Carbonation System in Soda Ash Process

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Solvay soda ash ammonia process remains one of the main methods for obtaining sodium carbonate, despite its considerable natural resources. This process consists of consecutive stages: absorption, carbonation, distillation and calcination. And performance of each stage is determined to considerable degree by performance of other stages. As in any chemical process thermal and barometric modes, besides concentration of initial material flows, significantly influence processes efficiency. Ammoniated brine carbonation is the main stage in soda ash process. In this article, basing on analysis of numerous data on existing carbonation systems performance, we considered peculiarities and basic ways for increase of these systems efficiency that influence plant operation in general.

Introduction

Soda ash process as a source for other anthropogenic and indispensable chemical substances and everyday products for human existence has passed a long way of methods searching, development and formation and efficient acceptance in the global community [1-4]. Environmental impact of large plants in particular soda ash ones promotes active search of ways for at least decrease of negative impacts if solution of such problems is impossible [5-8], but in many cases they are still under development and modeling by software and laboratory installations [5,9,10]. In 2004, five processes for reducing the negative environmental impact of soda production were studied at the laboratory level in Poland. These included obtaining calcium and magnesium phosphates, as well as precipitated ash and gypsum; flue gas desulfurization; and distillation waste recycling [5]. Recently, their pilot plant for absorbing off-gas CO_2 with ammonia condensate reduced CO_2 emissions by 634 kg/h [10].

In 2020, Spanish scientists investigated the use of off-gas CO_2 for methanol production and the potential for switching to renewable energy sources for a soda plant [7].

Global greenhouse gas emissions restrictions have stimulated the development of CO_2 capture and recycling processes. A 2019 review [11] evaluated and compared the carbonation of soda ash from trona and a method using sodium sulfate. A 2024 review [12] comprehensively identifies various methods, including the Solvay process, sodium hydroxide capture, and electrochemical CO_2 conversion, and examines ways to intensify sustainable CO_2 capture and mass transfer.

As early as 2005, Chinese scientists were searching for an efficient process for processing

sodium sulfate as a byproduct of industrial processes, with preliminary organic matter purification using coal, including for the production of sodium bicarbonate [13].

In recent years, Canadian and Chinese scientists [14] have been modeling the production of soda from sodium sulfate using Aspen Plus, intending to use organic matter to separate ammonium sulfate from unreacted sodium sulfate for its reuse. Korean scientists also used Aspen Plus to model the production of sodium and ammonium sulfate from mirabilite and conducted an energy analysis of the thermodynamic data obtained [15].

A 2026 article [16] describes the laboratory production of 99.38% pure soda ash from waste product - sodium sulfate, with pretreatment to remove total organic carbon, heterocycles, anilines, ketones, phenols, and long-chain alkanes, and to improve color, as well as the derivation of a kinetic equation throught reaction modeling. These studies are aimed at minimizing the environmental impact of waste from other industries.

However, a comparison of different methods for using waste CO_2 gas as feedstock for sodium bicarbonate production using Aspen Plus showed the highest profit from carbonating soda ash and less from carbonating sodium sulfate. [17].

The starting solution for the industrial production of soda using the Solvay method remains sodium chloride solution, and this classic method of production remains the most popular.

Analysis of carbonation stages

Carbonation of ammonia and salt solution is the main process that defines efficiency of ammonia soda ash process in general. This process is complicated as it depends on many factors, first of all on concentration of components fed to the process [17]. Carbonation can be provisionally divided into three continuously flowing stages:

1. Preliminary carbonation for increase of carbon dioxide concentration in the solution up to 60 DN/20 and more;

2. CO_2 absorption and exchange reaction with formation of $NaHCO_3$ crystals;

3. CO_2 absorption with obtained slurry cooling that promotes growth of $NaHCO_3$ crystals.

The first stage is preparatory, as increase of CO_2 concentration in the lye (C-liquor) fed to the column decreases NH_3 equilibrium pressure above this lye, and correspondingly, its blowing away.

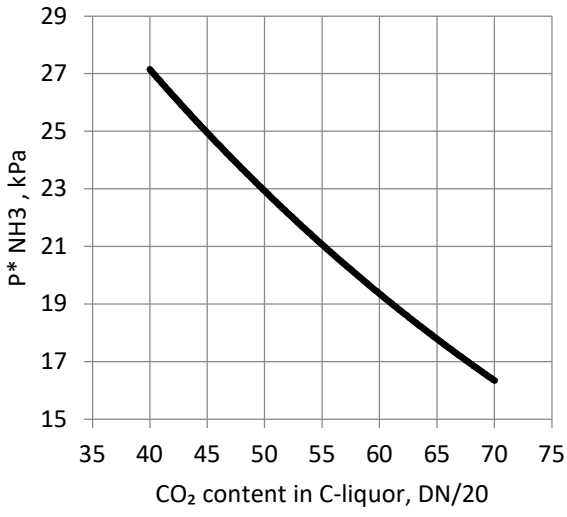

Figure 1. Dependency of NH_3 equilibrium pressure over C-liquor on CO_2 concentration in it.

Figure 1 shows diagram of NH_3 equilibrium pressure when CO_2 concentration increases in preliminarily carbonated lye (at NH_3 concentration in C-liquor 95-98 DN/20 and temperature 323-325 K). This diagram shows that is CO_2 concentration increases from 40 to 65 DN/20 NH_3 equilibrium pressure over the lye actually decreases 1.5 times, and correspondingly, its blowing away also decreases.

Second stage is defining, as basic chemical reactions take place during this stage. At this stage as CO_2 is absorbed ammonia carbonate is decomposed with formation of ammonia hydrocarbonate according to reaction:

$$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3 \quad (1)$$

After that in the so-called crystals formation zone exchange reaction takes place (exchange of HCO_3^- and Cl^- ions) with formation of $NaHCO_3$ crystals:

$$NaCl + NH_4HCO_3 \leftrightarrow NaHCO_3 + NH_4Cl \quad (2)$$

Creation and formation of $NaHCO_3$ crystals is the basic parameter of carbonation process that characterizes this process. This process determines temperature profile and efficiency of carbonation columns. Requirements to the quality of $NaHCO_3$ crystals are high: crystals should be large enough, have homogeneous form and size. On these qualities operation of adjacent filtration and calcination units depends. Small slimy or aggregated needle crystals are hard to filtrate and withhold much mother liquor. This in its turn requires increased heat flow during calcination and causes increased chlorides content in final product.

For obtaining large and homogeneous crystals period of crystal seeds formation and their further growth is very important. The more crystal seeds are formed in the initial period the more crystals will be obtained in the final result and the smaller they will be.

Part of small crystals can be agglomerated with each other forming crystal jams as “bundles” or “doppings” that are poorly washed from mother liquor and retain much moisture as we mentioned above. That is why for obtaining large monolithic crystals conditions should be created when amount of formed seeds is not too high and smaller seeds are dissolved.

As crystallization process depends on CO_2 absorption by ammoniated brine [18, 19] let’s study basic factors that impact this process. In this case chemical sorption besides physical absorption takes place where free ammonia is the active component that reacts with absorbed carbon dioxide.

CO_2 absorption in this system can be divided into two stages: first iniatial stage flows without $NaHCO_3$ sedimentation. At this stage, the absorption process occurs, accompanied by a reversible chemical reaction between CO2 and NH3:

$$2NH_{3\,g} + CO_{2\,g} + H_2O_l \leftrightarrow (NH_4)_2CO_{3\,l}$$

The amount of carbon dioxide absorbed per unit time per unit volume (N_{CO_2}) of solution is described by the kinetic equation:

$$N_{CO_2} = \left[NH_{3_{\text{своб}}}\right] \cdot K_a \cdot \left(p^g_{CO_2} - p^*_{CO_2}\right),$$

where

$\left[NH_{3_{\text{своб}}}\right]$ is the concentration of ammonia in the ammoniated brine.

K_a is a coefficient equal to the product of Henry's constant and the partial absorption coefficient for the boundary liquid film.

$p^g_{CO_2}$ is the partial pressure of CO2 in the carbonizing gas.

$p^*_{CO_2}$ is the equilibrium pressure of CO2 above the liquid.

Laboratory studies show that the constant K_a,depends on the liquid temperature T_l and is described by the equation:

$$\lg K_l = -\frac{760}{T} + 1{,}85$$

Second stage is complicated by $NaHCO_3$ crystallization. Change of CO_2 absorption velocity depending on the degree of solution carbonation is shown on **Figure 2**.

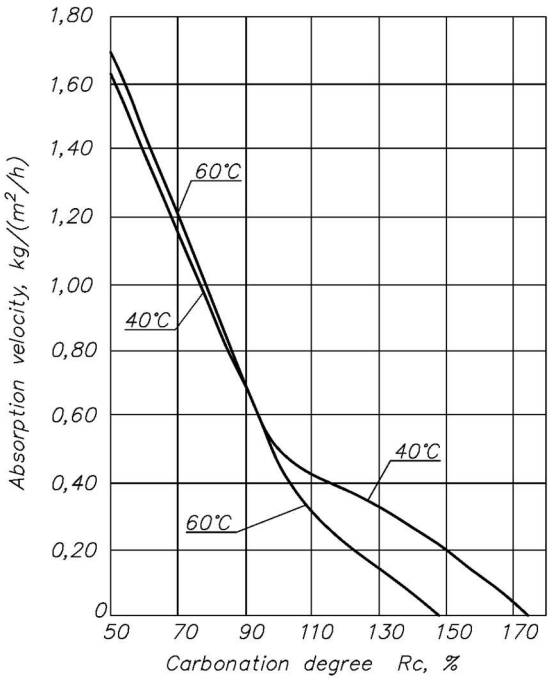

Figure 2. CO_2 absorption velocity during carbonation of ammoniated brine.

Here carbonation degree of solution Rc (%) is characterized by the quality of absorbed CO_2. It is defined by equation:

$$R_c = \frac{[CO_{2_{total}}] + 2[NH_4Cl]}{[NH_{3_{total}}]},$$

where concentration of all components are given in DN/20.

At this stage besides components concentration temperature profile is important, especially in the zone of crystals seeding. Operation experience shows that at 63ºC and higher in the zone of crystals seeding dissolution of formed small crystals increases and with further cooling larger seeds start to grow. This enhances crystals quality.

$NaHCO_3$ crystals mainly grow and, correspondingly, form during the third stage of the process simultaneously with CO_2 absorption and obtained slurry cooling [20]. At this stage, besides mass exchange, heat exchange with heat removal and, correspondingly, slurry cooling is very important.

Analysis of carbonation column structure

Basing on the above we can see that carbonation columns design shall ensure intense both mass and heat transfer. Typical carbonation column consists of two zones: top absorption and bottom cooling [20]. Basic chemical reactions and $NaHCO_3$ crystals seeding take place in the top zone, and crystals growth due to CO_2 absorption with heat exchange by slurry cooling in the bottom zone.

As CO_2 absorption and basic chemical reactions take place in the absorption zone it is determined by mass transfer coefficient, process moving force and chemical transformations. As a rule absorption zone is a cylindrical tank with contact elements installed along its height.

Mushroom elements are typical contact elements used in carbonation columns [21-23]. They provide absorption zone sectioning and homogeneous gas flow distribution along the column section. But these contact elements don't ensure sufficient intensity of gas and liquid interaction. Accumulation of sodium bicarbonate sediments negatively impacts homogeneous gas distribution. Countercurrent perforated contact elements with overflows are the most efficient for CO_2 absorption by ammonia salt solution [23]. These contact elements (trays) ensure long contact time for gas and liquid under intense gas and liquid interaction. For the bottom zone, i.e. cooling zone equipped with horizontal tube bundles mushroom contact elements fir better. Design of these elements actually prevents possibilities of high speed streams impact from perforation holes to the tubes thus preventing their quick erosion wear.

Then basing on tests data obtained during surveys of numerous carbonation systems we can tackle basic factors of their efficient operation.

Carbonation process includes three mass and heat exchange stages:

– CO_2 absorption, complicated due to chemical reactions;
– crystallization;
– carbonated slurry cooling,

so, carbonation columns design and operation profile should ensure the best conditions for these processes flow.

Results and discussion

Both heat and mass exchange processes are defined by kinetic coefficient values, process moving force and contact phases surface. Kinetic coefficients values are mainly defined by the process dynamics, i.e. intensity of phases interaction that ensures development of their contact surface. During CO_2 absorption in liquid phase chemical reaction flow at the same time. The latter as a rule take more time for the process, so larger operation volume of the units is required for them.

Intensity of heat exchange in the cooling zone is also defined by kinetic coefficient values, i.e. heat transfer coefficient from interpipe space to cooling water moving in the pipes.

Under the impact of upward gas phase flow part of cooled slurry is drawn to the absorption zone. This causes temperature decrease of the latter before entering cooling zone.

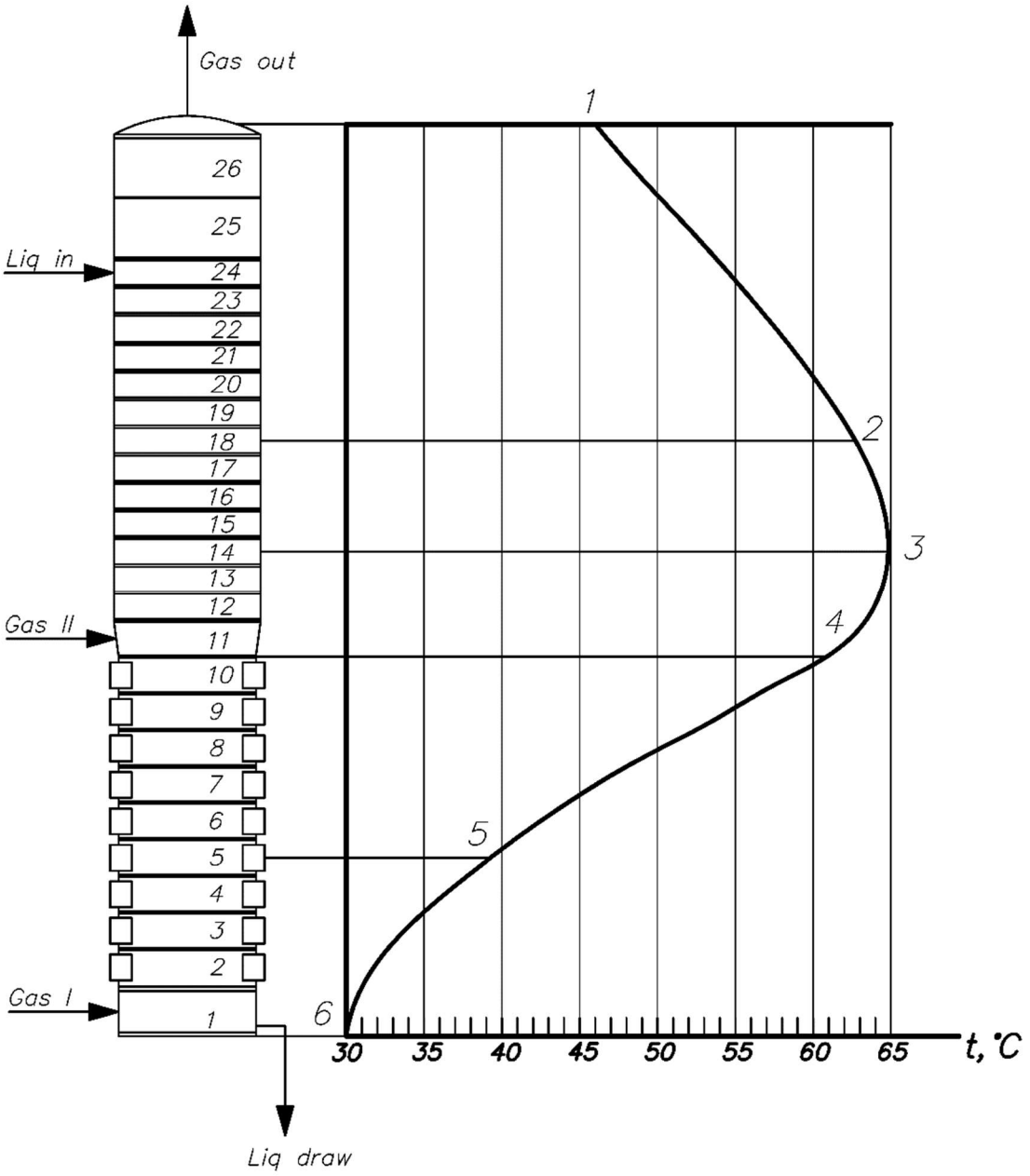

Figure 3. Temperature change diagram along carbonation column height.

On **Figure 3** temperature change diagram along carbonation column height is shown [20].

For process control and flow below listed temperature values are used as a rule:

– outlet gas 1;

– average in absorption 2 and cooling 5 zones;

– in the crystals see ding zone 3;

– in slurry feed zone to cooling zone 4;

– outlet slurry 6.

According to the diagram, liquid phase temperature gradually increases as it passes the column from the top to the bottom and reaches maximum the crystals seeding zone. Then it gradually decreases before the cooling zone, as it was mentioned above, due to mixing with cooled slurry blown away by gas flow from this zone. The best placement for crystals seeding zone allows to ensure gradual decrease of slurry temperature and, correspondingly, gradual crystals growth that create conditions for obtaining high quality crystals.

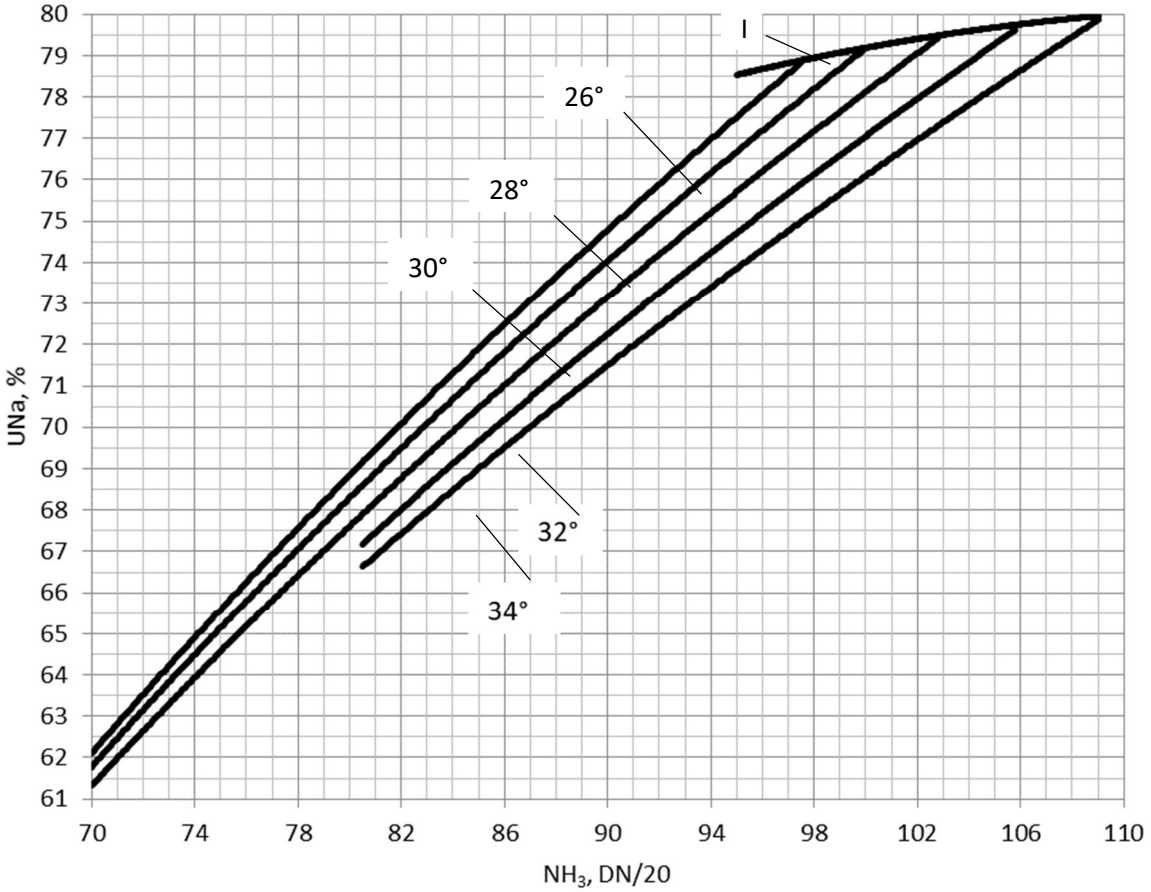

Figure 4. U_{Na} dependency on total NH_3 concentration in the carbonation columns slurry at various temperatures (I – slurry saturation line for $NaHCO_3$ and NH_4HCO_3).

Sinking of this zone facilitates cooling and, correspondingly, decreases quality of sodium bicarbonate crystals (forms and sizes).

Raise of crystals seeding zone causes failure to reach temperature required for small crystals dissolution that also impacts their quality.

Thus, carbonation process shall be managed by engineers with experience in corresponding equipment that allows to control, set and sustain crystals seeding zone at required level along the column height.

So, as we mentioned above design and operation mode shall ensure:

– intense gas and liquid interaction;
– required operation mode;
– required heat transfer surface.

One of basic performance indicators of efficient system operation is sodium recovery degree U_{Na}. Increase of this indicator and increase of crystals quality are mainly defined by initial solutions concentration, mainly by ammonia, carbon dioxide and sodium chloride and CO_2-containing gas [24-27].

Numerous research of ammonia concentration increase in solutions fed for carbonation showed that it causes extraction of ammonia hydrocarbonate to sediment that precipitated on the surfaces of contact elements and heat exchange pipes. It limited carbonation columns run between washes, broke process and decreased quality of $NaHCO_3$ crystals.

Increase of NaCl concentration is limited by its solubility in ammonia carbon salts. Though

feed of solid NaCl in certain amounts ensures its dissolution as reaction flows (2) allowing refined NaCl feed to carbonation process.

Basing on the above we can conclude that in order to prevent these adverse effects both components: ammonia and sodium chloride should be fed to the system simultaneously. Industrial tests with high ammonia content lyes saturated with sodium chloride slurry were fed to carbonation system.

Results of these tests showed that sodium chloride feed and increase of its concentration together with ammonia concentration allows to increase sodium recovery degree U_{Na} up to 75-78 %. Of course, refined sodium chloride salt should be used for dissolution in order not to contaminate the final product, i.e. sodium carbonate.

Another efficient way to increase U_{Na} is decrease of ammonia blow away from C liquor fed to basic carbonation. This can be reached by:

– increase of CO_2 concentration in this lye, as we mentioned above;

– decrease of fed lye temperature;

– pressure increase in the top of the columns by decreasing ammonia share in outlet gas.

Table 1. Data on carbonation column operation during its run

Inlet	**No**	C-liquor (temperature –41-42°C)			I input gas (flow–2200 nm³/h)		II input gas (flow– 3200-4000 nm³/h)
		Concentration, ND/20			CO_2 concentration, % vol.		
		NH_3 total	CO_2	Cl^- total			
	1	96,5-98,5	45	89	69,0		40,0
	2		49,6				
	3		54,8				
	4		60,5				
Outlet	**No**	Slurry					Exhaust columns gas
		Concentration, ND/20				U_{Na}, %	CO_2 concentration, % vol.
		NH_3 total	NH_3 fixed	CO_2	Cl^- total		
	1	90,0	70,3	30,0	99,5	70,6	7,9
	2	91,7	71,6	31,8	99,8	71,7	7,2
	3	93,5	72,5	34,0	99,5	72,8	6,8
	4	94,5	73,1	36,7	99,3	73,6	6,1

As ammonia blow away is defined by correlation of its total concentration in the final solution and ammoniated solution, diagram (**Figure 4**) clearly shows U_{Na} dependency on total NH_3 concentration in the final solution (slurry) at its various temperature values.

Table 1 shows the data from the inspection of the carbonation column during the run.

Conclusions

As above mentioned shows there are several ways for carbonation systems improvement. Main of them are:

– increase of basic components concentration;

– intensification of heat and mass exchange;

– decrease of NH_3 losses with exhaust gas.

Preliminary carbonation is very important for mass exchange. Increase of CO_2 concentration in the lye enhances NH_3 detention in the lye, decreases its blow away with exhaust gas thus increasing sodium recovery degree. Sodium chloride feed and increase of its concentration together with ammonia concentration also allows to increase sodium recovery degree thus increasing plant efficiency in general

References

[1] Rahimpour H, Fahmi A, Zinatloo-Ajabshir S. Toward sustainable soda ash production: A critical review on eco-impacts, modifications, and innovative approaches. Results in Engineering 2024;23:102399.

[2] Melnyk TV. From history of the development of basic chemical technology: production of soda. Questions of the history of science and technology 2011;4:47-53.

[3] Gryn GI, Hryntsova AV, Larina IV, Kobziev AV, Avina SI. Getting the soda ash ammonia method and methods of recycling of liquid waste. Young Scientist 2018;10(62):126-129.

[4] Cichosz M. Rozwój i stan przemysłu sodowego na świecie z uwzględnieniem rozwiązań przyjaznych dla środowiska. Przemysł Chemiczny 2018;1(3):17-23.

[5] Kasikowski T, Buczkowski R, Lemanowska E. Cleaner production in the ammonia–soda industry: an ecological and economic study. Journal of Environmental Management 2004;73(4):339-356.

[6] Suvorin O, Kravchenko I, Ozheredova M, Zubtsov Y, Píštěk V. The study of properties of soda production wastes as anti-icing reagents. Environmental Problems 2022;7(4):163-168.

[7] Rumayor M, Dominguez-Ramos A, Irabien A. Toward the Decarbonization of Hard-To-Abate Sectors: A Case Study of the Soda Ash Production. ACS Sustainable Chemistry & Engineering 2020;8(32):11956-11966.

[8] Cichosz M, Kiełkowska U, Skowron K, Kiedzik Ł, Łazarski S, Szkudlarek M, Kowalska B, Żurawski D. Changes in Synthetic Soda Ash Production and Its Consequences for the Environment. Materials 2022;15(14):4828.

[9] Cormos A, Cormos C, Ş. Agachi P. Making soda ash manufacture more sustainable. A modeling study using ASPEN Plus. Computer Aided Chemical Engineering 2007;24:551-556.

[10] Krótki A, Spietz T, Dobras S, Chwoła T, Tatarczuk A, Żórawski D, Skowron K, Skrzyniecki D, Hulisz P. Carbon capture pilot study in Solvay soda ash process. Applied Energy 2025;380:124995.

[11] Bonfim-Rocha L, Silva A, de Faria S, Vieira M, de Souza M. Production of Sodium Bicarbonate from CO2 Reuse Processes: A Brief Review. International Journal of Chemical Reactor Engineering 2019;18(1):20180318.

[12] Sibhat M, Yao G, Zhu N, Tsegay G, Fang K, Zhu Q, Zhou Y, Zhao J. Advancement in sodium carbonation pathways for sustainable carbon capture and utilization: A review. Results in Engineering 2024;23:102536.

[13] Wang T, Li Z. Novel process for manufacturing soda ash and sulfuric acid from sodium sulfate. Journal of Chemical Industry and Engineering 2005; 56(1):174-179.

[14] Li B, Asselin E, Li Z. New process for Na2CO3 production from Na2SO4 based on modeling the Na2SO4−(NH4)2SO4−MEA−MEG−H2O system. ACS Omega 2023;9(1):1265-1277.

[15] Pak K, Son S, Li B, Jang M, Jang P, Kim K, Pak S. Modeling and Simulation for the Production Process of Soda Ash by the Ammonium Sulfate-Soda Method.

Chemical Engineering & Technology 2021;44(10):1759-1767.

[16] Mao W, Zhang L, Gan S, Zhou Y, Li J, Cao J. Process for resource-based preparation of soda ash from waste sodium sulfate based on double displacement reaction: Optimization using response surface methodology. Journal of Cleaner Production 2026;546:147795.

[17] Hungaro Yoshi H, Silva A, de Souza M, Bernardo de Faria S, Bernardo A, Bonfim-Rocha L. Multi-criteria assessment of sodium bicarbonate optimized production through CO2 utilization strategies. Journal of Cleaner Production 2022;349:131419.

[18] Tseitlin MA, Frumin VM. Raschet odnovremennoi absorbtsii ammiaka i dioksida ugleroda v sodovom proizvodstve. Himicheskaia promyshlennost 1984;7:424–426.

[19] Yusupbekov N, Mukhitdinov D, Iskhakova F. Modeling of carbonization and absorption processes in soda ash production. Chemical Technology, Control and Management 2025;2025(3):05-13.

[20] Frumin VM, Bukhkalo SY, Tomenko VM. Carbonization of ammoniated brine in the production of calcined soda. Bulletin of the Kharkiv Polytechnic Institute: Series: Chemistry, chemical technologies and ecology 2006;25:115-119.

[21] Sharma MM, Mashelkar RA, Mehta VD. Mass transfer in plate columns. British chemical engineering 1969;14(1):70-76.

[22] Kulkarni SJ. Mass Transfer with Tray Tower and Its Modeling: A Review. International Journal of Research & Review 2016;3(11):51-55.

[23] Frumin VM, Burin VL, Pasichnychenko YuD. Hydraulic resistance of cross plates of large perforation. Bulletin of the Kharkiv Polytechnic Institute: Series: New solutions in modern technologies 2005;43:3-4.

[24] Skowron K, Sobczak W, Kiedzik L, Zelazny R, Buczkowski R, Wachowiak M, Cichosz M. Method for brine carbonization with additional amount of ammonia in a process of soda production and system of devices for carrying out this method. CIECH R&D Sp. z o.o., European patent 3312143A1. 2018 Apr 25.

[25] Panasenko VA, Mykhaylova EN, Mykhaylov VF, Kryvomlin VA, Kozub PA. Intensification of the carbonation process in soda production. Bulletin of the Kharkiv Polytechnic Institute: Series: Chemistry, chemical technologies and ecology 2006;44:3-7.

[26] Porokhnia M. Investigation of the influence of the main technological parameters (solution temperature, gas load) on the efficiency of the carbonization process in industrial conditions. Bulletin of the Kharkiv Polytechnic Institute: Series: Innovative studies in scientific works of students 2021;1(1361):56-61.

[27] Cichosz M, Kiełkowska U, Łazarski S, Kiedzik Ł, Szkudlare M, Skowron K, Kowalska B, Żurawski D. Influence of Ammonia Concentration on Solvay Soda Process Parameters and Associated Environmental and Energetic Effects. Energies 2022;15(22):8370.