



The association of independent consultants
in mineral resources, metallurgy and chemical industry

Sodium Bicarbonate Market Research in CIS

Sample PDF

*Moscow
September, 2007*

CONTENTS

Introduction	7
I. Production technology for sodium bicarbonate and raw materials used in the Industry	8
I.1. Manufacturing practice for sodium bicarbonate.....	8
<i>Sodium bicarbonate properties</i>	<i>8</i>
<i>Schematic diagram on obtaining purified sodium bicarbonate.....</i>	<i>10</i>
<i>Physicochemical fundamentals of separate stages of production of purified sodium bicarbonate</i>	<i>11</i>
<i>Carbonization of sodium solution.</i>	<i>13</i>
<i>Technological schemes of production of purified sodium bicarbonate</i>	<i>15</i>
<i>Dry method of sodium bicarbonate production.</i>	<i>18</i>
I.2 Key suppliers of raw materials in Russia and Ukraine.....	20
I.3. Destinations and volumes of supplies of raw materials in Russia.....	23
II. Production of sodium bicarbonate in the CIS countries.....	24
II.1. Quality of production.....	24
II.2 Volume of production of sodium bicarbonate in CIS in 1997-2006.....	25
II.3 The main company-producers of sodium bicarbonate in CIS countries	26
II.4 Current standing of key producers of sodium bicarbonate in the CIS	27
II.4.1. JSC “Soda” (Russia. Republic of Bashkortostan. the city of Sterlitamak)	27
II.4.2. Mikhailovsk Plant of Chemical Reagents (Russia, the Altay Area, village of Malinovoye Lake).....	29
II.4.3. JSC “Lisichansk Soda” (Ukraine, Lugansk Region, Lisichansk)	30
III. Export-import of sodium bicarbonate.....	32
III.1 Export-import of sodium bicarbonate in Russia.....	32
III.1.1 Exports of sodium bicarbonate in Russia.....	32
III.1.2. Imports of sodium bicarbonate	37
III.2. Export-import of sodium bicarbonate in the Ukraine	43
III.2.1. Exports of sodium bicarbonate	44
III.2.2. Imports of sodium bicarbonate	47
III.3. Export-import of sodium bicarbonate in Belarus	50
IV. Review of the prices for sodium bicarbonate.....	51
IV.1. Domestic prices for sodium bicarbonate in Russia.....	51
IV.1.1. Domestic prices in Russia	51
IV.1.2. Domestic prices in Ukraine	52
IV.2. Dynamics of export-import prices	52
IV.2.1. Dynamics of export-import prices in Russia	52
IV.2.2. Dynamics of export-import prices in Ukraine.....	54

V. Consumption of sodium bicarbonate in Russia.....	55
V.1 Balance of consumption of sodium bicarbonate	55
V.2 The structure of consumption of sodium bicarbonate.....	57
V.3 The main branches-consumers of sodium bicarbonate	61
V.4. The main enterprises-consumers	63
OOO “Procter & Gamble – Novomoskovsk” (Tula region, Novomoskovsk)	63
The company “Bryanconfi” (Bryansk)	64
JSC “Yashkino Food Factory” (Kemerovo Region, village of Yashkino).....	65
The company “United Bakers” (Voronezh).....	65
VI. Consumption of sodium bicarbonate in Ukraine.....	67
VI.1. Balance of consumption of sodium bicarbonate	67
VI.2. Major enterprises-consumers.....	68
Company “KONTI” (Donetsk).....	68
Confectionary Corporation ROSHEN (Kiev).....	69
The Company “Procter and Gamble” Ukraine (Kiev)	70
VII. The forecast for development of sodium bicarbonate market up to 2010	71
Contact information on company-producers of sodium bicarbonate in CIS countries	73

List of Tables

- Table 1: Solubility of sodium bicarbonate in water at different temperatures
- Table 2: Solubility of sodium carbonate in water at different temperatures
- Table 3: Density of NaHCO₃ water solutions at different temperatures
- Table 4: Solubility of NaHCO₃ with the presence of Na₂CO₃ at different temperatures
- Table 5: Equilibrium pressure of CO₂ over solutions, containing Na₂CO₃ and NaHCO₃
- Table 6: Distribution of common salt reserves of various commercial types in Russia as of 2007
- Table 7: Deposits of rock salt used in production of sodium bicarbonate in CIS
- Table 8: Main deposits of carbonate raw material for production of sodium bicarbonate in CIS
- Table 9: Quality index of produced sodium bicarbonate (GOST 2156-76)
- Table 10: Production of sodium bicarbonate in CIS in 1997-2007, thousand tons
- Table 11: Sodium bicarbonate production on CIS enterprises in 1997-2006, thousand ton
- Table 12: Quality characteristics of sodium bicarbonate produced by JSC “Soda” (GOST 2156-76)
- Table 13: External trade in sodium bicarbonate in the RF in 1997-2006 and in the first six months of 2007, 000 ton
- Table 14: Countries-importers of Russian sodium bicarbonate in 2005-2006 and in the 1st six months of 2007, 000 \$, \$/t
- Table 15: Key Consumers of Russian sodium bicarbonate in 2005-2006 and in the 1st six months of 2007, tons, 000 \$, \$/t
- Table 16: Countries-exporters of sodium bicarbonate to Russia in 2005-2006 and in the 1st six months of 2007 tons, 000 \$, \$/t
- Table 17: Suppliers of imported sodium bicarbonate to Russia in 2005-2006 and in the 1st six months of 2007 and its consumers. tons. thous. \$. \$/t
- Table 18: The biggest receivers of imported sodium bicarbonate in Russia in 2005-2006 and in the 1st six months of 2007, ton, 000 \$, \$/t
- Table 19: External trade in sodium bicarbonate in Ukraine in 1999-2006 and in the 1st six months of 2007, 000 ton
- Table 20: Countries-importers of Ukrainian sodium bicarbonate in 2005-2006 and in the 1st six months of 2007, tons, 000 \$. \$/t
- Table 21: The biggest consumers of Ukrainian sodium bicarbonate in 2005-2006 and in the 1st six month of 2007, tons, 000 \$, \$/t
- Table 22: Countries-exporters of sodium bicarbonate to Ukraine in 2005-2006 and in the 1st six months of 2007, tons, 000 \$. \$/t
- Table 23: The biggest receivers of foreign sodium bicarbonate in Ukraine in 2005-2006 and in the first six months of 2007, tons, 000\$, \$/t
- Table 24: Destinations of deliveries of Russian sodium bicarbonate to Belarus in 2004-2006, tons

- Table 25: Prices of JSC “Soda” for sodium bicarbonate in 2004-2007, rubles/t, VAT-exclusive
- Table 26: Prices of JSC “Leik” for sodium bicarbonate in August 2007, rubles/ton, VAT-exclusive
- Table 27: Export-import prices for sodium bicarbonate in Russia in 1999-2006 and in 1st six months of 2007, \$/t
- Table 28: Export-import prices for sodium bicarbonate in Ukraine in 1999-2006 and in the 1st six months of 2007, \$/t
- Table 29: Domestic consumption of sodium bicarbonate in Russia in 1997-2006, 000 ton
- Table 30: Structure of consumption of sodium bicarbonate in Russia in 2006, 000 ton, %
- Table 31: Regional structure of railway deliveries of sodium bicarbonate in Russia in 2005-2006, 000 ton, %
- Table 32: Domestic consumption of sodium bicarbonate in Ukraine in 1999-2006, 000 ton

List of Figures

- Figure 1: Flow diagram of an aggregate for sodium solution preparation through decarbonization of bicarbonate suspension
- Figure 2: Flow diagram for production of rectified sodium bicarbonate through “wet”
- Figure 3: Flow diagram for production of rectified sodium bicarbonate through “dry” method
- Figure 4: Sodium bicarbonate production dynamics in CIS in 1997-2006, 000 ton
- Figure 5: Dynamics of sodium bicarbonate production by JSC “Soda” in 1997-2006. 000 ton
- Figure 6: Dynamics of production of sodium bicarbonate by JSC “Lisichansk soda” in 1997-2006, 000 ton
- Figure 7: Dynamics of Russian export of sodium bicarbonate (000 ton) and prices for it (\$/t) in 1997-2006
- Figure 8: The share of export deliveries in production of sodium bicarbonate in Russia in 1997-2006, %
- Figure 9: Dynamics of Russian imports of sodium bicarbonate (tons) and prices for it (\$/t) in 1997-2006
- Figure 10: The average annual prices for imported sodium bicarbonate broken per country in 2005-2006. \$/t
- Figure 11: Dynamics of Ukrainian exports and imports of sodium bicarbonate in 1999-2006, 000 ton
- Figure 12: Dynamics of Ukrainian export of sodium bicarbonate (tons) and prices for it (\$/t) in 1999-2006
- Figure 13: Dynamics of Ukrainian imports of sodium bicarbonate (tons) and prices for it (\$/t) in 1999-2006
- Figure 14: Dynamics of average export-import prices for sodium bicarbonate in Russia in 1999-2006, \$/t
- Figure 15: Dynamics of average export-import prices for sodium bicarbonate in Ukraine in 1999-2006, \$/t
- Figure 16: Dynamics of production and consumption of sodium bicarbonate in Russia in 1997-2006, 000 ton
- Figure 17: Structure of consumption of sodium bicarbonate in Russia in 2006, %
- Figure 18: Structure of railway deliveries of sodium bicarbonate as per Federal Districts in Russia in 2006, %
- Figure 19: Dynamics of consumption of sodium bicarbonate in Ukraine in 1999-2006, 000 ton
- Figure 20: Growth indexes of production volume in sectors consuming sodium bicarbonate (% by 2001 г.)
- Figure 21: Forecast of development of commercial use of sodium bicarbonate in Russia up to 2010 (000 ton)

Introduction

Sodium bicarbonate (Natrii hydrocarbonas). Synonyms: baking soda, bread soda, cooking soda, bicarbonate of soda, sodium hydrogen carbonate, Natrium bicarbonicum, Natrium hydrocarbonicum, Sodium bicarbonate. Sodium bicarbonate is a white solid that is crystalline but often appears as a fine powder without odor, with slight alkali taste. It is water-soluble (1:2) with formation of alkaline solution (pH of 5% solution 8,1), practically non-soluble in spirit.

NaHCO₃ is a white crystalline powder with density of 2.16-2.22 g/sm³. When heated over 50°C, CO₂ starts being released, and when heated up to 100-150°C it gets decomposed completely, turning into Na₂CO₃. Water solutions of NaHCO₃ boast slight alkaline reaction.

Sodium bicarbonate was first classified by a German druggist B. Rose in 1801. In industry it is obtained by running CO₂ under pressure into saturated solution of Na₂CO₃ under 75°C:



Sodium bicarbonate NaHCO₃ (baking soda) is primarily used as a source of carbon dioxide in processes of bread baking, pastry baking, producing carbonated beverages and artificial mineral water, as a component of fire extinguishing compounds and medicinal agents. This is attributed to its easy decomposition (at 50-100°C).

I. Production technology for sodium bicarbonate and raw materials used in the Industry

I.1. Manufacturing practice for sodium bicarbonate

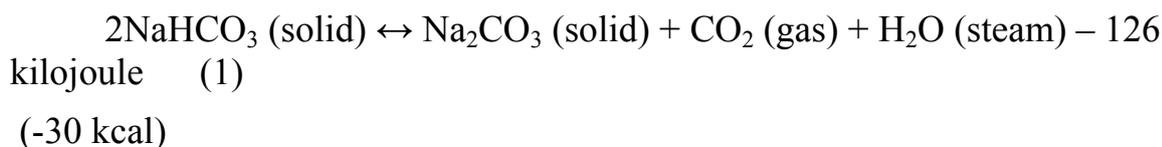
Sodium bicarbonate properties

Sodium bicarbonate NaHCO_3 , called sodium hydrocarbonate in pure form, is generated as a transitional product in the process of soda ash production through saturation of ammoniac-saline solution with carbon dioxide. Sediment separated from mother waters (that is called raw bicarbonate on plants) contains a number of admixtures: sodium chloride, ammonium chloride, iron salines, insoluble matters and others. In the process of raw bicarbonate drying, practically all the admixtures remain in the product. Therefore, its compound does not meet the requirements set forth by consumers in a number of cases and consequently needs purification.

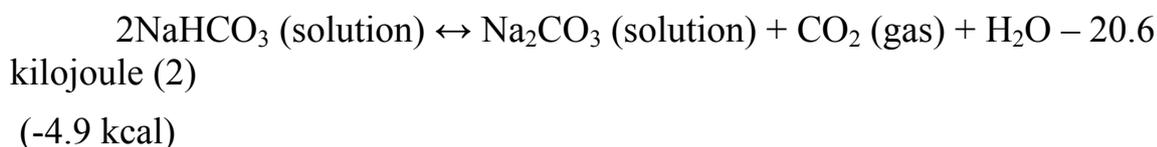
Production of rectified sodium bicarbonate is closely associated with sodium production, since soda ash, or raw bicarbonate and carbon dioxide of calcic furnaces are used in NaHCO_3 production process. That is why workshops for pure sodium bicarbonate are placed at sodium plants.

Sodium bicarbonate presents itself as white crystalline powder with average crystal size of 0.05-0.2 mm. Its molecular weight stands at 84.01, density at 2,200 kg/m^3 , apparent density 0.9 g/sm^3 . Sodium bicarbonate heat of solution is 205 kilojoule (48.8 kcal) for a kilo of NaHCO_3 , heat capacity 1.05 kilojoule/kg·K (0.249 kcal/g·°C).

Sodium bicarbonate is thermally low stable and when heated becomes decomposed with formation of solid sodium carbonate and with emission of carbon dioxide and water into gas phase:



Water solutions of sodium bicarbonate decompose similarly:



Water solution of sodium bicarbonate has slight alkaline character; therefore, it does not interact with animal or plant tissue. Solubility in water is moderate. With temperature increase, it grows slightly in size. Tables 1 and 2 shows data on solubility of NaHCO_3 and Na_2CO_3 in water at different temperatures.

Table 1: Solubility of sodium bicarbonate in water at different temperatures

Temperature °C	Solubility of NaHCO ₃			Temperature °C	Solubility of NaHCO ₃		
	g/100 g H ₂ O	%	n.d.*		g/100 g H ₂ O	%	n.d.
0	6.87	6.43	16.0	40	12.54	11.14	28.7
5	7.41	6.89	17.2	45	13.35	11.78	30.4
10	8.11	7.50	18.8	50	14.19	12.34	32.0
15	8.79	8.08	20.3	55	14.94	13.09	34.1
20	9.53	8.70	22.0	60	15.77	13.63	35.6
25	10.27	9.31	23.6	70	17.45	14.85	39.2
30	11.00	9.90	25.2	80	19.17	16.08	42.7
35	11.77	10.53	27.0				

* - concentration of salts is represented in normal divisions (n.d.). This concentration measuring is used at soda plants. One n.d. corresponds 1/20 g-equiv of matter in 1 liter of solution. Measurement of matter concentration in gram-equivalents simplifies calculations, eases browsing and comparative assessment of technical estimation and laboratory reports. For sodium bicarbonate coefficient of n.d. in g/l equals 4200, g/l in n.d. – 0,2381.

Source: Krashennokov S.A. “Technology of soda ash and purified sodium bicarbonate”, 1985

Table 2: Solubility of sodium carbonate in water at different temperatures

Temperature, °C	Solubility Na ₂ CO ₃	
	g/100 g H ₂ O	n.d.
20	22.95	83.5
30	39.20	144.0
40	48.90	182.0
60	46.50	173.0
80	45.40	170.5
100	45.20	170.0

Source: Krashennokov S.A. “Technology of soda ash and purified sodium bicarbonate”, 1985

As can be seen from the comparison of the presented data, solubility of sodium carbonate (soda ash) at the same temperature is 3-5 times higher than solubility of sodium bicarbonate.

The density of saturated aqueous solutions of NaHCO₃ due to small solubility comparatively little differs from pure water density. Table 3 shows some values of aqueous solutions of NaHCO₃ at different temperatures.

Table 3: Density of NaHCO₃ water solutions at different temperatures

Concentration of NaHCO ₃ , %	Density, kg/m ³ at temperature	
	18°	50°
1	1006	1006
2	1013	1013
3	1021	1020
4	1028	1027
5	1035	1034
6	1043	1041
7	1050	1048
8	1053	1055
10	-	1069
12	-	1084

Source: Krashenninokov S.A. "Technology of soda ash and purified sodium bicarbonate", 1985

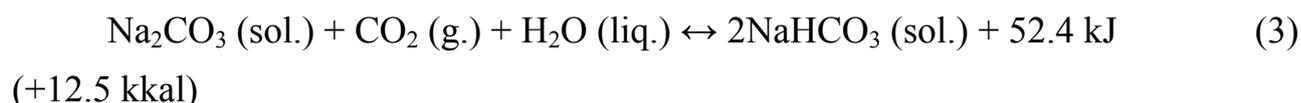
The following dependence of viscosity of water solutions of NaHCO₃ on their concentration at temperature 18° C is observed:

Concentration of solution, %	2,06	4,03	7,75
Viscosity, centipoise	1,204	1,851	2,238

Schematic diagram on obtaining purified sodium bicarbonate

Sodium bicarbonate is poorly water-soluble, and besides, it is thermally unstable; when it is heated, some part of it converts into soda, reducing NaHCO₃ solubility. The solubility of NaHCO₃ in presence of Na₂CO₃ at the temperature of 25° and 50°C is shown in Table 4.

On an industrial scale purified sodium bicarbonate is received by carbonizing soda solution according to reaction



The application of the carbonization method allows sufficient reduction of the volume of liquid necessary for obtaining a product unit, as soda solubility is several times higher than solubility of NaHCO₃.

Table 4: Solubility of NaHCO₃ with the presence of Na₂CO₃ at different temperatures

Temperature °C	Solubility NaHCO ₃ , %	Content Na ₂ CO ₃ , %	Temperature °C	Solubility NaHCO ₃ , %	Content Na ₂ CO ₃ , %
25	9.3	0.0	50	12.40	0.00
25	9.1	0.9	50	12.22	0.27
25	7.8	5.4	50	11.68	1.08
25	4.9	6.1	50	9.93	4.78
25	3.9	10.0	50	8.27	10.04
25	3.3	16.7	50	6.80	14.90

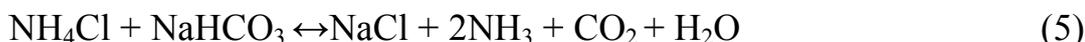
Source: Krashenninokov S.A. "Technology of soda ash and purified sodium bicarbonate", 1985

Soda solution for carbonization can be obtained by dissolving in water solid technical soda, generated during calcinations of wet bicarbonate (“dry” method), or decomposition of bicarbonate in aqueous medium when heated under the reaction (2) (“wet” method). The latter process is called decarbonization. In industry both methods are used. The “wet” method is more appropriate, as it requires less heat for decomposition of NaHCO_3 with obtaining of Na_2CO_3 in solution.

The pure sodium bicarbonate, precipitating during saturation of soda solution by carbon dioxide, is separated, and the mother liquid containing NaHCO_3 , Na_2CO_3 and dissolved impurity substances, for instance NaCl , are returned to the start of the process for getting initial soda solution. Because of multiple circulation of mother liquid, impurities are accumulated in it and likely to cause the appearance of these inclusions in the purified bicarbonate. That is why part of the mother liquid is withdrawn from the cycle and is usually directed to the brine cleaning for diluting of strong soda solution.

Physicochemical fundamentals of separate stages of production of purified sodium bicarbonate

The process of obtaining of initial solution by decarbonization of suspension of technical sodium bicarbonate. When water solution of sodium bicarbonate is heated, it transmits into soda according to the reaction (1), and the impurities contained in it, containing ammonia, are decomposed under reactions:



Sodium and sodium chloride remain in the solution, and carbon dioxide and ammonia are removed from the solution into gaseous phase.

The decarbonization process is aimed at obtaining soda solution with maximum concentration of Na_2CO_3 , possible at temperatures of the surrounding premises. It will approximately conform to the general alkalinity of the solution (as calculated for Na_2CO_3) 278 g/l, or 105 n.d. For obtaining soda solution of such concentration, the initial solution of sodium bicarbonate should contain at least 102 n.d. of NaHCO_3 . This concentration more than three times exceeds NaHCO_3 solubility. Therefore, aqueous suspension of NaHCO_3 is used for its decarbonization. As the dissolved NaHCO_3 decomposes, new quantities of it will pass to the solution from the solid phase until it is fully dissolved.

Rising of temperature shifts the balance of the reaction (2) to the right. Therefore, the process of decarbonization is carried out in industry at temperatures close to the boiling point of the solution. Below is shown the dependence of the level of decomposition of sodium bicarbonate, or decarbonization level on the temperature and the time of the heating:

Temperature, °C	102	102	102	102
Degree of decomposition, %	87	90	92	92
Duration of heating, min	30	40	50	70

(The degree of the decomposition of NaHCO_3 , or, which is the same, the degree of decarbonization, is determined by the ration of the content in n.l. Na_2CO_3 in the solution to its total alkalinity, expressed in per cent)

As can be seen from this data, the process of decomposition of NaHCO_3 does not proceed until the end and at high degrees of carbonization the rate of the process slows down.

The rate of decomposition of NaHCO_3 , like the rate of any chemical reaction, depends on the temperature. Growth of temperature has a positive effect both on the shift of balance to the desired direction and on the rate of reaction.

The process of decomposition of NaHCO_3 is facilitated by removal from the liquid of the product of CO_2 reaction. The driving force of desorption process is the difference between the equilibrium pressure of desorbed gas (CO_2) above the liquid and its partial pressure in the gaseous phase. The more the difference, the more intensive is the process. Desorption continues until the equilibrium pressure of CO_2 above the liquid becomes equal to its partial pressure in the gaseous phase.

Equilibrium pressure of CO_2 above the solution containing Na_2CO_3 and NaHCO_3 , as well as maximum obtainable degrees of decarbonization depending on the temperature and pressure of CO_2 in the gaseous phase can be calculated according to the following empirical equation:

$$\frac{X^2 C^{1.29}}{SP^*(1-X)(185-t)} = 26600 \quad (6)$$

where X – content of sodium, present in the form of NaHCO_3 ; $(I - X)$ – content of sodium, present in the form of Na_2CO_3 , C – concentration of total Na в in solution, n.d.; t – solution temperature °C, S - solubility of CO_2 in water at temperature t and pressure P_{CO_2} , equal to 1 atm, mole/l; P^* – equilibrium partial pressure of CO_2 above the solution, atm. (The received values of P^* in atmospheres are recalculated into kiloPascals).

The solubility of CO_2 in water at the pressure equal 1 atm is the following:

Temperature, °C	15	25	35	45	55	65	75	85	105
Solubility, CO_2, mole/l	0.045	0.033	0.026	0.021	0.017	0.015	0.012	0.009	0.001

Table 5 shows equilibrium pressures of CO_2 above the solutions, containing Na_2CO_3 and NaHCO_3 , depending on the temperature and degree of carbonization, calculated according to the equation (6). Calculations in the table are made for solutions, containing 1 g·equiv of total Na per 1 liter of solution. If Na concentration is increased by x times, partial pressures of CO_2 according to the equation (6) should be multiplied by $x^{1.29}$.

Table 5: Equilibrium pressure of CO₂ over solutions, containing Na₂CO₃ and NaHCO₃

Degree of decarbonization, °%	Equilibrium pressure of CO ₂ over solution, kilopascals (millimeter of mercury)		
	at 20°C	at 40°C	at 60°C
10	12.6(95.00)	24(180.00)	40(300.0)
75	0.15(1.10)	0.24(1.80)	0.37(2.80)
90	0.01(0.13)	0.03(0.22)	0.04(0.32)

Source: Krashenninokov S.A. "Technology of soda ash and purified sodium bicarbonate", 1985

Table 5 shows that increase of decarbonization degree results in sharp drop of equilibrium pressure of CO₂ above the solution, and when carbonization reaches 90% it makes only tenth of mm Hg. Therefore if decarbonization degree is increased, the driving force of desorption drops sharply, which greatly slows down the process of NaHCO₃ decomposition. Therefore in order to achieve high degrees of decarbonization not only high temperature, but long-time keeping of the liquid in the apparatus is needed, which can be achieved only in bubble-type apparatus (with bubble plates, with submerged muzzle and so on).

However in order to produce purified sodium bicarbonate it is not necessary to obtain high levels of decarbonisation, as the solution received further in a decarbonifier is subject to carbonization yielding NaHCO₃. The degree of decomposition of NaHCO₃ of about 85% or lower is enough.

The suspension of NaHCO₃ is heated up to the decomposition temperature by means of saturated water steam delivered to the suspension. During direct contact of the heating steam with liquid the intensity of the heat transfer increases, and CO₂ partial pressure in gas decreases, favorably affecting the intensity of the driving force of desorption, especially at the end of the decomposition process.

Carbonization of sodium solution.

Soda solution obtained by "wet" or "dry" method is subjected to carbonization for releasing NaHCO₃ from it as solid phase according to the equation (3) for the reaction.

If in the process of decarbonization the limiting phase is desorption of CO₂ from solution, the rate of decarbonization is determined by the reverse process - the rate of CO₂ absorption. As is in case of absorption of CO₂ by the ammonized solution, the rate of absorption of CO₂ by soda solution at rising temperature, on the one hand, will rise, as the reaction rate grows and viscosity of the solution falls, facilitating introduction of the active CO₂ component to the surface of phases contact, - but on the other hand, will reduce, as the driving force of absorption diminishes - the difference of CO₂ pressures in carbonizing gas and above the solution. These two factors, acting in two opposite directions, indicate the optimum for carbonization temperature. It is found within the range of 80-60°C. The first temperature is related to the soda solution coming for carbonization and containing little bicarbonate with low CO₂ equilibrium pressure, while the second one is related to the final carbonized

solution where the increased content of carbonate starts to influence noticeably, as the temperature grows, the equilibrium pressure of CO₂ above the solution, and therefore, to decrease the driving force of absorption.

The quantity of sediment NaHCO₃ produced by carbonization of soda solution depends on the concentration of the initial solution, on temperature and degree of carbonization, determined as the ratio of the total content of CO₂ in sediment and in the solution, to the general alkalinity of the initial solution.

This dependence may be expressed by the equation

$$x = 0.0088C_{init.Na} (R - 87) - 0.015t - 0.7, \quad (7)$$

where x – quality of sediment NaHCO₃ in the initial solution, g·equiv/l;

$C_{init.Na}$ – alkalinity of the initial soda solution, g·equiv/l;

R – carbonization degree, %;

$R_c = (total. CO_2/total. Na) 100$;

t – temperature, °C.

Thus at temperature of 50°C and carbonization degree of 160% NaHCO₃ precipitates as a solid phase from each liter of soda solution with initial alkalinity 4.5 g·equiv/l:

$$x = 0.0088 \cdot 4.5 (160 - 87) - 0.015 \cdot 50 - 0.7 = 1.44 \text{ g·equiv.}$$

It is evident that the higher the concentration of total Na in the initial solution and the lower the temperature of the suspension as well as its carbonization degree, the greater is the quantity of NaHCO₃ in the sediment. However, it should be noted that the final temperature of suspension is determined not by the quantity of the sediment sodium bicarbonate, but by its quality, therefore the level of carbonization is kept rather different from the equilibrium.

The significant operation in the process of obtaining purified sodium bicarbonate is crystallization of NaHCO₃. During crystallization of NaHCO₃ in the process of carbonization of soda solutions, direct dependence has been established between the rate of crystallization – W_{cr} and absorption of CO₂, as the latter determines the extent of the oversaturation of solution in NaHCO₃. On the other hand, the rate of crystallization of sodium bicarbonate influences the rate of absorption of CO₂, as in the process of crystallization of NaHCO₃ concentration falls of HCO₃⁻ ions adversely affecting the absorption of CO₂ by the solution. Crystallization of NaHCO₃ may be determined by hydrodynamic conditions – turbulization of the system (the intensity of its mixing), or the temperature. Under these conditions the rate of crystallization depends only on the temperature. For both regimes of crystallization behavior, called diffusion and kinetic, W_{cr} is generally expressed by equation

$$W_{kp} = K_k \Delta c^n, \quad (8)$$

where K_{cr} – constant of NaHCO₃ crystallization rate; Δc – oversaturation of the solution in NaHCO₃, or the difference between the current and equilibrium concentration of NaHCO₃ in solution; n – index of power, equal for the diffusion regime 1 and for kinetic regime 2.

Experiments have shown that low mixing conditions result in crystallization process under diffusion-limited regime, whereas intensive turbulent mixing condition – under kinetic-limited regime.

Big and easily filtrated NaHCO_3 crystals are obtained if high temperature of carbonized suspension is kept (60-70 °C) until its exit from the carbonizing column. The construction of the carbonizing column itself facilitates obtaining big NaHCO_3 crystals – with small amount of plates, providing for lengthways mixing of the liquid inside the column, the withdrawal of small NaHCO_3 crystals from the bottom part of the column to its upper part as inoculums, around which mass crystallization is going on. Oversaturation decreases, the rate of crystallization falls, and the crystals grow bigger.

Technological schemes of production of purified sodium bicarbonate

Technological schemes of production of purified sodium bicarbonate by means of “dry” and “wet” method differ mainly according to the procedure of preparation of the initial solution.

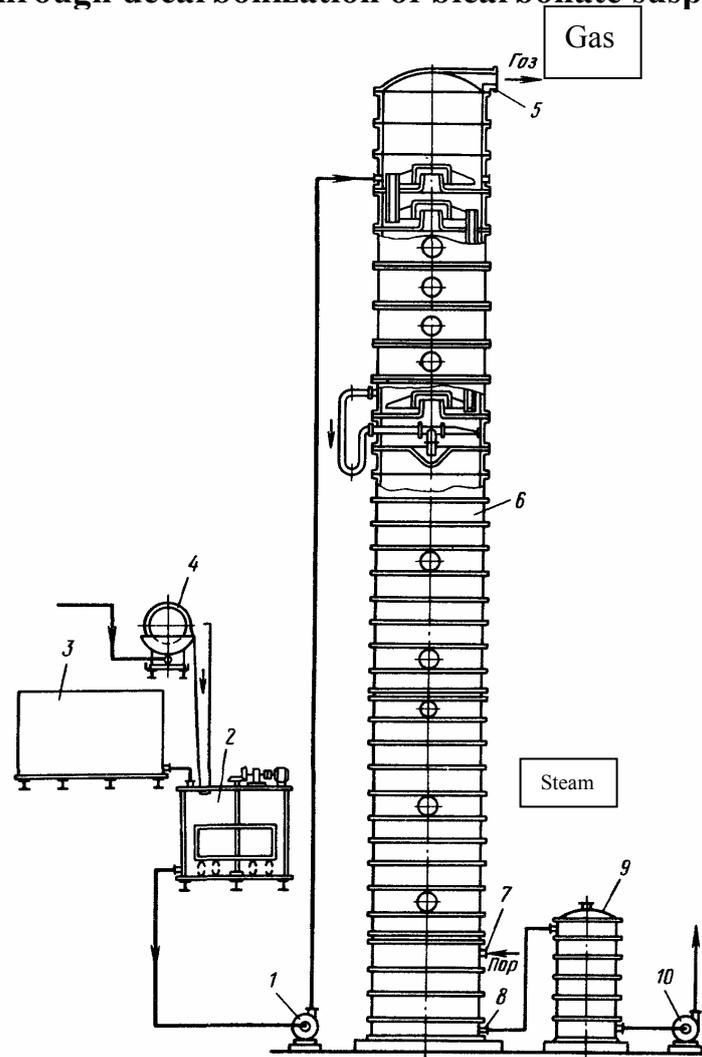
Production of purified sodium bicarbonate by means of “wet method”.

Figure 1 represents a schematic diagram of the compartment for preparation of initial sodium solution by decarbonization of bicarbonate suspension. Sodium bicarbonate from vacuum-filters 4 for sodium production is delivered to the reservoir with mixer 2 for preparation of suspension of NaHCO_3 , where the “return” sodium solution from vessel 3 also enters. The proportion between the “return” solution and solid NaHCO_3 should provide for the total alkalinity of the prepared suspension of 110-115 n. d.

The prepared suspension of NaHCO_3 is pumped by centrifugal pump 1 to the top of decarbonator 6. From the bottom through connector 7 water steam is fed under pressure of 3.9-4.9 Pa (0.4-0.5 atm), necessary for decomposition of NaHCO_3 . Sodium solution having concentration of total alkalinity 105-110 n. d. goes out from the bottom part of decarbonator 6 to collector 9, from where by pump 10 it is pumped out for production needs. The gases released from the top part of the decarbonizer contain up to 95-98 volume % of CO_2 as calculate for dry gas and some quantity of NH_3 . Therefore, they are not allowed to be released into the atmosphere, but directed through connector 5 to the gas collector of furnaces for soda ash production. During production of 1 ton of standard soda solution about 415 kg of CO_2 and 20 kg of NH_3 is released.

Further processing of soda solution into purified sodium bicarbonate both under “wet” and “dry” method is the same, and includes the following operations: clarification of sodium solution, carbonization of sodium solution, filtration of sodium bicarbonate, drying of wet sodium bicarbonate, sizing (crushing), magnetic separation and packing of the ready product.

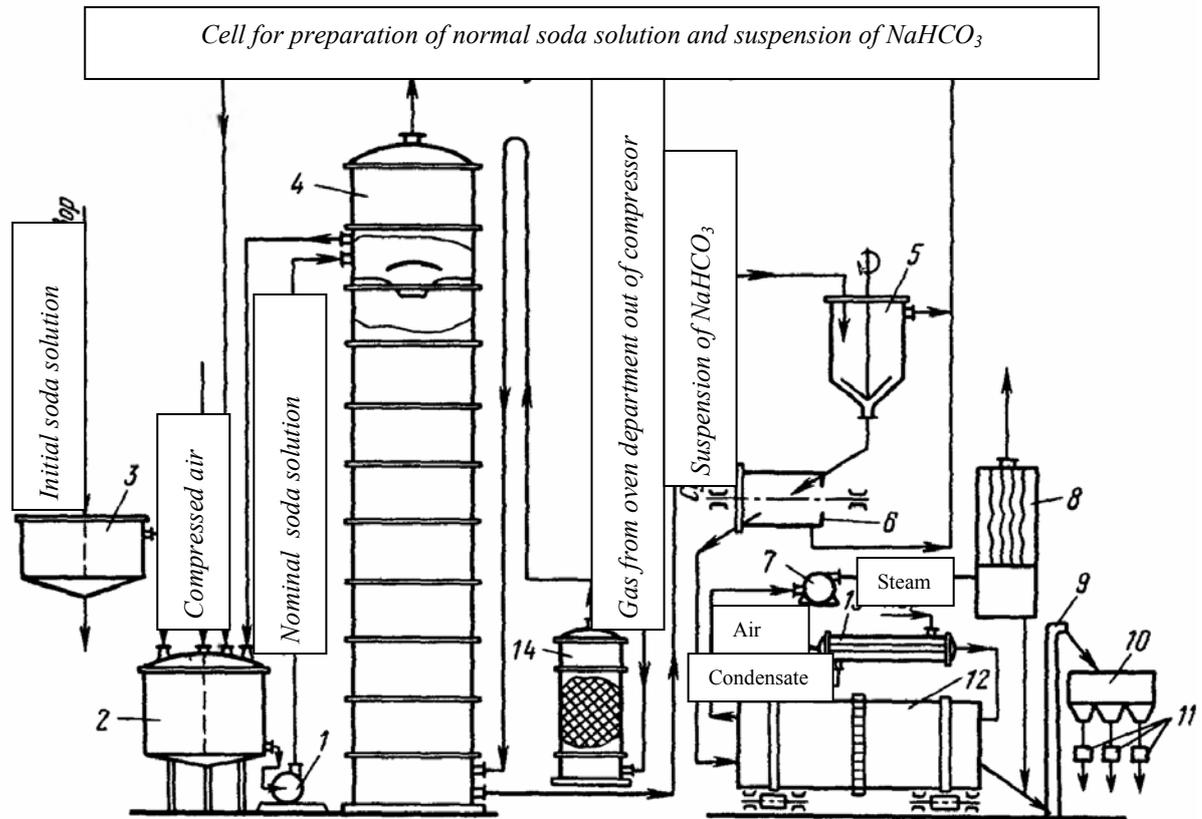
Figure 1: Flow diagram of an aggregate for sodium solution preparation through decarbonization of bicarbonate suspension



- 1, 10 - pumps, 2 – mixer for sodium bicarbonate suspension, 3 – vessel for solvent, 4 – drum vacuum -filter, 5 - connector for exit of steam-gas mixture, 6 - decarbonator, 7 – connector for steam feeding, 8 - connector for sodium solution exit, 9 - collector

Figure 2 shows technological scheme of production sodium bicarbonate by means of “wet” method (without transport devices and some auxiliary apparatus). Sodium solution having total alkalinity of 105-110 n. d. is pumped 3 from carbonization compartment to the collector 3 of the initial sodium solution for settlement. Very small amounts of precipitation which are generated are withdrawn from time to time out of collector 3 and are delivered for using to the compartment of solution clarification. The clarified sodium solution from collector 3 is pumped to the two alternatively working collectors 2, where normal sodium solution with total alkaline concentration of about 86 n. d. is prepared. Experience has shown that sodium solution of such concentration provides for high rate of CO₂ absorption, while production capacity of the carbonizing column stays rather high. For diluting initial sodium solution “return” solution is fed to collector 2, which is called weak liquid.

Figure 2: Flow diagram for production of rectified sodium bicarbonate through “wet”



- 1 - pump, 2 – collector for preparation of “normal” sodium solution, 3 – collector for the initial sodium solution, 4 – carbonizing column, 5 - precipitation-condensing tank,
 6 - centrifuge, 7 - blower, 8 - bag filter, 9 - elevator,
 10 – sizing sieve, 11 – magnetic separator, 12 – drum dryer,
 13 - heater, 14 – gas washer

For rapid mixing of liquids in tank 2 compressed air is delivered to it. From tank 2 normal soda brine, called column liquid, by pump 1 is pumped to the top of carbonizing column 4. Carbon dioxide from lime furnaces, cleaned from mechanical impurities in washer 14 is pumped from the bottom to the carbonizing column by the pump under pressure 24.5 Pa (2.5 atm). The content of CO_2 in carbonizing gas should be not less than 32%. Carbon dioxide is not fully absorbed in the column. Its content in the exhausted gas, released in the atmosphere is 16-20%.

The suspension of sodium bicarbonate, formed in the column, is diverted from below the column to the tank-thickener 5. The requirement for NaHCO_3 suspension thickening before delivering it to the centrifuge is needed because for proper centrifuge operation the suspension should have proportion L:S= 1.1:1.0, as diluted suspension is difficult to filter and considerably reduces centrifuge production capacity.

The thickened part of the suspension (pulp) from the bottom of the tank-thickener 5 enters centrifuge 6 for separation. The sediment NaHCO_3 , if necessary, is washed with water, discharged from the centrifuge and is delivered to the dryer 12.

The manifold and washing liquid from the centrifuge and clarified solution from the precipitation tank 5 go to the relevant tanks (not shown on Figure2), then they are mixed and in the form of the recirculated solution or weak liquid go to the vessel 2 for diluting soda solution and to the compartment of decarbonization for preparing of sodium bicarbonate suspension. The moisture content of NaHCO_3 sediment discharged from the centrifuge is 2.5-3%.

For drying sodium bicarbonate drum driers are used, in which wet sodium bicarbonate during rotation of the drum is moving alongside it and is being dried by the coming hot air with temperature of 105-110 °C. At the exit from the dryer the air temperature falls to 55-59 °C. Dry sodium bicarbonate, unloaded from the drum drier by the elevator 9, goes to the sieve screen sizer 10, where it is divided according to the size into several fractions. At some plants big size fractions are ground and after that it again goes to the sieve screen 10. Before packing sodium bicarbonate passes through magnetic separator 11 in order to remove random metallic fractions.

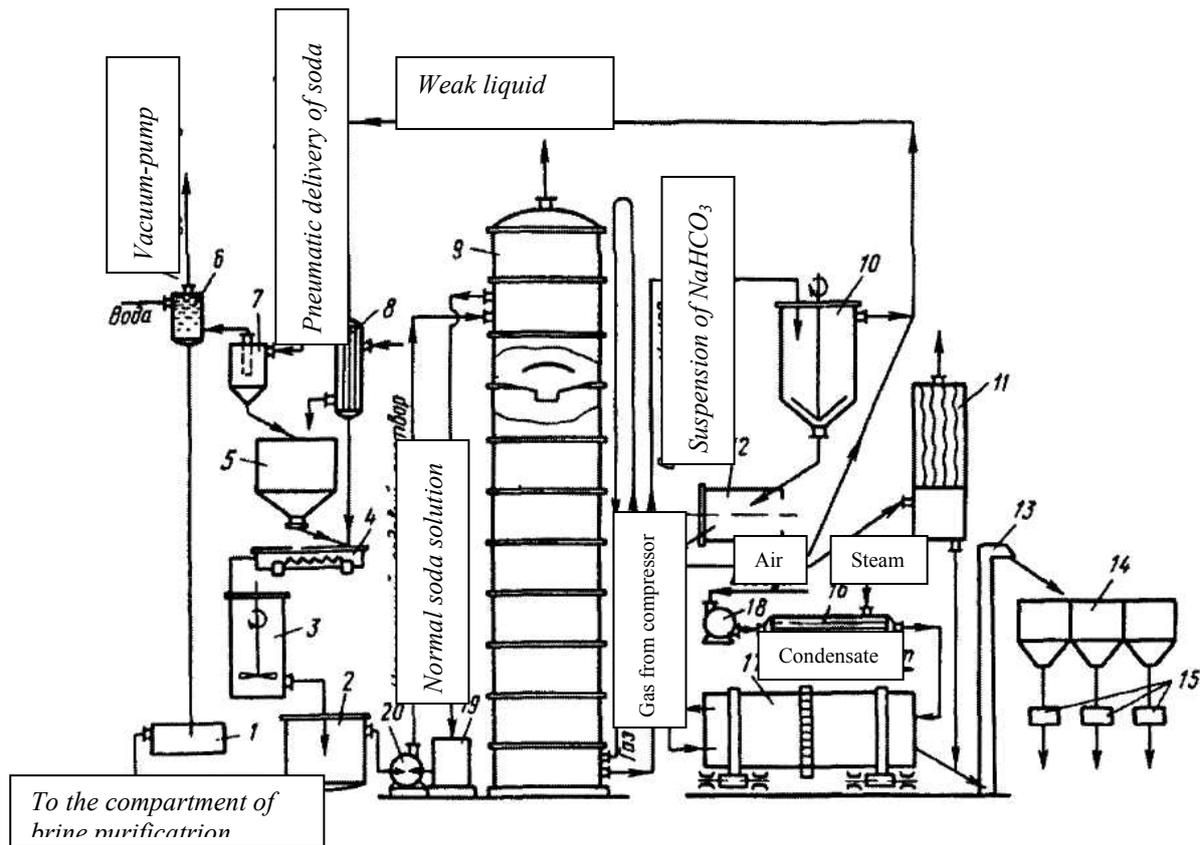
The air necessary for drying sodium bicarbonate passes through tube airheater 13, where it is heated by air steam up to 105-110 °C and by means of blower 7 penetrated through the dryer. Passing through the dryer, the air entraps up to 12% NaHCO_3 , therefore before being discharged into the atmosphere it is passes through the bag filter 8. From the filter the entrapped fractions of sodium bicarbonate get to the general current of NaHCO_3 , going to the sizing. The use of counterflow in drum dryers reduces the removal of dust, as the counterflow makes the air going out of the dryer contact wet sodium bicarbonate fractions.

Dry method of sodium bicarbonate production.

Solid soda ash is pumped from the calcinations compartment to the cyclone 7 (Figure 3). The air cleaned from soda dust passes through the washer 6 and is inhaled by a vacuum pump (not shown on the figure). The washing liquid from the washer 6 is collected in the bucket 1 and is transferred to the cleaning brine compartment. Soda ash from the bottom of cyclone 7 passes to the soda bin 5, from where it goes to screw diluter 4. Weak liquid, heated in the heater 8 up to 90-95°C is used as solvent.

The prepared soda solution is delivered to the storage tank of normal soda solution 4 from where it passes to precipitation tank 2. The clarified solution is pumped by the pump 20 to the top of the carbonizing column 9. The excess of the solution from column 9 through overflow goes to the bin 19. From the bottom carbon dioxide is pumped to the column by a gas compressor. The gas released from the column passes through a mist eliminator and is exhausted to the atmosphere. Sodium bicarbonate suspension from column 9 passes to precipitation-thickener 10. The compacted precipitation NaHCO_3 goes to centrifuge 12 and then to the dryer 17.

Figure 3: Flow diagram for production of rectified sodium bicarbonate through “dry” method



- 1 - bin, 2 – precipitation tank, 3 – collector of normal sodium solution, 4 – screw melter, 5 – sodium bin, 6 – air washer with barometer tube, 7 - cyclone, 8 - warmer, 9 – carbonizing column, 10 – precipitating tank, 11 - bag filter, 12 –centrifuge, 13 - elevator, 14 – sizing sieve, 15 – magnetic separator, 16 - heater, 17 – drum dryer, 18 - blower, 19 – overflow tank, 20 - pump

Sodium bicarbonate is dried by hot air injected to the dryer by the blower 18, The air is heated in the heater 16 by the air steam and is cleaned from NaHCO₃ fractions by bag filter 11, after which it is exhausted into atmosphere. For sizing particles of sodium bicarbonate shake-sieve 14 is used. Sodium bicarbonate divided into fractions passes through magnetic separator 15 and goes for packing.

During operating process the carbonizing column, whether “dry” or “wet” method is used, becomes gradually covered with sodium bicarbonate sludge. Hydrodynamic resistance starts growing, CO₂ concentration increases at the exit from the column, the quality of the crystals deteriorates, column production capacity falls. Therefore after 12-18 days of non-stop work a washer is installed on the carbonizing column. If there is another column in the workshop the output production is stopped, the column is discharged, terminating the delivery of liquid and gas, then the column is washed first by weak liquid, and then by water. Along with the liquid direct steam is delivered to the column, which allows to keep the liquid at 85-90 °C during its circulation through the column.