A PHYSICO-CHEMICAL ANALYSIS
OF CARBON AMMONIUM SALTS' PRODUCTION TECHNOLOGIES

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ABSTRACT

An analytical study of the cyclic method of obtaining ammonium salt in the process of water absorption of ammonia and carbon dioxide is carried out on the ground of the phase diagram of the three-component system $NH_3 - CO_2 - H_2O$. Taking into account the previously refined data on the solubility and the vapor pressure in the system, the temperature and the concentration conditions of the process at the stages of ammonization, carbonation and bicarbonation of the solution are substantiated with precipitation of the target product – ammonium bicarbonate NH_4HCO_3. Based on the results of a survey of an industrial unit, a working diagram of the production cycle is constructed. The reasons for its discrepancies with the theoretical diagram, resulting in a non-conforming product and a decrease of its yield, are identified.
Keywords: carbon ammonium salt, production cycle, working diagram.

INTRODUCTION

Carbon ammonium salt (CAS) is the technical name of the product produced by the chemical industry. It consists mainly of ammonium bicarbonate with an admixture of other ammonium carbonates. It is used in agriculture as ballast-free environmentally friendly fertilizers and preservatives of the agricultural products – sugar beet, forage grain of high humidity, pulpy fodder, etc. In industry, CAS is used in organic synthesis technologies, flotation processes, in the production of chemical reagents. CASs of food grades are used in baking, in the production of confectionery.

The use of CAS in fodder production instead of carbamide is a relatively new and very promising direction of its use [1]. The preservative effect is achieved by combining two well-known complementary preservatives, ammonia and carbon dioxide, in CAS, thereby reducing losses during harvesting, storage and processing of fodder. However, the addition of CAS increases the fodder nutritional value.

The further development of the technology and the increase of the product's quality are considered an urgent task in view of the variety of applications of CASs and the prospects of increasing their production. This in turn requires an additional research of the physico-chemical properties of $NH_3 - CO_2 - H_2O$ system, which includes CAS, a construction of a working diagram of the production cycle and an analysis of the process taking place.

AN ANALYSIS OF LITERATURE DATA AND A PROBLEM STATEMENT
CAS production technology

Several ammonium carbonates are formed in $NH_3 - CO_2 - H_2O$ system. They refer to: a neutral carbonate, anhydrous $(NH_4)_2CO_3$ and a monohydrate $(NH_4)_2CO_3 \cdot H_2O$, "one-and-a-half salt" or ammonium sesquicarbonate $2NH_4HCO_3 \cdot (NH_4)_2CO_3$, ammonium bicarbonate NH_4HCO_3, and ammonium carbamate NH_2COONH_4. All these compounds are unstable and gradually decompose releasing ammonia and carbon dioxide. Ammonium bicarbonate is the most stable salt. It is the main component of the commercial product CAS.

CAS is produced industrially on a ground of a cyclic scheme including sequential saturation of the aqueous solution circulating in the system with ammonia, then
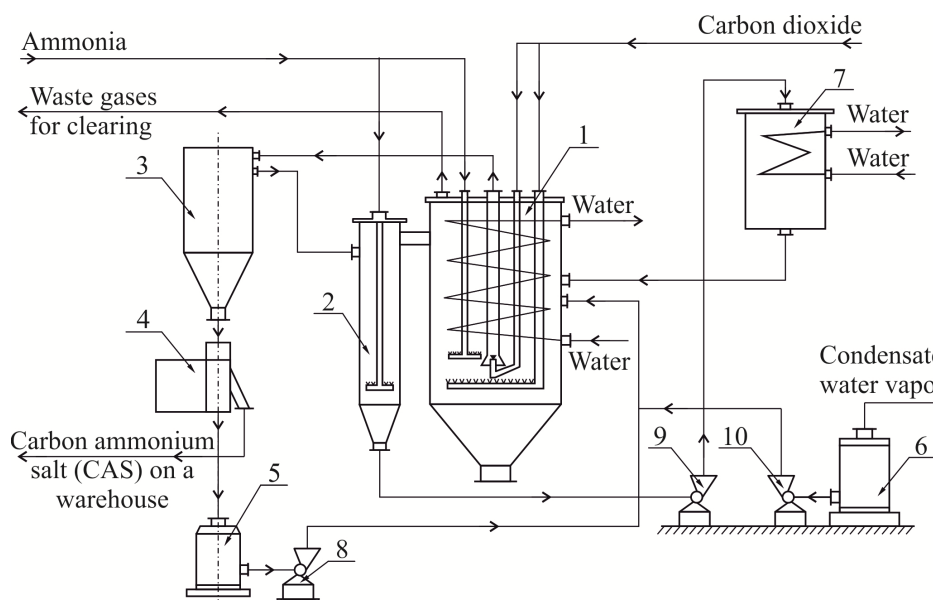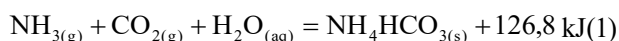
Fig. 1. Schematic diagram of the CAS production: 1 - saturator; 2 - ammonizer; 3 - sump;
4 - centrifuge; 5,6 - sectors; 7 - cooler; 8, 9, 10 - pumps.

with carbon dioxide with removal of chemical reactions heat, as well as ammonium bicarbonate crystallization. The overall process

$$NH_{3(g)} + CO_{2(g)} + H_2O_{(aq)} = NH_4HCO_{3(s)} + 126,8 \text{ kJ} \quad (1)$$

releases a suspension, which is separated. The crystalline product is sent to the warehouse, while the filtrate – the mother liquor, is returned to the process. The cycle described is repeated.

The technological scheme of CAS production by the cyclic scheme is presented in Fig. 1. Synthetic ammonia is the raw material, while a by-product of the ammonia synthesis, consisting mainly of carbon dioxide with an admixture of inert gases is used as an expansion gas. The stages and the chemistry of the process can be formally represented by the following scheme.

The system is filled with the mother liquor of the previous cycle and an equilibrium amount of water is added. Ammonia is supplied in the course of the solution circulation from ammonizer 2 via pump 9 through the external cooler 7 to saturator 1 and from the saturator via the gas lift through sump 3 again to ammonizer unit 2. There the bicarbonate of the mother liquor turns into carbonate

$$NH_4HCO_{3(aq)} + NH_{3(g)} = (NH_4)_2 CO_{3(aq)} \quad (2)$$
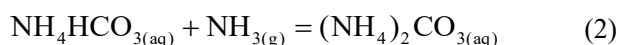
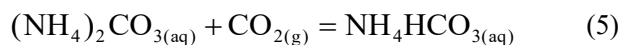while the crystalline bicarbonate remaining in the mother

liquor and on the heat exchange surfaces from the previous cycle dissolves. After completion of reaction (2), "free" ammonia is formed in the solution:

$$NH_{3(g)} + H_2O_{(aq)} = NH_4OH_{(aq)} \quad (3)$$
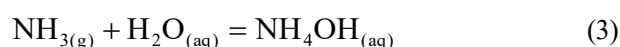
Then the supply of ammonia is stopped. The solution continues to circulate in the system and is saturated with carbon dioxide. The carbonation occurs in the solution in accordance with:

$$2NH_4OH_{(aq)} + CO_{2(g)} = (NH_4)_2 CO_{3(aq)} \quad (4)$$
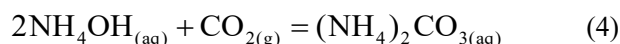
Then bicarbonation takes place:

$$(NH_4)_2 CO_{3(aq)} + CO_{2(g)} = NH_4HCO_{3(aq)} \quad (5)$$

As the concentration of the solution increases, saturation occurs and ammonium bicarbonate crystals precipitate. They are separated from the suspension on centrifuge 4. The crystals discharged from the centrifuge are sent to the packaging, while the mother liquor from collector 5 is returned to the saturator by pump 8 for the next cycle.

It is possible to use other sources of carbon dioxide for the production of CAS. These are the waste gases of the cement industry [2], the tank and the purge gases from the ammonia production [3].
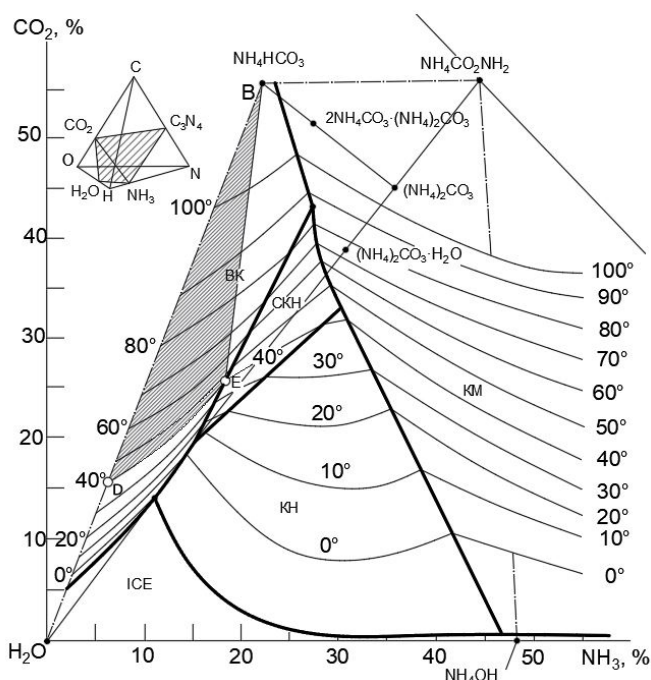
Fig. 2. The polytherm solution-solid phase of the system
$NH_3 - CO_2 - H_2O : B - NH_4HCO_3$; $KH - (NH_4)_2CO_3 \cdot H_2O$;
$KM - NH_4COONH_2$; $CKH - 2NH_4HCO_3 \cdot (NH_4)_2CO_3$.

The main technological parameters of the cyclic scheme described are worked out during the practical operation of units of a relatively low power. Due to the prospect of increasing CASs demand and creating large-capacity units, the development of the theoretical foundations of CASs technology with the aim of developing new technical solutions and their implementation becomes important. This is done in view of the operating experience of the existing workshops.

Phase and chemical equilibria in $NH_3 - CO_2 - H_2O$ system

A specific feature of $NH_3 - CO_2 - H_2O$ system refers to the fact that all three components are volatile, each one of them being in a gas and a condensed phase. Since crystallization and absorption are the main processes in the production of CASs, the L–S diagrams, i.e. the solubility diagrams, representing the equilibria of the liquid and solid phases, are of paramount importance for their analysis. The G–L diagrams represent the equilibrium between the gas phase and the solution. The final stage of the process – the bicarbonation of the saturated solution takes place during the absorption of carbon dioxide with simultaneous precipitation of ammonium bicarbonate. To analyze this stage, data is needed in the area of the three-phase G–L–S equilibrium.

Solubility diagrams

E. Janecke [4, 5] suggests the most extensive generalization of the graphical method for presenting data referring to the phase and chemical equilibrium in $NH_3 - CO_2 - H_2O$ system. He takes four elements, carbon, hydrogen, oxygen, and nitrogen, as initial components. They are positioned at the vertices of the tetrahedron, Fig. 2. The system considered with this choice of primary components is actually a private subsystem inside the tetrahedron (Fig. 2).

This diagram and its individual parts are used in the production of soda [6], carbamide [7], and other products. The inorganic part of the diagram limited by the triangle forming the system $NH_3 - CO_2 - H_2O$ (Fig. 2) is of interest for the technology of ammonium carbonates. It marks the boundaries between the fields of carbonates and ammonium carbamate, isolates the isotherm of 40^0C and outlines the field of crystallization of ammonium bicarbonate (BDE) where the process must be conducted. It is noted that despite the qualitative consistency, this data has a relatively low degree of accuracy. This is due to the experimental difficulties associated with the tendency of the system to form meta-

stable equilibria. The largest discrepancies are observed in the area of the joint crystallization of bicarbonate and ammonium sesquicarbonate. Some authors generally deny the existence of a sesquialteral salt [5].

G–L and G– L–S equilibria in $NH_3 - CO_2 - H_2O$ system

The published experimental data on the gas-liquid equilibrium in the temperature-concentration area of $NH_3 - CO_2 - H_2O$ system, corresponding to CAS production technology, is insufficient and often contradictory [6, 8]. Semi-empirical analytical methods for calculating the partial pressures of ammonia and carbon (IV) oxide are of interest. They take into account the ionic equilibria in the ammonium-carbon solutions. Such a method has been originally developed by Van Krevelen [9].

The Van Krevelen method is further elaborated in the work of S. Wicar [10], who accepts it as a basis of his own method for calculating G–L equilibrium at high values of the gross concentrations of solutions as applied to the conditions of distillation of carbamide's synthesis melt. Here the system $NH_3 - CO_2 - H_2O$ turns into the four-component one $NH_3 - CO_2 - CO(NH_2)_2 - H_2O$ through a hindered synthesis reaction. This provides its consideration as a pseudo-three-component one complicated by the presence of carbamide.

Modern methods for calculating the liquid–vapor equilibrium in $NH_3 - CO_2 - H_2O$ system in absence of a solid phase are developed on the basis of the UNI-QUAC model [11]. They are intended for modeling, analysis and optimization of the industrial processes of the carbamide synthesis [12], which occur at high temperatures under pressure.

Data on the equilibrium in the three-phase $G - L - S$ area of the system in the process of ammonium bicarbonate crystallization upon solutions saturation with carbon dioxide is very limited and insufficient.

The absence of a working diagram referring to CAS production process and the lack of data for its construction motivate the research in this direction.

THE PURPOSE AND THE RESEARCH TASKS

The conducted studies are aimed at determining the physicochemical features of the industrial process for the production of ammonium salts, the substantiation of the parameters of the technological regime and the possible new solutions for its implementation.

To achieve this goal, the following tasks are solved:

– A specification of $NH_3 - CO_2 - H_2O$ system diagram in the area of crystallization of ammonium bicarbonate and a sesquialteral salt;

– An identification of the nature of the composition changes of the gas phase above the solutions saturated with NH_4HCO_3 in the course of carbon (IV) oxide absorption aiming to assess the maximum degree of carbonation of the liquid phase at atmospheric pressure;

– A theoretical development of a working diagram of the process of CAS obtaining on the ground of the phase diagram of $NH_3 - CO_2 - H_2O$ system and its verification by production data.

A RESEARCH OF THE SALTS SOLUBILITY AND THE VAPOUR PRESSURE IN $NH_3 - CO_2 - H_2O$ SYSTEM

The polytherm of solubility in $NH_2COONH_4 - H_2O$ cross section, passing through the areas of these solid phases is studied in $NH_3 - CO_2 - H_2O$ diagram (Fig. 2) to clarify the possibility of joint crystallization of ammonium bicarbonate and a sesquialteral salt in the process of CAS production.

Chemically pure reagents were used in the studies. Ammonium carbamate was prepared by a gas-phase synthesis from ammonia and carbon dioxide with removal of the reaction heat. Ammonium carbonates were obtained by precipitation from solutions with subsequent air drying.

The order of the experiments was as follows. Ammonium carbamate solutions of increasing concentrations were prepared. They were kept for about 1 h after complete dissolution of the sample. Then the crystallization temperature was determined by an improved visual-polythermal technique. The experimental setup, presented in Fig. 3, included test tube 1 with the test solution, which was placed in Dewar vessel 2 with non-silver walls - illuminator 4. The tube was heated using a transparent electrically conductive film of tin oxides deposited on its outer surface and autotransformer 5. The cooling rate was controlled by moving the Dewar vessel with liquid nitrogen relative to the fixed tube. The illuminator with a narrow light beam facilitated the observation of the appearance and the disappearance of crystals during the slow heating (cooling) of the solution and its continuous mixing using stir bar 6 and electromagnets 3. The crystallization temperature was referred to the average value between the temperatures
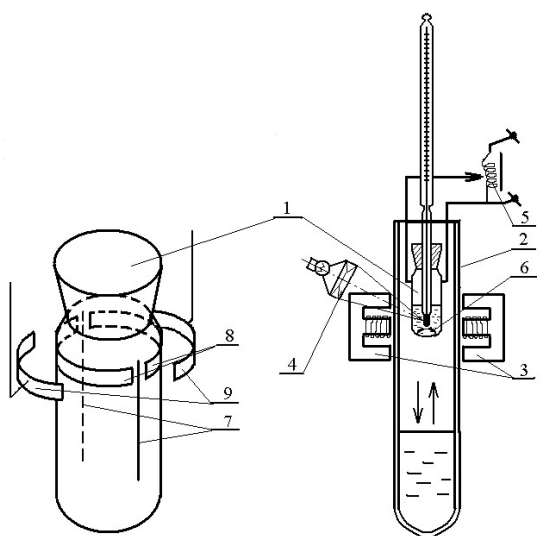
Fig. 3. Installation for the study of solubility by the visual-polythermal method: 1 - test tube with the test solution; 2 - Dewar vessel; 3 - electromagnets; 4 - illuminator; 5 - autotransformer; 6 - stir bars.

Fig. 4. The polytherm solution-solid phase of the system $NH_2COONH_4 - H_2O$.

of crystals appearance and disappearance, achieving a minimum difference. Seedings of the corresponding solid phases were added, if required, aiming to obtain reproducible stable results.

Fig. 4 shows the obtained S–L polytherm of the two-component subsystem $NH_2COONH_4 - H_2O$. The liquidus line consists of a branch of ice, branches of bicarbonate and ammonium sesquicarbonate. The identification of the solid phases was carried out by chemical analysis and crystal optics. As seen in Fig. 5, bicarbonate can be isolated from the solutions in the form of rather large bulk crystals, while the sesquialteral salt crystallizes in the form of thin rhomboid plates. This verifies the possibility of sesquicarbonate formation in the course of the joint absorption of ammonia and carbon dioxide by aqueous solutions. This should be taken into account when organizing CAS production process
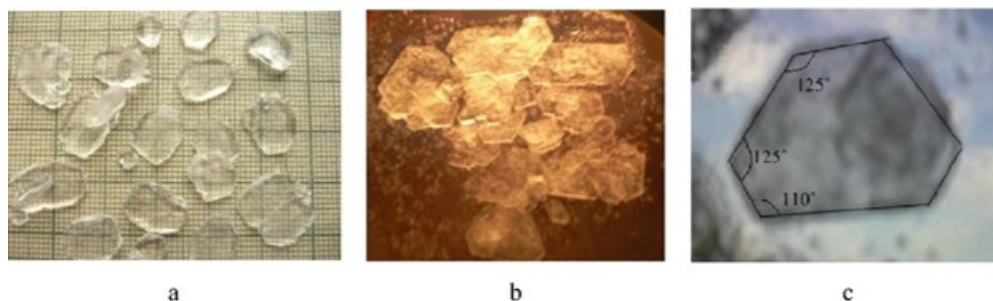
The nature of the change of the gas phase composition at the stage of absorption of carbon dioxide by solutions saturated with NH_4HCO_3 was determined by the method of Van Krevelen – Wicar. Fig. 6 presents the calculated values of the vapor pressure of NH_3 and CO_2 over ammonium bicarbonate solutions saturated at 40^0C depending on the degree of carbonation R of these solutions. It is equal to the ratio of the number of equivalents of carbon dioxide, E_{CO_2}, to the number of equivalents of ammonia, E_{NH_3}, E_{NH_3} i.e. $R = (E_{CO_2} / E_{NH_3}) \cdot 100$ %.

As expected, NH_3 pressure in this area (with R higher than 100 %) is small and tends to zero with the increase of the degree of carbonation. On the contrary, CO_2 pressure increases rapidly with R and reaches the atmospheric pressure at R = 150 %. Despite the approximate nature, these dependencies provide to

Fig. 5. The crystals of ammonium carbonates: a - ammonium bicarbonate NH_4HCO_3; b - ammonium sesquicarbonate; c - a separate crystal $2NH_4HCO_3 \cdot (NH_4)_2CO_3$.
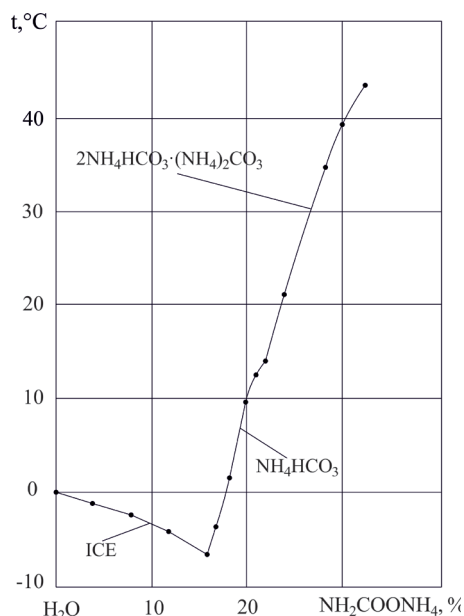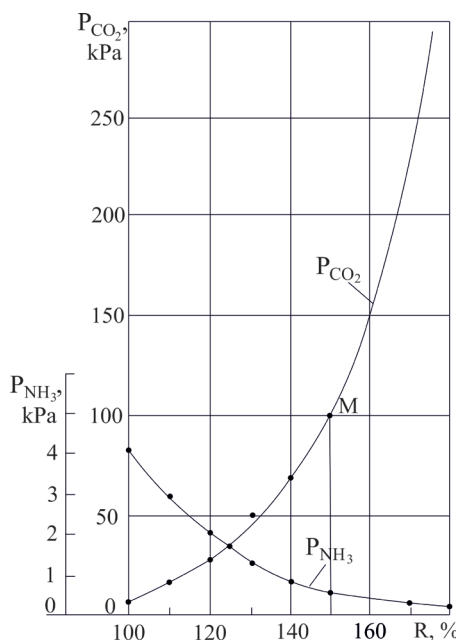
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Fig. 6. The vapour pressure of ammonia and carbon dioxide over saturated solutions of ammonium bicarbonate at 40°C.

substantiate the choice of the concentration norms of the solution carbonation stage taking into account the kinetics of the process.

AN ANALYTICAL INVESTIGATION OF THE CYCLIC PROCESS OF CAS OBTAINING

The theoretical basis of the technology of mineral salts refers to a method of physico-chemical analysis based on the phase equilibrium diagrams use. It applies the phase rule, the rule of the connecting line and the lever rule.

This analytical method is relatively simple and intuitive. It allows considering and comparing the options for the implementation of the process investigated and justifying the most rational one. The theory and practice of this method are set forth with examples of obtaining many important inorganic products described in monographs and periodicals. Recent investigations are presented by Sokolovsky and Yakhontova [13], Welles [14], etc. There is no such analysis of CAS technology. Some results referring to this issue have been partially published in a specialized collection [15], which is inaccessible to technologists. In this regard, the actual task undertaken is to study thoroughly the CAS production aiming its further development.

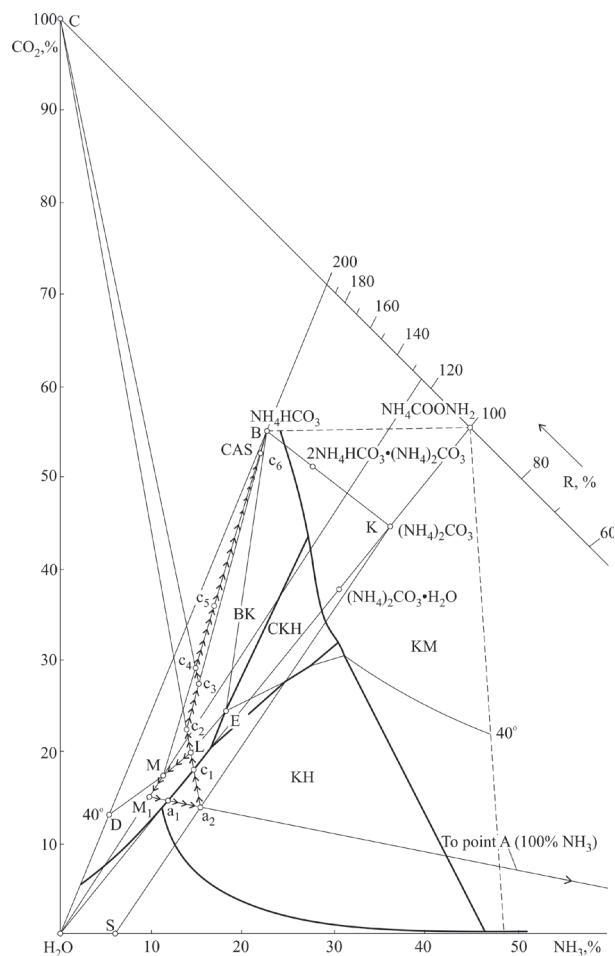Refined data on the vapor solubility and pressure

Fig. 7. The diagram of the cyclic process of obtaining CAS.

in the three-phase area of $NH_3 - CO_2 - H_2O$ system is used to construct the working diagram of CAS production cycle. It is presented in Fig. 7. The degree of the solutions carbonation, R (%), is the most important indicator of the technological regime. It is visualized by rays on the system phase diagram. Thus the ray attributed to R = 100 % passes through the points referring to $(NH_4)_2 CO_3 \cdot H_2O$, $(NH_4)_2 CO_3$ and NH_4COONH_2, while that attributed to R = 200 % goes through the point referring to NH_4HCO_3. The ray attributed to R = 125 % is found necessary for further constructions.

As shown above, it is possible to obtain a saturated ammonium bicarbonate solution at 40°C, $P_{CO_2} = 100$ kPa and a degree of carbonation of the order of 150 %. It is necessary to adopt a lower value of the degree of carbonation of the absorbing solution to ensure the driving of the overall absorption process of CO_2. Its value is maintained at the level of 125 % in the current

industrial unit on account of kinetic considerations. The intersection of this ray and the isotherm of 40° (Fig. 7) corresponds to the figurative point M of the mother liquor, which is the starting point of building the production cycle. Further constructions are carried out in accordance with the sequence of obtaining CAS according to the cyclic scheme presented in Fig. 1. The replenishment of the reactor, which refers to adding an equilibrtium quantity of water to the mother liquor of the previous cycle, is displayed on the diagram by a ray from point M to the origin (the dilution ray coincides with that referring to R = 125 %, but goes in the opposite direction). The figurative point M_1 on $M–H_2O$ segment, found by the rule of the lever, corresponds to the diluted mother liquor. The saturation of this solution by ammonia is displayed by the ammonization M_1A ray. During the process, the figurative point of the solution goes from the bicarbonate area to the ammonium carbonate area. At the site M_1a_1 of the ammonization ray, reaction (2) is underway, which ends when R = 100 % at point a_1. Next, reaction (3) takes place on a_1a_2 site.

At the completion of the ammonization stage, the figurative point a_2 can be thought of as referring to a solution of ammonium carbonate in ammonia water. The concentration of the latter can be determined by drawing a ray from point K through point a_2 to the intersection with the triangle side $H_2O – NH_3$ at point S. The degree of carbonation of solution a_2 (approximately 75 %) is determined using the R scale.

The next stage referring to the saturation of the solution by carbon dioxide is depicted in the diagram by the carbonation ray a_2C. Reaction (4) proceeds on segment a_2c_1 and the degree of carbonation increases from $R_{a_2} = 75$ % to $R_{c_1} = 100$ %. It is followed by the bicarbonation process described by reaction (5), where the value of R exceeds 100%. The solution becomes saturated and ammonium bicarbonate crystals start to precipitate at point L referring to the intersection of the carbonation ray and the isotherm of 40°C. Then a_2C ray passes through the crystallization field of NH_4HCO_3 and the mass of this salt increases in the suspension. The figurative point of the solid phase remains at the crystallization pole B, while the figurative point of the saturated solution moves from L to M. The degree of carbonation of the saturated solution increases from $R_L = 110$ % at the initial moment to the maximum accepted value $R_M = 125$ %. The break of the carbonation ray at c_2c_3 site

corresponds to the stage of ammonia solution saturation by ammonia, when ammonium bicarbonate is formed along overall reaction (1).

The figurative point of the suspension moves along the second carbonation ray c_3C when the ammonia supply stops (point c_3). The final composition of the suspension presented by point c_4 is located at the intersection of c_3C carbonation ray and that of MB crystallization. Point c_4 divides the segment MB in relation to Bc_4 / Mc_4, equal to the ratio of the mass of NH_4HCO_3 crystals and the mass of the saturated solution M in the suspension.

The final stage connected with the separation of the suspension is carried out in two stages: in a sump and in a centrifuge. The figurative point of the suspension moves to the crystallization pole along MB ray, while the figurative point of the saturated solution remains at point M. The composition of the suspension condensed in the sump is presented by point c_5. After centrifugation, the crystalline product retains up to 8 % of the occluded mother liquor M. The figurative point c_6 of the finished product CAS is determined through division of MB seg-
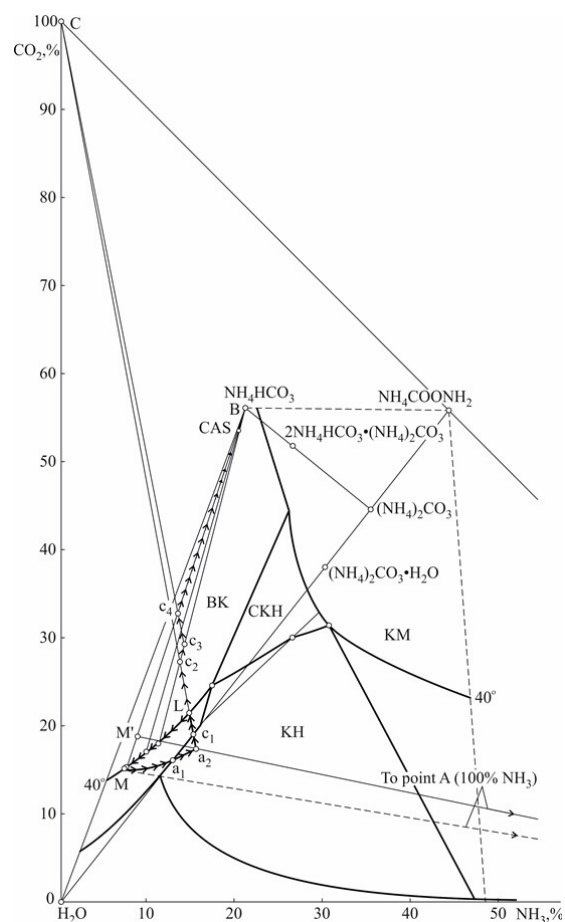

Fig. 8. The diagram of the production cycle of obtaining CAS.

ment length in a ratio of 92/8. Its gross composition can be represented through the common components of the system ($NH_3 = 20{,}6$ %; $CO_2 = 53{,}5$ %; $H_2O = 25{,}9$ %), or recalculated into the salt components.

A WORKING DIAGRAM OF CAS OBTAINING AT AN INDUSTRIAL UNIT

Fig. 8 shows a working diagram based on a survey of an industrial unit [15]. In general, it coincides with the theoretical diagram discussed above. The differences are as follows. The working diagram does not explicitly reflect the stage of replenishing the reactor with an equilibrium amount of water, since water in this cycle is added gradually during the ammonization stage. Another difference refers to the ammonization ray a_2A which deviates from the theoretical MA one (presented by a dotted line) towards the area of a higher concentrations of carbon dioxide. This is explained by the fact that the suspension is not fully separated in course of the previous cycle, and a significant amount of crystalline ammonium bicarbonate remains in the mother liquor. The dissolution of these crystals in the process of ammonization together with the salt deposited on the heat exchange surfaces leads to an increase of CO_2 concentration in the solution. The mass of the solid phase, which comes with the mother liquor of the previous cycle, can be calculated on the ground of the diagram. The extension of the ammonization ray a_2A to its intersection with MB crystallization one, provides finding point M' referring to the initial reaction mixture of the next cycle. The ratio of MM' and MB segments is equal to the proportion of the solid phase in respect to the mixture and can thus serve as an indicator of the completeness of the suspension separation in each cycle.

The analysis of the working diagram provides to explain the formation of fine, poorly filtered sediment called "light" crystals which is an undesirable phenomenon occurring often during the operation of an industrial unit. The main reason refers to the aim of increasing the product yield through an excessive saturation of the mother liquor by ammonia during the first stage of the process. This is visualized by the carbonation ray passing through the field of the sesquialteral salt in the course of the subsequent stage of carbon dioxide absorption. In this case, it is this salt that will precipitate out in the form of scaly crystals (Fig. 5(c)). The probability of the formation of such "light" crystals of $2NH_4HCO_3 \cdot (NH_4)_2CO_3$

is greater in case the suspension of the previous cycle is less fully separated. Thus, to bypass the field of the sesquialteral salt, the process must be conducted through a two-step supply of ammonia, i.e. through ammonization of the mother liquor and mixing the saturated suspension with carbon dioxide. This is required aiming to obtain the desired product of NH_4HCO_3 and to increase its yield.

CONCLUSIONS

A theoretical cyclic process of ammonium bicarbonate production by water absorption of ammonia and carbon dioxide is developed on the ground of the phase diagram of the three-component system $NH_3 - CO_2 - H_2O$. The reasons for the appearance of discrepancies between the working diagram of production and the theoretical cycles are identified. They are associated with violations of the technological regime. It is shown that the process must be conducted stepwise, bypassing the sesquialteral salt field, in order to obtain a standard CAS product and increase its yield.

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