

Module: 3

Lecture: 9

SODIUM CARBONATE

INTRODUCTION

Sodium carbonate (Na_2CO_3) also known as washing soda or soda ash, is a sodium salt of carbonic acid. Most commonly occurs as a crystalline heptahydrate, which readily effloresces to form a white powder, the monohydrate. Sodium carbonate is domestically well known as a water softener. It can be extracted from the ashes of many plants. It is synthetically produced in large quantities from salt and limestone in a process known as the Solvay process.

Soda ash is the most important high tonnage, low cost, reasonably pure, soluble alkali available to the industries as well to the laboratory.

MANUFACTURE

Sodium carbonate is manufactured by following process.

1. Leblanc process.
2. Solvay's ammonia soda process.
3. Dual process (modified Solvay's process)
4. Electrolytic process.

1. Leblanc process

The process has only historical importance, because is now been replaced completely by Solvay process or modified by Solvay process.

Raw materials

| | |
|--|----------|
| Basis: 1000kg Sodium carbonate (98% yield) | |
| Common salt | = 1126kg |
| Sulfuric acid | = 945kg |
| Lime stone | = 963kg |
| Coke | = 463kg |

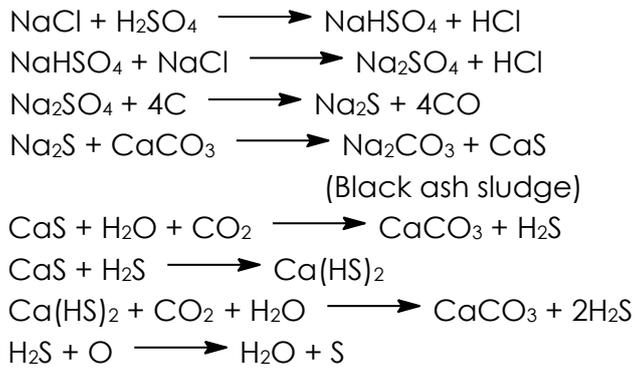
Sources of raw material

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

Sulfuric acid can be obtained by contact process as described in Module: 4, Lecture: 18

Lime stone is obtained from mineral calcite or aragonite, which can be used after removal of clay, slit and sand (silica).

Reactions



Manufacture

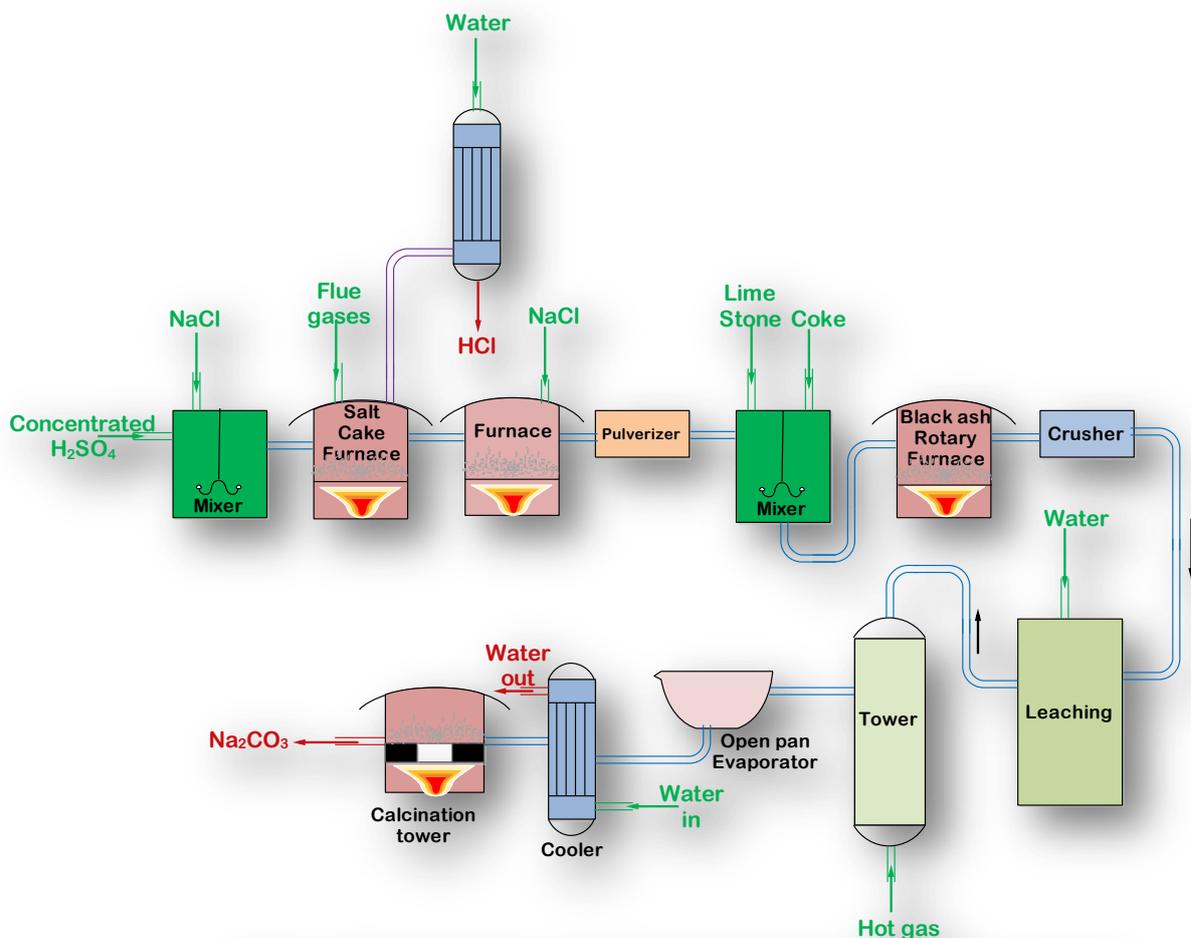


Figure: Manufacturing of Sodium Carbonate by Lablance process

[Block diagram of manufacturing process](#)

[Diagram with process equipment](#)

[Animation](#)

Common salt is first mixed with the conc. H_2SO_4 in equivalent quantities and heated in a cast iron salt cake furnace by flue gases from adjacent coal of fire. NaHSO_4 along with HCl gas is formed. HCl is passed to tower packed with coke and is absorbed through a spray of water comes down in the tower. The paste of NaHSO_4 is taken out and heated to a high temperature on the hearth of a furnace along with some more common salt. NaHSO_4 is thus converted into sodium sulfate, known as salt cake.

The salt cake is broken or pulverized, mixed with coke and limestone and charged into black ash rotary furnace consisting of refractory lined steel shells. The mass is heated by hot combustion gases entering at one end and leaving at the others. The molten porous gray mass thus formed known as black ash is separated from the calcium sludge and then crushed and leached with water in absence of air in a series of iron tank.

The extract containing Na_2CO_3 , NaOH , and other impurities is sprayed from the top of a tower in counter current to flow of hot gases from the black ash furnace. The sodium carbonate thus obtained is concentrated in open pans and then cooled to get sodium carbonate. The product is calcined to get soda ash which is re-crystallized to $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The sludge containing mostly CaS is left behind as alkali waste.

The liquor remaining after removal of first batch of soda ash crystals is purified and then causticized with lime to produce caustic soda.

Recovery of sulfur from alkali waste

Alkali waste is charged into cylindrical iron vessels arranged in series and CO_2 delivered from lime kilns is passed through it, the H_2S gas thus obtained is then conducted together with a regulated amount of air in a Claus kiln containing iron oxide as catalyst. The exothermic reaction proceeds without further external heat. Recovered sulfur is used in the manufacture of sulfuric acid.

2. Solvay's ammonia soda process

Raw materials

| | |
|--------------------------------|----------|
| Basis: 1000kg sodium carbonate | |
| Salt | = 1550kg |
| Limestone | = 1200kg |

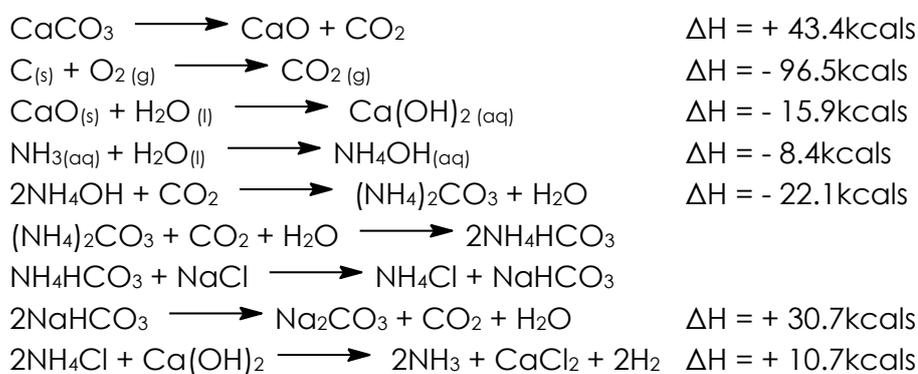
| | |
|-----------------------|-------------------|
| Coke | = 90kg |
| Ammonia as a catalyst | = 1.5kg (Loss) |
| High pressure steam | = 1350kg |
| Low pressure steam | = 1600kg |
| Cooling water | = 40000 - 60000kg |
| Electric power | = 210KWH |

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.

Lime stone is obtained from mineral calcite or aragonite, which can be used after removal of clay, slit and sand (silica).

Reactions



Overall reaction



Manufacture

[Block diagram of manufacturing process](#)

[Diagram with process equipment](#)

[Process equipment](#)

[Animation](#)

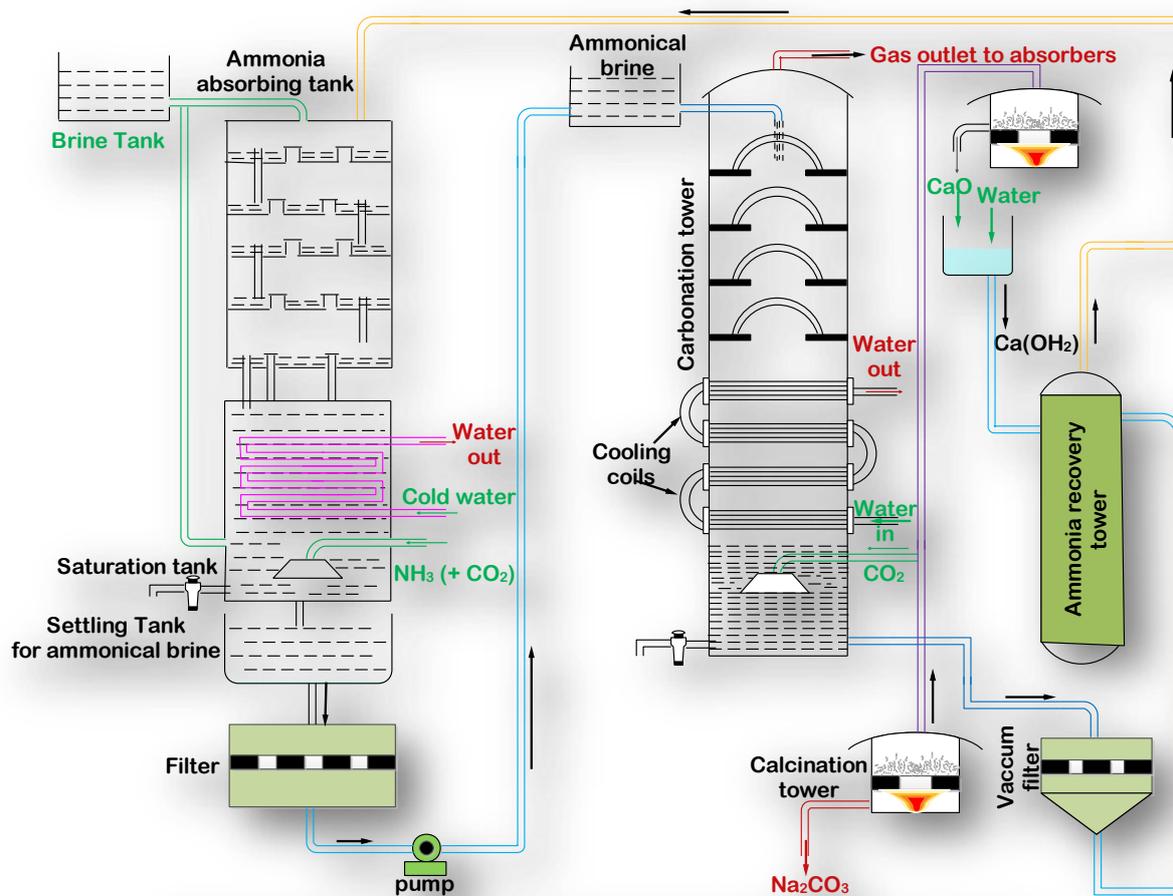


Figure: Manufacturing of Sodium Carbonate by Solvay's Process

Ammonia is dissolved in a salt solution and ammoniate brine solution is allowed to react with CO_2 which is obtained by calcining lime stone with coke. A precipitate of NaHCO_3 , thus obtain is then calcined to produce high purity Na_2CO_3 .

Preparation and purification of brine

Saturated solution of NaCl is used. Brine contains impurities such as calcium, magnesium and iron compounds. To remove calcium sulfate, magnesium and iron salts sodium carbonate and sodium hydroxide are added. The precipitated carbonates and hydroxide are removed by filtration. Sometimes sulfate are removed with BaCl_2 or the hot brine is treated with OH^- and CO_3^{2-} ions. The calcium, magnesium and iron salts from saturated brine may be precipitated by dilute ammonia and CO_2 in a series of washing towers. The brine is purified by allowing it to settle in vats, as a result of which precipitated CaCO_3 , MgCO_3 , $\text{Mg}(\text{OH})_2$ and iron hydroxide settle down and pure brine solution is pumped to the ammonia absorber tower, where it dissolve NH_3 with the liberation of heat.

Ammoniation of brine

The purified brine is allowed to percolate down the ammonia tower in which ammonia gas is passed through the bottom in a counter current fashion. The brine solution thus takes up the necessary amount of ammonia and liberates heat. The gas which escapes solution in the tank is absorbed by the brine falling down the tower. Some carbon dioxide is also absorbed by ammonia, as a result of which some insoluble carbonate is also precipitated. The ammoniated brine is allowed to settle, cooled to about 30°C and pumped to the carbonating tower.

Carbon dioxide formation

Limestone is calcined to get CO_2 in a lime kiln filled with coke. As a result of burning of coke necessary heat required for the decomposition of lime stone is generated. CaO obtained from the lime kiln is converted into slaked lime and pumped to the ammonia recovery tower.

Carbonation of ammonium brine

CO_2 from the lime kiln is compressed and passed through the bottom of carbonating tower down which ammoniated brine percolates. Carbonating towers operated in series with several precipitation towers are constructed of cast iron having 22-25meter height, 1.6-2.5meter in diameter. During the precipitation cycle, the temperature is maintained about 20-25°C at the both ends and 45-55°C at the middle by making use of cooling coils, provided at about 20ft above the bottom. The tower gradually becomes flooded as sodium bicarbonate cakes on the cooling coils and shelves. The cooling coils of the fouled tower are shut off. Then the fresh hot ammoniated brine is fed down the tower in which NaHCO_3 are dissolved to form ammonium carbonate solution. The solution containing $(\text{NH}_4)_2\text{CO}_3$, unconverted NaHCO_3 is allowed to fall down a second tower, called making tower. The making towers are constructed with a series of boxes and sloped baffles. Ammoniated brine and CO_2 gas (90-95%) from the bicarbonate calciner is recompressed and pumped to the bottom of the making tower. The ammonium carbonate first reacts with CO_2 to form ammonium bicarbonate and the latter reacting with salt, forms sodium bicarbonate. The heat of exothermic reaction is removed by cooling coils.

Filtration

NaHCO_3 slurry is then filtered on a rotary vacuum filter which helps in drying of bicarbonate and in recovering ammonia. The filter cake after removal of salt and NH_4Cl by washing with water, sent to a centrifugal filter to remove the moisture or calcined directly. During washing, about 10% NaHCO_3 also passes into filtrate. The filtrate containing NaCl , NH_4Cl , NaHCO_3 and NH_4HCO_3 is treated with lime obtained from lime kiln to recover NH_3 and CO_2 .

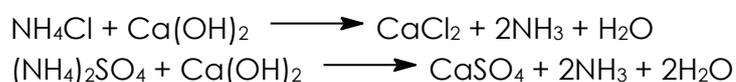
Calcination

NaHCO₃ from the drum filter is calcined at about 200°C in a horizontal calciner, which is either fired at feed end by gas or steam heated unit. The heating being through the shell parallel to the product, which prevent the formation of bicarbonate lumps.

The hot soda ash from the calciner is passed through a rotary cooler and packed in bags. The exit gases (CO₂, NH₃, steam etc.) are cooled and condensed to get liquid ammonia; the rich CO₂ gas is cooled and returned to the carbonating tower. The product from the calciner is light soda ash. To produce dense soda ash, sufficient water is milled with it to form more mono hydrate Na₂CO₃.H₂O and the mixture is recycled.

Recovery of ammonia

The ammonia is recovered in strong ammonia liquor still, consisting of two parts. The parts above and below the lime inlet is called as heater and lime still respectively. The filtrate obtained from washing of NaHCO₃ from the pressure type rotary filter is fed into the heater, where free ammonia and carbon dioxide are driven off by distillation. Dry lime or milk of lime (slaked lime) obtained from lime kiln is fed through the lime inlet and mixed with the liquor from the heater. As the liquor flows down the column, calcium chloride and calcium sulfate are formed and NH₃ gas is released.



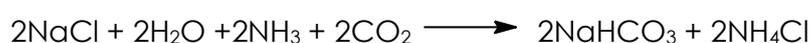
The liquor from the bottom of the lime still is free from ammonia and contains unreacted NaCl and largely CaCl₂, which is disposed off. The liquor is, therefore allowed to settle in settling ponds and the clear liquid is evaporated till the salt separates out and is sold as such for calcium chloride or further evaporated.

Kinetics and thermodynamics

The overall reaction shows that salt and calcium carbonate are the only raw materials which are continuously supplied in the process and that produce sodium carbonate and calcium chloride



Overall reaction of ammoniation of brine and then treatment of carbon dioxide to ammoniated brine is as under



The above reaction shows the role of ammonia and carbon dioxide in the process, and also determines the yield of the final product. There so conditions favourable to it are precisely defined. For these the reaction is divided in to two steps.



Reaction (a) is undoubtedly favoured by low temperature because it requires the dissolution of gas in water, is displaced to right by virtue of the fact that reaction (b), which utilizes the product by subtracting it from (a) is displaced in the same direction. Consequently, it is the precipitation of NaHCO_3 according to (b) which is the driving force behind the entire method.

The solubilities of the salts at various temperature is as under

| Temperature | Solubility in gm/litre | | | |
|-------------|------------------------|---------------------------|------------------------|------------------|
| | NaCl | NH_4HCO_3 | NH_4Cl | NaHCO_3 |
| 0°C | 357 | 120 | 298 | 69 |
| 20°C | 358.5 | 217 | 374 | 95.4 |
| 30°C | 359 | 269 | 467 | 109 |

Above data indicate that precipitation fortunately tends to take place preferentially with satisfactory yields. On the basis of data and common ion effect on precipitation of salts, physicochemical conditions most suitable for the forward step of reaction (b) which causes precipitation of NaHCO_3 are as under

- To maintain lowest possible temperature in order to lower the solubility off sodium bicarbonate
- To maintain the greatest possible concentration of one or both the salts appearing on the product side of reaction (b) with the aim of lowering still further solubility of sodium bicarbonate.

These conditions are nevertheless discerningly applied because they serve to bring about appreciable increase in the yields of NaHCO_3 and permit the most effective use of most costly reagent NH_4HCO_3 in reaction (b).

Attention is paid to the fact that, if precipitation temperature is always kept low, the sodium bicarbonate separates in a microcrystalline form which is with difficult to filter and it is soluble during subsequent washing on the filter, increase requirement of NaCl.

Experimentally, the conditions which are most effectively reconcile the physicochemical aspect of precipitation of sodium bicarbonate economically are as under

- 284gm/liter (≈ 4.9 mole/liter) of NaCl reacting with 76gm/liter (≈ 4.5 mole/liter) of NH_3 instead of equimolecular solution of two reagents
- Relatively high temperature (60-65°C) at the start so as to allow the formation of well-developed NaHCO_3 crystallization seeds and increasing the volume of these seeds to decrease the solubility of salt with gradual cooling.

Major engineering problem

Absorption units

The absorption units should be constructed to permit the downward travel of growing sodium bicarbonate crystals. This is done by having each unit simulate a very large single bubble cap with down sloping floors. The absorption is carried out in towers filled with liquid. Hence CO_2 must be compressed. Due to the compression the partial pressure and solubility of CO_2 increased at the end of carbonating cycle.

Making tower

Sodium bicarbonate formed in the making tower is drawn off as a suspension, it is necessary to ensure that the precipitated sodium bicarbonate is easily filterable and efficiently washable. It is carried out by regulating the temperature and concentration in the making tower. During the precipitation cycle, the temperature gradient is maintained at 20°C at the both ends and 45°C in the middle and fine crystals of sodium bicarbonate are allowed to grow. The temperature is increased from 20°C to 45-55°C by heat of reaction and reduced by using coils.

Development of suitable calcining equipment

Moist sodium bicarbonate will cake on sides of kiln, preventing effective heat transfer through shell. Kiln 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 calciner.

Filtration unit

Filtration should be carried out by using vacuum on the drum filter. It helps in drying the bicarbonate and in recovering ammonia

Ammonia recovery

Ammonia recovery costs 4-5 times that of Na_2CO_3 inventory so losses must be kept low. By proper choice of equipment design and maintenance, losses are less than 0.2% of recycle load or 0.5%/kg product or 1kg/ton of sodium carbonate.

Waste disposal

Large quantities of $\text{CaCl}_2\text{-NaCl}$ liquor is generated during the process. The uses of these liquor is to be find out or dispose it as waste.