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Dedicated to professor Gh. Marcu at his 80th anniversary

MODELING AND SIMULATION OF THE AMMONIA ABSORPTION PROCESS IN SODIUM CHLORIDE SOLUTION USING CHEMCAD

CALIN CORMOS*, ANA-MARIA CORMOS*, SERBAN AGACHI*

ABSTRACT. In this paper the mathematical modeling and the simulation results for ammonia absorption in sodium chloride solution (brine) have been presented. The ammoniacal brine is used to obtain sodium bicarbonate and sodium carbonate in soda ash plants (according to the Solvay process).

The ammonia absorption process is performed in the absorption columns sequence. Because the absorption process is an exothermic process, the absorption columns are provided with cooling systems.

Modeling and simulation of the ammonia absorption in sodium chloride solution were done using ChemCAD software package. The evolutions of the process parameters were studied during the absorption process. The model and the simulation results proved to be a reliable tool for analyzing the absorption 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). 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].

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 (the recovered ammonia from the residual liquid phase is used). 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 results. Sodium bicarbonate is filtered and the residual liquid phase is treated with calcium hydroxide solution (slaked lime) in order to recover the ammonia

* *Babes – Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Street, RO-400028, Cluj – Napoca, Romania, Tel: +40264593833, Fax: +40264590818, E-mail: cormos@chem.ubbcluj.ro, cani@chem.ubbcluj.ro, sagachi@chem.ubbcluj.ro*

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

2. MODELING AND SIMULATION OF THE PROCESS

The ammonia absorption process is done using an absorption columns sequence. Because the absorption process is exothermic the columns are provided with cooling systems. The ammonia absorption process is presented in figure 1 [1,2].

The purified brine is distributed in the ammonia recovering column I *2* and in ammonia recovering column III *4*. The sodium chlorine solution (brine) rich in ammonia passes in the ammonia recovering column II *3*, and into the first absorber *6*. In the absorbers *6* and *7*, the brine flows in counter-current with cold gas from distillation (the gas from distillation are cooled at 55-60^{o}C, in the refrigerator *8*). During the ammonia absorption process, the temperature increases and reaches 60-63^{o}C to the bottom of the absorption column *6*. The ammonia concentration in the first absorber is 15-20 DN. In the second absorber *7*, the temperature is kept constant in the interval of 60-65^{o}C, by cooling. The ammoniacal brine from the second absorber *7* (with concentration 100-106 DN/20 ammonia and 30-35 DN/20 carbon dioxide) is cooled at 30-35^{o}C, in the refrigerator *9* and collected in the ammoniacal brine tank 10 in order to be send to carbonation process. The condensed phase is collected in tank *11* and sent to ammonia distillation. The outlet gas from the first absorber *6* contains 9-17% ammonia and 55-60% carbon dioxide. The ammonia from the outlet gas of the absorber *6* is absorbed in the recovering column *3*, and the rich carbon dioxide gas passes to the calciner gas collector.

The main ionic reactions of the ammonia absorption in sodium chloride solution (brine) are presented below [2]. Most of the authors agreed to the following description of the ionic reactions that take place during the absorption process:

$$H_2O \leftrightarrows H^+ + OH^- \quad (1)$$

$$CO_2 + H_2O \leftrightarrows HCO_3^- + H^+ \quad (2)$$

$$HCO_3^- \leftrightarrows CO_3^{2-} + H^+ \quad (3)$$

$$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^- \quad (4)$$

$$NH_3 + HCO_3^- \leftrightarrows NH_2COO^- + H_2O \quad (5)$$

$$NaCl \leftrightarrows Na^+ + Cl^- \quad (6)$$

$$NH_4OH \leftrightarrows NH_4^+ + OH^- \quad (7)$$

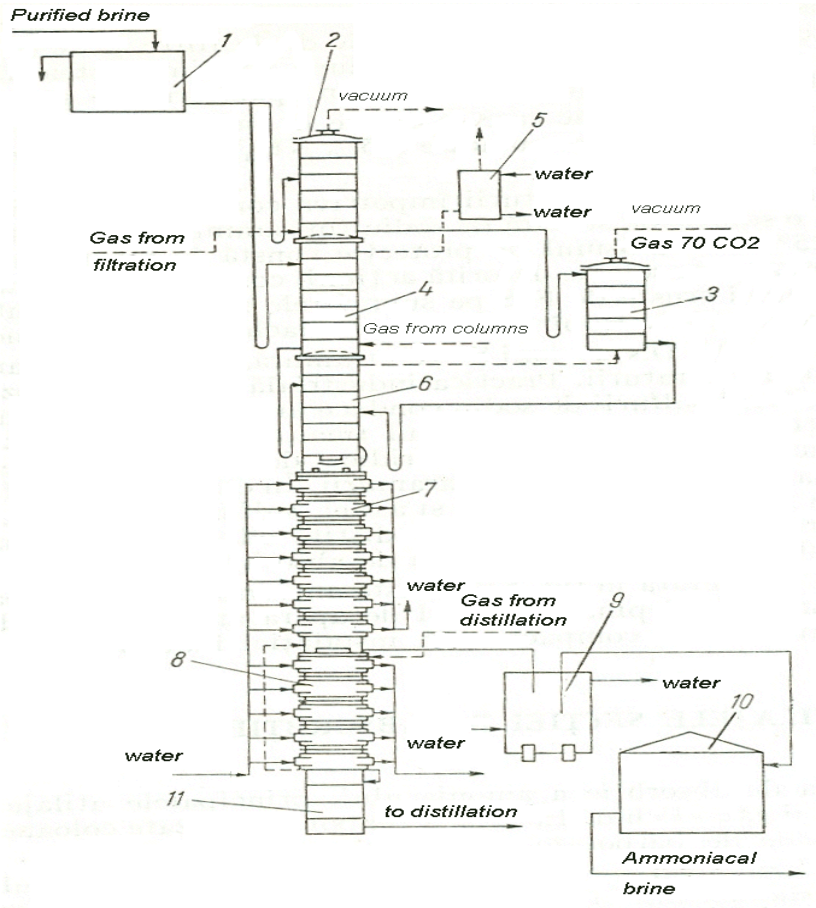

Figure 1. Ammonia absorption process [1]
1 - purified brine tank, 2 – ammonia recovering column I (from the filtration gas), 3- ammonia recovering column II (from absorption stage), 4- ammonia recovering column III (from the carbonation column gas), 5 – gas cleaner, 6 – ammonia absorber I, 7- ammonia absorber II, 8 – refrigerator of the distillation gas, 9 – refrigerator of the ammoniacal brine, 10- ammoniacal brine tank, 11- condensed tank

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

Table 1.

The properties of the inlet gaseous streams

Parameter	Measuring Unit	Gas coming from sodium bicarbonate filtration process	Gas coming from carbonation columns	Gas coming from ammonia distillation process
Temperature	[^oC]	25	50	60
Pressure	[bar]	0.5	1	0.9
CO_2	[mole %]	3.20	5.36	14.33
CO	[mole %]	0	1.00	0.03
O_2	[mole %]	18.42	1.50	0.05
N_2	[mole %]	73.68	68.52	0.33
H_2O	[mole %]	3.50	5.33	14.42
NH_3	[mole %]	1.20	18.28	70.83
Flow	[kg/h]	850	1016	1136.15

Table 2.

The properties of the inlet liquid stream (purified brine)

Parameter	Measuring Unit	Value
Temperature	[^oC]	20
Pressure	[bar]	1
NaCl	[weight %]	24,63
H_2O	[weight %]	75.47
Flow	[kg/h]	10600

Table 3.

Parameters of the absorption columns

Parameter	No. of stage	Feed tray for liquid stream	Feed tray for gas stream	Cooling duty
First absorber	6	1,4	6	0
Second absorber	6	1	6	1* 100′ J/h
Ammonia recovering column I	4	1	4	0
Ammonia recovering column II	6	1	6	0
Ammonia recovering column III	6	1	6	0

The modeling and simulation of the ammonia absorption process were done using ChemCAD (version 5.1.3) software package. The electrolyte package was used as thermodynamic option for simulation of the ammonia absorption process [4,5].

The main window of the application developed for ammonia absorption process is presented in the figure 2.

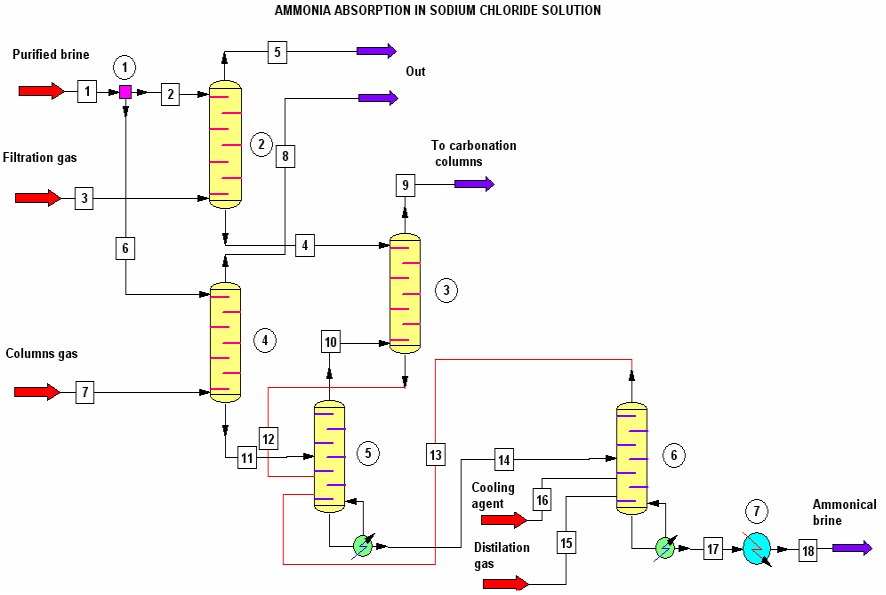

Figure 2. Simulation of the ammonia absorption process using ChemCAD

3. RESULTS AND DISCUSSIONS

The simulation results of ammonia absorption process in brine (sodium chloride solution) using ChemCAD, are presented below.

The properties of output gaseous streams resulted from the simulation in case of the recovering columns and absorber columns are presented in table 4 and 5.

Tabel 4.

The properties of the gaseous streams leaving the ammonia recovering columns

Parameter	Measuring Unit	Gas from ammonia recovering column I	Gas from ammonia recovering column III	Gas from ammonia recovering column II
Temperature	[^{o}C]	20	20	26
Pressure	[bar]	1	1	1
CO_2	[mole %]	2.2	0	49.45
CO	[mole %]	0	1.38	2.85
O_2	[mole %]	19.17	2.07	6.67
N_2	[mole %]	76.77	94.7	38.07
H_2O	[mole %]	1.86	1.85	2.9
NH_3	[mole %]	0	0	0
Flow	[kg/h]	820	775	80

Tabel 5.

The properties of the gaseous streams leaving the ammonia absorbers

Parameter	Measuring Unit	First absorber	Second absorber
Temperature	[^oC]	39	36
Pressure	[bar]	1	1
CO_2	[mole %]	0.16	0.12
CO	[mole %]	5.58	7.82
O_2	[mole %]	8.11	14.83
N_2	[mole %]	79.11	71.57
H_2O	[mole %]	5.57	4.70
NH_3	[mole %]	1.47	0.95
Flow	[kg/h]	8.2	8.6

The ammoniacal brine resulted in the absorption process has the following properties: temperature 62^{o}C, pressure 1 bar, flow 12000 kg/h, and composition (mass %): 64.88 % water, 15 % ammonia, 5.34 % NH_4OH, 3.11 % NH_2COO^-, 8.52 % Na^+, 1.39 % CO_3^{-2}, 0.56 % HCO_3^-, 1.93 % NH_4^+, 13.14 % Cl^-.

In the sequence of absorption columns, the temperature variations are: for the ammonia recovering column I the change is of 20-26^{o}C, for the ammonia recovering column III is of 20-39.5^{o}C, for the ammonia recovering column II the temperature is constant, for the first ammonia absorber is of 36-39^{o}C and for the second ammonia absorber is of 30-60 ^{o}C.

The variations of the temperature for the ammonia recovering columns are presented in the figures 3 and 4.

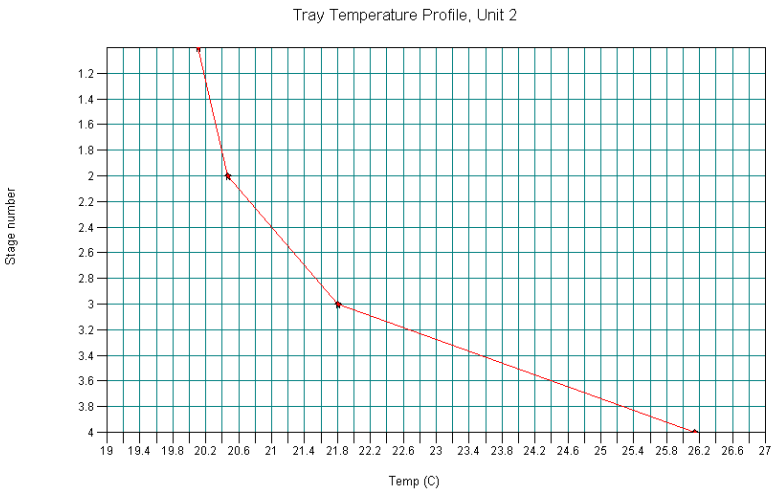

Figure 3. Variation of the temperature in the ammonia recovering column I

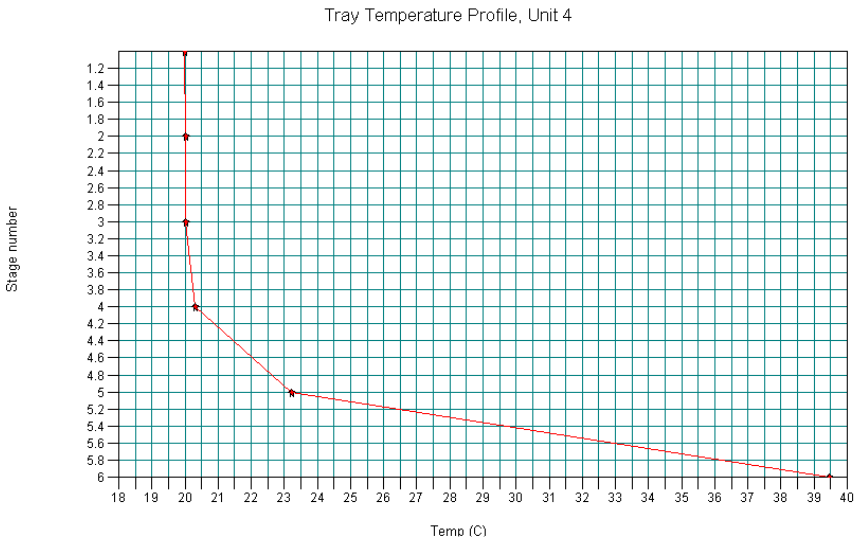

Figure 4. Variation of the temperature in of the ammonia recovering column III

The simulation results presented above were compared with data collected from real plant operation. The operation data collected from a real plant are presented in the table 6 [1, 2, 3].

Tabel 6.

The properties of the gaseous streams leaving the ammonia recovering columns (data collected from a real plant operation)

Parameter	Measuring Unit	Ammonia recovering column I	Ammonia recovering column III	Ammonia recovering column II
Temperature	[^{o}C]	-	-	25-30
CO_2	[mole %]	1.3	3.2	69.7
H_2O	[mole %]	1.8	3.2	5.1
NH_3	[mole %]	0.06	0.19	0.06
Inert	[mole %]	96.9	93.4	25.2

From the comparison of the simulation and real plant data, one can observe a close similarity between simulation results and experimental data. This fact validates the application developed for simulation 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 ammonia absorption process in sodium chloride solution (brine) was done using ChemCAD software package (version 5.1.3).

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

The mathematical model and the simulation results proved to be a reliable tool for analyzing and optimizing the real plant operation of the ammonia absorption in sodium chloride solution used in soda ash manufacturing process according to the Solvay technology.

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