6

The Chlor-Alkali Industry

6.1 Overview of the Chlor-Alkali Industry

Chlorine, Sodium Hydroxide, and Sodium Carbonate Are Primary Products of the Chlor-Alkali Industry

The caustics chain begins with sodium chloride (NaCl) and forms the basis for what is often referred to as the **chlor-alkali** industry. Major products of the chlor-alkali industry include **chlorine**, **sodium hydroxide (caustic soda)**, **soda ash (sodium carbonate), sodium bicarbonate, potassium hydroxide, and potassium carbonate**. Of these products, chlorine, sodium hydroxide, and soda ash account for the largest share of shipments from the chlor-alkali industry. These products are also very important economically, being the chemicals produced in the eighth, ninth, and tenth largest amounts in the United States (in 1997, their combined production was over 72 billion pounds) (CMA 1998).

U.S. Production of Major Products in the Caustics Chain (1997)

Chlorine (26.0 billion lbs)
Sodium Carbonate (23.7 billion lbs)
Sodium Hydroxide (22.7 billion lbs)

Source: CMA 1998.

Most of the **chlorine** produced in the United States (about 70 percent) is used to manufacture organic chemicals (e.g., vinyl chloride monomer, ethylene dichloride, glycerine, chlorinated solvents, glycols). Nearly 40 percent is used for the production of vinyl chloride, an important building block for poly vinyl chloride (PVC) and a number of petrochemicals (see Figure 6-1). Chlorine is also important to the pulp and paper industry, which consumes about 15 percent of the chlorine produced annually. Other major uses for chlorine include the manufacture of inorganic chemicals, disinfection of water, and production of hypochlorite (CMA 1998, Orica 1999).

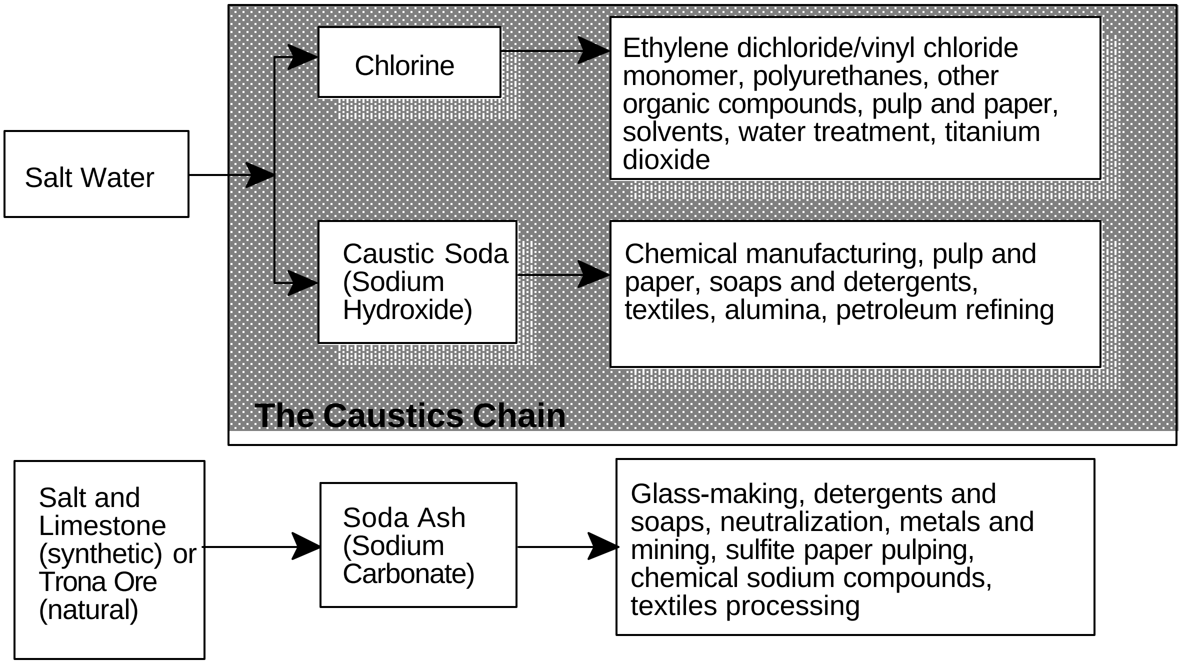


Figure 6-1. Chlor-Alkali Products Chain (CMA 1998)

About 30 percent of the **sodium hydroxide** produced is used by the organic chemical industry and about 20 percent is consumed by the inorganic chemical industry for neutralization and off-gas scrubbing, and as an input into the production of various chemical products (e.g., alumina, propylene oxide, polycarbonate resin, expoxies, synthetic fibers, soaps, detergents, rayon, cellophane). Another 20 percent of sodium hydroxide production is used by the pulp and paper industry for pulping wood chips and for other processes. Sodium hydroxide is also used to manufacture soap and cleaning products, and as drilling fluid for oil and gas extraction (CHEMX 1999, Orica 1999).

Soda ash is used primarily by the glass industry as a flux to reduce the melting point of sand. It is also a raw material in the manufacture of sodium phosphates and sodium silicates, important components of domestic and industrial cleaners. Other uses are in the production of metals in both the refining and smelting stages, in sulfite paper pulping processes, and in textiles processing. Soda ash is also an intermediate in the production of sodium compounds, including phosphates, silicates, and sulfites.

Demand for Sodium Hydroxide and Chlorine Is Impacted by Global Economies

The chlor-alkali industry has been growing at a slow pace over the last 10 years and this rate is expected to continue in the early years of the new century. Chlorine and sodium hydroxide are co-products, and the demand for one will highly influence the demand for the other. Over the last several decades, market forces have switched between chlorine and sodium hydroxide a number of times. Chlorine demand drives the chlor-alkali industry, but the demand is cyclical, with chlorine and caustic soda out of phase in the marketplace. When caustic soda reaches a high level of demand, the direction of product flow is dependent upon Asian and European economies and the foreign exchange rate. Foreign producers may often export caustic soda to the

United States to keep chlorine production high, which impacts both markets and production in this country (DOW 1999).

Prices for both chlorine and caustic soda are impacted by changes in vinyl exports to Asia and weakness in the pulp and paper industry. Important Asian economies (e.g., Japan) will continue to drive demand for both these products and set the pace of new production facilities in the United States. The fact that the United States remains competitive in the chlorine-caustic-vinyl cycle can be attributed to three factors: our large supplies of energy and raw materials (salt and ethylene), and our large-scale economy. With the exception of Taiwan, world scale vinyl plants are not being built in Asia (DOW 1999).

Other forces affecting the market for chlor-alkalis include environmental regulations aimed at curtailing chlorine use. For example, restrictions on the production or disposal of products that require large amounts of chlorine (e.g., PVC, chlorinated solvents) have had a negative impact on the chlorine market. Several environmental groups and initiatives (e.g., International Joint Commission of Great Lakes Water Quality) are calling for a gradual phaseout or immediate ban on chlorine and chlorinated compounds as industrial feedstocks, which is also impacting commercial use of chlorine (CCC 1995, EPA 1995a, CCC 1996, Ayres 1997).

However, demand for PVC has been a significant driver in the growth of chlorine use both in the United States and globally. The industrialization of Asia is expected to drive PVC demand and chlorine growth well into the next century. Until a non-chlorine replacement for PVC is developed, demand will remain strong (DOW 1999).

Demand for sodium hydroxide may also be impacted by users switching to soda ash to avoid shortages of sodium hydroxide (like the worldwide shortage that occurred in the late 1980s). Soda ash is very plentiful in the United States and is obtained almost entirely from natural sources of trona ore . However, it is more expensive to mine soda ash than to produce 50 percent caustic, so increased use of soda ash is not likely to occur unless the price of caustic is relatively high (Chenier 1992, DOW 1999). Demand for sodium hydroxide may also be impacted as pulp and paper mills increasingly look for cost-effective ways to recycle sodium hydroxide from spent pulping liquor. Currently, however, most of these alternatives cannot compete on a capital and cost basis with caustic soda production, and will only impact demand when they become economically viable (EPA 1995a, CHEMWK 1999).

Chlorine is difficult to store and transport economically. As a result, chlorine and caustic soda are usually produced in close proximity to end-users (primarily chemical manufacturers and pulp and paper mills). Geographically, about 72 percent of chlorine production takes place in chlor-alkali facilities located along the Gulf Coast; other production occurs in the vicinity of pulp mills of the Southeast and Northwest.

6.1.1 Manufacture of Chlorine and Sodium Hydroxide

Chlorine and Sodium Hydroxide Are Co-Products of Brine Electrolysis

Chlorine was first discovered in 1774 by the German chemist Scheele, and was identified as an element in 1810 by an English scientist named Davy. Caustic soda, or sodium hydroxide, has been an important industrial chemical since1853. Until 1892 sodium hydroxide was produced by the reaction of slaked lime and soda ash. That year, the electrolysis of brine was discovered as a method of making both sodium hydroxide and chlorine. Since the 1960s electrolysis has been the predominant technique employed to manufacture these two important chemicals (Chenier 1992, Orica 1999).

Although electrolysis of brine is the primary production method, technologies for converting aqueous hydrochloric acid to chlorine are also used in the United States and Europe. A process to convert anhydrous hydrochloric acid to chlorine, developed jointly by Dupont and Kvarner Chemetics, was also recently unveiled. Similar technology is also being marketed in Europe by DeNora, an Italian firm.

Chlorine and sodium hydroxide are co-products that are produced in roughly equivalent amounts through electrolysis of common salt in a brine solution (about 1.1 tons of sodium hydroxide for every ton of chlorine produced). Hydrogen is also produced in equal molar amounts with chlorine and caustic. Chemical demand for hydrogen on the Gulf Coast is significant, and it is often transported by pipeline long distances to meet the needs of oil refineries. There is also an opportunity to use fuel cell technology to closely couple the hydrogen produced with electrical power units that can feed DC power to chlorine cells. Some demonstration units using this technology are in operation outside the United States (DOW 1999).

During electrolysis, two electrodes are immersed in a brine solution. When a source of direct current is attached to the electrodes, sodium ions begin to move toward the negative electrode (cathode) and chlorine ions toward the positive electrode (anode) (Sittig 1977, IND CHEM 1990, EPA 1995a, Orica 1999).

If the primary products from salt electrolysis remain in contact after formation, they can react with each other to form oxygenated compounds of chlorine. Three electrolytic processes are available and use different methods to keep the chlorine produced at the anode separated from the caustic soda and hydrogen produced at the cathode. In historical order, these cells include diaphragm cells, mercury cathode or "amalgam" cells, and membrane cells. Table 6-1 provides a comparison of the various aspects of the three electrolysis cells, including electrical energy consumption.

Diaphragm cells use a simple and economical brine system and require less electrical energy than mercury cells. A primary disadvantage of the diaphragm cell is the low concentration of the caustic soda solution, which requires several concentrative operations to achieve the purity needed for industrial use. The caustic contains 2 to 3 percent NaCl, requiring further purification for some industrial uses. The diaphragm cell is also known to be a source of pollution from asbestos fibers, the primary material of the diaphragm.

Because of these disadvantages, mercury cathode cells began to compete with diaphragm cells early in the twentieth century. Mercury cells produce a much purer and extremely concentrated caustic product that can be used without further treatment in most cases. However, mercury has extremely serious ecological impacts and when dispersed from chemical process effluents, can enter the food chain and lead to mercury poisoning in humans.

Membrane cells are the most environmentally benign of all the cell technologies, and have electricity requirements similar to those of diaphragm cells. The caustic solution produced is also essentially salt-free and more concentrated than that produced from diaphragm cells. Chemical companies have been slow to adopt membrane technology because of operational problems encountered in early installations, and because existing facilities are fully depreciated but still functional (IND CHEM 1990, Ayres 1997).

Diaphragm and mercury cells include an anode and cathode in contact with a brine solution. The membrane cell cathode is only in contact with 20 to 32 percent NaOH, with very low chloride content. Features that distinguish the cells from each other include the method used to keep the three major products separated and unable to mix (chlorine gas, sodium hydroxide, and hydrogen), and the resulting product concentration (see Figure 6-2). Hydrogen *must* be separated from the chlorine gas as mixtures of these two gases can be explosive.

Diaphragm cells account for 71 percent of domestic production, mercury cells for 12 percent, and membrane cells for 16 percent, with other methods producing about 1 percent (CI 1999). Total production costs for using cells are a function of raw materials, energy, operating costs, and capital depreciation. Today, membrane cell technology is only a small factor in new capacity. Membrane cell technology requires a secondary brine treatment, disposal or recycling of spent anolyte, and has relatively high capital costs. Most diaphragm cell producers continue to rebuild their existing diaphragm cells, rather than convert to membranes.

Chemical Reaction in Salt Electrolysis

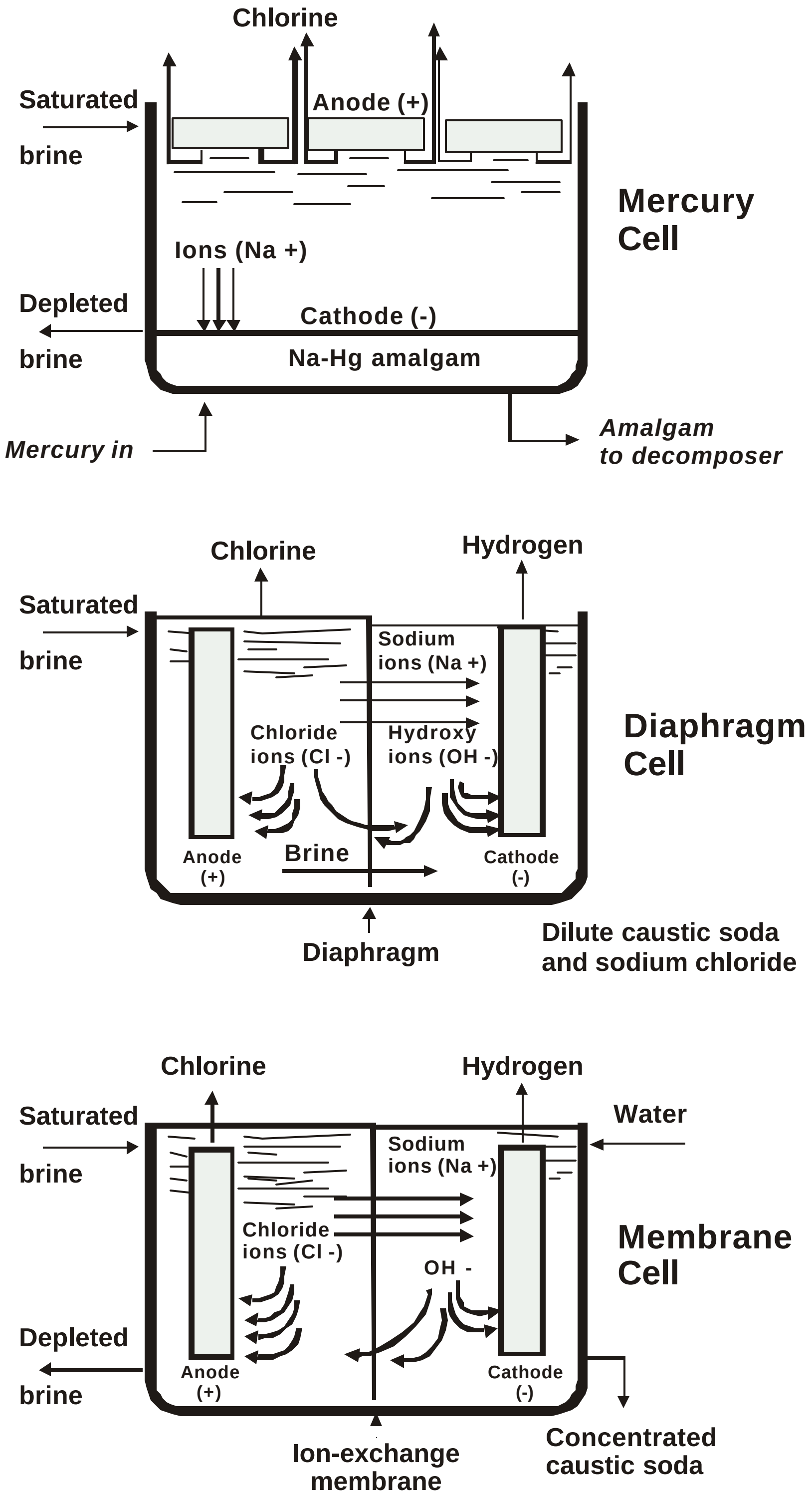
$$\underset{\text{Salt}}{2NaCl} + \underset{\text{Water}}{2\,H_2O} \rightarrow \underset{\text{Sodium Hydroxide}}{2NaOH} + \underset{\text{Chlorine}}{Cl_2} + \underset{\text{Hydrogen}}{H_2}$$

Table 6-1. Characteristics of Various Chlorine/Sodium Hydroxide Electrolysis Cells

Component	Diaphragm Cell	Mercury Cell	Membrane Cell
Cathode	Steel/steel coating with nickel	Mercury flowing over steel	Steel or nickel with a nickel-based coating
Anode	Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life	Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life	Titanium with ruthenium and titanium oxide coatings; iridium oxide added to improve performance and extend life
Diaphragm/ Membrane Material	Asbestos and fibrous polytetrafluoroethylene	None	Ion-exchange membrane (fluorinated polymers)
Cathode Product	10 to15% sodium hydroxide solution, containing 15 to17% salt (NaCl) (sent to evaporator for further processing); hydrogen gas	Sodium amalgam (sent for further processing through a decomposer cell)	30-33% sodium hydroxide solution (sent to evaporator for further processing); hydrogen gas
Anode Product	Chlorine gas containing some oxygen, salt, water vapor, and sodium hydroxide	Chlorine gas containing some oxygen, salt, and water vapor	Chlorine gas containing some oxygen, salt, and water vapor
Evaporator/Decom-position Product	50% sodium hydroxide solution containing 1% salt; solid salt from evaporator	50% sodium hydroxide solution; hydrogen gas	50% sodium hydroxide solution with very little salt
Electricity Consumption	2,550 to 2,900 kWh/ton chlorine gas	3,250 to 3,450 kWh/ton chlorine gas	2,530 to 2,600 kWh/ton chlorine gas

Sources: Sittig 1977, EPA 1990, EPA 1992b, EPA 1995b, DOW 1999.

Figure 6-2. Comparison of Chlorine/Sodium Hydroxide Electrolysis Cells (IND CHEM 1990, EPA 1995a)



In a **diaphragm cell**, multiple cells containing an anode and cathode pair are mounted vertically and parallel to each other (see Figure 6-3). Cathodes are usually a flat hollow steel mesh or perforated steel sheet covered with asbestos fibers and fibrous polytetrafluoro-ethylene (PFTE), and function as the diaphragm. The mix of fibers is typically about 75 percent asbestos and 25 percent PFTE. The anode is usually constructed of titanium plates covered with layers of Group VIII oxides with metal conductivity (ruthenium oxide, titanium oxide).

The overall process flow is shown in Figure 6-4. Brine flows continuously into the anode chamber and then through the diaphragm to the cathode. Chlorine gas is formed at the anodes, and sodium hydroxide solution and hydrogen gas are formed directly at the cathode. By allowing liquid to pass through to the cathode, but not the fine chlorine gas bubbles, the diaphragm prevents the mixing of hydrogen and chlorine. The diaphragm also limits the back-diffusion of hydroxide ions formed at the cathode. The back-migration of hydrogen

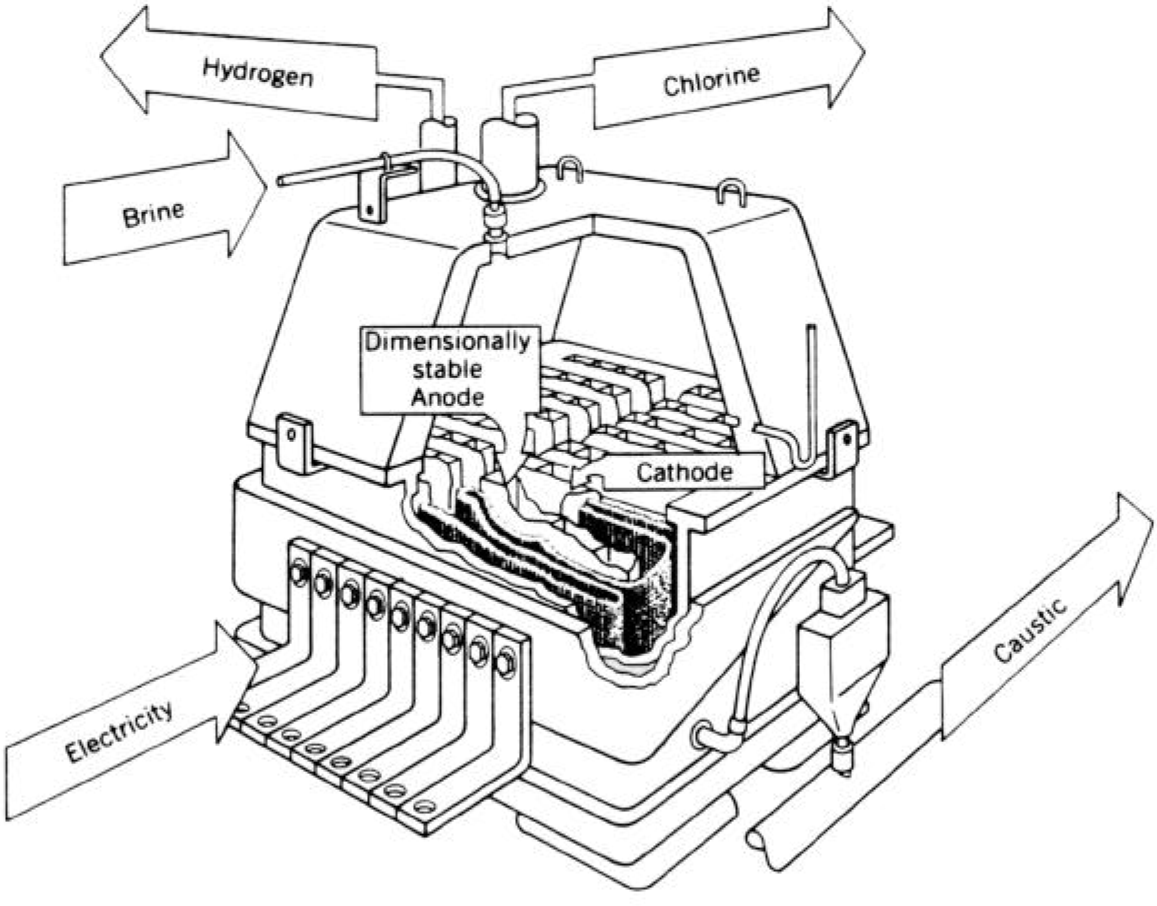


Figure 6-3. Typical Diaphragm Cell (Chenier 1992)

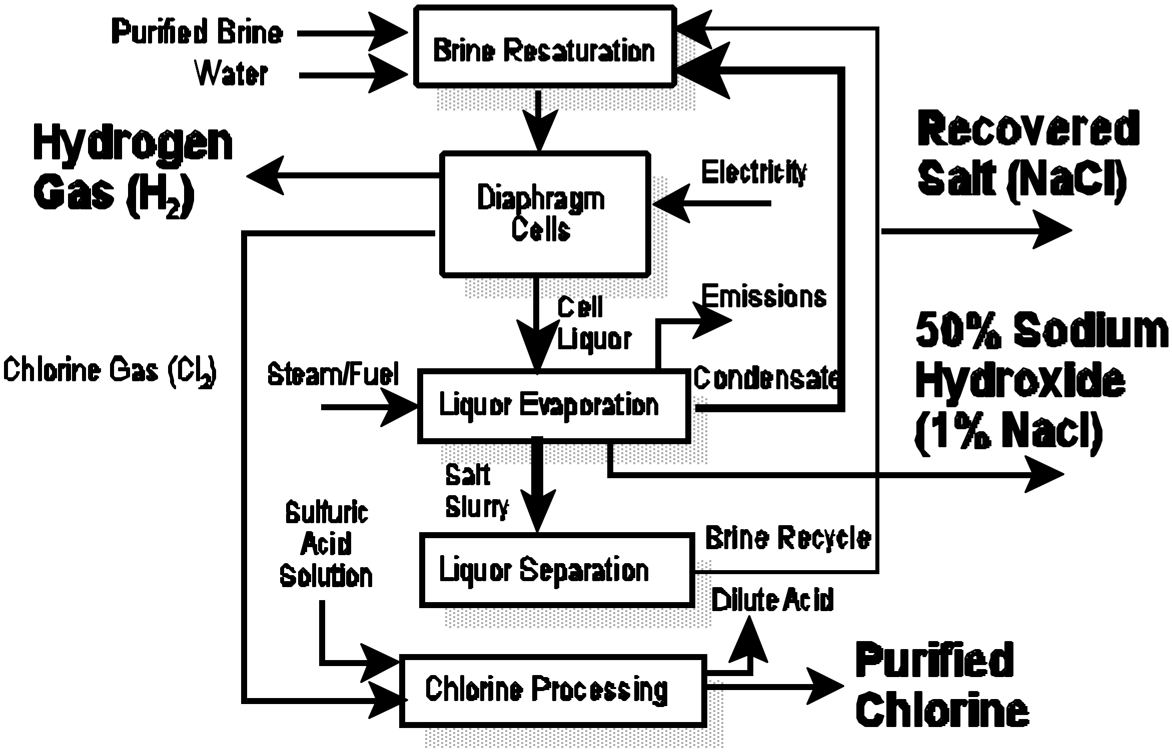


Figure 6-4. Diaphragm Cell Process (IND CHEM 1990, EPA 1992b, EPA 1995a)

Key Energy and Environmental Facts - Diaphragm Cell Process			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Electricity use: *4,649 Btu/lb chlorine* *2,725 kWhr/ton chlorine*	*Largest source - fugitive and point source emissions (chlorine gas, carbon dioxide, carbon monoxide, hydrogen, and Freon)*	*Largest source - wash water from chlorine processing (spent sulfuric acid, which is reclaimed and reused)*	*Scrapped diaphragms (lead, asbestos) and cell parts*

ions across the diaphragm represents the most inefficient aspect of the cell. The hydrogen gas and chlorine gas are drawn off separately from the top of the cell, and the residual brine containing 10 to 15 percent sodium hydroxide is taken from the bottom of the cell. After being de-humidified and cooled, the hydrogen is sent to storage. For a less pure product, the chlorine is first cooled (using a Freon or similar refrigerant), then washed with sulfuric acid in a packed column to dry it. The spent sulfuric acid is recovered and reused. Diaphragm cells will have dissolved air and carbon dioxide that enter with the brine, and leave the process via chlorine purification.

Demand for purified chlorine is high, and represents the largest share of chlorine produced. Purified chlorine is produced by compressing and cooling the gas to a liquid state. The liquid chlorine is fractionally distilled to remove chlorinated tars called “taffy” in the heavy fraction. The light fraction contains inerts such as air, carbon dioxide, and impurities such as bromine and iodine. Gaseous chlorine is transferred for use by pipeline or liquid chlorine is transported by rail car to offsite customers (DOW 1999). Rail cars and barges are generally purged with nitrogen to remove the chlorine and the chlorine is scrubbed in a tower with caustic. The resulting hypochlorite is treated with bisulfite and the effluent is treated for disposal.

The dilute sodium hydroxide solution contains residual salt and must undergo an evaporative process to produce a product at a usable concentration. The greatest disadvantage to diaphragm cells is the large amount of salt that must be removed at this stage. The need for salt columns, centrifuges, cyclones, clarifiers, and filters increases the complexity, capital cost, and energy use in a diaphragm-based caustic plant (DOW 1999).

Figure 6-5 shows the general arrangement for the concentration and production of the final sodium hydroxide product. This process concentrates the cell liquor from the diaphragm cell by evaporating water from the dilute caustic and separating the residual salt. The end result is a 50 percent sodium hydroxide solution with 1 percent residual sodium chloride.

The advantage of diaphragm cells is that they operate at a lower voltage than mercury cells and use less electricity. The brine feedstock can also be less pure than that required by mercury or membrane cells.

The **mercury cell** process (see Figure 6-6) uses two cells: an electrolyzer cell and a decomposer cell. The electrolyzer is essentially an electrolysis cell consisting of a large steel container shaped like a rectangular parallelogram with lined walls under a covering of flexible and anti-explosive rubber. A thin layer of mercury of about 3 millimeters in depth flows over the bottom of the steel container, serving as the cathode for the process. A saturated brine solution of about 25 percent NaCl by weight flows through the container above the mercury.

The anode, consisting of titanium sheet coated with ruthenium oxide and titanium oxide, is incorporated into the cell cover and suspended horizontally in the brine solutions. The height of the anodes in the brine is adjusted to obtain an optimum distance from the mercury cathode.

In the electrolyzer, chlorine evolves from the electrolytic decomposition of NaCl and moves upward through gas extraction slits in the cell cover. The chlorine gas is removed, purified, and sent to storage. Sodium ions are absorbed in the mercury layer, and the resulting sodium and mercury mixture (amalgam) is sent on to the decomposer cell.

The decomposer is essentially a short-circuited galvanic cell and consists of a small cylindrical steel tower divided into two parts. The amalgam is semi-decomposed in the upper section, and the decomposition is then completed in the lower part. Graphite serves as the anode and amalgam serves as the cathode. The amalgam and water flowing through the cell come into direct contact with the graphite. In both parts of the tower the amalgam is decomposed by water with the formation of sodium hydroxide, the reformation of mercury, and the production of hydrogen gas.

The mercury generated can be reused in the primary electrolytic cell. A relatively highly concentrated (50 percent) solution of sodium hydroxide is formed and can be used as it is or after it is further concentrated. The hydrogen gas is purified and used elsewhere in the plant.

The depleted brine leaving the cell contains a high concentration of NaCl (21 to 22 percent by weight). Dissolved chlorine is removed from this solution, and it is resaturated with NaCl and purified for re-use. The high concentration of sodium hydroxide solution produced and the absence of residual salt are the major advantages of the mercury cell. No further evaporation or salt separation is needed to produce the finished product. However, mercury cells require higher voltage than both diaphragm and membrane

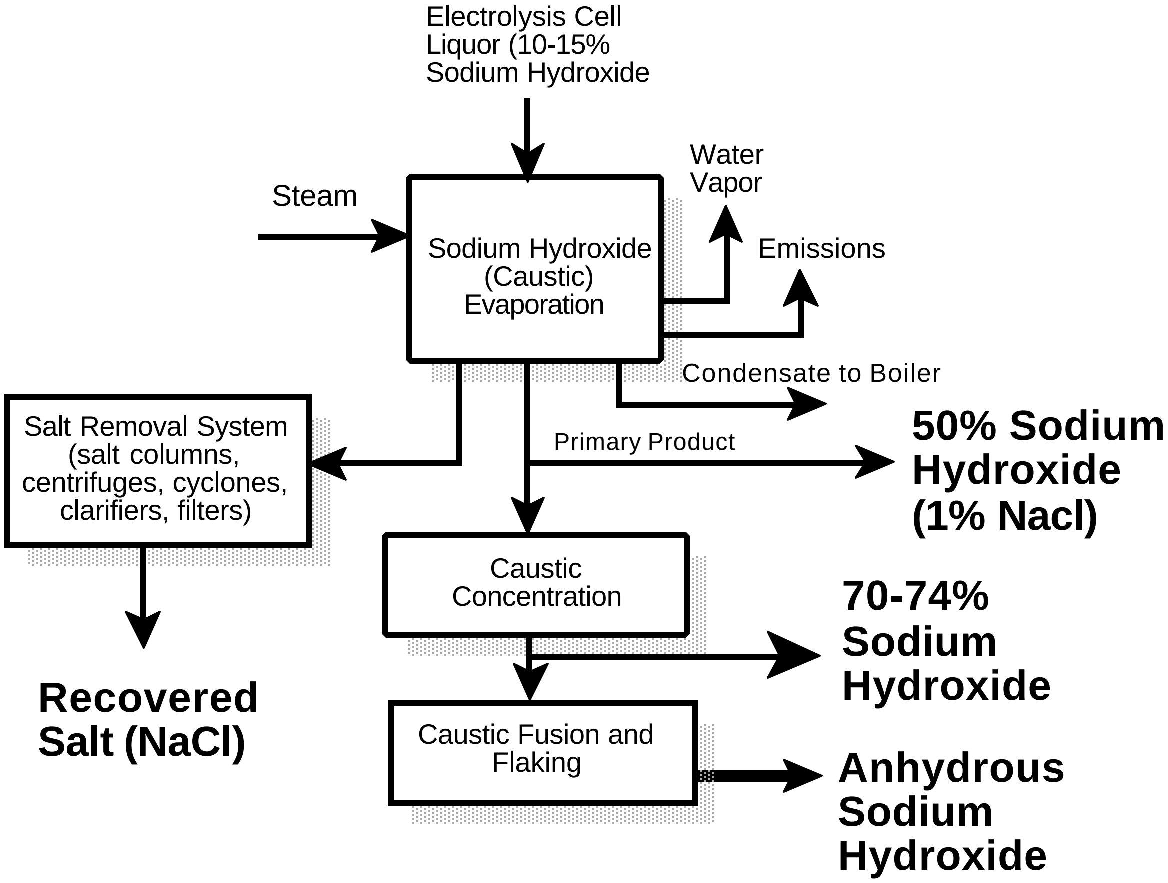


Figure 6-5. Sodium Hydroxide (Caustic) Evaporation Process
(Sittig 1977, IND CHEM 1990, Chenier 1992, EPA 1992b, Orica 1999)

cells, and use more energy. The process also requires as input a very pure brine solution without metal contaminants.

There are also environmental consequences to the use of mercury. Through contaminated effluents it can enter the food chain via plankton and accumulate in the adipose tissue of fish. Fish products can then act as a vehicle in conveying mercury compounds with neurotoxic properties (e.g., mercury poisoning). Tremendous improvements in the cell technology have significantly reduced emissions from these plants. However, precautions are taken to prevent releases of mercury to the environment. Liquid effluents from the mercury process are treated with sodium sulfide to remove mercury before any discharge. The mercury compounds are combined with brine treatment sludges for further treatment and disposal. Traces of mercury occur in caustic soda and hydrogen generated from the mercury cell process. These are removed from caustic soda by filtration. With hydrogen, they are removed by cooling followed by absorption with activated carbon (Orica 1999, DOW 1999).

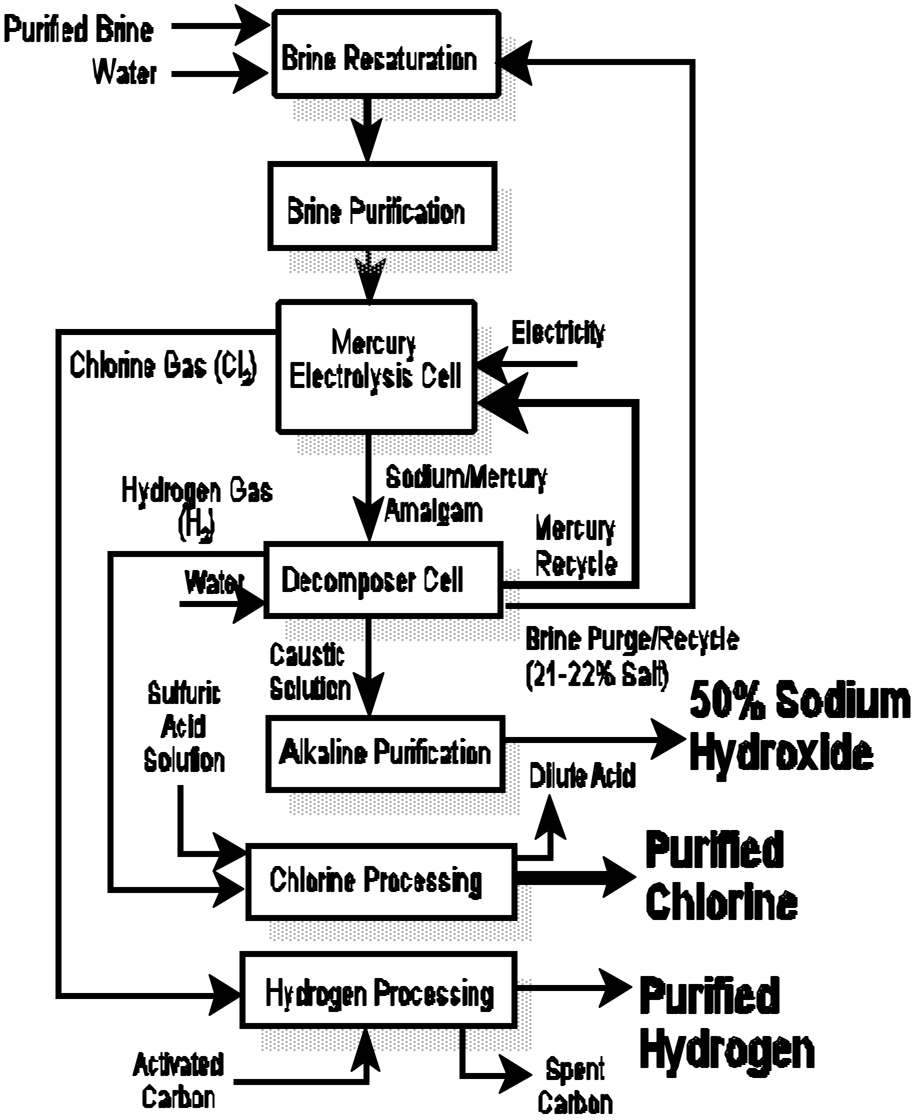


Figure 6-6. Mercury Cell Process
(IND CHEM 1990, EPA 1992b, EPA 1995a, Orica 1999)

Key Energy and Environmental Facts - Mercury Cell Process			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Electricity use: *Gross: 5,715 Btu/lb chlorine* *3,350 kWhr/ton chlorine*	*Largest source - fugitive and point source emissions (chlorine, Freon, and mercury)*	*Largest source - wastewater from brine pumps, cell wash water, sumps (small amounts of mercury); chlorine processing wastewater (sulfuric acid)*	*Spent graphite from decomposer cells, spent caustic filtration cartridges from the filtration of caustic soda solution, spilled mercury from sumps, and mercury cell "butters"*

In a **membrane cell** the anode and cathode are separated by a water-impermeable, ion-conducting membrane (see Figure 6-7). In this process the brine solution flows through the anode compartment and chlorine gas is generated at the anode. Sodium ions migrate through the membrane to the cathode compartment, where sodium hydroxide solution is flowing. Water hydrolizes at the cathode and releases hydrogen gas and hydroxide ions.

The combination of sodium and hydroxide ions produces sodium hydroxide which reaches a concentration of about 30 to33 percent before leaving the cell. The membrane preferentially passes positive sodium ions from the anode chamber to the cathode chamber. Negatively charged chloride and hydroxide ions are primarily rejected by the membrane. As a result, the sodium hydroxide solution typically contains less than 100 ppm NaCl. The depleted brine leaves the anode compartment and is resaturated with salt for reuse in the membrane cell.

Stainless steel or nickel is typically used as a cathode in the membrane cell. The cathodes are also often coated with a catalyst (nickel-sulfur, nickel-aluminum, nickel-nickel oxide, platinum group metals) to increase surface area and reduce the hydrogen evolution potential. Anodes are similar to those used in both diaphragm and mercury cells (ruthenium and titanium oxide on titanium).

The membrane's material and design are critical to cell operation. Membranes must maintain stability after exposure to both chlorine and strong caustic solution. They require low electrical resistance and must allow the transport of sodium ions but not chloride ions. Membrane materials currently in use are fluorinated polymers with pendant functional groups that make them ion-selective.

The advantage of membrane cells is the relatively pure sodium hydroxide solution produced and the lower electricity requirements than either diaphragm or mercury cells. In addition, membrane cells do not require the use of toxic materials (e.g., asbestos, mercury).

Disadvantages of the membrane cell include the need for processing of the chlorine gas to remove oxygen and water vapor, and for moderate evaporation to increase the concentration of the caustic solution. Another disadvantage is that the brine entering a membrane cell must be of very high purity to prevent contamination of the membrane, which requires costly purification of the brine prior to electrolysis. The membrane separator in these cells is expensive and easily damaged, and has a shorter lifetime than diaphragm and mercury separators.

6.1.2 Brine Production

Brine Production and Purification Are Required for All Cells

Regardless of the type of cell employed, a suitable brine must be prepared prior to entering the cell. Different levels of purification are required for the various cells, and some require removal of metals or other impurities.

Salt is obtained from the mining of natural deposits or from seawater (via solar evaporation), and contains impurities that must be removed before it can be used in the electrolytic cell. Impurities include primarily calcium, magnesium, barium, iron, aluminum, sulfates, and trace metals. Impurities can negatively affect the electrolytic cell by precipitating out and blocking or damaging membrane or diaphragm materials. Impurities can also poison the catalytic coating on the anode and cathode. In the case of the mercury cell, some trace metals (e.g., vanadium) can reduce efficiency and cause the production of potentially dangerous amounts of hydrogen gas. Impurities can also lead to the production of chlorinated compounds, a situation that can negatively impact cell performance (EPA 1995a).

The first phase of brine preparation includes the dissolution of sea salt and rock salt in a water and dilute brine mix (see Figure 6-8). The amount of material dissolved is a function of brine concentration, residence time, and temperature. In all cases the brine-solid salt mixture is allowed to reach equilibrium so that a saturated solution of approximately 25 weight percent is produced. Purification is accomplished through two steps:

- The addition of Na_2CO_3 (soda ash) and NaOH (caustic soda) to precipitate Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+} ions
- The addition of NaOCl if there is any ammonia present, and $CaCl_2$ to eliminate $(SO^{2-})_4$ ions

Sulfate levels in the brine can be controlled by adding calcium chloride to a side stream to precipitate the sulfate as calcium sulfate. The sludge containing this compound can then be removed and disposed of in a landfill. In some cases the brine is evaporated to a solid salt to remove sulfates (DOW 1999, Orica 1999).

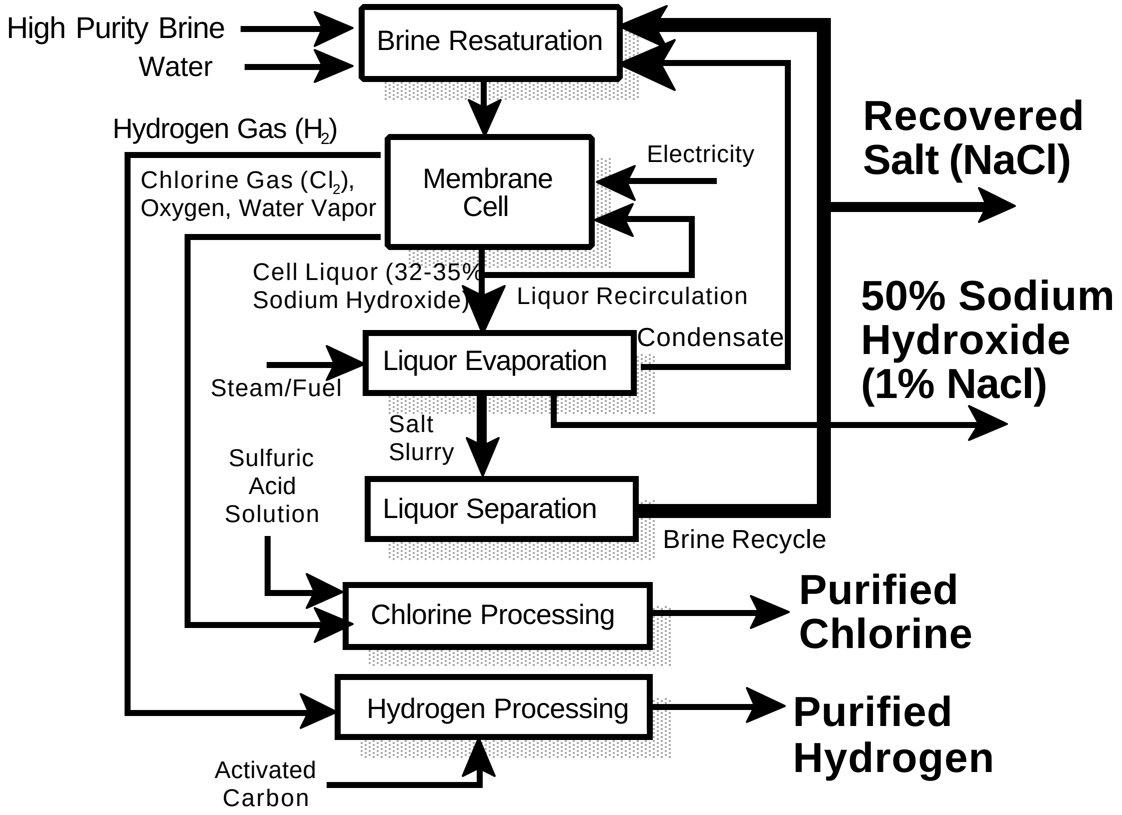


Figure 6-7. Membrane Cell Process
(IND CHEM 1990, EPA 1992b, EPA 1995a, Orica 1999)

Key Energy and Environmental Facts - Membrane Cell Process			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Electricity use: *4,375 Btu/lb chlorine* *2,565 kWhr/ton chlorine*	*Largest sources - fugitive and point source emissions (chlorine and Freon)*	*Largest source - chlorine processing wastewater (sulfuric acid); ion-exchange wash water.*	*Scrapped cell parts (used membranes, anodes, cathodes)*

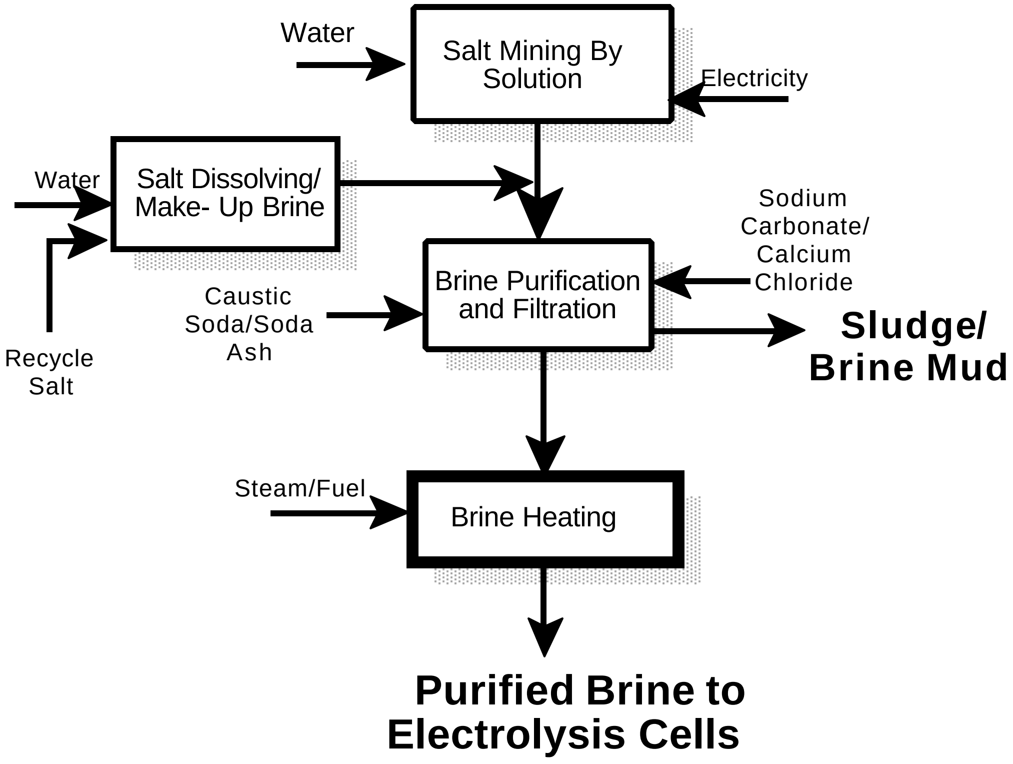


Figure 6-8. Brine Purification (Sittig 1977, EPA 1995a)

Key Energy and Environmental Facts - Brine Purification			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *1,424 Btu/lb chlorine*	*Largest sources - heater stack gas (CO, SOx, NOx, hydrocarbons, and particulates)*	*Recycle brine/brine purge*	*Brine mud (magnesium hydroxide, calcium carbonate, and barium sulfate; mercury in elemental form or as mercuric chloride; calcium sulfate; mercury sulfide)*

Purification creates a precipitation sludge (brine mud) that is washed to recover entrained sodium chloride and then disposed of in a landfill. If the mercury process is used, brine purification sludges will contain trace levels of mercury. In this case the sludge is treated with sodium sulfide to bind the mercury as mercury sulfide (an insoluble compound) and the sludge may be further bound by casting the sludge into concrete blocks. These blocks are tested for leachability and then disposed of into a controlled landfill.

The second step in brine preparation includes clarification, filtration, the addition of recycled brine, adjustment of pH value, and collection into tanks to feed the cells. Sand filters are commonly used for clarification and filtration.

Brine for mercury and diaphragm processes contains less than 4 parts per million (ppm)of calcium and 0.5 ppm of magnesium. Membrane cell processes require a more purified brine (less than 20 parts per billion of magnesium and calcium combined), which is usually passed through ion exchange columns to remove impurities to the needed level.

After purification the purified brine is heated to bring it up to the correct process temperature for each cell (Sittig 1977, EPA 1995a).

Table 6.2 Average Operating Conditions for Cells

Cell Type	Brine Concentration (g//l)	Limits on Impurities			Temperature °F	pH
		CaO	MgO	SO_2		
Diaphragm	315-330	5 ppm	0.8 ppm	0-0.3 g/l	194-221	10.5 - 11
Mercury	300-320	< 5 ppm	< 3 ppm	< 2g/l	165 -185	3-5
Membrane	~ 445	nil[a]	nil[a]	nil	165 - 195	7

[a] less than 20 parts per billion of calcium and magnesium combined.

Sources: IND CHEM 1990, Ayres 1997.

6.1.3 Manufacture of Soda Ash

Trona Ore Is the Feedstock for U.S. Soda Ash Production

In 1864, a Belgium chemist named Ernest Solvay invented the ammonia-soda or Solvay process for manufacture of **sodium carbonate (soda ash)**. While this process is still popular world-wide, in the United States all soda ash is produced from natural trona ore. In the 1940s, large deposits of this ore were found in Wyoming, which ultimately led to the closing of the last Solvay process plant in 1986. Conversion from the synthetic Solvay process to natural soda ash has been touted as one of the most successful transformations of the chemical industry during the 1970s and 1980s (Chenier 1992).

Trona ore, also called sesquicarbonate, is a complex of sodium, carbon, hydrogen, and oxygen ($2NA_2CO_3 \bullet NAHCO_3 \bullet 2H_20$). Upon heating it produces soda ash and carbon dioxide (see Figure 6-8). Approximately 1.8 tons of trona ore are required to produce one ton of soda ash.

There are four methods currently used to mine Wyoming trona ore: 1) solution mining, 2) room-and-pillar, 3) longwall, and 4) shortwall. In solution mining, dilute sodium hydroxide is injected into the trona ore to dissolve it. The solution is then treated with carbon dioxide to precipitate out sodium carbonate. The crystals are then dissolved again in water, precipitated with carbon dioxide, and filtered. Calcining is then employed to produce a dense soda ash.

All other methods of trona ore mining require blasting. A combination of prilled ammonium nitrate and fuel oil is the most commonly used blasting agent. In this process the trona ore is crushed, dissolved in water, filtered to remove insoluble impurities, subjected to vacuum crystallization to precipitate sesquicarbonate, then calcined to produce sodium carbonate.

Alternatively, a monohydrate process is employed. In this process crushed trona ore is calcined in a rotary kiln, yielding dense soda ash and carbon dioxide as byproducts. The calcined material is combined withwater to settle out impurities, and is then concentrated using triple effect evaporators or mechanical vapor recompression. For every pound of soda ash created in this process, 0.42 pounds of carbon dioxide are also produced and vented to the atmosphere (Brown 1996, EPA 1997g, EIA 1998).

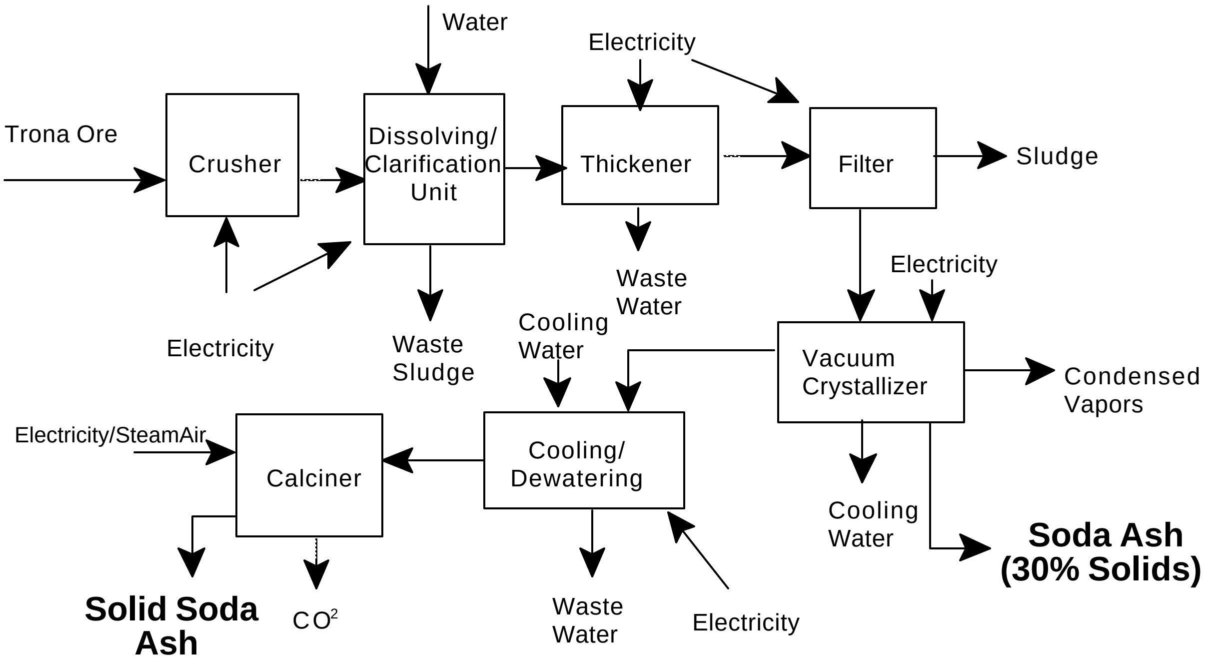


Figure 6-8. Manufacture of Soda Ash (Brown 1996)

Key Energy and Environmental Facts - Soda Ash Manufacture			
Energy	***Emissions***	***Effluents***	***Wastes/Byproducts***
Net Energy use: *3,393 Btu/lb*	*Largest sources - carbon dioxide, boiler emissions, particulates (soda ash)*	*Waste water*	*Clarification sludge, condensed vapors*

6.2 Summary of Inputs and Outputs

The following is a summary of inputs and outputs for important chemicals of the chlor-alkali industry.

Chlorine/Sodium Hydroxide

<u>Inputs:</u>	<u>Outputs:</u>
Purified Brine	Chlorine
Sulfuric Acid	Sodium Hydroxide
Hydrochloric Acid	Hydrogen
Water	Recycle Brine
Electricity	Water Vapor
Steam	Sludge
Cooling Water	Process Water
Anode/Cathode Materials	Salt

Soda Ash

Inputs:	Outputs:
Trona Ore	Soda Ash
Cooling Water	Carbon Dioxide
Steam/Fuel	Condensed Vapors
Electricity	Waste Sludge
Air	Waste Water

Brine Purification

Inputs:	Outputs:
Salt	Purified Brine
Water	Brine Mud/Sludge
Make-up Brine	
Sodium Carbonate	
Caustic Soda/ Soda Ash	
Steam/Fuel	
Electricity	

6.3 Energy Requirements

Electricity Is the Largest Energy Source Used for Production of Chlorine and Sodium Hydroxide

Data on the process energy used for the co-production of **chlorine and sodium hydroxide** is shown in Table 6-3. Electricity fuels the electrolysis process and represents the primary energy source. The amount of electricity required depends on the design of the cell, the design operating current, concentration of electrolytes, temperature, and pressure. The values shown in Table 6-3 represent an average of energy consumption for the various cell types. Energy in the form of fuels or steam is used primarily for evaporation of the sodium hydroxide solution to a useable state. Some fuels are also consumed in the production and purification of brine feedstock before it is sent to the electrolysis cell.

For every category, energy use for process heat is distributed according to the various fuel types used throughout the industry. Fuel distribution for 1997 was as follows: fuel oil and LPG - 3 percent; natural gas - 77 percent; coal and coke - 10 percent; other - 10 percent (CMA 1998). The "other" category includes any other fuel source (e.g., byproduct fuel gases).

Among the three types of chlorine cells, the mercury cell is the **most energy-intensive**, with electricity requirements of nearly 3600 kWhr per metric ton of chlorine. The membrane cell is the least energy-intensive in terms of both steam and electricity requirements. Steam requirements are less than half those of the diaphragm or mercury cell. Electricity requirements for the membrane cell are in the range of 2800 kWhr per metric ton of chlorine. The diaphragm cell is intermediate between these energy consumption ranges.

Overall, the **electrical energy requirements** for chlorine electrolysis cells are high, accounting for nearly 130 trillion Btu annually. When losses due to transmission and generation of electricity are considered, they reach nearly 400 trillion Btu annually. Thus, efficient operation of the cell is critical to optimized energy use and cost-effective production. Sources of energy losses in chlorine cells include anode or cathode overvoltage, too large a drop across the diaphragm, oxygen evolution on the anode, and failure to recover heat and energy from hydrogen, chlorine, and cell liquor streams.

A key consideration in membrane processes is the purity of the brine. Using very pure brine at an optimum flow rate minimizes blockage through the membrane and allows sodium to penetrate freely. Brine purity is also important in mercury cells. Impurities tend to increase hydrogen by-product and reduce the current efficiency.

Another issue is brine flowrate. Flowrates that are too high increase cell temperature and electrical conductivity of the medium. Brine rates that are too low create temperatures and high cell voltages that are higher than the most efficient voltage (3.1 to 3.7 volts) (Sittig 1977, Orica 1999).

Table 6-3. Estimated Energy Use in Manufacture of Chlorine/Sodium Hydroxide (Caustic Soda) Co-Products - 1997

Energy	Specific Energy[d] (Btu/lb of Cl_2)	Average Specific[d] Energy (Btu/lb of Cl_2)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	4,353 - 5,561	4,957	128.8
Fuel Oil and LPG[b]	62 - 112	87	2.3
Natural Gas	1,601 - 2,880	2,240	58.3
Coal and Coke	208 - 374	291	7.6
Other[c]	208 - 374	291	7.6
NET PROCESS ENERGY	6,432 - 9,301	7,867	204.5
Electricity Losses	9,039 - 11,547	10,293	267.6
Energy Export	0	0	0.0
TOTAL PROCESS ENERGY	**15,471 - 20,848**	**18,160**	**472.2**

[a] Does not Include losses incurred during the generation and transmission of electricity. Conversion factor: 3412 Btu/kWh. Based on range of cell currents for diaphragm, mercury, and membrane cells. Includes electricity for brine purification.

[b] Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.

[c] Includes net purchased steam, and any other energy source not listed (e.g., renewables).

[d] Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for diaphragm, mercury, and membrane cell technologies . Includes steam for brine purification and caustic evaporation (Sources: IND CHEM 1990, Brown 1996, Orica 1999, Ayres 1999).

[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values for chlorine (26 billion lbs) (CMA 1998). Note that 1.12 to1.43 lbs of sodium hydroxide are produced for every lb of chlorine.

At present, U.S. chlorine production is dominated by the diaphragm cell, and the use of the more energy-intensive mercury cell continues to decline. In Europe, however, production is still dominated by use of the mercury cell, although European manufacturers have committed to build no new mercury cells in the future (Ayres 1997).

Energy requirements for the manufacture of **sodium carbonate from trona ore** are shown in Table 6-4. A large share of the energy consumed is in the form of steam used for vacuum crystallization of the trona solution to produce an initial 30 percent solids solution of sodium carbonate, and for calcining. Electricity is used for dissolution, clarifying, thickening, precipitation, dewatering, and calcining. Overall electricity use for this process is very low, about 127 Btu per pound of solid product. Annual energy use for producing sodium carbonate, however, is considerable–over 80 trillion Btus–due to the large production value of nearly 24 billion pounds annually.

Table 6-4. Estimated Energy Use in Manufacture of Sodium Carbonate (Soda Ash) From Trona Ore - 1997

Energy	Average Specific[d] Energy (Btu/lb)	Total Industry Use[e] (10^{12} Btu)
Electricity[a]	127	3.0
Fuel Oil and LPG[b]	98	2.3
Natural Gas	2,515	59.6
Coal and Coke	327	7.7
Other[c]	327	7.7
NET PROCESS ENERGY	**3,393**	**80.4**
Electricity Losses	264	6.3
Energy Export	0	0.0
TOTAL PROCESS ENERGY	**3,657**	**86.7**

[a] Does not Include losses incurred during the generation and transmission of electricity.

[b] Includes ethane, ethylene, propane, propylene, normal butane, butylenes, and mixtures of these gases.

[c] Includes net purchased steam, and any other energy source not listed (e.g., renewables).

[d] Steam/fuel use estimated based on current distribution of fuels in chemical plants (CMA 1998). Values are based on published fuel use and electricity requirements for process based on trona ore (Brown 1996).

[e] Calculated by multiplying average energy use (Btu/lb) by1997 production values for sodium carbonate (23.7 billion lbs) (CMA 1998).

6.4 Air Emissions

Chlorine Gas and Freon Are Primary Air Emissions from Brine Electrolysis

Air emissions from brine electrolysis include chlorine gas and freon emissions (both fugitive and point source) and other vapors. Fugitive emissions arise from cells, scrubbers, and vents throughout the system. While individual leaks may be minor, the combination of fugitive emissions from various sources can be substantial. In 1995, nearly 3 million pounds of chlorine fugitive and point source emissions were reportedly released by the inorganic chemical industry (EPA 1997c). These emissions are controlled through leak-resistant equipment modifications, source reduction, and programs to monitor such leaks. Table 6-5 lists emission factors for mercury emissions from chlor-alkali production (EPA 1992b).

Diaphragm cells and **membrane cells** release chlorine as fugitive emissions from the cell itself and in process tail gases, which are wet-scrubbed with soda ash or caustic soda to remove chlorine. The spent caustic solution from this wash is neutralized and then discharged to water treatment facilities (EPA 1992b, EPA 1995a).

Mercury cells release small amounts of mercury vapor and chlorine gas from the cell itself. Process tail gases from chlorine processing, caustic soda processing, and hydrogen processing also release small amounts. Mercury is removed from the hydrogen gas stream by cooling followed by absorption with activated carbon. (EPA 1992b, Orica 1999).

Before the hazards of mercury emissions were fully recognized, actual emissions from mercury cells were as high as 3 kg per metric ton. Mercury emissions from chlorine production have dramatically declined in response to tighter regulations, better housekeeping, and technology improvements. However, there are considerable variations in the estimated mercury emissions from chlorine manufacture (Ayres 1997).

Varying Estimates of Mercury Emissions per Ton of Chlorine Manufactured

0.6 gram/metric ton (EPA 1992b)
0.47 gram/metric ton (Habersatter 1991)
2.47 gram/metric ton (Manzone 1993)
2.50 gram/metric ton (Euro Chlor 1995)
3.00 gram/metric ton (SRI 1989)

Brine preparation and caustic evaporation processes release emissions through the combustion of fuels in process heaters and in boilers that produce process steam. When operating in an optimum condition and burning cleaner fuels (e.g., natural gas, refinery gas), these heating units create relatively low emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbon emissions. A table of emission factors for combustion of fossil fuels in fired heaters and boilers is provided in Chapter 7, Supporting Processes.

During the production of **sodium carbonate**, particulate emissions are created from ore calciners, soda ash coolers and dryers, ore crushing, screening and transporting, and product handling and shipping. Combustion products (SO_x, NO_x, CO, particulates, and volatile hydrocarbons) are also emitted from direct-fired process heating units (ore calcining kilns, soda ash dryers). Little data is available on combustion products from these units, although emissions from similar equipment are categorized by the U.S. Environmental Protection Agency for the mineral industries, in *AP 42 Chapter 11, Mineral Products Industry*.

Production of sodium carbonate from trona ore also creates emissions of carbon dioxide, a suspected greenhouse gas. Emission factors for carbon dioxide emitted from this process are given in Table 6-6. Additional carbon dioxide may be emitted as sodium carbonate is processed in other manufacturing processes (glass-making, water treatment, flue gas desulfurization, soap and detergent production, pulp and paper making). Data is listed on releases of carbon dioxide from these processes.

According to a recent study (EIA 1998), approximately 113 metric tons of carbon are released for every 1000 metric tons of soda ash consumed in glass manufacturing or flue gas desulfurization. The same source indicates about 97 million metric tons of carbon released for every 1000 tons of trona ore produced annually for sodium carbonate production.

In 1997, reported annual emissions of carbon dioxide from manufacture of sodium carbonate were 1.08 million metric tons; emissions from use of sodium carbonate were 0.86 million metric tons (EIA 1998). More than 88 percent of emissions from the use of sodium carbonate were associated with flue gas desulfurization.

Controlled and uncontrolled emissions of filterable and total particulate matter from sodium carbonate production processes are shown in Table 6-7. Emissions of particulates from calciners and dryers are most often controlled by venturi scrubbers, electrostatic precipitators, or cyclones. The high moisture content of exiting gases makes it difficult to use baghouse-type filters. Control of particulates from ore and product handling systems, however, is often accomplished by baghouse filters or venturi scrubbers. These are essential to the cost-effectiveness of the process as they permit capture and recovery of valuable product.

Table 6-5 Mercury Emissions from Chlorine/Caustic Soda Manufacture

Source	Mercury Gas (lb/ton of chlorine produced)	Mercury Gas (grams/metric ton of chlorine produced)
Uncontrolled Hydrogen vent	0.0033	0.17
Controlled Hydrogen vents	0.0012	0.6
End Box	0.010	5.0

Source : EPA 1992b.

Table 6-6. Uncontrolled Emission Factors for Carbon Dioxide from Sodium Carbonate Production

Process	lb CO_2/ton of sodium carbonate
Trona ore process: rotary ore calciner	310
Trona ore process: fluid bed calciner	180
Rotary soda ash dryers	130

Source: EPA 1997g.

Table 6-7 Particulate Emission Factors for Sodium Carbonate Manufacture

Source	Controlled Emissions (lb/ton of sodium carbonate)		Uncontrolled Emissions (lb/ton of sodium carbonate)
	Filterable	Total	
Ore mining	0.0033	no data	3.3
Ore crushing and screening	0.0021	0.0035	3.5
Ore transfer	0.0002	0.0002	0.2
Trona ore process: rotary calciner	0.72	0.73	72
Trona ore process: fluid bed calciner	0.043	no data	4.3
Rotary soda ash dryers	0.50	0.52	50
Fluid bed soda ash dryers/coolers	0.030	0.39	3.0
Soda ash screening	0.019	0.026	19
Soda ash storage/loading/unloading	0.0041	0.0051	5.2

Source: EPA 1997g.

6.5 Effluents

Wastewater Is Treated To Remove Chlorine and Acids Prior to Discharge

Wastewater from **diaphragm and membrane cells** originates from caustic evaporation, chlorine drying, washing of the ion-exchange resin, and from purification of salt recovered from evaporators.

Caustic evaporation, where the sodium hydroxide solution is concentrated to a 50 or 70 percent solution, evaporates about 5 tons of water per ton of 50 percent caustic soda produced. The water vapor from the evaporators is condensed, and in the case of the diaphragm process, will contain about 15 percent caustic soda solution and a relatively high salt content of 15 to 17 percent. If sodium sulfate is not removed during the brine purification process, salt recovered from evaporators may be recrystallized to avoid buildup of sulfate in the brine. If the salt is recrystallized, the wastewater may contain sodium sulfates.

Wastewater from membrane processes contains caustic soda solution, but is virtually free of salt or sodium sulfates. Wastewater from caustic soda processing is usually neutralized with hydrochloric acid, then lagooned and discharged to and or to receiving ponds.

During **chlorine gas processing**, water vapor is removed by scrubbing with concentrated sulfuric acid. Between 6 kilograms and 35 kilograms of 79 percent sulfuric acid wastewater is generated per 1000 kilograms of chlorine produced (EPA 1995a). Most of this wastewater is shipped off-site for processing into concentrated sulfuric acid or for use in other processes. The remainder is used for pH control or discharged to water treatment facilities for disposal (EPA 1995a).

Ion-exchange wash water from **membrane cell** processes usually contains dilute hydrochloric acid with small amounts of dissolved calcium, magnesium, and aluminum chloride. This wastewater is usually treated along with other acidic wastewaters by neutralization.

Wastewater streams are generated from mercury cells during the chlorine drying process, brine purge, and from other sources. Mercury is present in the brine purge and other sources (floor sumps, cell wash water) in small amounts. This mercury is generally present in concentrations ranging from 0 to 20 parts per million, and is precipitated out using sodium hydrosulfide to form mercuric sulfide. The mercuric sulfide is removed through filtration before the water is discharged (EPA 1995a, Orica 1999).

Sodium carbonate manufacture creates significant volumes of wastewater that must be treated prior to discharge or recycling to the process. These may contain both mineral (e.g., shale) and salt impurities (EPA 1997g). Limitations for toxic or hazardous compounds contained in these wastewaters are given by the U.S. Environmental Protection Agency in 40 CFR, Chapter 1, Part 415, which was originally promulgated in 1974 and has been revised several times since then. The chemicals in the chlor-alkali industry and sodium carbonate are covered under Subparts F and O. Specific limitations for restricted compounds and total suspended solids (TSS) are shown in Tables 6-8 through 6-10. “BPT Standards” refers to the use of the best practicable control technology currently available. “BAT” refers to the best available technology economically achievable. “NSPS” refers to new source performance standards that apply to new process water impoundment or treatment facilities.

Table 6-10 provides BPT limitations only for the production of **sodium chloride** (the primary input to chlor-alkali manufacture) by solution brine-mining. In this process water is pumped into a salt deposit and a saturated salt solution is removed that is about one-third salt. Provisions are that no process wastewater pollutant may be returned to navigable waters. The exception is unused bitterns (saturated brine solution remaining after precipitation of sodium chloride), which may be returned to the body of water from which the process brine solution was originally withdrawn.

Table 6-8. Effluent Pretreatment Standards: Mercury Cells			
Effluent	**BPT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**BAT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**NSPS Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**
TSS	0.32	--	0.32
Mercury	0.00014	0.00010	0.00010
Total Residual Chlorine	--	0.0019	0.0019
pH	6-9	6-9	6-9

Source: 40 CFR Chapter 1, Part 415, Inorganic Chemicals Manufacturing Point Source Category, Subpart F.

Table 6-9. Effluent Pretreatment Standards: Diaphragm Cells			
Effluent	**BPT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**BAT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**	**NSPS Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**
TSS	0.51	--	0.51
Copper	0.0070	0.0049	0.0019
Lead	0.010	0.0024	0.0019
Nickel	0.0056	0.0037	--
Total Residual Chlorine	--	0.0079	0.0079
pH	6-9	6-9	6-9

Source: 40 CFR Chapter 1, Part 415, Inorganic Chemicals Manufacturing Point Source Category, Subpart F.

Table 6-10. Effluent Pretreatment Standards: Production of Sodium Chloride by Solution Brine-Mining	
Effluent	**BAT Standards: Average of Daily Values for 30 Consecutive Days (lb/1000 lb product)**
TSS	0.17
pH	6-9

Source: 40 CFR Chapter 1, Part 415, Inorganic Chemicals Manufacturing Point Source Category, Subpart P.

6.6 Hazardous Wastes and Byproducts

Brine Mud Constitutes the Largest Solid Waste Stream from Chlor-Alkali Production

Brine purification results in brine mud, one of the largest waste streams from the chlor-alkali industry. About 30 kilograms of brine mud are generated for every 1000 kilograms of chlorine produced, but this varies with the purity of the salt used to produce the brine. Pre-purified salts, for example, will generate only about 0.7 to 6.0 kilograms per 1000 kilograms of chlorine produced. The brine mud contains a variety of compounds, typically magnesium hydroxide and calcium carbonate formed during the addition of compounds to purify the brine. The sludge or brine mud containing these impurities must be disposed of in a landfill (EPA 1995a, Orica 1999). If a mercury process is being used, the brine mud may contain trace levels of mercury. In this case, the sludge is treated with sodium sulfide to create mercury sulfide, an insoluble compound. The sludge is further treated by casting it into concrete blocks, which are treated for leachability and sent to a controlled landfill.

Both **diaphragm and membrane cell** processes generate solid wastes from scrapping of cell parts (cell covers, piping, used diaphragms, used membranes, cathodes, and anodes). Discarded cell parts are landfilled on-site or shipped off-site for disposal. Used cathodes and anodes are shipped off-site to a third party recovery facility. Depending on the cell technology, the cathodes may be refurbished and reused, particularly those made of nickel. The anodes for diaphragm cells are refurbished and rec-coated with RuO_2/TiO_2 and returned to service.

Solid wastes from **mercury cells** include spent graphite from decomposer cells, spent caustic filtration cartridges from the filtration of caustic soda solution, spilled mercury from sumps, and mercury cell "butters." (The latter are semi-solid amalgams of mercury with barium or iron, formed when an excess of barium is used during purification). Mercury is recovered from these wastes where possible, and the remainder is disposed of in secure landfills to prevent migration of mercury, which can cause significant damage to the environment.

Mercury cell brine muds may also contain mercury in elemental form or as mercuric chloride. These muds are considered hazardous and must be disposed of in a RCRA Subtitle C landfill after treatment with sodium sulfide, which creates an insoluble sulfide compound (EPA 1995a). Other brine muds are segregated and stored in lagoons, which are periodically dredged or drained and covered over. The dredgings are usually landfilled off-site.

The **processing of hydrogen gas** from mercury cells also creates hazardous waste. In this process, small amounts of mercury present in the hydrogen gas are extracted by cooling the gas. A large part of the condensed mercury is removed in this fashion and returned to the electrolytic cell. Some facilities use activated carbon treatment to further purify the hydrogen of mercury, and the spent carbon is shipped off-site for disposal as a hazardous waste.

The effluents and solid wastes and hazardous wastes from chlor-alkali production are summarized in Table 6-11. Specific wastes from chlor-alkali manufacture that are listed by the EPA as **hazardous** as shown in Table 6-12. Most of the hazardous wastes are generated from the mercury cell process.

The dissolving and clarification steps in **sodium carbonate production** create a waste sludge containing non-hazardous impurities, such as salts and minerals. This sludge is disposed of in landfills.

Table 6-11. Summary of Effluents and Solid and Hazardous Waste Streams from Chlorine/Sodium Hydroxide Production

Source	Diaphragm/ Membrane Cells	Mercury Cells	Caustic Evaporation	Chlorine/ Hydrogen Processing	Brine Purification
Wastewater	Ion-exchange wash water, cell wash water, brine purge	Brine pumps, cell wash water, sumps (small amounts of mercury)	5 tons water/ton 50% caustic soda solution	79% sulfuric acid solution (6 to 35 kg/1000 kg chlorine)	
Solid Wastes	Scrapped cell parts (cell covers, piping, used diaphragms, used membranes, cathodes, and anodes)	Spent caustic filtration cartridges from the filtration of caustic soda solution, spent graphite from decomposer cells			Brine mud (0.7 to 30 kg/1000 kg chlorine)
Hazardous Wastes	Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process (K073)	Spilled mercury from sumps, and mercury cell “butters”; wastewater treatment sludge (K106)		Spent activated carbon	Brine mud containing mercury (K071)

Source: EPA 1995a.

Table 6-12. Hazardous Wastes from Chlor-Alkali Manufacture

Waste Classification	Description	Hazardous Constituents
K071	Brine purification muds from the mercury cell process in chlorine production, where separately pre-purified brine is not used	Mercury
K073	Chlorinated hydrocarbon waste from the purification step of the diaphragm cell process	Chloroform, carbon tetrachloride, hexachloroethane, trichloroethane, tetrachloroethylene, dichloroethylene, 1,1,2,2-tetrachloroethane
K106	Wastewater treatment sludge from the mercury cell process in chlorine production	Mercury

Source: BNA 1995.