## C1 CHLOR-ALKALI

### **ELECTROLYSIS**



## Let's start at the very beginning...

**Electrolysis** is a chemical decomposition reaction produced by passing an electric current through a solution containing ions.

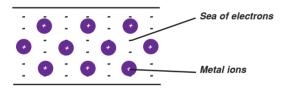
**Reduction** is when an atom, ion or molecule gains electrons. Examples can be shown using half reactions:  $Cl_2 + 2e^- \rightarrow 2Cl^-$  or  $Mg^{2+} + 2e^- \rightarrow Mg(s)$ 

**Oxidation** is when an atom, ion or molecule gives off (loses) electrons, for example:

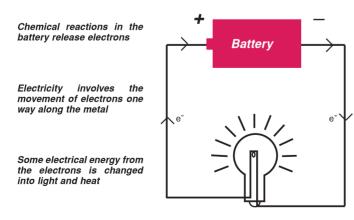
 $Na(s) \rightarrow Na^+ + e^- \text{ or } S^{2-} \rightarrow S(s) + 2e^-$ 

A **redox** reaction is a reaction that involves electron transfer. One species is oxidised while another is reduced.

Charge can move within a conductor. Metals are good conductors because they have delocalised electrons which can move without chemically changing the metal. These electrons are already present in the metal.



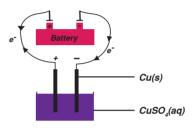
An **electrolyte** is a liquid that can conduct electricity. Electrons do not move freely through these liquids, rather it is charged ions present within the liquid that move. The effect is still moving charge. Many liquids with ions present are used as electrolytes. Some are pure liquid compounds and some are ions in solution.



A battery connected in a circuit sets up an electric field in the circuit which causes the electrons to move.

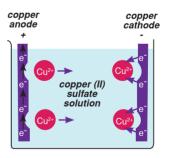
### Purifying metals

Let us take two copper electrodes submerged in blue copper (II) sulfate solution and connect them to a battery. Copper sulfate is an electrolyte as it has ions  $(Cu^{2+} \text{ and } SO_4^{2-})$  which are free to move.

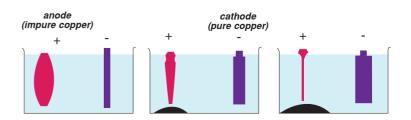


At the positive electrode (**anode**) copper atoms become copper ions and the released electrons move through the conductor towards the battery. Copper atoms are oxidised to form copper ions:  $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ . Oxidation occurs at the anode. Copper ions will go into solution at the anode.

Electrons moving to the negative electrode (**cathode**) combine with the positive copper ions from the solution to form copper atoms which then remain on the electrode. Copper ions are reduced to form copper atoms.  $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ . Reduction occurs at the cathode. Copper metal will be formed at the cathode.



The result is that the anode decreases in mass as the copper goes into the solution. The cathode increases in mass. This can be used as a purification method as impurities will be exposed as the anode erodes, but will not be attracted to the cathode.

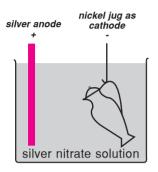


## Electroplating

This is just a variation of the previous concept. If the anode is made of silver metal and the electrolyte contains silver ions (silver nitrate in this example), then the item used as a cathode will have a silver layer formed around it. Oxidation will take place at the anode: Ag  $\rightarrow$  Ag<sup>+</sup> + e<sup>-</sup>

Reduction will take place at the cathode:

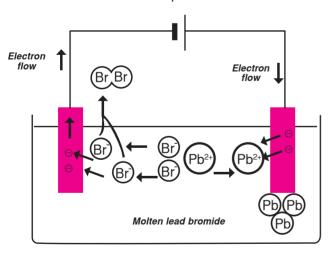
$$Ag^+ + e^- \rightarrow Ag$$





## Decomposition using electrolysis

Let us set up a similar situation with graphite electrodes dipped in molten lead bromide (PbBr<sub>2</sub>). (Graphite will conduct electricity but not take part in the reaction.) There are Pb<sup>2+</sup> ions and Br<sup>-</sup> ions present. The negative bromide ions will be attracted to the positive electrode. Here they will be oxidised (making this electrode the anode) into bromine atoms which will combine to form bromine gas. The positive lead ions will be attracted to the negative electrode where they will be reduced to form lead atoms. Brown bubbles are formed at the anode and the cathode is plated with lead.

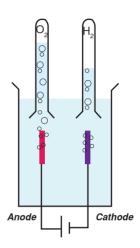


Two Br- ions each lose 1 electron to the anode... forming atoms of bromine gas.

At the anode: Br<sup>-</sup> → Br + e<sup>-</sup> Each Pb<sup>2+</sup> ion gains 2 electrons from the cathode... ...to form a lead atom.

At the cathode:  $Pb^{2+} + 2e^{-} \longrightarrow Pb$  Water, which can break up into H<sup>+</sup> ions and OH<sup>-</sup> ions, can be decomposed in a similar manner:

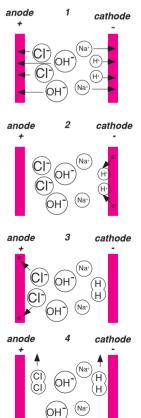
The reaction that takes place at the anode is an oxidation reaction (loss of electrons):  $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ The reaction that takes place at the cathode is a reduction reaction (gain of electrons):  $2H^+ + 2e^- \rightarrow H_2$ Therefore the net reaction is:  $2H_2O(\ell) \rightarrow 2H_2(g) + O_2(g)$ 



## Electrolysis of brine

Brine is sodium chloride (NaCl or table salt) solution and contains Na<sup>+</sup> and Cl<sup>-</sup>. Some H<sup>+</sup> and OH<sup>-</sup> ions are also present since water dissociates to a small extent. We find that some cations are better at accepting electrons than others, and that some anions lose their electrons easier than others. This is what happens in the electrolysis of brine:

- Positive ions attracted to negative electrode. Negative ions attracted to positive electrode.
- 2. Hydrogen ions accept electrons more readily than sodium ions. Hydrogen is therefore reduced at the cathode to form hydrogen gas: 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>o</sub>
- Chloride ions lose electrons more readily than hydroxide ions. Chlorine is therefore oxidised at the anode to form chlorine gas: 2Cl<sup>-</sup> → Cl<sub>2</sub> + 2e<sup>-</sup>
- 4. Chlorine gas bubbles are formed at the anode and hydrogen gas bubbles are formed at the cathode. The remaining solution becomes alkaline due to the presence of sodium hydroxide.



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## C2 CHLOR-ALKALI

SODIUM SALTS



### Salt

The word 'salt' is a general chemical term that refers to the ionic compound that is formed when an acid reacts with a base. They may be simple salts such as NaCl, KCl, and Na<sub>2</sub>SO<sub>4</sub>; acid salts like NaHCO<sub>2</sub> and NaH<sub>2</sub>PO<sub>4</sub>; or double salts like KAI(SO<sub>4</sub>)<sub>2</sub>. Table salt is sodium chloride, a chemical compound with the formula NaCl. Sodium chloride has been used to flavour and preserve food for thousands of years. As a result, salt became an essential part of commercial transactions and was often used as money or barter. Exchange of salt for slaves in ancient Greece gave rise to the expression 'not worth his salt'. The Romans gave a salarium (salary) to those who were 'worth their salt,' and Roman soldiers were given salt rations known as salaria argenta. Today, salt continues to be of major economic importance, with thousands of uses in addition to flavouring and preserving food.

Sodium chloride forms colourless, cubic crystals that are made up of large numbers of NaCl formula units, to give a three-dimensional crystalline lattice in which each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The strong electrostatic attractions between the positive and negative ions, known as ionic bonds, hold the solid sodium chloride together.

Sodium chloride occurs naturally as the mineral halite, commonly called rock salt, in large underground deposits on every continent. Natural brines, or salty waters other than seawater, are found in wells and lakes, such as the Great Salt Lake of Utah and the Dead Sea. Salt is also found in surface deposits in regions subject to arid climates.

The manufacture and use of salt is one of the oldest chemical industries. The three main methods for recovering salt are:

- Underground salt mining, which uses techniques similar to those for mining coal;
- Solar evaporation of seawater or natural brine in lakesor large lagoons; and
- Evaporation of brines obtained by pumping water into a rock salt deposit, dissolving the salt, and bringing the brine to the surface.

The annual world salt production is about 180 milliontonnes. The top producers are the United States and China with 40 million and 27 million tonnes, respectively.

#### Industrial use

Electrolysis of molten sodium chloride produces sodium metal and chlorine gas:

 $2 \text{ NaCl}(\ell) \rightarrow 2 \text{Na}(\ell) + \text{Cl}_2(g)$ 

Salt is also one of the raw materials used in the Solvay process for manufacturing sodium carbonate (soda ash).

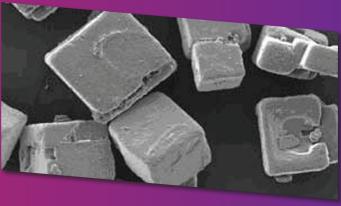
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#### A large pile of salt at a salt mine in Upington



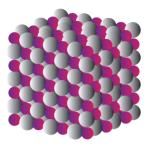
Source: www.chemistryexplained.com

#### Salt crystals magnified 100x



Source: California State University

#### A 3-D representation of a sodium chloride crystal



Source: Wikimedia Commons

## Salt in history

Salt's profound impact on human civilisation spans recorded history, and precedes it. Salt has influenced human existence virtually from the beginning. Neolithic settlements were at salt springs. Caravans trekked deserts trading salt ounce-for-ounce for gold.

Most cultures have folklore and art forms based on salt. And many cultures share traditions such as offering bread and salt to welcome visitors.

Salt's economic and military significance produced trading partnerships, or armed combat. Economies and cultures ranging from the Sahara in West Africa to the Himalayan peaks of Nepal gives a glimpse of the salt trading culture of centuries gone by.

Religious texts and liturgy frequently employ salt metaphorically, for example 'Ye are the salt of the Earth'.

Salt was involved in such historic events as the building of the Erie Canal, the French Revolution and the drive for India's independence from British colonial rule.

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Caption: A bar of salt



### **DID YOU KNOW?**

Seawater contains an average of 2.6% (by weight) NaCl, or 78 million tonnes per cubic kilometre.



## The role of salt

Table salt is pure salt that has been ground into fine particles. Because salt tends to cake in humid climates, an anti-caking agent such as magnesium carbonate or calcium silicate is often added. Table salt is also available as iodised salt with 0,1 percent potassium iodide by weight. Because iodide ion is essential to thyroid gland function, the routine use of iodised salt ensures adequate iodine in the diet.

Salt is used to cure meat and fish by soaking them in brine, rubbing salt onto them, or injecting them with a salt solution. Salt is also used to make pickles by soaking cucumbers in brine. Rock salt is sprinkled on highways to melt ice.

Nearly half of the 40 million tonnes of salt produced each year in the United States is used in the chemical manufacture of chlorine and sodium hydroxide (caustic soda) by electrolysis of brine solution.

Both sodium chloride and potassium chloride are essential to the electrolyte balance in body fluids. Good health depends on the proper ratio of potassium ions to sodium ions. One solution is to eat unprocessed, natural foods and to salt foods with a commercial product that contains both potassium and sodium chlorides called "Lite Salt" or "Low Salt".

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# C3 CHLOR-ALKALI

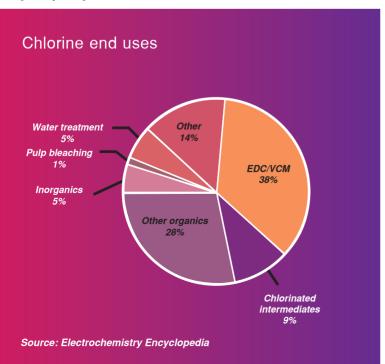
CHLORINE

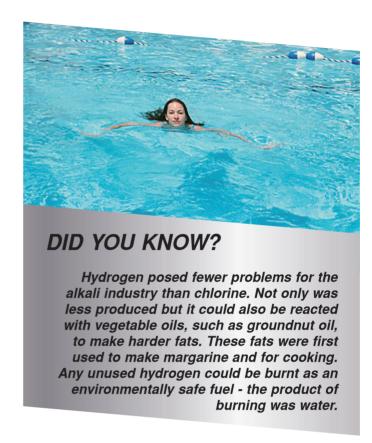


### The use of chlorine

The first use of chlorine for disinfection dates back to 1823, when it was used in hospitals. Chlorine water was employed in obstetric wards to prevent puerperal fever in 1826, and fumigation with chlorine was practised during the great European cholera epidemic. Following the discovery that bacteria were responsible for the transmission of certain diseases, several investigators studied chlorination of both sewage and potable water in the 1890's in an attempt to destroy these bacteria. By 1912, the use of chlorine for water treatment had become a common practice. There was significant reduction in the incidence of water-borne diseases, such as typhoid. For example, from October to December 1909, 549 cases of 'winter typhoid' were reported in Montreal, Canada. After chlorination of drinking water was begun in 1910, only 170 cases were reported for the same 4-month period. Thus, virtually all the chlorine manufactured during the 19th century was consumed by these two industries. The major turning event for the growth of the chlorine industry was its use in 1912 for water purification during the Niagara Falls typhoid epidemic. It should be noted that bleaching powder was used in 1897 to clean the polluted mains during a typhoid outbreak in England.

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Between 1920 and 1940, several new applications for chlorine were developed, for example, in the manufacture of ethylene glycol, chlorinated solvents, vinyl chloride, and others. World War II triggered the development of new uses for chlorine for military needs. This trend continued to produce new products for civilian use following the war. Progress in synthetic organic chemistry in the 19th century had led to the preparation of substitutes for natural products and entirely new and useful compounds including intermediates and final products. Chlorine, because of its reactivity, unique properties, and low price, was used in many of these, including solvents, pharmaceuticals and dyes. In 1795, dichloroethane was produced and in 1831 chloroform was synthesised. By 1848, the anaesthetic properties of chloroform were recognised and used in surgical practice.

The uses of chlorine include pulp and paper manufacturing operations for bleaching to produce a high quality whitened material, and in water treatment operations as a disinfectant. Other uses of chlorine include the production of organic and inorganic chemicals. The largest volume organic chemical manufactured that involves chlorine is polyvinyl chloride (PVC). PVC is a very versatile thermoplastic, used in a wide variety of daily products.

### Chlorine profile

Chlorine is a toxic yellowish green gas, which is heavier than air and has an irritating odour. Chlorine is a member of the halogens, along with fluorine, bromine, and iodine. It is the 11th most abundant element. Chlorine is highly reactive and combines readily with other elements to form compounds. It is found as sodium chloride (salt), potassium chloride or calcium chloride in seawater and rock salts, rather than in the form of an elemental substance in nature.

### Chlorine

The element chlorine was discovered in 1774 by a Swedish chemist named C.W. Scheele. The first industrial process for the production of chlorine was the so-called Weldon process (1866). This process employs the reaction between HCl and oxygen under the catalysis of manganese dioxide to form chlorine and water.

$$4\text{HCI} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{CI}_2$$

The Deacon process (1868) is a variation of the Weldon process using a cobalt catalyst instead of manganese dioxide. A variation of this process called the Shell-Deacon process is still of limited technical importance today.

$$4HCI + O_{2} \rightarrow 2H_{2}O + 2CI_{2}$$

In 1892 the first electrochemical manufacturing process for chlorine production was developed. Since then electrochemical processes have been the methods of choice for most chlorine production. One of the main reasons for this is the fact that electrochemical processes produce caustic soda and hydrogen simultaneously with chlorine. With caustic soda being consumed in large quantities by various industries, the electrochemical route offers the advantage of producing two saleable products at the same time thus making the whole process more economically viable. The simultaneous production of chlorine and caustic soda is the reason that the chlorine industry is also referred to as the 'chlor-alkali' industry.

#### Chlorine gas



#### Chlorine liquid



Source: Wikimedia Commons

### Salt water pool chlorinator



## Chlorine in pools

Pool owners make use of chlorine containing chemicals to keep their pools clear and disinfected. Common methods introduce the hypochlorite ion, which has bleaching and disinfecting properties, to the water. 'Chlorine pools' often use chemicals like calcium hypochlorite or sodium hypochlorite which are added to the water. Chlorine tablets are readily available and are either added to the pump unit or placed in floating devices that dissolve the tablet over time in the water. Some chlorine pool owners report bleaching of hair, burning eyes, dry skin and faster deterioration of swim wear as a result of these chemicals in the water.

'Salt water pools' have only salt (NaCl) added to the water and the pump unit uses electrolysis to form chlorine and sodium hydroxide. These two products react and yield the hypochlorite ion, which is then introduced into the pool. The pools are not chlorine free, but the concentration of chlorine is less than in chlorine pools. This lower concentration results in less damage to swimmers and clothing, but these pools take longer to clear up if there is bacteria present or the pH levels are not ideal.

Pool chemistry is sensitive to pH levels and therefore the pH needs to be monitored in both types of pools. Introduction of rainwater, urine, decomposing plant material and other contaminants can affect these levels and lead to the formation of other chemicals, like chloramines, which can also cause irritation to swimmers.

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## C4 CHLOR-ALKALI

### CHLORINE DERIVATIVES



### Bleach

Sodium hypochlorite is a chemical compound with the formula NaClO. Sodium hypochlorite solution, commonly known as bleach, is frequently used as a disinfectant or a bleaching agent.

Sodium hypochlorite

Sodium chlorate

$$Na^{+} \begin{bmatrix} O \\ C \\ O \end{bmatrix}$$

$$Na^{+} \begin{bmatrix} O \\ O \\ O \end{bmatrix}$$

Source: Wikimedia Commons

Hypochlorite was first produced in 1789 by Claude Louis Berthollet in his laboratory on the Quay Javel in Paris, France, by passing chlorine gas through a solution of sodium carbonate. The resulting liquid, known as "Eau de Javel" ("Javel water"), was a weak solution of sodium hypochlorite.

The Hooker process is the only large scale industrial method of sodium hypochlorite production. In this process sodium hypochlorite (NaClO) and sodium chloride (NaCl) are formed when chlorine is passed into cold and dilute sodium hydroxide solution. It is prepared industrially by electrolysis with minimal separation between the anode and the cathode. The solution must be kept below 40°C (by cooling coils) to prevent the undesired formation of sodium chlorate.

Sodium hydroxide and chlorine are commercially produced by the chlor-alkali process, and there is no need to isolate them to prepare sodium hypochlorite.

Household bleach sold for use in laundering clothes is a 3-6% solution of sodium hypochlorite at the time of manufacture. A 12% solution is widely used in waterworks for the chlorination of water and a 15% solution is more commonly used for disinfection of waste water in treatment plants. High-test hypochlorite (HTH) is sold for chlorination of swimming pools and contains approximately 30% calcium hypochlorite. The crystalline salt is also sold for the same use; this salt usually contains less than 50% of calcium hypochlorite.

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## Hydrochloric acid

Hydrochloric acid is amongst the top 25 industrial chemicals produced and used globally and in South Africa. It is used for mineral processing, metal pickling, regenerating water purification systems, and swimming pool neutralisation. Most chlor-alkali plants have a hydrochloric acid production plant on the same site.

$$H_2(g) + CI_2(g) \rightarrow 2HCI(g)$$

 $HCI(g) + H_2O(\ell) \rightarrow H_3O^{\dagger}(aq) + CI^{\dagger}(aq)$ 

hydrogen chloride gas → hydrochloric acid (HCl(aq))

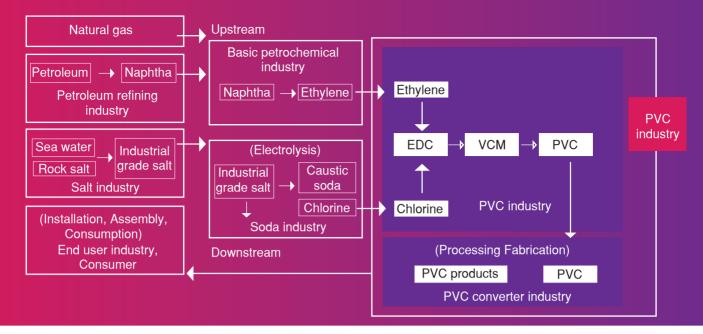
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Bottle of hydrochloric acid

Bottle of bleach





### How is PVC made?

The chemical process for making polyvinyl chloride (PVC) involves taking the simplest unit, called the monomer, and linking these monomer molecules together in the polymerisation process. molecular chains, called polymers, are formed. This is the case for PVC, which is made from vinyl chloride monomer (known usually by its initials VCM), through polymerisation. Polymers such as PVC, which are manufactured from monomers through polymerisation, are solid and chemically stable substances. VCM is a gas at room temperature but is usually stored in liquid form under pressure. It is also known as chloroethene or ethylene chloride. Ethylene and chlorine are raw materials for PVC. Upstream industries are those that provide these materials. They include producers of basic petrochemicals, which supply ethylene; and the chlor-alkali (caustic soda) industry, which supplies chlorine.

By thermal cracking of naphtha or natural gas, the basic petrochemical industry manufactures ethylene and propylene amongst other products. Naphtha is mainly supplied from the petroleum refinery industry, which uses crude oil as raw material. The chlor-alkali industry produces caustic soda, chlorine and hydrogen via electrolysis using industrial grade salt as main raw material. As a first stage in the PVC production process, ethylene and chlorine are combined to produce an intermediate product called ethylene dichloride; this is then transformed into vinyl chloride, the basic building block of polyvinyl chloride or PVC. The process of 'polymerisation' links together the vinyl chloride molecules to form chains of PVC. Most commodity plastics have carbon and hydrogen as their main component elements. PVC differs by containing chlorine (around 57 per cent by weight), in addition to carbon and hydrogen. The presence of chlorine in the molecule makes PVC particularly versatile because it makes it compatible with a wide range of other

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materials. The chlorine content also helps to make PVC flame retardant.

The formation of PVC can be represented with the following equations:

poly(vinyl chloride) or PVC

### The uses of PVC

As a hard plastic, it is used as vinyl siding, magnetic stripe cards, window profiles, gramophone records (which is the source of the name for vinyl records), pipe, plumbing and conduit fixtures. The material is often used in plastic pressure pipe systems for pipelines in the water and sewer industries because of its inexpensive nature and flexibility. It can be made softer and more flexible by the addition of plasticisers, the most widely used being phthalates. In this form, it is used in clothing and upholstery, and to make flexible hoses and tubing, flooring, roofing membranes, and electrical cable insulation.

The formation of PVC

Different representations of polyvinylchloride or PVC

# C5 CHLOR-ALKALI

**HYDROGEN** 



## Hydrogen profile

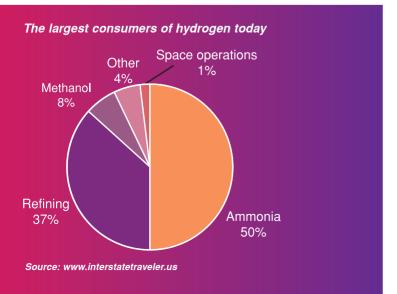
- · Hydrogen is the lightest element.
- It is by far the most abundant element in the known universe and makes up about 90% of the universe by weight. Hydrogen in water (H<sub>2</sub>O) is absolutely essential to life and it is present in all organic organisms.
- Hydrogen gas was used in lighter-than-air balloons for transport but is far too dangerous because of the fire risk.
- It burns in air to form only water as product.
- If hydrogen could be made on sufficient scale from other than fossil fuels then there might be a possibility of a hydrogen economy.

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## A timeline for hydrogen

1766 Hydrogen was first identified as a distinct element by British scientist Henry Cavendish after he evolved hydrogen gas by reacting zinc metal with hydrochloric acid. In a demonstration to the Royal Society of London, Cavendish applied a spark to hydrogen gas yielding water. This discovery led to his later finding that water (H<sub>2</sub>O) is made of hydrogen and oxygen.

1783 Jacques Alexander Cesar Charles, a French physicist, launched the first hydrogen balloon flight. Known as 'Charliere', the unmanned balloon flew to an altitude of three kilometres. Only three months later, Charles himself flew in his first manned hydrogen balloon.



**1800** English scientists William Nicholson and Sir Anthony Carlisle discovered that applying electric current to water produced hydrogen and oxygen gases. This process was later termed 'electrolysis.'

**1874** Jules Verne, a French author, prophetically examined the potential use of hydrogen as a fuel in his popular work of fiction entitled "The Mysterious Island".

1920s German engineer, Rudolf Erren, converted the internal combustion engines of trucks, buses, and submarines to use hydrogen or hydrogen mixtures. British scientist and writer, J.B.S. Haldane introduced the concept of renewable hydrogen in his paper "Science and the Future" by proposing that there will be great power stations where during windy weather the surplus power will be used for the electrolytic decomposition of water into oxygen and hydrogen.

1937 After ten successful trans-Atlantic flights from Germany to the United States, the Hindenburg, a dirigible inflated with hydrogen gas, crashed upon landing in Lakewood, New Jersey. The mystery of the crash was solved in 1997 when retired NASA engineer, Addison Bain, challenged the belief that hydrogen caused the Hindenburg accident. A study concluded that the explosion was not due to the hydrogen gas, but rather to a weather-related static electric discharge which ignited the airship's silver-coloured canvas exterior covering which had been treated with the key ingredients of solid rocket fuel.

**1958** The United States formed the National Aeronautics and Space Administration (NASA). NASA's space program currently uses the most liquid hydrogen worldwide.

**1959** Francis T. Bacon of Cambridge University in England built the first practical hydrogen-air fuel cell. The 5-kilowatt (kW) system powered a welding machine. He named his fuel cell design the 'Bacon Cell'.

**1973** The OPEC oil embargo and the resulting supply shock suggested that the era of cheap petroleum had ended and that the world needed alternative fuels. The development of hydrogen fuel cells for conventional commercial applications began.

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### Hydrogen

Based on the world chlorine production of 49,1 million tons in 2005, it can be estimated that the world production of hydrogen in the chlor alkali industry in 2005 was around 1,4 million tons per annum. It is rather difficult to comment on the world demand for hydrogen because this varies drastically from country to country. In some areas hydrogen has virtually no value, while in others it can be quite valuable. However, with the proposed entry into hydrogen technology based fuel production and a more widespread use of fuel cell technology on the cards, it is very likely that there will be dramatic changes in the hydrogen market in the near future. In South Africa hydrogen is mainly used for the production of HCl and Sorbitol.

A representation of a hydrogen molecule



## Cling wrap

Plastic wrap was invented in 1953 by a scientist who was trying to make a hard plastic cover for his car; his experiment was completely unsuccessful but he then found the usefulness of plastic wrap which he happened to create instead. The original cling wrap material was Saran, the commercial name for polyvinylidene chloride.

The material was given approval for direct dry food contact and for paperboard coating for contact with fatty and aqueous foods.

### Purification and disinfection

Chlorine is an important chemical for water purification (such as water treatment plants), in disinfectants, and in bleach. Chlorine in water is more than three times more effective as a disinfectant against *Escherichia coli* than an equivalent concentration of bromine, and is more than six times more effective than an equivalent concentration of iodine.

Chlorine is usually used (in the form of hypochlorous acid) to kill bacteria and other microbes in drinking water supplies and public swimming pools. In most private swimming pools chlorine itself is not used, but rather sodium hypochlorite, formed from chlorine and sodium hydroxide, or solid tablets of chlorinated isocyanurates. Even small water supplies are now routinely chlorinated.

It is often impractical to store and use poisonous chlorine gas for water treatment, so alternative methods of adding chlorine are used. These include hypochlorite solutions, which gradually release chlorine into the water, and compounds like sodium dichloro-s-triazinetrione (dihydrate or anhydrous), sometimes referred to as "dichlor", and trichloro-s-triazinetrione, sometimes referred to as "trichlor". These compounds are stable while solid and may be used in powdered, granular, or tablet form. When added in small amounts to pool water or industrial water systems, the chlorine atoms hydrolyse from the rest of the molecule forming hypochlorous acid (HOCI) which acts as a general biocide killing germs, micro-organisms, algae, and so on.

This article was obtained online from the Wikipedia. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list. Wikipedia. 2010. Chlorine. [Online]. Available: http://en.wikipedia.org/wiki/Chlorine#Purification \_ and \_ disinfection. [19 July 2010].

#### Cling wrap



The terms 'Saran Wrap' and 'Glad Wrap' are used in many countries and areas to refer to any brand of cling/plastic wrap.

Shell Hydrogen
Fuel station Vetnisstöö

A hydrogen filling station in Reykjavik, Iceland

Source: http://feedthesink.com/2010/05/17/cling-wrap-history-future

# C6 CHLOR-ALKALI

SODIUM HYDROXIDE



## Sodium hydroxide

Sodium hydroxide, a chemical compound, NaOH, is a white crystalline substance that readily absorbs carbon dioxide and moisture from the air. It is very soluble in water, alcohol, and glycerin. It is corrosive and a strong base. Commonly known as caustic soda. Ive. or sodium hydrate, it is available commercially in various solid forms, for example pellets, sticks, or chips, and in water solutions of various concentrations; both solid and liquid forms vary in purity. The major use of sodium hydroxide is as a chemical in the manufacture of other chemicals; because it is inexpensive, it is widely used wherever a strong base is needed. It is also used in producing rayon and other textiles, in making paper, in etching aluminium, in making soaps and detergents, and in a wide variety of other uses. The principal method for its manufacture is electrolytic dissociation of sodium chloride; chlorine gas is a co-product. Small amounts of sodium hydroxide are produced by the soda-lime process in which a concentrated solution of sodium carbonate (soda) is reacted with calcium hydroxide (slaked lime); calcium carbonate precipitates, leaving a sodium hydroxide solution.

This material was obtained from The Columbia Electronic Encyclopedia. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: The Columbia Electronic Encyclopedia, 6th ed. 2007. Sodium Hydroxide. [Online]. Available: http://www.infoplease.com/ce6/sci/A0845794.html. [19 July 2010].

#### Hand made soap



Source: Wikimedia Commons

### **DID YOU KNOW?**

'Soda ash' is sodium carbonate, while 'potash' is a term used to refer to many potassium chloride and various potassium sulphates.

#### Global caustic soda demand



2005 demand = 52.5 million dry metric tons



Sodium hydroxide pellets Source: Wikimedia Commons

### Caustic soda history

The Egyptians used caustic soda to manufacture coarse soaps. For centuries, the main use remained the saponification of fatty acids. In 1791, Leblanc invented a process for the production of sodium carbonate which was a major milestone in the evolution of commercial production. However, this was superseded by Ernest Solvay who, in 1861, manufactured this same sodium carbonate using ammonia. His efficient production methodology overtook all other processes. Producing sodium carbonate of such a high purity was not possible at the time. The Solvay process therefore gave a vigorous impulse to the consumer industries by providing unlimited quantities of sodium carbonate at a low cost. Among these, the manufacture of caustic soda by the caustification of sodium carbonate was obviously the first beneficiary discovery. Towards the end of the 19th century, thanks to technological advances, another process for the manufacture of caustic soda, the electrolysis of a solution of sodium chloride, became feasible industrially. Solvay became interested in the process and built its first electrolysis plant in 1898. Since then this technique has been continuously improved.

This material was obtained from Solvay Indupa. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: Solvay Indupa. 2010. Sodium Hydroxide History. [Online]. Available: http://www.solvayindupa.com/nossosprodutosquimicos/soda/historia/0,,58919-2-0,00.htm. [19 July 2010].

### **DID YOU KNOW?**

A surfactant is a wetting agent that lowers the surface tension of a liquid, allowing it to spread more easily. Soap is a surfactant that is used with water for washing and cleaning. Soap is made by reacting a fat with either sodium hydroxide (NaOH) or potassium hydroxide (KOH).

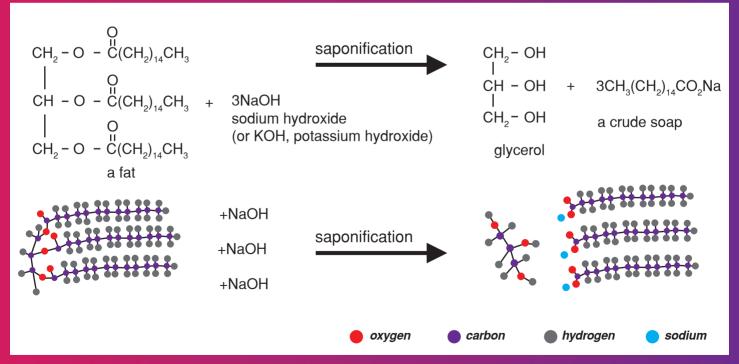
Caption: Making soap ducks



Source: @BrokenSphere / Wikimedia Commons

## How soaps are made

The two diagrams below show how sodium hydroxide reacts with a fat to form a soap and glycerol. fat (ester) + sodium hydroxide → glycerol + soap



One of the organic chemical reactions known to ancient man was the preparation of soaps through a reaction called saponification or soap-making. Natural soaps are sodium or potassium salts of fatty acids, originally made by boiling lard or other animal fat together with lye or potassium hydroxide. Hydrolysis of the fats and oils occurs, yielding glycerol and crude soap.

## C7 CHLOR-ALKALI

SOAPS AND DETERGENTS



### Introduction

Large amounts of caustic soda are used in the manufacture of soap. The chemistry behind soap production has not changed since it was made from animal fat and ash from wood fires about 5 000 years ago. Today humans still make soap by boiling animal fat or plant oils with a strong base, such as sodium or potassium hydroxide. Soap is a waxy substance that enhances the ability of water to wash away grease and oil from our bodies, clothes and dishes. Soaps usually consist of 90% by mass neat soap and 10% moisture. Pigments, dyes, perfumes, germicides and antioxidants may be added depending on the application and market segment for which the product is targeted.

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### Soap

Soap is a mixture of sodium salts of various naturally occurring fatty acids. Air bubbles added to a molten soap will decrease the density of the soap and thus allow it to float on water. If the fatty acid salt contains potassium rather than sodium, a softer lather is the result. Soap is produced by a saponification or basic hydrolysis reaction of a fat or oil. Sodium carbonate or sodium hydroxide is used to neutralise the fatty acid and convert it to the salt.

The general overall hydrolysis reaction is:

fat + NaOH → glycerol + sodium salt of fatty acid

Although the reaction is shown as a one step reaction, it is in fact two steps. The net effect is that the ester bonds are broken. The glycerol turns back into an alcohol. The fatty acid portion is turned into a salt because of the presence of a basic solution of NaOH. In the carboxyl group, one oxygen now has a negative charge that attracts the positive sodium ion.

Types of soap: The type of fatty acid and length of the carbon chain determines the unique properties of various soaps. Tallow or animal fats give primarily sodium stearate (18 carbons), a very hard, insoluble soap. Fatty acids with longer chains are even more insoluble. As a matter of fact, zinc stearate is used in talcum powders because it is water repellent. Coconut oil is a source of lauric acid (12 carbons) which can be made into sodium laurate. This soap is very soluble and will lather easily even in sea water. Fatty acids with only 10 or fewer carbons are not used in soaps because they irritate the skin and have unpleasant odours.

This material was obtained from the Virtual Chembook, Elmhurst College. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: Ophardt, C.E. 2003. Soap. [Online]. Available: www.elmhurst.edu/~chm/vchembook/554soap.html. [19. July 2010]

### Investigating soaps

Take two jars and fill them half full of water.

Add a drop or two of food colouring and shake.

Add plain cooking oil to the jars, leaving some space at the top. Add a few squirts of liquid soap to one of the jars. Put the lids back on tight and shake them for about 30 seconds. When you first put them down, there's not much difference between the two jars. The oil and water molecules are all quite well mixed together. Wait a while and observe.

**Explanation:** Some molecules are hydrophilic, meaning they are attracted to water, and some molecules are hydrophobic meaning they are repelled by water. Soap is actually a very long molecule that has one hydrophilic end and one hydrophobic end. The water sticks to or associates with the hydrophobic end and the oil sticks to or associates with the hydrophobic end. This is what has happened in the soap-containing jar. The jar with just oil and water quickly separates. In the jar with the soap added, however, the oil and water stay mixed together for much longer.



### **Micelles**

Each soap molecule has a long hydrocarbon chain, sometimes called its 'tail', and a carboxylate 'head'. In water, the sodium or potassium ions float free, leaving a negatively-charged head. Soap is an excellent cleanser because of its ability to act as an emulsifying agent. An emulsifier is capable of dispersing one liquid into another immiscible liquid. This means that while oil (which attracts dirt) doesn't naturally mix with water, soap can suspend oil/dirt in such a way that it can be removed.

The hydrocarbon chains are attracted to each other by dispersion forces and cluster together, forming structures called micelles. In these micelles, the carboxylate groups form a negatively-charged spherical surface, with the hydrocarbon chains inside the sphere. Because they are negatively charged, soap micelles repel each other and remain dispersed in water. Grease and oil are non-polar and insoluble in water.

When soap and soiling oils are mixed, the non-polar hydrocarbon portion of the micelles break up the non-polar oil molecules. A different type of micelle then forms, one with non-polar soiling molecules in the centre. Thus, grease and oil and the 'dirt' attached to them are caught inside the micelle and can be rinsed away. Although soaps are excellent cleansers, they do have disadvantages. As salts of weak acids, they are converted by mineral acids into free fatty acids:

$$CH_2(CH_2)_{16}CO_2Na + HCl(aq) \rightarrow CH_2(CH_2)_{16}CO_2H + Na^+ + Cl^-$$

These fatty acids are less soluble than the sodium or potassium salts and form a precipitate or soap scum. Because of this, soaps are ineffective in acidic water. Also, soaps form insoluble salts in hard water, such as water containing magnesium, calcium, or iron.

$$2CH_3(CH_2)_{16}CO_2Na + Mg^{2+} \rightarrow [CH_3(CH_2)_{16}CO_2]_2Mg + 2Na^+$$

The insoluble salts form bathtub rings, leave films that reduce hair lustre, and gray/roughen textiles after repeated washings.

## How does soap clean?

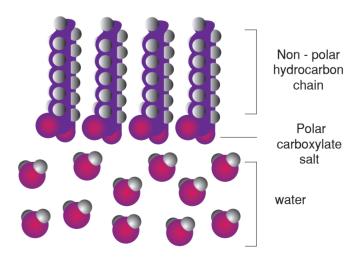
Modern detergents contain more than just surfactants. Cleaning products may also contain enzymes to degrade protein-based stains, bleaches to de-colour stains and add power to cleaning agents, and blue dyes to counter yellowing. Like soaps, detergents have hydrophobic or water-hating molecular chains and hydrophilic or waterloving components. The hydrophobic hydrocarbons are repelled by water, but are attracted to oil and grease. The hydrophilic end of the same molecule causes the one end of the molecule to be attracted to water, while the other side is binds to oil. Neither detergents nor soap accomplish anything except binding to the soil until some mechanical energy or agitation is added into the equation. Swishing the soapy water around allows the soap or detergent to pull the grime away from clothes or dishes and into the larger pool of rinse water. Rinsing washes the detergent and soil away. Warm or hot water melts fats and oils so that it is easier for the soap or detergent to dissolve and pull them away into the rinse water. Detergents are similar to soap, but they are less likely to form films (soap scum) and are not as affected by the presence of minerals in water (hard water). Other additives are sometimes added to soap for antibacterial or antifungal effects, but these are not the main ingredients, they just enhance the primary function of emulsifying oils in water.

The cleansing action of soap: grease is not soluble in water. In (a) the hydrophobic tails of the soap molecules dissolve in the grease. In (b) the grease is finally in the form of an emulsion.

This article was obtained online from the About.com Guide. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list. Helmenstine, A.H. 2010. How Soap Cleans. [Online]. Available http://chemistry.about.com/od/cleanerchemistry/a/how-soap-cleans.htm. [19 July 2010].

## Forming a soap film

When soap is added to water, the ionic-salt end of the molecule is attracted to water and dissolved in it. The non-polar hydrocarbon end of the soap molecule is repelled by water. A drop or two of soap in water forms a monolayer on the water surface as shown in the graphics below. The soap molecules "stand up" on the surface as the polar carboxyl salt end is attracted to the polar water. The non-polar hydrocarbon tails are repelled by the water, which makes them appear to stand up.



This material was obtained from the Virtual Chembook, Elmhurst College. Learners – if you use any part of it you need to write it in your own words and include the following in your reference list: Ophardt, C.E. 2003. Soap [Online]. Available: www.elmhurst.edu/~chm/vchembook/554soap.html [19 July 2010].

## C8 CHLOR-ALKALI

THE DIAPHRAGM CELL



## Electrolytic cells

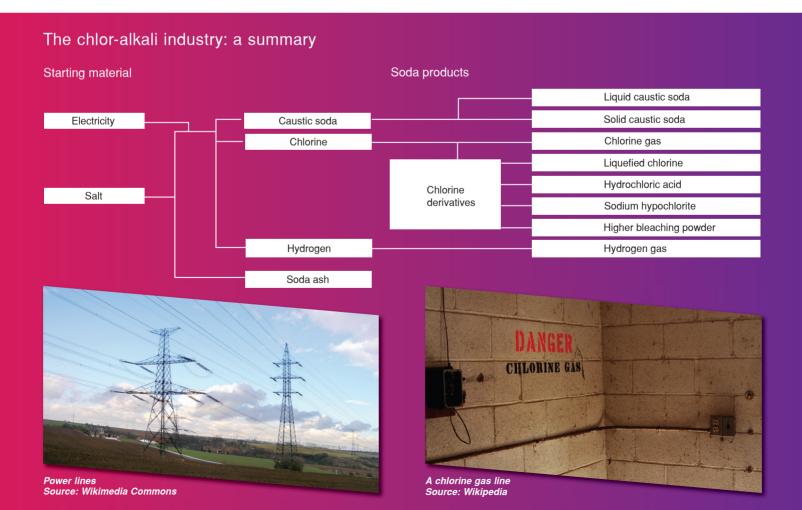
The first commercial production of chlorine through electrolysis was in 1888, and today more than 95% of the world chlorine production is achieved through this process. There are three different types of electrolytic cell that can be used for this process - the mercury cell, the diaphragm cell and the membrane cell. All three types have the same net reaction, but each technology uses a different way to separate the products when they form. Regardless of the technology used, cells are arranged in series, with each circuit consisting of several rows of cells. All electrochemical processes include some provision to separate the caustic and the hydrogen from the anode products. These provisions include:

- Asbestos diaphragm (Diaphragm process)
- Ion exchange membrane (Membrane process)
- Producing hydrogen and caustic in separate reactors (Amalgam process)



Chlorine is used to make polyvinylchloride (PVC), a versatile polymer used in sewerage pipes, drain pipes and gutters

Source: Wikimedia Commons



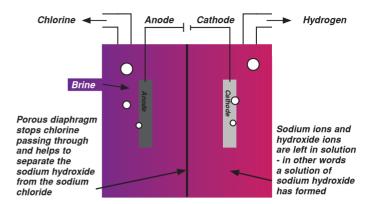
### The diaphragm cell

The development of the diaphragm process started in 1885 with the Griesheim cell. However, this early cell had no diaphragm as such and relied on the flow of the anolyte towards the cathode to prevent the hydroxide ions from backmigrating. E.A. Le Sueur is credited with the design of a cell incorporating a percolating asbestos diaphragm, which is the basis for all diaphragm chlor-alkali cells currently in use.

To separate the chlorine from the sodium hydroxide, the two half-cells were traditionally separated by a porous asbestos diaphragm, which needed to be replaced every two months. This was environmentally detrimental owing to the need for disposing of large quantities of asbestos. Such frequent replacement is fortunately

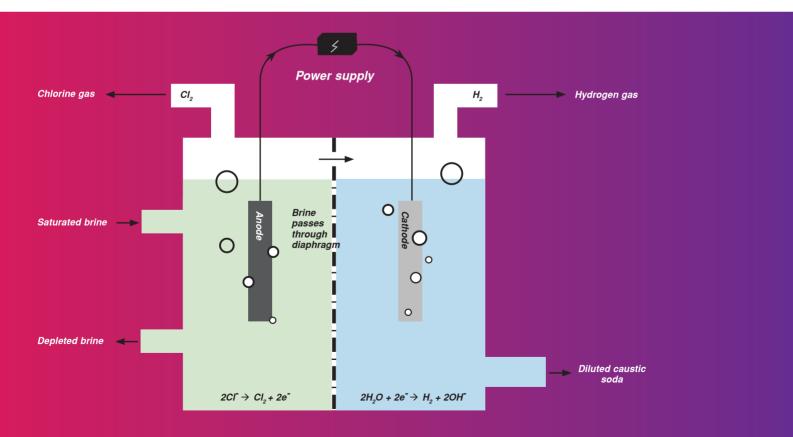
no longer necessary, the asbestos having now been replaced in part by polymers resulting in diaphragms with a much longer life.

#### The basic design of a diaphragm cell



Advantages of the diaphragm cell	Disadvantages of the diaphragm cell	
Use of well brine	Use of asbestos	
Low electrical energy consumption	High steam consumption for caustic concentration in expansive multistage evaporators	
	Low purity caustic	
	Low chlorine quality	
	Cell sensitive to pressure variations	

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Sodium and chloride ions enter the anode compartment. Chloride ions are oxidised at the anode to give chlorine molecules. Sodium and chloride ions pass through the diaphragm. Water is reduced at the cathode to form hydroxide ions and hydrogen molecules. Sodium, chloride and hydroxide ions exit the cathode compartment.

## C9 CHLOR-ALKALI

THE MEMBRANE CELL



## Producing chlorine using electrolysis

Electrochemical processes for chlorine production are mainly based on the electrolytic decomposition of sodium chloride (NaCl). In the majority of processes NaCl is dissolved in water forming a saturated solution (brine) that is subjected to a number of purification steps and fed into the anode side of an electrolytic cell. Direct current (DC) is applied to the cell solution resulting in the formation of three products: chlorine gas (Cl<sub>2</sub>), hydrogen gas (H<sub>2</sub>) and caustic soda (NaOH). The reactions taking place during this process are the following:

- Na<sup>+</sup>(aq) + Cl<sup>-</sup>(aq) are present due to the dissolution of sodium chloride: NaCl(s) → Na<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)
- H<sup>+</sup> and OH<sup>-</sup> are present due to water dissociating:
   H<sub>2</sub>O(ℓ) → H<sup>+</sup>(aq) + OH<sup>-</sup>(aq)
- Oxidation reaction at the anode: 2Cl<sup>-</sup> → Cl<sub>2</sub> + 2e<sup>-</sup>
- Reduction reaction at the cathode: 2H<sup>+</sup> + 2e<sup>-</sup> → H<sub>a</sub>
- Overall:

 $2NaCl(s) + 2H_2O(\ell) \rightarrow Cl_2(g) + H_2(g) + 2NaOH(aq)$ 

The first membrane plants came on-line in 1975, but it was only in the early 1960's that membrane plants started to become economically viable. The main reason for this was the unsatisfactory performance of the early generation of membranes. Once the membranes became more durable, the membrane process increasingly became the process of choice. Today nearly every new chlorine plant that comes online is based on the membrane process.

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### Using membranes

The most modern systems use a selective ion-exchange membrane to keep the products apart. The ion-exchange membrane is typically a fluoropolymer and can contain sulfonic acid groups. A saturated solution of brine flows into the anode compartment where CI- ions are oxidised to CI2 gas. Water enters the cathode compartment where it is reduced to H2 gas. OH- ions stay behind in the water. The selective ion-exchange membrane between the two compartments is permeable to cations and small amounts of water, but not to anions. The membrane keeps the CI2 gas and OH- ions apart but allows the Na+ ions to flow into

the cathode compartment, thus allowing the current to flow and maintaining electrical neutrality in the compartments. An aqueous solution of NaOH flows out of the cathode compartment. If the membrane malfunctions then hydroxide ions will migrate to the anode compartment and will react to form oxygen according to the following reaction:

 $2OH^{-} \rightarrow O_{2} + 2H^{+} + 4e^{-}$ 

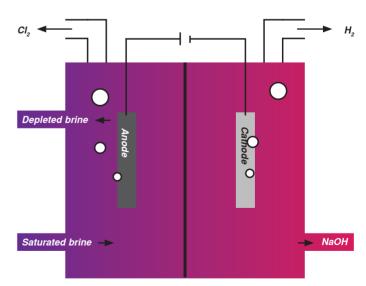
Alternatively it will react with the chlorine, forming chlorates:

 $2OH^- + Cl_2 \rightarrow OCl^- + H_2O + Cl^-$ .

### **DID YOU KNOW?**

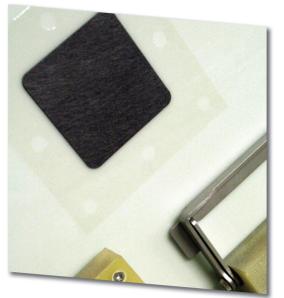
Modern membranes are manufactured from fluoro-substituted polymers that have COO and SO<sub>3</sub><sup>3-</sup> side groups. These side groups are responsible for preventing anions like OH and Cl<sup>-</sup> from migrating from one compartment to the other.

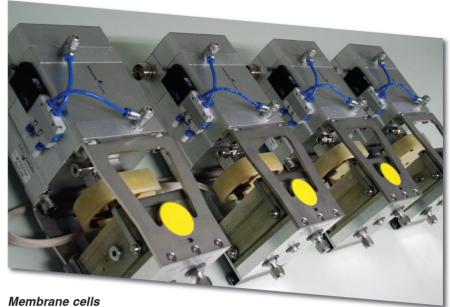
#### The basic structure of the membrane cell



Source: Wikimedia Commons

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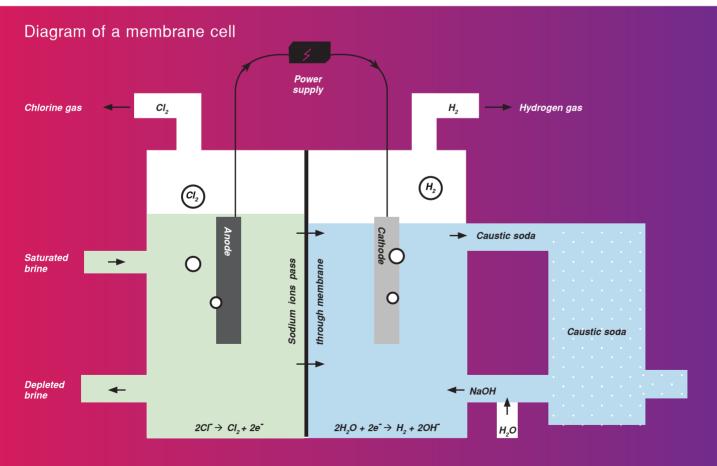


Nafion	mem	hrane

Advantages of membrane cells	Disadvantages of membrane cells
Low total energy consumption	High purity brine is required
Low capital investment	High cost of membranes
Inexpensive cell operation	High oxygen content in chlorine

High purity caustic solution obtained

Insensitive to cell load variations and shut downs



Sodium and chloride ions enter the anode compartment. Chloride ions are oxidised at the anode to give chlorine molecules. Sodium ions pass through the membrane and are attracted to the hydroxide ions. Water is reduced at the cathode to form hydroxide ions and hydrogen molecules. Sodium and hydroxide ions exit the cathode compartment.

# C10 CHLOR-ALKALI

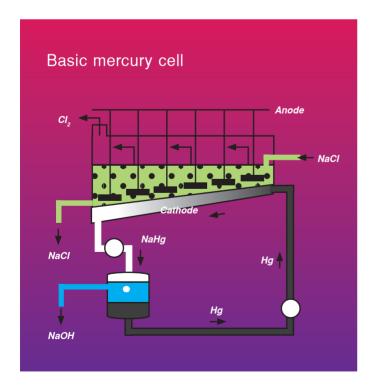
THE MERCURY CELL



## The mercury cell

The mercury cell was developed in 1892 by H.Y. Castner and C. Kellner. The mercury process is one of the oldest electrochemical processes used for the manufacture of chlorine. In this process brine is pumped through a basin with a bottom that slopes by 1 - 2°. A thin layer of mercury flows on this bottom. This layer acts as cathode. Due to the high overvoltage of hydrogen at the mercury electrode, hydrogen and caustic are not produced at this cathode; instead sodium is produced and dissolves in the mercury as an amalgam (a solution in liquid mercury). This is also the reason why this process is often referred to as the Amalgam Process. The liquid amalgam is removed from the cell to a separate reactor, called a decomposer, where it reacts with water in the presence of a catalyst (activated carbon) to form sodium hydroxide and hydrogen. The anodes are placed in the brine so that there is a small gap between the anode and the mercury cathode. These anodes were originally made from graphite and later from titanium.

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Electrolysis of brine would normally generate hydrogen at the cathode, but if mercury is used as the cathode material this does not occur.

Source: IUPAC

### Quality of caustic soda

The greatest advantage of the mercury cell is the superior quality of caustic soda produced, 50% solution with trace levels of sodium chloride, 0,002-0,003%. The amalgam caustic is widely used in the rayon industry which requires high purity caustic soda without chlorides. In contrast, the diaphragm cell produces weak 10% caustic soda solution containing 15% sodium chloride. The weak solution is concentrated to 50% solution with 1% sodium chloride in a triple effect evaporation. The membrane cell produces higher concentration, 30-35% caustic soda containing trace levels of 0,001-0,002% sodium chloride. The caustic soda is evaporated to 50% solution but at a lower cost of steam usage.

## Choice of process technology

The membrane cell process, compared with diaphragm and the mercury cell processes, has superior economic characteristics. The membrane cell process operates in modules. It therefore provides for easy reduction or expansion of capacity to the demand for caustic soda and chlorine. It has low power consumption as a result of low voltage drops at the electrodes and membranes, closer electrode spacing, and lower chlorine and hydrogen over voltages. The membrane cell process produces high purity caustic soda. The cell design does not use hazardous materials such as mercury or asbestos. Operating in modules and combining superior economic characteristics, the membrane cell process is considered most appropriate choice for the electrolysis of brine.

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### **DID YOU KNOW?**

The only three raw materials used for the production of chlorine are table salt, water and electricity. Electricity represents around 50% of the production cost. The industry consumes around 1% of the global electricity generated.

### The mercury process

Chlorine is produced at the positively charged anodes, which traditionally consisted of a series of suspended graphite rods but are now being replaced by more expensive, but more durable, Ti or Pt-steel alloys. The chlorine which is formed collects at the top of the cell.

The sodium atoms combine with mercury to form an amalgam. This also protects the sodium from contact (and therefore reaction) with water, so the problem of the alkaline medium is avoided. The sodium amalgam is run off from the bottom of the cell into a separate chamber containing graphite balls. The graphite catalyses the dissociation of sodium amalgam. The sodium released reacts with water to form sodium hydroxide and hydrogen, the mercury being recovered and returned to the electrolysis cell.

The reaction for the separation of the mercury and sodium is as follows:

$$2NaHg(\ell) + 2H_2O \rightarrow H_2(g) + 2NaOH(aq) + 2Hg(\ell)$$

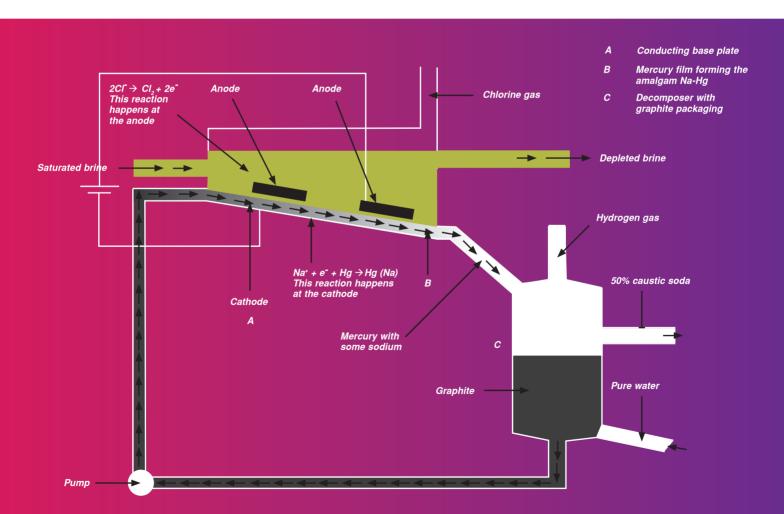
The mercury process is capable of producing caustic of very high purity without the need for a process plant.

However, the process itself has high power consumption and a mercury plant requires a large area of space. Another disadvantage is the fact that the high current densities result in high electromagnetic fields, giving rise to the need for shielding the control room properly against the interferences of these fields or moving it away from the cell house.

The process itself is quite sensitive to a number of parameters like salt concentration, sodium concentration in the amalgam and trace metal concentration. If the process runs outside these parameters it can result in high hydrogen concentrations in the cell and the possibility of a hydrogen chlorine explosion.

The diaphragm process is a very robust process for the production of chlorine. It is easier to run in terms of process safety than the mercury process and the danger of explosive mixtures of hydrogen and chlorine forming is much lower than during the mercury process. However, the product purity is much lower than for products from the mercury process and the energy requirements are higher.

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Sodium and chloride ions enter the anode compartment. Chloride ions are oxidized at the anode to give chlorine molecules. Sodium ions are attracted to the mercury (which acts as cathode) to form an amalgam. The amalgam is decomposed in a separate step and combined with water. Mercury is recycled. Sodium and hydroxide ions and hydrogen gas exit the decomposer.

## C11 CHLOR-ALKAL





### Overview

Until recently the South African chlor-alkali industry mainly consisted of Sasol Polymers and NCP Chlorchem plus Mondi who are producing small amounts of chlorine for captive use. However, another player recently entered the scene in the form of Straits Chemicals as part of the Coega Development Initiative. The following table gives an overview of the capacities, technology used and main products of the South African chlorine producers.

Chlor-Alkali producers in South Africa							
Company	Straits	Sasol Polymers	NCP Chlorchem	Mondi			
Capacity	200 000 tpa (proposed)	Approx 120 000 tpa	Approx 90 000 tpa	Approx 15 000 tpa			
Location	Coega	Sasolburg	Kempton Park	Richards Bay			
Technology	Membrane	Membrane/ Diaphragm	Membrane	Membrane			
Use	Export, various down- stream plants	PVC, HCI, CsCl <sub>2</sub> , Hypochlorite	Water treatment, HCI, Hypochlorite	Paper production			
Comment	At the moment in the project state		Busy expanding to 170 000 tpa				

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## Straits Chemicals to invest R5,8bn in Coega chlorine, desalination plant

23 April 2007

Straits Chemicals on Monday inked a deal which will see it spending R5,8-billion on a chlorine manufacturing and water desalination plant at the Coega Industrial Development Zone, near Port Elizabeth.

The plant will have the capacity to produce 600 t of chlorine a day and will supply to both export and domestic markets. Straits Chemicals will introduce a new state-of-the-art membrane technology that is cleaner and friendlier to the environment. This project is expected to create 600 jobs during construction and, once operational, will employ

about 250 people on a three shift basis, excluding management positions.



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### Sasol

Phosphoric acid is produced in Phalaborwa as raw material for the detergent industry. Sasol is the only sodium tri-polyphosphate (STPP) producing company in Sub-Saharan Africa. STPP is used as builder in soap manufacturing for the detergent industry. Sasol produces fatty (long carbon chain) alcohols that are also used in detergents. Sasol polymers produce caustic soda. They also produce 2121 tonnes per annum (2007) of sodium hypochlorite.

Source: www.sasol.com



### **AECI**

AECI is a leading supplier of chemicals and related products to a wide range of industries. Its three main subsidiaries are African Explosives Limited, Chemical Services Limited and Heartland Properties. AECI produces caustic soda and hydrochloric acid. It also produces oleum, urea and tall oil/vegetable fatty acids/derivatives which are used in detergent manufacturing.

Source: www.aeci.co.za



## Chlor-Alkali Holdings (Pty) Ltd

Chlor-Alkali Holdings (Pty) Ltd is the holding company of a South African based manufacturer and distributor of salt, chlor-alkali products and derivatives targeted at the water treatment-, industrial-, paper- and chemical markets. It has about 35% of current chlor-alkali capacity in South Africa (2005). The business is comprised of two distinct operations, the chlor-alkali operations at Chloorkop, trading as NCP Chlorchem (Pty) Ltd and the salt operation at Walvis Bay, trading as Walvis Bay Salt Refiners (Pty) Ltd. Waterchem, a division of NCP Chlorchem (Pty) Ltd, came into existence in May 2004 following the Competition Board's approval of the purchase of Sasol Polymers packed chlorine business.

Source: www.ncp.co.za



## Mondi

Mondi South Africa, has a paper mill in Durban and a pulp and linerboard mill and wood chipping plant in Richards Bay. They also own and manage more than 327 000 hectares of forestry plantations. Mondi produced 28291 tonnes per annum (2007) of sodium hypochlorite which is used in the production of paper.

Source: www.mondigroup.com



## Protea Chemicals (a member of the Omnia Group)

Protea Chemicals produces sodium hypochlorite (5000 tonnes, 2007) from chlorine. Sodium hypochlorite is used as a bleaching agent and disinfectant. Protea Chemicals operates sodium hypochlorite plants in the Eastern and Western Cape.

Source: www.proteachemicals.co.za



### Zetachem

Zetachem was founded in 1986. They are a major supplier of speciality polymers and chemical management systems to the leading companies in the water treatment, mining and pulp and paper industries. Zetachem is the largest producer of organic coagulants in Africa and in the Southern Hemisphere. Zetachem manufactures 10 000 tonnes per annum of sodium hypochlorite in Durban, KZN.

Source: www.zetachem.co.za

## C12 CHLOR-ALKALI

**ENVIRONMENTAL ISSUES** 



## Detergent making a mess?

In recent years, the laundry detergent industry has been faced with two environmental challenges, both of which seem to have been dealt with successfully. Environmentalists were concerned that phosphate builders added large amounts of phosphorus compounds to the nation's waterways. Acting as a fertiliser, the phosphorus stimulated the growth of algae, and these unnaturally large crops of algae significantly depleted the amount of dissolved oxygen in water. This decrease in free oxygen harmed other marine life, thus threatening to disrupt normal ecological patterns.

This problem, and the environmental pressure and legislation it prompted in the late 1960s, led manufacturers to develop effective builders that did not contain phosphates. Today, detergents sold in many countries are phosphate-free. Although this adjustment did not entail a change in the manufacturing process, it did require a research effort to devise a satisfactory alternative that took several months. An earlier environmental problem was that of excess detergent foam appearing in the nation's waterways. In the early 1950s, when home use of washing machines and laundry detergents grew at an explosive rate,

there were several instances of large amounts of foam appearing in rivers and streams, although detergent may not have been the only cause of the foaming. Over a period of five years, from 1951 to 1956, it was found that a common surfactant, ABS (alkyl benzene sulphonate), the detergent ingredient that contributed to foaming, was responsible. ABS's complex molecular structure did not biodegrade rapidly enough to keep it from foaming once washing water was discharged. A proven replacement was not immediately available. Beginning in 1956, however, manufacturers replaced ABS with LAS (linear alkylate sulfonate), which biodegrades rapidly, and since that time, LAS has been the primary foaming agent in detergents.

This material was obtained from www.madehow.com. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: www.madehow.com. 2010. Laundry Detergent. [Online]. Available http://www.madehow.com/Volume-1/Laundry-Detergent.html. [19 July 2010].

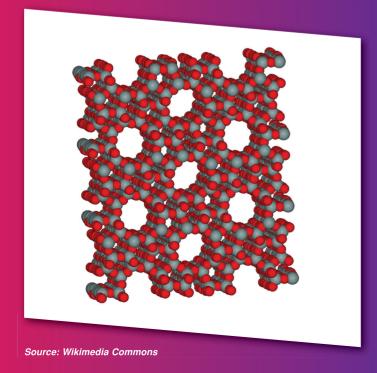
## Environmental impact of synthetic detergents

The first soapless detergents caused pollution problems because they could not be broken down by bacteria. The foam they created caused pollution in rivers and streams. We now have biodegradable detergents that can be broken down by bacteria. Detergents that contain phosphates still create pollution problems. When the phosphates enter streams and rivers they act as fertilisers and water plants grow rapidly. When the plants die, bacteria in the rivers feed on them and use up all the oxygen in the water. Fish and other animals die from lack of oxygen. This process is called eutrophication.

Trends in world markets in respect of laundry detergent formulations have focused on (a) the volume of surfactant in the formulation, (b) environmental pressures on phosphate builders, and (c) the use of bleaches. In the Northern Hemisphere, there has been a move to liquid and super concentrated laundry detergents leading to changes in the surfactant, bleach, filler and enzyme concentrations in formulations. However, in developing countries, where product price is a major factor, there has been a more gradual decline in the consumption of phosphate builders, such as sodium tripolyphosphate, and a slower crossover to zeolite-built formulations.

This material was obtained from the Sasol Group Services. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: UCT Chemical Engineering Schools Project. 2010. Chemical Industries Resource Pack. Cape Town.

#### A model of a zeolite



## Getting the balance right

The key to any understanding of the chlor-alkali industry, either in Europe or any other region, is an understanding of the inseparable production of caustic soda and chlorine in approximately equal volumes. Electrolysis of common salt (sodium chloride) or brine solution accounts for in excess of 99% of all production of caustic soda and chlorine. While supplies of chlorine and caustic soda are in approximately equal quantities, the end-use profiles of demand for chlorine and caustic soda are quite different. Thus, as economic cycles influence chemical demand, with different industries experiencing up-cycles and down-cycles at different points in the general economic cycle, demand for chlorine and caustic soda are rarely balanced.

Normally, one of the products is in greater demand than the other. Furthermore, chlorine gas cannot be readily stored in large volumes, whereas substantial inventories of caustic soda can be held at any one time. This feature also affects the chlorine and caustic soda supply-demand balance.

Production of either chlorine or caustic soda is always limited by demand for and ability to store the other. Pricing of each of the two materials is heavily influenced by whether chlorine or caustic soda is in greatest demand at any one time.

Any contraction in chlorine production would eventually impact on PVC manufacture, since chlorine cannot be transported over large distances. This would also have a knock-on effect on hydrochloric acid availability as a by product from some chlorination processes.



This material was obtained from an article by Stephen Harriman on www. icis.com. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: Harriman, S. 2002. Getting the balance right. [Online]. Available: http://www.icis.com/Articles/2002/10/04/181939/getting-the-balance-right.html.[19 July 2010].

# Minamata mercury poisoning

A major factor in the development of the membrane process was the so-called Minamata incident where mercury organic compounds that were discharged into the sea entered the food chain. The mercury then poisoned the people via the fish they consumed leading to several deaths among the population of a small Japanese village. The Minamata incident sparked a ban on processes utilising mercury or mercury compounds in Japan. This forced the chlor-alkali chemical industry in Japan to phase out the mercury process for chlorine production. The last chlorine plant based on the mercury process in Japan was closed in 1984.

This material was obtained from Wikipedia. Learners – if you use any part of it you need to write it in your own words and include the following in your reference list: Wikipedia. 2010. Minamata disease. [Online] Available: http://en.wikipedia.org/wiki/Minamata \_ disease [19 July 2010].

## Chlorine as a weapon

"It was Thursday evening, April 22nd, 1915. Towards evening, at around 5 pm, the bombardment began afresh - except that sentries posted among the French and Algerian troops noticed a curious yellow-green cloud drifting slowly towards their line. This was the first use of chlorine gas on the battlefield. The effects of chlorine gas were severe. Within seconds of inhaling its vapour it destroyed the victim's respiratory organs, bringing on choking attacks."

"Plainly something terrible was happening. What was it? Officers, and Staff officers too, stood gazing at the scene, awestruck and dumbfounded; for in the northerly breeze there came a pungent nauseating smell that tickled the throat and made our eyes smart. The horses and men were still pouring down the road, two or three men on a horse, I saw, while over the fields streamed mobs of infantry, the dusky warriors of French Africa; away went their rifles, equipment, even their tunics that they might run the faster.

One man came stumbling through our lines. He was frothing at the mouth, his eyes started from their sockets, and he fell writhing at the officer's feet."

This article was adapted from a memoir from www.firstworldwar.com. Learners - if you use any part of it you need to write it in your own words and include the following in your reference list: Hossack, A. R. 1930. Everyman at War. [Online]. Available http://www.firstworldwar.com/diaries/firstgasattack.htm. [19 July 2010].