Soda Ash (Sodium carbonate) Manufacture
Pertinent properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value/Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. Wt.</td>
<td>106</td>
</tr>
<tr>
<td>M.P.</td>
<td>851 deg.C.</td>
</tr>
<tr>
<td>B.P.</td>
<td>Decomposes</td>
</tr>
<tr>
<td>Soluble in water</td>
<td>8.9 gm/100gm at 20 deg.cel.</td>
</tr>
</tbody>
</table>

Grade s: 99% sodium carbonate washing soda (Na₂CO₃ .10 H₂O)
Methods of production:

(i) Solvay or ammonia soda process
(ii) dual process
(iii) natural soda ash deposits
(i) Solvay or ammonia soda process

Reactions:
2 NaCl + CaCO₃ → Na₂CO₃ + CaCl₂

Raw material: They are salt, coal and limestone
Quantitative requirements:
Basis: 1 ton of Na₂CO₃
salt  1.55 tons
Limestone  1.2 tons
Coke  0.09 tons
High pressure steam  1.35 tons
Low pressure steam  1.60 tons
Ammonia losses: 1.5 kg
Cooling water  40-60 tons
Electric power  210 KWH
Plant Capacity: 200,-2000 tons/day
Process Description:

In 1869 Solvay discovered that NH₃ dissolved in an NaCl solution and then reacted with CO₂. A precipitate of NaHCO₃ was obtained which could be calcined to produce high purity Na₂CO₃.

Saturated salt brine is purified in series of wash towers with NH₃ and then with CO₂ to remove Ca, Mg and sludge.

The purified brine is pumped to the ammonia absorber tower where it dissolves NH₃ with liberation of heat. Some CO₂ dissolves in this tower.
The ammoniated partially carbonated brine is cooled to 30 deg. cel. and pumped to the carbonating tower that is on cleaning duty.

Weak CO$_2$ gas is admitted below the tower. This gas serves to further carbonate the liquor to just below precipitation point.

The carbonating towers are about 22-25 m high and 1.8 – 2.5 m in diameter and constructed of cast iron.

During precipitation cycle the tower temperature gradients is maintained as 20-25 deg. C. at both ends and 45-55 deg. C. in middle.
The remainder process concerns ammonia recovery and recycle.
Chemistry of Solvay process

The Solvay process results in soda ash (predominantly sodium carbonate (Na$_2$CO$_3$)) from brine (as a source of sodium chloride (NaCl)) and from limestone (as a source of calcium carbonate (CaCO$_3$)). The overall process is:

$$2 \text{NaCl} + \text{CaCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CaCl}_2$$

The actual implementation of this overall reaction is done is four steps.

In the first step in the process, carbon dioxide (CO$_2$) passes through a concentrated aqueous solution of sodium chloride (NaCl) and ammonia (NH$_3$).

$$\text{NaCl} + \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl} \quad (I)$$
Chemistry of Solvay process

The carbon dioxide required for reaction (I) is produced by heating ("calcination") of the limestone at 950 - 1100 °C. The calcium carbonate (CaCO$_3$) in the limestone is partially converted to quicklime (calcium oxide (CaO)) and carbon dioxide:

$$\text{CaCO}_3 \rightarrow \text{CO}_2 + \text{CaO}$$ (II)
Chemistry of Solvay process

The sodium bicarbonate (NaHCO$_3$) that precipitates out in reaction (I) is filtered out from the hot ammonium chloride (NH$_4$Cl) solution, and the solution is then reacted with the quicklime (calcium oxide (CaO)) left over from heating the limestone in step (II).

$$2 \text{NH}_4\text{Cl} + \text{CaO} \rightarrow 2 \text{NH}_3 + \text{CaCl}_2 + \text{H}_2\text{O} \text{ (III)}$$

CaO makes a strong basic solution. The ammonia from reaction (III) is recycled back to the initial brine solution of reaction (I).
Chemistry of Solvay process

The sodium bicarbonate (NaHCO$_3$) precipitate from reaction (I) is then converted to the final product, sodium carbonate (Na$_2$CO$_3$), by calcination (160 - 230°C), producing water and carbon dioxide as byproducts:

$$2 \text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \text{ (IV)}$$
The carbon dioxide from step (IV) is recovered for re-use in step (I). When properly designed and operated, a Solvay plant can reclaim almost all its ammonia, and consumes only small amounts of additional ammonia to make up for losses. The only major inputs to the Solvay process are salt, limestone and thermal energy, and its only major byproduct is calcium chloride, which is sold as road salt.
Major engineering problems:
(a) Development of suitable calcining equipment:

Moist NaHCO$_3$ will cake on sides of klin, preventing effective heat transfer through the shell.

The klin must be equipped with heavy scraper chain inside and wet filter cake must be mixed with dry product to avoid caking.

These problems can be avoided by using fluidized bed calciners in newer installations.
Major engineering problems contd:

(b) Economic balance on tower design: the tower height, pressure and temperature are optimized, giving approximately 75% yield of NaHCO$_3$ from NaCl.

(c) Ammonia recovery: NH$_3$ inventory costs 4-5 times that of Na$_2$CO$_3$ inventory so losses must be kept low.

(d) plant modernization

(e) waste disposal.
USES OF SODA ASH

Soda ash is used in many industrial processes, and its production is sometimes used as an indicator of economic health. The principal current uses include:

Glass making: More than half the worldwide production of soda ash is used to make glass. Bottle and window glass (Soda-lime glass) is made by melting a mixture of sodium carbonate, calcium carbonate and silica sand (silicon dioxide (SiO$_2$)).
USES OF SODA ASH

Soda ash is used in many industrial processes.

Water treatment: Sodium carbonate is used to soften water (precipitates out $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ carbonates). This is used both industrially and domestically (in some washing powders).

Making soaps and detergents: Often sodium carbonate is used as a cheaper alternative to lye (sodium hydroxide (NaOH)).

Paper making: Sodium carbonate is used to make sodium bisulfite (NaHSO$_3$) for the "sulfite" method of separating lignin from cellulose.
USES OF SODA ASH

As a common base in many chemical factories because it is cheaper than NaOH and far safer to handle.

Making sodium bicarbonate: baking soda and fire extinguishers. Although NaHCO₃ is produced in the SolvNaHCO₃ is used in solvay process, heating it to remove the ammonia it is contaminated with decomposes some NaHCO₃, so it is actually cheaper to react the finished Na₂CO₃ product with CO₂.

Removing sulfur dioxide (SO₂) from flue gases in power stations. This is becoming more common, especially where stations have to meet stringent emission controls.
<table>
<thead>
<tr>
<th>Consuming Industry</th>
<th>Metric Kilotons per Year</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>4150</td>
<td>50</td>
</tr>
<tr>
<td>Manufacture of chemicals</td>
<td>1735</td>
<td>18</td>
</tr>
<tr>
<td>Soap and detergents</td>
<td>377</td>
<td>5</td>
</tr>
<tr>
<td>Pulp and paper</td>
<td>226</td>
<td>3</td>
</tr>
<tr>
<td>Water and sewage treatment</td>
<td>226</td>
<td>3</td>
</tr>
<tr>
<td>Miscellaneous (incl. exports)</td>
<td>830</td>
<td>21</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>7544</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

USES AND ECONOMICS. Soda ash is a lightweight solid, moderately soluble in water, usually containing 99.3% \( \text{Na}_2\text{CO}_3 \). It is sold on the basis of its sodium oxide content, which is generally 58%. Figure 13.1 and Table 13.3 summarize the more important uses. The production of soda ash from natural trona deposits now exceeds that from ammonia-soda. The synthetic process has been plagued by high costs and pollution problems and is disappearing in the United States.

Pure caustic soda is a brittle white solid that readily absorbs moisture and carbon dioxide from the air. It is sold on the basis of its \( \text{Na}_2\text{O} \) content and usually contains about 76% \( \text{Na}_2\text{O} \) equivalent to 98% \( \text{NaOH} \). The term caustic soda is widely used because this compound is corrosive to the skin. Table 13.4 presents its diversified distribution. The traditional uses in the fields of soap, textiles, and petroleum refining are still substantial, and there is increasing use in the field of chemicals.
Current status of soda ash industry

In the eighteenth century soda ash was produced by LeBlanc process based on roasting salt cake with carbon and limestone.

The synthetic process for the manufacture of soda ash by ammonia soda process was developed by Ernest Solvay in 1861.

Natural deposits of soda containing sodium carbonate (known as Trona) mostly occur in America, East Africa, Mexico and China.

About 30% of world soda ash production (90% of this is in U.S. alone) is from natural deposits and the rest 70% from synthetic process.
Current status of soda ash industry

The main consuming industries of soda ash are glass, detergent, laundry soap, sodium silicate, cotton yarn, dyes and dyestuff, paper board and other chemical industries.

For countries which do not possess natural resources of soda ash, the following synthetic processes are available:

— Solvay Process
— Akzo Dry Lime Process
— Dual Process
— New Ashai (NA) Process
Current status of soda ash industry

The cost of production of indigenous soda ash is much higher compared to that of international soda ash market due to inferior quality of raw materials and also higher cost.

The ex-work price of soda ash in India is Rs 7000-8000 per MT while European price is $130-159 per MT and US price is $145-170 per MT.
Current status of soda ash industry

The minimum viable capacity and the estimated cost of such a soda ash plant are as under:

a) 1000 TPD Solvay process plant costing Rs 700.0 crores investment

b) 300 TPD Dual process plant costing Rs 300.0 crores investment