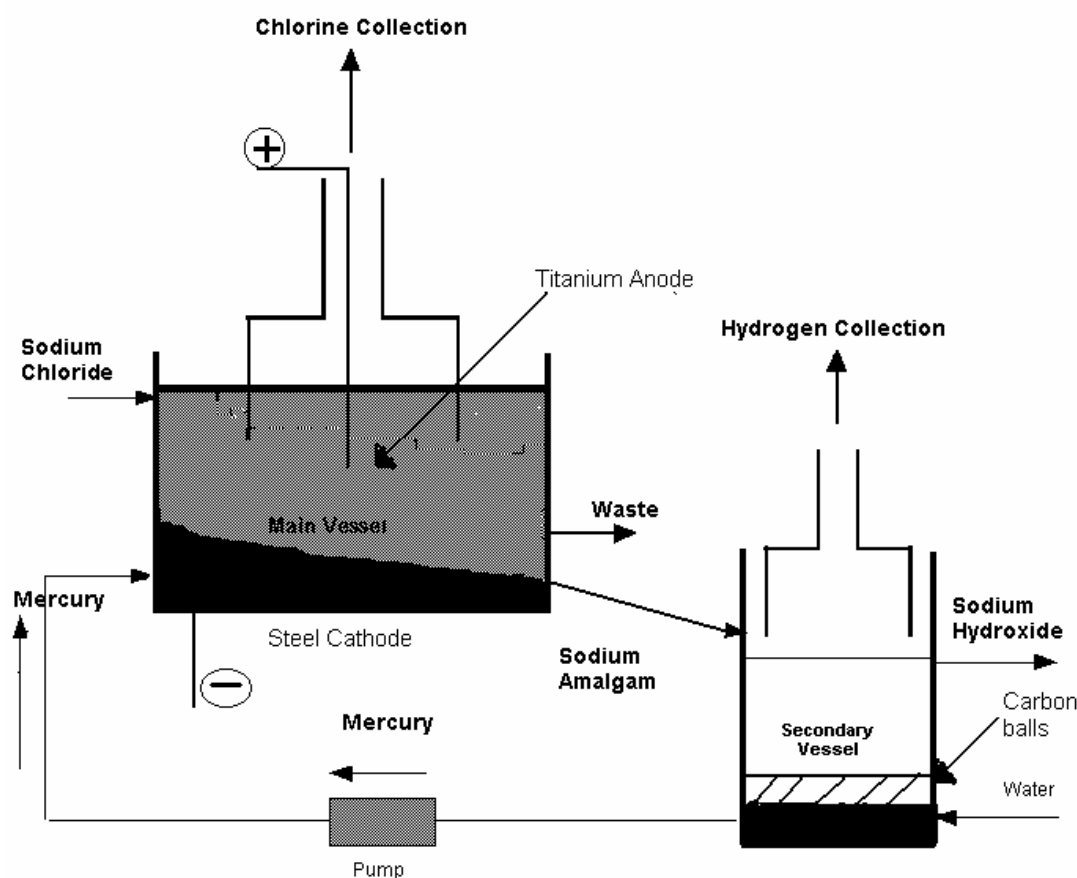# Further information on the mercury cell

Here is some further information to assist you.

The anode reaction involves chloride ion being converted to chorine gas. Mercury flows over the steel base of the cell and, in this way, the mercury acts as the cathode. Sodium is released in preference to hydrogen on the mercury surface, the sodium dissolving in the mercury. This is then carried into the secondary cell where it reacts with water to release sodium hydroxide.

In the secondary reactor, the sodium amalgam reacts with water to produce sodium hydroxide and hydrogen. **Write the equation for this reaction**.

To increase the rate of this reaction, the secondary reactor contains carbon balls, which catalyse the reaction.

The sodium hydroxide is produced at up to 50% concentration. This is the sales specification and therefore no further purification is required. Additionally, the amount of sodium chloride produced is low at 30 ppm, making the mercury cell a highly effective means of producing sodium hydroxide.
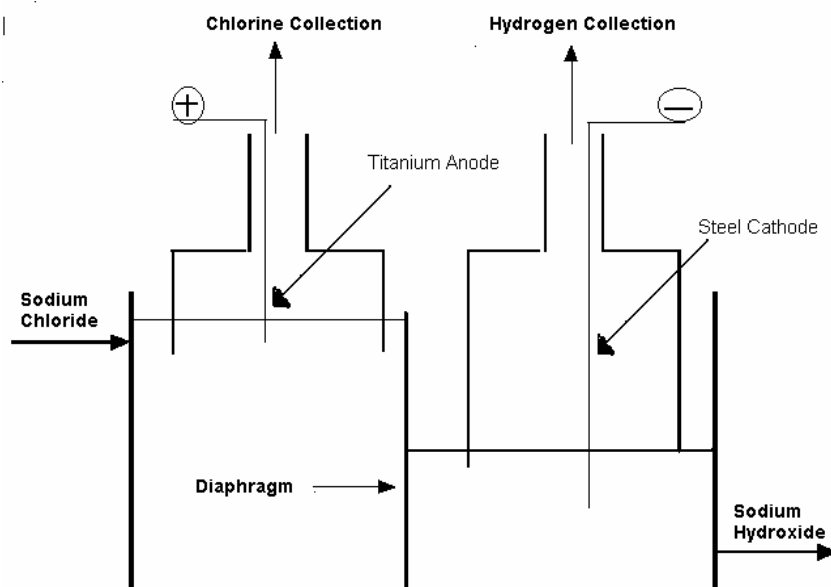
Further information on the diaphragm cell

Here is some further information to assist you.

The anode reaction involves chloride ion being converted to chlorine gas, while, at the cathode, hydrogen is released. The porous diaphragm is a means of separating chlorine liberated at the anode from sodium hydroxide and hydrogen produced at the cathode. Due to a hydraulic gradient, it prevents the reverse flow of hydroxyl ions formed in cathode section from passing into the anode section where they can react to form sodium hypochlorite (NaClO) and sodium chlorate ($NaClO_3$).

Due to reactions described in the section on *The problem with electrolysis*, sodium hypochlorite, sodium chlorate and oxygen are formed as bi-products in a commercial cell. However, the major problem is that the electrolysis current only converts about half of the original sodium chloride feed to sodium hydroxide, leading to high concentrations of sodium chloride in the product liquor. The concentration level can be as high as up to 15 wt % NaCl, which has to be removed.

The sodium hydroxide is produced at up to 12% concentration. The sales specification is 50% therefore further purification is required. This is achieved by a series of evaporators. As the sodium hydroxide concentration increases, the sodium chloride crystallises out and is removed by filters and/or centrifuges. However, solubility levels are such that most diaphragm cell products still contain up to 1% w/w salt, and this can restrict its use, *e.g.* in the rayon industry. The energy requirement for these additional purification steps is 700 kWh per ton of chlorine produced.

The diaphragm is made by fusing a fibrous polymer (polytetrafluoroethylene, PTFE) with asbestos. Asbestos is used because of its chemical and physical stability and because it is a relatively inexpensive and abundant raw material.

Further information on the membrane cell

Here is some further information to assist you.

The anode reaction involves chloride ion being converted to chorine gas while hydrogen is formed at the cathode.

The membrane is a means of separating chlorine liberated at the anode from sodium hydroxide and hydrogen produced at the cathode. It does this by allowing the sodium ions only to pass in the anode → cathode direction. This inhibits the reverse flow of OH ions, where they can react to form sodium hypochlorite (NaClO) and sodium chlorate ($NaClO_3$) and oxygen due to reactions described in the section on 'The Problem with Electrolysis'.

Sodium chloride concentrations are low at 50 ppm.

The sodium hydroxide is produced at up to 30% concentration. The sales specification is 50% therefore further purification is required. This is achieved by means of a simple evaporation system. The energy requirement for this purification step is 250 kWh per ton of chlorine produced.

Membranes are made from perfluoro polymers. They consist of a film of perfluorosulfonate polymer, a Teflon reinforcing fabric and a perflurocarboxylate polymer all bonded together.
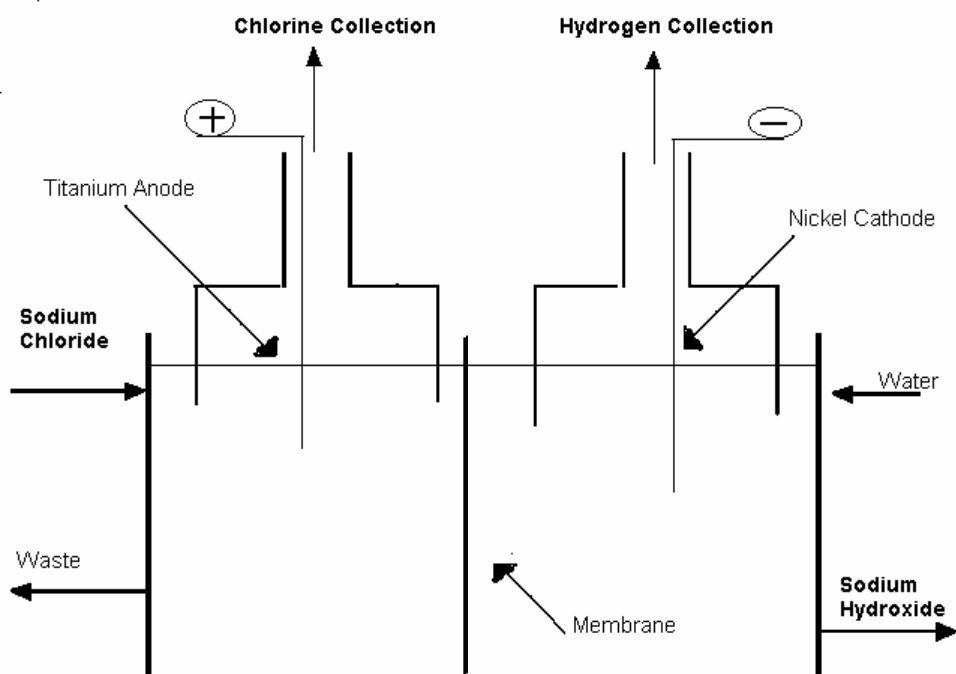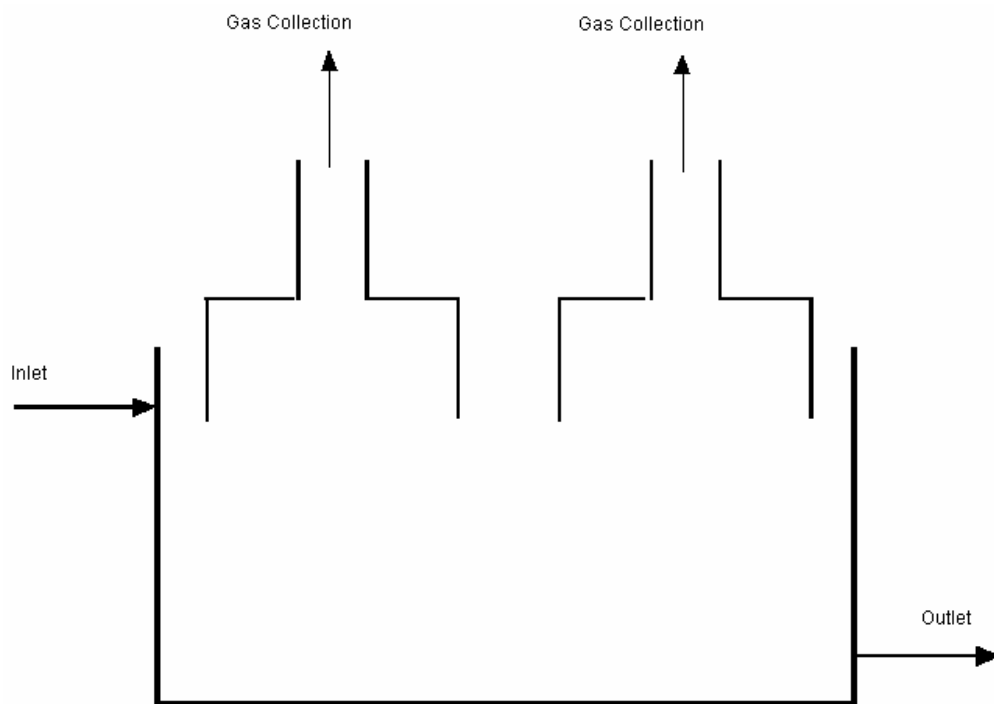
Mercury, membrane or diaphragm

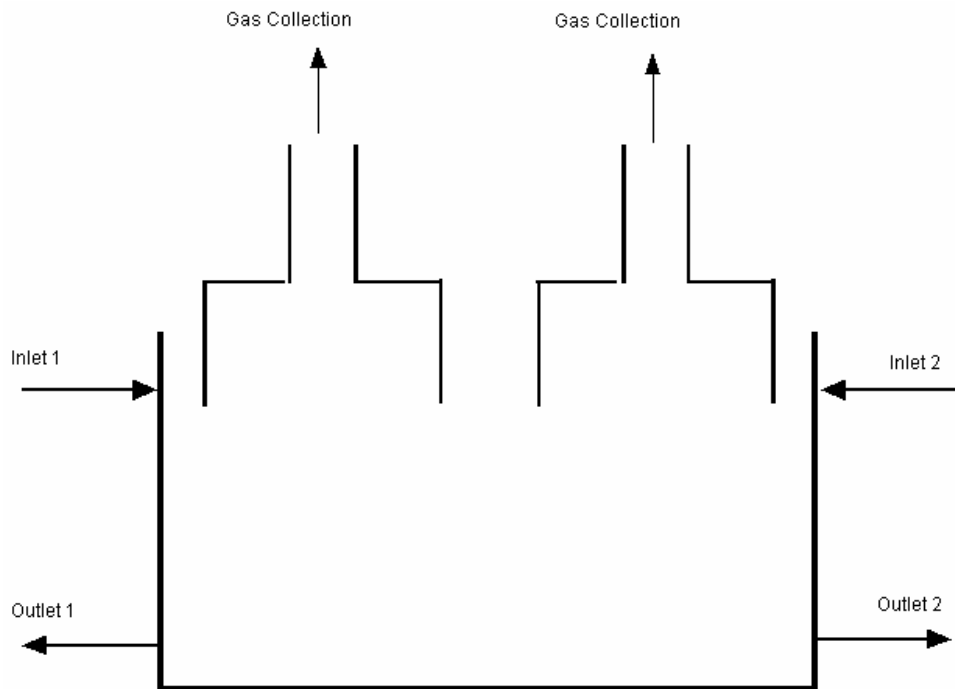## Technical presentation – Mercury electrochemical cell
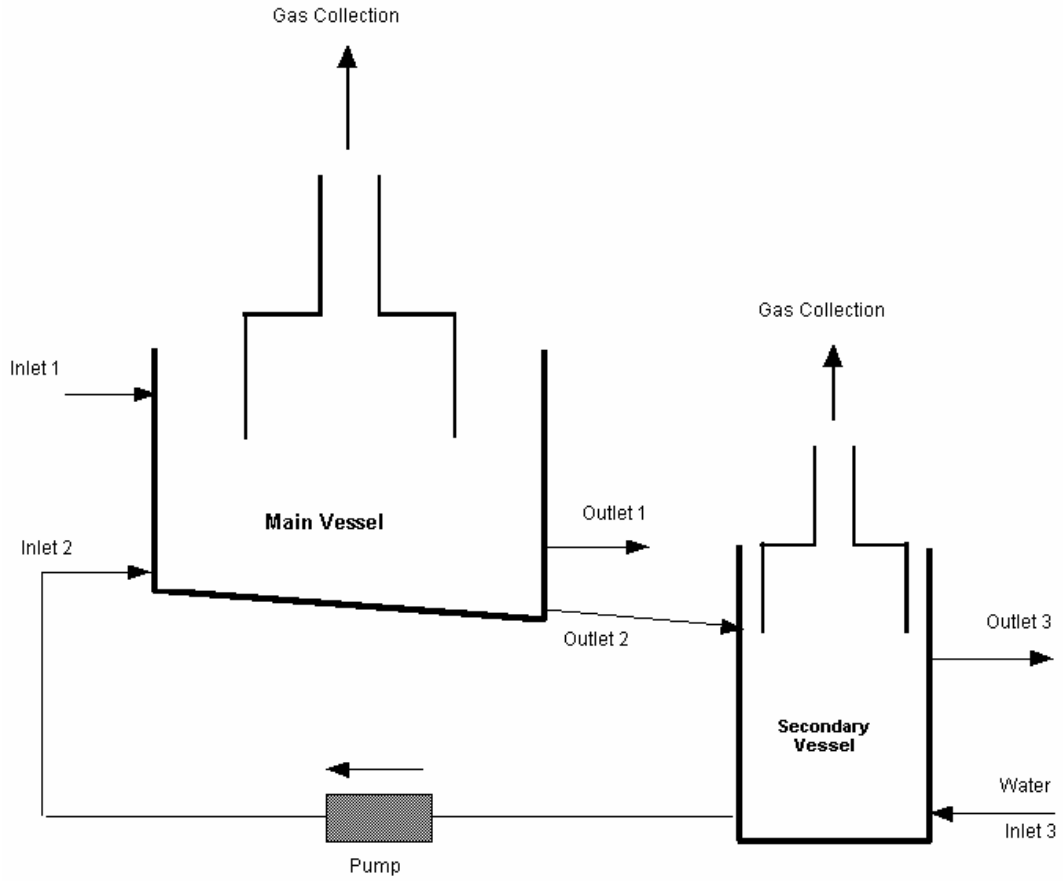
Mercury, membrane or diaphragm

Technical presentation – Diaphragm electrochemical cell

Mercury, membrane or diaphragm

Technical presentation – Membrane electrochemical cell

Gas Collection

Gas Collection

Inlet 1

Inlet 2

Outlet 1

Outlet 2

Mercury, membrane or diaphragm

<u>Presentation to Technical Director</u>

1. Why the company should adopt the <u>mercury</u> <u>electrochemical</u> <u>cell</u> to produce chlorine, sodium hydroxide and hydrogen:-

2. How does the mercury cell effectively separate the products/reagents?

3. Economic issues.

4. Environmental issues.

5. Advantages of mercury cells over diaphragm and membrane cells.

Mercury, membrane or diaphragm

<u>Presentation to Technical Director</u>

1. Why the company should adopt the <u>diaphragm</u> <u>electrochemical</u> <u>cell</u> to produce chlorine, sodium hydroxide and hydrogen:-

2. How does the diaphragm cell effectively separate the products/reagents?

3. Economic issues.

4. Environmental issues.

5. Advantages of diaphragm cells over mercury and membrane cells.

Mercury, membrane or diaphragm

<u>Presentation to Technical Director</u>

1. Why the company should adopt the <u>membrane</u> <u>electrochemical</u> <u>cell</u> to produce chlorine, sodium hydroxide and hydrogen:-

2. How does the membrane cell effectively separate the products/reagents?

3. Economic issues.

4. Environmental issues.

5. Advantages of membrane cells over mercury and diaphragm cells.

Mercury, membrane or diaphragm

<u>Sub-group summary sheet</u>

<u>Preferred electrochemical cell(s)</u>
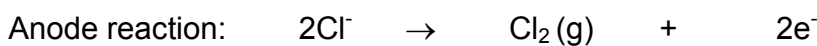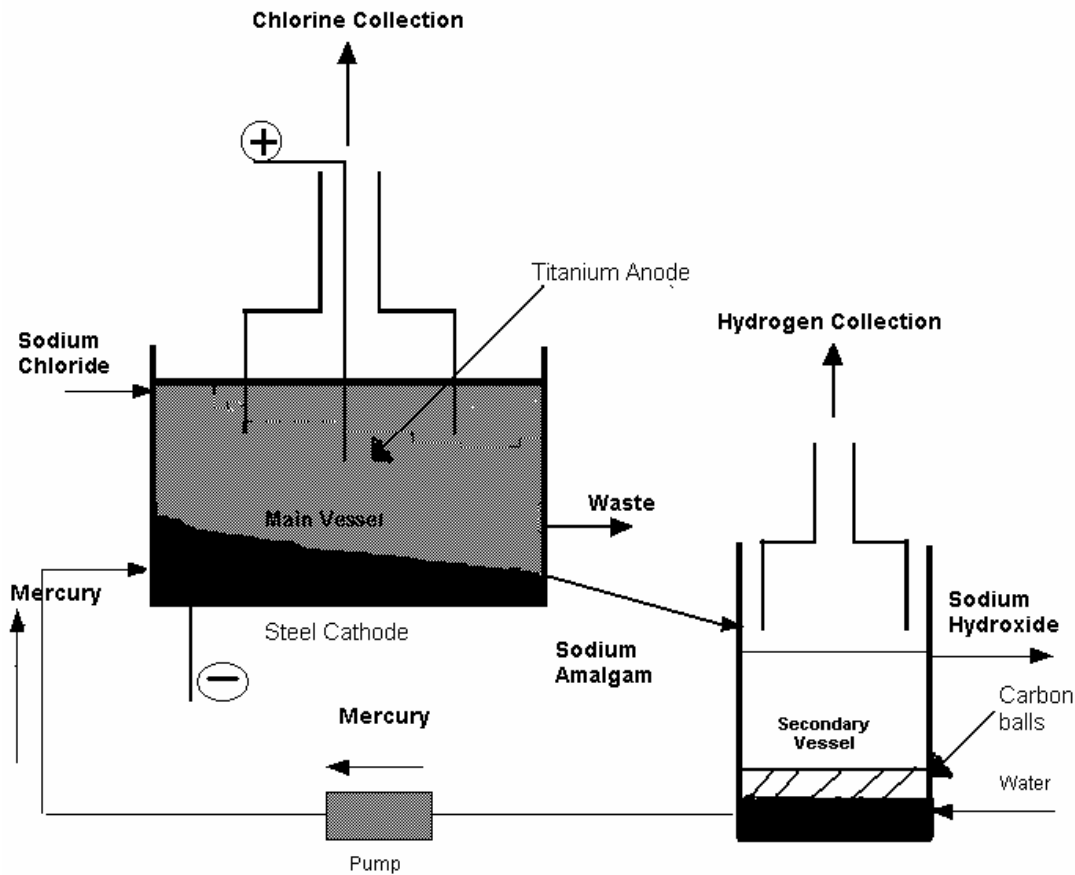
A.

B.

C.

D.

Mercury, membrane or diaphragm

Group conclusions

Group:

1. Which electrochemical cell(s) do you recommend to the Main Board should go into production?

2. Advantages:-

3. Disadvantages:-

Completed diagram of cells - The mercury cell

Anode reaction: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathode reaction: $Na^+ + e^- \rightarrow Na$ (dissolved in mercury)

In the secondary vessel, the following reaction occurs:

$$2Na/Hg(l) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) + 2Hg(l)$$

The main vessel is filled continuously with brine (sodium chloride solution). Mercury enters this vessel at the bottom and flows down the steel base, converting to sodium amalgam along the way. The steel base is connected to the negative supply and the mercury acts as the negative electrode (cathode). As electrolysis proceeds, chlorine is liberated at the anode and collected as a single gas. Sodium amalgam enters the secondary vessel where it reacts with water to liberate hydrogen and form sodium hydroxide. This reaction is catalysed by carbon, which is present in the secondary reactor (often termed the decomposer) as carbon balls. Hydrogen is collected as a gas and sodium hydroxide removed. The mercury is pumped

back to the main vessel for continuous operation. Waste ('spent brine') is removed continuously from the main vessel, where it can be either re-saturated and recycled or dumped.
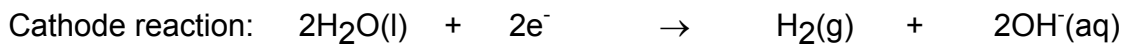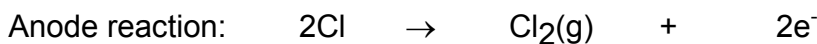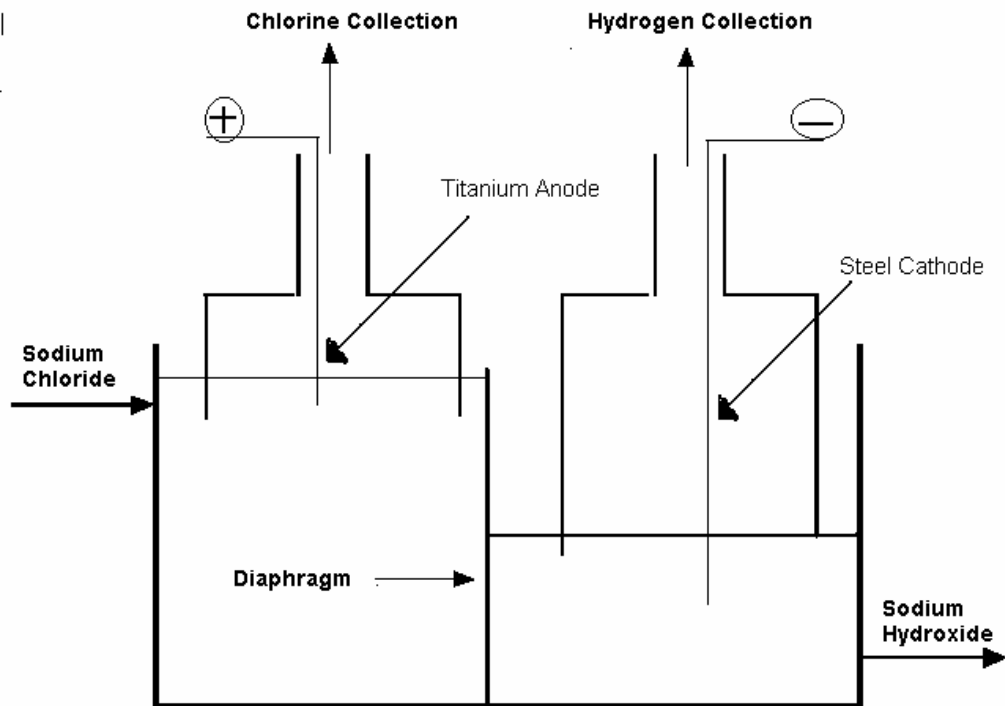
The sodium hydroxide purity is very high, with typical concentration being 50% sodium hydroxide by weight, contaminated with 30 ppm sodium chloride.

This cell design offers excellent separation between the chlorine and sodium hydroxide and consequently the impurity levels of sodium hypochlorite, sodium chlorate and oxygen are low. The major drawback of this cell is that it uses mercury, which is highly toxic. Electrolysis cell buildings need to be well ventilated to avoid the build-up of mercury vapour. Mercury can also be lost in the effluent stream. Obviously it is undesirable for this to enter the environment. Industrial handling practices have been refined over the years so that mercury discharge levels are minimal and safe.

Another problem is that some of the amalgam reacts with water in the main vessel to liberate hydrogen which can then contaminate the chlorine and which constitutes an explosion hazard in the chlorine treatment system.

Despite these issues, the modern mercury cell is still a highly effective way of producing chlorine, hydrogen and high quality sodium hydroxide.

Completed diagram of cells - The diaphragm cell

Chlorine Collection

Hydrogen Collection

$(+)$

$(-)$

Titanium Anode

Steel Cathode

Sodium Chloride

Diaphragm

Sodium Hydroxide

Anode reaction: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathode reaction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

The diaphragm is placed down the middle of the cell to make two separate compartments. The anode (coated titanium) is placed in the left compartment and the cathode (steel) in the right compartment, each below a gas collector.

The left compartment is filled continuously with sodium chloride (brine). Brine percolates through the diaphragm to enter the right compartment. As electrolysis proceeds chlorine is liberated at the anode and collected as a gas. Hydrogen is liberated at the cathode and collected as a gas. Hydroxide ions are also formed at the cathode and combine with sodium ions (aqueous sodium chloride can pass through the diaphragm) to give sodium hydroxide. This is removed continuously. Brine is maintained at a higher level in the left compartment to minimise the diffusion of hydroxyl ions through the diaphragm from the right compartment, helping to prevent chlorate and hypochlorite formation.

Brine can pass through the diaphragm which leads to the product sodium hydroxide containing sodium chloride. Typical concentrations are 12% sodium hydroxide by weight and 15% sodium chloride by weight. This mixture is concentrated in a separate evaporation

stage, resulting in the formation of crystalline salt which can then be removed by filtration. However, the 50% sodium

hydroxide by weight produced by this method still contains about 1% sodium chloride by weight.

The major drawback of this cell, apart from the low purity sodium hydroxide, is the use of asbestos in the diaphragm. Inhaled asbestos is known to cause lung cancer. White asbestos, rather than the considerably more toxic blue asbestos, is used and modern safe handling practices ensure a generally low health risk. Small quantities of sodium hypochlorite, sodium chlorate and oxygen are present as bi-products, further complicating the industrial exploitation of this technology.

Completed diagram of cells - Membrane cell

Anode reaction: $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Cathode reaction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
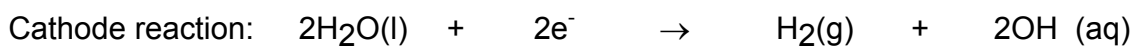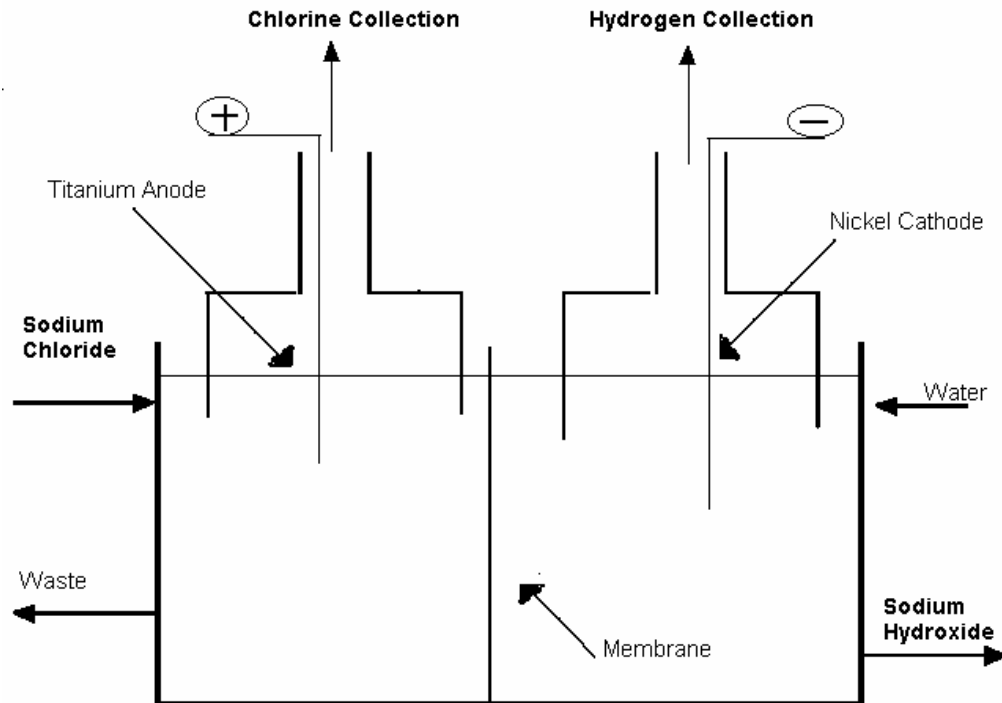
The membrane is placed down the middle of the cell to make two separate compartments. The anode (coated titanium) is placed in the left compartment and the cathode (nickel) in the right compartment, each below a gas collector.

The left compartment is filled continuously with sodium chloride (brine). The right compartment is filled continuously with water. As electrolysis proceeds chlorine is liberated at the anode and collected as a gas. Hydrogen is liberated at the cathode and collected as a gas. Hydroxide ions are also formed at the cathode and combine with sodium ions (sodium ions can pass through the diaphragm) to give sodium hydroxide. This can be removed continuously from the right hand compartment. Waste ('spent brine') is emptied continuously from the left compartment. The membrane does not allow hydroxyl ions to enter the left compartment, thus minimising hypochlorite formation, though some is still produced.

The sodium hydroxide purity is high, typical concentration is 30% sodium hydroxide by weight, contaminated with 50 ppm sodium chloride.

Early problems with membrane cells were concerned with the lifetime of the membrane itself as the conditions inside the cell are quite severe. Modern membranes are quite expensive, but will function for approximately 3 years. A small number of companies manufacture these membranes which have strict patent protection rights pending. The concentration of the sodium hydroxide produced is not sufficiently high (as demanded by many commercial applications), requiring a separate evaporation stage to bring it up to the desired concentration of 50% by weight.

In addition to sodium chloride, sodium hypochlorite, sodium chlorate and oxygen are also present as impurities in small quantities.

Mercury, membrane or diaphragm

Summary

Up until the 1970s, virtually all commercial electrolysis cells were of the mercury or diaphragm design. However, in 1965 Japan experienced a mercury poisoning scare in Minamata Bay. Mercury effluent collected at the bottom of the sea where it was converted into the highly toxic dimethyl mercury by micro-organisms. This substance worked its way into the food chain of the local population, by people eating fish caught in the bay, and led to severe health problems, including brain damage.

As a consequence, the Japanese government brought in legislation requiring all mercury cells to be phased out. Initially, conversion to diaphragm cells was thought to be the solution, but diaphragm cells are not able to produce sodium hydroxide of sufficient purity for all applications. The sodium hydroxide is contaminated with sodium chloride as brine can pass through the diaphragm. Even after purification by evaporation/filtration, itself a high energy process, about 1% sodium chloride still remains. By contrast, sodium hydroxide from mercury cells is virtually sodium chloride free. This gave the impetus for advancement in membrane technology and, today, virtually all Japanese electrolysis uses membrane cells.

The coated titanium anode is often referred to as the dimensionally stable anode (DSA) and was introduced in the 1970s as a replacement for carbon based anodes. The DSA is longer lasting, is electrochemically more efficient and is less labour intensive than carbon. It also plays an <u>electrocatalytic</u> role. This technological invention represents a major milestone in the chloro-alkali industry.

A major problem concerned the development of a membrane material that could resist the demanding conditions within the chlor-alkali cell. Modern membranes are based on a backbone of carbon and fluorine with side chains terminating in sulfonic and carboxylic acid groups. Sodium hydroxide produced in membrane cells contains only a trace of sodium chloride. This is a consequence of the main difference between the membrane cell and the diaphragm cell: only sodium ions can pass through the membrane while both sodium and chloride ions can pass through the diaphragm.

In 1997, the distribution of chlorine production in Western Europe is as follows:

Mercury cells	64%
Diaphragm cells	24%
Membrane cells	11%

Total: 4 million tonnes per year

The worldwide distribution reflects the historical and geographical usage of the different production methods. Europe and Japan originally favoured the mercury cell while the diaphragm cell was the preferred option in North America. The world membrane cell capacity is shown in *Figure 12*.
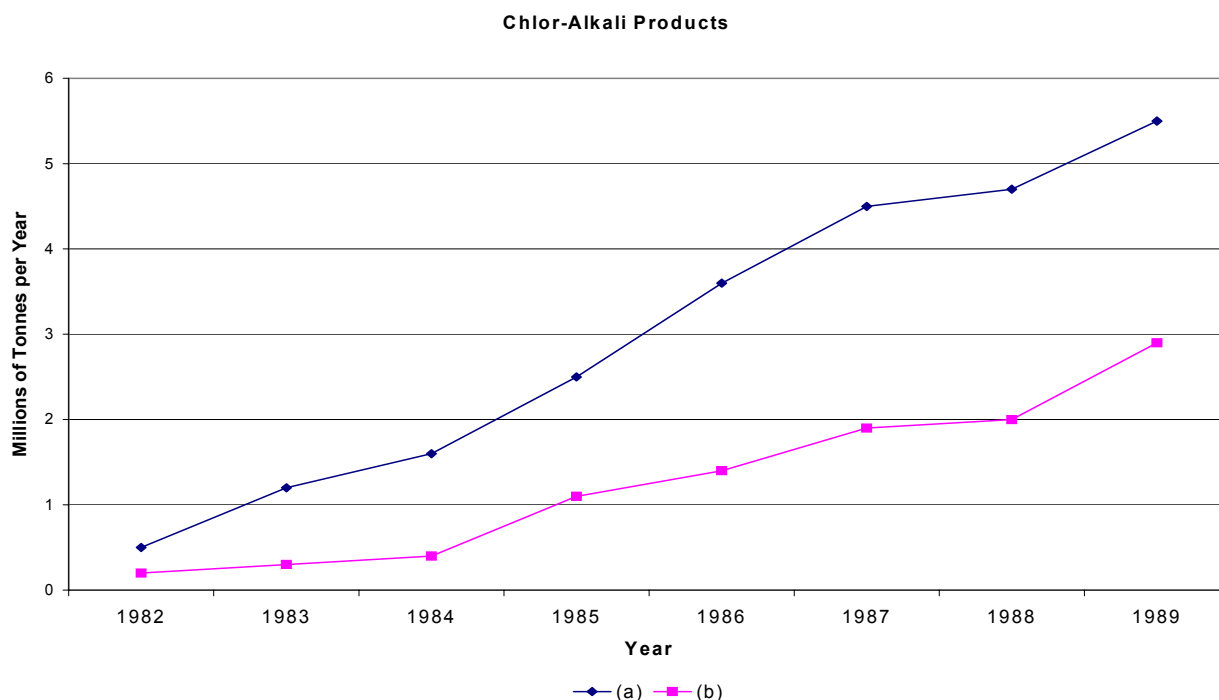
Chlor-Alkali Products

Figure 12: (a) Including Japanese licensees; (b) Excluding Japanese licensees

Electricity accounts for approximately 60% of the total cost of the products. Total power consumptions for each cell type are:

Mercury cell	3400 kWh/ton of Cl produced
Diaphragm cell	3600 kWh/ton of Cl produced
Membrane	2950 kWh/ton of Cl produced

As energy costs and environmental factors continue to increase in importance, there is little doubt that membrane cells will become the preferred technology in industry. Nevertheless mercury cells continue to be used today, where considerable investment has been made to minimise their environmental impact. In fact a recent study established that mercury emissions from chlorine production in Europe are now lower than background emissions from natural sources (*e.g.* geological emissions).

Summary

This unit has demonstrated the degree of complexity that is common in modern industrial chemistry. The successful implementation of new manufacturing procedures for an ever changing market place is a demanding task, where chemists play an important and critical role.

Coursework

Prepare a short technical report (one page of text *ca* 500 words) describing a process to produce chlorine, sodium chloride and hydrogen on an industrial scale.

You can highlight any electrochemical cell(s), however the advantages/disadvantages of your designated cell(s) compared to alternatives should be addressed.

You can structure your report according to the following headings:-

1. *Chlorine demand*
2. *Proposed method of production*
3. *The chemical process*
4. *Economic issues*
5. *Environmental issues*

No single answer is correct and a spectrum of opinion is acceptable, as long as the central science-based issues are presented.

The report needs to be well structured, neat and easy to read. Typed reports are not obligatory. Diagrams and chemical equations are encouraged. Marks will be deducted for poor grammar and spelling.

Essays are to be handed in to your sub-group tutor <u>two weeks after completing</u> the unit. Late course work will incur a penalty and course work received > one week late will not be marked. All scripts will be returned to students.

Acknowledgements

This unit has been developed with assistance from the Teaching and Learning Service, the Centre for Science Education at the University of Glasgow and ICI Chemicals and Polymers Ltd.