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MODELING AND SIMULATION OF THE CARBONATION PROCESS OF AMMONIACAL BRINE USING CHEMCAD

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ABSTRACT. In this paper the model and the simulation results for carbonation process of ammoniacal brine solution have been presented. Carbonation process of ammoniacal sodium chloride solution (brine) is used to obtain sodium bicarbonate and sodium carbonate in soda ash plants (according to Solvay process).

The carbonation process of ammoniacal sodium chloride solution is done using tray absorption columns, typically in a three columns sequence. The first absorption column is used to saturate the ammoniacal brine with carbon dioxide. The second column is a scrubbing unit used to recover residual carbon dioxide from the gaseous effluent coming from first and third columns. In the third column, the final saturation of the liquid phase with carbon dioxide and the precipitation of sodium bicarbonate take place.

The carbonation process of ammoniacal sodium chloride solution is a complex process because of chemical reactions that involve the species present in the liquid phase. Modeling and simulation of the carbonation process of ammoniacal sodium chloride solution and precipitation of sodium bicarbonate were done using ChemCAD software package.

The evolutions of the process parameters were studied during the carbonation process. The model and the simulation results proved to be a reliable tool for analyzing the carbonation and precipitation processes and can be used to improve the real plant operation.

1. INTRODUCTION

Sodium carbonate is a common inorganic industrial chemical, also known as soda ash (Na_2CO_3). It is widely used in the manufacture of glass, chemicals, such as sodium silicates and sodium phosphates, the pulp and paper industries, the manufacture of detergents and for the treatment of water.

The synthesis process of soda ash (sodium carbonate) using Solvay process is done starting from sodium chloride, limestone, coke and ammonia as raw materials [1, 2, 3].

The natural sodium chloride solution (brine) is extracted from soil and purified (removal of solid impurities by filtration and removal of calcium and magnesium ions by precipitation).

Into the purified sodium chloride solution, ammonia is absorbed. After ammonia absorption, the solution is carbonated with gaseous carbon dioxide coming from two main sources: thermal decomposition of the limestone and sodium bicarbonate calcination process.

After carbonation of ammoniacal brine, a suspension of sodium bicarbonate is obtained. Sodium bicarbonate is filtered and the residual liquid phase is treated with calcium hydroxide solution (slaked lime) in order to recover the ammonia from ammonium salts (ammonium chloride, carbonate, bicarbonate etc.). The recovered ammonia is recycled into the process at absorption stage into the sodium chloride solution (brine).

Sodium bicarbonate resulted after filtration is washed, dried and calcined in order to obtain sodium carbonate (soda ash).

The main chemical reactions involved in sodium carbonate (soda ash) synthesis are presented below [2]:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O \quad (3)$$

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3 \quad (4)$$

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl \quad (5)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \quad (6)$$

The carbonation process is done using tray absorption columns, typically in a three columns sequence. The first absorption column is used to saturate the ammoniacal brine with carbon dioxide coming from limestone decomposition process (35 – 40 % CO_2 mole fractions).

The second column is a scrubbing unit used to recover residual carbon dioxide from the gaseous effluent coming from the first and the third columns (5 – 10 % CO_2 mole fractions).

The third absorption column has two gaseous inlets: one situated at the bottom of the column and one situated at the middle of the column. The bottom inlet gas is coming from sodium bicarbonate calcination process (60 – 70 % CO_2 mole fractions). The middle inlet gas is coming from the limestone decomposition process (35 – 40 % CO_2 mole fractions). In the third column the final saturation of the liquid phase with carbon dioxide and the precipitation of sodium bicarbonate take place.

2. MODELING AND SIMULATION OF THE PROCESS

The carbonation process of ammoniacal sodium chloride solution is a complex process because of the following factors: presence of a three phase system (gas – liquid – solid), chemical species present in the liquid phase, chemical reactions that take place, the carbonation process is exothermic, precipitation of sodium bicarbonate that affects the heat transfer coefficients etc.

Most of the authors agreed with the following description of the chemical reactions that take place during the carbonation process of ammoniacal brine and the precipitation process of sodium bicarbonate [1, 5, 6]:

$$CO_2 + OH^- \leftrightarrows HCO_3^- \quad (7)$$

$$CO_2 + 2OH^- \leftrightarrows CO_3^{2-} + H_2O \quad (8)$$

$$CO_2 + CO_3^{2-} + H_2O \leftrightarrows 2HCO_3^- \quad (9)$$

$$CO_2 + NH_3 \leftrightarrows NH_2COO^- + H^+ \quad (10)$$

$$H^+ + NH_3 \leftrightarrows NH_4^+ \quad (11)$$

$$NH_2COO^- + NH_4^+ \leftrightarrows CO_2 + 2NH_3 \quad (12)$$

$$HCO_3^- + NH_3 \leftrightarrows NH_4^+ + CO_3^{2-} \quad (13)$$

The parameters used for modeling and simulation of the carbonation process of ammoniacal sodium chloride solution (brine) are presented in the tables 1, 2 and 3.

Table 1.

The properties of the inlet gaseous streams

Parameter	Unit	First column - bottom -	Third column - bottom -	Third column - middle -
Temperature	[^oC]	30	30	30
Pressure	[bar]	2.6	2.8	1.5
CO_2	[mole %]	37.3	68	40
CO	[mole %]	0.6	0.2	0.5
O_2	[mole %]	2	0.2	0.5
N_2	[mole %]	58.6	30.5	58
H_2O	[mole %]	1.5	1	0.5
NH_3	[mole %]	0	0.1	0.5
Flow	[kg/h]	1033	1420	760

Table 2.

The properties of the inlet liquid stream (ammoniacal brine)

Parameter	Unit	First column
Temperature	[^oC]	30
Pressure	[bar]	1
NaCl	[mass %]	22.7
NH_3	[mass %]	7.5
H_2O	[mass %]	69.8
Flow	[kg/h]	11460

Table 3.

The parameters of the absorption columns

Parameter	Column 1	Column 2	Column 3
No. of stage	35	10	35
Top pressure	1 bar	1 bar	1 bar
Feed tray for liquid stream	1	1	1
Feed tray for gas stream	35	10	25 35
Cooling duty	$2 * 10^7$ J/h	0	$1.9 * 10^9$ J/h

The modeling and simulation of the carbonation process of ammoniacal brine, precipitation and filtration of sodium bicarbonate were done using ChemCAD (version 5.1.3) software package. As thermodynamic option used for simulation of the carbonation process, the electrolyte package was used [6, 7].

The main window of the application is presented in the figure 1.

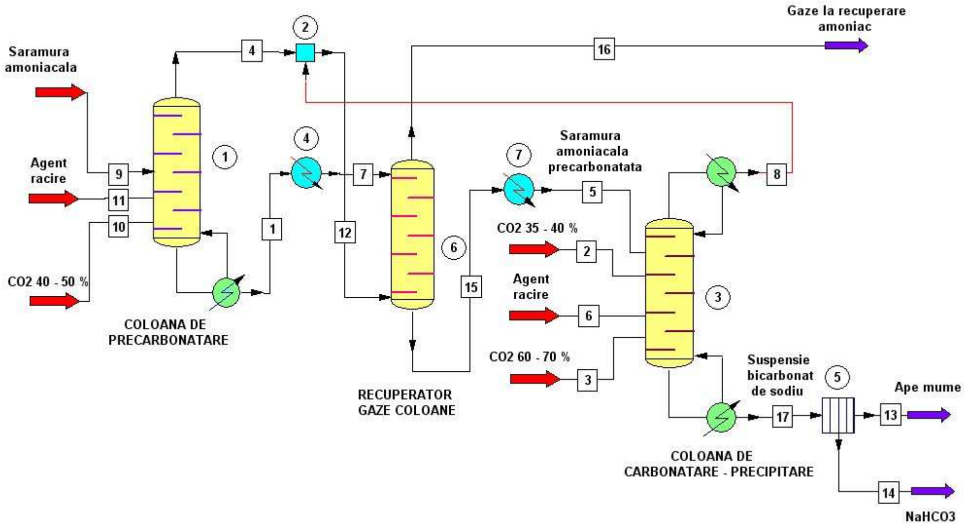

Figure 1. Simulation of the carbonation process using ChemCAD

3. RESULTS AND DISCUSSIONS

In the first column, the ammoniacal brine is saturated with carbon dioxide coming from thermal limestone decomposition process.

The variation of total vapor flow, total liquid flow and temperature for the first absorption column are presented in the figures 2, 3 and 4.

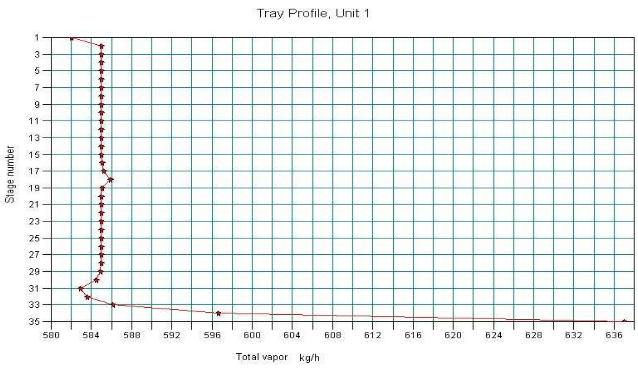

Figure 2. Variation of the total vapor flow for the first column

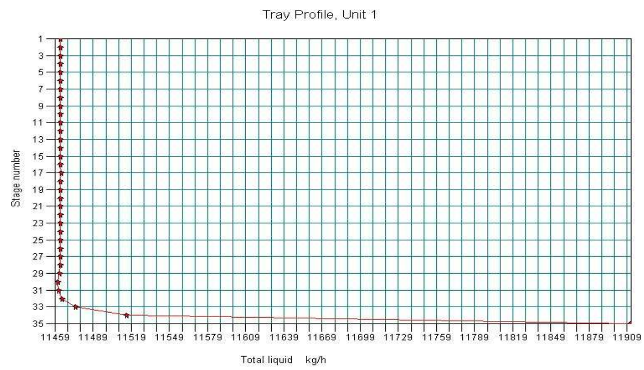

Figure 3. Variation of the total liquid flow for the first column

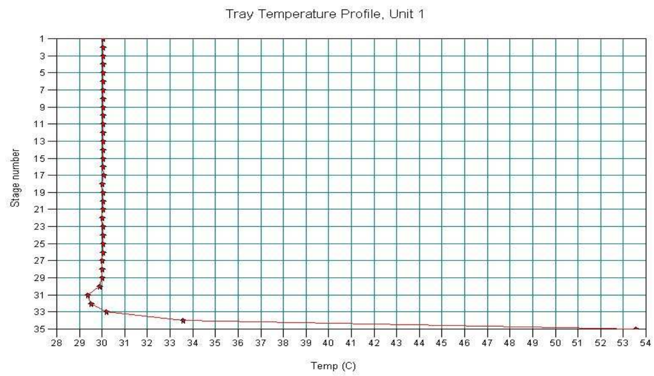

Figure 4. Variation of the temperature for the first column

The variation of total vapor flow, total liquid flow and temperature for the second column (scrubbing unit) are presented in the figures 5, 6 and 7.

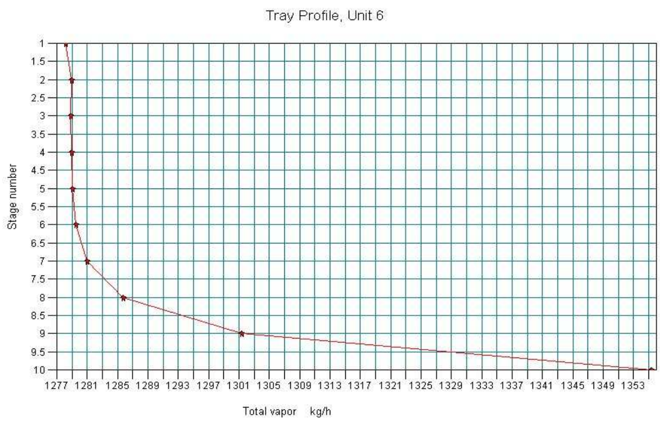

Figure 5. Variation of the total vapor flow for the second column (scrubber)

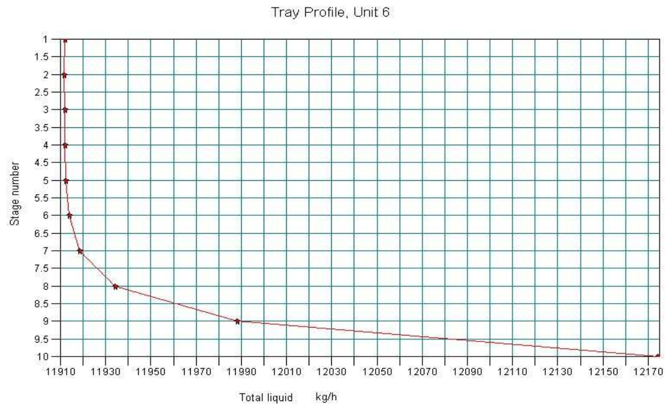

Figure 6. Variation of the total liquid flow for the second column (scrubber)

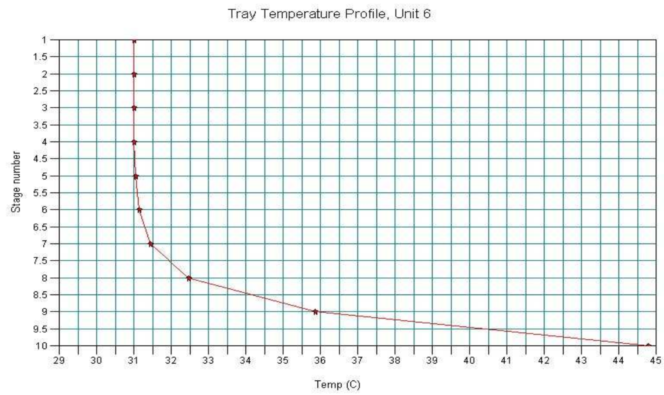

Figure 7. Variation of the temperature for the second column (scrubber)

The variation of total vapor flow, total liquid flow and temperature for the third column are presented in the figures 8, 9 and 10.

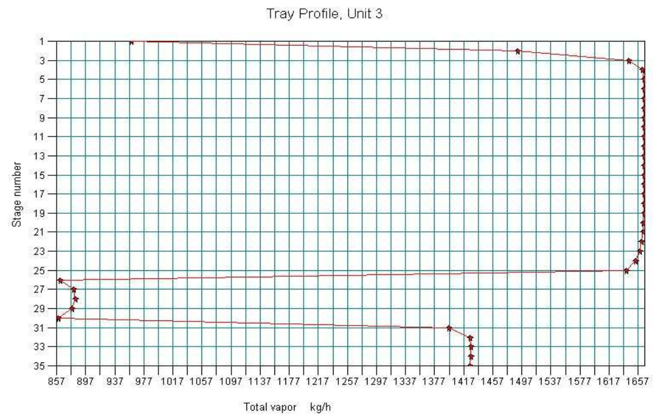

Figure 8. Variation of the total vapor flow for the third column

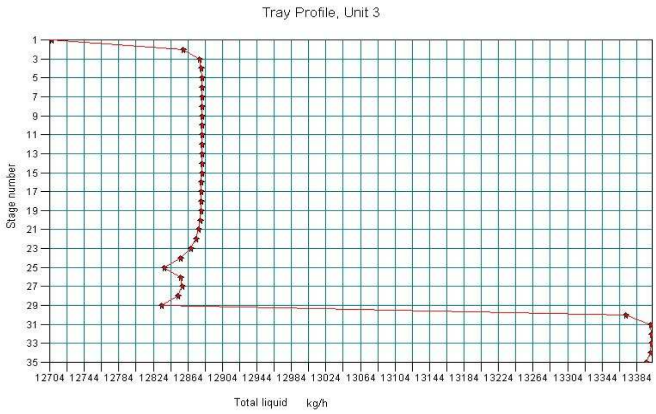

Figure 9. Variation of the total liquid flow for the third column

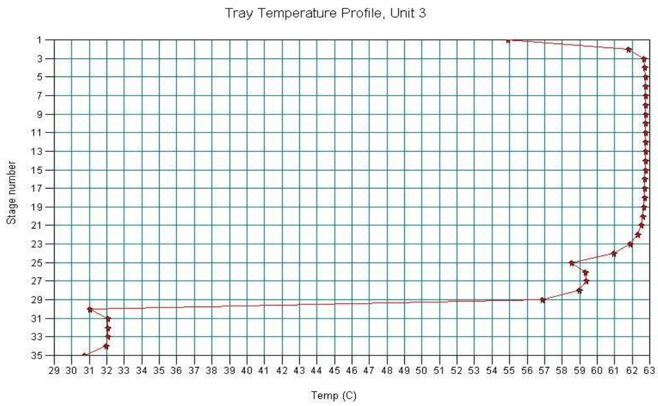

Figure 10. Variation of the temperature for the third column

The calculated properties of the output liquid streams resulted from the simulation of the carbonation columns are presented in the table 4.

Table 4.

The properties of the column liquid streams (simulation results)

Parameter	Unit	First column	Second column	Third column
Temperature	[°C]	53.5	44.8	30.7
Pressure	[bar]	1	1	1
H_2O	[mass %]	63.8	63	53.86
NH_3	[mass %]	1.4	1.07	0.06
NH_4OH	[mass %]	5.29	4.5	0.22
$NaHCO_3$	[mass %]	0	0	15.66
Na^+	[mass %]	8.6	8.4	3.34
NH_4^+	[mass %]	2	2.56	6.1
Cl^-	[mass %]	13.25	12.95	11.77

Parameter	Unit	First column	Second column	Third column
OH^-	[mass %]	0.00025	0.00012	0.0000023
H^+	[mass %]	$2.3 * 10^{-12}$	$2.2 * 10^{-12}$	$5.49 * 10^{-11}$
HCO_3^-	[mass %]	1.15	1.56	8.19
CO_3^{2-}	[mass %]	1.01	1.18	0.16
NH_2COO^-	[mass %]	3.5	4.78	0.71
Flow	[kg/h]	11911	12175	13395

The calculated properties of output gaseous streams resulted from the simulation of the carbonation columns are presented in the table 5.

Table 5.

The properties of the column gaseous streams (simulation results)

Parameter	Unit	First column	Second column	Third column
Temperature	[^oC]	30	31	55
Pressure	[bar]	1	1	1
CO_2	[mole %]	2.15	0.09	10.95
CO	[mole %]	0.8	0.77	0.53
O_2	[mole %]	2.83	1.72	0.55
N_2	[mole %]	81.04	89.09	69.93
H_2O	[mole %]	2.88	3.22	11.55
NH_3	[mole %]	10.43	5.11	6.49
Flow	[kg/h]	582	1278	960

The suspension of sodium bicarbonate resulted at the bottom of the third column is filtrated on a rotary drum filter and 2918 kg/h wet product is obtained. The wet product obtained after filtration contains 2100 kg/h sodium bicarbonate.

The overall yield of the carbonation process of ammoniacal sodium chloride solution (transformation of sodium chloride into sodium bicarbonate) is 72 %.

The simulation results presented above were compared with data collected from real plant operation [1, 3, 4]. Regarding the liquid streams compositions, data collected from a real plant operation are presented in the table 6.

Table 6.

The properties of the column liquid streams (real plant operation)

Parameter	Unit	First column	Second column	Third column
Temperature	[^oC]	40 – 55	35 – 45	30 – 40
Pressure	[bar]	1	1	1
H_2O	[mass %]	60 – 65	60 – 65	50 – 55
NH_4OH	[mass %]	4 – 7	3 – 6	0 – 0.5
NH_4HCO_3	[mass %]	0	0	6 – 7
$NaHCO_3$	[mass %]	0	0	15 – 22
NaCl	[mass %]	15 – 22	15 – 22	3 – 5
NH_4Cl	[mass %]	0	0	12 – 15
Na_2CO_3	[mass %]	0 – 0.5	0 – 0.5	0
$(NH_4)_2CO_3$	[mass %]	10 – 15	10 – 15	0

Regarding the gaseous streams compositions, data collected from a real plant operation are presented in the table 7.

Table 7.

The properties of the column gaseous streams (real plant operation)

Parameter	Unit	First column	Second column	Third column
Temperature	[^oC]	30 – 40	30 – 40	45 – 55
Pressure	[bar]	1 – 1.2	1 – 1.1	1 – 1.2
CO_2	[mole %]	2 – 5	1 – 3	8 – 12
N_2	[mole %]	79 – 85	80 – 90	65 – 72
H_2O	[mole %]	2 – 5	2 – 5	10 – 15
NH_3	[mole %]	5 – 10	5 – 12	5 – 10

In a real plant, the overall carbonation yield of ammoniacal brine (transformation of sodium chloride into sodium bicarbonate) is 72 – 75 %.

From the comparison, one can observe a close similarity between simulation results and data collected from a real plant. This fact validates the application developed for simulation of the process and proves the utility of the model in analyzing and optimization of the real plant operation.

4. CONCLUSIONS

Modeling and simulation of the carbonation process of ammoniacal sodium chloride solution (brine) was done using ChemCAD software package (version 5.1.3).

The carbonation process of ammoniacal brine and precipitation of sodium bicarbonate were done in three absorption columns. The first absorption column is a precarbonation column and is used to saturate the liquid phase with carbon dioxide, the second column is a scrubbing unit used to recover the remaining carbon dioxide from the other two columns and the third column is used to complete the carbonation process and to precipitate sodium bicarbonate from the liquid phase.

The evolutions of the process parameters (liquid and gaseous flows, composition of the streams, temperatures) were studied during the carbonation process of ammoniacal brine. The simulation results were compared with real plant operation data in order to validate the application developed for the carbonation process.

The mathematical model and the simulation results proved to be a reliable tool for analyzing and optimizing the real plant operation of the carbonation process of ammoniacal sodium chloride solution used is soda ash manufacture according to Solvay technology.

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