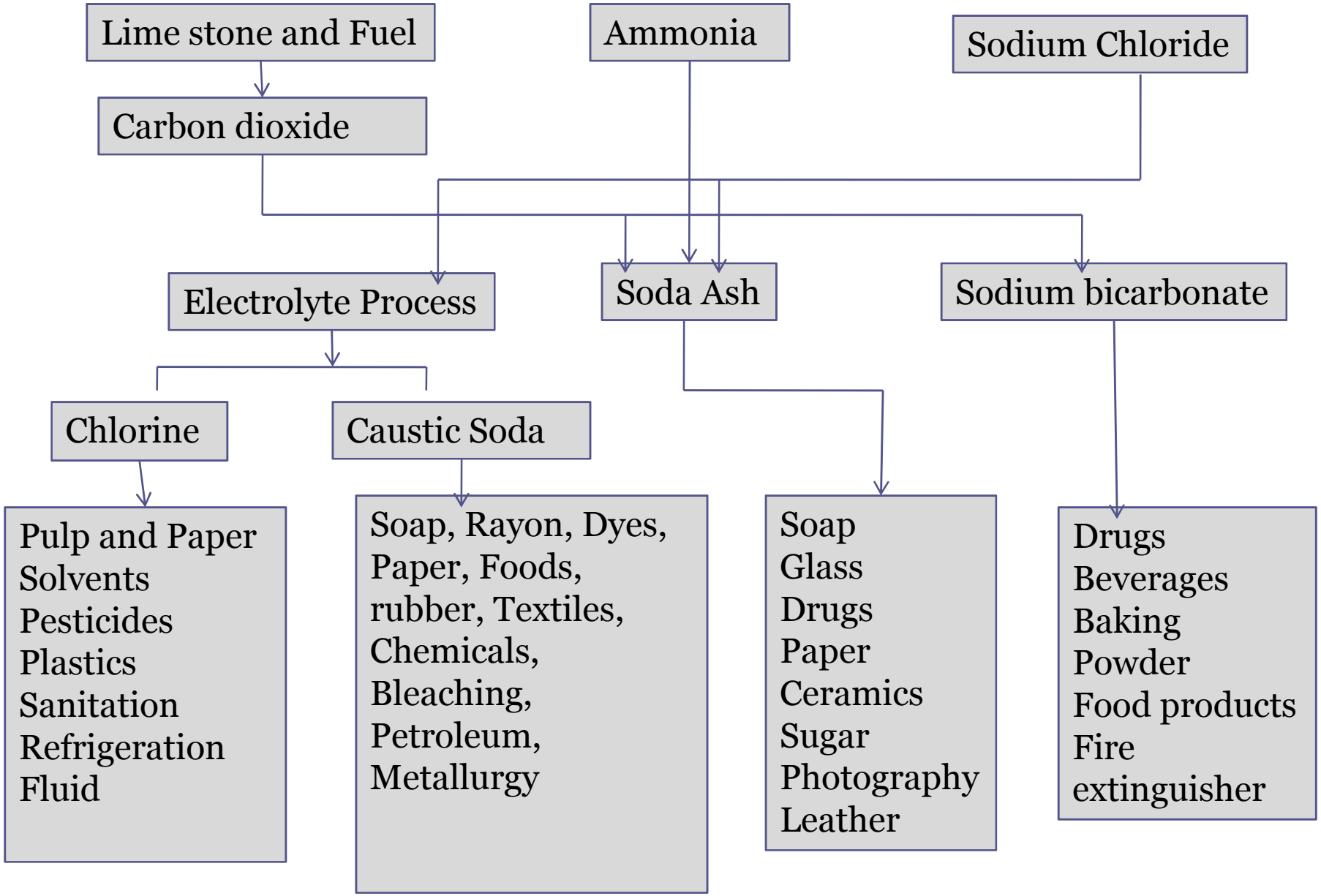
ChE 308
Lecture 3

Chlor-Alkali Industries: Caustic soda, Chlorine, Soda Ash

Chlor-Alkali Industry



Manufacture of Chlorine and Caustic Soda

Sodium Hydroxide:

- White, solid material that picks up moisture from air.
- If put in water, it produces a large amount of heat.
- Very corrosive and can cause severe burns

Caustic Soda and Chlorine Processes

- Sodium Chloride solution (brine)is electrolytically decomposed to **elemental chlorine** (in the anode compartment), and **sodium hydroxide solution and elemental hydrogen** (in the cathode compartment) in all the processes
- The overall reaction for the electrolytic production of caustic soda and chlorine is:

$$\mathbf{2\ NaCl\ (aq) + 2\ H_2O = Cl_2\ (gas) + H_2\ (gas) + 2\ NaOH\ (aq)}$$

Anode

Cathode

Manufacture of Chlorine and Caustic Soda cont'd

Reactions:

$$NaCl + H_2O = NaOH + ½\ H_2 + ½\ Cl_2$$

Decomposition Voltage and voltage efficiency:

$$E = \frac{-J\Delta H}{nF} + \frac{T\,dE}{dT}$$

Where, E= Theoretical decomposition voltage
ΔH= enthalpy change of reaction
J= electrical equivalent of heat
T= absolute temperature
F= Faraday constant
n= number of equivalents involved

Manufacture of Chlorine and Caustic Soda cont'd

Decomposition Voltage and voltage efficiency (cont'd):

- The ratio of theoretical voltage to that actually used is the **Voltage efficiency** of the cell(ranges from 60-75%).
- The ratio of the theoretical to the actual current consumed is defined as the **Current efficiency**(ranges from 95-97%).
- The product of voltage efficiency and current efficiency is the **energy efficiency** of the cell.

Manufacture of Chlorine and Caustic Soda cont'd

Methods of manufacture

1. Chemical: Lime soda Process
2. Electrochemical: Chloro Alkali Process

- **Diaphragm Cell**
- **Mercury Cell process**
- **Membrane cell process**

Electrochemical methods of manufacture

Diaphragm cell process:

- This process uses a steel cathode, and the anode area is separated from the anode area by a permeable diaphragm.
- A diluted caustic brine leaves the cell.
- The caustic soda must usually be concentrated to 50% and the salt removed.

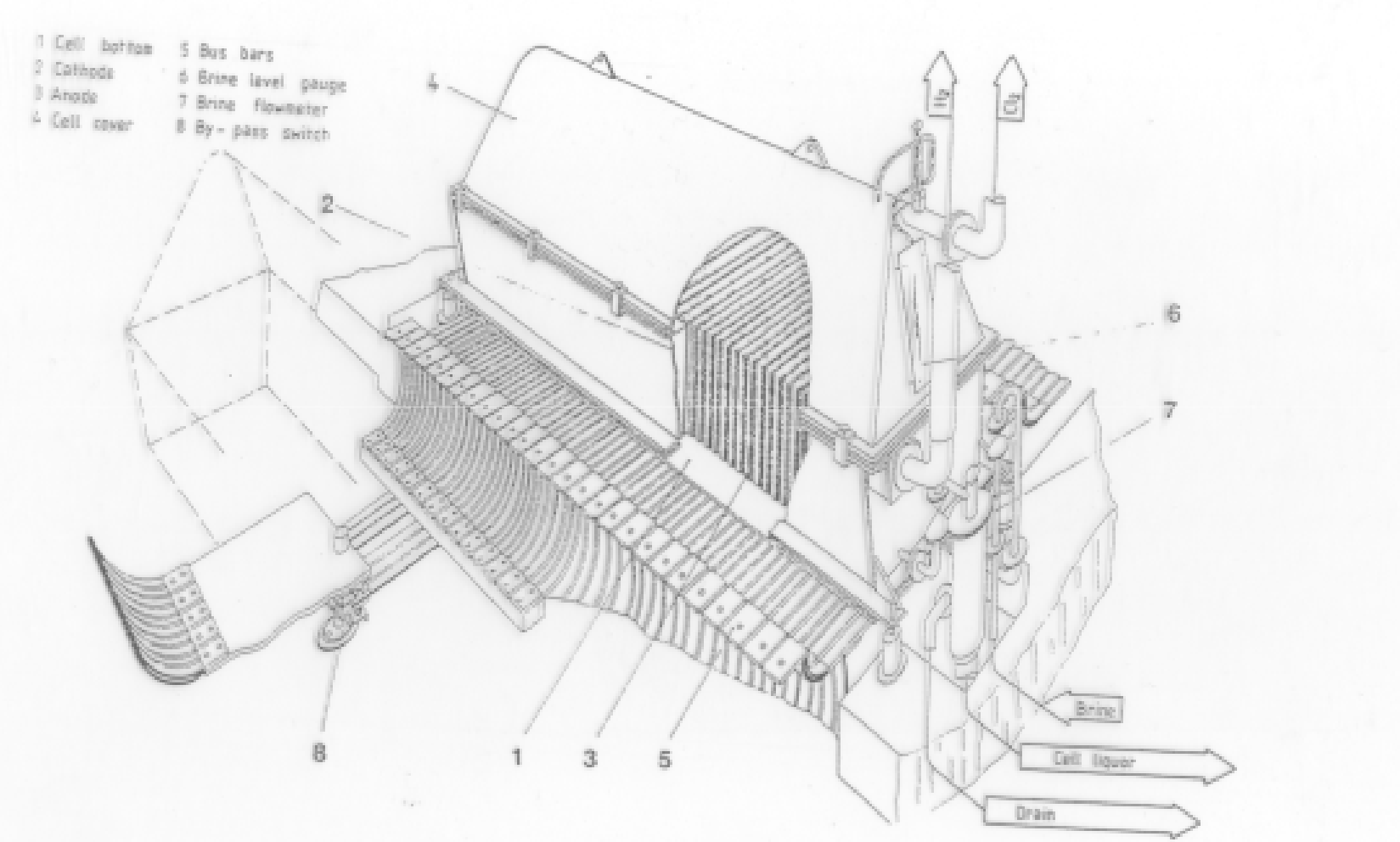
Mercury cell process:

- Sodium metal forms an amalgam at a mercury cathode.
- This sodium is then reacted with water to produce NaOH.

Membrane cell process:

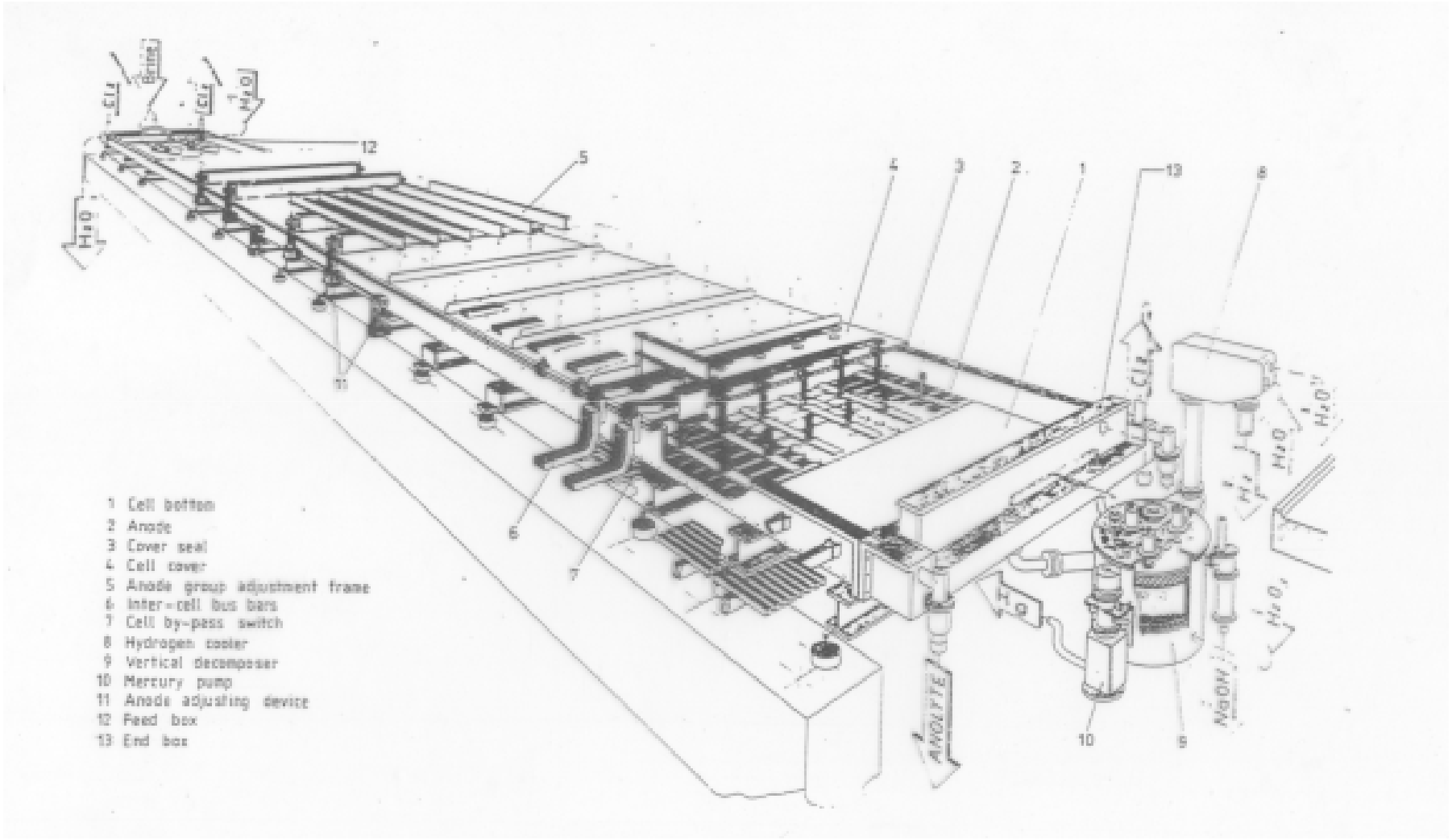
- This process is similar to the diaphragm cell process.
- Here a Naflon membrane is used to separate the cathode and the anode reactions. Only sodium ions and a little water pass through the membrane.
- It produces a high quality of NaOH.
- Of the three processes , it requires the lowest consumption of electric energy and the amount of steam needed for the concentration of the caustic soda is relatively small.

Electrochemical methods of manufacture cont'd



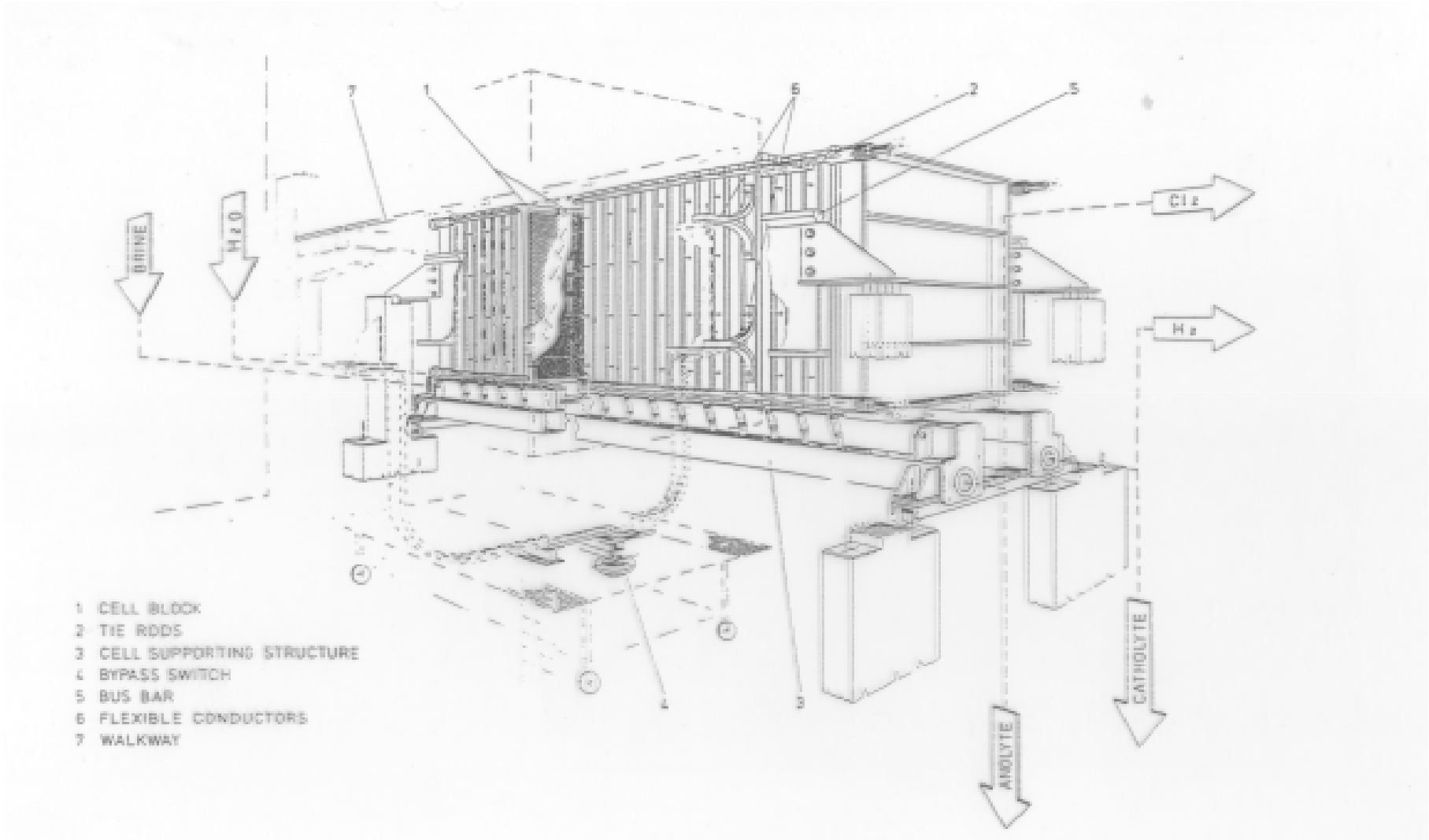
Diaphragm Cell type Process

Electrochemical methods of manufacture cont'd



Mercury Cell type Process

Electrochemical methods of manufacture cont'd



Membrane Cell type Process

Electrochemical methods of manufacture cont'd

Chlor/alkali manufacturing process

Electrochemical and chemical reactions occurring in mercury cells

[1] $2Cl^- \Longrightarrow Cl_2 + 2e^-$ (anodic reaction)

[2] $2Na^+ + 2Hg + 2e^- \Longrightarrow 2Na\ (in\ Hg)$ (cathodic reaction)

[3] $2Cl^- + 2Na^+ + 2Hg \Longrightarrow Cl_2 + 2Na\ (in\ Hg)$ (overall cell reaction)

[4] $2Na\ (in\ Hg) + 2H_2O \Longrightarrow H_2 + 2NaOH + Hg$ (decomposer reaction)

[5] $2NaCl + 2H_2O \Longrightarrow Cl_2 + 2NaOH + H_2$ (overall process reaction)

Electrochemical methods of manufacture cont'd

Electrochemical and chemical reactions occurring in diaphragm and membrane cells

[1] $2Cl^- \Longrightarrow Cl_2 + 2e^-$ (anodic reaction)

[6] $2H_2O + 2e^- \Longrightarrow 2OH^- + H_2$ (cathodic reaction)

[7] $2Cl^- + 2H_2O \Longrightarrow Cl_2 + H_2 + 2OH^-$ (overall ionic reaction)

[5] $2NaCl + 2H_2O \Longrightarrow Cl_2 + 2NaOH + H_2$ (overall reaction)

[8] $Cl_2 + 2NaOH \Longrightarrow NaOCl + NaCl + H_2O$ (side reaction)

[9] $3NaOCl \Longrightarrow NaClO_3 + 2NaCl$ (side reaction)

Reaction [9] will contaminate the caustic product with chlorate.

Chemical reactions occurring in brine processing

[10] $Na_2SO_4 + BaCl_2 \Longrightarrow 2NaCl + BaSO_4$ ($BaSO_4$ precipitates)

[11 $CaCl_2 + Na_2CO_3 \Longrightarrow CaCO_3 + 2NaCl$ ($CaCO_3$ precipitates)

[12] $MgCl_2 + 2NaOH \Longrightarrow Mg(OH)_2 + 2NaCl$ ($Mg(OH)_2$ precipitates)

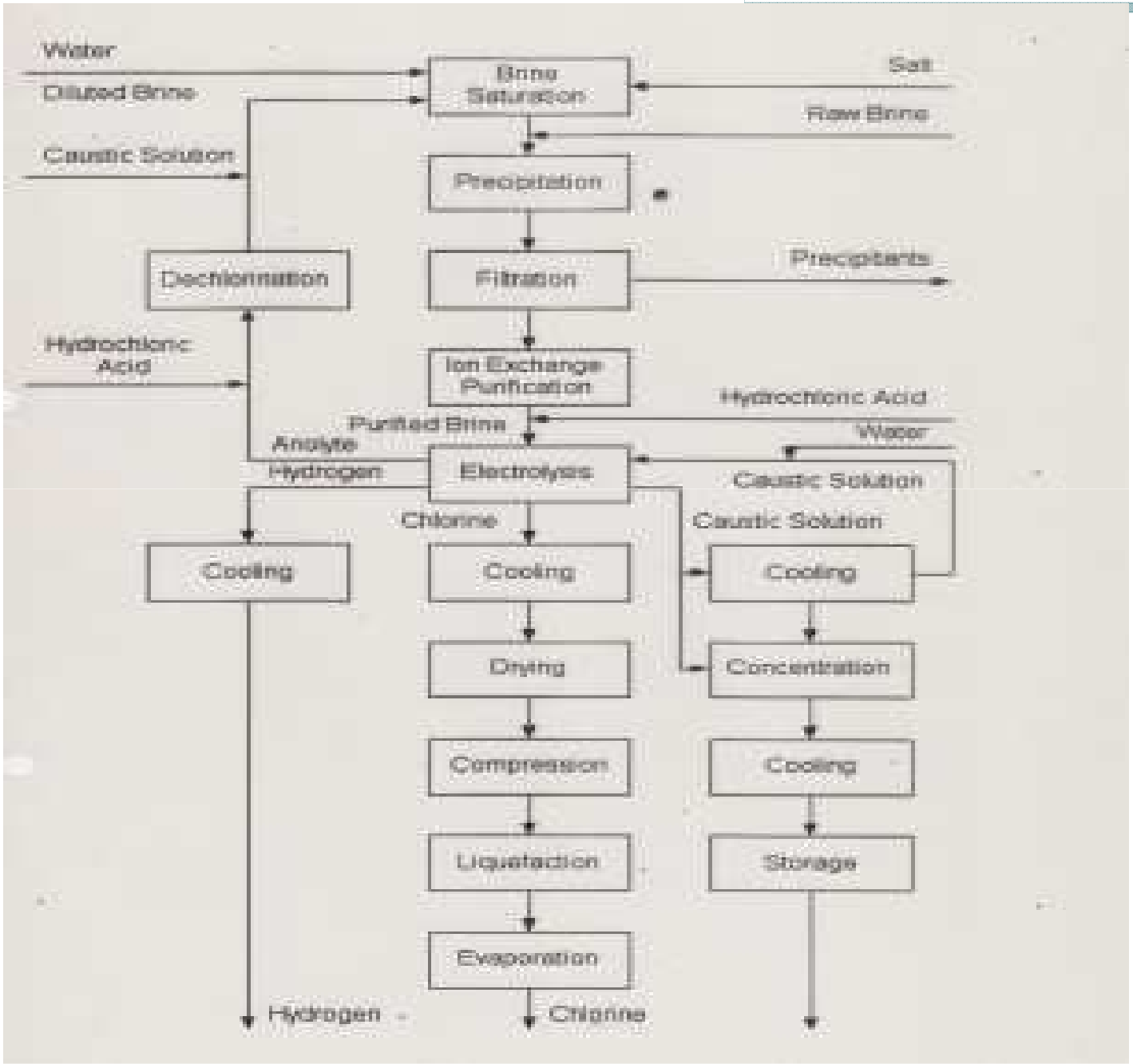
Advantages and Disadvantages of Electrochemical methods of manufacture

Process	Advantages	Disadvantages
Diaphragm Process	•Use of well brine • Low electricity consumption	•Use of asbestos •High steam consumption •Low purity caustic •Low chlorine quality
Mercury Process	•50% caustic direct from cell •High purity chlorine and hydrogen •Simple brine purification	•Use of mercury •Expensive cell operation •Large floor space •Costly environment protection
Membrane Process	•Low energy consumption •Low capital investment •High purity caustic •Insensitivity to cell load variations and shutdowns	•Cost of membrane •Use of solid salt, high purity brine •High oxygen content in chlorine

Comparison of cell technologies

	Mercury	Diaphragm	Membrane
Operating current density(KA/m^2)	8-13	0.9-2.6	3-5
Cell voltage (V)	3.9- 4.2	2.9- 3.5	3.0-6.0
NaOH strength(wt%)	50	12	33-35
Energy Consumption(KWh/MT Cl_2)	3360	2720	2650
Steam Consumption (KWh/MT Cl_2) for concentration to 50% NaOH	0	610	180

Membrane cell process Flow sheet


Water
Diluted Brine
Caustic Solution
Brine Saturation
Salt
Raw Brine
Precipitation
Dechlorination
Filtration
Precipitants
Hydrochloric Acid
Ion Exchange Purification
Hydrochloric Acid
Purified Brine
Water
Anolyte
Hydrogen
Electrolysis
Caustic Solution
Chlorine
Caustic Solution
Cooling
Cooling
Cooling
Drying
Concentration
Compression
Cooling
Liquefaction
Storage
Evaporation
Hydrogen
Chlorine

Dorr Continuous Causticization Process

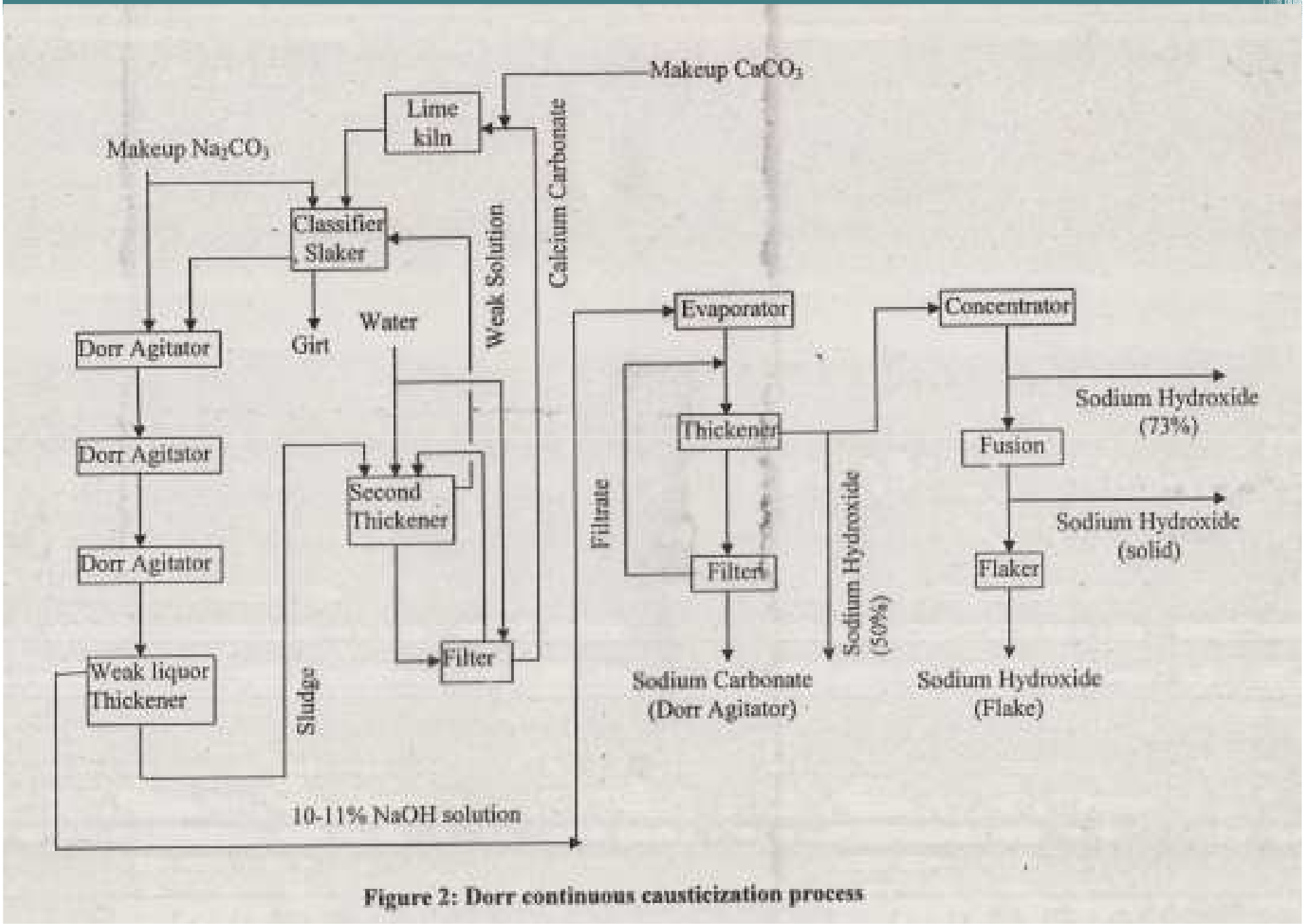


Figure 2: Dorr continuous causticization process

Other Chlor-Alkali Products

Liquid Chlorine

Chemical Formula: Cl_2

Appearance: Clear amber color

Product Quality: Cl_2 purity 99.5%

Uses:

- Manufacture of various chemical compounds e.g., carbon tetrachloride, chlorinated lime, PVC, HCl, etc.
- Water purification, manufacture of metallic chlorides, chlorinated lime, chlorobenzene, etc.
- Shrink proofing wool, in flame-retardant compounds, manufacture of trichloroethylene, neoprene etc.
- Processing of meat, fish, vegetables and fruit, in special batteries (with lithium or zinc)

Hydrochloric acid

Chemical Formula: HCl

Product quality: 30-32% HCl

Appearance: Colorless or slightly yellow fuming liquid

Uses:

- Metal picking and cleaning, industrial acidizing, boiler scale removal
- Processing of bone in gelatin manufacturing industry, food processing (corn syrup, sodium glutamate).
- Manufacture of dyestuffs, casein, pharmaceuticals, synthetic rubber, laboratory reagent etc.
- Effluent treatment and the regeneration of ion-exchange resin in water treatment.

Bangladesh demand: 150- 200 TPD

Sodium Hypochlorite

Chemical Formula: NaOCl

Product quality: Available Cl2

Appearance: Pale greenish liquid

Uses:

- Disinfection, odor control, specification, bleaching.
- Chlorination of drinking and process water, oil refineries, petroleum refineries.
- Textile industry, pulp and paper industry, soap manufacturing, food processors, wood processing.
- Elimination of slime and algae in swimming pool and boiler water.

Bangladesh demand: 40- 50 TPD

Stable Bleaching Powder

Chemical Name: chlorinated lime

Chemical Formula: Ca(OCl)Cl

Product quality: 30-32% HCl

Appearance: Dry free flowing dull white powder

Product quality: Available chlorine conc. 35-37% min

Uses:

- Sewage disposal, odor control, BOD reduction and removal of poisonous matter.
- Potable water purification, mosquito control, control of epidemic etc.
- Bleaching agent (paper & textile), algaecide, bactericidal and deodrant.
- Elimination of algae and slime in swimming pool, sanitation and general hygiene.

Bangladesh demand: 100- 150 TPD

Na_2CO_3

Shall be discussed on next class……