CLEANER PRODUCTION OPPORTUNITIES

IN

CAUSTIC SODA /CHLOR-ALKALI INDUSTRIES
Introduction to Caustic soda / Chlor Alkali Industry

The Chlor-Alkali industry in India forms an important component of basic chemicals industry, comprising around 74% of the basic chemicals production in India. Caustic soda, soda ash, chlorine alongside hydrogen and hydrochloric acid comprise the Chlor-alkali industry’s components. These chemicals find their applications in a number of industries such as textiles, chemicals, paper, PVC, water treatment, alumina, soaps & detergents, glass, chlorinated paraffin wax, among others. The demand for the two sub-segments – caustic soda & soda ash, has increased significantly registering a compound annual growth rate (CAGR) of 5.6% and 4.7% respectively, over the past five years.

The Chlor-Alkali Industry in the country produces mainly Caustic Soda, Chlorine and Soda Ash. The products of the industry are of vital importance and their uses are:-

a) Caustic Soda
   - Soaps and Detergent Industry
   - Pulp and Paper Industry
   - Textile Processing Industry
   - Aluminum Smelting
   - Dyes and Dyestuff Industry
   - Plastic Polymers
   - Rayon Grade Pulp
   - Pharmaceuticals
   - Electroplating
   - Adhesives/Additives.

b) Chlorine, By-product of Caustic Soda Industry is very important for manufacturing of PVC, one of the five major Thermoplastic Commodity Plastics. Besides this, it is used in disinfection of drinking water, pharmaceutical industry and various other chemical industries. Because of the strong oxidizing properties of Chlorine, it is effectively used to control bacteria and viruses in drinking water that can cause devastating illness such as Cholera. Use of Chlorine is very important for the Countries like India especially in case of floods. 85% of the pharmaceuticals rely on Chlorine Chemistry including medicines that treat heart disease, cancer, AIDS and many other life threatening diseases. Chlorine tablets are also used by public health workers in rural areas.

c) Soda Ash is used in Glass Industry, Soaps & Detergents, Silicates and various other Chemical Industries.
As stated above the growth of Caustic Soda and Soda Ash Industry is very important for the Nation and if competitiveness of this Industry is maintained, it can certainly grow at a much faster rate.

**Highlights of processes for Chloralkali/ caustic soda**

The Chloralkali process (also chlor-alkali and chlor alkali) is an industrial process for the electrolysis of sodium chloride solution (brine). Depending on the method, several products besides hydrogen can be produced. If the products are separated, chlorine and sodium hydroxide (caustic soda) are the products; by mixing, sodium hypochlorite or sodium chlorate are produced, depending on the temperature.

There are three basic processes for the electrolytic production of chlorine, the nature of the cathode reaction depending on the specific process. These three processes are the diaphragm cell process (Griesheim cell, 1885), the mercury cell process (Castner–Kellner cell, 1892), and the membrane cell process (1970). Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode.

The basic principle in the electrolysis of a sodium chloride solution is the following:
- At the anode, chloride ions are oxidised and chlorine (Cl₂) is formed.
- At the cathode: In the mercury process a sodium/mercury amalgam is formed and hydrogen (H₂) and hydroxide ions (OH⁻) are formed by the reaction of the sodium in the amalgam with water in the denuder. In membrane and diaphragm cells, water decomposes to form hydrogen (H₂) and hydroxide ions (OH⁻) at the cathode.

For all processes the dissolving of salt, sodium chloride, is:
\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \]

The **anode** reaction for all processes is:
\[ 2 \text{Cl}^- \text{(aq)} \rightarrow \text{Cl}_2 \text{(g)} + 2 \text{e}^- \]

The **cathode** reaction is:
\[ 2 \text{Na}^+ \text{(aq)} + 2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 \text{(g)} + 2 \text{Na}^+ \text{(aq)} + 2 \text{OH}^- \text{(aq)} \]

The **overall** reaction is:
\[ 2 \text{Na}^+ \text{(aq)} + 2 \text{Cl}^- \text{(aq)} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Na}^+ \text{(aq)} + 2 \text{OH}^- \text{(aq)} + \text{Cl}_2 \text{(g)} + \text{H}_2 \text{(g)} \]
(Flow diagram of the three main Chlor-alkali processes)
(Simplified scheme of chlorine electrolysis cells)

The main characteristics of the three electrolysis processes are presented in Table

<table>
<thead>
<tr>
<th></th>
<th>Mercury</th>
<th>Diaphragm</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caustic quality</td>
<td>High, &lt;30 ppm NaCl; 5-150 μg Hg/l (Before treatment the Hg level is between 2.5-25 mg Hg/l)</td>
<td>1.0-1.5% by weight NaCl (Before treatment the NaCl content is about 18%) 0.1% NaClO₃ Not suitable for some applications</td>
<td>High, &lt;50 ppm NaCl</td>
</tr>
<tr>
<td>Caustic concentration</td>
<td><strong>50%</strong></td>
<td><strong>12%</strong>, requires concentration to 50% for some applications</td>
<td><strong>33%</strong>, requires concentration to 50% for some applications</td>
</tr>
<tr>
<td>Chlorine quality</td>
<td>Contains low levels of Oxygen content</td>
<td>Oxygen content</td>
<td>Oxygen content</td>
</tr>
</tbody>
</table>

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### Auxiliary processes

There are various auxiliary processes attached to all the three technologies, which are listed below:

- salt processing; unloading/storage
- brine purification and re-saturation
- chlorine processing
- caustic processing
- hydrogen processing

### Caustic Processing

*Process for Caustic Soda*

Sodium hydroxide (caustic soda) is produced in a fixed ratio of 1.128 tonnes (as 100% NaOH) per tonne chlorine produced.

The caustic soda solution from the three technologies is treated in slightly different ways due to the difference in composition and concentration.

In the mercury cell process, 50% caustic soda is obtained directly from the decomposers. The caustic soda is normally pumped through a cooler, then through a mercury removal system and then to the intermediate and final storage sections. In some cases the caustic is heated before filtration. The most common method for removal of mercury from caustic soda is a plate (or leaf)
filter with carbon precoat. Under normal operating conditions, mercury-cell caustic soda (as 100% NaOH) contains 20-100 ppm of sodium chloride and 40-60 μg Hg/kg NaOH. In the case of diaphragm and membrane technologies the caustic soda is concentrated by evaporation before final storage.

(The flow to storage of caustic soda from the different technologies)

**Emissions in Chlor Alkali Industry**

**Emission from Mercury cell process**

<table>
<thead>
<tr>
<th>Air Emission</th>
<th>Water emissions</th>
<th>Solid Waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Releases of mercury are specific to the amalgam technology. Air emissions consist of mercury vapour coming from: - cell-room ventilation - process exhausts - brine purification - stack of caustic evaporators</td>
<td>- the process: bleed from brine purification, condensate from hydrogen drying, condensate from caustic soda concentration units, brine leakage, ion-exchange eluate from process water Treatment. - the wash water from the cell cleaning operations: inlet and outlet boxes - the rinsing water from the electrolysis hall:</td>
<td>- Solids from brine purification - Solids from caustic filtration - Graphite and activated carbon from treatment of gaseous streams</td>
</tr>
</tbody>
</table>
- hydrogen burnt or vented to atmosphere  
- mercury retorting  
- maintenance outside cell room  
cleaning of the floors, tanks, pipes and dismantled apparatus  
- the rinsing water from maintenance areas outside the electrolysis hall, if they are cleaned with water

### Emission from Diaphragm cell process

<table>
<thead>
<tr>
<th>Air Emission</th>
<th>Water emissions</th>
<th>Solid Waste</th>
</tr>
</thead>
</table>
| Three sources of asbestos emission can be identified in the cell room maintenance area:  
- from the off-gas compressor,  
- from the off-gas drying oven,  
- from the off-gas asbestos weighing room | Waste water streams from the diaphragm cell process mainly originate from  
- the condenser  
- caustic soda evaporation,  
- chlorine drying,  
- brine purification of salt recovered from The evaporators. | Bagged asbestos from scrap diaphragms |

### Emission from the Membrane Cell Process

<table>
<thead>
<tr>
<th>Air Emission</th>
<th>Water emissions</th>
<th>Solid Waste</th>
</tr>
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</table>
| - | Waste water from the membrane cell process originates from  
- caustic evaporation,  
- chlorine drying and  
- Wash water from the ion exchange resin used to purify the brine. | Precoat and body feed material made of cellulose  
- Spent membranes and gaskets from membrane cells |

### Environmental Issues in Chlor alkali/ caustic soda Industry and CP options

- Implementation of cleaner processes and pollution prevention measures can yield both economic and environmental benefits. In MBCP (membrane process), the chlorine (at the anode) and the hydrogen (at the cathode) are kept apart by a selective polymer membrane that allows sodium ions to pass into the cathodic compartment and react with the hydroxyl ions to form caustic soda. The depleted brine is de-chlorinated and recycled to the input stage. The major waste stream from the MBCP consists of brine mud - the sludge from the brine purification step, which may contain magnesium, calcium, iron, and other metal hydroxides, depending on the source and purity of the brine.
- The pollution emission target namely wastewater generation target of 0.1 m³ per ton of
  1. Having an emergency preparedness and response plan for potential uncontrolled chlorine and other releases.
  2. Using carbon tetrachloride with levels below 4% to avoid explosion.
  3. Using metal rather than graphite anodes in DCP to reduce lead and chlorinated organics.
  4. Re-saturate brine in closed vessels to reduce the generation of salt sprays.
  5. Use non-contact condensers to reduce the amount of process wastewater.
  6. Scrub chlorine tail-gases to reduce chlorine discharges and to produce hypochlorite. Scrub chlorine tail-gas using suitable quantity of water for preparation of caustic solution for pH maintenance to reduce chlorine discharge and to produce sodium hypo chloride
  7. Recycle condensates and waste process water to the brine system, if possible.
  8. Recycle brine wastes, if possible
  9. Preferable use of substitutes for carbon tetrachloride as this is hazardous
  10. chlorine produced can be achieved by adopting preventive measures such as:

- Indian Chlor-alkali plants have achieved huge benefits through technology shift i.e. Technology shift from Mercury cell to Membrane cell, which are tabulated below:
  1. Given the fact that Chlor-alkali production relies on energy intensive electrochemical technology, approximately 70-75% of the production cost primarily comprises of energy costs in case of mercury cell based technology. On the other hand in case of membrane cell technology, there is a significant reduction in energy consumption and the total energy cost only constitutes 60% of the production cost. Therefore, immediate reduction of production cost of about 24% can be achieved by technology shifts.
  2. The membrane cell plant is an environment friendly and energy efficient technology. Any end products or gas, generated from this plant are completely free of mercury with no chances of mercury contamination to the soil or water;
  3. The membrane cell based plant would ensure no emission of mercury into the air;
  4. No chances of negative impacts on humans as well as the environment remains as the mercury itself is a toxic element;
  5. Net energy saving of about 24 percent, thereby reducing the amount of carbon foot print

- Mercury cell Chlor-alkali plants are subject to special regulations due to the use of mercury. In the case of mercury as well as membrane cell process, the initial investment on pollution control measures remains unchanged; thereby the conversion in technology did not envisage any additional investment. Converting to a mercury free process will lead to the savings of several relevant costs, which in approximate order of economic significance include:
  1. Avoiding costs of recycling, retorting, transporting, inventorizing and/or disposing of mercury wastes;
  2. Elimination of the mercury wastewater treatment facility;
  3. Reduced labor costs due to reduced need for maintenance;
4. Reduced labor costs due to reduced need for monitoring mercury emissions and occupational exposures, health testing, reporting and abatement measures;
5. Avoidance of costs of storage of residual mercury;
6. Elimination of mercury monitoring equipment, as well as equipment for cleaning mercury from product streams, flue exhausts, other clean-up related costs (spillages) etc;
7. This cannot be easily quantified; however, at least 5% of the total benefits listed above, can be achieved, which include, improved community relations, decreased legal liability, improved public/investor image of the company, improved attractiveness of the company as a place to work (employee satisfaction), reduced energy demand during the time of raised energy consciousness, reduced CO₂ emissions related to energy demand etc.
8. Reduced costs on medical testing of workers and relevant insurances as well as costs related to potential need of rehabilitation in case workers had to take time off.

- Fundamental research programmes related to mercury technology are not being developed since it is very unlikely that any new mercury plants will be built. The only recent improvements in mercury cells concerns the anode geometry with the aim of improving gas release in order to decrease electrical energy usage and increase anode coating life. In diaphragm technology, with the exception of non-asbestos technology referred earlier, improvements are minor and related to reducing power consumption in the cell. An interesting example is a specific development of activated cathode technology which is the pre-cathode concept.
- Oxygen depolarized cathodes in membrane cells have the potential to save around 500-600 kWh/tonne of chlorine produced and are now being tested at the industrial scale.
- The membrane is being developed that can produce high concentration (50%) caustic soda and believes that it could be available at an acceptable cost within a few years
- For MBCP (membrane technology) the cleaner options include:
  1. Minimizing the discharge of chlorate and bromate to water by applying: acid conditions in the anolyte (pH: 1-2) to minimize the formation of chlorate (ClO₃⁻) and bromate (BrO₃⁻) – chlorate destruction in the brine circuit to remove chlorate before purging.
  2. The acidity of the anolyte is a design parameter of membrane cell plant and cannot be adjusted without affecting the operation of the membrane cell. If this is not the chosen option, a chlorate decomposer may be necessary to remove chlorate before purging.
  3. The chlorate level associated with BAT in the brine circuit is 1-5 g/l and the associated bromate level is 2-10 mg/l (note that the bromate level depends on the bromide level in the salt).
  4. Appropriate handling of spent membranes and gaskets.

**Environmental Issues in Caustic Soda Manufacturing and CP options**

- Steam is used as the source of evaporative energy. The presence of salt in the diaphragm cell liquor requires that the evaporator is equipped with scraper blades or other devices to draw off the precipitated salt. This high quality sodium chloride can then be used to enrich depleted
brine, sometimes it is used as a raw material for an amalgam or membrane process. The residual level of sodium chloride in sodium hydroxide from diaphragm cell is about 1% and sodium chlorate 0.1%. For this reason, it is unsuitable for certain end applications such as the manufacture of rayon.

- Salt and sodium chlorate in the caustic soda from diaphragm cells can be reduced by ammonia extraction to increase marketability, but at increased cost.
- The caustic soda from membrane cells is of high quality, although the caustic soda produced (usually around 33% NaOH) needs concentration to 50% NaOH for some applications. The salt content of the membrane-cell caustic soda lies between 20-100 ppm (in 100% NaOH), but is on average slightly higher than mercury cell caustic.
- In some plants the caustic soda is further concentrated to a 73% solution and to 100% as solid caustic prills or flakes.
- Some Chlor-alkali production facilities can combine the caustic production process from mercury and membrane cells in order to minimize energy costs. It is possible to feed 33% caustic from the membrane cells to the decomposer to produce 50% caustic without the need for evaporation.

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