dyes and $Na_2S$. In the case of sulfur dyes, byproduct leach liquor contains thiosulfate, which can be recovered by evaporation and crystallization in stainless steel equipment. Much of this is sold as the pentahydrate. Of less importance today is the older soda ash-sulfur process. A liquor containing $NaHSO_3$ (made by absorbing $SO_2$ into soda ash solution) is heated with powdered sulfur in an agitated stainless steel digestion tank. Evaporative crystallization again yields the pentahydrate. After centrifuging, washing, and drying, this material is packaged in airtight containers, in order to prevent efflorescence.

$Na_2S_2O_3 \cdot 5H_2O$ is the photographer's "hypo." While many photographic markets are declining or growing only slowly because of the advance of digital technology, this remains the principal use of the product. Its value lies in its ability to dissolve water-insoluble silver salts. Other uses include leather processing, water treatment, and oil recovery. It is also used as an active chlorine scavenger, particularly in Western Europe. It has the advantage of an average sulfur valence state of only +2, giving it twice the reducing power of other sulfur-based agents. However, other reactions can occur at low pH [17], and $Na_2S_2O_3$ is fully effective only at pH 11 and higher [18].

## Sodium Sulfite

Sodium sulfite ($Na_2SO_3$) is produced by reacting sulfur dioxide with an alkaline solution, either sodium carbonate or sodium hydroxide. It is also recovered as a byproduct of various processes. Its principal use historically has been in the pulp and paper industry. While improvements in mill efficiency and substantial reductions in sulfur discharges have tended to reduce its use there, the spread of chemithermomechanical processing from Europe has helped to keep this market strong. The pulp industry accounts for about 55% of the market in the United States [19]. Other large uses are in water treatment (20%), the photographic industry (10%), and oil recovery (5%).

Sodium sulfite is a white crystalline or powdered compound. It is readily soluble in water and decomposes on heating. It is a strong reducing agent and so is subject to oxidation; the solid compound is more stable than solutions in this regard. $Na_2SO_3$ is used in water treatment as an oxygen and free chlorine scavenger and in the photographic industry to protect developer solutions from oxidation. Miscellaneous applications are in the textile industry as a bleaching, desulfurizing, and dechlorinating agent; in the leather trade in the sulfitization of tanning extracts; and in the organic chemical industry as a sulfonation and sulfomethylation agent. It forms adducts with aldehydes and ketones and so plays a role in purifying and isolating those compounds. Other applications include ore flotation, oil recovery, food preservation, dye making, detergent production, and the production of sodium thiosulfate (*supra*).

Yearly production in the United States is about 90,000 t, with an installed capacity of about 245,000 t/year. These figures are inexact largely because they exclude the substantial and variable captive production and use [19].

## Sodium Bisulfite

Sodium bisulfite may be supplied as a solution or as a solid. The solution normally contains 23–27 wt.% $SO_2$ equivalent. The solid product actually is in the form of sodium metabisulfite, which is the anhydride $Na_2S_2O_5$. Commercial metabisulfite is about 98% pure, typically containing 1.5% $Na_2SO_3$ and 0.5% $Na_2SO_4$.

Methods of production are all variations on the same theme:

$$Na_2CO_3 + 2SO_2 \rightarrow Na_2S_2O_5 + CO_2$$
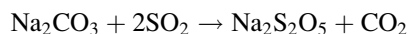
In one version, $SO_2$ is sparged into a stainless steel absorber through which a solution of $Na_2CO_3$ flows. The product crystallizes when the saturated solution is cooled. Recovery is by centrifugation, and then the crystals are dried. The last step must be rapid, as in a flash dryer, in order to avoid air oxidation to sulfate.

Markets for sodium bisulfite are diverse [20]. They include chemical intermediates, pharmaceuticals, food preservation, water treatment, and dye fixing. Additionally, sodium bisulfite is used in photography, in the manufacture of sodium hydrosulfite (*infra*), and as an active chlorine scavenger in pulp bleaching and chlor-alkali brine dechlorination.

Sodium sulfite and bisulfite are interchangeable in many applications, and some producing plants can switch between the two forms. Their reducing power (and that of $SO_2$) in all cases depends on the oxidation of $S^{+4}$ to $S^{+6}$. Proton shifts between $HSO_3^-$ and $SO_3^{2-}$ are rapid [21], and so the form of the anion actually present in solution is determined by the pH.

## Sodium Hydrosulfite (Sodium Hyposulfite)

$Na_2S_2O_4$ is variously referred to as sodium hydrosulfite, sodium hyposulfite, and dithionite. It is a powerful reducing agent used principally for the reduction of vat dyes and the brightening of mechanical wood pulps and clays. There are several methods for its production, all of which involve reduction of $SO_2$ or $NaHSO_3$. Reducing agents include sodium amalgam, sodium formate, and sodium borohydride. Previous editions of this handbook also described two methods for reduction by zinc powder. These are obsolescent because of the environmental problems associated with the release of zinc.

The amalgam process [22] uses the dilute (<0.5%) sodium amalgam from a chlorine cell (*infra*). Reaction of the amalgam with bisulfite solution at pH 5–7 produces the hydrosulfite along with a sodium sulfite co-product:

$$4NaHSO_3 + 2Na(Hg) \rightarrow Na_2S_2O_4 + 2Na_2SO_3 + 2H_2O + (Hg)$$
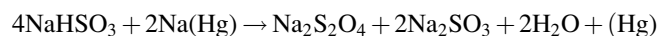
The parentheses indicate that mercury is not involved in stoichiometric quantities. The mercury returns to the electrolytic cell to form more amalgam. The sulfite is reacted with $SO_2$ in aqueous solution to regenerate bisulfite for recycle:
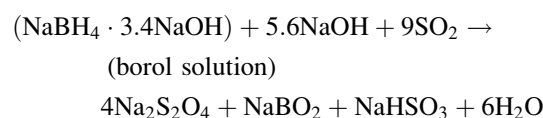
$$Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$$

$SO_2$ normally supplies the sulfur value in the formate process:

$$HCOONa + NaOH + 2SO_2 \rightarrow Na_2S_2O_4 + H_2O + CO_2$$
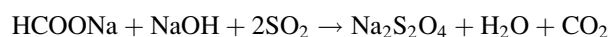
This reaction requires the use of acidified methanol. The anhydrous sodium hydrosulfite precipitates and is recovered by filtration.

In pulp and paper mills, the hydrosulfite often is produced in situ at low concentrations (5–7%). Here, $SO_2$ reacts with alkaline sodium borohydride:

$$(NaBH_4 \cdot 3.4NaOH) + 5.6NaOH + 9SO_2 \rightarrow$$
$$\text{(borol solution)}$$
$$4Na_2S_2O_4 + NaBO_2 + NaHSO_3 + 6H_2O$$

Finally, hydrosulfite can be produced by the direct electrolysis of a bisulfite solution [23]. The cathode reaction is:

$$2HSO_3^- + 2H^+ + 2e \rightarrow S_2O_4^{2-} + 2H_2O$$
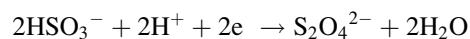
Such a process might be useful for on-site production.

## Sodium Silicates

In the sodium silicate family, a series of derivatives is produced by reacting $Na_2CO_3$ with varying amounts of silica. The products normally are referred to by their ratios of $SiO_2$ to $Na_2O$. The custom in the United States, followed here, is to express these in terms of weight. In some other parts of the world, molar ratios are used. Since the formula weights of the two species are nearly equal (60 and 62), the numerical differences are not large but still may confuse the unwary. The normal product is called *water glass* because while solid it actually is a glass, but, unlike lime-soda glass, it is soluble in water.

In the standard process, high-purity sand and soda ash are fused in a large tank furnace similar to the type used for flat glass. The raw materials, often premixed, are introduced at one end of the furnace and the product

**Table 26.11** Properties of typical commercial sodium silicate solutions

| Ratio, $SiO_2$/$Na_2O$ | Wt. % $SiO_2$ | Wt. % $Na_2O$ | Density, g/mL | Viscosity, cp | pH |
|---|---|---|---|---|---|
| 3.22 | 28.7 | 8.9 | 1.38 | 180 | 11.3 |
| 3.22 | 29.5 | 9.1 | 1.41 | 400 | 11.3 |
| 2.88 | 31.7 | 11.0 | 1.48 | 960 | 11.5 |
| 2.58 | 32.1 | 12.4 | 1.52 | 780 | 11.8 |
| 2.40 | 33.2 | 13.8 | 1.56 | 2100 | 12.3 |
| 2.00 | 29.4 | 14.7 | 1.53 | 400 | 12.8 |
| 1.80 | 23.7 | 13.1 | 1.42 | 655 | 13.1 |
| 1.60 | 26.2 | 16.4 | 1.53 | 280 | 13.5 |

Ratio $\pm 0.05$; %$SiO_2$ $\pm 1.0$; %$Na_2O$ $\pm 0.2$. Physical properties at 20°C
*Source*: PQ Corporation, Bulletin 17-2A (2007)

drawn off at the other. The product ratio is set by the raw material mixture:

$$Na_2CO_3 + nSiO_2 \rightarrow Na_2O(SiO_2)_n + CO_2$$
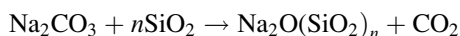
The reaction temperature is about 1,300°C. Large furnaces are regenerative or recuperative, in order to reduce heat loss by way of combustion offgas. Particularly on smaller scale, electrically heated melters may replace the fuel-fired version. Another variation has been the use of a rotary kiln in place of a stationary furnace. As the melt leaves the furnace, a stream of cold water shatters it into fragments, or it is collected and cooled in molds that form a moving chain. The solid material can be dissolved in hot water/superheated steam in tall steel cylinders. Sodium silicates normally are sold in solutions of varying density and viscosity. Compositions and physical properties of typical commercial grades are shown in Table 26.11. Dry solids also are marketed, usually with ratios between 2.0 and 3.25 [24]. Since some solid silicates are hygroscopic, they may be blended with $Na_2SO_4$ to prevent caking.

Caustic soda is a possible replacement for soda ash in the silicate process:

$$2NaOH + nSiO_2 \rightarrow Na_2O(SiO_2)_n + H_2O$$
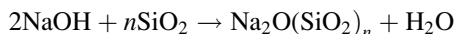
Those who can use either NaOH or $Na_2CO_3$ as a source of alkalinity must continually be aware of the comparative economics of the two, and it is useful to have the option to switch materials when desired. Unfortunately, the use of caustic soda, solid or liquid, is not practicable in the glass furnace. Instead, standard practice is to use an autoclave to dissolve sand in NaOH solution. Results are limited by the solubility of crystalline silica to ratios less than about 2.4.

The buffering capacity of silicate solutions is important to the many applications that depend on their alkalinity (e.g., detergents, oxide bleaching of wood pulp, de-inking of waste paper). Figure 26.2 shows that silicate solutions are
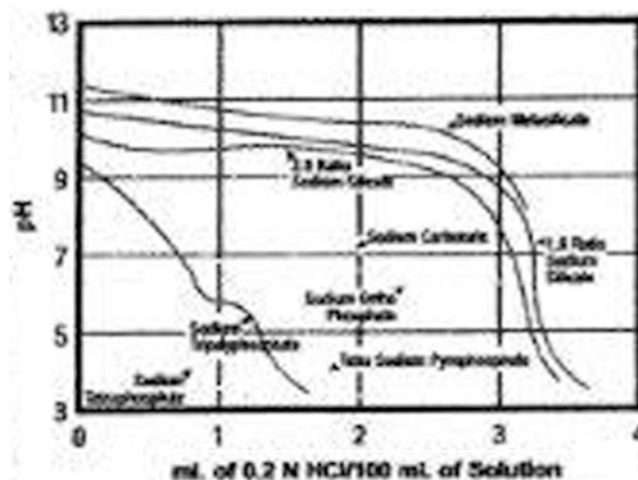


**Fig. 26.2** Alkaline buffering capacities of several compounds (Courtesy of PQ Corporation)

superior in this respect to the other salts shown. The increased use of peroxide bleaching of wood pulp and the growing importance of waste paper de-inking have increased sodium silicate demand in the pulp and paper industry. Silicates sequester iron and other metal ions that reduce the efficiency of the peroxide. They also buffer the pH in the alkaline range required for bleaching. In the de-inking process, in addition to its buffering and sequestering action, silicate provides detergency and helps to prevent redeposition.

While the uses of dissolved silicates are extraordinarily diverse, the most rapid growth in the sodium silicate market is in custom derivatives such as precipitated silicas and zeolite catalysts. Processing of silicate solutions with mineral acids yields hydrated silica, which forms silica gel when dried. Silica gel finds wide application as an adsorbent and is used in the manufacture of catalysts (petroleum cracking and hydrocracking, hydrocarbon isomerization, etc.). Modified processing can yield silica sols, which are useful in water treatment. Zeolites primarily are aluminosilicates, made in many different grades. Properties depend on $SiO_2$/$Al_2O_3$ ratio, particle size, and cell structure. Varying the positive counterion and incorporating different metals into the structure give a wide variety of catalytic functions.

Other specialized products are those of higher alkalinity, such as the metasilicate, $Na_2SiO_3$ (molar ratio 1.0), and the orthosilicate, $Na_4SiO_4$ (molar ratio 0.5). Such high alkalinity would be corrosive to normal furnace refractories, and so these products are made in special apparatus by adding caustic soda to sil4icates of higher ratio [25]. The metasilicate is supplied in the anhydrous form and as the pentahydrate. Solid products with the $SiO_2$/$Na_2O$ ratio of orthosilicate may be supplied as the compound or as a mixture of solid metasilicate and anhydrous NaOH beads.

## Chlor-Alkali (Chlorine and Caustic Soda)

The most important use of salt in the chemical industry is the production of chlorine and caustic soda (sodium hydroxide, NaOH). Each is among the world's ten largest volume commodity chemicals. In 2009, combined production in the United States was 21.5 million metric tons [26]. This may have been a recessional anomaly, as in each of the preceding 5 years the total was between 22.8 and 24.7 million tons. Global production of chlorine alone in 2008 was about 42 million metric tons, distributed by region as shown in Table 26.12 [27].

Historically, electrolysis of NaCl brine accounts for about 96% of all chlorine production. It consumes about 2% of the electrical power generated in much of the industrial world. One of the difficulties faced by chlorine/caustic soda merchants is the fixed ratio of the amounts of the two products that are generated. Theoretically, nearly 1.13 kg of NaOH accompany each kilogram of chlorine. In the United States, the ratio in the electrolytic industry has hovered around 1.05–1.06. The same ratio applies to the data in Table 26.12. This reflects the fact that some plants produce chlorine without NaOH. Co-products may be Na, Mg, or KOH. There is also some production of chlorine by electrolysis of HCl. At the same time, there is some production of caustic soda without chlorine by reaction of sodium carbonate with lime. These alternative processes are described in standard texts [28, 29].

The chlor-alkali industry in the United States has been consolidating. Some merchants who supplied the pulp and paper industry, for instance, have left the business. Growth has been in the form of large plants integrated forward to produce EDC. The number of producers has been declining. Table 26.13 shows that four of them accounted for more than 80% of the capacity in 2010. Applications of caustic soda are quite diverse. Table 26.14, in which 30% is assigned to the very broad category of "organics," confirms this. The uses of chlorine historically were just as diverse, but social and environmental pressures have removed certain market segments (e.g., pulp bleaching, some chlorinated solvents). As a result, the chlorine market depends more heavily on vinyl chloride monomer (VCM) and its polymers. Table 26.15 shows 43% of the American market in this single use [27].

The heart of the chlor-alkali process is an electrolytic cell in which a nearly saturated solution of purified NaCl is decomposed. The three types of cell now in use are shown schematically in Fig. 26.3. The anode reaction is the same in every case:

$$2Cl^- \rightarrow Cl_2 + 2e$$
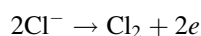
**Table 26.12**  Worldwide production data for caustic soda and chlorine

| Area | Caustic soda production[a] | Chlorine production[a] |
|---|---|---|
| Asia | 15.7 | 14.8 |
| Europe | 12.2 | 11.5 |
| North America | 11.5 | 10.9 |
| South America | 1.8 | 1.7 |
| Others[b] | 3.6 | 3.4 |
| Total | 45.0 | 42.3 |

[a]Millions of metric tons; 2008
[b]Includes India, Middle East, etc.
Courtesy of Consulting Resources Corporation

**Table 26.13**  Leading producers of chlorine in the United States

| Company | % of total capacity |
|---|---|
| Dow | 31.8 |
| Occidental | 23.3 |
| PPG | 13.6 |
| Olin | 13.5 |
| Formosa Plastics | 5.9 |
| Georgia Gulf | 3.1 |
| Others | 8.8 |

*Source*: The Chlorine Institute, Inc. [26]

**Table 26.14**  Caustic soda end use pattern in USA (Courtesy of Consulting Resources Corporation)

| Market segment | % of total |
|---|---|
| Organics | 30 |
| Inorganics | 19 |
| Pulp and paper | 12 |
| Petroleum | 6 |
| Soap and detergents | 5 |
| Miscellaneous | 13 |
| Export | 15 |

**Table 26.15**  Chlorine consumption pattern in USA (Courtesy of Consulting Resources Corporation)

| Market segment | % of total |
|---|---|
| EDC/VCM | 43 |
| Other organics | 29 |
| Inorganics | 12 |
| Water treatment | 4 |
| Miscellaneous | 12 |

Simple discharge of the sodium ion cannot occur in an aqueous medium; the favored reaction instead would be

$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$
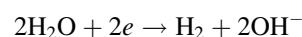
Chlorine and hydroxide ion would react immediately to form chloride and hypochlorite if the anolyte and catholyte were
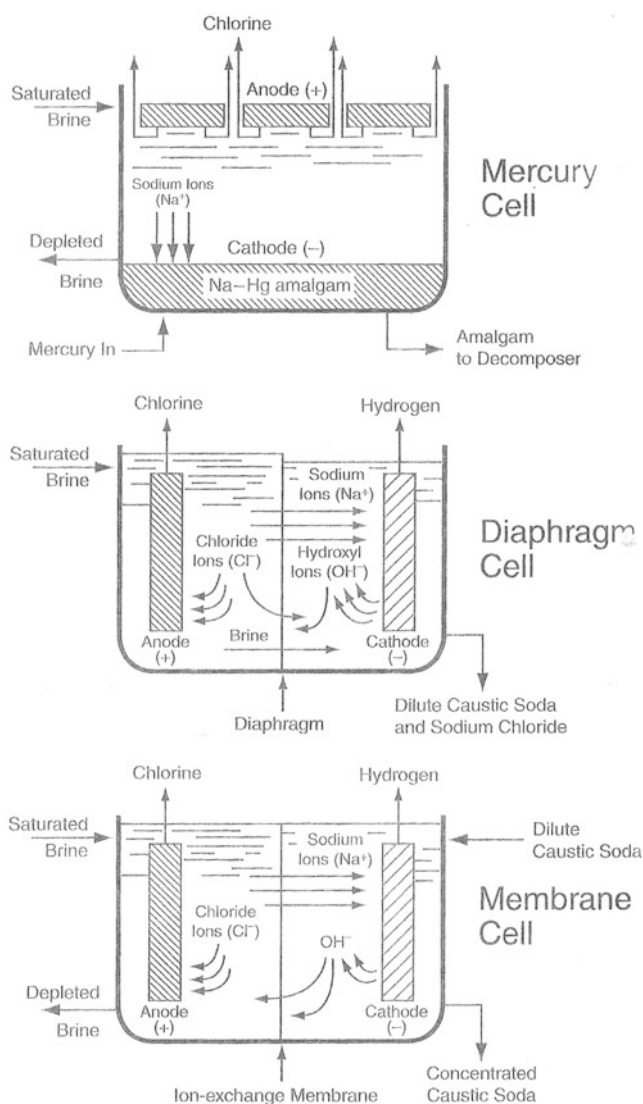
**Fig. 26.3** Schematics of mercury, diaphragm, and membrane chlor-alkali cells (Reproduced from Handbook of Chlor-Alkali Technology, vol. I, p. 38. Copyright 2005 Springer Science + Media and reproduced with permission.)

allowed to mix. Chlor-alkali cells must be designed to prevent this mixing. Diaphragm and membrane cells physically separate anolyte and catholyte. Mercury cells rely on a different chemistry. The cathode there is a dilute sodium amalgam flowing over a sloped floor of carbon steel. The sodium ion discharges to $Na^0$, amalgamated with the mercury. The amalgam that leaves the main part of the cell then flows through a decomposer, or denuder, forming caustic soda by its reaction with purified water:

$$2Na(Hg) + 2H_2O \rightarrow 2NaOH + H_2 + (Hg)$$
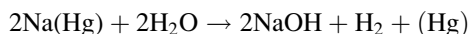
The parentheses indicate that mercury is not involved in stoichiometric quantities; the amalgam is in fact quite dilute

(<0.5%) in sodium. The flow rate of water, when correctly proportioned to the rate of production, controls the strength of the NaOH solution. The denuded amalgam is recycled to the cell.

In the diaphragm cell, a fibrous mat separates anolyte and catholyte. The feed brine enters the anode side of the cells, and the anolyte flows through the diaphragm into the cathode side. The chlorine formed at the anode passes off as a gas. Not all the chloride ion is oxidized; practical considerations limit its conversion to about 50%. The unreacted chloride ion goes into the catholyte. Hydrogen gas and caustic soda form at the cathode. Figure 26.4 shows the components of a modern diaphragm cell.

Diaphragm-cell liquor contains roughly equal amounts of chloride and hydroxide (molar basis). This is the fundamental disadvantage of the diaphragm cell because extensive processing is required to produce a high-quality NaOH product and recover the unconverted salt for recycle. Another disadvantage, which also goes to explain the continuing gradual replacement of diaphragm cells, is that the fiber used to form the diaphragms classically has been asbestos. Modern cells use a modified form into which a fused fluoropolymer is incorporated. All such formulations are gradually disappearing, largely because of the toxicity of asbestos and increasing restrictions on its use. Synthetic diaphragms free of asbestos are available and are gradually replacing the older types [30].

The technical advantage of membrane cells over diaphragm cells lies in the selectivity of the interelectrode barrier, shown as an ion-exchange membrane in the bottom part of Fig. 26.3. Membranes are sheets of perfluorinated polymer that are designed to permit the flow of water and alkali metal ions from anolyte to catholyte and to block the flow of anions in either direction. This means that chloride ions do not pass into the catholyte to any great extent, and so their concentration in the final product caustic usually is measured in tens of parts per million. To a lesser extent, the passage of hydroxide from catholyte to anolyte also is restricted. The hydroxide flow is a few percent of the total ionic flux through a properly performing membrane. The efficiency of its rejection is determined by the nature of the polymer facing the catholyte. For best efficiency, the ion-exchange group in the polymer will be based on a carboxylic acid. Carboxylate polymers have the disadvantage of low electrical conductivity. Perfluorosulfonate polymers are more conductive but operate at lower current efficiency. The typical membrane therefore has composite construction. It may also include PTFE fibers for physical reinforcement and a surface coating that promotes the release of gas bubbles when the gaps between cell components are small. Figure 26.5 shows how these features are combined in a commercial membrane.
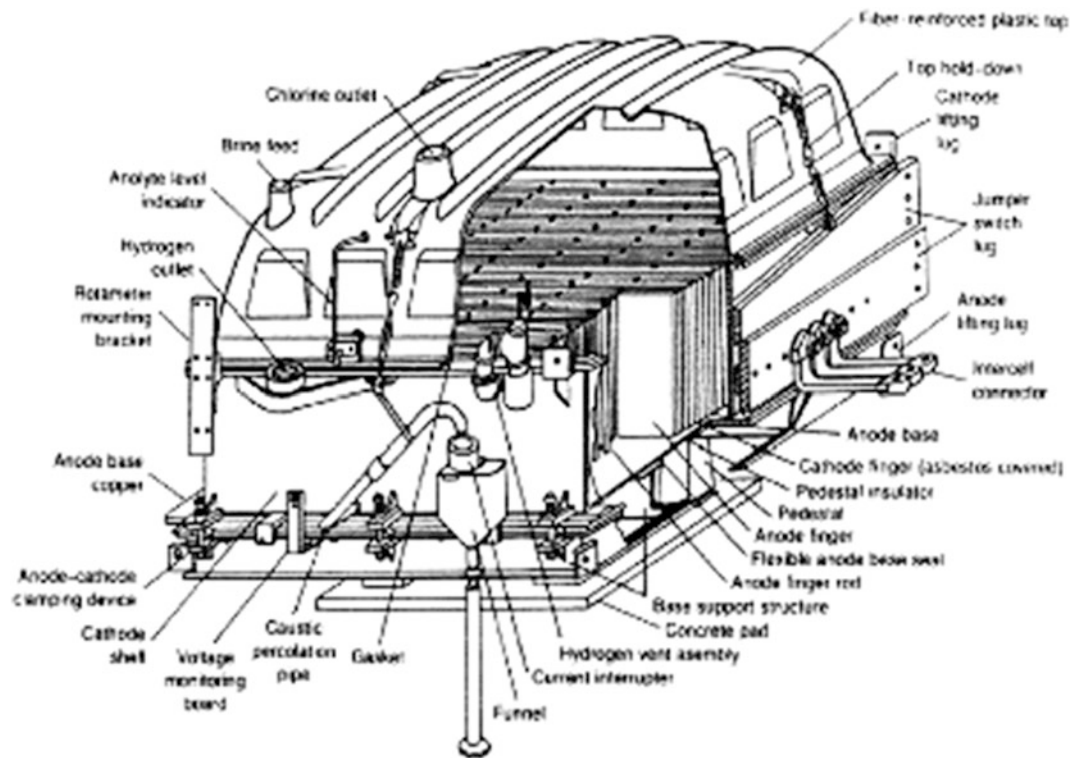
**Fig. 26.4** Cut view of ELTECH diaphragm cell (Courtesy of ELTECH Systems Corporation)
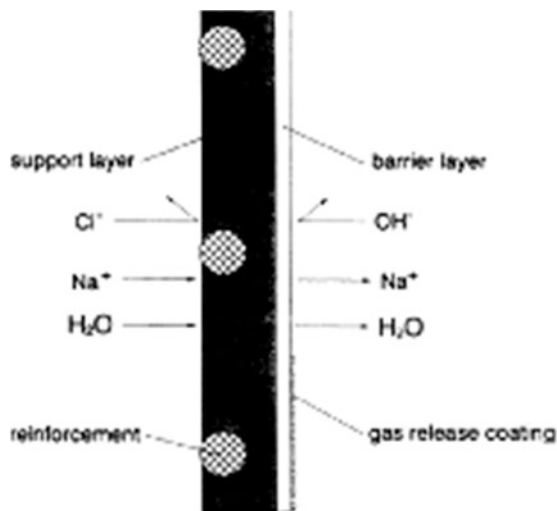


**Fig. 26.5** Chlor-alkali membrane cross-section

Before the commercial advent of the membrane cell, diaphragm and mercury technologies competed primarily on the bases of energy consumption and product quality. Mercury cells consume more electrical energy, and this is their chief economic drawback. On the other hand, they operate at much higher current densities and produce caustic soda at commercial strength without extensive processing. The liquor produced in a diaphragm cell is much weaker and has a high concentration of dissolved salt. Expensive multi-effect crystallizing evaporators are required, with large steam consumption and the need to recover and recycle salt. Removal of the dissolved salt is not perfect, and 50% diaphragm-cell caustic soda typically contains 1% residual NaCl. Mercury-cell caustic, often referred to as "rayon-grade," therefore was preferred for some applications and often could be sold at a premium price. The cells are sensitive to a different set of brine impurities, i.e., those that can interfere with amalgam chemistry. Their defining disadvantage, however, is simply the presence and inevitable release of small amounts of the highly toxic mercury. Societal and regulatory pressures against the use of mercury continue to increase. The use of mercury cells has been in steady decline, and their days are numbered.

Membrane cells generally consume less electrical energy than do diaphragm cells. Evaporators are required, but they are simpler in construction and consume much less steam than their diaphragm-cell counterparts. The caustic product is somewhat less pure than mercury-cell caustic, and the stringent brine purity requirements add to the cost and complexity of the process. The advantages outweigh the disadvantages, and the membrane cell is now the technology of choice. It is the universal choice for new installations and frequently is used in conversion of plants from the older technologies. A typical installation of new bipolar membrane cells is shown in Fig. 26.6. Figure 26.7 shows the

**Fig. 26.6** Membrane-cell installation at BorsodChem Zrt., Kazinbarcika, Hungary (Courtesy of Chlorine Engineers Corporation, Ltd.)
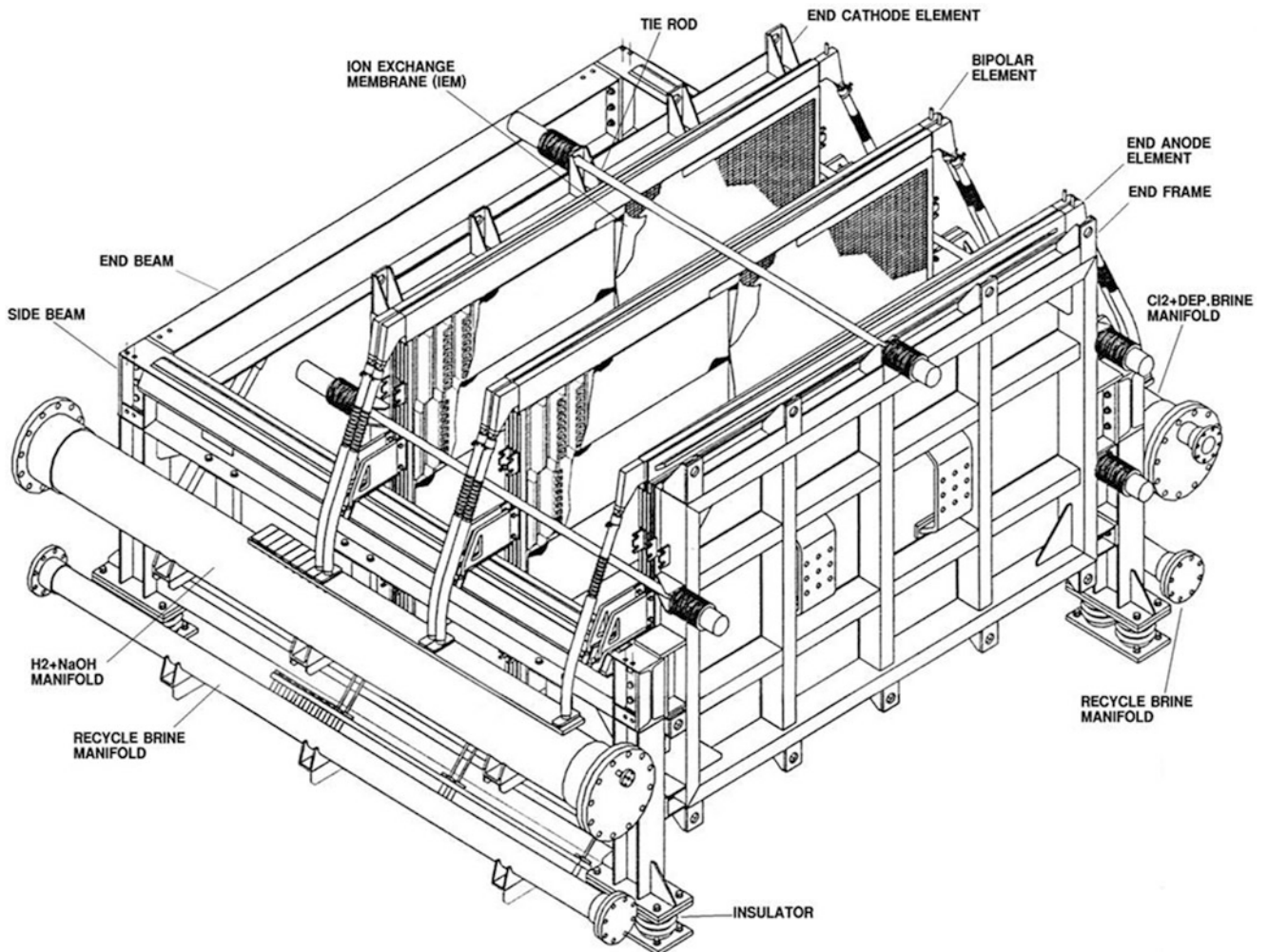


**Fig. 26.7** Overview of BiTAC® bipolar membrane electrolyzer (Courtesy of Chlorine Engineers Corporation, Ltd)

assembly of a typical state-of-the-art electrolyzer. Cells such as these can operate at 3 V or less at membrane current densities of 6 kA/m$^2$ (Table 26.16).

The United States has resisted the change to membrane-cell technology longer than most countries. Most US capacity (>70%) is on the Gulf Coast, where several factors continue to favor diaphragm cells. There are extensive salt deposits, and solution-mined brine is readily available. Diaphragm cells can operate without penalty when salt is supplied as concentrated brine, which Table 26.5 shows to be the cheapest form. Fuel is plentiful and relatively cheap, so the large evaporative demand of the diaphragm cell is less of a liability. Also, the balance between electrical and thermal demand of a diaphragm plant is better suited to the operation of a cogeneration system. Finally, continued improvement in cell components has reduced energy consumption and

increased on-line time between maintenance shutdowns [31]. In 2008, 67% of US chlorine capacity was in diaphragm cells. Membrane cells provided 26% and mercury cells, expected to phase out within the current decade, 4%. The situation in Europe was different. Mercury cells had been favored, but there, too, they are being phased out. Membrane-cell capacity became more than 50% of Europe's total in 2011 [32].

Membrane cells provide more compact installations, and conversion from one of the older technologies frequently has allowed an increase in capacity within an existing footprint. Evolution of the technology has continually increased the maximum practicable current density. Any new project requires an economic balance between the lower capital cost associated with increasing current density and the resulting higher operating voltage that increases energy cost. The recent trend in the industry is to higher current densities and little improvement in energy consumption. It is interesting to note that this parallels the history of development of the mercury cell many years ago [33].

Figure 26.8 shows the elements of the electrolyte processing required with each type of cell. In every case, NaCl brine is the major feed material. The first step in its treatment is the removal of hardness elements and heavy metals by chemical precipitation. The solids that form are removed by settling and one or two stages of filtration. The resulting brine, with a few ppm of hardness remaining, is suitable for use in diaphragm or mercury cells. Membrane

**Table 26.16** Components of membrane electrolyzer voltage (Courtesy of Chlorine Engineers Corporation, Ltd)

| Component | Voltage | % of total |
|---|---|---|
| Decomposition voltage | 2.26 | 76.3 |
| Anodic overpotential | 0.06 | 2.0 |
| Cathodic overpotential | 0.07 | 2.4 |
| IR losses[a] | 0.57 | 19.3 |
| Total | 2.96[b] | 100.0 |

[a]Include gas effects and IR drops through solution, membrane, and structure
[b]32% NaOH, 90 °C, 6 kA/m$^2$
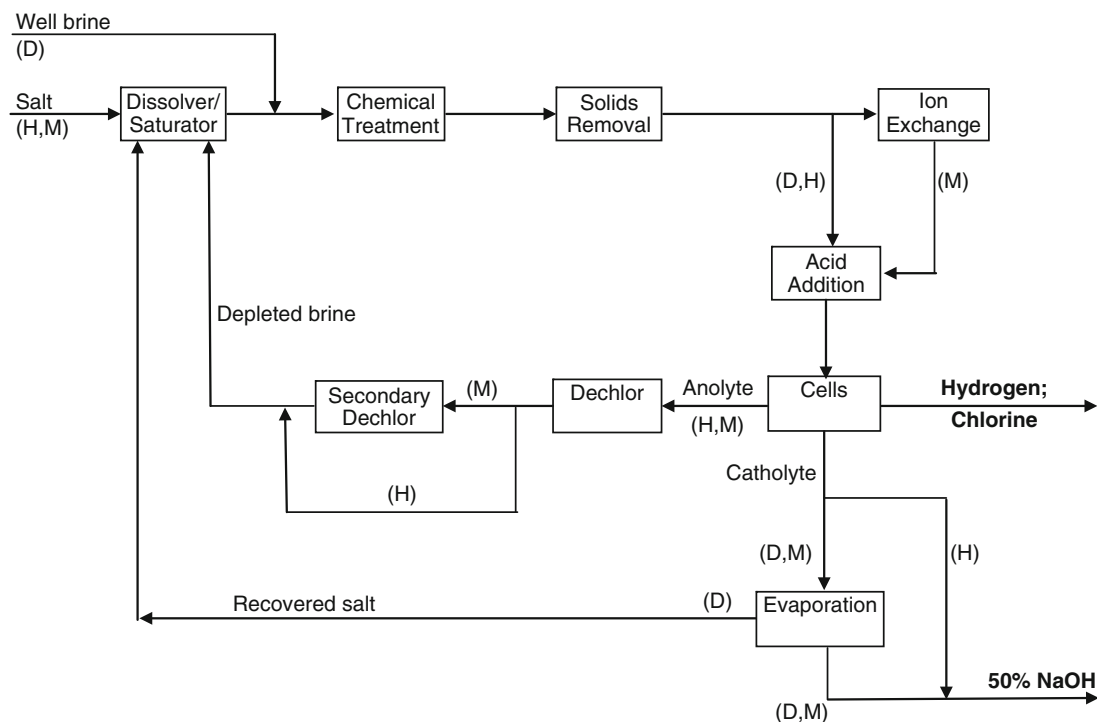


**Fig. 26.8** Chlor-alkali electrolyte processing key: D, diaphragm cells; H, mercury cells; M, membrane cells

cells require additional treatment with a chelating ion-exchange resin to reduce hardness to a low ppb level. The treated brine will be alkaline and will contain dissolved $CO_2$. The addition of acid has several advantages including the removal of the $CO_2$, improving the quality of the cell gas, and scavenging of some of the $OH^-$ that leaks back from the catholyte in some cells.

The cells produce hydrogen and chlorine gases at their electrodes. The quality of the gases does not depend greatly on the type of cell. The hydrogen is quite pure, and extensive processing is required only for special applications. At the anode, several reactions compete with chlorine formation. Impurity concentrations in the chlorine gas will amount to several percent.

The processing of hydrogen depends on its end use. It is frequently used for its fuel value. All that is required then is to deliver it at a useful pressure and with an acceptable water content. Membrane cells can operate under modest positive pressure. This at least relieves the problem of ingress of air and may also eliminate the need for compression. Other cells may require a blower. The cooling duty depends strongly on the type of cell. Latent heat being a large fraction of the total, process duty correlates with the amount of water accompanying the hydrogen. With mercury cells, the duty is quite small. Membrane cells are the intermediate case. The hydrogen is saturated with water over 30–35% NaOH. In diaphragm cells, the catholyte is more dilute in NaOH, and so the water content of the hydrogen is higher. To choose single values for comparison, with unity assigned to membrane-cell hydrogen, one might say that the cooling duty with mercury-cell hydrogen is about 0.1 and with diaphragm-cell hydrogen about 3 or 4 [34].

Chlorine may be used on site, transferred by pipeline, or liquefied for export. Broadly, about half the chlorine produced is consumed as the liquid. The full process then includes cooling, drying, compression, and liquefaction. Modern practice is to cool the gas, incidentally removing most of its water, in vertical shell-and-tube exchangers with titanium on the process side. Drying is by countercurrent contact with concentrated sulfuric acid [35]. As more water is removed during the cooling process, the cost of supply and disposal of sulfuric acid goes down. Design, however, does not involve simply an economic balance; there are technical limits on the amount of water that can safely be removed. Below 10°C, a solid hydrate of chlorine forms (approximate composition $Cl_2 \cdot 7.2H_2O$). This can deposit in equipment and cut off flow. Upon shutdown, it will melt, causing very rapid corrosion. Next, the titanium used in the coolers is suitable for service in wet chlorine because a resistant oxide film forms by hydrolysis of the metal. The film must be continuously renewed to prevent contact and rapid reaction of the metal with $Cl_2$. Cooling must not deplete the water content of the gas to a level where it cannot maintain the $TiO_2$ film.

Dry gas can be handled in ferrous-metal equipment. Centrifugal compressors are standard in large plants; liquefaction is by indirect contact with boiling refrigerant [36]. Centrifugal compressors in chlorine service are restricted in compression ratio, because temperature must be limited in order to prevent combustive reaction between the gas and the metal of the compressor. Compression then becomes a multistage process, with gas coolers operating between stages. In older and smaller plants, liquid-ring compressors are a frequent choice. The sealing liquid is concentrated sulfuric acid. These compressors have much lower energy efficiency, but the circulating acid removes much of the heat of compression, and so the compression ratio can be higher without producing excessive temperature.

The final pressure on the chlorine normally is 2–10 atm. It is determined by downstream needs if the chlorine is to be processed immediately or by a balance between refrigeration and chlorine compression costs when the gas is to be liquefied.

The impurities present in chlorine are mostly permanent gases that do not condense in the liquefaction system. They leave as a vent stream, carrying chlorine at a partial pressure equal to its vapor pressure at liquefaction temperature. The extent of liquefaction therefore increases at higher pressure and lower temperature. It, too, may be a multistage operation. Since deeper liquefaction requires higher severity, energy can be saved by liquefying most of the chlorine under relatively mild conditions and then increasing the severity to reach the desired recovery.

The presence of chlorine in the uncondensed tail gas is a problem that must be dealt with. It can be destroyed by conversion to an innocuous waste, converted to another useful product, or recovered as the element. There are many processes for treating tail gas. The paper by Silver [37] remains a good summary. Destruction most often is by scrubbing with an alkaline liquor. This absorbs the chlorine from the gas and first converts it to hypochlorite, as in the equation above. Some of this will react to form chlorate (*infra*), and the rest can be chemically or catalytically reduced to chloride.

Controlled absorption with precautions not to decompose the hypochlorite is one example of conversion to a useful product. Production of hypochlorite bleach in this way is discussed below. Another option is the production of hydrochloric acid (*infra*). This can be an especially attractive operation as it upgrades some of the hydrogen from the cells and provides a material for internal consumption in brine treatment and dechlorination. Still another option is production of ferrous and ferric chlorides from the metal.

For recovery as the element, absorption/desorption processes suggest themselves. Chlorine would be absorbed from the tail gas at high pressure and low temperature and then released under opposite conditions as a nearly pure vapor.

The ideal characteristics of a solvent have been enumerated [38]. Several plants have operated with carbon tetrachloride as solvent. Environmental restrictions on $CCl_4$ have put a stop to this practice, and some recovery units have been scrapped. The usual choice for their replacement has been enhanced liquefaction. This might take the form of a tertiary stage where the gas after further compression is exposed again to the lowest temperature in the liquefaction process.

Anolyte, which is a separate stream only with mercury and membrane cells, will contain dissolved chlorine. Most of this can be removed by adding acid to reverse its hydrolysis and reducing the operating pressure. It can join the chlorine from the cells for processing. A small amount of chlorine will remain in the brine. With mercury cells, this is tolerable and may even be beneficial by keeping mercury in solution and preventing deposits of the metal in the brine system. In the membrane-cell process, the residual $Cl_2$ is not tolerable. A second stage of dechlorination then is necessary. Here, $Cl_2$ and $OCl^-$ are chemically or catalytically reduced to $Cl^-$. The depleted and dechlorinated brine then returns to the brine feed process.

Differences in caustic soda processing are profound, reflecting the differences among the various cell products:

1. Mercury cells: NaOH at sales or use concentration, low levels of impurities
2. Membrane cells: 30–35% NaOH, some anionic impurities ($Cl^-$, $ClO_3^-$, $SO_4^{2-}$)
3. Diaphragm cells: 10–12% NaOH, ~15% NaCl, other anionic impurities

Mercury-cell caustic requires very little processing. The evaporation of membrane-cell caustic is a straightforward process in which the amount of water to be removed is roughly equal to the amount of contained NaOH. A typical evaporation system will have two or three effects. The nature of diaphragm-cell caustic complicates the evaporation process. The combined presence of NaCl and NaOH will exceed the limits of solubility well before reaching the desired concentration of 48–50% NaOH. NaCl then begins to drop out of solution. Evaporation of about 85% of the water releases about 95% of the salt as crystals that form a concentrated slurry in NaOH solution. The salt, recovered on centrifuges, returns to the brine system for another pass through the cells. The solution is then cooled, releasing more dissolved salt, and is at its final concentration. The newly crystallized salt is removed from the solution by another set of centrifuges. Filtration of the product NaOH solution, which in the 50% grade still contains about 1% dissolved NaCl, normally is necessary to remove the last traces of solid salt.

Most diaphragm-cell caustic is sold with its residual dissolved NaCl. This has been a marked disadvantage in some applications. The less attractive composition of the product, the complexity and cost of an evaporation plant,

and the increased energy requirement all favor the replacement of diaphragm with membrane cells. The evaporative load is about five times as great as that in a membrane-cell evaporator. As a result, diaphragm-cell evaporators generally have three or four effects.

A small fraction of the diaphragm-cell caustic output is purified to remove anionic impurities, principally $Cl^-$. This involves extraction by anhydrous ammonia in a column at high pressure. Extensive processing removes traces of ammonia from the purified caustic and reconstitutes the ammonia for recycle. The byproduct of this process is a stream of caustic soda with an elevated concentration of impurities. It may become a waste or may be used as a source of alkalinity.

In some applications, the water accompanying the caustic is undesirable or unacceptable in further processing. The cost of shipping it along with the caustic is always undesirable. Approximately 5% of the NaOH produced therefore is concentrated beyond 50%. Simple concentrating evaporators can produce 70–73% NaOH in one stage. More complex processing gives products that are 98–99.5% solids. Typically, this involves evaporation in vertical units heated by a molten salt followed by vacuum flashing to remove further traces of water. The molten product may be merely cast in drums. More elaborate processes include the formation of flakes on a cooled roll equipped with doctor knife and the formation of nearly spherical particles by atomization into a stream of dry, relatively cool air.

All the products of a chlor-alkali plant are hazardous, and the hazards are diverse. It would be unwise to provide an inadequate summary here. The interested reader may consult the voluminous safety literature, the guides and publications of industry associations [39, 40], and the standard references already cited here [41, 42].

## Hydrochloric Acid

More than 93% of the hydrogen chloride used in the United States is obtained as a byproduct. The chief source is the chlorination of hydrocarbons. Other important sources are isocyanate and fluorocarbon production and the thermal oxidation of chlorinated organic wastes. In substitution chlorination of paraffinic hydrocarbons, HCl is generated in the chlorination reaction. Chlorine never enters the organic molecule during the preparation of isocyanates. Its function is that of a carbonyl carrier, being used first to produce phosgene. Phosgenation of an amino compound then produces two molecules of byproduct HCl.

After addition chlorination of olefins, HCl may be generated by a pyrolysis that leaves a monochlorinated olefin product. In the classical process, this is so in the case of

VCM, the principal derivative of chlorine (*supra*). Addition of $Cl_2$ to ethylene produces ethylene dichloride. VCM results when a molecule of HCl is split off. If all VCM were produced this way, there would be a serious glut of HCl. This fact provided much of the incentive for development of the oxychlorination process in which HCl is oxidized as it forms to regenerate chlorine:

$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$$
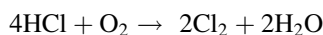
Ideally, all of the chlorine value goes into the product, with no net formation of HCl.

Most synthetic HCl is the product of combustion of chlorine with hydrogen. This is a convenient way to upgrade the tail gas from chlorine liquefaction (*supra*). HCl is recovered as the acid, and much of it is recycled for internal use. Accurate data on hydrogen chloride production and consumption are difficult to obtain because of the large numbers of producers and consumers, the variety of grades, and the confidentiality of information relating to captive use of HCl.

Hydrogen chloride is marketed both as anhydrous HCl and as hydrochloric acid, typically a 32% solution. HCl normally is absorbed in a falling film column followed by a packed tails tower that vents inerts into the atmosphere. The weak acid from the tails tower flows to the primary absorber. The heat of absorption of HCl is about 400 kcal/kg and requires that the primary absorber be water-cooled. With the addition of a ceramic burner to produce HCl from $H_2$ and $Cl_2$, similar apparatus becomes an HCl synthesis unit.

Acid made by burning hydrogen in chlorine tail gas is quite pure and requires no further treatment except, in some cases, for the removal of traces of dissolved chlorine. Byproduct acid requires purification in packed scrubbers in which the parent hydrocarbon is circulated in the scrubbing tower before flowing to the chlorinator. Frequently, the absorption efficiency is improved by cooling the scrubbing liquor with a refrigerant.

## Bromine and Sodium Bromide

Bromine has long been produced by the displacement of bromides from seawater. While this is an inexhaustible source ($10^{14}$ metric tons Br), operation is expensive because of the low concentration of bromide (about 65 ppm [43]), and the process no longer operates in the United States. Rather, underground brines found in Arkansas at depths of about 2,400 m and containing up to 0.6% Br are the favored source. There are two US producers with combined capacity of 278,000 t/year [44].

The United States is the world's largest producer of bromine (about one-third of the total), but China and the Dead Sea countries account for a large and growing share.

**Table 26.17** US production and consumption of bromine

|  | 2007 | 2008 | 2009 | 2010 |
|---|---|---|---|---|
| Production | 243 | w[a] | w[a] | w[a] |
| Exports | 8.6 | 9.6 | 8.1 | 8.0 |
| Imports | 32.2 | 41.2 | 34.2 | 45.0 |
| Consumption[b] | 277 | w[a] | w[a] | w[a] |

*Source*: US Geological Survey Mineral Commodity Summary, *Bromine*, 2011
All quantities in thousands of metric tons bromine equivalent
[a]Quantities withheld; fewer than three domestic producers
[b]Apparent consumption = production + imports–exports

**Table 26.18** Worldwide production and reserves of bromine, 2010

| Country | Production (est.) | Reserves |
|---|---|---|
| United States | – | 11,000 |
| Israel | 185 | (Dead Sea) |
| China | 150 | 130[a] |
| Jordan | 85 | (Dead Sea) |
| Japan | 20 | NR |
| Ukraine | 4 | 400 |
| Azerbaijan | 3.5 | 300 |
| Spain | 0.1 | 1,400 |
| Turkmenistan | 0.15 | 700 |
| Others | 3 | (from bitterns) |
| Total non-US | 450 | Large |

*Sources*: US Geological Survey: Mineral Commodity Summary, *Bromine*, 2011; advanced release of 2010 Minerals Yearbook
All quantities in thousands of metric tons bromine equivalent
[a]China has a total of 3.5 million metric tons of base reserves of uncertain quality and value (reported elsewhere)

Table 26.17 shows that production and consumption rates in the United States are hard to obtain because data are not reported when there are fewer than three active producers. Table 26.18 shows worldwide production and reserves. Non-US production in 2010 was about 10% higher than the average of the previous 4 years. Bitterns of potash production from Dead Sea brines, used in Israel and Jordan, are very rich in bromide, containing 1.0–1.2% Br (w/v). The total amount of bromine available there is about $10^9$ metric tons. Some countries produce relatively small amounts of bromine by recovering it from solar salt or potash bitterns.

There are four major steps in the recovery of bromine from brine: (1) oxidation of $Br^-$ by injection of chlorine, (2) stripping of elemental bromine from solution, (3) recovery of bromine from vapor, and (4) purification. The first step depends on the equilibrium between chlorine and bromine:

$$Cl_2 + 2Br^- \leftrightarrow 2Cl^- + Br_2$$
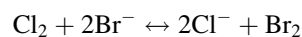
In the second step, elemental bromine is released by contact of the solution with air or steam. There is an economic balance here between the cost of steam and the difficulty of recovering bromine from air in the third step.

Generally, steam is favored when processing brines and air when processing the much more dilute seawater. The use of air requires the bromine to be trapped in an alkaline or reducing solution to concentrate it.

Operating a steam-based process under vacuum allows bromine to be stripped at lower temperature. Claimed benefits are increases in steam economy and plant capacity and reductions in chlorine loss, spent brine treating requirements, maintenance costs, and atmospheric emissions [45, 46].

Primary uses of bromine and bromine chemicals are in flame retardants, drilling fluids, water treatment, and pesticides. The once-prominent market in petroleum additives has declined with the phase-out of lead-based antiknocks, which consumed ethylene bromide. Similarly, certain brominated flame retardants are being withdrawn from the market [44]. A growing application is the use of bromine to bond with mercury in flue gases. In some cases, it replaces chlorine as a scavenger. The mercuric bromide that forms is relatively easy to remove in flue-gas scrubbers. One process uses fine powdered carbon impregnated with about 10% bromine [47].

Sodium bromide sometimes is recovered as a byproduct of other operations, and it can be prepared by adding excess bromine to a solution of NaOH. After evaporation to dryness, treatment with a reducing agent converts sodium bromate to NaBr. It is used as an intermediate in production of other chemicals, often by double decomposition with organic chlorides. Bromides are the proverbial sedatives, and other uses are as algaecides and photographic chemicals. Their major use has been in drilling fluids, where the high density of concentrated aqueous solutions (up to 1.55 g/cm$^3$) is useful in well completions. NaBr is the form of supply when using bromine as a biocide. The active form is released by activators such as hypochlorites and chlorinated isocyanurates.

Recovery of bromine from byproduct solutions and HBr emitted in organic brominations is the source of roughly one-third of total production. Incineration of plastics that contain brominated flame retardants also provides bromine for recovery [48].

## Bleaches and Disinfectants

The oxidative and biocidal properties of chlorine have been widely exploited from the beginnings of the chemical industry. Textile manufacturers and the paper industry have long recognized the value of bleach in their operations. The extensive use of chlorine and its derivatives to bleach wood pulp is described in Chap. 28.

Active chlorine compounds also find wide use as disinfectants and in laundry bleaching. The spread of the great killer diseases cholera and typhoid was checked by the addition of small amounts of chlorine bleach to wastewater and drinking water. Today, potable water disinfection accounts for only a few percent of the world's chlorine consumption (see Table 26.15) but remains perhaps its most important and most beneficial use. The use of chlorination is widespread only in the developed world, and an estimated one-third of deaths and 80% of all diseases in developing countries are due to consumption of contaminated water [49].

When chlorine is added to water, it hydrolyzes to form hydrochloric and hypochlorous acids:

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$$

HOCl is a strong disinfectant that is not ionized at low pH. Rather than transport and handle liquid chlorine, both hazardous undertakings, treatment plant operators may use solutions of sodium hypochlorite. This is produced, along with an equal amount of salt, by absorption of chlorine into a solution of caustic soda:

$$Cl_2 + 2NaOH \rightarrow NaCl + NaOCl + H_2O$$

The strength of the solution may vary to suit the application. The use of 20% NaOH gives a 16% solution of NaOCl, which is regarded as commercial strength. At high pH, hypochlorite is completely ionized. It is less effective in this form, and, at lower pH at the point of application, it may convert to the more active HOCl.

Before the commercialization of chlorine liquefaction, bleaching compounds were the only transportable form of chlorine. The earliest practice was to absorb chlorine in hydrated lime, Ca(OH)$_2$. This forms chloride of lime, CaOCl$_2$, which is easily transported as a solid. Dissolved in water, it forms equal moles of CaCl$_2$ and Ca(OCl)$_2$:

$$2CaOCl_2 (\text{dissolved}) \rightarrow CaCl_2 + Ca(OCl)_2$$
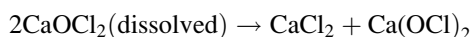
Chlorination of milk of lime or of a slurry of lime produces the same mixture, in which calcium hypochlorite is the active ingredient [50]. If sodium hypochlorite is separately produced or if a mixture of lime and caustic soda is used, the lower solubility of Ca(OCl)$_2$ allows double decomposition of NaOCl and CaCl$_2$, and all the calcium value can be converted to bleach. The overall reaction becomes, ideally:

$$2Cl_2 + Ca(OH)_2 + 2NaOH \rightarrow 2NaCl + 2H_2O + Ca(OCl)_2 \downarrow$$
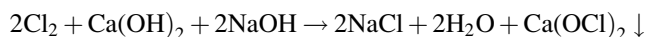
Ca(OCl)$_2$ has characteristics similar to those of NaOCl, but it is approximately neutral and in its granular form has a high available chlorine content. The chloride of lime as produced in the past contained only about 35% available chlorine.

The term "available chlorine" describes the bleaching capacity of a substance or solution referred to an equal weight of elemental chlorine. The chloride ion that results from hydrolysis of $Cl_2$ is not a bleaching agent, but the hypochlorite ion can abstract two electrons (the chlorine atom is in the +1 oxidation state, and $Cl^{1+}O^{2-}$ is a more informative notation). The net result of hydrolysis and bleaching is as if each chlorine atom picked up one electron in oxidation of the material being treated. A hypochlorite group, it will be seen, then has all the bleaching capacity of a molecule of chlorine. Pure calcium hypochlorite, noted above, therefore contains $2 \times 100 \times 71/143 = 99.3\%$ available chlorine. The commercial product actually is the dihydrate $Ca(OCl)_2 \cdot 2H_2O$. Its strength varies with the purity of the lime used in its preparation, the purity of the mixed crystals formed in precipitation, the degree of contamination by unreacted lime, and the final processing conditions. Centrifugation, granulation, and air drying normally yield a product with 65–70% available chlorine. This is the form packaged for sale.

Chlorine/hypochlorite has largely been displaced from wood pulp bleaching in the move to elemental chlorine-free (ECF) bleaching. It still is widely used in household bleaches because of its ease of manufacture and handling, as well as its low cost. Many plants are dedicated to the production of bleach and operate on purchased chlorine and caustic soda. Others are attached to chlor-alkali plants (*supra*) and frequently operate on liquefaction plant tail gas. Commercial soda bleaches vary in their NaOCl content up to 15–16%, the higher NaOCl contents requiring higher excess concentrations of caustic to maintain stability. Household bleach is relatively dilute and normally contains 5–6% available $Cl_2$. Lacking the additives found in many consumer products, bleach has few residual effects, and the Centers for Disease Control and Prevention recommend its use for all sanitizing purposes [51].

The conventional expression "trade %" is simply the available chlorine content in weight/vol.%. Thus,

$$(\text{trade } \% \text{ available } Cl_2) = (\text{weight } \% \text{ available } Cl_2) \\ \times (\text{specific gravity})$$

Since pure sodium hypochlorite has 95.3% available chlorine, one also can write

$$(\text{trade } \% \text{ available } Cl_2) = (\text{gpl NaOCl}) \times 0.0953$$

Bleach also can be produced by the absorption of chlorine from liquefaction tail gas. Even the liquor from an emergency vent scrubber may be a useful bleach. Maintaining the quality of the bleach often is at cross purposes with the function of an emergency scrubber. Design and operating technique can overcome some of the difficulties. Some key points as well as the problems of decomposition of hypochlorite and the use of filtration and proper materials of construction to improve product stability are discussed elsewhere [52].

A much weaker bleach results from electrolysis of seawater in undivided cells. The electrode products, NaOH and $Cl_2$, react as noted above to produce hypochlorite. As a low-level bleach and disinfectant, it can serve as a utility-type water and sewage treating agent. It is a natural choice for marine sanitation and as an algaecide in seawater evaporation plants.

Dilute sodium hypochlorite is approved for sanitization of food processing equipment. A concentration of 200 ppm available chlorine is acceptable without washing if equipment is adequately drained [53]. More concentrated solutions may be used along with proper rinsing protocols.

The insoluble components in lime-based products are especially objectionable in laundry and dishwashing uses. Sodium compounds are preferred, and sometimes in spite of their greater cost, lithium compounds. LiOCl can be prepared by absorbing chlorine in LiOH or by adding LiCl to soda bleach. In the latter case, it is the insolubility of NaCl in concentrated solution that drives the double decomposition:

$$NaOCl + LiCl \rightarrow LiOCl + NaCl \downarrow$$
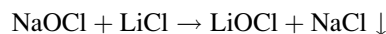
The demand for chlorine dioxide was an early beneficiary of the move away from chlorine bleaching of wood pulp. For many years, $ClO_2$ had been used late in many pulp-bleaching sequences. It is a strong bleaching agent that can remove certain compounds that resist bleaching by chlorine. Its use thus increases the brightness of the final product. It also produces fewer waste products that require disposal [54] and in particular produces much less adsorbable organic halide and no dioxin [55]. The use of more $ClO_2$ in earlier stages permitted the reduction or elimination of chlorine bleaching.

The shift to $ClO_2$ increased the market for sodium chlorate. Chlorine dioxide is very unstable and cannot be safely and economically transported. Instead, it is produced at the point of use by treating a solution of $NaClO_3$ and $NaCl$ with acid and a reducing agent. There are several different types of commercial chlorine dioxide generator in operation, classified by acid medium (sulfuric, hydrochloric) and reducing agent (sulfur dioxide, methanol, sodium chloride, hydrochloric acid). Most processes generate some elemental chlorine as a byproduct. The use of sulfuric acid or $SO_2$ also produces sodium sulfate or waste acid for disposal. As an example of the chemistry, consider HCl, which serves both as acid and as reducing agent:

$$NaClO_3 + 2HCl \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O$$
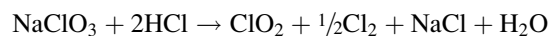
Generators must be operated with care to avoid $ClO_2$ concentrations above 10%, which can lead to explosive decomposition. The reactor offgas therefore is diluted with air, and the $ClO_2$ is immediately absorbed in water. The molar ratio of $ClO_2$ to $Cl_2$ formed is typically 2:1. If this level of $Cl_2$ is objectionable, the gas is passed through a tower in contact with circulating chilled water. This dissolves all the $ClO_2$ but only about 25% of the $Cl_2$, raising the molar ratio to $8ClO_2$:$1Cl_2$. The remaining $Cl_2$ can be removed by scrubbing with alkali.

Since the oxidation state of chlorine in $ClO_2$ is +4, it abstracts five electrons as it is reduced to chloride. A chlorine molecule, as we have seen, transfers only two. The available chlorine content of $ClO_2$ therefore is $5/2 \times 100 \times 71/67.5 = 263\%$.

## Sodium Chlorate

Sodium chlorate is produced by the electrolysis of NaCl brine in a cell similar to a chlor-alkali cell but lacking means to separate the products of the two electrodes. The chlorine and caustic soda produced in the cell therefore react immediately, producing sodium hypochlorite:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O$$

The cell liquor is kept hot (80–95°C) in a vessel that provides enough residence time for the hypochlorite to disproportionate into chlorate and chloride:

$$3NaOCl \rightarrow NaClO_3 + 2NaCl$$

The overall reaction, requiring 6 F/mole, becomes

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$$
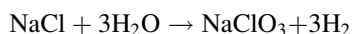
Optimum cell conditions are 80–90°C and pH 6–6.5. The liquor contains 550–750 gpl $NaClO_3$ and 100–120 gpl NaCl [56]. Coated titanium anodes and steel cathodes are used, and small amounts of dichromate are added to the cell liquor to prevent the cathodic reduction of chlorate or hypochlorite. Resulting current efficiencies are above 90%, and energy consumption is in the vicinity of 4,500 kWh/metric ton.

The adoption of permanent metal anodes permitted an increase in sodium chlorate and a reduction in salt concentrations in the liquor without loss of current efficiency. This in turn allowed direct recovery of sodium chlorate by evaporative crystallization [57]. This was an advance on the process described in previous editions of this handbook. The earlier process yielded solid salt when the liquor was evaporated. After removal of the salt, cooling of the liquor produced $NaClO_3$ crystals.

Nearly all the sodium chlorate made in North America is used in the on-site manufacture of chlorine dioxide for pulp bleaching. The surge in demand due to the industry's adoption of ECF bleaching has run its course. The rest is used to produce other chlorates, perchlorates, and chlorites; in water treatment; and in the hydrometallurgical recovery of uranium. Sodium chlorate also is a nonselective herbicide. While this market might tend to increase along with GDP, there is also pressure to convert to total chlorine-free (TCF) bleaching. The market for $NaClO_3$ has been growing faster where conditions are more favorable. In Asia and South America, the abundance of faster-growing pulps presents more opportunity. Russia, with 22% of the world's forest and relatively cheap electricity, also has seen some growth. Where electricity is more expensive, the higher cost of $NaClO_3$ has allowed $H_2O_2$ to penetrate the bleaching-chemical market. In Europe and Japan, where $ClO_2$ accounts for only 90 and 84% of consumption, respectively, the use of sodium chlorate as a herbicide is more common. However, this market is threatened by a European Union directive to withdraw sodium chlorate products from the market [58].

Potassium chlorate can in some circumstances be produced electrolytically from KCl. It is more common to produce it from $NaClO_3$ by double decomposition:

$$KCl + NaClO_3 \rightarrow KClO_3 + NaCl$$
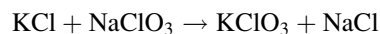
After the reaction is carried out in solution, crystallization yields solid $KClO_3$. $KClO_3$ is used in matches, pyrotechnic products, explosives, cosmetics, and pharmaceuticals [59].

Bromates are produced electrolytically, like chlorate, or by bromination of the respective carbonates. Bromates are used in small quantities, but they are important in the bread-making industry for maturing flour and conditioning dough. They also are used in permanent-wave lotions and in the manufacture of dyes.

Both chlorates and bromates have substantial oxidizing power, and care must be taken in their storage and handling. Contact with reducing agents or combustibles can be disastrous.

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