engineering proceedings

MDPI

Proceeding Paper

Modeling and Optimization of the Ammonium Solution Extraction Process †

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† Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: https://asec2023.sciforum.net/.

Abstract: Calcined soda production is one of the important parts of the industry. One of the main problems in the production of soda is the waste of raw materials. Disposing of some raw materials as waste not only causes economic damage but also has a negative impact on the environment. Absorption is the main process in the production of calcined soda. By finding the optimal consumption of the chemical components involved in absorption process, it will be possible to reduce the amount of raw materials released into the waste. In this work, initially, the kinetic model of the absorption process was found using the stoichiometric matrix method. Based on the stoichiometric matrix, the main components (NH_3, CO_2, NH_4HCO_3, NaCl) participating in the chemical reaction were identified. Using the found kinetic model, a computer model of the absorption process was simulated in the MATLAB program. Based on the simulated computer model, a diagram of changes in the concentration of components in the absorption process over time was obtained. The use of the considered mathematical model as part of the absorption process control system allows: (1) Reduce the loss of the amount of gases used in the absorption process; (2) Provide the required concentration of liquid saturated with ammonia; (3) Determine the required temperature regime along the entire length of the absorber.

Keywords: calcined soda; absorption; stoichiometric matrix; kinetic model; computer simulation

Citation: Usmanov, K.; Eshbobaev, J.; Yakubova, N. Modeling and Optimization of the Ammonium Solution Extraction Process. *Eng. Proc.* **2023**, *52*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s): Name

Published: date

1. Introduction

One of the salient attributes of contemporary oil refining procedures is the pursuit of enhancing technologies, augmenting productivity, and elevating the unit capacity of facilities. Simultaneously, the advancement of contemporary production is accompanied by a persistent escalation in the demands for the efficacy of technological systems, necessitating consideration during the design phase of process control systems [1] The practical organization of contemporary production management necessitates reevaluating conventional control mechanisms and adopting a novel system engineering approach towards formulating control and automation strategies. In this particular scenario, the design does not include the creation of distinct automation nodes. Instead, a unified technological system is developed, including all control devices and considering their connectivity and mutual effect [2].

The acquisition of ammoniated brine is a crucial step in the production of soda ash by the ammonia technique. The conventional procedure involves the saturation of brine, which is an aqueous solution of sodium chloride, with a gas-vapor combination including ammonia and carbon dioxide emanating from the distillation unit. Ammonized brine

obtained by interaction with distillation gases [3]. The ammoniated brine, which is formed by the reaction between brine and distillation gases, is then sent to the carbonization phase in order to facilitate the precipitation of sodium bicarbonate [4].

Absorption saturates pure brine with gaseous ammonia and carbon dioxide. The absorption process is complicated by reversible reactions. Many components react in three steps, and unstable raw materials complicate the process. Any component concentration change in the reaction mixture affects the absorption process.

Ammonization may cause unwanted reactions if the brine is poorly purified from calcium and magnesium salts. Calcium carbonate and magnesium hydroxide deposits occur when ammonia and carbon dioxide interact with calcium and magnesium compounds. These deposits may build on equipment and pipes. Deposits on equipment and pipe walls from systematic brine cleaning violations can hinder the absorption unit's operations [5].

The regular functioning of the absorption unit can be disrupted when there is a systematic violation of the brine cleaning regime, leading to the formation of $CaCO_3$ and $Mg(OH)_2$ deposits on the walls of apparatuses and pipes.

The complete assimilation procedure is primarily determined by two factors:

1. The absorber receives gases from both the distillation column and the bicarbonate calcination furnace.
2. The control of the absorption process involves controlling the flow of brine to ensure that the resulting liquid, saturated with ammonia, achieves the desired concentration. This is achieved by adjusting the quantity of brine entering the distillation process.

In order to achieve saturation of the cleaned brine, a gas-vapor combination including ammonia and water vapor containing carbon dioxide, obtained via distillation, is employed. By decreasing the quantity of water vapor, it becomes possible to enhance the concentration of ammonia and sodium chloride inside the brine solution [6].

The gas-vapor mixture from distillation usually contains 52% ammonia (NH_3), and 25% carbon dioxide (CO_2), the rest is water vapor and has a temperature of 60 ^{0}C. The formation of ammonium carbamate creates favorable conditions for the absorption of ammonia and carbon dioxide since this reduces the equilibrium pressure of NH_3 and CO_2 over the solution.

2. Methodology

The absorption process will be examined through the utilization of the kinetic model of reactions as a mathematical representation. The precise processes underlying the absorption process remain incompletely elucidated. However, in technical calculations, it is customary to employ the following chemical reactions.

We find out the chemical reaction of the process [7], and then we use the stoichiometric matrix approach to build a mathematical model of that process.

$$\begin{aligned} &NH_3 + CO_2 + H_2O \leftrightarrow NH_4HCO_3 \\ &NaCl + NH_4HCO_3 \leftrightarrow NaHCO_3 + NH_4Cl \\ &NH_3 + H_2O \leftrightarrow NH_4OH \\ &2NH_3 + CO_2 + H_2O \leftrightarrow (NH_4)_2CO_3 \end{aligned} \quad (1)$$

We mark each component in the above chemical reactions as x_1

Ammonia	$x_1 - NH_3$
Carbon dioxide	$x_2 - CO_2$
Water	$x_3 - H_2O$
Ammonium bicarbonate	$x_4 - NH_4HCO_3$
Sodium chloride	$x_5 - NaCl$
Sodium bicarbonate	$x_6 - NaHCO_3$

(2)

Ammonium chloride	$x_7 - NH_4Cl$
Ammonium hydroxide	$x_8 - NH_4OH$
Ammonium carbonate	$x_9 - (NH_4)_2CO_3$

Considering the given notation (2), it can be observed that chemical reactions (1) will manifest in the subsequent manner.

$$\begin{aligned} &x_1 + x_2 + x_3 \rightarrow x_4 \\ &x_5 + x_4 \leftrightarrow x_6 + x_7 \\ &x_1 + x_3 \leftrightarrow x_8 \\ &2x_1 + x_2 + x_3 \leftrightarrow x_9 \end{aligned} \quad (3)$$

The matrix of stoichiometric coefficients $\nu_{IJ}, i = \overline{1,9},\ j = \overline{1,4},$ corresponding to the kinetic equation is given Table 1.

Table 1. Matrix of stoichiometric coefficients.

	NH_3	CO_2	H_2O	NH_4HCO_3	NaCl	$NaHCO_3$	NH_4Cl	NH_4OH	$(NH_4)_2$
ω_1	−1	−1	−1	1	0	0	0	0	0
ω_2	0	0	0	−1	−1	1	1	0	0
ω_3	−1	0	−1	0	0	0	0	1	0
ω_4	−1	−1	−1	0	0	0	0	0	1

The resultant matrix is a representation of stoichiometric coefficients, formally indicating the rate of change of chemical reaction components. The equations representing the kinetic equations for the absorption process of ammonization of brine may be derived from the law of mass action and the matrix of stoichiometric coefficients. These equations correspond to the chemical changes outlined in the scheme (3).

$$\begin{aligned} \omega_1 &= k_1 C_{x1} C_{x2} C_{x3} \\ \omega_2 &= k_2 C_{x5} C_{x4-} k_3 C_{x6} C_{x7} \\ \omega_3 &= k_4 C_{x1} C_{x5-} k_5 C_{x8} \\ \omega_4 &= k_6 C_{x1}^2 C_{x2} C_{x3} - k_7 C_{x9} \end{aligned} \quad (4)$$

C_{xi} −vector of molar concentrations of substances, mol/m^3; k—rate constants (sec^{-1}) of the chemical reaction of the corresponding direction, the defining Arrhenius equation:

$$k = k_0 e^{-\frac{E}{RT}}; \quad (5)$$

k_0 −pre-exponential factor.

E −activation energy of the stage, (cal/mol)

T −absolute temperature.

R −universal gas constant (cal/(mol K)).

Using the stoichiometric matrix method, we can write the mathematical model of the change in the concentration of each component in the device as follows

$$\begin{aligned} g_{x_1} &= -\omega_1 - \omega_3 - \omega_4 \\ g_{x_2} &= -\omega_1 - \omega_4 \\ g_{x_3} &= -\omega_1 - \omega_3 - \omega_4 \\ g_{x_4} &= \omega_1 - \omega_2 \\ g_{x_5} &= -\omega_2 \\ g_{x_6} &= \omega_2 \\ g_{x_7} &= \omega_2 \\ g_{x_8} &= \omega_3 \\ g_{x_9} &= \omega_4 \end{aligned} \quad (6)$$

Within the field of chemical reactions, it is possible to discern between essential and non-essential elements among the many components. The quantity of fundamental constituents involved in a chemical reaction is equivalent to the order of the matrix of stoichiometric coefficients. Given that the rank of the stoichiometric matrix is, it may be inferred that the chemical reaction under consideration involves essential components.

We define the key components ($g_{x_1} = g_{x_1}$; $g_{x_3} = g_{x_1}$; $g_{x_5} = -g_{x_5}$; $g_{x_7} = g_{x_5}$; $g_{x_2} = g_{x_2}$; $g_{x_4} = g_{x_4}$; $g_{x_6} = g_{x_5}$; $g_{x_8} = g_{x_2} - g_{x_1}$; $g_{x_9} = -g_{x_4} - g_{x_5} - g_{x_2}$;) that directly affect the course of the absorption process.

The major components involve NH_3, CO_2, NH_4HCO_3, and NaCl. Due to the spatial variation of the total concentration over the length of the absorption column, the material balance equations will exhibit a certain shape [8].

$$\frac{d(\nu x_i)}{dl} = G_{i(l)}^{\Sigma}; \quad (7)$$

l—reactor length;
V^R—volume of absorption column
ν—volumetric flow rate of the mixture
$G_{i(l)}^{\Sigma}$—intensity
$G_{i(l)}^{\Sigma} = G_{i(l)}^{\Sigma}/L$ и $G_i^{\Sigma} = V^R \cdot g_{x_i}$
For the stationary mode, Equation (8) has the following form:

$$\frac{d(\nu x_i)}{dl} = \frac{V^R}{L} \cdot g_{x_i} \quad (8)$$

The constituents of Equation (8) can be expressed in the subsequent format:

$$\begin{aligned}
\frac{d(Cx_1)}{dl} &= \frac{V^R}{L} \cdot (-k_1 \cdot C_{x_1} \cdot C_{x_2} - k_4 \cdot C_{x_1} \cdot C_{x_5} + k_5 \cdot C_{x_8} - k_6 \cdot C_{x_1}^2 \cdot C_2 \cdot C_3 + k_7 \cdot C_{x_9}) \\
\frac{d(Cx_2)}{dl} &= \frac{V^R}{\nu L} \cdot (-k_1 \cdot C_{x_1} \cdot C_{x_2} \cdot C_{x_3} - k_6 \cdot C_{x_1}^2 \cdot C_2 \cdot C_3 + k_7 \cdot C_{x_9}) \\
\frac{d(Cx_3)}{dl} &= \frac{V^R}{L} \cdot (-k_1 \cdot C_{x_1} \cdot C_{x_2} \cdot C_{x_3} - k_4 \cdot C_{x_1} \cdot C_{x_5} + k_5 \cdot C_{x_8} - k_6 \cdot C_{x_1}^2 \cdot C_2 \cdot C_3 + k_7 \cdot C_{x_9}) \\
\frac{d(Cx_4)}{dl} &= \frac{V^R}{\nu L} \cdot (k_1 \cdot C_{x_1} \cdot C_{x_2} \cdot C_{x_3} - k_2 \cdot C_{x_5} \cdot C_{x_4} + k_3 \cdot C_{x6} \cdot C_{x_7}) \\
\frac{d(Cx_5)}{dl} &= \frac{V^R}{\nu L} \cdot (-k_2 \cdot C_{x_5} \cdot C_{x_4} + k_3 \cdot C_{x6} \cdot C_{x_7}) \\
\frac{d(Cx_6)}{dl} &= \frac{V^R}{\nu L} \cdot (k_2 \cdot C_{x_5} \cdot C_{x_4} - k_3 \cdot C_{x6} \cdot C_{x_7}) \\
\frac{d(Cx_7)}{dl} &= \frac{V^R}{\nu L} \cdot (k_2 \cdot C_{x_5} \cdot C_{x_4} - k_3 \cdot C_{x6} \cdot C_{x_7}) \\
\frac{d(Cx_8)}{dl} &= \frac{V^R}{L} \cdot (-k_4 \cdot C_{x_1} \cdot C_{x_5} + k_5 \cdot C_{x_8}) \\
\frac{d(Cx_9)}{dl} &= \frac{V^R}{L} \cdot (k_6 \cdot C_{x_1}^2 \cdot C_2 \cdot C_3 - k_7 \cdot C_{x_9})
\end{aligned} \quad (9)$$

3. Result and Discussion

The build of a computer modelling system for the calculation and prediction of the ideal technical operating mode of the absorption column is founded upon the kinetic model of the process. In order to address this issue, it is recommended to employ the MATLAB software platform to construct a computer simulation model of the process depicted in Figure 1. This model will enable the characterization of the manner in which the concentration of components varies along the length.

For the stationary mode, the initial values corresponding to the technological regulation are inputted into the variables, resulting in the following graphs of the change of the components with regard to the column height.

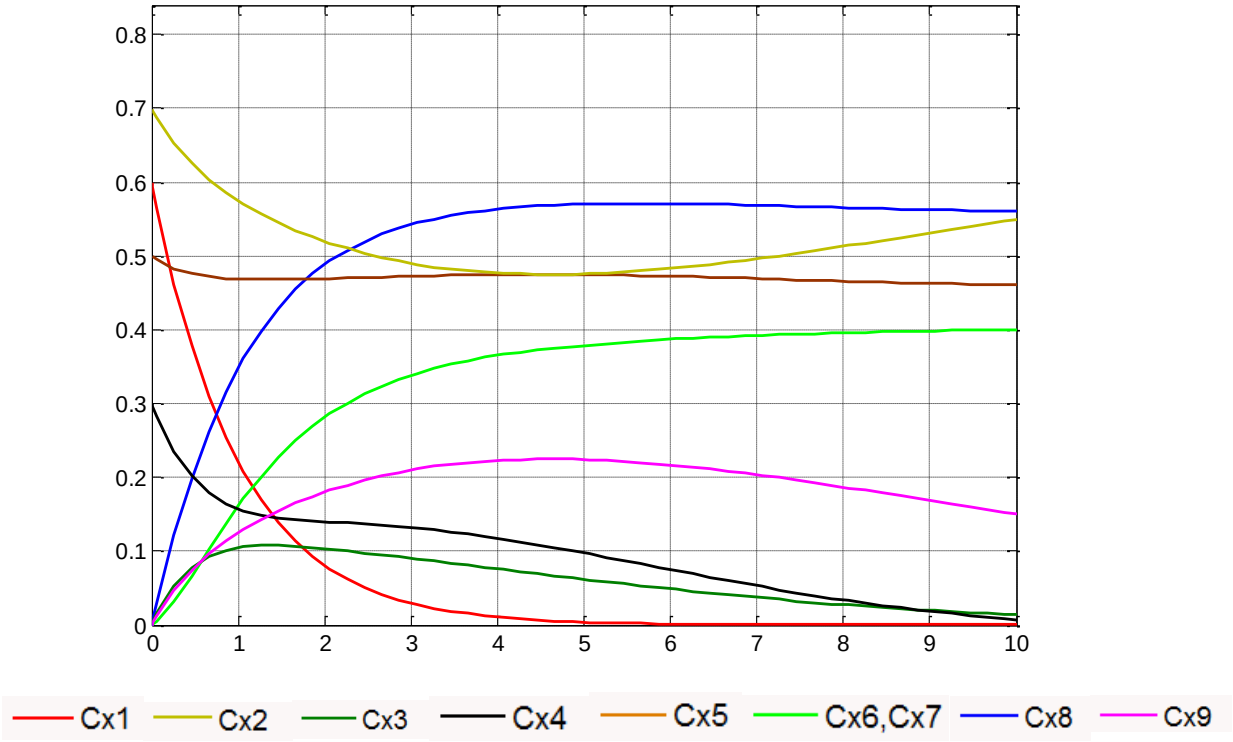

Figure 1. Transient processes of the distribution of the concentration of substances in the process of ammonization of brine.

Based on the findings of the simulated experiment, the comparison between the composition of chemical components and the laboratory analysis reveals a discrepancy of no more than 5%. This observation serves as evidence for the dependability of the results, as indicated in Table 2.

Table 2. The results of laboratory analyze and simulation experiments comparative analysis.

Components Name	Ammonium Salt Content at the Outlet of the Absorber, in Mole Percent		Relative Error
	Laboratory Results	Calculation Results	
$x_1 - NH_3$	0.05897	0.0588	0.24
$x_2 - CO_2$	0.00067	0.0007	1.49
$x_3 - H_2O$	0.7310	0.7271	0.54
$x_4 - NH_4HCO_3$	0.0918	0.0917	0.09
$x_5 - NaCl$	0.000579	0.0006	3.92
$x_6 - NaHCO_3$	0.037	0.0352	4.76
$x_7 - NH_4Cl$	0.0846	0.0843	0.39
$x_8 - NH_4OH$	0.0702	0.0723	3.85
$x_9 - (NH_4)_2CO_3$	0.00196	0.00191	3.06

It is required to maintain the optimal mode in the absorption column in order to manage the absorption process in order to produce the maximum product (ammonium solution). This is done in order to achieve the goal of controlling the absorption process. As a consequence of this, the concentration of the product that is discharged from the absorption column is 0.0738 mole fraction, which is equal to 1843 kg/t; however, under the conditions of industrialized production, this value is reduced to 1657 kg/t.

4. Conclusions

In this work, a mathematical model of the absorption process based on chemical kinetics and taking into account the uncertainties of the reaction mixture was developed in the production of soda ash. The model allows determining the limits of quality indicators of the process efficiency and calculating the parameters of the optimal mode of the absorption column.

Author Contributions: Conceptualization, K.U. and J.E.; writing—original draft preparation, K.U. and J.E.; visualization, N.Y., J.E. and K.U.; writing—review and editing, K.U.; supervision, K.U., J.E. and K.U. contributed equally to this paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The first and second authors acknowledge the members of the Department of IT, Automation, and Control (Tashkent Institute of Chemical Technology), for their guidance and motivation.

Conflicts of Interest: The authors declare no conflict of interest.

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