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## The Chlor-Alkali Process – *Work in Progress*

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### Abstract

The chlor-alkali process has come a long way from the days of the diaphragm and mercury cell process to the present membrane cell process, with huge reduction in power consumption, and hence it's carbon footprint. Although there is reduction in the release of highly toxic mercury to the environment, there is increased release of less harmful substances such as chloride and chlorate because the membrane cell is less tolerant to contaminants, and hence requires higher purity brine. The technology providers have continued to improve upon the process to reduce power consumption and to reduce the plant's footprint. This review looks briefly at the three technologies and attempts to look at where we currently are at. All new chlor-alkali plants being built are of the membrane process. This review mentions some of the areas where improvements can be made to the process.

### 1. Introduction

The chlor-alkali industry generally refers to the industry that produces chlorine and sodium hydroxide (an alkali), hence the term chlor-alkali (Environment Canada 1989)(IPPC 2011, Dec). The term chlor-alkali industry also includes the production of chlorine with potassium or lithium hydroxide. Sodium hydroxide is commonly known as caustic soda or just caustic.

Chlorine and caustic soda are products that are widely used in industry. They are used in producing detergents, herbicides, pesticides, pharmaceuticals, plastics, and soaps (Bommaraju, Orosz, Sokol 2007; Euro Chlor 2007). The single largest usage area for chlorine is in the manufacture of polyvinyl chloride (Euro Chlor 2007; IPPC 2001), while its largest use in inorganic chemicals is for the manufacture of titanium dioxide. In the polyvinyl chloride molecule, more than half its content by weight is from chlorine (Euro Chlor 2011, Sept). The manufacture of some plastics such as polyurethanes and epoxy resins that do not contain chlorine in their molecule also require chlorine in their process (Euro Chlor 2011, Sept). The chlorine tree in Fig 1 shows the various uses of chlorine (Euro Chlor 2011, Sept).

Today, in organic chemicals manufacture, polyvinyl chloride (PVC) is the largest consumer of chlorine, while its largest use in inorganic chemicals is for the manufacture of titanium dioxide (Bommaraju, Orosz, Sokol 2007). It's co-product from the chlor alkali manufacturing process, sodium hydroxide also finds wide application in industry.

For the production of sodium hydroxide and chlorine, the raw material used is sodium chloride. Sodium chloride, also known as common salt, has the chemical formula NaCl and contains the elements sodium and chlorine. Sodium chloride crystals vary in colour from colourless when pure to white or grey.

The solar evaporation method for producing salt (Varjian 2003) is possible in areas with warm climates and where there is a higher evaporation rate than precipitation rate (O'Brien, Bommaraju, Hine 2005a). In this process, the salt water is collected in shallow ponds. Energy in the form of heat from the sun is used to evaporate the water. The salt content of sea water is less than 3%. As the water evaporates and the brine solution increases in concentration, the sodium chloride starts to precipitate. This precipitate is collected and is processed to remove impurities such as bromide, chloride, and sulphate as well as calcium carbonate, sulphate and potassium chloride (O'Brien, Bommaraju, Hine 2005a).

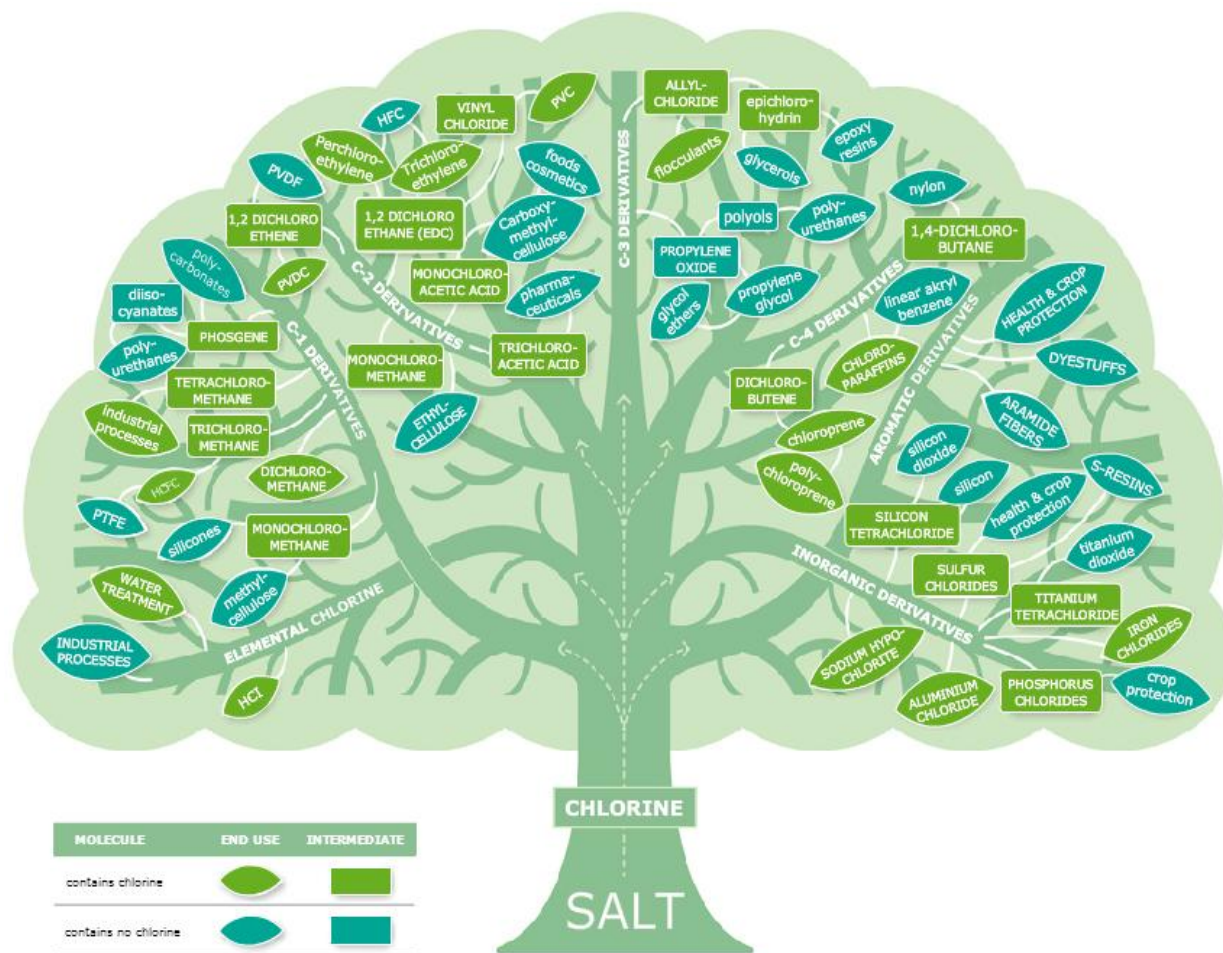


Fig. 1 The Chlorine Tree (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)

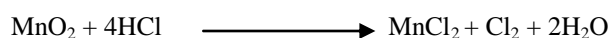
In the chlor-alkali process, sodium chloride is converted into sodium hydroxide and chlorine by impressing an electric current through the solution (Clark 2007). This electro-chemical process is referred to as electrolysis (Rhees 2007). Electrolysis occurs in reactors that are known as electrolytic cells (Varjian 2003)(Grotheer, Alkire, Varjian 2006).

The electrolysis cell generally comprises of a containment device, and an anode and a cathode through which an electrical charge is passed to cause the electrolysis to occur. Some cells may have a separator such as a diaphragm or membrane to keep the products produced at the anode and cathode apart from each other (Grotheer, Alkire, Varjian 2006).

Sodium chloride electrolysis is today the largest scale electro synthesis, and is a huge consumer of electricity (Euro Chlor 2011, Sept; Sathaye and others 2005; Shojaikaveh and others 2009). In the past, due to its high energy consumption, such plants were located near hydroelectric or steam power plants (Grotheer, Alkire, Varjian 2006)(Euro Chlor 2011, Sept) and where there were sources of salt nearby.

## 2. Brief history of the process

In the 1800's chlorine was produced via the Weldon process for use in the textile and paper industry. This process involved using manganese dioxide and hydrochloric acid (O'Brien, Bommaraju, Hine 2005a) in the following manner:-

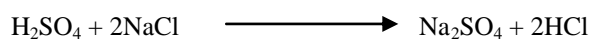


Later the Deacon process came about (O'Brien, Bommaraju, Hine 2005a). This process involved the use of hydrochloric acid which was reacted with oxygen to produce Chlorine gas and water according to the reaction:-

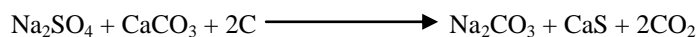


(A Copper Chloride catalyst is used in the reaction which occurs at 400-450°C.)

The hydrochloric acid (HCl) for both these processes came from the LeBlanc soda ash process (O'Brien, Bommaraju, Hine 2005a), which was a batch or stage-wise reaction and is described further below. In the first stage sodium chloride is reacted with sulphuric acid to form sodium sulphate and hydrochloric acid gas as shown below.



This reaction was discovered by Carl Wilhelm Scheele in 1772 (Bommaraju, Orosz, Sokol 2007)(Kiefer 2002). LeBlanc took this reaction further. In the second stage, LeBlanc reacted the salt cake (sodium sulphate) with calcium carbonate to produce a solution containing sodium carbonate as shown below.



Due to the insoluble nature of calcium sulphide and calcium carbonate, the liquor was taken away and evaporated to recover soda ash or sodium carbonate. For many years, this remained the major route for producing soda ash, and hydrochloric acid was a by-product of the process.

The development of the Solvay process (Kiefer 2002; Varjian 2003) for the direct manufacture of soda ash in the 1860's, replaced the LeBlanc soda ash process and resulted in a lack of HCl for use in the Weldon and Deacon processes (O'Brien, Bommaraju, Hine 2005a). This is because HCl was previously obtained as a by-product of the first stage of the LeBlanc process. This made it necessary to find a new process for generating chlorine and resulted in the development of the electrolysis of sodium chloride to produce both sodium hydroxide and chlorine.

## 2.1 Diaphragm Cells

It was in 1851 that the combined processing of caustic and chlorine came about, in what is today known as the diaphragm cell process. In the late 1880's to 1890 several commercial diaphragm plants went into operation (IPPC 2001). The Griesham diaphragm cell went into operation in Germany in 1890 (Schneiders, Zimmerman, Henben 2001). They underwent continuous improvements until around 1920 when asbestos became the major material used for the diaphragm and remained the major material used for the following 80 years (O'Brien, Bommaraju, Hine 2005a). In the diaphragm cell process, asbestos or other suitable materials were used to separate the caustic soda from the chlorine (Euro Chlor 2007). The diaphragm cell produced caustic soda solution of around 12%, but its major drawback was the high salt content (Bommaraju, Orosz, Sokol 2007) in its caustic soda.

Platinum or magnetite were the early material used for the anodes of the diaphragm cells. However due to cost considerations as well as limitation on the current density when using magnetite, graphite became the major anode material until the 1970's. It was in the 1970's that a titanium base coated with a catalytic layer comprising of mixed oxides was developed (Bommaraju, Orosz, Sokol 2007). They were successfully used with long life and low cell voltage. These anodes became to be known as Dimensionally Stable Anodes and were used by all the technology suppliers (Bommaraju, Orosz, Sokol 2007).

There were developments made to improve the asbestos diaphragms such as mixing asbestos with polytetrafluoroethylene which produced a dimensionally stable diaphragm (O'Brien, Bommaraju, Hine 2005a). Then came a stabilized diaphragm, which had a polymer added into the asbestos slurry, and produced a diaphragm that did not swell (IPPC 2001). This was followed by the development of bipolar diaphragm cells with one side as the anode and the other side as the cathode. They were assembled together into a cell and tightened in place with tie rods which made them appear to look like plate and frame filter presses.

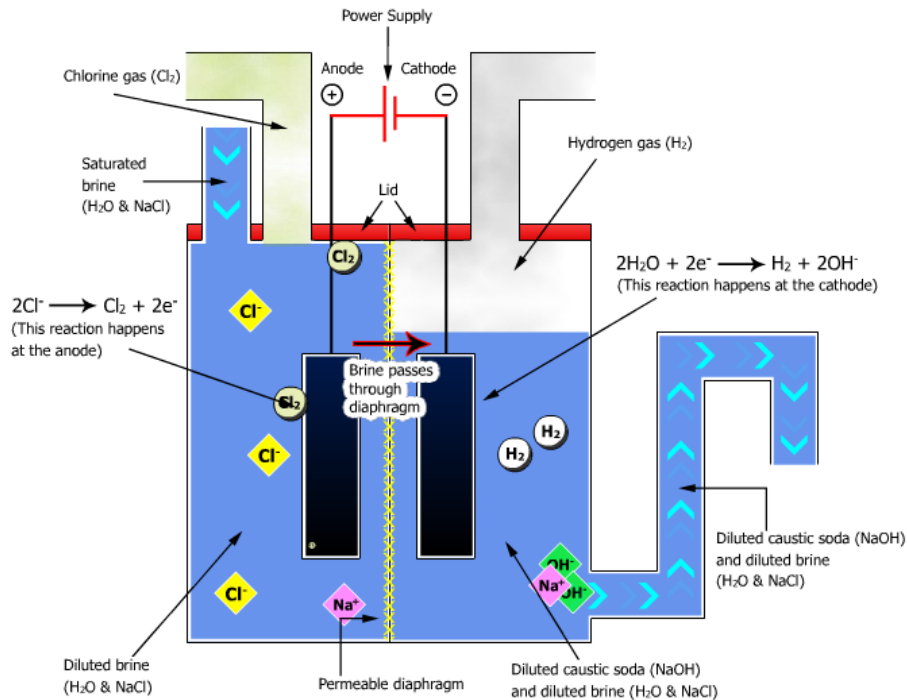
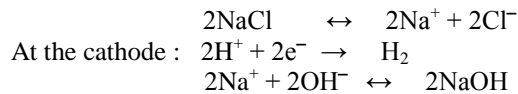


Fig 2 Diaphragm Cell process (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)

Fig 2 shows the layout of the diaphragm cell. The reactions occurring in the diaphragm cell are as follows (Wiberg 2001):-





As the sodium hydroxide concentration increases at the anode, there is a greater likelihood for it to be discharged into oxygen and water (Wiberg 2001). For this reason, diaphragm grade caustic is only produced at around 12-15% concentration in the electrolysis cell.

The height of brine in the anode compartment is maintained above the level in the cathodic side to enable brine to slowly permeate through the diaphragm (Varjian 2003). Saturated brine is fed to the anode compartment, where electrolysis of the brine takes place. Chlorine is formed at the anode. While sodium ions travel through the diaphragm, some sodium chloride is also transported along with it. At the cathode, hydrogen forms and the weak caustic soda containing around 14% sodium chloride is sent for further processing. The solution is then channeled through 3 or 4 evaporation processes to achieve a concentration of 50%. The salt crystallizes out on saturation of the caustic soda and is separated from it via crystallization and filtration and reused in the process. The caustic soda quality from diaphragm cells is considered to be low due to its high salt content of upto 1.3% and high sodium chlorate content of upto 0.3% with other impurities also at levels exceeding that from the other electrochemical processes.

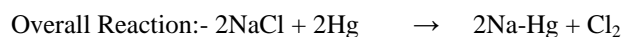
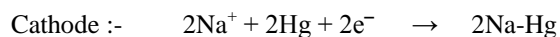
The caustic soda produced from the diaphragm cell is also known as Diaphragm Cell Grade and finds application in industries without stringent quality requirements.

The diaphragm cells have used chrysotile asbestos for the diaphragm. Despite the ban imposed on the use of asbestos, the diaphragm cells in the European Union are permitted to continue to use these asbestos diaphragms until the technology is phased out (Euro Chlor 2007)(Concentrates 2007; Giannasi 2007). With the banning of asbestos in many countries (Giannasi 2007), came the development of asbestos free diaphragms. Chemical businesses now face a real business risk in the form of asbestos related health claims. Legislation is making it easier for individuals exposed to asbestos to take legal action against their employers (Pelham 2010)(Smith and Wright 1996).

## 2.2 Mercury Cells

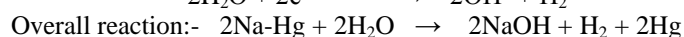
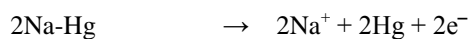
The Castner-Kellner mercury cell went into operation in 1892 (IPPC 2011, Dec). The process within a mercury cell differs somewhat from that in a diaphragm cell. The mercury cell is composed of an electrolyzer and a denuder or sometimes called a decomposer (O'Brien, Bommaraju, Hine 2005b).

The reactions in the electrolyzer are as follows:-



Mercury acts as the cathode in this reaction and also forms an amalgam with sodium. Mercury is not consumed in the process. This amalgam is reacted with water in the denuder to produce caustic soda at the desired concentration. i.e. Caustic soda of 50% concentration can be produced directly from the denuder, without any need for further concentrating it (Euro Chlor 1998). Fig 3 shows how the mercury cell functions.

In the denuder the following reactions occur:-



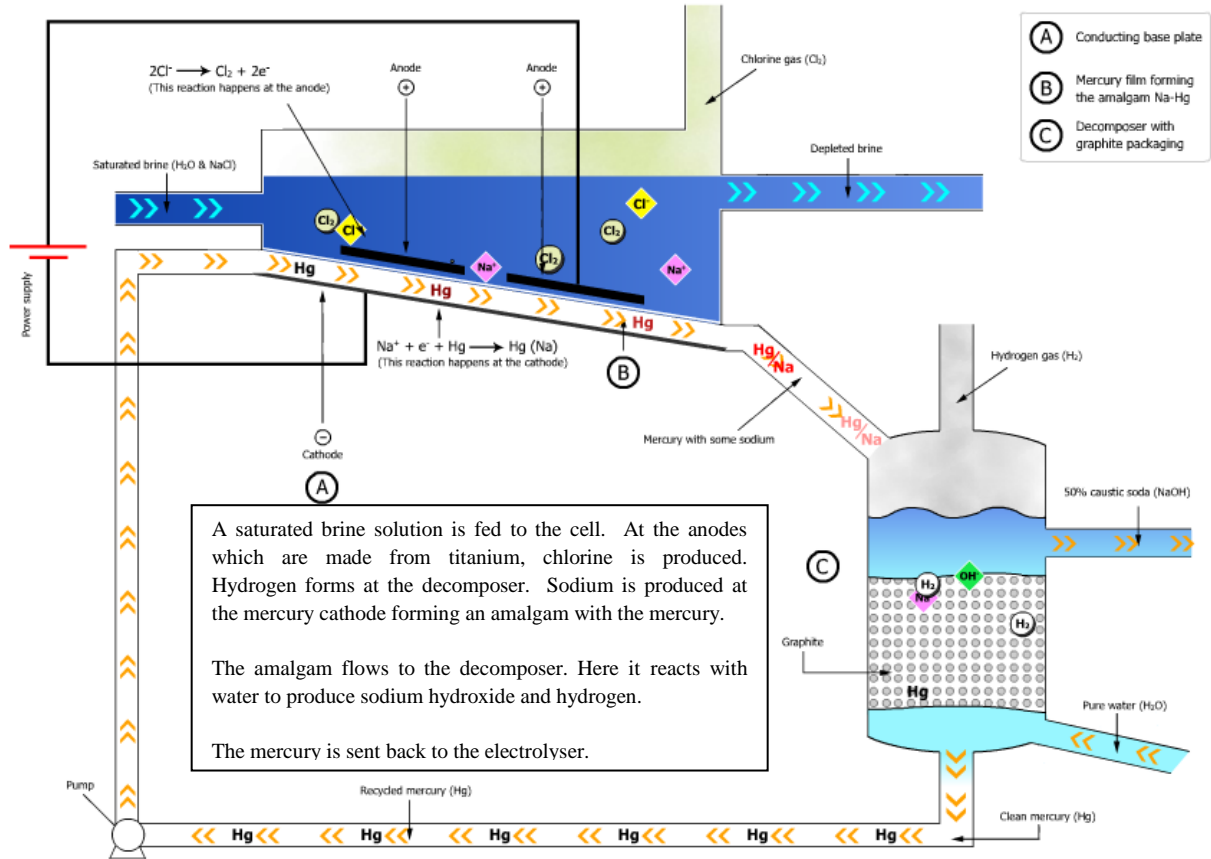


Fig 3 Mercury Cell process flow diagram (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)

At the outlet of the decomposer, the sodium hydroxide which is at 50% strength does not require further processing.

The mercury cell process is known to produce the highest quality caustic soda, but its major drawback is that its products has some mercury present (Wiberg 2001). Mercury levels are typically below 1ppm while sodium chloride content is typically below 10ppm, and sodium chlorate content is below 1ppm. The caustic soda produced from this process is referred to as Mercury Cell Grade or Rayon Grade. This is because the production of rayon prefers caustic soda such as that produced via the mercury cell (O'Brien, Bommaraju, Hine 2005a) process.

Due to its polluting nature and the move away from mercury, there are no more new mercury cells being installed in the world. There are still a few old mercury cell units operating, but due to calls for greener technologies, their days are numbered. Chlorine manufacturers have voluntarily agreed to reduce mercury consumption by 50% by 2005 over the base year 1990-1995. This target has been achieved and exceeded (Chlorine Institute 2006). In 2006, 43% of European chlorine capacity came from the mercury process (Euro Chlor 2007). Diaphragm technology made up 15% of the capacity, with 39% coming from membrane technology. As at end 2011, mercury process has dropped to 31%, diaphragm process to 13% and the membrane process has increased to 52% (IPPC 2011, Dec).

Globally, the number of mercury process plants have reduced from 92 plants in 2002 with a capacity of 9million mt/yr down to 57 plants in 2010 with 5.5million mt/yr capacity (Euro Chlor 2011a). There is a voluntary commitment to phase out the use of the mercury cell process by 2020 by European manufacturers(Euro Chlor 2012).

The chlor-alkali industry claims that the levels of mercury from chlorine manufacture have reduced substantially over the years, and that the industry is now a minor contributor to environmental mercury levels (Euro Chlor 2011, Sept; Singh 2010). One of the points of concern from mercury cells is the residual levels of mercury (typically 0.5ppm and below) present in products from the cell (Dufault and others 2009a) and the use of mercury containing chemicals for food processing applications and possible bioaccumulation and potential microbial action that converts mercury to methyl mercury which is highly toxic(Gochfeld 2003; Román 2007; Stern and others 2001). It's use in food applications such as for the manufacture of high fructose corn syrup is cause for concern (Dufault and others 2009b).

Other disadvantages of the mercury cell process are the potential hazards from exposure to mercury and mercury vapours which are a known neurotoxin. They also require larger floorspace than diaphragm cells and membrane cells and consume more energy for the production of chlor alkali products.

Some former mercury process chlor-alkali plant sites show signs of soil contamination with mercury. Remedial works are required to contain or remove the mercury from such soils. One such site is in Botany, Australia which operated a mercury process chlor-alkali plant on that site from 1944 to 2002 before switching to the membrane cell process. The soil at the plant and surrounding sites have been found to be contaminated with some elemental and some dissolved mercury leaving a bad legacy for chemical industry and requiring costly remedial measures (Golder Associates Pty Ltd 2012). Some former mercury based chlor-alkali sites in Europe have shown signs of contamination and require cleanup (Bernaus and others 2006; Biester, Müller, Schöler 2002). Some former mercury based chlor-alkali plants such as Saltville in Virginia, and Lavaca Bay in Texas have been classified as Superfund sites (Rule and Iwashchenko 1998; Sager 2002).

### **2.3 Current best available technology - Membrane Cells**

Global chlor-alkali production capacity in 2008 was 62.8 million tons per year, with the fastest growth recorded in China, making China today's largest producer and consumer of chlor-alkali products (IPPC 2011, Dec). With the growth in membrane cell and conversion to membrane technology, as at 2011, mercury process capacity stood at below 10% of global production capacity and is set to decline further. Japan is the first major chlor alkali producing country to switch entirely to membrane cells (O'Brien, Bommaraju, Hine 2005a).

Due to incidents of mercury poisoning in Minamata and Niigata in 1972, Japan started switching to membrane cells, and today has no more mercury cells in operation (O'Brien, Bommaraju, Hine 2005a)(Gochfeld 2003).



The power consumption in the membrane cell is the lowest comparing the three technologies (Euro Chlor 2011b; IPPC 2011, Dec; Wiberg 2001). However certain industries such as the rayon industry consider the caustic soda quality from membrane cells to be slightly inferior to that produced via the mercury cell method due to the higher chloride and chlorate content.

The key principle of the membrane process is the selective permeability of the membrane. The membrane allows only specific components to permeate through it. The actual transport processes occurring within the membrane are yet to be understood fully (Grotheer, Alkire, Varjian 2006). Research is on-going in an effort to better understand how these membranes work so as to tailor make membranes with highly selective permeability and exhibiting low electrical resistance (Grotheer, Alkire, Varjian 2006).

The ion exchange membrane separates the cathode side from the anode side as shown in Fig. 4. The membrane currently used in industry is comprised of two layers to be able to withstand the significantly different conditions on either side of it. The two layers are made of perfluorosulfonic acid and perfluorocarboxylic acid films.

Fig 4 shows the membrane cell process. A saturated brine solution that has been treated is channeled to the anodic compartment while demineralized water is fed to the cathodic compartment. During the electrolysis, sodium ions and some water permeates through the membrane and enters the cathode compartment. Chlorine gas is formed in the anode compartment. In the cathode compartment, water molecules are electrolyzed, releasing hydrogen gas. The hydroxyl ions will combine with the sodium that permeates through the membrane, to form sodium hydroxide. The depleted brine that leaves the anodic compartment is sent for processing and re-concentration before it is fed back to the anodic compartment.

In the cathodic compartment, only a portion of the sodium hydroxide of 32% concentration is taken out for further processing, while demineralized water is continuously fed to the compartment to maintain the sodium hydroxide concentration in the compartment at around 30%. Based on current technology, the highest sodium hydroxide concentration that can be produced in the membrane electrolyser is 35% (Moorhouse 2001)

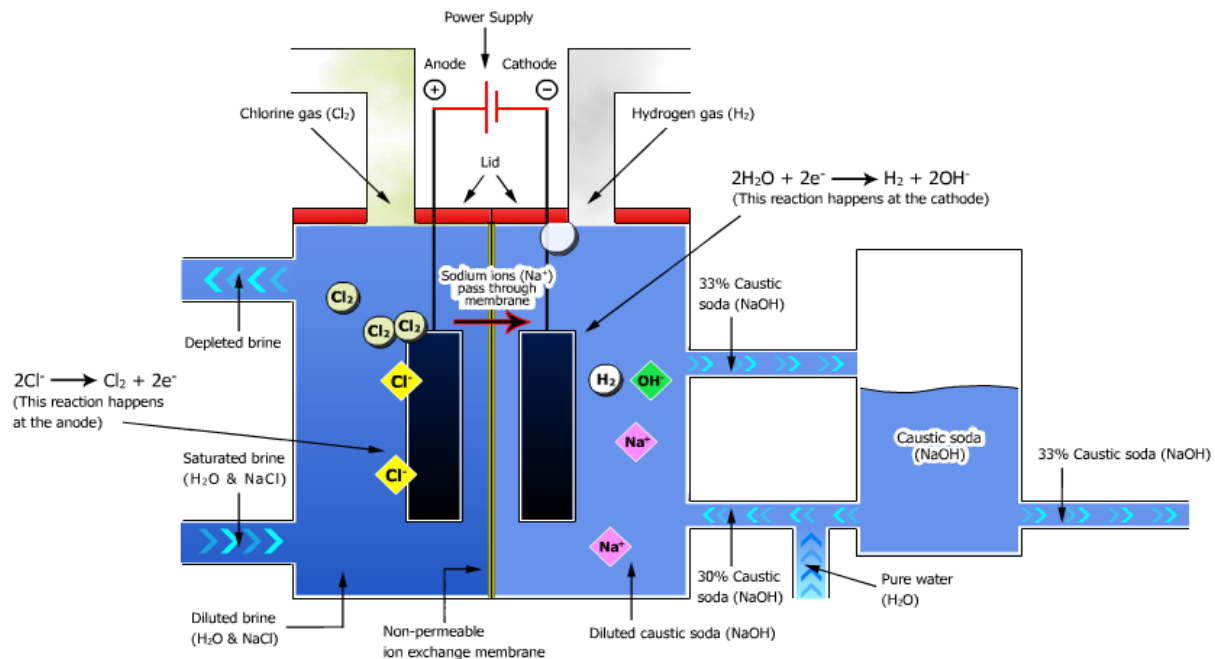


Fig 4 Process flow of the membrane cell process (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)

As can be seen from the figures above, all three processes produce chlorine at the anode. For the mercury cell, sodium hydroxide is produced in the denuder, to the desired concentration, i.e. 50%. Separation of the anolyte and

catholyte is done using a diaphragm in diaphragm cells, while an ion exchange membrane is used for the membrane cell. For the mercury cell, mercury which acts as the cathode also acts as the separator by forming a sodium mercury amalgam.

### 2.3.1 Recent advances in Membrane cell process

One of the significant developments in the chlor-alkali industry is the oxygen-depolarized cathode (ODC) process in which, oxygen is introduced into the electrolysis chamber via a porous cathode. This process yields a significant reduction in electrical power consumption of around 30%, with hydrogen no longer evolved from the cathode. Instead of hydrogen, oxygen is released from the cathode of ODC cells (Kiros and Bursell 2008). Initial studies indicate that the existing membrane plants cannot be modified to the ODC process due to differences in operating conditions and use of the special cathodes (Chlistunoff 2005).

A demonstration electrolyzer with a capacity of 20,000 tons per annum of chlorine has been operational for Bayer at its site in Uerdingen since May 2011. Research work is ongoing to determine types of electrode coatings to be used (Moussallem and others 2012).

The ODC process has also been put to commercial use for electrolysis of HCl to produce chlorine, with significant savings in electrical costs. Here too, oxygen is introduced at the cathode and no hydrogen is evolved. This is a significant development given that in most synthesis reactions using chlorine, one major by-product is hydrochloric acid. The use of the ODC process helps recover chlorine from HCl.

Table 1 below summarizes some of the more recent developments in the chlor-alkali industry which shows there is still much development work going-on.

Table 1 Recent developments in the chlor-alkali industry

	Improvement	Year	Remarks
1	Membrane	2012	Dupont developed N2030/NE2040 membranes exhibiting lower voltage drop. <a href="http://www.abiclor.com.br/cong2012/apresentacoes/11-0812-DuPont-Nafion-Membranes-R&amp;D-update-and-Product-Technology-Overview-Patricia-Strabelli.pdf">www.abiclor.com.br/cong2012/apresentacoes/11-0812-DuPont-Nafion-Membranes-R&amp;D-update-and-Product-Technology-Overview-Patricia-Strabelli.pdf</a>
2	Brine treatment – sulphate	2012	e.g. Akzo Nobel developed a nano-filtration method for removing sulphates from brine. <a href="http://www.akzonobel.com/ic/system/images/AkzoNobel_Nano_GB-med_tcm18-75380.pdf">http://www.akzonobel.com/ic/system/images/AkzoNobel_Nano_GB-med_tcm18-75380.pdf</a>
3	Ultrapure salt use	2012	Using ultrapure salt to reduce salt consumption and processing costs. <a href="http://www.salt-partners.com/publications.htm">www.salt-partners.com/publications.htm</a>
4	Better resins	2012	Lanxess developed new smaller resins with greater adsorption capacity, extending resin on-line time by 50-100%. <a href="http://www.ionexchange.com/ion/en/applications/chem_env/">http://www.ionexchange.com/ion/en/applications/chem_env/</a>
5	Electrolyser	2012	Uhdenora reduced power consumption in the electrolyser from 2130 kWhr/t Cl <sub>2</sub> (in 2004) to 2035 (in 2012) via their version 6 BM2.7 electrolyser. <a href="http://www.thyssenkrupp-uhde.de">www.thyssenkrupp-uhde.de</a>
6	Oxygen depolarized cathode (ODC)	2011	Uhdenora tied up with Bayer to develop and test the NaCl-ODC with significant power reduction of 25%. <a href="http://www.abiclor.com.br/cong2012/apresentacoes/10-0812-Development-update-of-UHDENORA-technologies-%20Werner-Graichen.pdf">http://www.abiclor.com.br/cong2012/apresentacoes/10-0812-Development-update-of-UHDENORA-technologies-%20Werner-Graichen.pdf</a>

The list is by no means exhaustive, but shows that there is much work being done to improve the process further.

### 3. Comparison of the Membrane Cell process vs the Diaphragm and Mercury Cell

There are distinct advantages in using the membrane cell technology. This together with the polluting nature of and environmental concerns of using the other technologies, has resulted in all new plants being built, to be of the membrane cell process. Table 2 below summarizes some of the advantages and disadvantages of using the membrane cell in comparison with the other two technologies.

Table 2 Advantages and disadvantages of the membrane cell as compared to the mercury cell and diaphragm cell process

Advantages of the Membrane Cell	Disadvantages of the Membrane Cell
<p>a) Does not use harmful substances such as mercury or asbestos and hence there can be no potential release of these materials into the product, ground or environment.</p> <p>b) Lowest power consumer when compared to mercury and diaphragm cells. (Electric power consumed in kWhr/t Cl<sub>2</sub> (Moussallem and others 2008) Mercury cell – 3100-3400 Diaphragm cell – 2300-2900 Membrane cell – 2100-2600</p> <p>Total power consumed Mercury – 3100-3400 Diaphragm – 3200-3800 Membrane – 2400-2900)</p> <p>c) Higher quality of sodium hydroxide when compared to the diaphragm cell.</p>	<p>a) Higher quality salt and brine required. Resulting in higher cost</p> <p>b) More processing steps required to purify the brine, again higher cost</p> <p>c) Higher unit consumption of salt</p> <p>d) Lower quality sodium hydroxide vs mercury grade in terms of sodium chloride content.</p> <p>e) The sodium hydroxide produced may contain higher chlorate levels than mercury grade.</p> <p>f) Higher internal consumption of sodium hydroxide and hydrochloric acid for regeneration of the ion-exchange resins and for brine acidification for chlorate decomposition.</p> <p>g) Higher maintenance or operating cost for replacement of membranes – typically needs to be replaced every 4 years (or earlier depending on treated brine quality).</p> <p>h) The purging of brine streams will release chlorate to the environment through the waste water. Chlorates are known to be persistent and records show that it can adversely affect certain strains of algae such as <i>fucus vesiculosus</i> or bladder-wrack (brown algae) at µg/l levels (Rosemarin and others 1994). Safe limits as specified in Canada are at 5 µg/l level (Warrington 2002).</p> <p>i) The production of perfluorocarboxylic acid and perfluorosulfonic acid used in the membranes also do result in the release of pollutants (Kärrman and others 2010)(Jeon and others 2010).</p>

### 4. The way forward

Some of the areas that could be looked into to further improve upon the process are:-

- a) To reduce electricity consumption by reducing the power loss in the cells and across the membranes by the use of better materials with lower electrical resistance while still exhibiting the desired chemical resistance (Beckmann and Lüke 2000).
- b) To reduce effluent discharge. The water consumed in the membrane cell process is quite large, and generates large amounts of effluent. The current practice of purging brine also contributes to high effluent discharge from membrane cell plants. One option would be to site alternative processes beside the membrane cell plants which can consume the brine being purged from such plants. Possible plants include chlorate producing plants (Bommaraju and Chen 1999).
- c) To recover raw material from its effluent streams – the brine stream that is being purged by the chlor alkali plant contains sodium chloride. Sodium chloride is the raw material for the chlor alkali process. The sodium chloride content within the brine solution that is purged from membrane cell plants is typically around 20% (DeNora 1995). The purging of such streams hence results in loss of its raw material.

- d) To reduce chlorate content in its products – the process has to be optimized to reduce the generation of sodium chlorate in the electrolyser, by adjusting operating parameters to minimize its generation (Bergner 1990; O'Brien 2008, May).
- e) To reduce chlorate content in its effluent – The chlorate in the effluent comes about when brine is purged. Brine is purged mainly due to high chlorate and sulphate levels in the brine. Hence the process should be modified to either eliminate the generation of chlorate or to remove it once it has been produced so that significant amounts of the brine can be reused in the plant, without the need for purging the brine solution (Bergner 1990).
- f) Legislation should be introduced to limit chloride and chlorate release from chlor-alkali plants. E.g. for pulp and paper mills, legislation in Canada requires the release of chlorate to be less than 15ppb (Warrington 2002).
- g) To have higher brine quality, to enable longer membrane life. The current technology calls for brine with 20ppb levels of calcium and magnesium to enable the membranes to have a useful life of 4 years. Over that period, the calcium and magnesium will be precipitating on the membranes, but this occurs very gradually and results in a gradual decline in the efficiency of the cell as well as an increase in the power consumed by the cell. Significantly improving the brine quality will also help prolong the life of the membranes as well as the cell elements, resulting in lower operating costs.
- h) To have self cleaning/non-fouling membranes or to design membranes such that the precipitation on them can be reversed. When the cell is taken off-line for some routine maintenance, perhaps introducing a process to remove the precipitates from the membrane, and thus returning the membrane to high efficiency and low power consumption.
- i) Better membranes with less break-through, hence higher quality products. Design of membranes could be enhanced to produce membranes that have lower power drop and are less susceptible to precipitation by the anions and cations.

## 5. Summary

The chlor-alkali industry has come a long way from the days of the Deacon and Weldon process. There are continuous efforts to improve the process in areas such as power consumption, better membranes, brine purification and improved resins. However, there are several challenges and opportunities for the chlor-alkali industry. Asbestos claims are a threat that could be made against the diaphragm cell process and the mercury cell process has its own problems with mercury exposure. The membrane cell process has to learn from its predecessors and become a cleaner process and ensure that its own emissions do not cause it similar problems in the future. The development of the ODC process has helped in significantly reducing the power consumption and carbon footprint of chlor-alkali plants. One area of improvement to the process that would impact several of the areas mentioned above would be the removal of chlorate from the depleted brine stream. This would enable the brine stream to be fully recovered, doing away with the need to purge brine. There would then be less raw material and water consumed by the process, and less waste released to the effluent stream all contributing to reduce the carbon footprint of the chlor-alkali plant. The removal and destruction of chlorate will result in reduction of chlorate being released to the environment.

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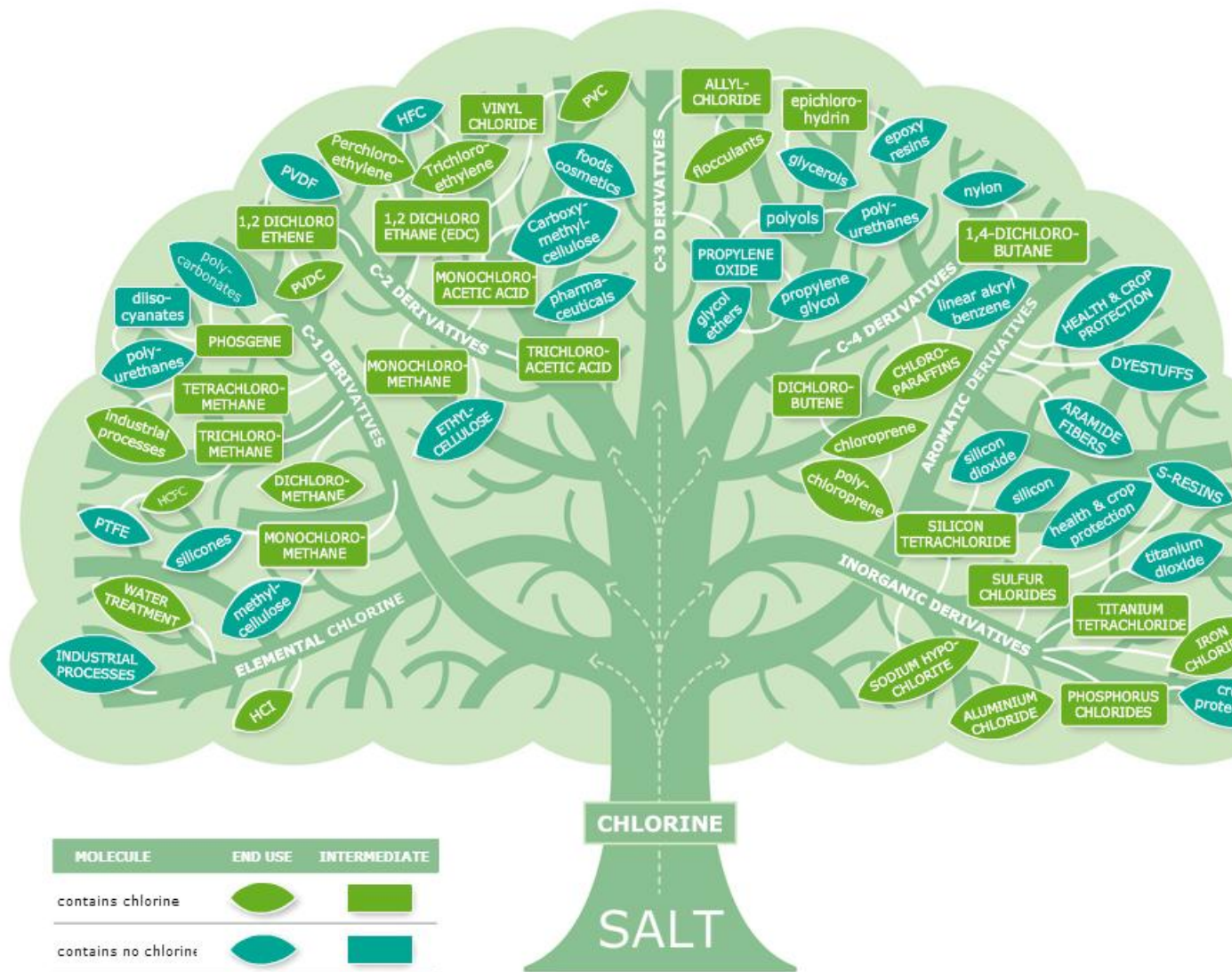


Fig. 1 The Chlorine Tree (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)



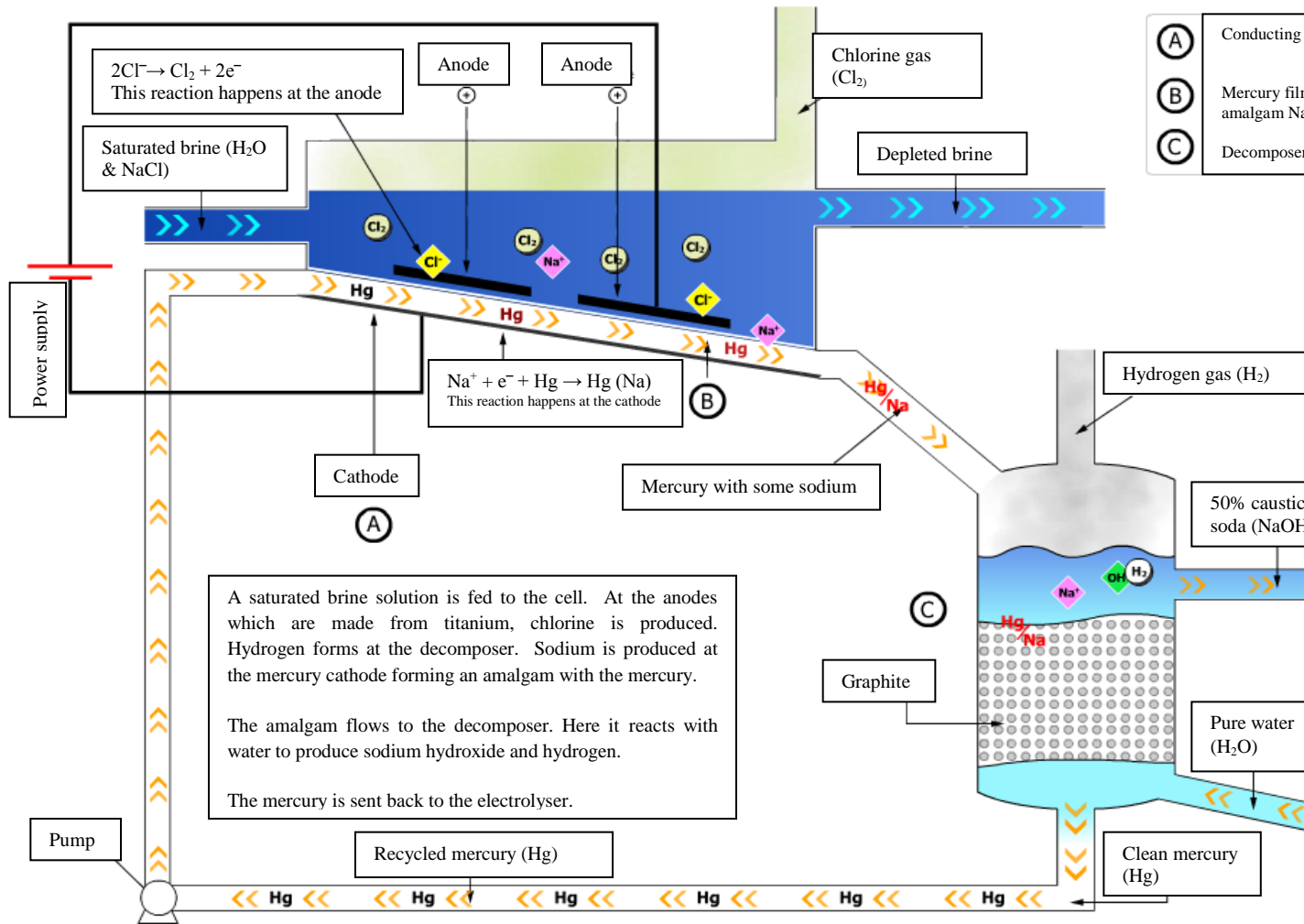


Fig 3 Mercury Cell process flow diagram (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)

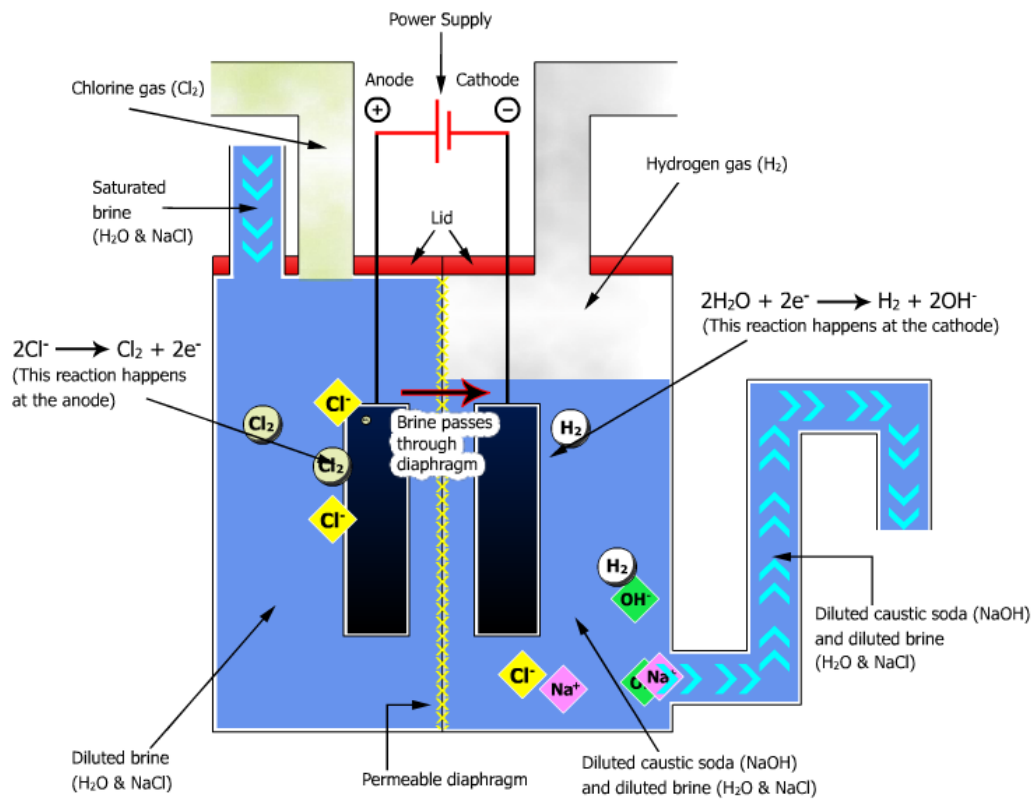


Fig 2 Diaphragm Cell process (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)

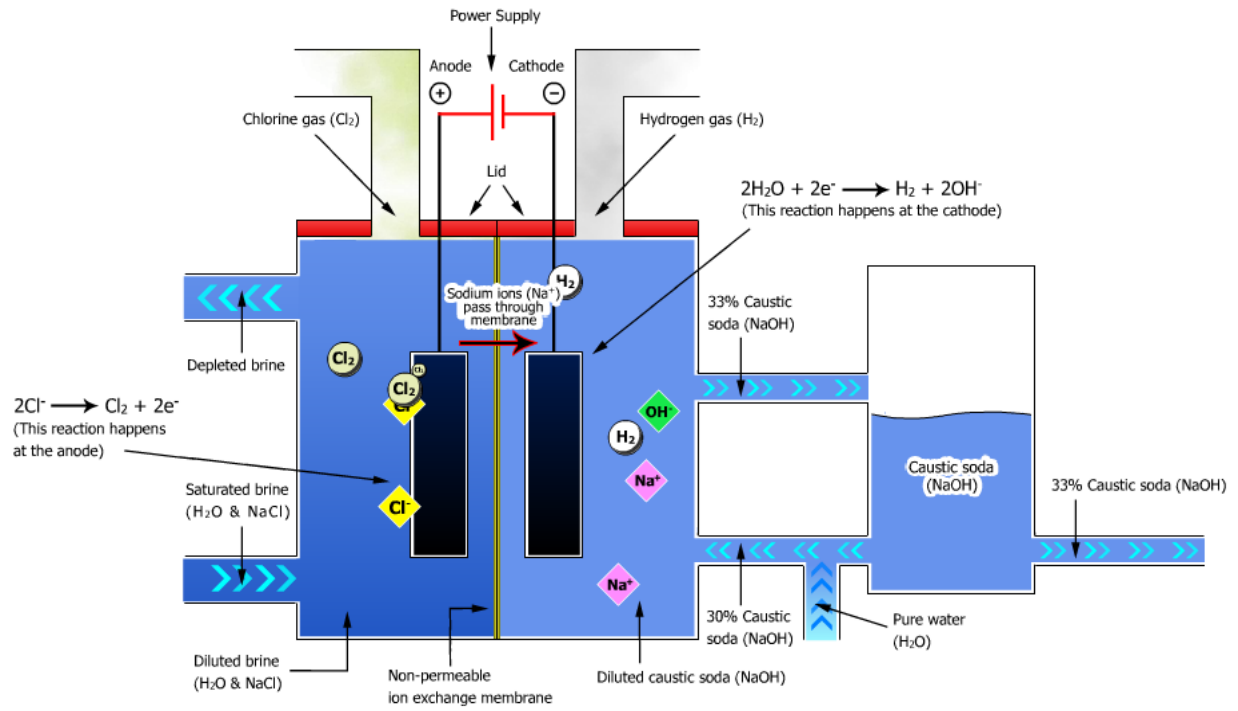


Fig 4 Process flow of the membrane cell process (reproduced with permission of Euro Chlor <http://www.eurochlor.org/>)