Part 4

Manufacturing sodium carbonate by the Solvay process

An overview of the process for post-16 students
Manufacturing sodium carbonate by the Solvay process

Sodium carbonate 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 hydrogen carbonate as well as calcium chloride as 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 more efficient to transport.

Sodium hydrogen carbonate 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.

Figure 1 gives an approximate breakdown of the uses of light 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. Importation 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 uses sodium chloride to provide the sodium ions and calcium carbonate for the carbonate ions in 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 pumped to the Northwich 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.

At first sight, the reaction below seems to be the obvious way to prepare sodium carbonate from sodium chloride and calcium carbonate.

\[ 2 \text{NaCl(aq)} + \text{CaCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{CaCl}_2(aq) \]

Unfortunately salt and limestone do not react together. In fact the reverse reaction actually takes place between calcium chloride and sodium carbonate to give the original starting materials, so an indirect route must be found. Furthermore, the overall reaction is endothermic and so a significant energy input 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 hydrogen carbonate. It occurs in 25 metre high Solvay towers.

\[ \text{NaCl(aq)} + \text{NH}_3(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \leftrightarrow \text{NH}_4\text{Cl(aq)} + \text{NaHCO}_3(s) \]

Energy is provided by burning coke, and the heat generated is used to decompose the calcium carbonate to provide carbon dioxide for the process.

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]

Returning to the key reaction.

\[ \text{NaCl(aq)} + \text{NH}_3(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g) \leftrightarrow \text{NH}_4\text{Cl(aq)} + \text{NaHCO}_3(s) \]

At low temperatures the sodium hydrogen carbonate is much less soluble than ammonium chloride and crystallises out. This moves the equilibrium in the Solvay tower reaction to the right. The sodium hydrogen carbonate is filtered out and heated to form sodium carbonate.

\[ 2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g) \]

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

\[ \text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(s) \]

The calcium hydroxide is used to regenerate the ammonia.

\[ \text{Ca(OH)}_2(s) + 2\text{NH}_4\text{Cl(aq)} \rightarrow \text{CaCl}_2(aq) + 2\text{NH}_3(aq) + 2\text{H}_2\text{O}(l) \]

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.
Three different products are formed from this process, light sodium carbonate (light ash), granular sodium carbonate (heavy ash) and refined sodium hydrogen carbonate. The main by-product 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 it is disposed of in the nearby river Weaver.
Light sodium carbonate (light ash)

This is made by taking the filtered sodium hydrogencarbonate and heating it. This drives off the water and the 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 mix easily, 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 crystals of sodium hydrogencarbonate 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.