

# CHLOR-ALKALI INDUSTRY

Soda ash

Chlorine and Caustic Soda

Chemical process Technology

CHE F419





Aiguille verte

Aiguille du Dru

Aiguille de Talèfre

Aiguille de Leschaux

Col des Hirondelles  
Grandes Jorasses

Dent du Géant

Aiguille du Plan

Col du Plan

Aiguille du Midi

Mont Blanc du Tacul

Mont Maudit

Mont-Blanc

Dôme du Goûter

# Soda Ash (Sodium carbonate)

## ▶ Properties

- Mol wt: 106
- Appearance: White solid, hygroscopic
- M.P. : 106.0 C

## ▶ Grades

- 99% Sodium carbonate as light (0.5 g/cc) and dense (1 g/cc) grades of granular product
- Washing Soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ )

## ▶ Uses

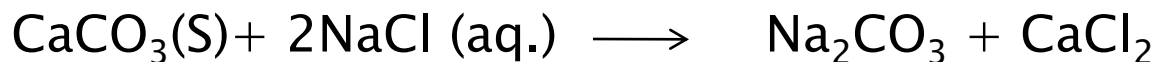
- Soap detergents; Glass; Sodium silicate, water softening, reagent, paper-paint-textile industry.

# Classification of processes

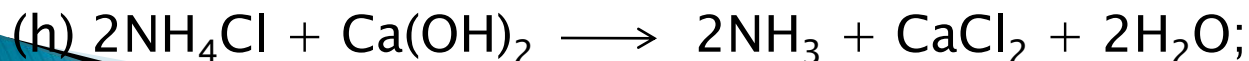
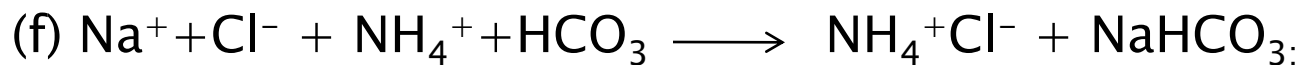
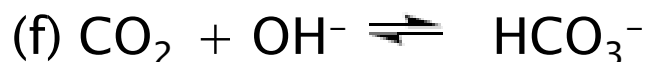
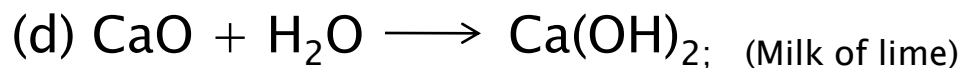
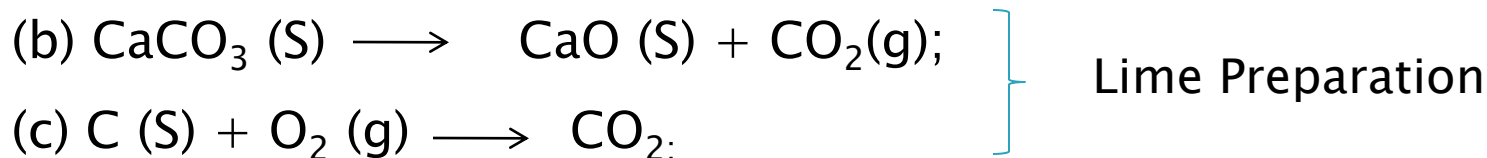
- It can be extracted from some plants, or produced from naturally occurring trona or produced synthetically by chemical process like Leblanc process and Solvay process.
- **Le-blanc Process**
  - Used sulfuric acid, inefficient, large waste, Obsolete
- **Natural soda-ash from deposits (Trona)**
  - Trona ore is calcined. Simple process but depend on natural ore resource.
- **Solvay or ammonia-soda**
  - Uses ammonia, dominant technology, used through out world
- **Dual Process ( $\text{Na}_2\text{CO}_3 + \text{NH}_4\text{Cl}$ )**
  - ammonium chloride is produced as a co-product in equivalent quantities and differs from conventional solvay process

# Solvay Process

## (a) Overall reaction



**This reaction takes place in a number of steps**



Ammonia absorption  
&  
Carbonation

# Process description

## (1) Brine preparation

- Prior purification is required to remove impurities as Mg and Ca salts

## (2) Lime preparation

- limestone is usually mixed with about 7% metallurgical – grade coke or anthracite and then burned in vertical shaft kilns. Air is admitted continuously into the bottom of the kiln.

## (3) Ammonia absorption

- The strong brine is saturated with ammonia gas in the ammonia absorption tower. Small amounts of ammonia are added to make up for losses. The brine descends through the main part of the absorber countercurrent to the rising ammoniacal gases.

## (4) Precipitation of bicarbonate

- The ammoniated brine from the absorber coolers is pumped to the top of one column in a block of columns used to precipitate bicarbonate.
  - Cleaning Tower
  - Making Tower



- ▶ Crystals formed during the carbonation step gradually foul the heat – exchange surfaces and thus a crystallizing column must alternately be the “cleaning” column.

## **(5) Filtration of bicarbonate**

- The slurry, collected from the crystallizing towers, is fed to continuous vacuum filters or centrifuges which separate the crystals from the “filter liquor.” The filter cake, often called “crude bicarbonate” or “ammonia soda”, liquor and is made up of sodium bicarbonate.

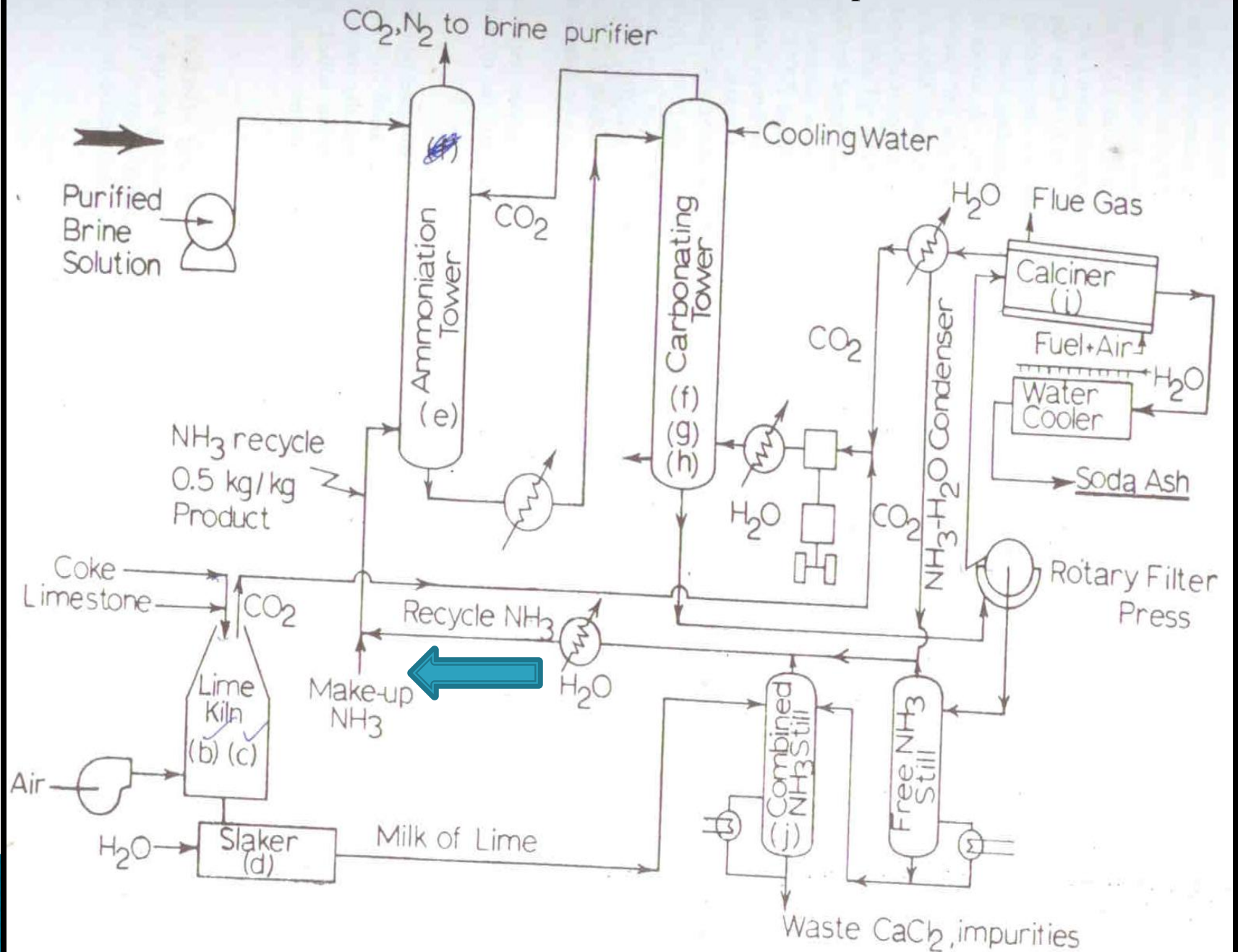
## **(6) Calcining the bicarbonate to soda-ash**

- The crude filtered bicarbonate is continuously calcined by indirect heating. The hot soda ash discharged from the calciner is cooled, screened, and packaged or shipped in bulk. This product, called “light ash” because of its low bulk density. It can be converted to dense ash.

## **(7) Recovery of $\text{NH}_3$**

- The “filter liquor” contains unreacted sodium chloride and substantially all the ammonia with which the brine was originally saturated, present as “fixed” (as ammonium chloride) and “free” ammonia (as ammonium hydroxide, decompose at moderate temperature).

Can we replace this with a 3D flow sheet?



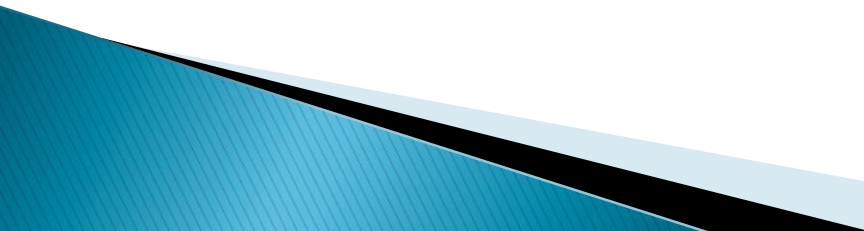


# Advantages and disadvantages with Solvay Process

## Advantages

- Can use low-grade brine
- Less electric power
- Less corrosion problems
- No co product dispose
- Does not require ammonia plant investment

## Disadvantages

- Higher salt consumption
  - Higher investment in ammonia recovery unit verses crystallization units for ammonium chloride
  - Waste disposal of calcium chloride, brine stream
  - More steam consumption
- 

# Major engineering problems

## ▶ Development of suitable calcining equipment

- Heavy scraper chain to avoid caking
- Wet filter cake mixing with dry product
- Fluidized bed calciner

## ▶ Economic balance on tower design

## ▶ Ammonia recovery

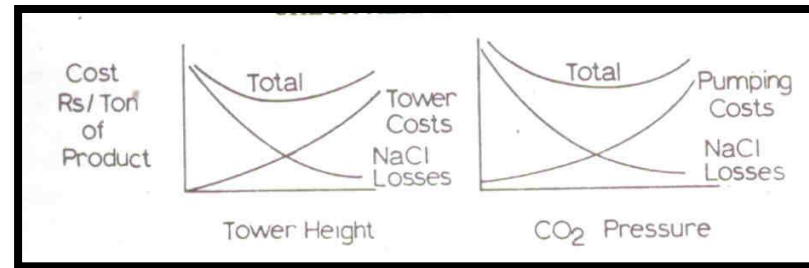
- By choice of equipment design
- Maintenance

## ▶ Plant modernization

- Better material of construction

## ▶ Waste disposal

- Use of  $\text{CaCl}_2$  -NaCl liquor



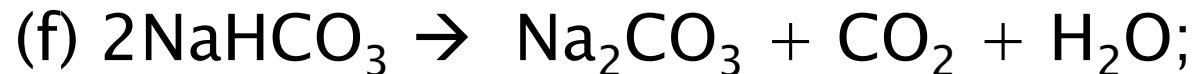
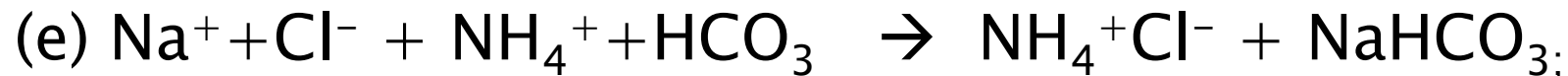
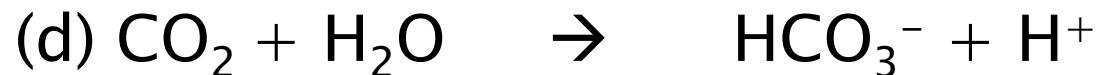
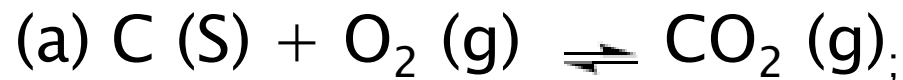
•Automatic control

•CO<sub>2</sub> and calcining exhaust

# Dual Process (Modified Solvay)

- ▶ In this process ammonium chloride is produced as a co-product in equivalent quantities.

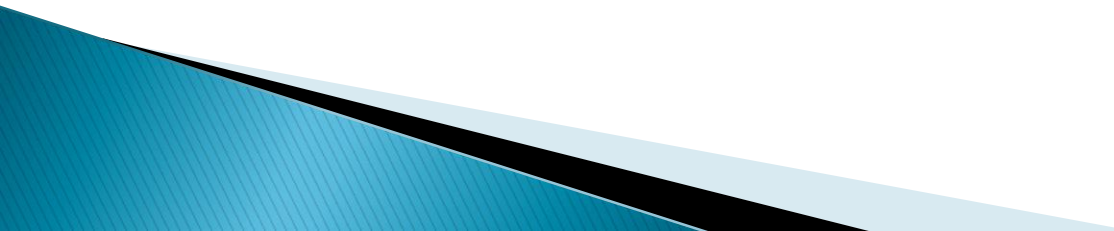
## Chemical Reactions



# Process Steps

- ▶ The principal modification is in the recovery of  $\text{NH}_4\text{Cl}$  as co-product.
- ▶ The liquor from the bicarbonate filters is mixed with washed salt feed to aid in precipitation of ammonium chloride.
- ▶ The  $\text{NH}_4\text{Cl}$  is crystallized in a refrigerated tank unit at 0 C.
- ▶ The Slurry is centrifuged and crystals are dried in a rotary drum dryer.

## ▶ Engineering Problems

- Salt purification
  - Corrosion
  - Refrigeration
- 

# Caustic Soda (NaOH)

- ▶ Sodium hydroxide is a highly caustic metallic base.
  - **Mol wt: 40**
  - **B.P. : 1,390 °C**
  - **M.P. : 318 °C**
- ▶ It is a white solid available in pellets, flakes, granules, and as saturated (50 and 73%) solution.
- ▶ Sodium hydroxide is soluble in water, ethanol and methanol.
- ▶ **Uses:**
  - Sodium hydroxide is used in many industries, mostly as a strong chemical base in the manufacture of pulp and paper, textiles, drinking water, soaps and detergents and as a drain cleaner.

# Production Methods

## ▶ Lime Soda Process

- $\text{Na}_2\text{CO}_3 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{NaOH} + \text{CaCl}_2$
- Old process, require soda ash (high cost).

## ▶ Electrolytic Route (using brine)

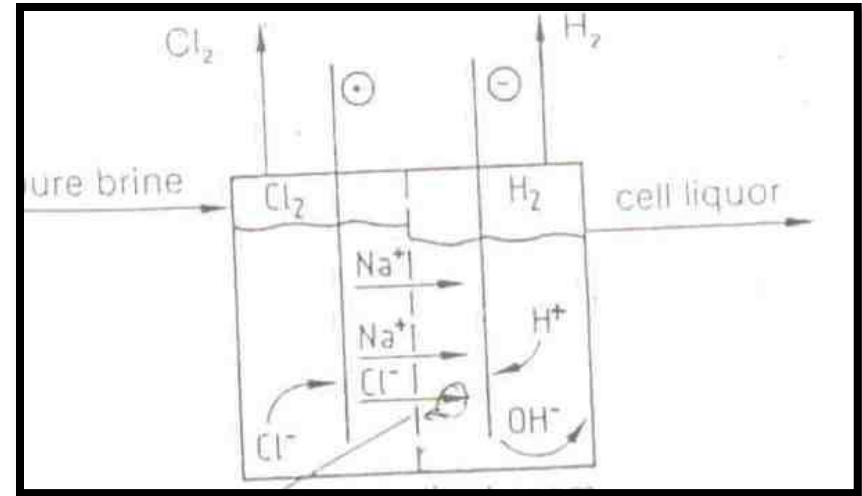
- $\text{Na}^+ + 1\text{e}^- \rightarrow \text{Na}$  (or with water  $\rightarrow \text{NaOH} + 1/2 \text{H}_2$ )
- $\text{Cl}^- - 1\text{e}^- \rightarrow 1/2 \text{Cl}_2$
- Current method of manufacturing
- Additional to NaOH, chlorine and hydrogen co-product
- Products need to be keep apart, otherwise react vigorously to give NaCl and NaClO.
- Three main methods are used
  - Porous vertical Diaphragm
  - Flowing Mercury Cathode
  - Ion selective Membrane (most recent development)



# Diaphragm cell

## ▶ Cell reactions

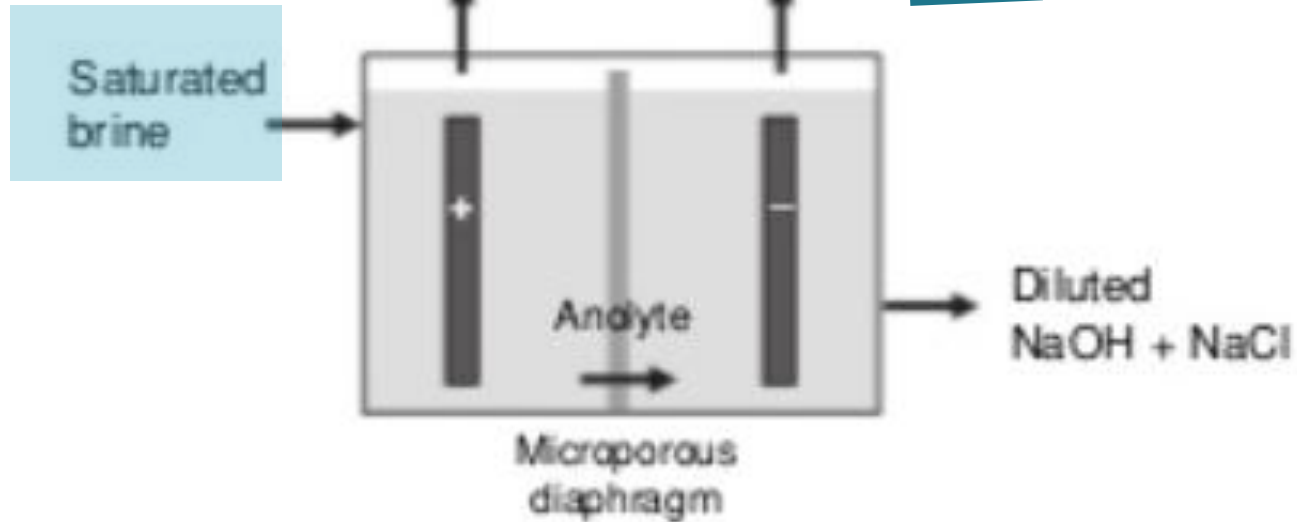
- Anode :
  - $\text{Cl}^- - \text{e}^- \rightarrow \frac{1}{2} \text{Cl}_2$
- Cathode :
  - $\text{Na}^+ + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Na}^+ + \text{OH}^- + \frac{1}{2} \text{H}_2$
- Overall :
  - $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2$



- Percolating diaphragm allows the continuous passage of ions and brine solutions from anode to cathode compartment.
- An outlet is placed at the cathode side ( at level lower than anode side). It allows the continuous removal of nonelectrolyzed brine and the caustic product.
- Diaphragm of most modern cells consists of a thick asbsetos fiber pad/polymer with metal oxide.
  - Anode : Graphite    Cathode : Iron
- Electrolyze 30-40 % of the sodium chloride present in feed.

What are the secondary reactions that are caused due to  $\text{H}_2$  liberation?

Why saturated brine?



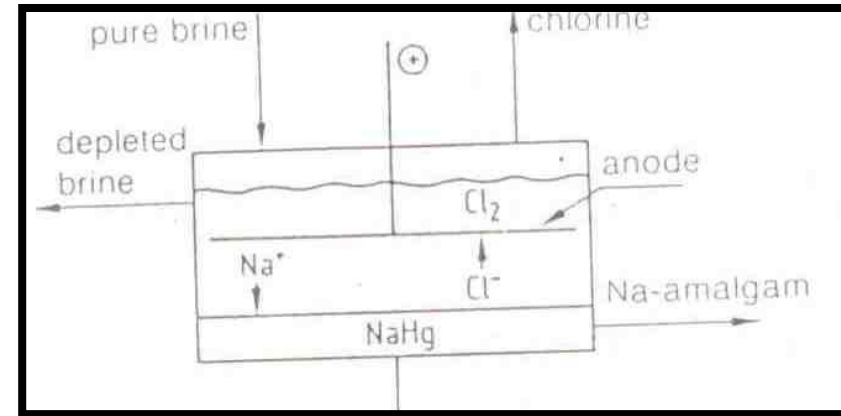
*Figure 8.14 Representation of the diaphragm cell process.*

What happens as chlorine is liberated at anode?

# Mercury Cell

## ▶ Cell reactions

- Anode :  $\text{Cl}^- - \text{e}^- \rightarrow \frac{1}{2} \text{Cl}_2$
- Cathode :  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}^0$   
 $\text{Na}^0 + \text{Hg} \rightarrow \text{NaHg (Amalgam)}$
- Denuding:
  - $\text{NaHg} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 + \text{Hg}$
- Overall :  $\text{NaCl} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{Cl}_2$



- This cell employ mercury as cathode which cause sodium deposition in mercury (to form amalgam).
- No direct contact between the brine and sodium hydroxide streams, so produces a **high purity 50% NaOH** solution directly.
- Modern mercury cells comprise of two key parts
  - Electrolyzer : Produce sodium amalgam product
  - Decomposer/ denuder : Sodium amalgam is feed at the top and deionized water counter-currently from bottom.

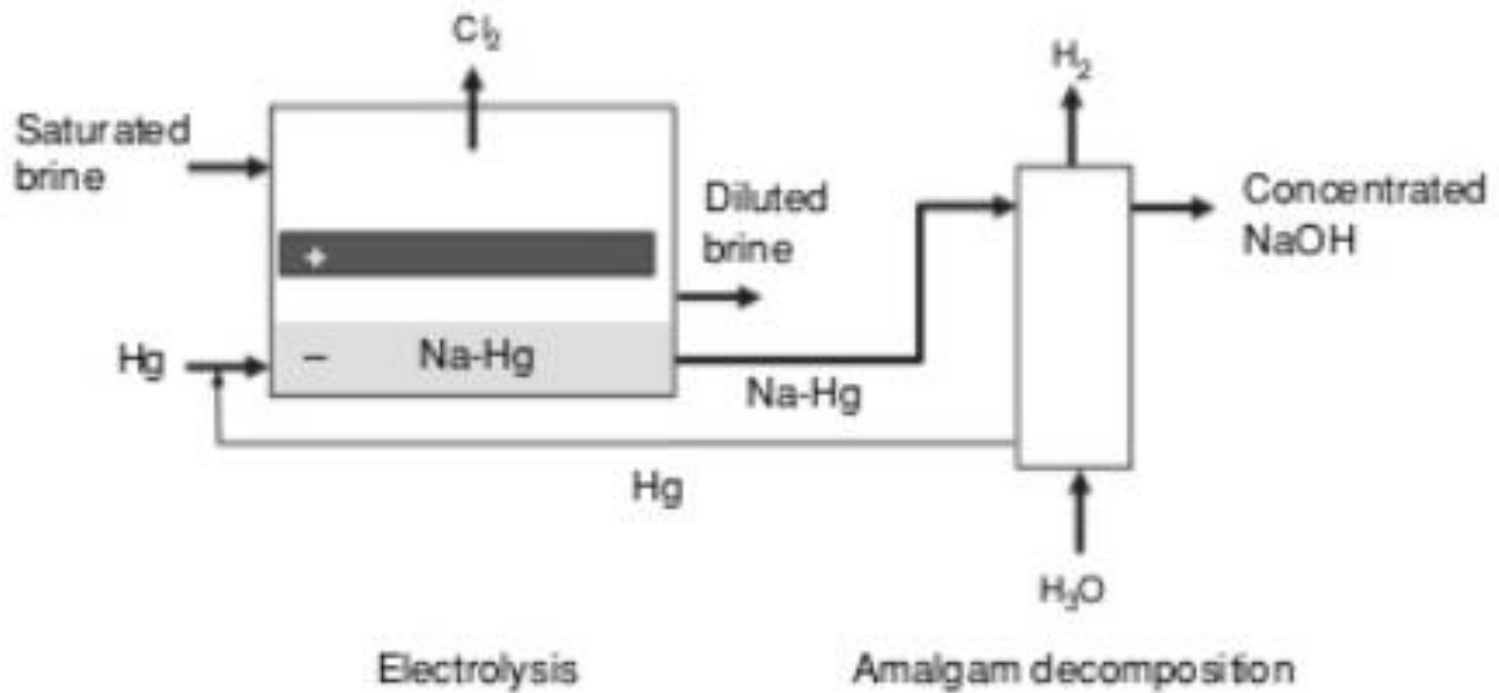
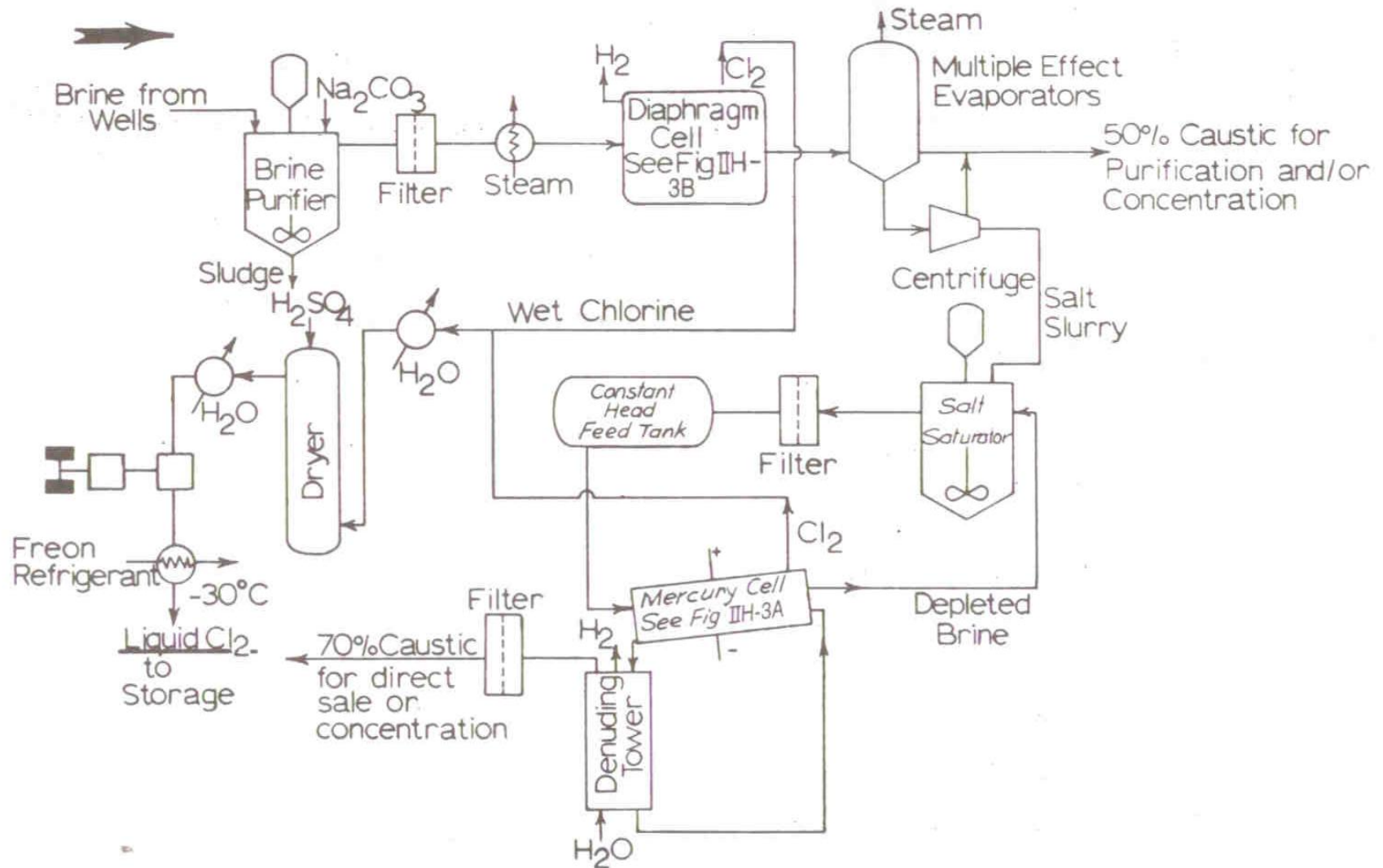


Figure 8.13 Representation of the mercury cell process.



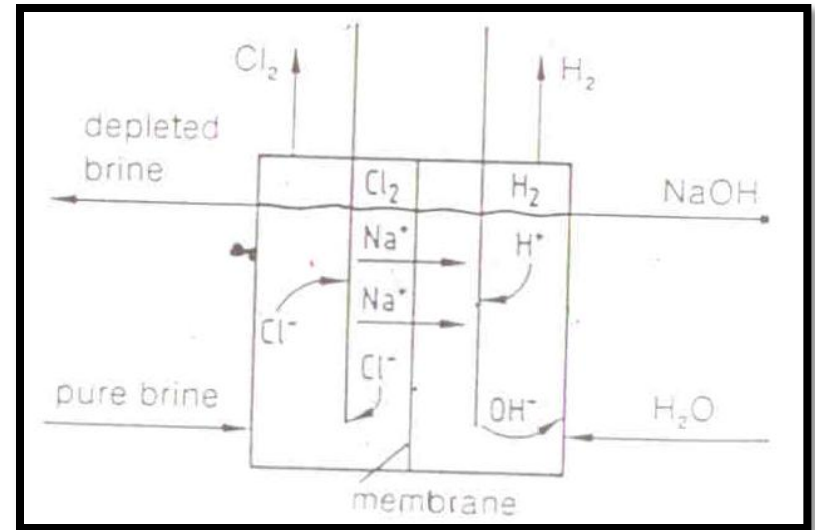
Why more voltage is required for Mercury cell?

# Process flow sheet



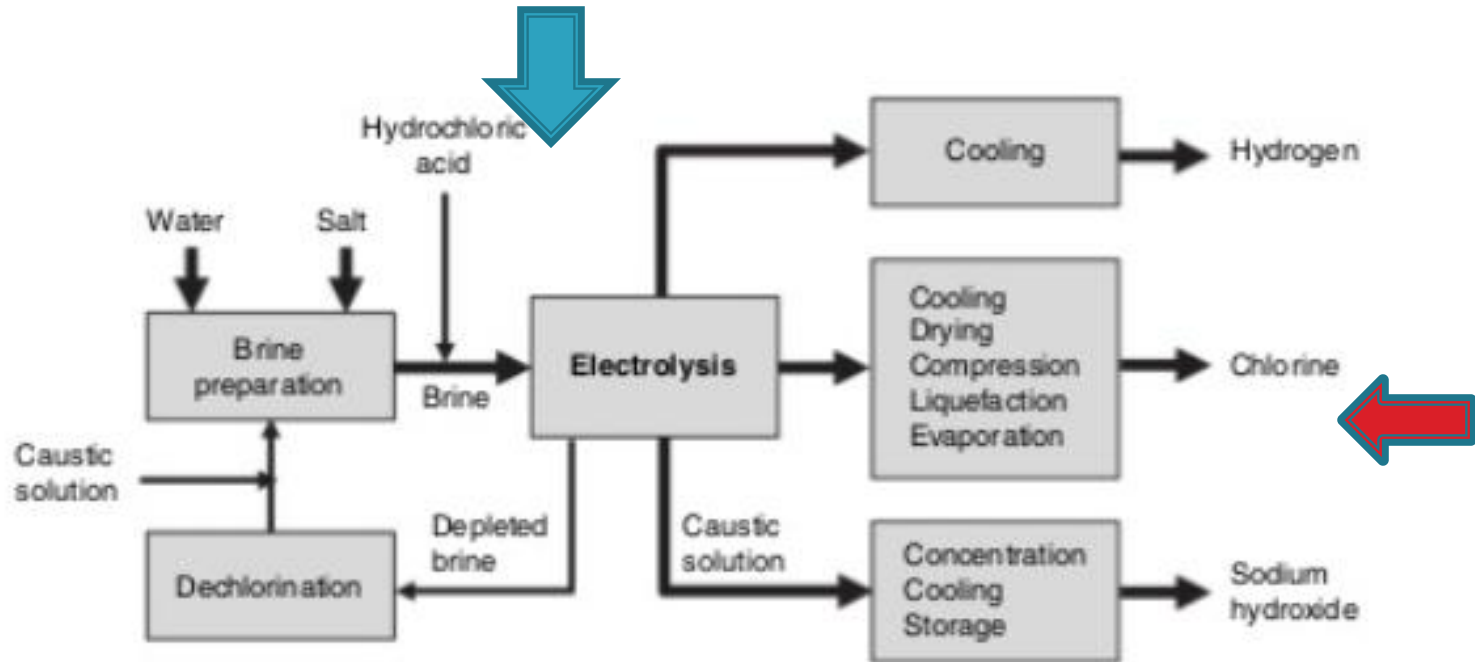
# Membrane Cell

- ▶ Ion-selective membrane separates anode and cathode
  - Use polytetrafluoroethylene, ion permeable membrane (ex: Nafion)
  - **Membrane Properties:** Durability; High selectivity; Negligible transport of chloride, hypochlorite and chlorate ion ; Zero back migration of hydroxide ion; Low electrical resistance.
  - Carboxylate or sulfate group on surface of the membrane makes it selective to pass sodium ions and reject chlorine ions.
- Saturated brine passes through the anode compartment forming chlorine gas and sodium ion.
- Negatively charged groups on membrane surface prevent both the forward diffusion of chlorine ion and backward diffusion of hydroxyl ion.
- Purified water, added to the cathode compartment is partially electrolyzed to hydrogen gas and hydroxide ions.
- Concentration 15-35% obtained.

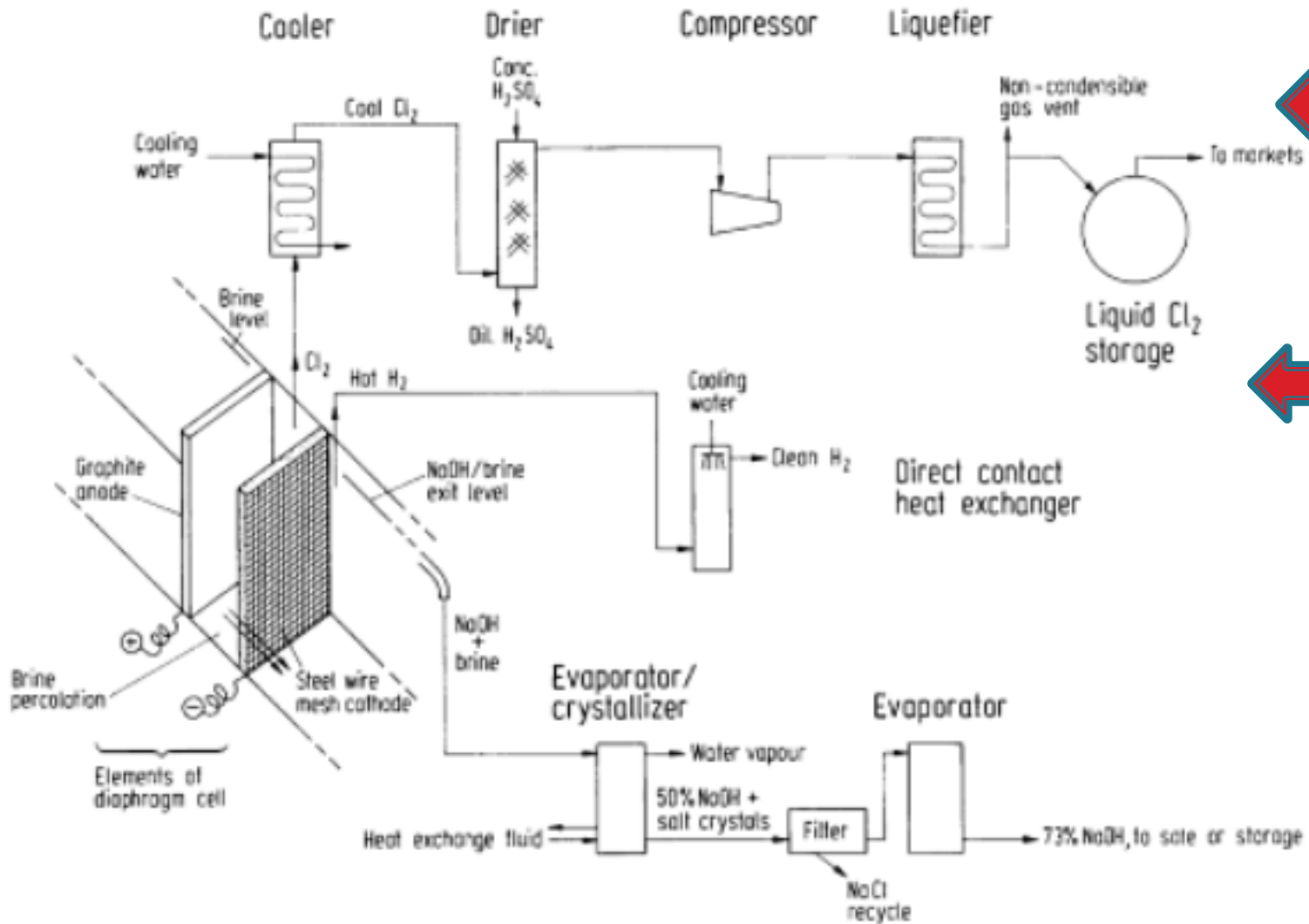




Why hydrochloric acid has to be added before electro dialysis?



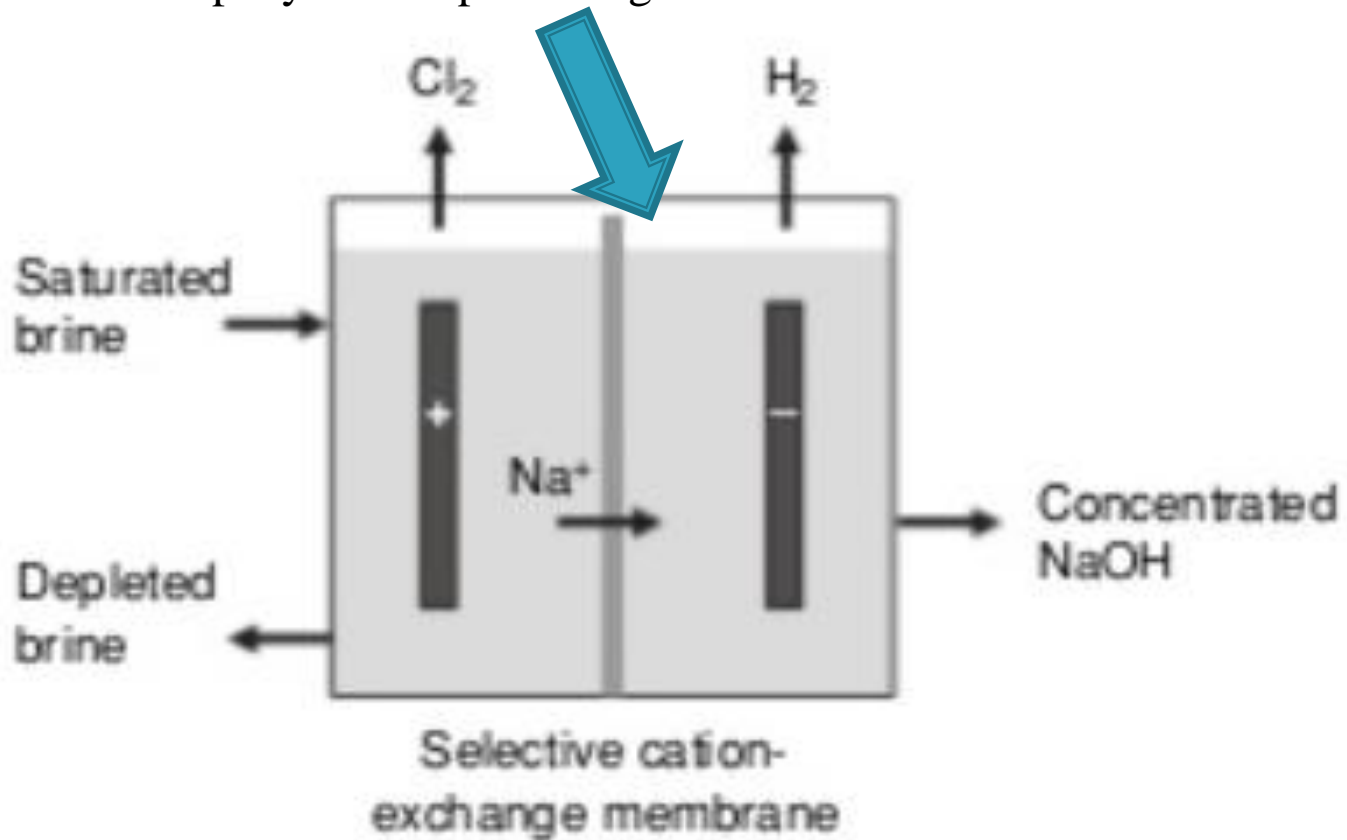
*Figure 8.16* Simplified flow diagram of the membrane cell process.



**FIGURE 8.2** Diagram of the components of a commercial asbestos diaphragm cell, and flowsheet

What was replaced with Asbestos and why?

What is the role of cation exchange membrane here?  
Which company started producing Nafion®?



*Figure 8.15 Representation of the membrane cell process.*

# Characteristic of different cells

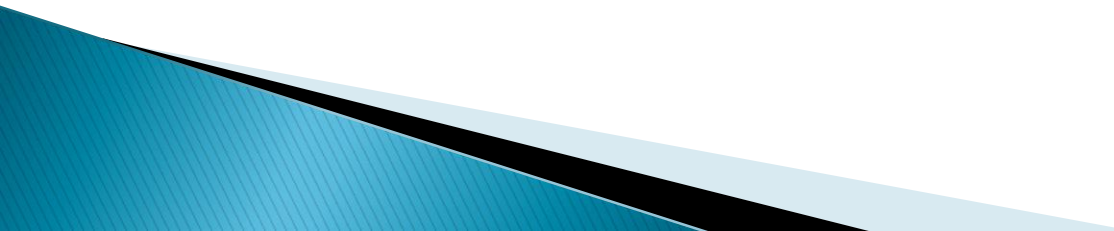
Characteristic	Diaphragm Cell	Mercury Cell	Membrane Cell
Utilization of less pure brine	Yes	No	Very high purity brine
Voltage	Lower than mercury	Higher	Lower
Purity of product	Dilute and chloride contaminated	Pure 50% NaOH	Pure NaOH
Contamination	Asbestos	Mercury	No mercury/ asbestos

# Major engineering problems

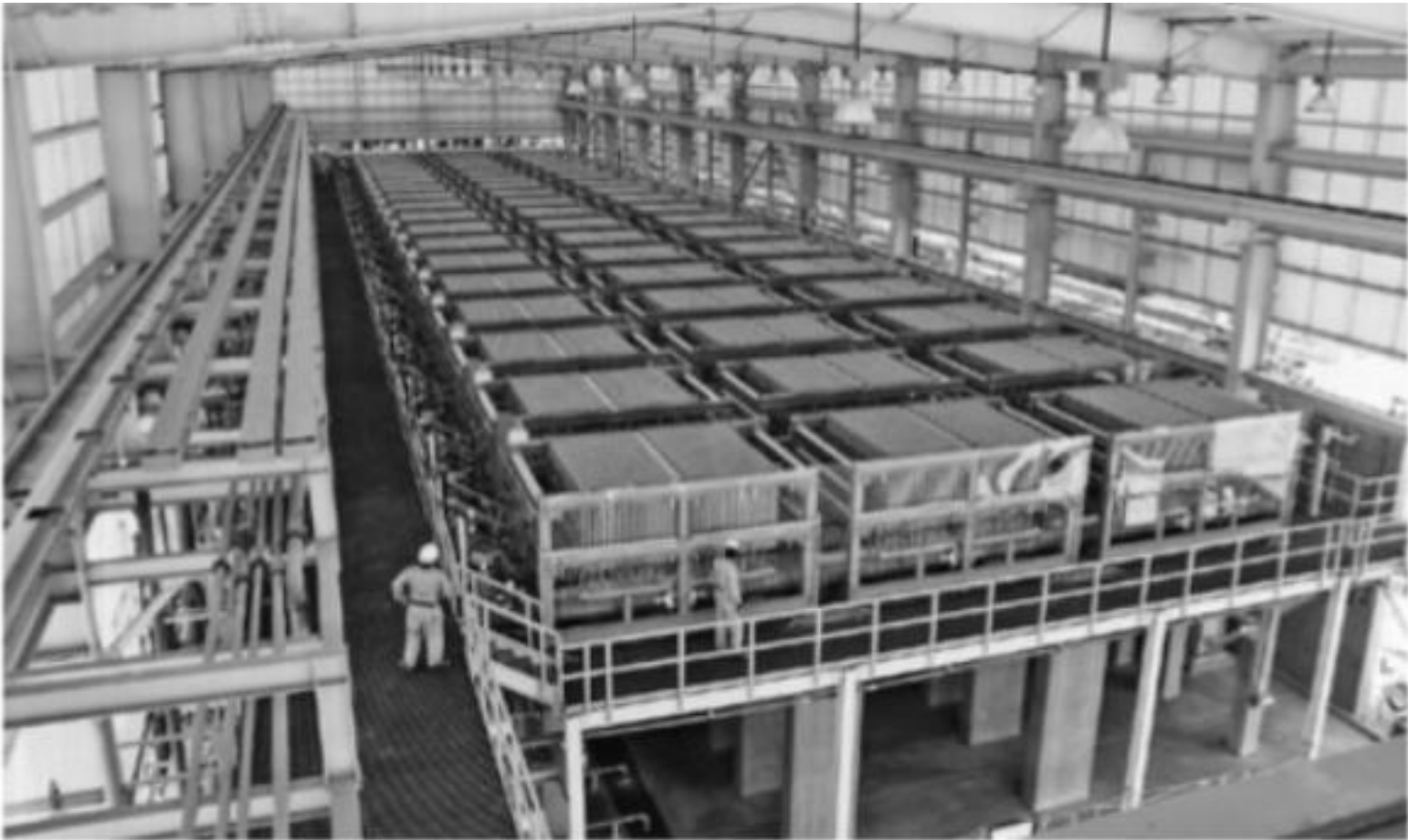
## ▶ Choice of cell design

- Membrane technology : most modern, energy efficient, pollution free
- Conversion cost of existing cells, high capital equipment, high technology transfer fees

## ▶ Corrosion

- Wet chlorine: Require stoneware, plastic, glass or rubber-lined equipment
  - Brine solution: Highly corrosive at higher temp.
  - Ni lined evaporators to avoid iron-contamination
  - Remainder plant equipment: Cast iron, steel, wood
- 

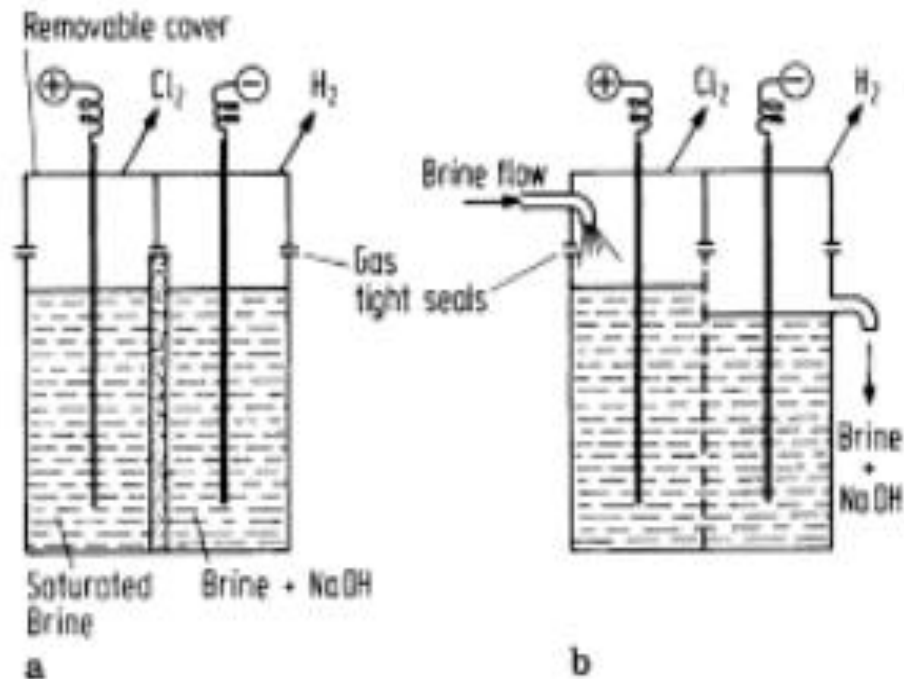
## Bull or Bear?



*Figure 8.17 Bipolar cell room by Krupp Uhde. Reprinted with permission from [13] Copyright (200*



# Griesheim type cell



**FIGURE 8.1** (a) Schematic diagram of a Griesheim-type cell which operated on a batch basis. The product was pumped out after electrolysis for about 3 days. (b) Schematic diagram showing the LeSueur percolating diaphragm which changed the mode of cell operation to a continuous basis and decreased