

# **Part 1**

# **Manufacturing sodium carbonate**

**An overview for teachers**

# Manufacturing sodium carbonate – an overview for teachers

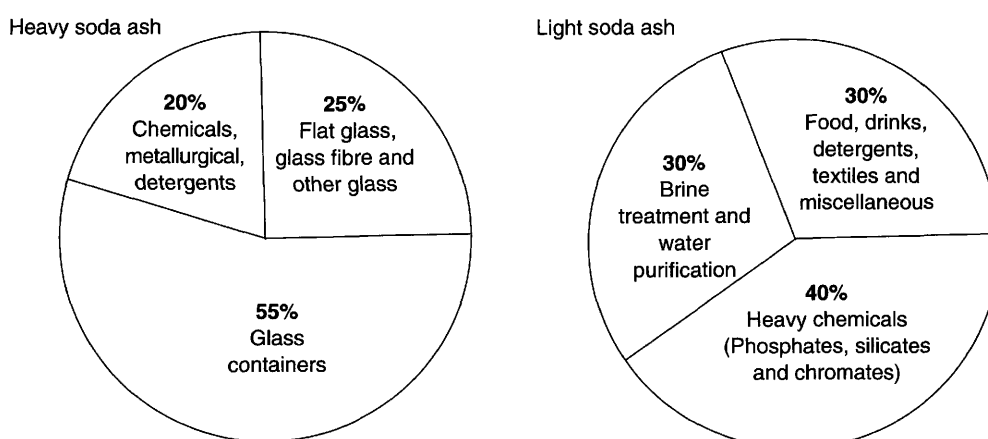
Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is used by many different industries as a raw material, and about one million tonnes is produced each year in the UK – all of it by the Brunner Mond Company in Northwich, Cheshire. Also produced in smaller quantities is sodium hydrogencarbonate ( $\text{NaHCO}_3$ ) as well as calcium chloride ( $\text{CaCl}_2$ ) – a by-product, a little of which can be sold.

Industrially, sodium carbonate is usually referred to as 'soda ash' and is produced and sold in two grades:

- ▼ 'light ash' – a fine powder; and
- ▼ 'heavy ash' – which has a bigger particle size and is more dense, making it less bulky to transport.

Sodium hydrogencarbonate is used in:

- ▼ water treatment;
- ▼ as an additive in food and drinks – eg baking powder;
- ▼ for blowing foams such as expanded polystyrene;
- ▼ in pharmaceutical products as an antacid;
- ▼ in personal care products such as toothpaste; and
- ▼ as an additive in animal feeds.



**Fig 1 The uses of sodium carbonate**  
Exact percentages will vary with economic and social factors

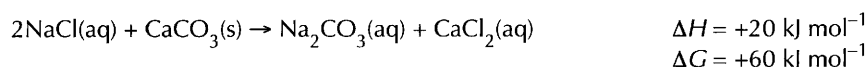
Figure 1 gives an approximate breakdown of the uses of light ash and heavy ash but these are subject to change depending on a number of social and economic factors. For example, in a recession, fewer cars and houses are built, which reduces the demand for glass. Importing of alcoholic drinks from the continent due to more liberal customs regulations has led to a decrease in the number of glass bottles made in the UK and thus a drop in demand for heavy ash.

## The Solvay process

This process has been used for making sodium carbonate and sodium hydrogencarbonate since the late 19th century when it began to replace the Leblanc process. No more effective process has been found. The Solvay process uses salt (sodium chloride) to provide the sodium ions and limestone (calcium carbonate) for the carbonate ions in the sodium carbonate.

Salt and limestone are cheap and plentiful raw materials. Salt is found in underground deposits in Cheshire. It is extracted by solution mining as brine which is then pumped to the site and treated to precipitate out calcium and magnesium ions. The calcium carbonate is quarried as limestone near Buxton in Derbyshire and arrives on site by rail.

The reaction below seems to be the obvious way to prepare sodium carbonate from sodium chloride and calcium carbonate.



Unfortunately salt and limestone do not react together. The value of  $\Delta G$  shows that the equilibrium lies well to the left, so an indirect route must be used. In fact calculating  $K_c$  from the expression  $\Delta G = -RT \ln K_c$  gives a value of

$K_c \approx 1 \times 10^{-10} \text{ dm}^3 \text{ mol}^{-1}$ . Furthermore, the overall reaction is endothermic and so a significant input of heat energy is required. This is provided by burning coke which thus becomes the third raw material. This is transported to the site by road.

The key reaction is that between sodium chloride solution and carbon dioxide in the presence of ammonia. This is a reversible reaction forming ammonium chloride and sodium hydrogencarbonate. It occurs in 25 metre-high Solvay towers where a downward flow of ammonia dissolved in brine meets an upward flow of carbon dioxide.



Energy for the overall process is provided by burning coke.



The heat generated by this reaction is used to decompose the calcium carbonate to provide the carbon dioxide.

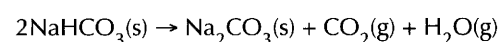


The  $\Delta H$  values show that two moles of calcium carbonate can be decomposed with the heat energy from one mole of coke, and this approximate ratio is used in practice. Both reactions produce carbon dioxide for the process.

Returning to the key reaction.



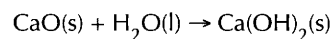
Sodium hydrogencarbonate is much less soluble than ammonium chloride at low temperature and crystallises out. The equilibrium in the Solvay tower reaction thus moves to the right. The reaction is exothermic ( $\Delta H = -79 \text{ kJ mol}^{-1}$ ), so the tower is cooled to keep the temperature at its base down to about 25 °C. The sodium hydrogencarbonate is filtered out and heated to form sodium carbonate ('light ash').



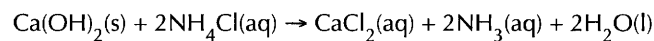
The carbon dioxide is recycled.

The calcium oxide from the decomposition of the limestone is slaked with water to form calcium hydroxide.

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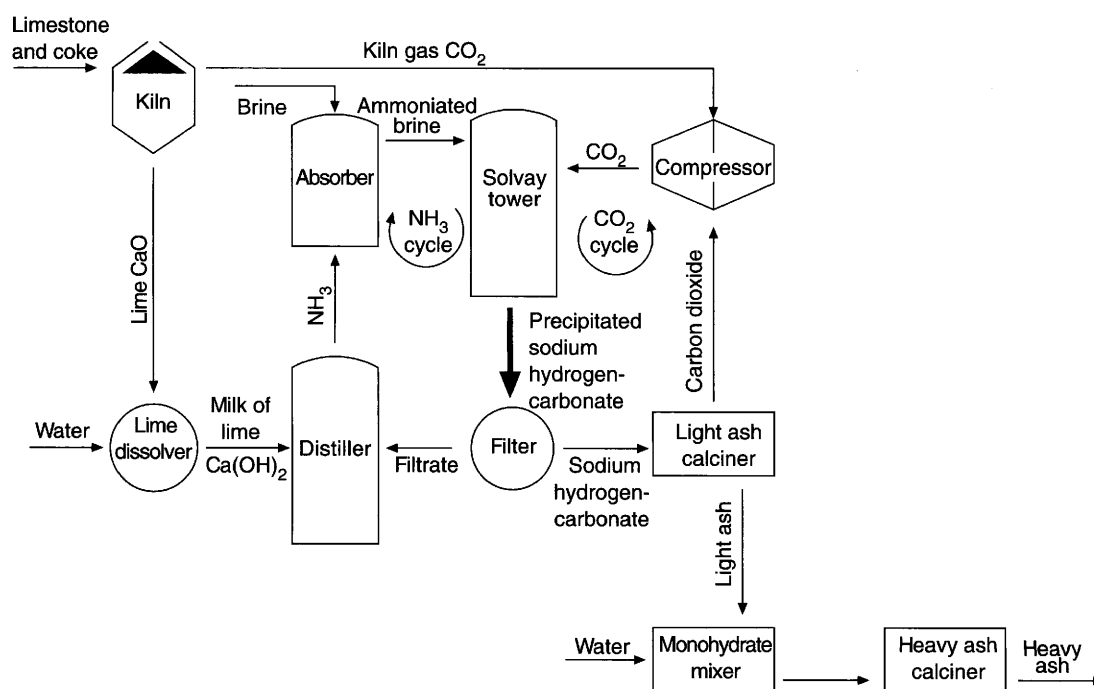


This is used to regenerate the ammonia in the distiller.

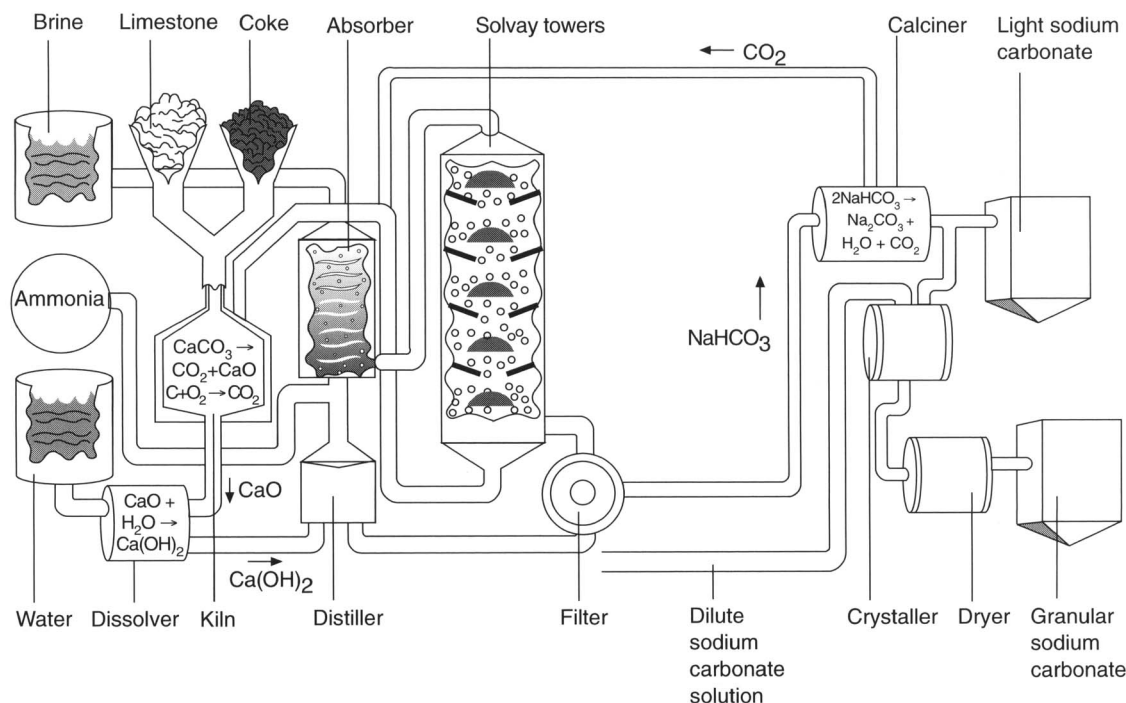


The ammonia is recycled.

The overall process is shown in a simplified form in *Figure 2* and more pictorially in *Figure 3*. It operates as two cycles, an ammonia cycle and a carbon dioxide cycle. In theory, no ammonia is used up; it is all recycled. In practice, a little is required to make up losses.



**Fig 2 A simplified flow diagram for the Solvay process showing the ammonia and carbon dioxide cycles**



**Fig 3 The Solvay process**

The Solvay process manufactures three different products – light sodium carbonate (light ash), granular sodium carbonate (heavy ash) and refined sodium hydrogencarbonate.

#### **Light sodium carbonate (light ash)**

This is made by taking filtered sodium hydrogencarbonate and heating it. This drives off water and carbon dioxide, which can be recycled. The product is a very fine white powder.

#### **Granular sodium carbonate (heavy ash)**

Light sodium carbonate is made into a slurry with water, to form sodium carbonate monohydrate. This is then heated to produce the anhydrous form as much larger crystals. These crystals have a particle size similar to that of sand so that the two make a homogeneous mixture which is important for glass making – the major use for heavy ash.

#### **Refined sodium hydrogencarbonate**

Crude sodium hydrogencarbonate is filtered and decarbonated and dehydrated by heating to give sodium carbonate. This is dissolved in water and the resulting solution is filtered to remove impurities. Highly pure sodium hydrogencarbonate crystals are formed by reacting the filtered solution with carbon dioxide. These crystals are then centrifuged and dried in a carbon dioxide atmosphere. The product is one of the purest industrial chemicals, and can be added to foods and pharmaceutical products.

The main by-product of the Solvay process is calcium chloride. A little of this can be sold for use in refrigeration, curing concrete and as a suspension in oil drilling. The bulk of calcium chloride is disposed of in the nearby river Weaver.

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## Alternative sources of sodium carbonate

So-called natural ash can be obtained from lakes containing alkaline brine and sodium sesquicarbonate dihydrate, (trona) ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ). Such deposits are found in a number of areas of the world including Kenya, Egypt and the US. In Wyoming, US, the deposits are about 500 m below the surface and are accessed by deep mining techniques.

Trona can be converted to soda ash by heating to 500 °C followed by recrystallisation from aqueous solution.

## Interesting facts concerning the industrial process

### Corrosion of the plant

The ammonia used in the process comes, not from the Haber process as might be expected, but as a by-product of making coke for this and other processes. (The Solvay process, of course, pre-dates the Haber process.) This ammonia contains traces of both hydrogen sulfide and cyanide ions. Most of the Solvay process plant is made of cast iron and those parts of it which are kept at a high temperature (such as the distillers) tend to corrode in contact with a hot, aqueous solution containing chloride ions.

However, hydrogen sulfide reacts with the iron to form hard, insoluble iron(II) sulfide which coats the inside of the plant and prevents corrosion. In some locations, where hydrogen sulfide is driven out by boiling, the cyanide ions react to form hexacyanoferrate(II) ions which react further with the iron to give a very hard, dark blue coating of  $(\text{NH}_4)_2\text{Fe}[\text{Fe}(\text{CN})_6]$ .

When this impure ammonia was replaced by purer Haber process ammonia the distillers corroded severely within a matter of months. Nowadays, the plant uses coal tar ammonia or, if Haber process ammonia is used, small quantities of cyanides and sulfides are added as corrosion inhibitors.

### The limestone kilns

The coke and limestone are mixed in a kiln and ignited. While the kiln is in continuous operation, the incoming coke ignites automatically at the temperature of the kiln. The coke used is produced to very detailed specifications. It must be strong enough to withstand being crushed by the limestone when it is tipped into the kiln. It must also have a specified calorific value – ie the amount of heat given out on burning a specified amount of coke – to produce the correct amount of energy. Because it is stored outside in heaps and may absorb rainwater, it is measured by volume and not mass.

Not all of the limestone decomposes in the kiln. After slaking, the unreacted calcium carbonate (called 'backstone') is removed from the dissolver and returned to the kiln. About 6 per cent of the limestone is returned as backstone.

### Lighting the kilns

The kilns normally run continuously. However when they do need to be relit (a process which occurs only once every 12–15 years), the process is somewhat arcane. Railway sleepers and rags soaked in creosote are placed in the kiln along with a small amount of coke. A gunpowder charge is used to ignite this and then more coke added as it catches light, producing puffs of smoke from the top of the kiln. This process is irreverently called 'electing the Pope'. Gradually the coke being added is enriched in limestone until the correct proportions are reached.

### Hot water effluent

Hot water from the process is put into the nearby river Weaver. This has encouraged the local fish in this area to migrate to the outflow pipe. 30 lb carp have been caught close to the plant.

**Aggregate tax**

The government has proposed (1999) a tax of £5 per tonne on limestone quarried for aggregate – the stone used for road building. If this tax is also levied on limestone used as a chemical (as in the Solvay process), it will affect the cost of sodium carbonate and hence the cost of glass *etc.*

**Commodity chemicals and speciality chemicals**

Commodity chemicals are those with reasonably high specifications which are sold in thousands of tonnes but at relatively low prices. Speciality chemicals have very high specifications and are sold in much smaller quantities but at higher prices. There is no precise definition of either term. Both sodium carbonate and sodium hydrogencarbonate can be considered as a commodity chemical or a speciality chemical depending on the exact specification in terms of purity, particle size, *etc.*

**Further information**

Further details of the Solvay process can be obtained from the following sources.

*The essential chemical industry (4th ed)*. York: The Chemical Industry Education Centre, 1999.

Sodium carbonate, R D A Woode, *Steam*, issue 7, April 1987.

There is a section on solution mining for salt in Cheshire in the clip *Chemicals from salt* in the video *Industrial chemistry for schools and colleges*, London: RSC, 1999.

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