SOLVAY PROCESS FOR MANUFACTURE OF SODA ASH

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INTRODUCTION

1.1 About Solvay Process

The **Solvay process** or **ammonia-soda process** is the major industrial process for the production of sodium carbonate (soda ash). The ammonia-soda process was developed into its modern form by Ernest Solvay during the 1860s. The ingredients for this are readily available and inexpensive: salt brine (from inland sources or from the sea) and limestone (from quarries). The worldwide production of soda ash in 2005 has been estimated at 42 million metric tons, which is more than six kilograms (13 lb) per year for each person on Earth. Solvay-based chemical plants now produce roughly three-quarters of this supply, with the remainder being mined from natural deposits.

1.2 About Soda Ash

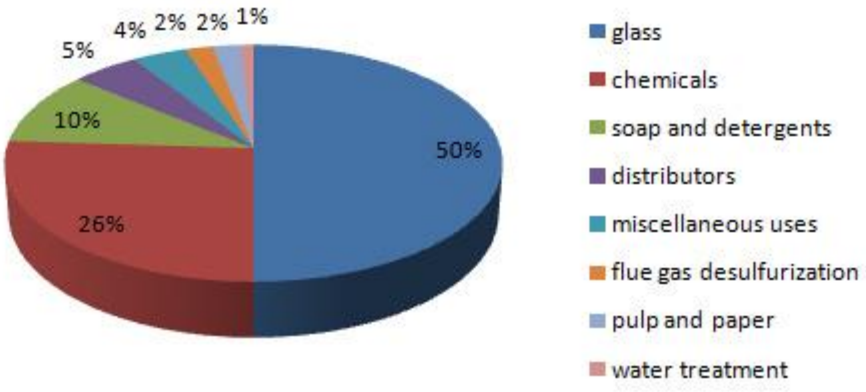
Soda ash, the trade name for sodium carbonate (Na_2CO_3), is a white, anhydrous, powdered or granular material. It is an essential raw material used in the manufacturing of glass, detergents chemicals and other industrial products.

Soda ash is made in three main grades - light, medium and dense. These have the same chemical properties and only differ in physical characteristics, such as bulk density and particle size and shape (which affect flow characteristics and angle of repose).

When companies process and produce soda ash, a number of other sodium compounds are made as co-products, including sodium bicarbonate (also known as baking soda), sodium sulphite, sodium tripolyphosphate, and chemical caustic soda.

1.3 Product usage

Soda ash is an essential raw material used in many applications such as the manufacture of glass, detergents and soaps, chemicals and many other industrial processes.



1.4 General chemical properties of soda ash

Chemical Name		Sodium Carbonate
Molecular Weight		105.989
Melting Point		851^{o}C 1564^{o}F
Specific Gravity	20^{o}/4^{o}C	2.533
Specific Heat	25^{o}C	0.249 cal/gm/^{o}C
	77^{o}F	0.249 Btu/lb/^{o}C
	45^{o}C	0.256 cal/gm/^{o}C
Heat of Fusion	854^{o}C	75.5 cal/gm 135.9 Btu/lb
Heat of Formation	25^{o}C	-2550 cal/gm -4590 Btu/lb
Heat of Hydration	Monohydrate, $Na_2CO_3 \cdot H_2O$	30.0 cal/gm Na_2CO_3 54.0 Btu/lb Na_2CO_3
	Heptahydrate, $Na_2CO_3 \cdot 7H_2O$	156.4 cal/gm Na_2CO_3 281.5 Btu/lb Na_2CO_3
	Decahydrate, $Na_2CO_3 \cdot 10H_2O$	208.8 cal/gm Na_2CO_3 375.8 Btu/lb Na_2CO_3

Solubility	0^oC	7 gms Na_2CO_3 in 100 gms H_2O
	100^oC	44.7 gms Na_2CO_3 in 100 gms H_2O
	35.37^oC (max.)	49.5 gms Na_2CO_3 in 100 gms H_2O
Alkali equivalent		100 % Na_2CO_3 = 58.48 % Na_2O
Acid equivalent		1 lb Na_2CO_3 = 0.6881 lb HCl

REACTIONS AND PROCESS DESCRIPTION

The Solvay process results in soda ash (predominantly sodium carbonate (Na_2CO_3)) from brine (as a source of sodium chloride (NaCl)) and from limestone (as a source of calcium carbonate ($CaCO_3$)). The overall process is:

$$\mathbf{2\,NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2}$$

The steps in the Solvay Process are:

i. Brine Purification
ii. Sodium Hydrogen Carbonate Formation
iii. Sodium Carbonate Formation
iv. Ammonia Recovery

i) Brine Purification

Brine is concentrated by evaporation to at least 30%
Impurities such as calcium, magnesium and iron are removed by precipitation, example

$$\mathbf{Ca^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \rightarrow CaCO_{3(s)}}$$
$$\mathbf{Mg^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mg(OH)_{2(s)}}$$
$$\mathbf{Fe^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)}}$$

Brine solution is then filtered and passed through an ammonia tower to dissolve ammonia.
This process is exothermic, releases energy, so the ammonia tower is cooled.

ii) Sodium Hydrogen Carbonate Formation

Carbon dioxide is produced by the thermal decomposition of limestone, $CaCO_{3(s)}$, in the lime kiln:

$$\mathbf{CaCO_{3(s)} \rightarrow CO_{2(g)} + CaO_{(s)}}$$

Carbon dioxide is bubbled through the ammoniated brine solution in the carbonating tower.

The carbon dioxide dissolves to form a weak acid:

$$\mathbf{CO_{2(g)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + H^+{}_{(aq)}}$$

The ammonia in the brine reacts with H^+ to form ammonium ions:

$$\mathbf{NH_{3(aq)} + H^+{}_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)}}$$

The HCO_3^- then reacts with the Na^+ to form a suspension of sodium hydrogen carbonate:

$$\mathbf{HCO_3^-{}_{(aq)} + Na^+{}_{(aq)} \rightleftharpoons NaHCO_{3(s)}}$$

$NaHCO_3$ precipitates because of the large excess of Na^+ present in the brine which forces the equilibrium position to shift to the right by Le Chatelier's Principle ($NaHCO_3$ is quite soluble in water).
The overall molecular equation for the formation of sodium hydrogen carbonate in the carbonating tower is:

$$\mathbf{NH_{3(aq)} + CO_{2(g)} + NaCl_{(aq)} + H_2O_{(l)} \rightarrow NaHCO_{3(s)} + NH_4Cl_{(aq)}}$$

The net ionic equation for the formation of sodium hydrogen carbonate in the carbonating tower is:

$$\mathbf{NH_{3(aq)} + CO_{2(g)} + Na^+{}_{(aq)} + H_2O_{(l)} \rightarrow NaHCO_{3(s)} + NH_4^+{}_{(aq)}}$$

where Cl^- is a spectator ion

iii) Sodium Carbonate Formation

Suspended sodium hydrogen carbonate is removed from the carbonating tower and heated at 300°C to produce sodium carbonate:

$$\mathbf{2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}}$$

The carbon dioxide produced is recycled back into the carbonating tower.

iv) Ammonia Recovery

CaO is formed as a by-product of the thermal decomposition of limestone in the lime kiln.
This CaO enters a lime slaker to react with water to form calcium hydroxide:

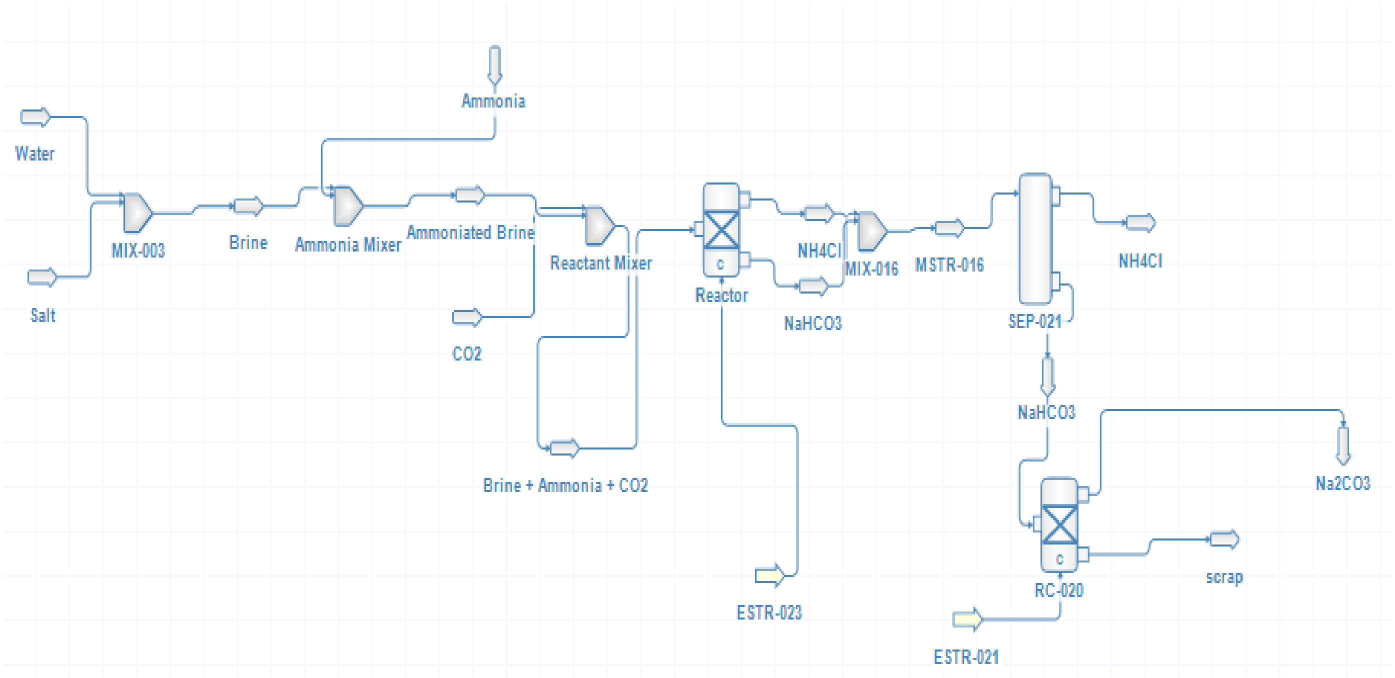
$$\mathbf{CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}}$$

The calcium hydroxide produced here is reacted with the ammonium chloride separated out of the carbonating tower by filtration:

$$\mathbf{Ca(OH)_{2(aq)} + 2NH_4Cl_{(aq)} \rightarrow CaCl_{2(aq)} + 2H_2O_{(l)} + 2NH_{3(g)}}$$

The ammonia is recycled back into the process to form ammoniated brine.
Calcium chloride is formed as a by-product of the Solvay Process.

PROCESS FLOW DIAGRAM



Summary:

Components	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5
Temperature (K)	298.41	298.12	298.15	298.15	298.15
Pressure (Pa)	115000	86000	194000	256000	296000
Mass Flow rate (kg/hr)	117429.78	45990.56	163420.26	37456.548	200876.83
Molar Flow rate (mol/hr)	6523.87	786.16	7310.03	2203.32	9513.35
Mixtures Molar Fractions					
Sodium chloride	0	1	0.107955	0	0.082637
Carbon dioxide	0	0	0	0	0
Ammonia	0	0	0	1	0.231569
Water	1	0	0.892044	0.	0.685759
Ammonium chloride	0	0	0	0	0
Sodium bicarbonate	0	0	0	0	0
Sodium carbonate	0	0	0	0	0

Components	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10
Temperature (K)	298.48	298.55	316.15	314.15	315.15
Pressure (Pa)	48000	244000	34000	27000	289000
Mass Flow rate (kg/hr)	34591.19	235465.02	31544.80	49528.30	81073.10
Molar Flow rate (mol/hr)	786.16	10299.51	539.22	589.62	1128.84
Mixtures Molar Fractions					
Sodium chloride	0	0.076329	0	0	0
Carbon dioxide	1	0.076329	0	0	0
Ammonia	0	0.213924	0	0	0
Water	0	0.633415	0	0	0
Ammonium chloride	0	0	1	0	0
Sodium bicarbonate	0	0	0	1	0.522323
Sodium carbonate	0	0	0	0	0.477676

Components	Stream 11	Stream 12	Stream 13	Stream 14
Temperature (K)	298.44737	298.15	784.15	784.15
Pressure (Pa)	17000	16000	33000	77000
Mass Flow rate (kg/hr)	31544.80	49528.30	55079.72	5551.42
Molar Flow rate (mol/hr)	298.22	297.62	573.62	572.32
Mixtures Molar Fractions				
Sodium chloride	0	0	0	0
Carbon dioxide	0	0	0	0.106523
Ammonia	0	0	0	0
Water	0	0	0	0.744556
Ammonium chloride	1	0	0	0
Sodium bicarbonate	0	1	0	0.164562
Sodium carbonate	0	0	1	0

References:

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