

**CHEMSYSTEMS**  
PERP PROGRAM

# Chlor-Alkali

PERP 2011-7

Report Abstract  
May 2012

# *Chlor-Alkali*

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## **CHEMSYSTEMS** PERP PROGRAM



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### INTRODUCTION

Chlorine and caustic alkali (caustic soda, sodium hydroxide) are large scale commodity chemicals.

Caustic soda is commonly sold in both anhydrous form and in solution (typically 50 or 73 percent solution). It is used throughout the chemical industry particularly in neutralization reactions, as well as in the manufacture of soaps and detergents, textiles, paint, and alumina etc.

Chlorine is generally liquefied and stored at low or ambient temperatures as compressed gas (typically in 45 to 68 kg cylinders, 1 ton containers or 55 and 90 ton rail tankers). The main application of chlorine, accounting for nearly half of its production, is in the production of polyvinyl chloride (PVC) via ethylene dichloride (EDC) and vinyl chloride monomer (VCM) intermediates.

Frequently chlor-alkali plants are integrated downstream to avoid transport issues. The majority of chlorine and sodium hydroxide production occurs by electrolysis of a sodium chloride solution using a diaphragm, membrane or mercury cell.

A small amount of chlorine production (about five percent of global supply) occurs by use of other technologies, such as electrolysis or oxidation of hydrogen chloride, as a co-product in metal production (such as during the electrolytic decomposition of magnesium and sodium chlorides to produce the metal), and electrolysis of potassium chloride which uses the same technology but produces potassium hydroxide as co-product (as opposed to sodium hydroxide).

With respect to sodium hydroxide production, the lime-soda process is an alternative, depending on the price/availability of sodium carbonate.

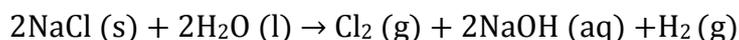
The historical growth of the industry has largely been dictated by the cost of energy. Any cell able to offer lower specific electrical energy consumptions has significant economic advantages. The evolutionary trend has seen membrane cells dominating the process technologies being used by producers in recent years. Now the membrane cells are being advanced to incorporate fuel cells or alternative gas diffusion electrodes reducing the energy demand.

This PERP report includes:

- In depth reviews of current and developing technology (including a list of technology holders and licensors )
- Cost of production estimates for current commercial technologies (mercury, diaphragm, and membrane cells) and speculative cost of production estimates for developing technologies (membrane with oxygen diffusion electrode and membrane with fuel cell)
- Regional commercial market analysis (supply, demand, and trade data and discussion)

## COMMERCIAL TECHNOLOGY

Chlorine production occurs overwhelmingly via electrolysis of a sodium chloride solution. The overall chlor-alkali process may be summarized as:



The various technologies differ by the method of separating the solution that surrounds the anode (anolyte) and the solution that surrounds the cathode (catholyte). This separation may be achieved by a porous separator (diaphragm), an ion exchange membrane (membrane cell); or, in the case of mercury cells, the cathode itself acts a separator by producing a sodium amalgam which is then reacted with water to produce sodium hydroxide.

Historically, mercury cells and asbestos based diaphragm cells were the major electrolysis technologies used to produce chlorine. However, due to environmental concerns and poor economics, these technologies are being phased out. Increased process efficiency and the requirement to meet more stringent environmental regulations has led to the increasing dominance of the more efficient, less hazardous/lower emission membrane-based technologies.

Following a general overview of electrochemical process technology (including brine and electricity supply, and electrode configurations), detailed discussion of the following technologies are given:

- Mercury Cells
- Diaphragm Cells
- Membrane Cells
- Fuel Integrated Systems
- Oxygen Depolarized Electrode

Brief overviews of electrical energy consumption and heating; as well as hydrogen, chlorine, sodium hydroxide, and effluent processing, are given.

## ALTERNATIVE AND DEVELOPING TECHNOLOGY

Following the trend to reduce costs by reducing electrical energy consumptions the conventional technology has evolved.

Oxygen diffusion electrodes have been studied for many years. They are already employed commercially in the less complex hydrogen chloride electrolysis in China. More recently, in 2011 a 20 000 tons per year chlor-alkali demonstration plant came on stream in Europe.

NASA used fuel cells in the 1970s, though they were too expensive to integrate into a chlor alkali system (cost to NASA of approximately \$600 000 per kilowatt). The technology uses hydrogen generated electrochemically to produce electricity in a fuel cell, avoiding the Carnot

limitations inherent to hydrogen's combustion. After numerous technology advances leading to a reduction in capital investment costs, renewed interest for incorporating fuel cells into a chlor-alkali system has been expressed by a number of producers.

## PROCESS ECONOMICS

Costs of producing Chlorine and Sodium Hydroxide have been developed for the following technologies:

- Mercury Cell (N.W. Europe basis)
- Diaphragm Cell (N.W. Europe basis)
- Monopolar Membrane Cell (N.W. Europe basis)
- Bipolar Membrane Cell (China, N.W. Europe, USGC bases)
- Membrane Cell with Oxygen Diffusion Electrode (China and N.W. Europe basis)
- Membrane Cell with Integrated Fuel Cell (China and N.W. Europe basis)

Various sensitivity analyses have been carried out, i.e., impact of sodium chloride price, electricity price, and plant scale on bipolar membrane process; and impact of oxygen and hydrogen prices on bipolar membrane, oxygen diffusion electrode, and integrated fuel cell processes).

Detailed cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities consumed (electrical energy, cooling water, fuel etc.), direct and allocated fixed costs, by unit consumption and per metric ton and annually, as well as contribution of depreciation to arrive at a cost estimate. Capital costs are broken down according to inside battery limits (ISBL), outside battery limits (OSBL), other project costs, and working capital. Major equipment items used in ISBL and OSBL is listed.

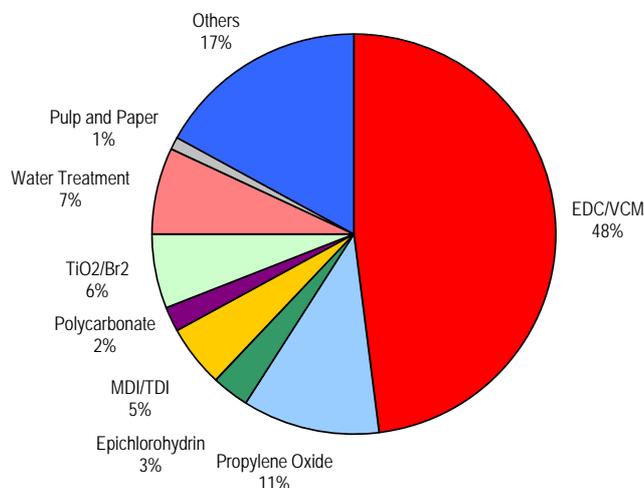
Note that in the cost of production tables, operating costs are presented in terms of \$ per electrochemical unit (ECU). This is the typical industry standard and reflects the fact that for every one ton of chlorine produced, 1.1 tons of sodium hydroxide is also produced (as well as 24 kg of hydrogen), this is what is known as the ECU.

## COMMERCIAL MARKET REVIEW

Chlor-alkali products are considered a keystone of the chemical industry. The major use of chlorine is to produce ethylene dichloride which in turn is used to make the vinyl chloride monomer and PVC. Phosgene and epichlorohydrin are other end use derivatives for chlorine. Traditionally chlorine has been used extensively by the pulp and paper industry for bleaching, though since the turn of the century this application has largely disappeared in developed economics over environmental concerns.

Figure 1.1 below gives a breakdown of global chlorine consumption by application and Figure 1.2 gives a breakdown of global caustic soda consumption by application.

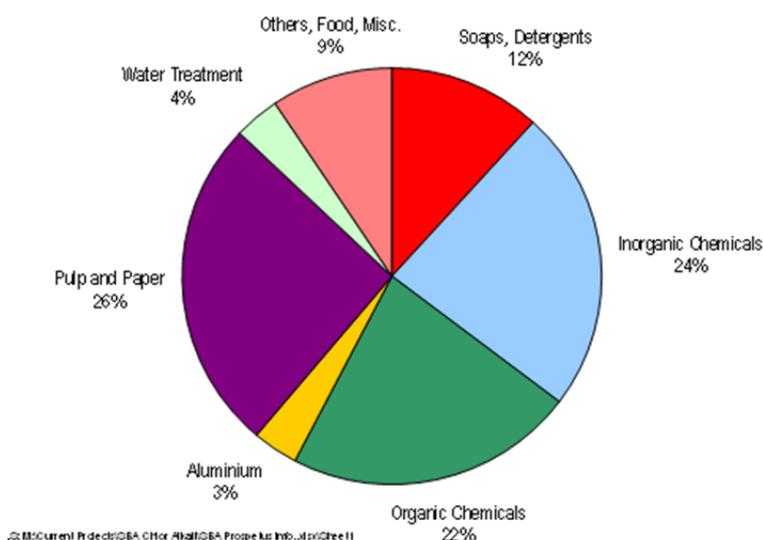
Figure 1 Global Chlorine Consumption by Application  
(2011)



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Sodium hydroxide is mainly used in the pulp and paper industry, aluminium, and soap and detergents production. It is also valued for its neutralising ability, and used in that capacity throughout the chemical industry, controlling acidity and neutralising acidic waste discharges. Similarly to chlorine, it is used as an intermediate in many products such as sodium phenolate used in the production of aspirin amongst other pharmaceuticals.

Figure 2 Global Caustic Soda Consumption by Application  
(2011)



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The report includes data and discussion on the following:

- Global demand, supply, and net trade
- Supply, demand and trade data according to region (i.e., North American, Western European, Asia Pacific and Rest of the World)
- A list of plants in each region above is given showing specific plant capacities, owning company, location and annual tonnage produced



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