More than 97% of world chlorine production is achieved using the chlor-alkali process.

This process applies a direct electrical current to a brine (water and salt) solution to produce chlorine and sodium hydroxide or potassium hydroxide (alkali) solution and hydrogen.

Chlorine is produced and collected at the anode, with any hydrogen and hydroxide ion being produced and collected at the cathode.

The first commercial production of chlorine using electrolysis was in 1888.

There are two main electrolytic production technologies used in the chlor-alkali industry – the diaphragm cell and membrane cell. Mercury-based cells were an alternative technology, but this is in the process of being phased out under the global Minamata Convention on mercury. Another technology is based on an oxygen depolarised cathode (ODC) which does not produce any hydrogen so requires less energy. Other processes produce chlorine from the electrolysis of HCl resulting in chlorine and hydrogen (or in the case of ODC, chlorine and water) or from metal salts producing chlorine and the desired metal (e.g. magnesium, nickel etc.).

Each technology uses a different way to keep chlorine separated from hydrogen and caustic solution. Currently, it is estimated that at least 95% of all chlorine is produced using membrane and diaphragm cells in approximately 580 plants located around the world.

Diaphragm technology is widely used on the American continent and in Russia and Arabic countries. In the rest of the world, production is mainly based on membrane technology.

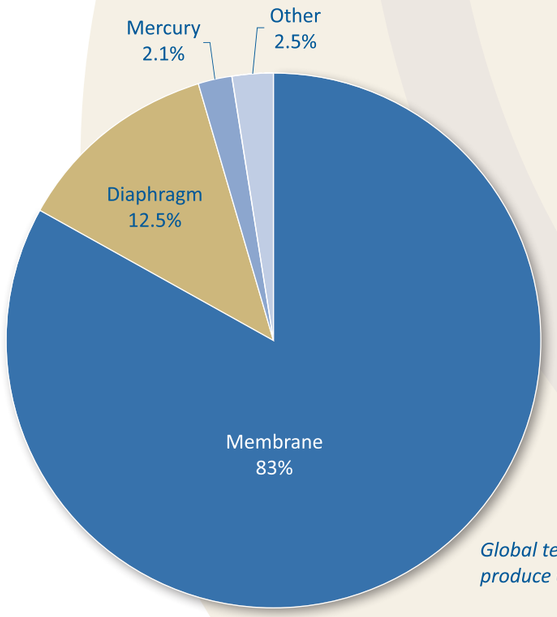
Regardless of the technology used, cells are arranged in series electrically, with each circuit consisting of several rows of cells. Two adjacent rows of cells may share a brine distribution line and collection systems for chlorine and hydrogen though. Each row is equipped with a pipeline on its aisle 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. The other gas that can be generated, hydrogen, is similarly collected.

For details on chlorine's many uses, please see the 'Chlorine Trees' available in the Resources section at www.worldchlorine.org.

The sodium ion concentration builds up in the brine and is eventually removed as sodium hydroxide or potassium hydroxide.

For details on caustic soda's many uses, please see the 'Caustic Soda Trees' available in the Resources section at www.worldchlorine.org.

Chlorine gas, at approximately 85 °C (185°F), is water-saturated when it exits the cell. Cooling this gas removes some moisture. Further drying is then accomplished using sulfuric acid. After compression, and cooling, the gas is liquefied via refrigeration/cooling water and transferred to storage containers for transportation, or it is sent directly to other plants by pipelines (sometimes without liquefaction).



Global technologies to produce chlor-alkali

Turning Salt into Chlorine and Caustic Soda

Chlorine manufacturing plant
Photo credit: Spolchemie

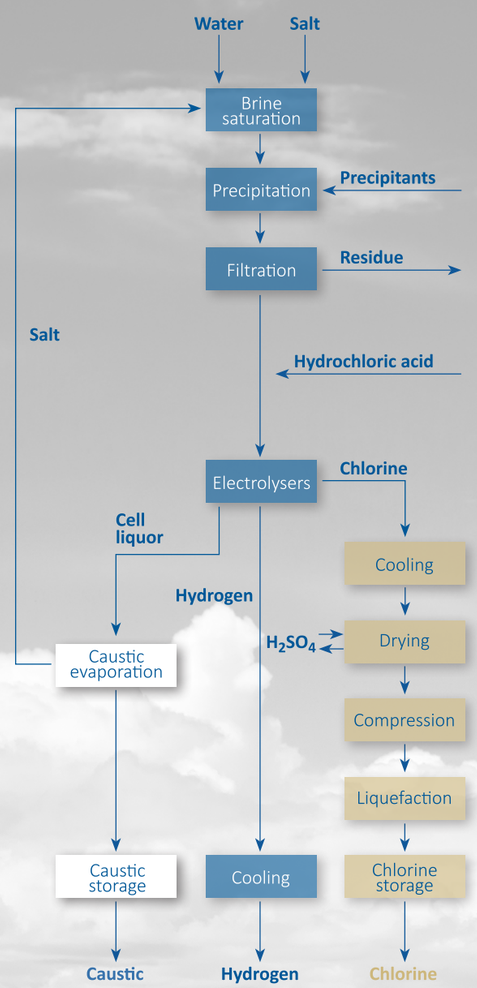
Chlor-Alkali Manufacturing Processes

worldchlorine.org

Diaphragm Cell Technique

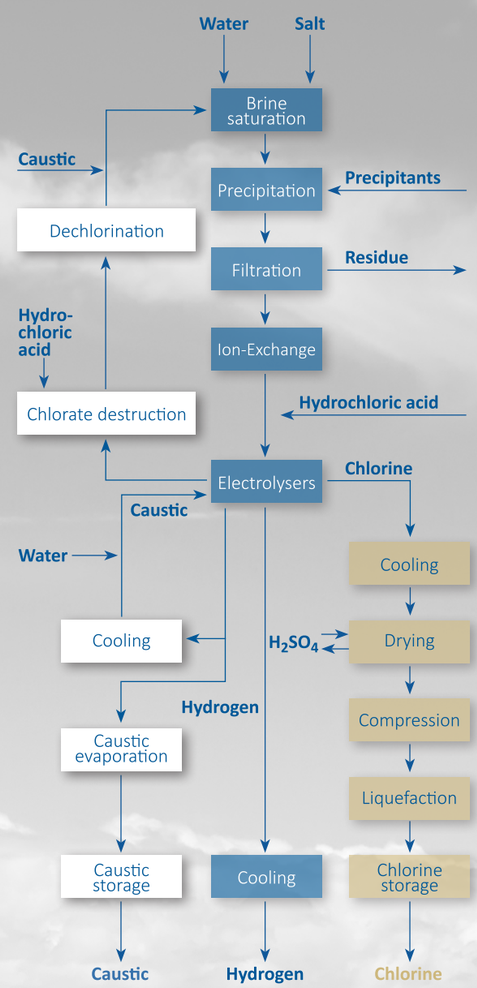
The diaphragm cell design is characterised by anode and cathode separation by a diaphragm consisting of a deposited layer of asbestos fibre mixed with an additive such as Teflon® (polytetrafluoroethylene), or other artificial non-asbestos type fibre that coats each cathode. The diaphragm keeps the caustic soda and hydrogen separated from the anolyte and affords control of the flow of electrolyte to the cathode. The produced material is a mixture of a salt and alkaline solution. In an evaporation process, the alkaline solution is concentrated to 50% whilst separating the majority of the salt by crystalisation. The diaphragm process produces the lowest caustic quality compared to other processes.

®Trademark of DuPont



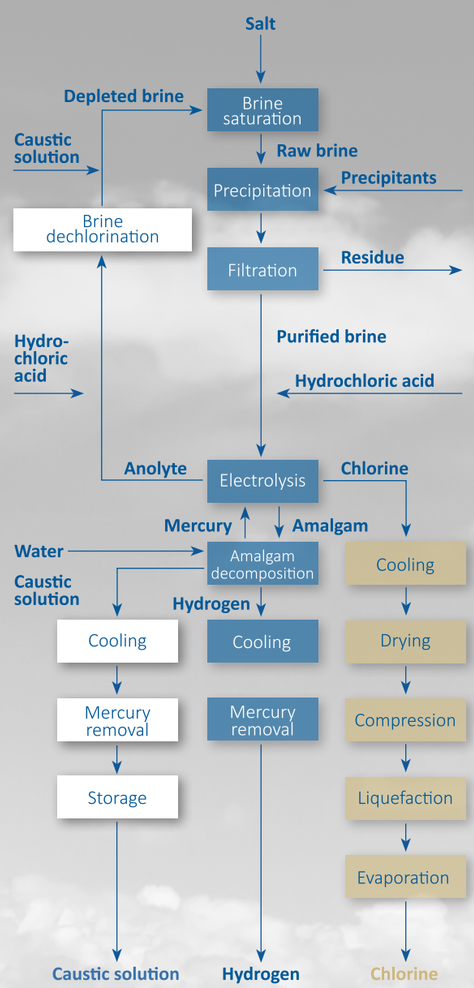
The membrane cell design is characterised by anode and cathode separation by a membrane. The membrane keeps the caustic soda and hydrogen separated from the anolyte and chlorine. The membrane only allows the sodium ion (or potassium) to pass through (along with water) and must prevent the back diffusion of the hydroxide ion. The process produces a 32-33% caustic solution which is normally concentrated to a 50% caustic solution. In an evaporation process, the alkaline solution is concentrated to 50%.

In the **Oxygen Depleted Cathode (ODC)** version of membrane electrolysis, the cathode reaction is different to the normal membrane electrolysis. In the ODC version, pure oxygen is added to the cathode. This reacts with water to the hydroxide ion. This process does not produce hydrogen and requires less electricity compared to the normal membrane electrolysis, and it requires pure oxygen at the cathode.



Mercury Cell Technique

The use of the **mercury cell** cathode is being phased out under global agreements on the use of mercury. The cell used to consist of a slowly flowing layer of mercury across the cell bottom producing sodium amalgam, whilst on the anode, chlorine is produced. In a separate reactor, known as the decomposer, the amalgam reacted with water to produce hydrogen gas and an alkaline solution. When mercury functions as an electrode, it is not consumed in such closed-loop processes. A 50 percent caustic solution is produced directly from the cell. Due to the toxic nature of mercury it has potential for adverse environmental and health effects. As such, strict safety procedures and process controls are followed to prevent workplace exposure and to minimise mercury emissions. Since the end of 2017, the mercury cell process was phased out in Europe. The mercury process represents approximately 2% of global chlorine production. Mercury emissions from chlor-alkali producers declined significantly over the years; the contribution of this industry to total natural and anthropogenic mercury emissions is less than 0.1%.



Membrane Techniques

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