

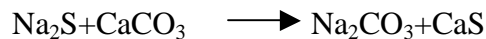
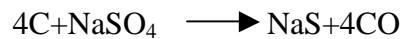
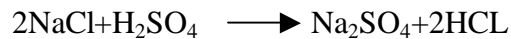
VARIOUS CHEMICAL PROCESSES PRODUCTION OF SODA ASH

(1) Le Blanc Process

This process was invented by Nicolas Le Blanc, a French man ,who in 1775, among several others submitted an outline of a process for making soda ash from common salt, in response to an offer of reward by the French academy in paris. Le Blanc proposal was accepted and workable on a commercial scale.

Process Description

Reactions



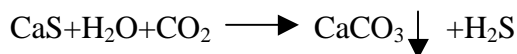
A mixture of equivalent quantities of salt and concentrated sulphuric acid is heated in cast iron salt cake furnace. Hydrochloric acid gas is given off and sodiumhydrogen sulphate is formed. The gas is dissolved in water and the mixture is raked and transferred to the muffle bed reverbratory furnace where it is subjected to stronger heat. Here sodium sulphate called salt cake is formed.

The cake is broken, mixed with coke and limestone and charged into black ash furnace. The mass is heated and a porous grey mass know as black ash is withdrawn.

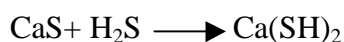
The black ash is cursed and leached with water in the absence of air in a series of tanks. The extract containing sodium carbonate, sodium hydroxide and many other impurities ,is sprayed from the top of a tower counter current to the flow of hot gases from the black-ash furnace. This converts sodium hydroxide, aluminate,silicate, cyanate to sodium carbonate. The liquor is concentrated in open pans until the solution is concentrated in open pans until the solution is concentrated enough to precipitate sodium carbonate on cooling. The product is calcined to get crude soda ash which is purified by

recrystallisation. The liquor remaining after removal of first crop of soda crystals is purified to remove iron and causticised with lime to produce caustic soda.

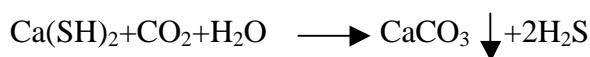
The mud remaining in the leaching tanks containing calcium sulphide is suspended in water and lime kiln gas is passed through it. The following reaction occurs.



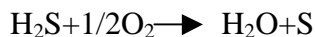
The lean gas containing hydrogen sulphide is passed through another tank containing suspension of calcium sulphide.



This solution is again treated with lime kiln gas liberating a gas rich in hydrogen sulphide.



The hydrogen sulphide is burnt in limited supply of air in a special furnace in presence of hydrated iron oxide as a catalyst to obtain sulphur.



The sulphur is sublimed and collected.

(2) Trona purification process

Several processes are used to refine trona ore and are simpler than solvay process. In general, they are of two types. In one process trona ore is calcined to impure soda ash, which is then purified. The other type produces soda ash by calcinations of purified sodium sesquicarbonate obtained from the trona. The first route is now used predominantly although the latter route was practiced first.

Monohydrate Process

In this process, the trona ore is crushed and then calcined in a rotary kiln at 160-200⁰ C, decomposing the sodium sesquicarbonate and liberating water and carbon dioxide. The calcined material, which is impure soda ash, is agitated in tanks with water

or weak soda ash liquors to dissolve the soda ash and soluble impurities, such as sodium chloride and sodium sulphate. Insoluble material, consisting of shale, clay, and complex salts containing calcium carbonate, is separated from the hot, near-saturated soda ash solution. To reduce soda ash losses, waste solids from this step are washed before being discarded.

The filtered liquor is usually treated with activated carbon to remove soluble organic compounds and reduce foaming during evaporation to produce crystals of sodium carbonate monohydrate. Crystallization is carried out in multiple effect evaporators at a maximum temperature of about 100°C , which is below the transition temperature of monohydrate to anhydrous soda ash. A purge from the crystallizers may be maintained to remove impurities. The slurry is centrifuged to separate the crystalline sodium carbonate monohydrate from the mother liquor which is returned to the crystallizers. The monohydrate crystals are dehydrated at about 150°C . because the crystal size of the soda ash is carefully controlled in the crystallizer only nominal screening is required before the dense ash product is cooled and loaded.

Sodium sesquicarbonate process

In this process, the crushed trona ore is fed into a series of dissolves to produce a saturated mother liquor, which is clarified, filtered, and freed of organic compounds by carbon treatment. Corrosion of the equipment by the mother liquor is controlled by a low concentration of sulfide ion. The treated liquor is evaporated in vacuum crystallizers and cooled to 40°C . The Sodium sesquicarbonate crystals formed are centrifuged and the mother liquor recycled to the dissolvers. The sesquicarbonate crystals are decomposed to sodium carbonate in rotary caliners at approximately 200°C . the anhydrous soda ash product has a bulk density of about 800kg/m^3 and must be double calcined to prepare dense ash. After calcinations, the soda ash is cooled and is ready for shipment.

(3) Dual process

In this process ammonium chloride is produced as a coproduct in equivalent quantities and differs from conventional ,solvay process and it does not recycle ammonia.

Process description:

The mother liquor from the carbonating system, containing ammonium chloride, unreacted salt and traces of carbonate is ammoniated in ammonia absorber. The ammoniated mother liquor is passed through a bed of salt in a salt dissolver. Exit liquor from the dissolver, saturated with salt, is gradually cooled from 40⁰ C to 10⁰ C by evaporation under vacuum to separate ammonium chloride. The slurry containing ammonium chloride is centrifuged and dried. The product is 98% pure and is marked as ammonium chloride fertilizer with nitrogen content of 25%.

The mother liquor obtained after the separation of ammonium chloride crystals is recycled to the carbonation vessels placed in series. Carbon dioxide obtained from ammonia plant and the calciner section of soda ash plant is injected in the carbonation vessels. There is provision of cooling coils in the lower carbonation vessels. Sodium bicarbonate is formed. The growth of crystals, of sodium bicarbonate is controlled by the supply of cooling water to cooling water to cooling coils in carbonation vessels.

sodium bicarbonate is thickened in a thickener and centrifuged. The sodium bicarbonate is calcined to soda ash.

Raw material consumption per ton of co-product

Salt	1.3 tons
Ammonia	335 kgs
Power	250 kwh
Fuel oil	18 litres
Steam(including refrigeration)	5.2 tons

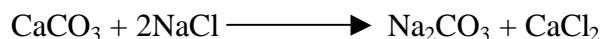
The plant has several advantages over the conventional Solvay process in as much as it uses less raw material, has no effluent disposal problem, and both sodium and chloride radical of salt are fully utilized giving valuable ammonium as a byproduct.

(4) Solvay process or Ammonia-soda process

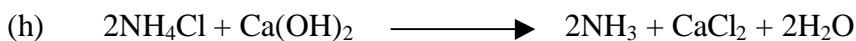
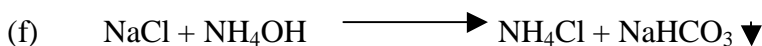
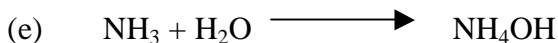
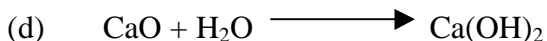
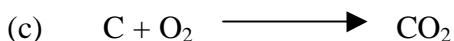
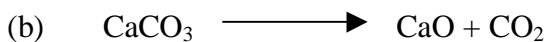
The discovery of the chemistry of the ammonia-soda process can be traced back to the early 1800s. A few British and French plants operated in 1840-1860, but without success. The ammonia-soda process is usually called the Solvay process because in 1865 Ernest Solvay started the first really successful plant at Couillet in Belgium. In 1874, the first successful ammonia-soda plant was erected in England. The ammonia-soda process is the dominant technology used throughout the world, hence this process is selected for production of soda ash.

Chemical reactions

(a) Overall reaction



This reaction takes place in a number of steps



Brine Preparation: Sodium chloride solutions are occasionally available naturally but are more often obtained by solution mining of salt deposits to give raw, near saturated brine containing low concentrations of impurities such as magnesium and calcium salts. Some brines contain significant quantities of sulfates. Brine purification is required to

prevent scaling of processing equipment and contamination of the product. Brine is usually purified by a lime soda treatment where the magnesium is precipitated with $\text{Ca}(\text{OH})_2$ (milk of lime) and the calcium is precipitated with soda ash. The brine, separated from precipitated impurities, is sent to the ammonia absorbers.

Ammonia Absorption: The strong brine is saturated with ammonia gas in the absorption tower. The ammonia, recycled from various process steps, contains water vapor and carbon dioxide. Small amounts of ammonia are added to make up for losses. During ammoniation, the brine requires cooling (approx 1650 MJ/t or 394 kcal/kg of product soda ash). The absorption operation is generally carried out at atmospheric pressure. The brine descends through the main part of the absorber countercurrent to the rising ammoniacal gases. The temperature of inlet brine is about 30°C and that of exit is about 36° to 42°C .

Precipitation of Bicarbonate: The ammoniated brine from the absorber coolers is pumped to the top of one column in a block of columns used to precipitate bicarbonate. This column which has been fouled or partially plugged with sodium bicarbonate after several days of crystallization is referred to as a “cleaning” column. Lime kiln gas, compressed to about 414 kPa (60psi), enters the bottom of the cleaning column and bubbles up through the solution to absorb most of the carbon dioxide. The concentration of carbon dioxide in the liquor is kept below the precipitation concentration. Relatively little cooling is required. The scale is dissolved off the cooling surfaces of the cleaning column by the fresh ammoniated brine, assisted by gas agitation. The liquor leaving this column is fed in parallel to the top of the remaining columns in to block. A stronger carbon dioxide gas made up of a mixture of kiln gas and bicarbonate calciner gas is fed to these crystallizing or “making” columns and bubbles up through the solution. This process precipitates sodium bicarbonate and is accompanied by the evolution of considerable heat which must be removed to improve yield. Crystals formed during the carbonation step gradually foul the heat – exchange surfaces and thus a crystallizing column must alternately be the “cleaning” column. The gases, which are predominantly

nitrogen, but also contain carbon dioxide and ammonia, are vented from the cleaning and making columns and collected of recycling to the absorber.

Filtration of Bicarbonate: The slurry, collected from the crystallizing towers, is fed to continuous vacuum filters or centrifuges which separate the crystals from the “filter liquor.” The filter cake is carefully washed with fresh water to control the residual chloride to meet customer specifications. The dewatering characteristics of the bicarbonate crystals are very dependent on operating conditions in the crystallizing columns. Air drawn through the vacuum filter (or the vent gas from the centrifuge operation) is returned to the absorption section. The filter cake, often called “crude bicarbonate” or “ammonia soda”, liquor and is made up of sodium bicarbonate and small amounts (5 mol% on a dry basis) of ammonia primarily in the form of ammonium bicarbonate. The cake is then conveyed to the calcining operation.

Recovery of Ammonia: The “filter liquor” contains unreacted sodium chloride and substantially all the ammonia with which the brine was originally saturated, present as “fixed” and “free” ammonia. The “fixed” ammonia or ammonium chloride corresponds stoichiometrically to the sodium bicarbonate that had been precipitated. “Free” ammonia includes ammonium hydroxide, bicarbonate, carbamate, and the several possible carbon compounds of ammonia that decompose at moderate temperatures. Before preheating, sulfide solution may be added for corrosion protection. The sulfide is distilled for eventual absorption by the brine in the absorber. The filter liquor is preheated by indirect contact with the gases leaving the distiller. The warmed feed liquor then enters the main coke-, or bubble cap – filled sections of the distiller where heat decomposes free ammonium compounds and steam strips almost all of the free ammonia and carbon dioxide.

The carbon dioxide – free solution is usually treated with milk of lime (or anhydrous lime) in an external well agitated limiting tank called a “prelimer”. Here the ammonium chloride reacts with the milk of lime and evolved ammonia gas is vented back to the distiller. The resulting hot calcium chloride solution, containing residual ammonia in the

form of ammonium hydroxide, flows back to a lower section of the distiller. Low pressure steam sweeps practically all of the ammonia out of the limed solution. The final solution, known as “distiller waste”, contains calcium chloride, unreacted sodium chloride, and the excess lime, and is diluted by the condensed steam and the water in which the lime was conveyed to the reaction. Distiller waste also contains the inert of this solution. However, the waste liquors are usually pumped to settling basins where the suspended solids are deposited. The clear overflow contains dissolved salts, which are objectionable contaminants are locations where the quality of the receiving waters is materially affected. Close control of the distillation is required to thoroughly strip carbon dioxide to avoid waste of lime and achieve nearly complete ammonia recovery. The hot (56°C) mixture of wet ammonia and carbon dioxide leaving the top of the distiller is cooled to remove water vapor before being sent to the absorber.

Lime Preparation: The most suitable limestone, hard and strong with low concentrations of impurities, is graded to reasonably uniform coarse size. Although other fuels may be used, the limestone is usually mixed with about 7% metallurgical – grade coke or anthracite and then burned in vertical shaft kilns. Air is admitted continuously into the bottom of the kiln and gas is sucked off the top. The fuel burns in a zone a little below the middle of the kiln, and the stone “burns” to lime. Carbon dioxide is generated by decomposition of limestone and combustion of carbon in the fuel. The kiln gases are diluted with nitrogen from the air used to burn the fuel and usually stone dust, ash particles, and gaseous impurities. The gas is partially cooled in the kiln by the upper layers of stone, and further cooled and cleaned before entering the compressors feeding the carbonating columns.

The lime, cooled somewhat by the entering air in the lower parts of the shaft kiln is discharged intermittently and usually in rotary slackers that produce a thick suspension, commonly called “milk of lime”, which is stored in agitated tanks. The heat of the reaction produces milk of lime at a temperature of 90-100°C; water addition is controlled to give a free calcium oxide. In some operations, dry lime is used in place of the milk of lime. It is pulverized and added continuously to the preimer in the distillation step, thus

reducing the water added and steam consumption and producing a concentrated distiller waste.

Calcining the Bicarbonate to Soda Ash: To prevent dilution of the decomposition gases, the crude filtered bicarbonate is continuously calcined by indirect heating. Various techniques are used to heat the material in which is recycled after compression to enrich the makeup kiln-gas feed to the carbonation operation. The hot soda ash discharged from the calciner is cooled, screened, and packaged or shipped in bulk. This product, called “light ash” because of its low bulk density, is converted to dense ash.

By-Products:

Calcium Chloride: Relatively few synthetic soda ash plants recover calcium chloride, and most of those that do utilize only a small part of the total amount available in the distiller waste. To produce calcium chloride, the distiller waste liquor is settled and then evaporated in multiple – effect evaporators. During concentration most of the sodium chloride separates. The remaining solution is further concentrated to the equivalent of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. this solution is cooled, forming flakes which are dried in a rotary dryer, giving a product sold as 77-80% calcium chloride. A small amount is processed to the anhydrous state. Calcium chloride is used on unpaved roads as a dust abater and as a deicer on highways in winter. It is used for freeze proofing and dust proofing coal and coke, in refrigeration brines, as a drying agent, and in cement products.

Ammonium Chloride: Ammonium chloride is the principal salt present in the mother liquor from the crude sodium bicarbonate filtration in the ammonia – soda process. Small amounts have been produced in soda ash plants by carbonation of the filter liquor, concentration, and crystallization of the ammonium chloride. Most of the demands in the United States are low – tonnage. The end uses are primarily in dry cells and fluxing agents.

However, ammonium chloride is also a good fertilizer for important crops in rainy climates, particularly for rice. In Japan, the production of by-product ammonium

chloride is quite large. In one process for manufacturing large quantities of by-product ammonium chloride, more ammonia is first added to the filter liquor, which is chilled to approximately 10°C. Solid sodium chloride is added, dissolved, and ammonium chloride precipitates, which is separated for sale, the mother liquor being recycled to the carbonation operation. There are significant differences in equipment of the conventional ammonia – soda process and the ammonium chloride producing soda ash process. For example, there is no ammonia recovery and therefore no distillation tower, likewise, no milk of lime and consequently no lime kilns which are also the source of carbon dioxide for bicarbonation. However, the ammonium chloride producing process requires, unlike the regular ammonia – soda plant, equipment to process solid salt, and of the ammonium chloride production, crystallizers, filters, dryers, and cooling equipment of corrosion resistant materials. In addition, an ammonia source is required which preferably also supplies carbon dioxide for the bicarbonation.

Advantages of Solvay process

- Can use low-grade brine
- Less electric power
- Less corrosion problems
- No co-products to dispose of
- Does not require ammonia plant investment

Disadvantages of Solvay process

- Higher salt consumption
- Higher investment in ammonia recovery unit verses crystallization units for ammonium chloride
- Waste disposal of calcium chloride brine stream
- More steam consumption
- Higher capacity plant for economic break-even operation
- With current fertilizer shortage, all of the ammonium chloride will be used as a mixed chemical fertilizer ingredient, so co-product disposal no problem.