Chemistry

How is chlorine produced by electrolysis?
And what are the implications for large scale
Chlorine production for society?

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The two key ideas under investigation are Energy and Chemical Reactions.
The two chemical concepts are the application of Faraday's Law's and the electrolytic production of chlorine using aqueous electrolytes: the effect of redox properties of the chemicals involved and the design features of an electrochemical cell.

Chlorine is an important chemical, which has many uses. ICI Australia produces approximately 100,000 tonnes of chlorine per annum.[1]

Because of its extreme reactivity, chlorine is not found naturally in the free state. Thus, it exists only in compounds, found mainly in chloride minerals such as sodium chloride. Chlorine is a member of Halogen (salt forming) family, and tends to combine with other elements by accepting electrons form them due to strong oxidising nature.

Because chlorine is a weak reductant, strong oxidising conditions are needed for conversion to Cl_2. For this reason, electrolysis of concentrated NaCl (brine) is employed.[2] Electrolysis is the process by which an electric current is passed through a liquid, causing a chemical reaction to take place. Chlorine production incorporates redox reactions, involving electron transfer from one chemical to another. The conversion of Cl^- to Cl_2 is an endothermic process as system requires input of energy, therefore the chemical yield of the products is higher than the energy of the reactants.

During electrolysis, electrical energy is converted into chemical energy. Reactions in electrolytic cells would not normally happen without the application of electrical energy, therefore they are non-spontaneous reactions. Chemicals formed by electrolysis are often difficult to obtain by other means.

Chlorine is mostly obtained by the electrolysis of a concentrated aqueous solution of sodium chloride.[3]

Before looking at industrial methods for manufacturing chlorine, we shall consider simple electrolytic cell to demonstrate principals of electrolysis. The following is a portion of electrochemical series, showing possible equations likely to occur.

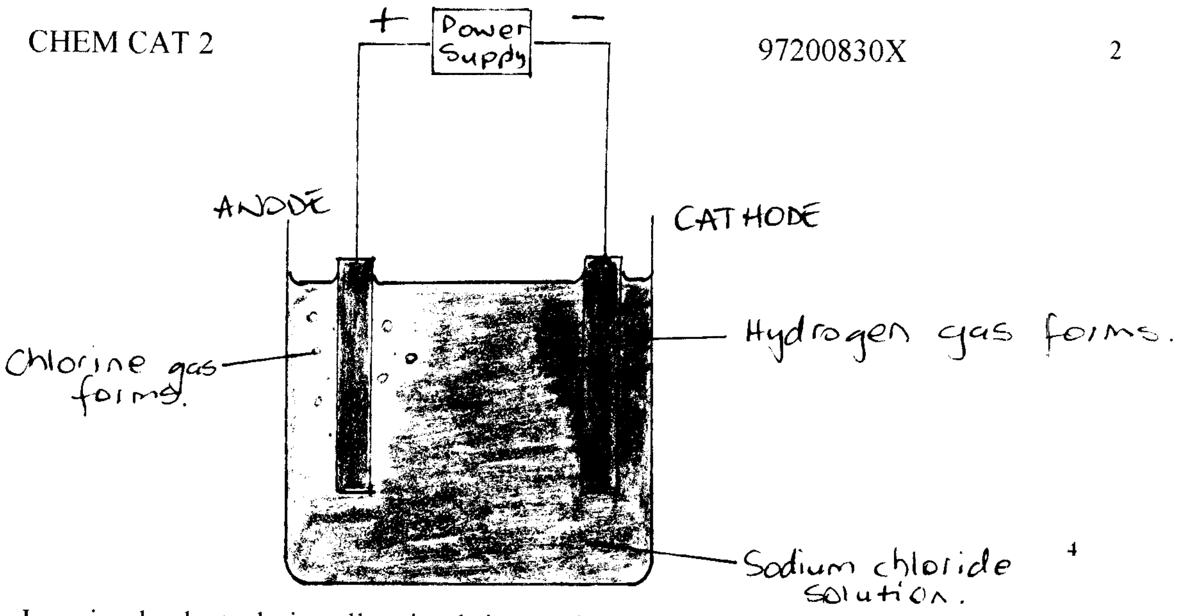
Oxidants **Reductants**

Increacing oxidising strength

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$
$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$$
$$2H_2(aq) + 2e^- \rightleftharpoons H_2(g)$$
$$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$$
$$Na^+(aq) + e^- \rightleftharpoons Na(s)$$

increacing reducing strength

[1] ICI Australia. "Chlorine chemical fact sheet." (Page 1)
[2] McTigue. P.T. " Chemistry key to the Earth." (Page 380)
[3] McTigue. P.T. "Chemistry Key to the Earth." (Page 380)



[4]

In a simple electrolytic cell, using brine as the electrolyte and unreactive electrodes, cathode will become negatively charged as the polarity of connected power supply causes electrons to migrate to this region, resulting in a reduction reaction. Chemicals present at cathode include $H_2O(l)$, $Na^+(aq)$, and $Cl^-(aq)$. From electrochemical series,

$$\mathbf{2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)}$$
$$\mathbf{Na^+(aq) + e^- \rightleftharpoons Na(s)}$$ [5]

Using electrochemical series, water molecules behave as stronger oxidants than sodium, ie. accepting electrons more readily. Sodium ions are located lower in series, behaving as weaker oxidant. ie, giving up electrons more readily. Reactions higher in series are more likely to occur as reduction reactions; thus, first equation will proceed.

At anode, electrons are drawn away causing anode to become positively charged. Thus, oxidation occurs. Chemicals present include, $H_2O(l)$, $Na^+(aq)$ and $Cl^-(aq)$. Two possible half equations include;

$$\mathbf{Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)}$$
$$\mathbf{O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)}$$ [6]

Competition between chlorine ions and water molecules is strong because of their positions in electrochemical series. Chlorine ions higher in series, behaving as weaker reductant, while water is behaving as a stronger reductant. Reactions lower in series have a greater tendency to occur as oxidation reactions (lose electrons more readily), thus second reaction would proceed. However, because these reactions are so close together, it is possible for the reverse reaction to occur, resulting in undesirable formation of O_2. This may be related to conditions other than standard, which include

; concentrations of 1M of substances,
Gas pressure of 1atm, and
Temperature of 25°C. [7]

Altering standard conditions will cause one reaction to be favoured by another.

To yield large amounts of chlorine, high concentrations of brine must be used, low concentrations will favour production of O_2 and H_2.
Electrolysis of chlorine requires that products formed must not be exposed to one another. Careful technological design ensures this.

Three main types of cells used in production of chlorine; mercury cell, diaphragm cell and membrane cell.

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[4] Commons. C "Chemistry Two" Second edition (Page 233)
[5] ibid
[6] ibid
[7] ibid

Diaphragm cell.

Within diaphragm cell, porous asbestos barrier prevents mixing of reaction products. This diaphragm separates anode compartment, containing brine fed into cell, chlorine produced from cathode compartment. The cathode compartment contains sodium hydroxide (caustic soda), produced as solution of undecomposed brine and hydrogen gas. Although ions and molecules are able to pass through, diaphragm prevents mixing of OH^- with Cl_2, therefore formation of chlorate,

$$NaCl(aq) + 3H_2O(l) \rightarrow NaClO_3(aq) + 3H_2(l)$$ [8]

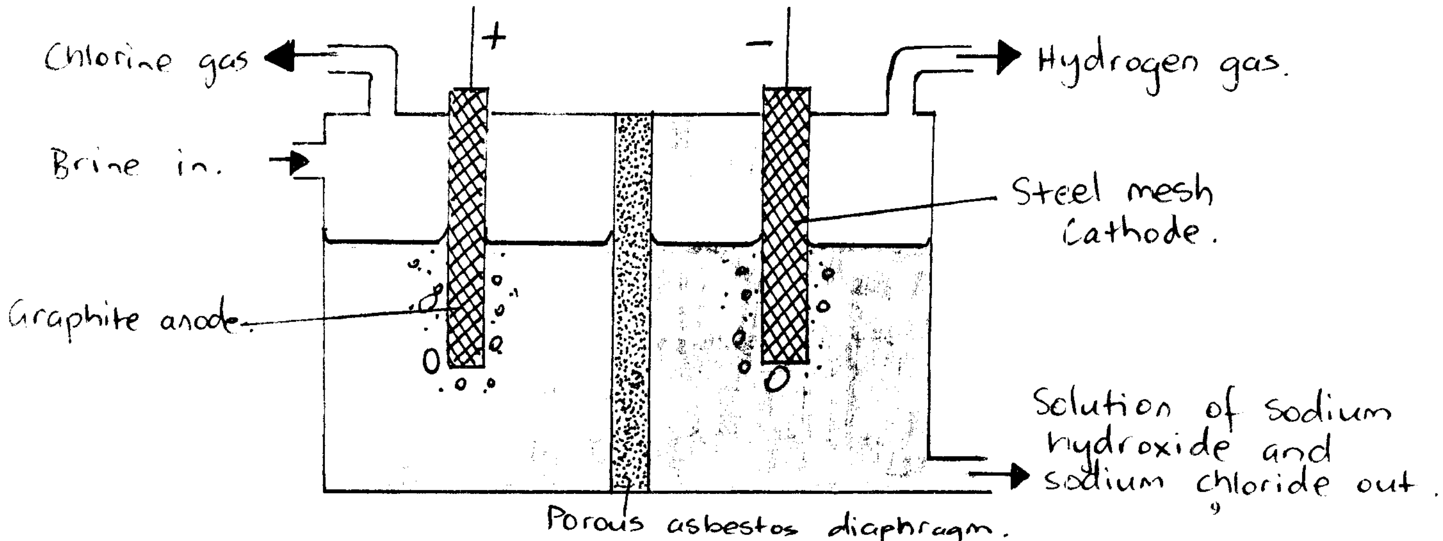
is minimised and the yields of Cl_2 and NaOH are maintained. Anode half equation given by:

$$2Cl^-(aq) \rightleftharpoons Cl_2(g) + 2e^-$$

Cathode half equation given by;

$$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$$

Overall; $2NaCl(aq) + 2H_2O(l) \rightleftharpoons 2NaOH(aq) + Cl_2(g) + H_2(g)$



[9]

Cell is normally steel and diaphragm normally made of asbestos deposited on fine wire. Traditionally anodes made of graphite and impregnated with linseed oil or other organic materials preventing electrolytic corrosion.[10] Chlorine produced on graphite anodes, which are covered with incoming salt brine. Chlorine bubbles rise to top of anode and collected form chlorine pipelines connected by each cell. Chlorine gas produced contains water vapour, making it a very corrosive material.

At cathode, hydrogen liberated. Evaporation of aqueous solution yields sodium hydroxide, known as caustic soda. Flow rate through diaphragm is faster than the salt can be electrolysed, preventing back diffusion and migration of caustic soda; ie movement of OH^- ions to the anode.

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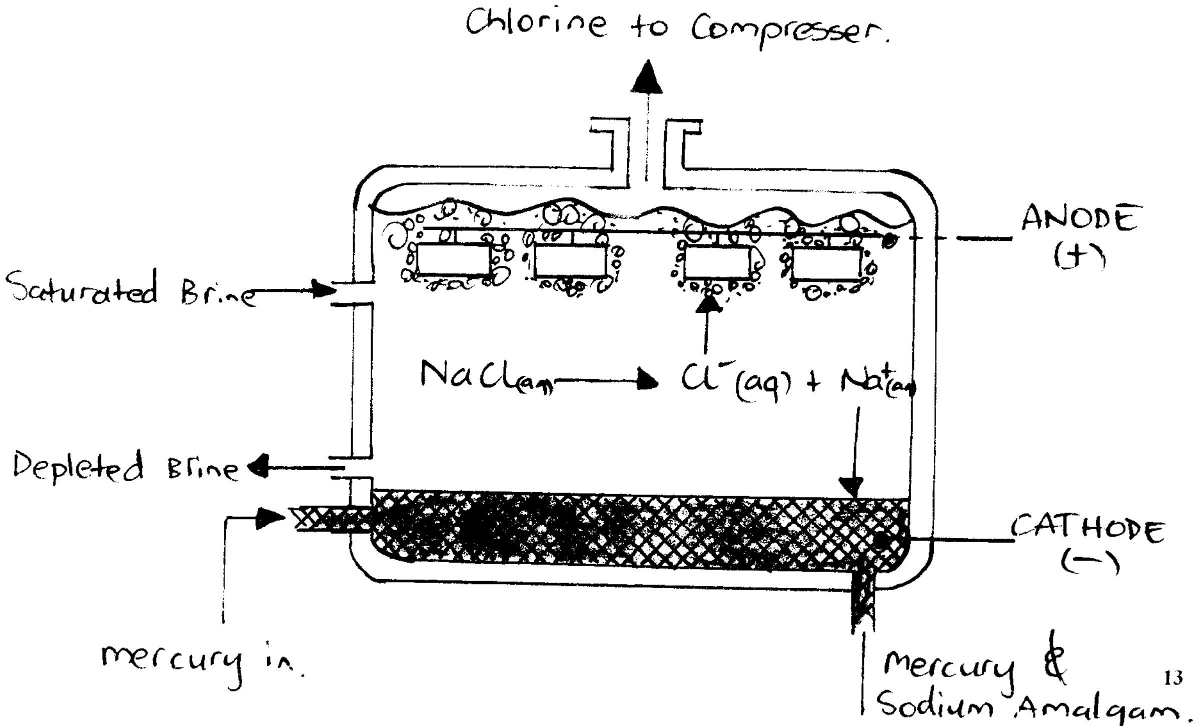
[8] McGraw-Hill Encyclopedia of Science and technology (Page 570)
[9] Commons. C "Chemistry Two" Second Edition (Page 234)
[10] McTigue. P.T "Chemistry Key to the Earth" (Page 381)

Diaphragms must be renewed if brine is not adequately purified because oils from the graphite anodes will cut down flow rate.[11] Diaphragms collect impurities.

Mercury Cell.

Mercury cell is more complex but produces sodium hydroxide at higher purity. Within mercury cell, saturated brine travels down steel trough between flowing film of mercury (cathode) and platinised titanium plates (anodes). Direct current is applied between anode and cathode. Chlorine liberated at anodes, collected above the brine let off as a hot, wet corrosive gas. [12]



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At mercury cathode, sodium cations are discharged at surface forming sodium amalgam with mercury, given by equation;

$$\mathbf{Na^{+}(aq) + Hg + 2e \rightarrow 2Na(Hg)(l)}$$ 14

At anode, Cl^- ions are oxidised to Cl_2 ions, given by

$$\mathbf{2Cl^{-}(aq) \rightleftharpoons Cl_2(g) + 2e^{-}}$$

Overall, equation for the electrolysis of chlorine by mercury cells is given by,

$$\mathbf{2NaCl\,(aq) + Hg(l) \rightarrow Cl_2(g) + 2Na(Hg)(l)}$$

Cells are normally constructed of steel, and are rubber lined where necessary for protection against wet chlorine.[15] Graphite anodes are parallel to the mercury surface, and are suspended from cover by graphite or other conducting pins.

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11 "McGraw-Hill Encyclopedia of science and Technology" McGraw-Hill (page 572)
12 ICI Australia "Chemical fact sheet" (page 3)
13 ICI Australia. "Chemical fact sheet." (page 10)
14 ICI Australia. "Chemical fact sheet." (page 10)
15 "McGraw-Hill Encyclopedia of Science and Technology" McGraw-Hill (page 573)

Mercury cells operate 0.8V higher than diaphragm cells, corresponding to higher power costs.[16] In addition, cost of mercury is considerable.

Because of great health hazards associated with asbestos and mercury, membrane cell was produced. However they are not widely used today, these cells are likely to replace diaphragm and mercury cells in future.

Membrane cell.

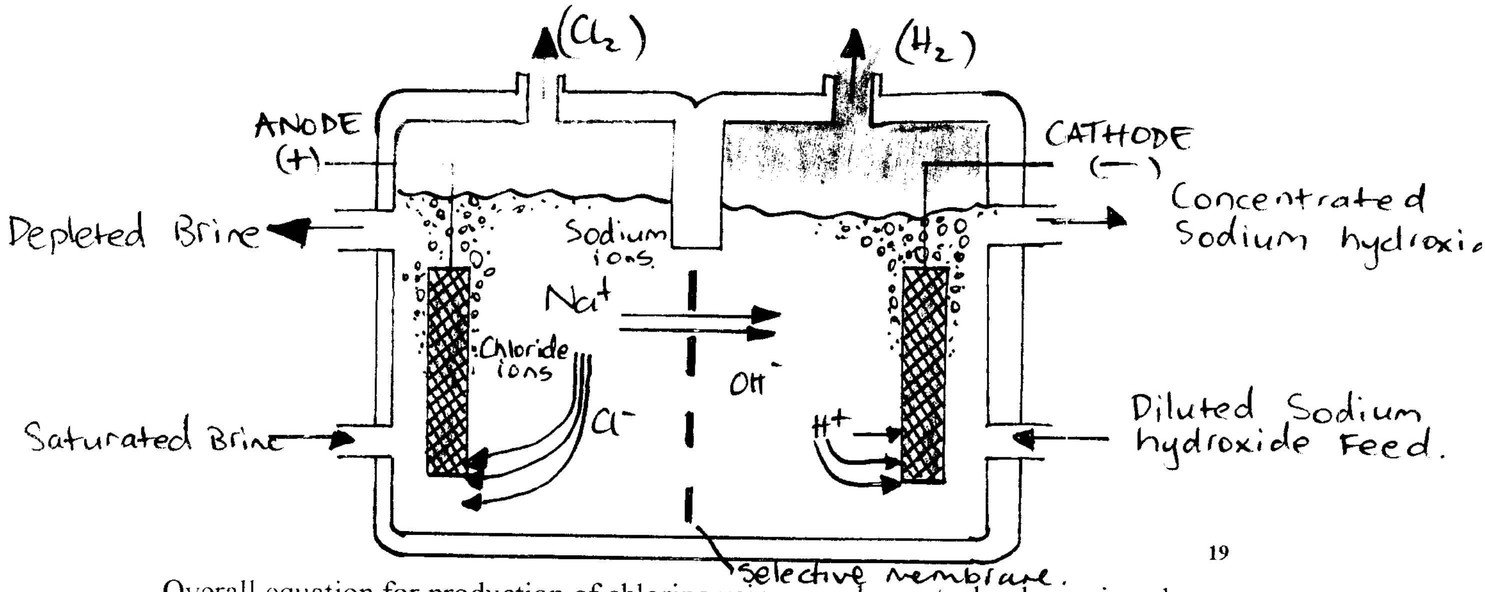
This is similar to diaphragm cell, however a specially developed plastic sheet, or membrane, is the feature of the membrane cell. This sheet is selective as it only allows movement of sodium ions across membrane from anode to cathode. There is no bulk flow of liquid across the membrane.

Cl^- ions in anode chamber cannot move to cathode and contaminate sodium hydroxide produced there.

$$2NaCl\,(aq) \rightarrow Cl_2(g) + 2Na^+(aq) + 2e^-$$ [17]

OH ions formed in cathode are prevented form returning to anode.

$$2H_2O(l) + 2Na^+(aq) + 2e^- \rightarrow H_2(g) + 2NaOH\,(aq)$$ [18]



[19]

Overall equation for production of chlorine using membrane technology given by

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

Anode chamber is made form titanium and cathode chamber is made form nickel. These metals are favoured as they resist chemicals produced and will not contaminate product.[20] Average operating life of anode and cathode varies form three to six years.

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[16] "McGraw-Hill Encyclopedia of Science and technology" McGraw-Hill (page 573)
[17] ICI Australia. "Chemical Fact sheet" (page 10)
[18] ICI Australia. "Chemical Fact sheet" (page 10)
[19] Commons. C "Chemistry Two." Second edition (page 234)
[20] ICI Australia. "Chemical Fact sheet" (page 4)

Faraday's second law states *in order to produce one mole of metal, one, two or three or another whole number of moles of electrode must be consumed.* [21]

The relationship between quantities of energy consumed and chemical change occurring by electrolysis is vital for production of chlorine

The total charge on one mole of electrons is known as one Faraday, where 1 Faraday = 96 500 coulomb mol^{-1}. The charge on electrons can be represented mathematically by the equation

$$Q = n(e^-) \times 96\,500$$

Where Q = Total charge (coulombs)
N = mole of electrons.

[22]

Cells are connected in series and generally have voltages between 3.5V – 5.0V, with currents ranging from 1000A – 80,000A. [23]

From Faraday's laws, we can calculate the amount of chlorine produced per day and the energy required.

We will now consider a voltage and current of 5V and 20,000A respectively.

$$Q = I\,t$$
$$= 20{,}000 \times 86{,}400$$
$$= 1.73 \times 10^{9}\,C$$

(Note: Time is expressed is seconds. Time = 24hours × 60 × 60 = 84,600s)

$$\therefore n(e^-) = \frac{Q}{F} = \frac{1.73 \times 10^{9}}{96{,}500} = 1.8 \times 10^{4}\,mol.$$

From the electrochemical series, 2 mol of electrons is needed to oxidise 1 mol of chlorine.

$$2Cl^-(aq) \rightleftharpoons Cl_2(g) + 2e^-$$ [24]

Now using Faraday's second law of electrolysis

$$n(Cl_2) \times 2 = n(e^-)$$

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[21] Commons. C "Chemistry Two." Second Edition (page 229)
[22] Commons. C "Chemistry Two." Second Edition (page 229)
[23] Commons. C "Chemistry Two." Second Edition (Page 234)
[24] Commons. C "Chemistry Two." Second Edition (page 213)

$\therefore \quad n(Cl_2) = \frac{n(e^-)}{2}$

$\therefore \quad n(Cl_2) = \frac{1.8 \times 10^4}{2}$

$= 9.0 \times 10^3$ mol.

To calculate the mass produced in one day.

$M(Cl_2) = n(Cl_2) \times Mr(Cl_2)$
$= 9.0 \times 10^3 \times 70.91$
$= 6.4 \times 10^5$ grams per day
$= 6.4 \times 10^2$ kg produced per day.

Up to 40 cells can be connected in series,[24] if these cells operate for 24hours approximately 2.56×10^4 kg would be produced.

The power consumed can also be calculated.

$P = I\ V$
$= 20{,}000 \times 5.0$
$= 100{,}000$ W
$= 100$kW

The amount of energy consumed in a day

$E = P\ t$
$= 100{,}000 \times 86{,}400$
$= 8.64 \times 10^9$ J

The electrical power requirements of the plants are enormous. The Largest mercury cells use enough power to service 175,000 Australian homes per day.[25]

Half of chlorine produced in Australia is used in manufacture of vinyl at the petrochemical complex in Botany, New south Wales.[26] Chlorine is useful in production of hydrochloric acid, aluminium refining and production of weed killers. Other uses include:

Disinfection of Town water supplies; The correct use of chlorine provides effective water protection against the spread of water borne diseases.

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[24] Commons. C "Chemistry Two." Second Edition (Page 232)
[25] McTigue, P.T "Chemistry Key to the Earth" (page 381)
[26] ICI Australia "Chlorine chemical Fact sheet." (page 1)

Swimming Pool Treatment; technique known as 'breakpoint chlorination' is used which supplies a sanitary and pleasant environment for pool users. Eye irritation is caused by insufficient chlorine, caused by chloramines, which are destroyed by addition of more chlorine. Given by equation;

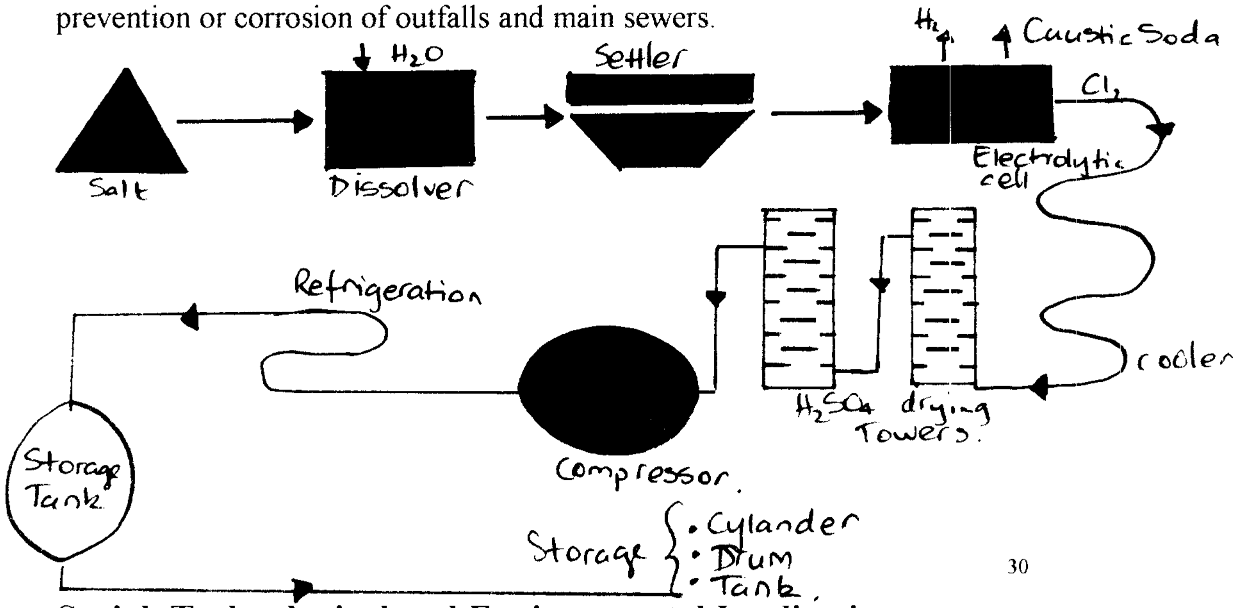
$$H_2O(l) + Cl_2(g) \rightarrow \underbrace{HOCl(aq) + HCl(aq)}_{\text{(Hypochlorous acid)}}$$ [27]

Treatment of cooling water; Growth of algae, bacteria or even shellfish can cause cooling water installations to suffer expensive failures or losses in efficiency. Chlorine helps prevent such matters arising.[28]

Bleach for Paper manufacture; Chlorine prevents discolouration of paper during storage or exposure to sunlight. It's also used to produce high quality pulp necessary for manufacture of printing and photocopy paper. Reaction of chlorine and sodium hydroxide to produce liquid bleach given by

$$Cl_2(g) + 2NaOH\ (aq) \rightarrow NaOCl\ \ (aq) + H_2O(l) + NaCl(aq)$$ [29]

Sewage Treatment; Chlorine is used to destroy or control harmful bacteria and the prevention or corrosion of outfalls and main sewers.



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Social, Technological and Environmental Implications

Current method of manufacture (diaphragm and mercury cells) present various health hazards to society and environment. Asbestos fibres in diaphragm cells cause degenerative heart disease of lungs.[31] Mercury, when discharged as waste material may enter aquatic food chain by building up fish, increasing risk of mercury

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[27] Knapp. B "Elements; Chlorine, Fluorine, Bromine and iodine." (page 17)
[28] ICI Australia, "Chlorine Handbook" (page 3)
[29] Knapp. B "Elements; Chlorine, Fluorine, bromine and iodine." (page 14)
[30] ICI Australia, "Chlorine handbook." (page 4)
[31] Commons. C "Chemistry Two" Second edition (Page 235)

poisoning for society. Because of this, Japan has banned use of mercury cells,[32] as bulk of Japanese diet consists of seafood.

Chlorine odour can be detected at levels as low as 0.5ppm. Exposure to any form of chlorine can result in blistering of skin, dental corrosion and reduced respiratory capacity. Storage of chlorine involves extreme precautions. Chlorine must be stored away from sources of heat and combustible materials. Ventilation must be provided in areas where chlorine stored, either naturally or by mechanical means.

Energy use during chlorine production is considerable, though demand for chlorine production is an essential process (ranked tenth in world chemical production).[33] Most likely source of energy would be from coal fired power stations. However, availability of fossil fuels becomes scarce, cost of chlorine production will increase.

Using fossil fuels increases environmental pollution.

- Carbon dioxide- contributes to greenhouse effect.
- Sulphur dioxide- contributes to acid rain.

Considerations must be given to cost of such pollution, which includes impaired health and the visual impact.

Its possible to decrease environmental pollution by considering different forms of electrical energy, such hydro-electricity, solar-energy, situated close to plants.

Current efficiency (percentage of the total current used to yield the required products) is 95%. The 5% inefficiency is related to undesirable reactions.
Eg. Diaphragm cell, anode reaction that generates oxygen

$$2H_2O(l) \rightleftarrows O_2(g) + 4H^+(aq) + 4e^-$$ [34]

To increase efficiency, ruthenium oxide and titanium coated anodes have been developed to replace graphite anodes (Which are replaced periodically). These reduce cost operating at lower voltages and having longer life spans. Other steps taken to increase the efficiency of production include;

- Ensuring brine is pure, reducing need to purify brine, reducing energy consumption.
- Ensuing electrical contacts are clean and tight, reducing electrical resistance and power wastage through heat.

Conclusion

Chlorine is produced by electrolysis using mercury, diaphragm and membrane technology. Most probable production method of chlorine in future will involve membrane technology, providing safe and economic alternative to diaphragm and mercury cells.

[32] Commons, C "Chemistry Two." Second edition (page 235)
[33] Commons, C "Chemistry two." Second Edition (page 232)
[34] McTigue, P.T "Chemistry Key to the Earth." (page)

Electrolysis of chlorine provides variety of useful materials for society that is obtained form brine, a cheap abundant material (chlorine and sodium hydroxide).

Application of Faraday's laws and effect in redox properties of chemicals involved on design features of each electrochemical cell are vital in determining energy required by society for production. Redox reactions are also an essential concept, which allows determination of chemicals produced by each electrolytic method.

To be commercially viable, electrolysis of chlorine should be located in places with cheap electrical power, easy access to brine, and must operate continuously for chlorine plants to be feasible.

Evaluation of information

Information used during the investigation was assumed relevant and accurate as it came directly from encyclopedias and chemistry textbooks. However, there was a slight discrepancy between sources about the accuracy of equations explaining chemical processes. For this reason, equations form ICI pamphlets were assumed the most accurate as they specialise in the area of chlorine production.

There was bias between sources, as ICI Australia did not produce sufficient information about the disadvantages associated with chlorine production.

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