

## CHAPTER I INTRODUCTION

The presence of hydrogen gas as an impurity in chlorine gas and caustic soda generated by electrolysis of an aqueous sodium chloride solution in a chlor-alkali plant leads to two principal operational problems. First is reducing plant efficiencies and increasing the specific energy consumption with the production of the useful products, NaOH and Cl<sub>2</sub>. Second, hydrogen gas in the presence of chlorine can be hazardous if the hydrogen concentration exceeds 6 %. The explosive limit of a mixture after the chlorine has been liquefied can give an enriched-gas phase containing more than 6 % hydrogen.

The presence of H<sub>2</sub> in Cl<sub>2</sub> gas from the caustic/chlorine plants differs depending on the employed technology.

Diaphragm cell:

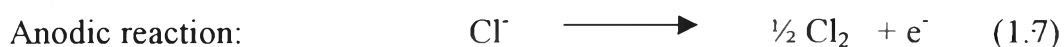
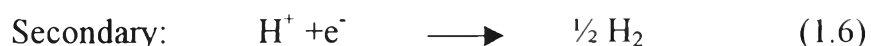
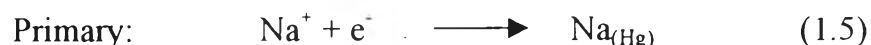
Cathodic reaction:



The primary reaction is desired since this produces NaOH, but it also produces H<sub>2</sub> at the cathode. The H<sub>2</sub> gas enters Cl<sub>2</sub> gas stream presumably by entrainment in following reactions.

Mercury cell:

Cathodic reaction:



Amalgam (NaHg) flows to reactor where H<sub>2</sub> produces NaOH. Hydrogen produced by the secondary reaction mixes with Cl<sub>2</sub>. The secondary reaction is undesirable since current efficiency (related to NaOH production) is lowered. A typical example of gas composition from mercury cell is 96 % Cl<sub>2</sub>, 1-2 % air, 2-3 % H<sub>2</sub> (dry basis).

The hydrogen concentration in chlorine is measured by a catharometer, the function of which depends on the large difference in thermal conductivities between hydrogen and chlorine. However, this equipment is expensive and massive and is not easily operated in the cell room. In addition, the gas needs to be dried before introduction into this instrument. As gas samples from a number of plant locations are taken to the laboratory for analysis of the hydrogen concentration, this method does not give continuous monitoring.

The development of an instrument for the continuous monitoring for the hydrogen concentration in moist chlorine gas at various locations of the chlor-alkali plant should have the following advantages:

1. The instrument would yield an early warning of a mal-functioning of a cell due to excessive hydrogen concentration in chlorine and allow for immediate corrective action.
2. The equipment could indicate a high hydrogen concentration in any location where a danger may be present.

The objective of this work is to identify the potential coating material which can be used to cover metals (palladium) and withstand long term exposure to moist chlorine gas at temperature up to 80 °C. This coating should completely block chlorine from the metal surface, but at the same time allow the passage of hydrogen to the metal beneath the coating. The Pd/H sensor cannot function in the presence of chlorine since palladium metal catalyzes the reaction between hydrogen and chlorine. Such a reaction would alter the absorption of hydrogen by the palladium and nullify the principle on which the sensor operates. It is desirable that this coating be applied in a reproducible manner with a known and controlled thickness. The procedure for application should be simple so that it can be part of a manufacturing process.

## **1.1 Description of Chlor-alkali Plant**

### **1.1.1 Raw Materials**

Usually, an aqueous solution of sodium chloride is employed as the electrolyte in electrolyte cells. Other metal chlorides such as KCl are used, but to a much smaller degree. As a whole, NaCl is obtained either from brine wells, underground deposits of solid salt, or the ocean. Before use, raw brine is treated to remove impurities (Environment Protection Agency, 1971). Purification of brine is necessary to remove such ions as  $Mg^{2+}$  since such impurities act to promote undesirable secondary cathodic reaction.

### 1.1.2 Electrolytic Decomposition of Sodium Chloride

Chlorine and caustic soda as well as hydrogen gas are co-products of electrolysis of aqueous sodium chloride solution, NaCl, (commonly called brine) by the following overall chemical reaction (Kirk, 1890-1957):



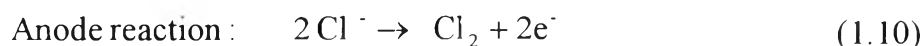
This reaction has a positive Gibbs free energy of 422.2 kJ / kg of NaCl (100.9 kcal/kg of NaCl) at 25 °C and hence energy has to be supplied in the form of d-c electricity to drive the reaction in a forward direction. Therefore, in order to achieve the overall reaction, the amount of electrical energy required for the reaction depends on electrolytic cell parameters such as current density, voltage, anode and cathode material, and the cell design.

According to the type of electrolytic cell, conversion of aqueous NaCl to Cl<sub>2</sub> and NaOH is achieved: *the diaphragm cell, the membrane cell, and the mercury cell*. The distinguishing features of these cells are the manner by which the electrolysis products are prevented from mixing with each other, thus ensuring products with high purity.

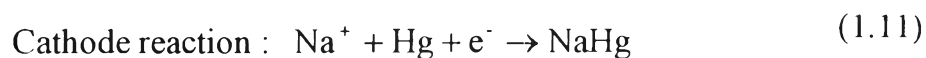
### 1.1.3 Cell Description and Operation

#### 1.1.3.1 *The Mercury Cell Process*

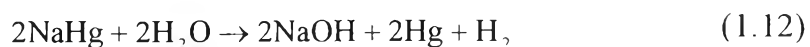
Refer to Figure 1.1, a mercury cell is composed of two electrochemical cells: the Electrolyzer and the decomposer (or the denuder). In the electrolyzer, saturated (25.5 % wt) sodium or potassium brine flows uniformly along a flat-bottomed steel trough that is inclined approximately 1 to 2.5°. Mercury, which is the cathode, flows concurrently with the brine over the steel base. Anodes of activated titanium are suspended in the brine from above. The sodium chloride electrochemical reactions are the discharge of chloride ion,  $\text{Cl}^-$ , at the anode,



At the cathode, the discharge of sodium ion,  $\text{Na}^+$ , takes place to form dilute sodium amalgam ( $\text{NaHg}$ ), which is mercury containing about 0.1-0.3 % Na.



The resulting amalgam flows from the electrolyzer to the decomposer where the amalgam is reacted with water and it becomes to a short-circuited electrical cell which graphite acts as the cathode and the amalgam as the anode. The reaction is given by:



The hydrogen gas is cooled and compressed. Moreover, hydrogen from mercury cells contains traces of mercury vapor. Most of it is removed in a direct-contact scrubber or in the condenser. There is obtained approximately 99.9%  $H_2$  on a dry basis which contains 20-30 mg of  $Hg / m^3$ .

Caustic produced in this cell is usually pure since there is no direct connection between the brine solution in the electrolyzer and the caustic solution in the decomposer.

Investment costs are higher in mercury cells costs because of mercury loss, and a higher energy requirement per ton of products.

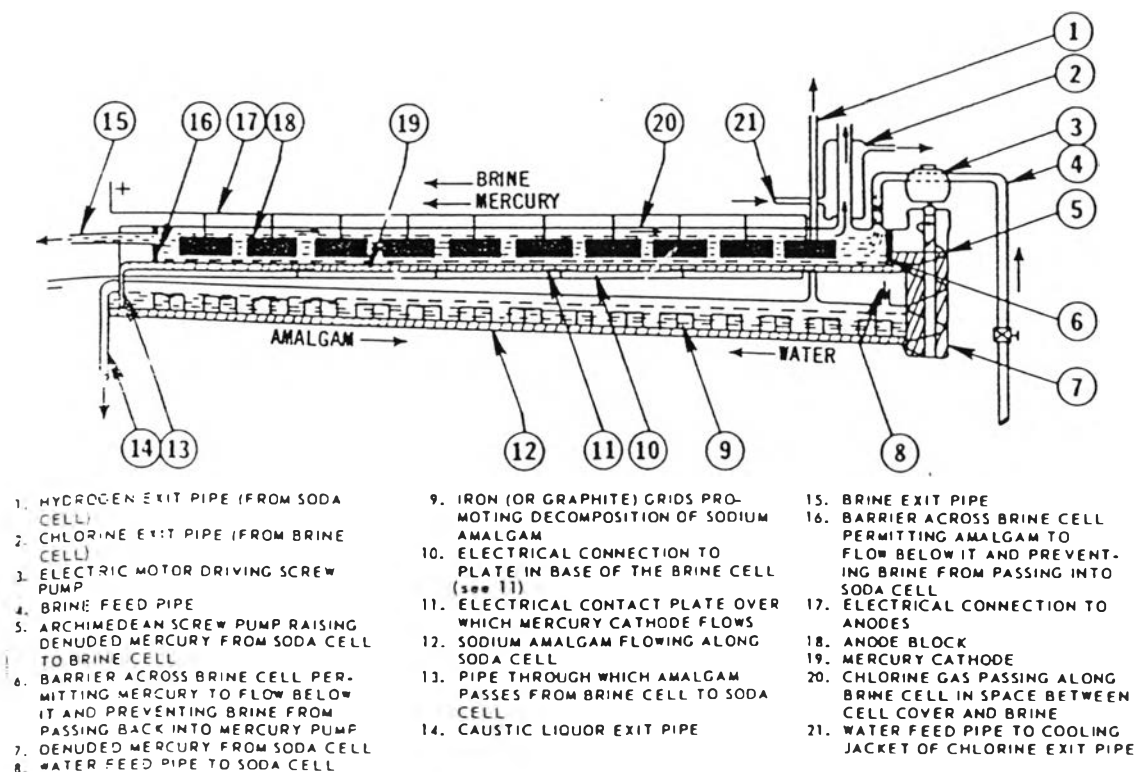


Figure 1.1 Typical mercury-cathode cell.

### 1.1.3.2 The Diaphragm Cell Process

Figure 1.2 shows a flow diagram of a typical chlor-alkali diaphragm-cell installation. The overall reaction for this cell is eq (1.1).

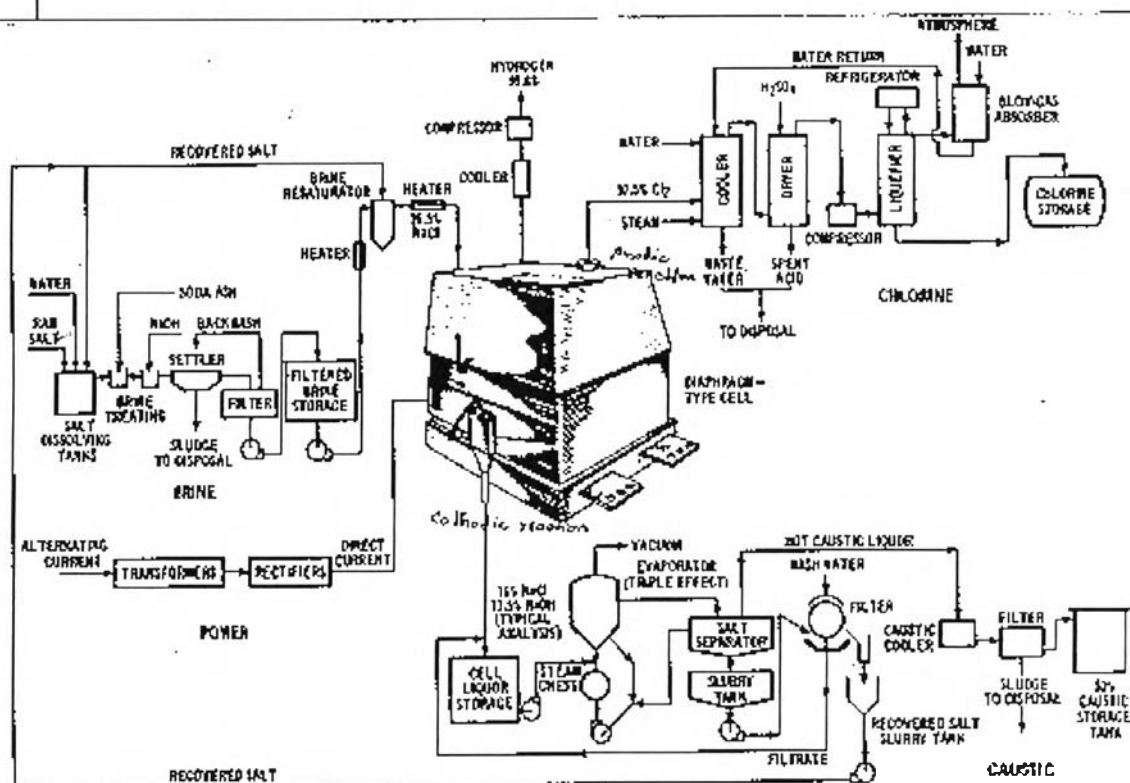


Figure 1.2 Flow diagram of a typical diaphragm-cell chlor-alkali installation.

KCl may be used instead of NaCl in diaphragm cells, in which case KOH is produced. However, the demand for KOH is small when compared with that of NaOH.

**Anodic reaction** - In most diaphragm cells, brine, known as anolyte, flows continuously into the anode compartment and directly contacts the oxide coated Ti anodes as they do not suffer erosion (see Table 1.1). Chlorine gas is produced at the anode and leaves the cell saturated with water vapor and is subsequently cooled in direct or indirect water coolers to condense most of the water. It is dried in direct-contact with sulfuric acid drying towers to remove liquid, condensable vapors, and solid impurities.

**Cathodic reaction** – The anolyte passes from the anode section into the cathode section through a porous asbestos diaphragm, which separates the chlorine liberated at the anode from the NaOH and H<sub>2</sub> produced at the cathode. The liquor, leaving the cathode compartment, contains about 11 % caustic (NaOH) and 15 % salt (NaCl). It is sent to evaporators where it is concentrated to 50 % or, up to 73 % caustic. During the evaporation step, excess salt precipitates. The NaOH produced is contaminated with small amounts of NaCl. This salt is filtered, washed, and returned as a slurry to the brine system.



### 1.1.3.3 The Membrane Cell Process

For the membrane cell, a cation-exchange membrane separates the anolyte and catholyte. Brine is fed into the anode compartment and chlorine gas is produced. The sodium ions and associated water of hydration migrate through the membrane into the catholyte. The cation-exchange membrane prevents the migration of chloride ions into the catholyte. Water is electrolyzed at the cathode and strong caustic (32-35 % wt) is produced either by controlling the water addition rate directly to the catholyte or by recirculating caustic to which water has been added. However, there is some back-migration of hydroxyl ions into the anolyte, which causes some loss of current.

Table 1.1 shows the components of Diaphragm, Membrane, and Mercury Cells.



**Table 1.1** Components of diaphragm, membrane, and mercury cells

Component	Mercury Cell	Diaphragm Cell	Membrane Cell
Anode	RuO <sub>2</sub> + TiO <sub>2</sub> coating on Ti substrate	RuO <sub>2</sub> -based coating on Ti substrate	RuO <sub>2</sub> based coating on Ti substrate
Cathode	Mercury on steel	Steel or steel coated with activated nickel	Steel or Ni based catalytic coating on nickel
Diaphragm	None	Asbestos, polymer-modified asbestos , or Polyramix	Ion-exchange membrane
Cathode product	Sodium amalgam	10-12 % NaOH + 15-17 % NaCl and H <sub>2</sub>	30-33 % NaOH + < 0.01 % NaOH and H <sub>2</sub>
Decomposer product	50 % NaOH and H <sub>2</sub>	None	None
Evaporator product	None	50 % NaOH with ~ 1.1 % salt and solid salt	50 % NaOH with ~0.01 % salt
Steam consumption	None	1500-2300 kg/t NaOH	450-550 kg/t NaOH
Cell voltage , V	4-5	3-4	2.8-3.3
Current density , kA/m <sup>2</sup>	7-10	0.5-3	2-5

#### 1.1.4 Electrolytic Cell Operating Characteristics

The greatest volume of chlorine production is currently by the diaphragm cell, followed by that of the mercury cell and lastly the membrane cell.

### 1.2 Concentration of Gas above Electric Cells

According to the design and operation of chlorine liquefaction plants, the hazards of excessive temperature as well as excessive pressure must be avoided (The Chlorine Institute, 1992). The common practice for preventing excessive pressure from a hydrogen explosion is to dilute with injected air to keep the hydrogen content below 4 % v/v in the gas leaving any stage of liquefaction. The costs of supplying the carefully dried dilution air and in reduced yield of liquid chlorine are significant. Liquefied and compressed chlorine gas in two stages with no air dilution gives a vent gas containing about 16 % hydrogen. With dry chlorine, there was no visible flame at the lower explosive limit of 3.5 % H<sub>2</sub>. A flame was observed at 7 % H<sub>2</sub> and an audible detonation at 17.5 % H<sub>2</sub>. On the other hand, the lower explosive limit was observed at 4 % H<sub>2</sub>, a flame at 7 % H<sub>2</sub>, and a detonation at 24 % H<sub>2</sub> with moist chlorine (87 % relative humidity). However, the explosive limits were not dependent on initial pressure and for H<sub>2</sub>-O<sub>2</sub> as well as H<sub>2</sub>-air mixtures. Addition of up to 80 % oxygen had no significant effect on the lower explosive limit. With regard to chlorine from electrolysis cell, chlorine gas is compressed to 1.5-2 atm gauge and liquefied in a multi-stage refrigerated cooling system with a final coolant temperature of about -60 °C. In the first stage (15 to -20 °C) 90 % of the chlorine is liquefied, giving an exhaust gas of 4 % hydrogen which is not explosive. In the second stage, virtually all chlorine is liquefied, giving a gas phase containing about 16 % hydrogen, which is in the explosive region.

### 1.3 Use of Hydrogen Concentration as an Indication of Cell Efficiency

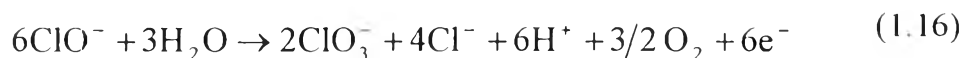
The current efficiency of an electrolytic process producing caustic soda and chlorine is the ratio of the amount of material produced to the theoretically expected quantities. Inefficiencies arise from secondary reactions occurring at the anode and cathode and in the bulk solution.

There are 2 parasitic reactions affecting anode efficiency;

- 1) Co-generation of oxygen,  $O_2$ , from the anodic discharge of water



- 2) Hypochlorite ion,  $OCl^-$ , electrochemical oxidation to chlorate,  $ClO_3^-$



Both of the oxygen oxidations are dependent on the anode material and the pH of the medium. In addition, if a graphite anode is used, another overall reaction leading to inefficiency, the oxidation of carbon to  $CO_2$  takes place.

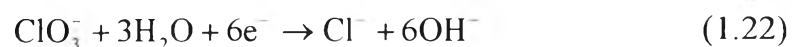
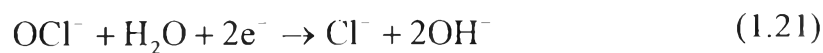


At the cathode, water molecules are discharged to yield  $H_2$  gas and hydroxide ion,  $OH^-$ . Caustic formed in the cathode compartment may back

migrate to the anodic compartment and react with the dissolved chlorine ( $\text{Cl}_{2(aq)}$ ) to form chlorate ion;



There are two reductions of  $\text{OCl}^-$  and of  $\text{ClO}_3^-$  that influence the cathodic efficiency;



These reactions are thermodynamically favorable, but are not kinetically significant under normal operating conditions. Hence the anodic efficiency is usually high (>95 %) in diaphragm and membrane cells. The cathodic efficiency is dependent upon the discharge of  $\text{H}_2$  at the cathode resulting from impurities in the brine ( $\text{NaCl}$ ) whereas the anodic inefficiency is the same as those of diaphragm and membrane cells.

*Current Efficiency* – For caustic soda, the current efficiency can be estimated from the production of caustic over a period of time and from knowledge of the number of coulombs of electricity passed during that time period. An alternative method involves gas analysis generated by the electrolytic cell which determines the anolyte composition. Material balance consideration indicates the caustic efficiency for membrane cells as following (Kirk, 1890-1957);

$$\eta_{\text{NaOH}} = 100 \left\{ \frac{1 - (2F/I)(A - B + Y - D)}{1 + (2\%O_2 / \%Cl_2)} \right\} \quad (1.16)$$

in which

$$A = \frac{3qC_{\text{NaClO}_3}(d)}{106.45} \quad B = \frac{3pC_{\text{NaClO}_3}(f)}{106.45}$$

$$Y = \frac{qCl_2(a)}{70.91} \quad D = \frac{pX}{70.91}$$

$C_z(y)$  is the concentration in grams per liter of  $z$  in medium  $y$ ;  $a$  is anolyte,  $c$  is catholyte;  $f$  is feed brine,  $d$  is depleted brine;  $Cl_2(a)$  is  $Cl_2$  (soluble) +  $HOCl$  +  $OCl^-$ ;  $F$  is the Faraday constant (= 96,487 C/mol);  $I$  is the load in A;  $p$  is the feed brine flow rate in L/s;  $q$  is the depleted brine flow rate in L/s; and

$$X = 1.338C_{\text{Na}_2\text{CO}_3}(f) + 0.844C_{\text{NaHCO}_3}(f) + 1.773C_{\text{NaOH}}(f) \quad (1.17)$$

For determining  $Cl_2$  efficiency ( $\eta_{Cl_2}$ ), the term  $Cl_2(a)$  in equation (1.16) should be dropped. Therefore, the corresponding expression for caustic efficiency for diaphragm cells is

$$\eta_{\text{NaOH}} = \left[ \frac{100}{1 + (2\%O_2 / \%Cl_2) + (80/C_{\text{OH}})(E - F)} \right] \quad (1.18)$$

where  $C_{\text{OH}}$  is the catholyte caustic concentration in g/L,

$$E = \frac{3C_{\text{NaClO}_3}(a)}{106.45} \quad F = [Cl_2(a) - X] / 70.91$$

Therefore, the chlorine efficiency in diaphragm cells is given by

$$\eta_{\text{Cl}_2} = \frac{100}{1 + (2\% \text{O}_2 / \% \text{Cl}_2) + (2.2546G) / C_{\text{OH}}} \quad (1.19)$$

where  $G = C_{\text{NaClO}_3}(\text{a}) - C_{\text{NaClO}_3}(\text{f})$

There are many approximate versions used to estimate the efficiency. The one closest to equation (1.19) is the “six equation” i.e. equation (1.20);

$$\eta_{\text{Cl}_2} = \left[ \frac{100}{1 + (2\% \text{O}_2 / \% \text{Cl}_2) + 6C_{\text{NaClO}_3}(\text{c}) / C_{\text{OH}}} \right] \quad (1.20)$$