SODIUM CARBONATE (continued)

3. **Dual process**

**Raw materials**

- **Basis:** 1000kg Sodium carbonate
- Crystalline Salt = 1260kg
- Ammonia = 325kg
- High pressure steam = 1350kg
- Low pressure steam = 100kg
- Cooling water = 50000 - 80000kg
- Electric power = 450KWH
- Co-product (NH₄Cl) = 620kg

**Sources of raw material**

Common salt can be obtained from sea water, salt lake and sub–soil water as described in Module: 3, Lecture: 8.

Ammonia can be synthesized by Haber – Bosch or Modern process as described in Module: 2, Lecture: 6.

**Reactions**

\[
\begin{align*}
C + O_2 & \rightarrow CO_2 \\
NH_3 + H_2O & \leftrightarrow NH_4^+OH^- \\
CO_2 + H_2O & \rightarrow HCO_3^- + H^+ \\
CO_2 + OH^- & \rightarrow HCO_3^- \\
Na^+ + Cl^- + NH_4^+ + HCO_3^- & \rightarrow NH_4Cl + NaHCO_3 \\
2NaHCO_3 & \rightarrow Na_2CO_3 + CO_2 + H_2O
\end{align*}
\]

**Manufacture**

- **Block diagram of manufacturing process**
- **Diagram with process equipment**
- **Animation**
The liquor from carbonation tower, containing ammonium chloride, unreacted NaCl and traces of sodium carbonate is ammoniated in ammonia absorber. The ammoniated liquor is sent to a bed of washed salt in salt dissolver. The resulting liquor is gradually cooled to 0°C in refrigerating tank unit, resulting into crystallize out ammonium chloride. The slurry containing ammonium chloride is thickened and NH₄Cl is centrifuged and dried. In this process ammonium chloride is obtained as co-product. These is the principal modification of dual process in which ammonium chloride is recovered as co-product rather than liberation of the contained ammonia for recycle as in the Solvay process.

The liquor obtained after separation of NH₄Cl is charged to series of carbonation towers in which CO₂ is passed from bottom in the counter current flow of liquor. The resulting sodium bicarbonate is thickened into thickener and centrifuged. It is then calcined into sodium carbonate.

**Major engineering problem**

**Salt purification**

Solid salt which is used to obtain better crystallization yields of NH₄Cl cannot be purified as with brine feeds in Solvay process. Only purification method is mechanical washing and dewatering.
Corrosion

Ammonium chloride solution is quite corrosive to equipment involved in crystallization and solids recovery. So, corrosion resistant material or rubber-lined units are preferred.

Refrigeration Cost

Actual refrigeration cost is variable but to maintain the temperature around 0°C, the electric requirements are still double than Solvay’s operation.

Choice of process

Advantage of Solvay process

- Less electric power
- Less corrosion problem
- Use of low grade brine
- Not a problem of disposal of co-product
- Does not require ammonia plant

Disadvantage of Solvay process

- Higher salt consumption
- Waste disposal of CaCl₂-brine stream
- Higher investment in ammonia recovery units than crystallization unit of NH₄Cl
- More steam consumption
- Higher capacity plant set up require for economic break even operation (100 v/s 55tons/day)
- NH₄Cl will be used as mixed fertilizer ingredient which minimizes the disposal problem of Duel process.

Plant location

One ton of soda ash production requires 8 tons of brine. As the salt sources are the key factor and they are less widely distributed than limestone or coal. There so plant should be located nearby the salt sources.

4. ELECTROLYTIC PROCESS

Raw materials

Basis: 1000kg Sodium carbonate (98% yield)
Salt = 563kg
Carbon dioxide = 424kg

Sources of raw material

Common salt can be obtained from sea water, salt lake and sub –soil water as described in Module: 3, Lecture: 8.
Reactions

\[ \text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^- \quad 2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}_2 + \text{OH}^- \]

At cathode

\[ 2\text{H}_2\text{O} + 2e^- \rightleftharpoons \text{H}^+ + 2\text{OH}^- \]
\[ \text{Na}^+ + \text{OH}^- \rightleftharpoons \text{NaOH} \]
\[ 2\text{NaOH} + \text{CO}_2 \rightleftharpoons \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]

At Anode

\[ \text{Cl}^- - e^- \rightleftharpoons \text{Cl} \]
\[ \text{Cl}^- + \text{Cl}^- \rightleftharpoons \text{Cl}_2 \]

Manufacture

Electrolytic cell consists of a perforated steel tube having a thin lining of asbestos on the inside. The steel tube acts as the cathode and is suspended in an outer steel tank. Brine is placed inside the cathode tube and a graphite rod is immersed in it acts as anode. When an electric current is passed, the salt solution undergoes electrolysis and its ions pass through the diaphragm as a result of electrical migration. Hydrogen and caustic soda are formed at the cathode and chlorine at the anode. Hydrogen gas is allowed to escape through an opening provided at the top of the cell. Chlorine liberated at the anode is led away through
a pipe and compressed into steel cylinders. The space between the cathode and outer tank is kept full of steam and Carbon dioxide.

Sodium ions pass through the asbestos and reach the cathode, where $\text{H}^+$ ions and $\text{OH}^-$ ions are formed as a result of reduction of water. Hydrogen escapes through an opening at the top and $\text{Na}^+$ ions combine with $\text{OH}^-$ ions to form caustic soda. Sodium hydroxide is reacted with pressurized $\text{CO}_2$ yielding Sodium carbonate which is collected from bottom of the cell.

**PROPERTIES**

- Molecular formula : $\text{Na}_2\text{CO}_3$
- Molecular weight : 105.978 gm/mole
- Appearance : White crystalline solid
- Odour : Odourless
- Boiling point : 1633°C
- Melting point : 851°C
- Density : 2.54 gm/mL (Anhydrous)
- Solubility : Soluble in water

99% sodium carbonate (58% Na$_2$CO$_3$) is known as light soda ash (solid density 1.86). Dense soda ash has solid density of 1.91. Both grads (lightly and dense) are granular. Na$_2$CO$_3$. 10H$_2$O is known as washing soda.

**USES**

- Widely used in the manufacture of glass,
- Used in manufacture of sodium bicarbonate, caustic soda,
- Used in soap, pulp and paper, textiles industries
- Used in petroleum and dyes industries
- Used in foods, leather and water softening industries.
- As a photographic film developing agent
- As an electrolyte
- As a washing soda in household uses.