Kirk-Othmer Encyclopedia of Chemical Technology.

SODIUM CARBONATE

Sodium carbonate [497-19-8], Na_2CO_3, also known as soda ash, is produced from both natural deposits and synthetic methods based on the Solvay process. Annual world production capacity is estimated at almost 44×10^6 metric tons. It is an essential ingredient in the production of glass, chemicals, soaps, detergents, pulp and paper.

1. Occurrence

Sodium carbonate deposits and brines exist around the world (1–7). Although there are several minerals that contain sodium carbonate, traditionally only trona, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$, and more recently nahcolite, $NaHCO_3$, are of commercial interest. Each deposit has its own distinctive characteristics and requires slightly different processing techniques.

The Green River Formation in Wyoming contains bedded trona deposits over an area of about 3400 km^2 (1, 2). Beds range in thickness from 1 to 11 m; mining heights are usually 2 to 3 m. The trona is interbedded with fine silt and shale containing associated organic materials such as oil shale. Estimates are that the deposit contains over $100{,}000 \times 10^6$ metric tons of trona, sufficient to satisfy world demand for over 2000 years. Room and pillar, longwall and shortwall mining techniques along with solution mining methods are used.

The Piceance Creek area in Colorado contains nacholite. This deposit is being solution mined by the newly formed American Soda Corporation.

Searles Lake, California is a large evaporite deposit about 78 km square and 46 m deep. The brine contains a complex mixed salt system that includes trona along with potassium, boron and other salts (8, 9).

Lake Magadi, about 19 km long and 3 km wide, is in the Great Rift Valley of East Africa (10). It is about 1830 m above sea level, has no outlet, and is fed by alkali springs which upon evaporation leave behind trona and other salts. Raw trona is dredged up from the lake and sent to an on-shore refining plant.

Lake Texcoco, a few miles northeast of Mexico City, is in the lowest part of the Valley of Mexico. The lake is mostly dry and alkali is recovered from brine wells that have been drilled into the underlying structure.

Owens Lake is a relatively small alkali deposit in Southern California where small amounts of crude trona are recovered and sold (11, 12).

Sodium carbonate brines are also produced near Sua Pan, Botswana (13, 14).

2. Properties

Physical properties of the various hydrates of sodium carbonate are given in Table 1. It is readily soluble in water (see Table 2) and the resulting solutions are alkaline, as expected from a salt formed from a strong base and a weak acid. At 25°C the pH of 1, 5 and 10 wt% solutions are 11.37, 11.58 and 11.70, respectively.

Table 1. Physical Properties of Sodium Carbonate[a]

	Value			
Property	Na_2CO_3	$Na_2CO_3 \cdot H_2O$	$Na_2CO_3 \cdot 7H_2O$	$Na_2CO_3 \cdot 10H_2O$
melting point	825			
bulk density, g/mL	0.59–1.04			
specific gravity	2.533			
heat of formation, ΔH_f, kJ/mol[b] at 0°C	−1131	−1459	−3201	−4082
temperature, °C, stable solid phase	>109	35.4–109.0	32.0–35.4	0–32.0

[a] Refs. 15–18.
[b] To convert kJ/mol to kcal/mol, divide by 4.184.

Table 2. Solubility Data for Sodium Carbonate[a]

Temperature, °C	Na_2CO_3 in saturated solution, wt %
0	6
10	8.5
20	17
30	28
40	32.3
50	32.0
60	31.7
70	31.0
80	30.8
90	30.8
100	30.8

[a] Ref. 17.

3. Manufacture and Processing

Sodium carbonate is readily produced from either natural deposits or by synthetic pathways. Discussion here focuses on production from trona and from the Solvay synthetic process since these two account for the vast majority of current industrial capacity.

3.1. Recovery From Trona

Two basis types of processes are used to produce sodium carbonate from trona: the monohydrate process and the sesquicarbonate process, both named after the crystalline intermediates formed in each process. Most ash is made using the monohydrate process. Figure 1 outlines the main steps for each process.

In the monohydrate process (19), trona is ground and calcined (150–300°C) to a crude soda ash in either a rotary gas-fired or coal grate-fired calciner. The calciner product is then leached with hot water and the clear, hot liquor is sent to a set of evaporative crystallizers (40–100°C) where sodium carbonate monohydrate is produced. Both multiple effect and mechanical vapor recompression (MVR) crystallizers are used. Some producers send the liquor through activated carbon beds before crystallization to remove trace organics from the solution. The organics, solubilized from the oil shale, can affect crystallizer performance by foaming and changing crystal growth rates and habit. Other trace contaminants are removed from the system by purging small amounts of mother liquor. Weak liquors and insolubles are removed by clarifiers and subsequent filtration. The insolubles are washed to recover any additional alkali.

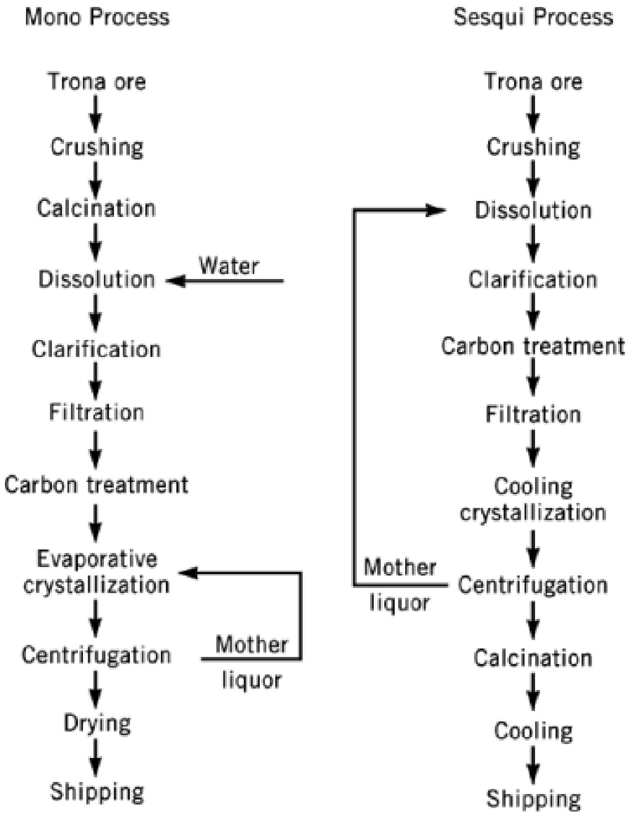

Fig. 1. Simplified flow diagrams for soda ash from trona.

Sodium carbonate monohydrate crystals from the crystallizers are concentrated in hydroclones and dewatered on centrifuges to between 2 and 6% free moisture. The centrifuge cake is sent to dryers where the product is calcined (150°C) to anhydrous soda ash, screened, and readied for shipment. Soda ash from this process typically has a bulk density between 0.99–1.04 g/mL with an average particle size of about 250 μm.

In the sesqui process (20), the crushed ore is dissolved in hot (95°C) return liquor, clarified, filtered and sent to cooling crystallizers where sodium sesquicarbonate [6106-20-3], $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ is formed. Carbon is added to the filters to control any crystal modifying organics. The sesquicarbonate crystals are hydrocloned, centrifuged, and calcined (110–175°C) using either indirect steam heat or combustion gases. This product has a typical bulk density of around 0.89 g/mL. Densities similar to the monohydrate ash may be achieved by subsequently heating the material to about 350°C. Alternatively, the ash can be converted to the monohydrate and then calcined.

3.2. Solvay Process

The first plant using the Solvay process was built in 1863. Although the chemistry is more involved compared to extraction from natural sources, plants based on the Solvay process have the advantage that the required raw materials are more widely available than natural alkali deposits. The natural alkali processes enjoy low production cost advantages, but synthetic processes often enjoy logistical advantages.

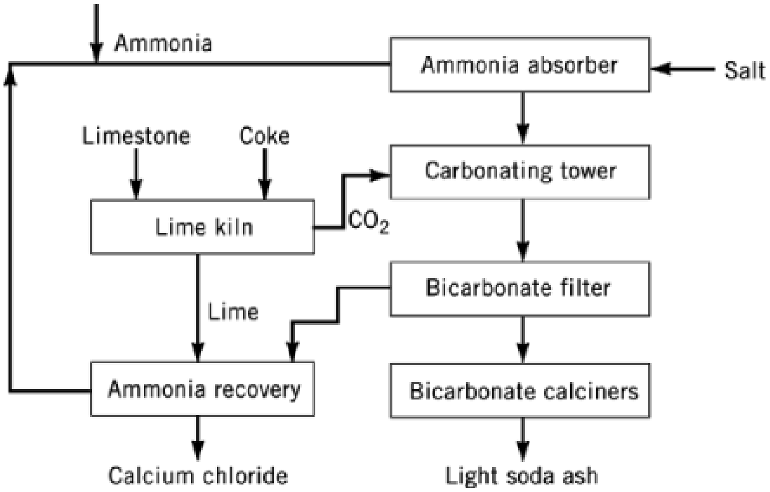

Fig. 2. Simplified Solvay flow diagram.

The overall chemical reaction,

$$2\ NaCl + CaCO_3 \longrightarrow Na_2CO_3 + CaCl_2$$

takes place in a series of process steps. A simplified flow diagram for the Solvay process is given in Figure 2.

Crude sodium chloride brine is first purified to prevent scaling of downstream process equipment and to prevent contamination of the final product. Magnesium ions are precipitated with milk of line, $Ca(OH)_2$, and the calcium ions are precipitated with soda ash.

After purification, the brine solution is contacted with ammonia gas:

$$NH_3 + H_2O \longrightarrow NH_4OH$$

The absorption is exothermic, requiring the removal of 1650 MJ/t. Most of the ammonia is recycled from downstream steps, although some make-up is required.

The ammoniated brine is then sent to the carbonating columns where sodium bicarbonate is precipitated by contacting the brine with carbon dioxide

$$2\ NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$
$$(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow 2\ NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow NH_4Cl + NaHCO_3$$

Sodium bicarbonate is less soluble and precipitates on the internals of the carbonating column. At the end of the make cycle, the slurry is drained and the solid bicarbonate is filtered. However, considerable amounts of bicarbonate remain in the column after the slurry is drained. The column is cleaned by passing fresh feed liquid feed through the column with only a limited amount of carbon dioxide feed to keep the effluent below the saturation limit for sodium bicarbonate. The liquid from the cleaning column is used as the feed to other columns in the make cycle, thus a series of five or more columns with appropriate piping interconnections are used for continuous operation.

The carbonation is favored by higher pressures since this forces the carbon dioxide into solution. Typical operating pressures are around 414 kPa (60 psi). The reactions in the carbonating column are exothermic, requiring the removal of 1450 MJ/t. This heat is removed by internal cooling coils in the column. Temperature profile in the column is closely controlled since this affects crystal nucleation and growth, which in turn influences filtration characteristics. Typically, the top of the make column is ca 25°C, the middle is ca 55°C and the bottom is ca 20°C.

The slurry from the carbonating columns is fed to continuous vacuum filters or centrifuges where the sodium bicarbonate crystals are recovered. The filter cake is carefully washed to control residual chloride while maintaining acceptable yield. Yield losses on washing are on the order of 10%.

The filtrate is then calcined at 175–225°C to produce sodium carbonate, carbon dioxide and water vapor:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

Carbon dioxide is recovered, compressed and recycled back to the carbonating columns as needed. Various calciner designs have been developed to deal with the caking tendencies of the sodium bicarbonate feed.

The hot soda ash discharged from the calciner is cooled, screened, and either packaged or shipped in bulk. This product, called light ash or technical grade soda ash, has a bulk density of around of 0.590 g/mL.

Dense ash is manufactured by hydrating light ash to produce the larger sodium carbonate monohydrate crystals, followed by dehydration. Hydration is accomplished either by feeding light ash and water to a blender or by adding light ash to a saturated soda ash solution containing monohydrate crystals. The monohydrate crystals are then fed to a continuous dryer and the dehydrated product is screened before packaging and shipping. Bulk densities typically run between 0.960–1.040 g/mL.

The original Solvay process was developed prior to the Haber process for ammonia production, thus ammonia was considered as a valuable chemical at the time. The traditional Solvay process recovers ammonia by reacting the ammonium chloride in the filtrate liquor with milk of lime

$$2\,NH_4Cl + Ca(OH)_2 \longrightarrow 2\,NH_3 + CaCl_2 + H_2O$$

This reaction is carried out in a steam stripping system of special design to prevent precipitation of calcium carbonate. The calcium chloride by-product solution was traditionally discharged into local waterways, although this practice is no longer acceptable in the United States. Asahi Glass (21–23) has developed alternatives to the traditional Solvay process in which the ammonium chloride is recovered as a marketable fertilizer product, thus circumventing the calcium chloride waste issue.

The milk of lime and much of the carbon dioxide needed in the Solvay process are produced from limestone. The reaction is carried out in a kiln at 950–1100°C.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Usually metallurgical grade coke is mixed with the limestone as a fuel. Carbon dioxide is recovered from the exhaust by filtration to remove entrained dust, compressed and sent to the carbonization columns. The lime is cooled and slaked with water.

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

An excess of water is used to produce a thick suspension called milk of lime. In some operations, dry lime is used to produce a more concentrated calcium chloride by-product stream.

Table 3. U.S. Soda Ash Producers[a]

Company	Location	Capacity, 10^3 t/yr
American Soda Corporation	Parachute, Colorado	727[b]
FMC	Green River, Wyoming	4,409
General Chemical	Green River, Wyoming	2,545
IMC	Argus, California	1,409
OCI Wyoming	Green River, Wyoming	2,000
Solvay Minerals	Green River, Wyoming	2,091
Total		*12,455*

[a] Ref. 26

[b] Was Scheduled for Nov. 2000 start-up; not included in total.

3.3. Other Processes

The Leblanc process is of historical interest. It was developed in the late 1700s. In this process, sodium chloride reacts with sulfuric acid to produce sodium sulfate and hydrochloric acid. The sodium sulfate is then roasted with limestone and coal and the resulting sodium carbonate–calcium sulfide mixture (black ash) is leached with water to extract the sodium carbonate. Poor economics and excessive pollution caused by the hydrochloric acid and calcium sulfide by-product led to the eventual demise of the Leblanc process. Reference 24 presents a historical case study of the English and German chemical industries that illustrates why the Leblanc process continued to be used for 50 years after the introduction of the Solvay process, even though the Solvay process is a better process.

4. Economic Aspects

The share of world production held by natural soda ash is climbing. In 1993, world production was split 70/30 in favor of synthetic. By 1997, this ratio had decreased to about 67/33 and by 2002 it is expected to reach 63/37. Low production costs and limited environmental impact favor continuation of this trend.

Annual world capacity is estimated at almost 44×10^6 metric tons in 1998 (25). The United States, China and Russia combined have a 60% share of installed world capacity. India, Germany, Ukraine, France, the United Kingdom, Italy, Bulgaria and Romania also have significant capacity.

Table 3 lists current United States producers and the year 2000 capacities. Consolidation has reduced the number of producers to five. Several Asian and Western European companies have recognized the long term strategic advantages posed by the U.S. natural resources and have acquired equity stakes in U.S. operations.

In October 1999, FMC announced it would temporarily idle 650,000 short tons of capacity pending improved markets. OCI brought on a new 800,000 short ton facility in late 1998 while at the same time idled 900,000 short ton/yr of older capacity. Solvay Minerals has announced a 400,000 short ton/yr expansion for late 2000. A new producer, American Soda Corporation, was scheduled to begin operation in November 2000.

Historical lists prices during 1994–2000 range from \$108–115/t (\$98–105 per US ton) dense ash for carloads fob Green River, Wyoming. Market prices are in the range of \$79–83/t (\$72–75 per US ton) for large quantities.

Table 4. Typical Properties of Commercial Soda Ash

			Synthetic ash		Natural ash (U.S.)	
Property			Light	Dense	Intermediate	Dense
bulk density, g/mL			0.59	1.04	0.80	1.04
NaCl, ppm			8000–1000	5000–300	300	300
Na_2SO_4, ppm			200	200	300	300
Fe_2O_3, ppm			80–20	80–20	5	3
size distribution, cumulative % on sieve no.	+ 40	size, μm 420	3	11	10	11
	+ 100	149	17	90	89	90
	+ 200	74	63	99	99	99
	+ 325	44	86	99	99	99
pore volume, mL/g			0.4	0.1	0.3	0.1
shape[a]			A	M	N	M

[a] Particle shapes are classified as acicular, A, monoclinic and blocky, M, or monoclinic and needle, N.

5. Grades, Specifications and Quality Control

All commercial grades are chemically similar. As shown in Table 4, bulk density differences are the main distinguishing feature.

6. Environmental Concerns

The major waste products from the natural soda ash processes are the tailings which are mostly insoluble shale and other minerals associated with the trona. These solids along with purge liquors containing organic and trace impurities are sent to large evaporation ponds for recovery of the residual alkali.

Traditional Solvay plants produce large quantities of aqueous calcium chloride. The major market for calcium chloride is as a road de-icer. Unfortunately the calcium chloride market is small compared to the quantities produced by Solvay plants. Pricing and volumes often do not justify recovery of calcium chloride. The solution is often disposed as a liquid waste into local waterways or deep underground wells. This practice is not allowed in the United States; The United States currently only produces sodium carbonate from natural deposits.

7. Health and Safety Factors

Under National Fire Protection Association (NFPA) Designation 704, soda ash is classified as a moderate health hazard. Exposure to soda ash dust may cause severe eye and slight nose and throat irritation. Repeated contact may affect the skin causing redness, dryness, and cracking. First aid procedures are to flush or wash the affected part with water for 15 minutes, obtaining medical attention if the irritation persists.

Simultaneous exposure to the dusts of lime and soda ash should be avoided. The two react to form caustic soda in the presence of moisture or perspiration.

Soda ash is strongly alkaline and should not be stored with acids. It is midly hygroscopic and generally stored in closed bins or multiwalled kraft bags.

Table 5. Soda Ash Use[a]

Category	% of U.S. consumption
glass	
container	21.6
flat	18.6
fiber insulation	4.4
other	4.4
Subtotal	*49.0*
chemicals	27.0
soap and detergents	11.0
flue gas desulfurization	3.0
pulp and paper	2.0
water treatment	2.0
miscellaneous	6.0
Total	*100.0*

[a] Ref. 26

8. Uses

Table 5 gives a breakdown of uses for sodium carbonate by market segment. Projected growth rates are 0.8–1.0 %/yr (26). These low growth rates are owing to recent slowing of the world economy and a decline in glass production as plastic continues to displace glass in many applications.

Sodium carbonate is used as a fluxing agent in glass manufacture. Dense ash is preferred because its particle size and bulk density minimizes segregation when mixed with other glass batch materials.

Sodium carbonate is used as an alkali in many soap and detergent applications. Light and intermediate grades of soda ash are preferred for some of these applications where surfactant carrying capacity and dissolution are important.

Aqueous soda ash solutions are used to remove sulfur dioxide from combustion gases, forming sodium sulfite and sodium bicarbonate. Similar solutions are also used in the sulfite paper pulp process (27).

Commercial interest in production of sodium hydroxide by the lime soda process has been revived because of imbalances in the chlorine and caustic markets. FMC and Solvay have about 223,000 t/yr of installed capacity in Wyoming. Similar chemistry is used in green liquor recovery section of the Kraft pulping process and in the bauxite digesters used in the production of alumina.

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