

8.11 Chlor-Alkali

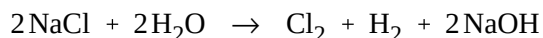
8.11.1 General¹⁻²

The chlor-alkali electrolysis process is used in the manufacture of chlorine, hydrogen, and sodium hydroxide (caustic) solution. Of these 3, the primary product is chlorine.

Chlorine is 1 of the more abundant chemicals produced by industry and has a wide variety of industrial uses. Chlorine was first used to produce bleaching agents for the textile and paper industries and for general cleaning and disinfecting. Since 1950, chlorine has become increasingly important as a raw material for synthetic organic chemistry. Chlorine is an essential component of construction materials, solvents, and insecticides. Annual production from U. S. facilities was 9.9 million megagrams (Mg) (10.9 million tons) in 1990 after peaking at 10.4 million Mg (11.4 million tons) in 1989.

8.11.2 Process Description¹⁻³

There are 3 types of electrolytic processes used in the production of chlorine: (1) the diaphragm cell process, (2) the mercury cell process, and (3) the membrane cell process. In each process, a salt solution is electrolyzed by the action of direct electric current that converts chloride ions to elemental chlorine. The overall process reaction is:



In all 3 methods, the chlorine (Cl_2) is produced at the positive electrode (anode) and the caustic soda (NaOH) and hydrogen (H_2) are produced, directly or indirectly, at the negative electrode (cathode). The 3 processes differ in the method by which the anode products are kept separate from the cathode products.

Of the chlorine produced in the U. S. in 1989, 94 percent was produced either by the diaphragm cell or mercury cell process. Therefore, these will be the only 2 processes discussed in this section.

8.11.2.1 Diaphragm Cell -

Figure 8.11-1 shows a simplified block diagram of the diaphragm cell process. Water (H_2O) and sodium chloride (NaCl) are combined to create the starting brine solution. The brine undergoes precipitation and filtration to remove impurities. Heat is applied and more salt is added. Then the nearly saturated, purified brine is heated again before direct electric current is applied. The anode is separated from the cathode by a permeable asbestos-based diaphragm to prevent the caustic soda from reacting with the chlorine. The chlorine produced at the anode is removed, and the saturated brine flows through the diaphragm to the cathode chamber. The chlorine is then purified by liquefaction and evaporation to yield a pure liquified product.

The caustic brine produced at the cathode is separated from salt and concentrated in an elaborate evaporative process to produce commercial caustic soda. The salt is recycled to saturate the

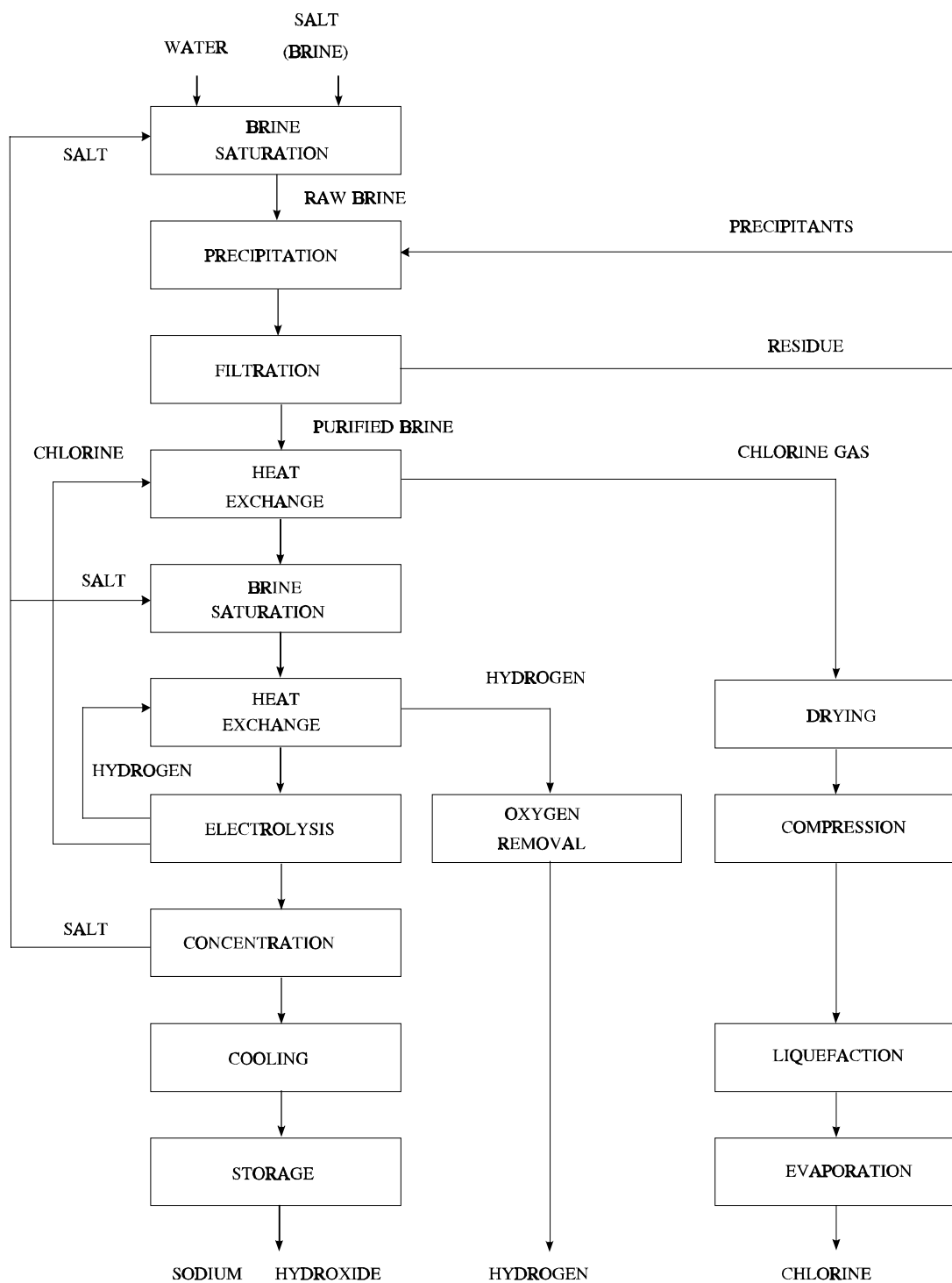


Figure 8.11-1. Simplified diagram of the diaphragm cell process.

dilute brine. The hydrogen removed in the cathode chamber is cooled and purified by removal of oxygen, then used in other plant processes or sold.

8.11.2.2 Mercury Cell -

Figure 8.11-2 shows a simplified block diagram for the mercury cell process. The recycled brine from the electrolysis process (anolyte) is dechlorinated and purified by a precipitation-filtration process. The liquid mercury cathode and the brine enter the cell flowing concurrently. The electrolysis process creates chlorine at the anode and elemental sodium at the cathode. The chlorine is removed from the anode, cooled, dried, and compressed. The sodium combines with mercury to form a sodium amalgam. The amalgam is further reacted with water in a separate reactor called the decomposer to produce hydrogen gas and caustic soda solution. The caustic and hydrogen are then separately cooled and the mercury is removed before proceeding to storage, sales, or other processes.

8.11.3 Emissions And Controls⁴

Tables 8.11-1 and 8.11-2 are a summaries of chlorine emission factors for chlor-alkali plants. Factors are expressed in units of kilograms per megagram (kg/Mg) and pounds per ton (lb/ton). Emissions from diaphragm and mercury cell plants include chlorine gas, carbon dioxide (CO₂), carbon monoxide (CO), and hydrogen. Gaseous chlorine is present in the blow gas from liquefaction, from vents in tank cars and tank containers during loading and unloading, and from storage tanks and process transfer tanks. Carbon dioxide emissions result from the decomposition of carbonates in the brine feed when contacted with acid. Carbon monoxide and hydrogen are created by side reactions within the production cell. Other emissions include mercury vapor from mercury cathode cells and chlorine from compressor seals, header seals, and the air blowing of depleted brine in mercury-cell plants. Emissions from these locations are, for the most part, controlled through the use of the gas in other parts of the plant, neutralization in alkaline scrubbers, or recovery of the chlorine from effluent gas streams.

Table 8.11-3 presents mercury emission factors based on 2 source tests used to substantiate the mercury national emission standard for hazardous air pollutants. Due to insufficient data, emission factors for CO, CO₂, and hydrogen are not presented here.

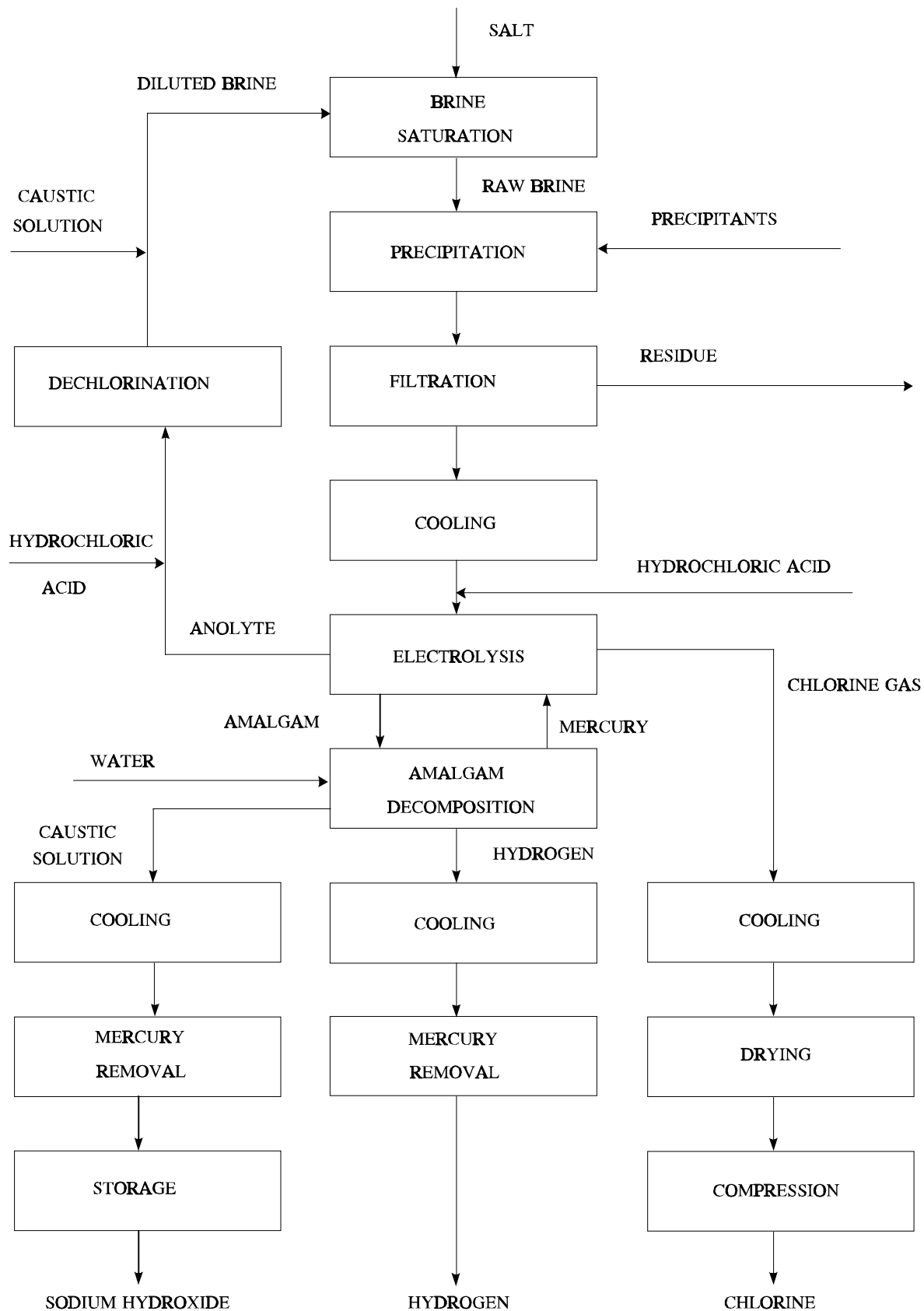


Figure 8.11-2. Simplified diagram of the mercury cell process.

Table 8.11-1 (Metric Units). EMISSION FACTORS FOR CHLORINE FROM
CHLOR-ALKALI PLANTS^a

EMISSION FACTOR RATING: E

Source	Chlorine Gas (kg/Mg Of Chlorine Produced)
Liquefaction blow gases	
Diaphragm cell (SCC 3-01-008-01)	10 - 50
Mercury cell (SCC 3-01-008-02)	20 - 80
Water absorber ^b (SCC 3-01-008-99)	0.830
Caustic scrubber ^b (SCC 3-01-008-99)	0.006
Chlorine loading	
Returned tank car vents (SCC 3-01-008-03)	4.1
Shipping container vents (SCC 3-01-008-04)	8.7
Mercury cell brine air blowing (SCC 3-01-008-05)	2.7

^a Reference 4. SCC = Source Classification Code.

^b Control devices.

Table 8.11-2 (English Units). EMISSION FACTORS FOR CHLORINE FROM
CHLOR-ALKALI PLANTS^a

EMISSION FACTOR RATING: E

Source	Chlorine Gas (lb/ton Of Chlorine Produced)
Liquefaction blow gases	
Diaphragm cell (SCC 3-01-008-01)	20 - 100
Mercury cell (SCC 3-01-008-02)	40 - 160
Water absorber ^b (SCC 3-01-008-99)	1.66
Caustic scrubber ^b (SCC 3-01-008-99)	0.012
Chlorine loading	
Returned tank car vents (SCC 3-01-008-03)	8.2
Shipping container vents (SCC 3-01-008-04)	17.3
Mercury cell brine air blowing (SCC 3-01-008-05)	5.4

^a Reference 4. SCC = Source Classification Code.

^b Control devices.

Table 8.11-3 (Metric And English Units). EMISSION FACTORS FOR MERCURY FROM
MERCURY CELL CHLOR-ALKALI PLANTS^a

EMISSION FACTOR RATING: E

Type Of Source	Mercury Gas	
	kg/Mg Of Chlorine Produced	lb/ton Of Chlorine Produced
Hydrogen vent (SCC 3-01-008-02)		
Uncontrolled	0.0017	0.0033
Controlled	0.0006	0.0012
End box (SCC 3-01-008-02)	0.005	0.010

^a SCC = Source Classification Code.

References For Section 8.11

1. *Ullmann's Encyclopedia Of Industrial Chemistry*, VCH Publishers, New York, 1989.
2. The Chlorine Institute, Inc., Washington, DC, January 1991.
3. *1991 Directory Of Chemical Producers*, Menlo Park, California: Chemical Information Services, Stanford Research Institute, Stanford, CA, 1991.
4. *Atmospheric Emissions From Chlor-Alkali Manufacture, AP-80*, U. S. Environmental Protection Agency, Research Triangle Park, NC, January 1971.
5. *B. F. Goodrich Chemical Company Chlor-Alkali Plant Source Tests, Calvert City, Kentucky*, EPA Contract No. CPA 70-132, Roy F. Weston, Inc., May 1972.
6. *Diamond Shamrock Corporation Chlor-Alkali Plant Source Tests, Delaware City, Delaware*, EPA Contract No. CPA 70-132, Roy F. Weston, Inc., June 1972.