CHAPTER I
INTRODUCTION

The manufacture of caustic and chlorine is one of the important heavy chemical industries. The electrolytic production of caustic soda was known in the eighteenth century. By the middle of the twentieth century, the electrolytic process produced more than 99% of the world's chlorine. Brine electrolysis (NaCl) produces chlorine at the anode and hydrogen (H_2) along with the alkali hydroxide (NaOH) at the cathode. In the electrolysis of NaCl solutions, the OH ions are prevented from passing to the anode by using a magnetite anode. This anode is made by fusing Fe_2O_3 in an electric furnace. When chlorine and the alkali hydroxide are to be the final products, it is necessary to design a cell that keeps them from mixing. A device that can detect changes in hydrogen concentration in the presence of the moist chlorine can be used for better cell control and the improvement of plant safety.

1.1 Background

In the chlor-alkali industry, three types of electrolytic cells, mercury cells, diaphragm cells and membrane cells, are in commercial use. The objective of each cell is to isolate the separate reaction products to ensure the generation of products having proper purity as much or substantial as possible.

Hydrogen presence in the chlorine gas stream is a consequence of different operating conditions in each electrolytic cell. The development of a sensor, for continuously monitoring of the hydrogen concentration in the wet chlorine gas at various locations within the chlor-alkali plant, would create the following benefits:

1. The instrument could determine a high hydrogen presence at any location, which is not desirable for safety reasons.

2. The instrument could give an early warning of a mal-functioning cell causing an increase in hydrogen concentration in the wet chlorine gas which allows corrective action.

The development of an inexpensive compact and robust sensor has been undertaken. Modification of the sensor to H_2-Cl_2-H_2O system has to account for the following particular factors:

1. The gas mixture is reactive and corrosive.
2. The gas stream temperature is between 60°C and 90°C.

The objective of this work is to identify a sheathing material for the sensor. This material will have the property of blocking chlorine while permitting hydrogen to pass to the sensing element. It is believed to be undesirable to permit access of the chlorine to the sensor that catalyzes the reaction between hydrogen and chlorine. Such a reaction would clearly alter the detection of hydrogen and nullify the principle of the sensor. The sensor also needs to have a capability of monitoring the presence of hydrogen in the chlorine gas in the wet conditions. In order to determine if any of the above materials would be acceptable sheathing materials, the rate of transfer of both chlorine and hydrogen through the test materials had to be quantified. The ratio of the hydrogen to chlorine permeability coefficients for an acceptable barrier material would be more than 10 000 (Center for Nuclear Energy Research, 2000).

Various materials have been tested in a previous study. It is indicated that epoxy vinyl ester resin is capable of blocking chlorine but allowing hydrogen to pass. The problem occurs when applying the co-monomer named epoxy vinyl ester resin to certain surfaces, since it is brittle and does not adhere well to the surface. Therefore, a material that has suitable properties would stick to the surface and be easy applied and control its thickness.

The operating conditions of the industrial electrochemical cells for the production of chlorine gas and sodium hydroxide solution is at 80°C and one atmospheric pressure in a gas composition of 96% chlorine, 3% air and 1% hydrogen, saturated with water vapor.

1.2 Importance of Measuring Hydrogen Concentration

The presence of hydrogen in the chlorine gas is undesirable. This causes two major operational problems as follows:

1. An increase in the specific energy consumption for the production of the desirable products, which are sodium hydroxide (NaOH) and chlorine (Cl_2). An increase in hydrogen gas above an electrical cell indicates operational cell inefficiencies, for example, the current efficiency.
2. The explosive limit of hydrogen in chlorine is 6% (Tufts, 1992). If the concentration of hydrogen in the chlorine exceeds such a limit a hazardous situation arises. This situation can arise in the second stage of the chlorine liquefaction where virtually all chlorine is liquefied and gives 16% hydrogen containing in a gas phase, which is in the explosive region.

The present device used to measure the concentration of hydrogen in chlorine gas is a catharometer. It determines the hydrogen concentration depending on the significant difference between the chlorine and hydrogen thermal conductivities. This device is expensive and not readily located in the cell room. In addition, gas samples from any locations are taken for hydrogen analysis in the laboratory because such gas samples must be dried before introduced into the device. As a result the catharometer does not allow continuous monitoring the hydrogen concentration.

1.3 Reactions and Energy Consumption

Austin (1984) explained the method to determine the decomposition voltage and the voltage efficiency of an electric cell, considered from the Gibbs Equation. The amount of energy consumed in the brine electrolysis is the product of the current flowing and the potential of the cell. The theoretical voltage required for the process can be approximated from the Gibbs-Helmholtz equation.

$$E = \frac{-J\Delta H}{nF} + \frac{TdE}{dT} \tag{1.1}$$

where:

E = theoretical decomposition voltage

ΔH = enthalpy change of reaction

J = electrical equivalent of heat

T = absolute temperature

F = Faraday's constant

n = number of equivalents involved.

The heat of reaction for the electrolysis of salt may be found from the heats of formation of the compounds of the overall reaction, as follows

$$NaCl_{(aq)} + H_2O_{(l)} \rightarrow NaOH_{(aq)} + \frac{1}{2}H_{2\,(g)} + \frac{1}{2}Cl_{2\,(g)} \tag{1.2}$$

$$Na_{(s)} + \tfrac{1}{2}Cl_{2\,(g)} \rightarrow NaCl_{(aq)} \qquad \Delta H = 407\ \text{kJ} \tag{1.3}$$

$$H_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} \rightarrow H_2O_{(l)} \qquad \Delta H = 256\ \text{kJ} \tag{1.4}$$

$$Na_{(s)} + \tfrac{1}{2}O_{2\,(g)} + \tfrac{1}{2}H_{2\,(g)} \rightarrow NaOH_{(aq)} \qquad \Delta H = 459\ \text{kJ} \tag{1.5}$$

which has the reactions of formation as given,

the net ΔH for the overall reaction results from equation (1.2) is

$$+407 + 286 - 469 = 224\ \text{kJ}.$$

When this value of ΔH is substituted in the Gibbs-Helmholtz equation and the change in voltage with temperature is neglected, the value of E is found to be 2.31V. The omission of TdE/dT involves an error of less than 10 percent for most cells.

The ratio of this theoretical voltage to that actually used is the "*voltage efficiency*" of the cell. Voltage efficiencies range from 60 to 75 percent. According to Faraday's law, 96 500C of electricity passing through a cell produce 1-gram equivalent of chemical reaction at each electrode. Because of side reactions, cells usually require more than this amount. The ratio of the theoretical to the actual current consumed is defined as the "*current efficiency*". Current efficiencies run 95 to 97 percent and, unless otherwise specified, are understood to be *cathode* current efficiencies. The current divided by the area on which the current acts is known as the "*current density*". A high value is desirable. The product of voltage efficiency and current efficiency is the "*energy efficiency*" of the cell. Another consideration is the "*decomposition efficiency*", which is the ratio of equivalents produced in the cell to equivalents charged. In the usual commercial cell, this decomposition efficiency is about 60 to 65 percent. Some newer, larger membrane cells claim efficiencies as high as 75 to 80 percent. Diaphragm cells operated to obtain very high decomposition efficiencies encounter difficulties with the migration of hydroxyl ions back to the anode, resulting in the formation of hypochlorite ion. Hydroxyl ions are decomposed on the anode by the reaction:

$$2OH^- \rightarrow H_2O + \tfrac{1}{2}O_2 + 2e \qquad (1.6)$$

The oxygen formed reacts with the graphite of the anodes, causing decreased anode life. In cells with metal anodes, the oxygen does not react.

1.4 Manufacturer of Chlorine and Caustic Soda

Henglein (1969) has divided electrolytic cells that produce chlorine gas and sodium hydroxide solution into 3 classes.

1.4.1 Stationary Electrode with Diaphragm Cell

There are both vertical and horizontal cells for the diaphragm process. The current yield in both types amounts to 90-92% and the voltage of 3.2-3.8 volt is measured between the anode and the cathode. It contains a diaphragm, usually made of asbestos, to separate the anode from the cathode as shown in Figure 1.1.

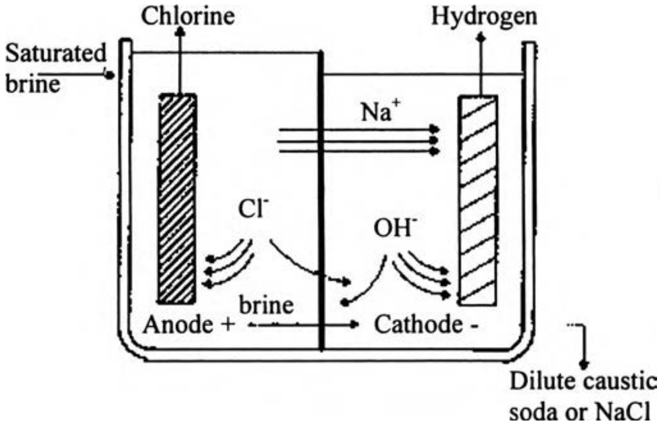

Figure 1.1 Ordinary asbestos-diaphragm cell (Raymond, 1985).

The diaphragm permits a flow from anode to cathode and thus greatly lessens or prevents side reactions (e.g., sodium hypochlorite formation). The generation of hydrogen, H_2 and hydroxide ion, OH^- occurs at the cathode.

At the anode:

$$Cl^- - 1e \rightarrow \frac{1}{2}Cl_2 \tag{1.7}$$

At the cathode:

$$H_2O + 1e \rightarrow \frac{1}{2}H_2 + OH^- \qquad (1.8)$$

Diaphragm cells are suitable if NaCl is supplied as brine and the fuel costs are low. A major advantage of the diaphragm cell is that it can run on dilute (20%), fairly impure brine. Such dilute brines produce dilute sodium hydroxide (typically 11%NaOH with 15%NaCl) contaminated with sodium chloride as a product. It is expected that diaphragms made of plastics having corrosion-resistant property will increase service life and remove the objection from the environmentalist to any process that may release asbestos fibers into the environment. The process of the production of diaphragm cells is shown in Figure 1.2.

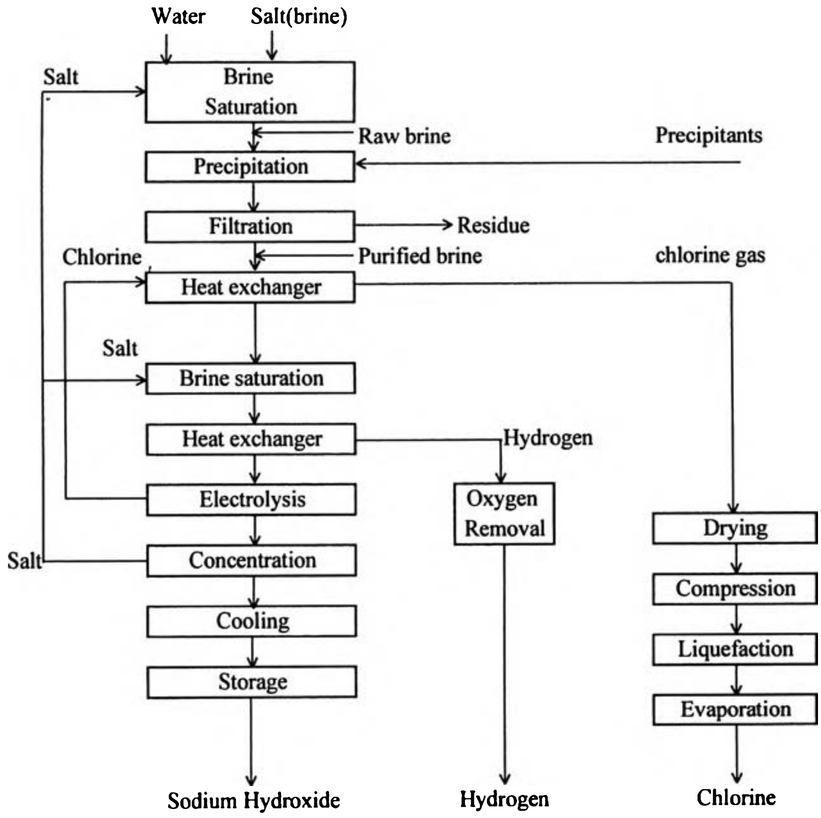

Figure 1.2 Flow diagram of diaphragm chlor-alkali process (Raymond, 1998).

1.4.2 Movable Electrode cells or Mercury Cell

The cathode consists of mercury, which reacts with the separating sodium and forms a mercury-sodium alloy (amalgam) of 0.2% concentration. This amalgam is then decomposed with water and produces NaOH and H_2. The decomposition reaction of an amalgam is

$$2Na{\cdot}Hg + 2H_2O \rightarrow 2NaOH + H_2 + Hg$$

The mercury is returned to the electrolytic cell. Figure 1.3 shows an example of the horizontal mercury cell with the cell voltage of 5 volt and the potential between cathode and anode is 3.9-4.2 volt. The operation of mercury cells in chlor-alkali plant is shown in Figure 1.4.

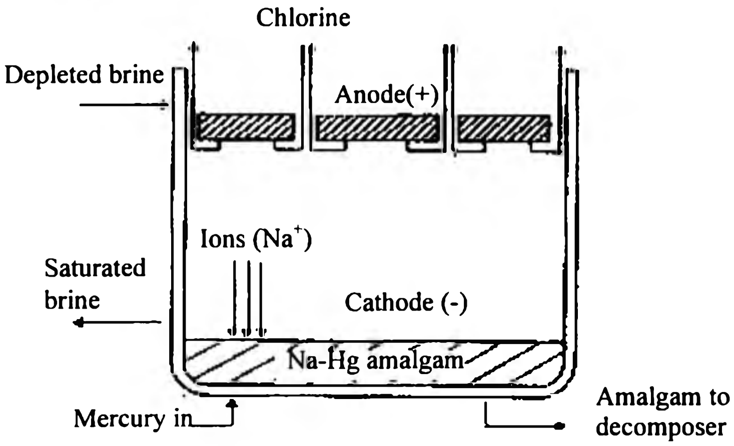

Figure 1.3 Mercury cell (Raymond, 1985).

The common processes in the mercury cell are as follows.

At the anode:

$$Cl^- - 1e \rightarrow \frac{1}{2}Cl_2 \tag{1.9}$$

At the cathode:

Primary reaction:

$$Na^+ + 1e \rightarrow Na \tag{1.10}$$

$$Na + xHg \rightarrow NaHg_x \tag{1.11}$$

Secondary reaction:

$$H^{+} - le \rightarrow \frac{1}{2}H_2 \qquad (1.12)$$

Chlorine is produced at the anode while the cathodic reaction in mercury cells is the discharge of sodium ion, Na^+ to form dilute sodium amalgam.

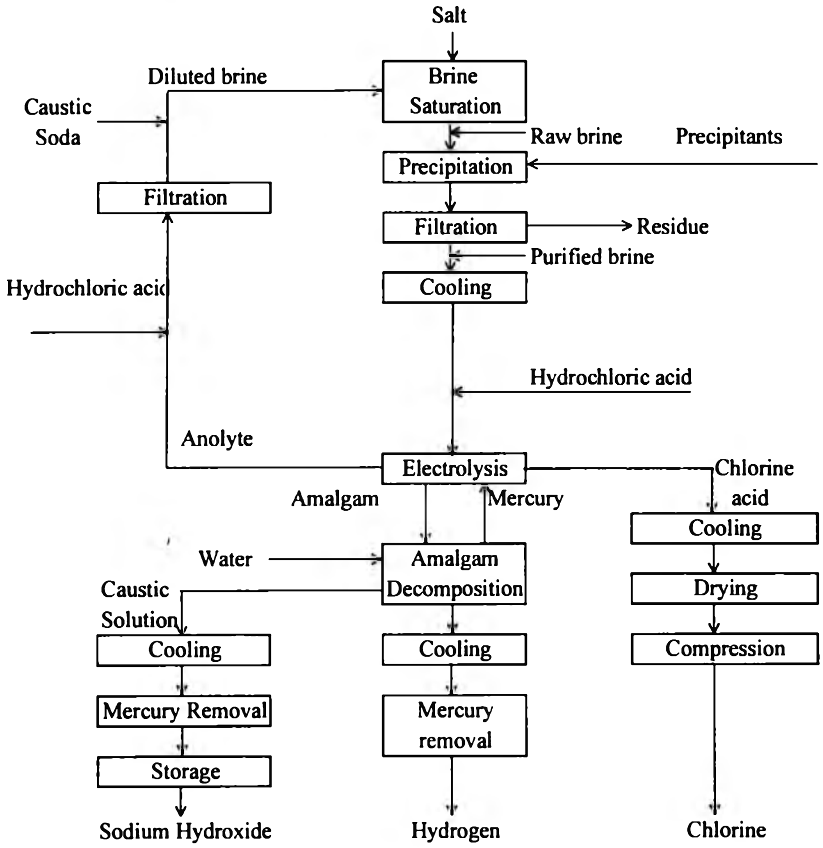

Figure 1.4 Flow diagram of mercury chlor-alkali process (Raymond, 1998).

1.4.3 Membrane Cell

A semipermeable membrane is used for separation of the anode and cathode compartments (See Figure 1.5). Membrane cells separate the compartments with porous chemically active plastic sheets that allow sodium ions to pass but reject hydroxyl ions. Several polymers have been developed for this required operation. The purpose of the membrane is to exclude hydroxyl and chloride ions from the anode chamber, therefore making the product much lower in salt concentration than the diaphragm cell. Membrane cells operate using a more concentrated brine and produce a purer, more concentrated product. The component electrochemical reactions are the discharge of chloride ions, Cl^-, at the anode,

$$Cl^- - 1e \rightarrow \frac{1}{2}Cl_2 \tag{1.13}$$

At the cathode:

$$H_2O + 1e \rightarrow \frac{1}{2}H_2 + OH^- \tag{1.14}$$

Figure 1.6 shows an example of the unit operation of membrane cells.

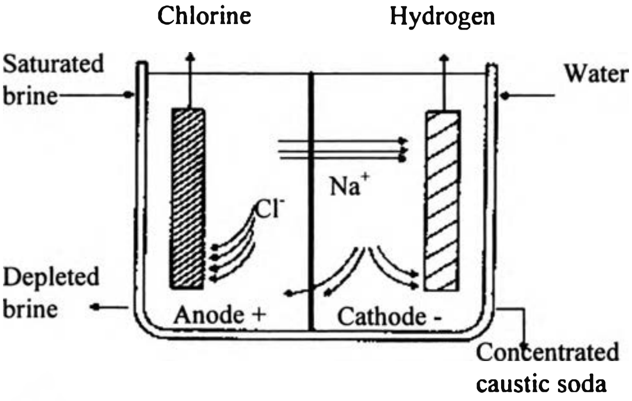

Figure 1.5 Perfluorosulfonic acid resin membrane (Raymond, 1985).

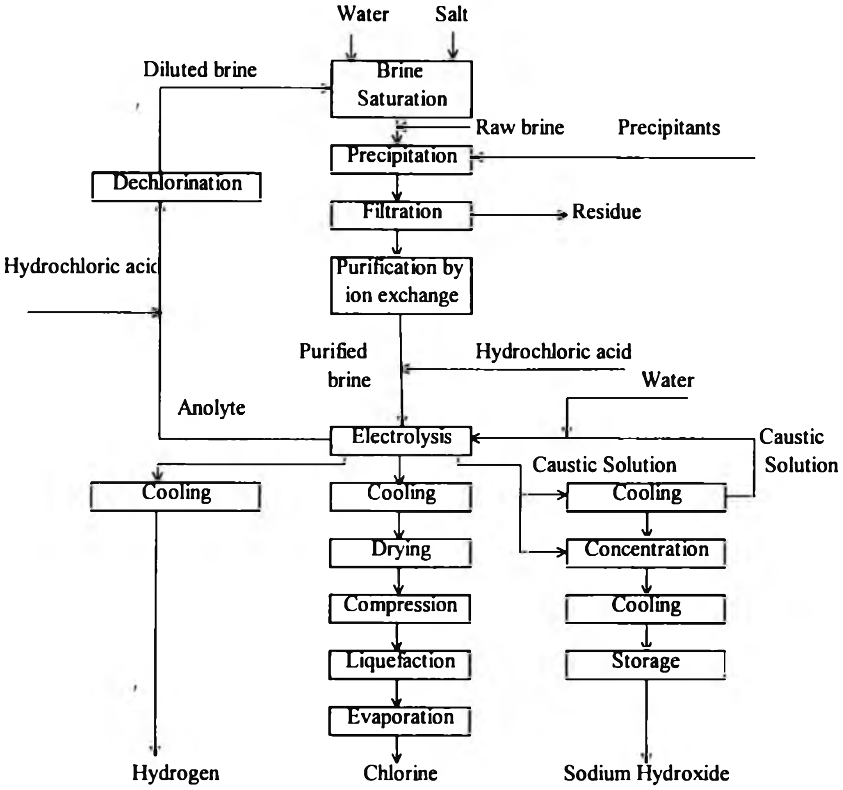

Figure 1.6 Flow diagram of membrane chlor-alkali process (Raymond, 1998).

Serious suggestions have been made that a combination plant using the output of the membrane cells as feed to the diaphragm cells might result in the optimum application of both and make a considerable cost reduction overall.

The mercury process yields a more pure and stronger caustic soda and reduces the cost of evaporation but consume higher energy than diaphragm cells. However, if high purity product is the criteria then mercury cells are superior, for example, for the synthetic fiber industry. The physical properties of the products from chlor-alkali plant are shown in Table 1.1 and Table 1.2. Diaphragm cells and membrane cells use about the same amount of electrical energy. The ratio of the electrical energy between diaphragm/membrane cells and mercury cells is approximately 3:4. In evaluating a cell, the following must be taken into consideration: yield on current, cell-voltage, concentration of caustic soda and the purity of gas product(s). The operational conditions of the three-type of the electrolytic cell, compares to each other are shown in Table 1.3.

Table 1.1 Physical constants of chlorine (Raymond, 1985).

Property	Value
Melting point, °C	-100.98
Boiling point at 101.33 kPa (760 mm Hg), °C	-34.05
Density of dry gas at 0°C and 101.33 kPa, g/L	3.209
Density of saturated gas at 0°C and 366.49 kPa (53.155 psia), g/L	12.07
Density of liquid at 0°C and 366.49 kPa, g/L	1468.4
Critical density, g/L	573
Critical pressure, MPa	7.71
Critical temperature, °C	1144
Critical volume, L/g	0.001745
Latent heat of vaporization, J/g(cal/g)	287.4(68.7)

Table 1.2 Physical constants of pure sodium hydroxide (Raymond, 1985).

Property	Value
Specific gravity, 20°/4°C	2.130
Melting point, °C	318
Boiling point at 101.3 kPa(760 mm Hg), °C	1390
Index of refraction	1.3576
Latent heat of fusion, J/g	167.4
Heat of transition, alpha to beta, J/g	103.3

Table 1.2 Physical constants of pure sodium hydroxide (Raymond, 1985), (Cont.).

Property	Value
Heat of formation from the elements:	
Alpha form, kJ/mol	422.46
Beta form, kJ/mol	426.60
Transition temperature, °C	299.6
Solubility at 20°C, g/100g water	109

Table 1.3 Comparison of the electrolytic cells.

Factor	Diaphragm	Mercury Cell	Membrane
anode	graphite or titanium-based	(same material)	(same material)
cathode coating	steel or nickel-coated steel	mercury on steel	steel or nickel
diaphragm membrane	asbestos or ion-exchange	None ion-exchange	membrane
cathode product	$NaOH_{(aq)}$, $NaCl_{(aq)}$ and $H_{2(g)}$	amalgam	$NaOH_{(aq)}$ and $H_{2(g)}$
decomposer product	$NaOH_{(aq)}$, $NaCl_{(aq)}$ and $H_{2(g)}$	None	None
evaporator product	$NaOH_{(aq)}$, $NaCl_{(aq)}$ and $NaCl_{(s)}$	None	$NaOH_{(aq)}$, $NaCl_{(aq)}$
steam consumption	1500-2300 kg/ton of $NaOH_{(aq)}$	None	450-550 kg/ton of $NaOH_{(aq)}$
cell voltage (V.)	3-4	4-5	2.8-3.3
current density (kA/m^2)	0.5-3	7-10	2-5