

# Chlor-Alkali Manufacturing Processes

More than 95 percent of world chlorine production is achieved using the chlor-alkali process. This process applies a direct electric current to a brine (water and salt) solution to produce chlorine and hydrogen gas and sodium hydroxide, or caustic soda solution. Chlorine is produced and collected at the negatively charged electrode, known as the cathode, and hydrogen and caustic soda are produced and collected at the positively charged electrode, known as the anode. The first commercial production of chlorine using electrolysis was in 1888.

There are three main electrolytic production technologies used in the chlor-alkali industry – the diaphragm cell, mercury cell and membrane cell. Each technology incorporates a different way of keeping chlorine separated from hydrogen and caustic soda.

Currently, it is estimated that 70 percent of all chlorine is produced using mercury and diaphragm cells in the approximately 650 plants located around the world. Diaphragm technology predominates in the United States, Russia and China, while 54 percent of the chlor-alkali plants in Western Europe use the mercury cell process.

Due to economic and ecological advantages, the use of membrane cells in Europe and the United States increased from 11 and 10 percent of production capacity, respectively, in 1996 to 21 and 19 percent, respectively, in 2000. All plants in Japan use this technology.

Regardless of the technology used, cells are arranged in series electrically, with each circuit consisting of several rows of cells. Two adjacent rows of cells may share a brine distribution line and collection systems for chlorine and hydrogen. Each row is equipped with a pipeline on its aisle side for collecting caustic. Brine flow is individually controlled for each cell.

Electrolysis occurs when direct current electricity flows between anodes (positive electrodes) and cathodes (negative electrodes), through the brine. Chlorine then collects at the plates, bubbling up through the brine, and is carried away by the chlorine-collecting system. (For details on chlorine's many uses,

please see insert *Chlorine Chemistry's Role in Our Daily Lives*.) The other gas generated, hydrogen, is similarly collected. The sodium ion concentration builds up in the brine and is eventually removed as caustic

soda (sodium hydroxide). (For details on caustic soda's many uses, please see insert *Chlorine's Important Co-product: Caustic Soda*.)

Chlorine gas, at approximately 93.3°C (200°F), is water-saturated when it exits the cell. Cooling the gas removes some moisture. Further drying is accomplished using sulfuric acid. After further purification, compression, and cooling, the gas is liquefied under refrigeration and transferred to storage containers for transportation, or it is sent to other plants on-site without liquefaction.

Since 1970, activated titanium anodes have replaced the graphite anodes used in the diaphragm and mercury cell processes. These anodes have improved productivity and are more environmentally acceptable than the formerly used carbon electrodes.

## ENERGY EFFICIENCY

- The chlorine industry has reduced power usage by 50 percent
- Using co-generation results in efficiencies that almost double that of power acquired from utilities.

## Co-generation of electricity

The chlorine chemistry industry has long employed co-generation, an energy efficiency attained through the co-production of electricity and process heat (also called combined heat and power or CHP) from a plant that is located at the chemical manufacturing facility. Significant efficiencies are gained from the productive use of the by-product heat, usually in the form of steam (this by-product heat is typically not recovered at a utility-type power plant). While the efficiency gains can vary widely among individual sites, at its peak co-generation can be over 70 percent efficient.

In addition, hydrogen gas produced as a by-product of chlorine is captured and used as a fuel in these on-site power stations. Hydrogen is considered a "clean fuel" – meaning it does not emit carbon dioxide, one of the greenhouse gases. Recovering and burning the hydrogen also preserves existing reserves such as coal, oil and natural gas. Considering the vital and growing role of energy in global economic and environmental issues, the chlorine industry is likely to increase its use of co-generation.



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## Chlorine and Caustic Soda Chlor-Alkali Manufacturing Processes

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## Diaphragm Cell

The diaphragm cell is the dominant electrolytic technology used in the United States and Canada. The cell design is characterized by anode and cathode separation by a diaphragm consisting of a deposited layer of asbestos fibre mixed with an additive such as Teflon® (polytetrafluoroethylene), or other fibre that coats each cathode. Any asbestos used is totally confined in the cell. The diaphragm keeps the caustic soda and hydrogen separated from the anolyte and affords control of the flow of electrolyte to the cathode.



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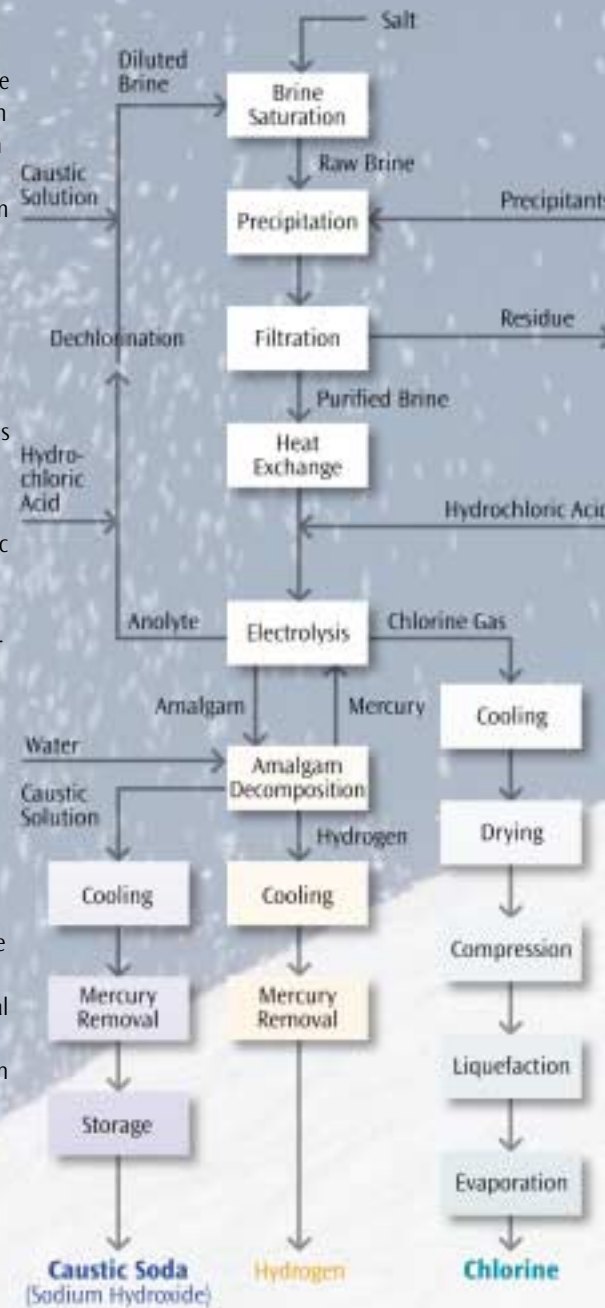


## Mercury Cell

The mercury cell cathode consists of a slowly flowing layer of mercury across the cell bottom. Sodium amalgam is produced at the cathode. In a separate reactor, known as the decomposer, the amalgam is reacted with water to produce hydrogen gas and caustic soda solution. When mercury functions as an electrode, it is not consumed in this closed-loop process. A 50 percent caustic solution is produced directly from the cell.

On the negative side, the toxic nature of mercury is associated with the greatest potential for adverse environmental and health effects. Strict safety procedures and process controls are followed to prevent workplace exposure and to minimize mercury emissions.

Mercury emissions from chlor-alkali producers have declined significantly over the years; the current contribution of this industry to total natural and anthropogenic mercury emissions is less than 0.1 percent. Western European mercury process plants reduced mercury emissions from 26.60 grams per metric tonne in 1977 to 1.25 grams per metric tonne in 2000. In 1995, U.S. producers made a voluntary commitment to the U.S. Environmental Protection Agency to reduce mercury by 50 percent.



Mercury cell use has declined since 1972 and now represents less than 20 percent of all worldwide production. In the future, there will be fewer and fewer mercury cells operated,

as the older plants are shut down or converted into membrane cells. European and North American producers have committed to not building any new mercury cell facilities.

## Membrane Cell

The membrane cell design resembles the diaphragm cell design except that the diaphragm is replaced with an ion exchange membrane. There are no special environmental problems associated with this method. Newer plants use the membrane process exclusively. About 30 percent of all production is achieved using membrane technology.

