UDC 628.316=111

I. M. Demchuk, *postgraduate student,*
e-mail: AnnaviAnnavi@yandex.ua
G. S. Stolyarenko, *D.Sc., professor, the head of the department*
of chemical technologies and water purification,
e-mail: htnr@rambler.ru
N. I. Tupytska, *master of the department*
of chemical technologies and water purification,
e-mail: nat.tupitska@yandex.ru
Cherkasy State Technological University
Shevchenko blvd, 460, Cherkasy, 18006, Ukraine

RECUPERATION OF BOUND NITROGEN BY PROCESSING INTO HYDRAZINE SULFATE IN INDUSTRIAL WASTEWATER

The work is aimed to reduce nitrogen-containing wastewaters of chemical plants by their utilization as secondary raw material.

The possibility to utilize contaminated water as secondary raw material not only reduces the value of production, but also saves water resources.

The objective of this project is to develop the method of recuperation of ammonia and urea as the main constituents of nitrogen-containing wastewater in mineral fertilizers manufacturing. In general, nitrogen-containing wastewater with ammonia concentration of 3–10 % and urea concentration of 1–5 % is desorbed and hydrolyzed. Desorption and hydrolysis are energy-intensive processes, as they are carried out at high temperatures and excessive pressure. The majority of wastewater after desorption and hydrolysis with urea mass concentration of max.300 mg/dm^3 and ammonia mass concentration of max.100 mg/dm^3 goes to advanced treatment at nitri-denitrification installations. Nitri-denitrification installations also require significant investments. Therefore the recuperation of wastewater is still important and the possibility of recuperation and reutilization of nitrogen-containing compounds might become a new phase of recovery technologies.

The synthesis of hydrazine as intermediate material in the production of hydrazine sulfate out a mixture of ammonia and urea has not been considered until now.

Keywords: *nitrogen-containing water, ammonia, urea, hydrazine, hydrazine sulfate, utilization synthesis, research.*

The work is aimed at reducing of nitrogen-containing runoffs of chemical plants, by using them as secondary raw materials.

The ability to use contaminated water as secondary raw material can not only reduce the cost of production, but also save water resources.

Typically, nitrogen-containing runoffs with ammonia concentration 3-10 % and urea 1-5 % are subjected to desorption and hydrolysis. Desorption and hydrolysis are energy-intensive processes, because they occur at high temperatures and under excess pressure. The main part of the wastewater after desorption and hydrolysis with urea mass concentration of less than 300 mg/dm^3 and ammonia mass concentration of less than 100 mg/dm^3 comes to repurification to nitri-denitrification installations (NDI). NDI installations also require significant investment [1–3].That is why the theme of wastewater recuperation does not lose its relevance still and the opportunity of processing and return of nitrogen-containing compounds in production can become a new stage of the development of utilization technologies.

Mineral fertilizers plant, specifically urea production unit, has been taken as the research base. After the analysis of wastewater (Table 1) the possibility of its usage in the synthesis of hydrazine has been established [3].

Table 1

Quality parameters of ammonia water in urea production before desorption and hydrolysis stages, provided for experiments by urea production unit M-2 of JSC «Azot»

Parameter	$CO(NH_2)_2$,	NH_3,	$C_2H_5N_3O_2$,	Fe,	Cu,	Ni,	Cr
	%	%	%	mg/dm^3	mg/dm^3	mg/dm^3	mg/dm^3
Concentration	less than 2	less than 5.5	less than 0.5	less than 0.3	less than 0.002	less than 0.01	less than 0.02

The synthesis of hydrazine from a mixture of ammonia and urea has not been considered till now. Since wastewater (as a raw material) is used for the synthesis process, this kind of research is appropriate in three areas:

1. Cleaning of nitrogen-containing runoffs (until now the only way to clean urea-containing wastewater consists in hydrolysis and purification at NDI plants).
2. Improving of hydrazine synthesis as intermediate substance in the production of hydrazine sulfate and hydrazine.
3. Reducing of urea production expenses by 5–7% (depending on installation design and synthesis units performance) via eliminating the purification step of condensates of juice steam.

In Ukraine, till 2013 there was one production of hydrazine and its derivatives. Today, hydrazine and its derivatives market is entirely dependent on import [4]. The main importers of this substance in our country are the following: France, Germany, Japan («OTSUKA-MGC CHEMICAL COMPANY, INC», Osaka), South Korea, the United States («Arch Hydrazine») and China.

The main task at hydrazine synthesis is to stabilize formed hydrazine and withdraw it from the process, as it is a strong reducing agent. The presence of even small amounts of impurities (oxygen, metals and metal oxides, particularly copper) leads to immediate oxidation of hydrazine. This phenomenon is connected with the fact that between p-orbitals of nitric system (>N-N<) there is repulsion, which makes the N-N bond longer (1,40Å), than the sum of the radii of two nitrogen atoms N≡N (0,53Å). In elementary nitrogen N_2 p-orbitals are mutually attracted, which further stabilizes the bond between atoms, so the system tends to the formation of nitrogen.

The synthesis temperature and reaction mixture temperature after hydrazine formation greatly influence on hydrazine stabilization [8]. Therefore, the temperature of hydrazine collapse at 50^0C is 0.01% per day, at 100^0C – 0.1% per day, at 250^0C – 10% for 1 minute [9].

To prevent the process of hydrazine collapse and reduce its reactivity in the laboratory it is possible to acidify newly formed hydrazine with sulfuric acid at low temperatures without the access of air, that leads to the formation of hydrazine sulfate salt, which is volatile and has a lower reactivity [6, 7].

Due to the toxicity of hydrazine (applies to the first class of dangers, TLV in the air of working area = 0.1 mg/m^3), the conduction of laboratory experiments is dangerous, therefore, the conduction of hydrazine sulfate release is determined after the formation of hydrazine sulphate salt [14, 15].

For laboratory researches of hydrazine sulfate synthesis guidelines for the implementation of research on "Utilization of bound nitrogen in industrial wastewater by processing in hydrazine sulfate" are developed.

The main methods of the synthesis of hydrazine as an intermediate product in the production of hydrazine sulfate and hydrazine itself, which are used in the industry, are listed below:

1. The synthesis of hydrazine by Raschig method from ammonia:

$$NH_3 + NaOCl \rightarrow NH_2Cl + NaOH, \quad (1)$$

$$NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O, \quad (2)$$

$$2NH_2Cl + N_2H_4 \rightarrow 2NH_4Cl + N_2. \quad (3)$$

Hydrazine formation occurs through the oxidation of ammonia with sodium hypochlorite. Chloramine is formed during the first phase. This reaction proceeds very quickly and can be expressed by equation (1). The reaction occurs at a temperature of 160 ^{0}C and a pressure of 2.5–3.0 MPa. Hydrazine synthesis is caused by the action of excess ammonia on chloramine according to equation (2). Reaction (2) proceeds slowly; it competes with reaction (3), which occurs, complicating the process. The reaction (3) proceeds much faster and is especially sensitive to impurities, that greatly reduces the output of hydrazine [5].

2. The synthesis of hydrazine by Hoffman method from urea by oxidation of carbamide (urea) with sodium hypochlorite:

$$(H_2N)_2CO + NaOCl + 2NaOH \rightarrow N_2H_4 + H_2O + NaCl + Na_2CO_3 \qquad (4)$$

3. The synthesis of hydrazine by the method of Eugene–Kuhlman from acetone, ammonia and hydrogen peroxide.

The reaction occurs in several stages. Acetone reacts with ammonia to form imine, which is oxidized by hydrogen peroxide with the formation of 3,3–dimethyloxapyridine, and then to azine, which forms a hydrazone with acetone, which hydrolyzes to hydrazine and acetone. The process goes at 50 ^{0}C and atmospheric pressure. The chemistry of the process is shown in Fig. 1.

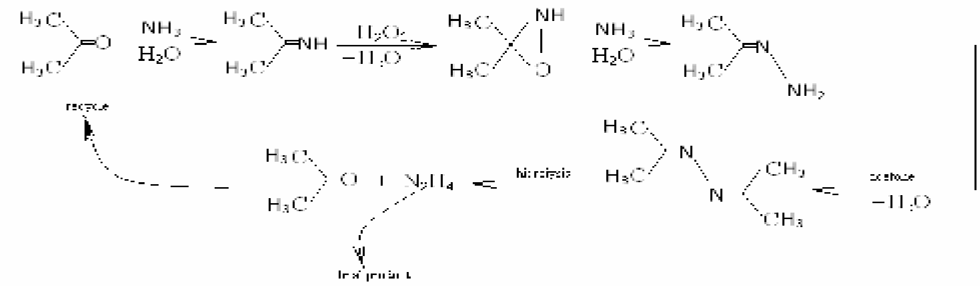


Fig. 1. The chemistry of Eugene-Kuhlman process

Techniques and methods of the synthesis of hydrazine and hydrazine sulfate, which are not implemented at industrial scale due to low profitability of these production methods, are listed below:

- the technology of hydrazine direct synthesis through nitrogen fixation, using two-photon absorptions by activating molecules of nitrogen and hydrogen on catalyst surface at the expense of discharge with the use of solid catalyst as the opposite electrode [10];

- the synthesis of hydrazine by Baer method from ammonia and hydrogen peroxide [11];

- direct synthesis of hydrazine sulfate from benzequinoxaline in the presence of dilute sulfuric acid [16].

As a raw material for this process nitrogen runoffs, mainly ammonia, urea, biuret; sodium hypochlorite; sodium hydroxide; gelatin; sulfuric acid are used.

For the provided technology as a foundation Raschig and Hoffman method is taken. The syntheses, designed by Raschig and Hoffman, seem simple, if written as equations, but the implementation of these chemical processes is complex and power-intensive.

After the improvement and adaptation of the proposed methods of hydrazine synthesis as intermediate product in the production of hydrazine sulfate, for this work the chemism of synthesis process is developed, which is shown below:

a) the basic synthesis reactions:

$$CO(NH_2)_2 + NaOCl + 2NaOH \rightarrow N_2H_4 + H_2O + NaCl + Na_2CO_3, \qquad (5)$$

$$2C_2H_5N_3O_2 + 2NaOCl + 2NaOH \rightarrow 3N_2H_4 + 2NaCl + Na_2CO_3 + CO_2, \qquad (6)$$

$$NaOCl + NH_3 \rightarrow NH_2Cl + NaOH, \qquad (7)$$

$$NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O, \qquad (8)$$

$$N_2H_4 + H_2SO_4 \rightarrow N_2H_4 \cdot H_2SO_4. \qquad (9)$$

b) adverse reactions of hydrazine sulfate synthesis:

$$NH_2Cl + N_2H_4 \rightarrow N_2 + NH_4Cl + NH_3, \qquad (10)$$

$$3NH_2Cl + 2NH_3 \rightarrow 3NH_4Cl + N_2, \qquad (11)$$

$$H_2O + NH_3 \rightarrow NH_4OH, \qquad (12)$$

$$N_2H_4 \cdot H_2SO_4 + 2NH_3 \rightarrow N_2H_4 + (NH_4)_2SO_4, \qquad (13)$$

$$2NaClO + H_2SO_4 \rightarrow Na_2SO_4 + 2HClO, \qquad (14)$$

$$3NH_2Cl + 3NaOH \rightarrow 3NaCl + N_2 + NH_3 + H_2O, \qquad (15)$$

$$H_2SO_4 + NH_3 \rightarrow (NH_4)_2SO_4 + H_2, \qquad (16)$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O, \qquad (17)$$

$$CO(NH_2)_2 + H_2SO_4 + H_2O \rightarrow (NH_4)_2SO_4 + CO_2, \qquad (18)$$

$$2N_2H_4 + H_2SO_4 \rightarrow (N_2H_4)_2 \cdot H_2SO_4 \rightarrow N_2H_4 \cdot H_2SO_4 + N_2H_4, \qquad (19)$$

$$N_2H_4 + 2H_2SO_4 \rightarrow N_2H_4 \cdot 2H_2SO_4 \rightarrow N_2H_4 \cdot H_2SO_4 + H_2SO_4, \qquad (20)$$

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3, \qquad (21)$$

$$(NH_4)_2CO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2O + CO_2, \qquad (22)$$

$$2NH_4Cl + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2HCl, \qquad (23)$$

$$N_2H_4 + 2NaOCl + 10H_2O \rightarrow 2NH_4Cl + 2\,NaOH + H_2O_2 + 8H_2O, \qquad (24)$$

$$NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O, \qquad (25)$$

$$2NaOCl \rightarrow 2\,NaCl + 2O_2, \qquad (26)$$

$$3NaOCl \rightarrow^{t\uparrow} NaClO_3 + 2\,NaCl, \qquad (27)$$

$$NaOCl + 2\,NaCl \rightarrow NaCl + Cl_2 + H_2O, \qquad (28)$$

$$4HClO^{(pH<3)} \rightarrow 2Cl_2 + O_2 + 2H_2O. \qquad (29)$$

The reaction between chloramine and hydrazine (10) is catalyzed by ions of certain metals, so without the use of inhibitors the formation of hydrazine practically will not occur. Also, to remove the run of adverse reaction (10), we create a slight excess of ammonia, that leads to the reaction (11), which is considerably faster than (10). To ensure optimum pH of the substance we use sodium hydroxide, which catalyzes the reaction (8). Ammonolysis reaction, expressed by the equation (13), requires a large excess of ammonia, that's why under these conditions the formation of ammonium sulphate according to the reaction (11) is not possible. The reaction (15), whose kinetics in these conditions has not been investigated, can also occur, but after a series of experimental studies the presence of ammonia in exhaust gases is established.

The excess of sulfuric acid provides the run of reactions (14) and (17), allowing to neutralize the balance of sodium hydroxide (reaction (17)) and sodium hypochlorite (reaction (14)). The decomposition of urea with sulfuric acid is limited by low temperature of the process, since the reaction (18) is endothermic and because of the conditions of hydrazine sulfate synthesis (12-18 ^{0}C) runs slowly. Dyhydrazine sulfate, formed by the reaction (19), and hydrazine dysulfate (reaction (20)) are unstable, decomposing to form hydrazine sulfate, hydrazine and sulfuric acid, according to reactions equations, so they can be ignored. Since urea hydrolyzes to form ammonium carbonate very slowly, the equation (21), and, as a consequence, the equation (22) can also be ignored.

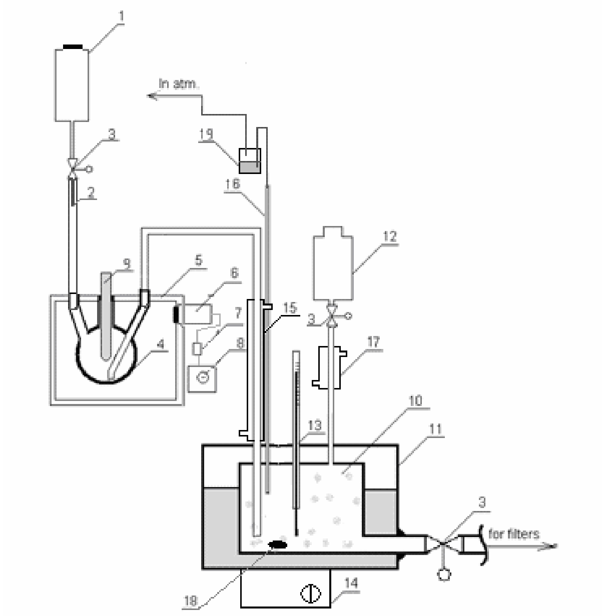
The main problem in the synthesis of hydrazine and hydrazine sulfate under this scheme consists in oxygen formation according to reactions (26) and (29), which oxidizes hydrazine with the formation of nitrogen, ammonia and water.

Before experimental testing a new model of hydrazine synthesis is developed (Fig. 2).

This flow-chart, through the use of alternative heat sources and conducting the process without ejectors and pumps, is less power-intensive. According to this technology it is possible to conduct continuous synthesis of intermediate hydrazine.

As a heating element of reaction mixture electromagnetic waves with the length from 1 mm to 1 m (ν> 300 MHz) are used. High frequency radiation provides a non-contact heating of reaction mixture. In this process heating occurs not only because of heat transfer from the surface of heating element, but also throughout the volume of reaction mixture as it contains polar molecules. This phenomenon makes it possible to ensure even temperature distribution in reaction environment.

In this process temperature control of hydrazine synthesis is impossible for this scheme. As an alternative it is decided to measure the temperature of reaction mixture at the outlet of synthesis reactor. To do this, the thermogram of synthesis process (Fig. 3) is taken from heat vision TH 9100 NEC, which allows to measure the temperature of the wall of connective capillary tube.



1 – pressure tank with reaction mixture; 2 – flow meter; 3 – check valves;
4 – intermediate (hydrazine) synthesis reactor; 5 – protective capacity; 6 – magnetron; 7 – condenser;
8 – transformer; 9 – compensator of magnetic waves; 10 – hydrazine sulfate synthesis reactor;
11 – cooling capacity; 12 – pressure tank of sulfuric acid; 13 – thermometer; 14 – magnetic stirrer;
15, 17 – refrigerator; 16 – diverter tube; 18 – stirrer in a glass flask; 19 – water seal

Fig. 2. Flow-chart of laboratory installation of hydrazine sulfate synthesis

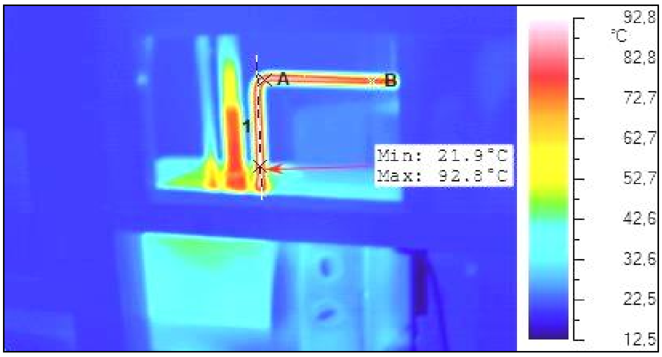


Fig. 3. The thermogram of the process of hydrazine sulphate synthesis

For further calculation of the temperature of hydrazine synthesis the dependence of the value of specific heat flow (q, W/m•K) on the temperature of outlet wall tube is derived (Fig. 4).

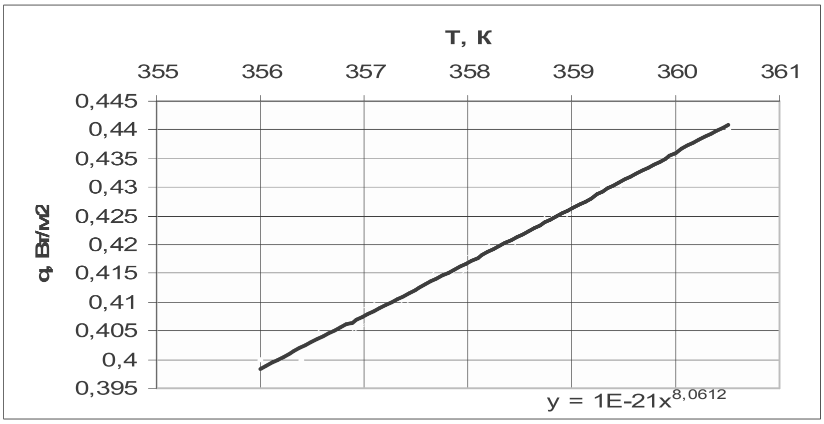


Fig. 4. The dependence of the value of current heat flow on outlet tube wall

Using Mathcad program (the system of computer algebra from the class of automated projecting systems), the algorithm for determining reaction mixture temperature with the following parameters of the process: wall thickness (in this laboratory installation $\delta = 0,002$ m), the coefficient of thermal conductivity of wall material, surface area of outlet wall, the coefficient of wall heat transfer, the coefficient,of thermal conductivity of wall material (for this material $\lambda = 1.14$ W/m•K), the viscosity of reaction mixture and other parameters is established [12, 13].

Then, having determined specific heat flow q, we calculate approximate temperature of reaction mixture at the outlet of hydrazine synthesis reactor (T_R), measuring the temperature of outlet pipe wall of reaction mixture (T_w) according to the equation (30).

$$T_R = \frac{q \cdot \delta}{\lambda} + T_w, K \qquad (30)$$

After the syntheses of hydrazine sulphate the following has been established:

- The outlet of hydrazine depends on molar ratio of input components of reaction mixture (NaOCl, NaOH) at constant composition of waste water ($C_{(CO\ (NH2)2)} = 0,5\%$, $C_{(S2H5N3O2)} = 0,06\%$, $C_{(NH3)} = 4.15\%$, $C_{(CO2)} = 3.5\%$).

- The degree of hydrazine collapse after the synthesis of hydrazine sulfate, which is 50-70%, depending on the temperature of hydrazine sulfate synthesis, sulfuric acid volume and the time of the synthesis, is established. This phenomenon confirms the occurrence of adverse reactions (14), (26), (29).

- A qualitative and quantitative analysis of hydrazine sulfate solution on the presence of ammonium ions is made. The complete absence of ammonium ions in the solution is established that allows to neglect the reactions (10), (11), (16), (18), (21) and, as a consequence, reactions (22), (23), (24) and (25).

- After hydrazine sulfate synthesis the intensification of gas phase release (residual CO_2 and Cl_2 formed by reactions (28) and (29)) is observed. Taking into account oxygen solubility in acidic environment in current circumstances (at 12-18 ^{0}C oxygen solubility in sulfuric acid is small and located within 0,001-0,02 mg/dm^3) the gassing of the last one is also possible.

- Since the process of hydrazine stabilization with sulfuric acid is limited by hydrazine decomposition temperature, the presence of the reaction (26) is confirmed by the degree of hydrazine conversion in a hydrazine sulfate. The loss of hydrazine from the termination of the synthesis of intermediate product – hydrazine before the termination of the synthesis of hydrazine sulphate ranges from 50–70% depending on temperature control of the process of hydrazine sulfate synthesis.

- Non-reacted ammonia is released in gas phase, that is confirmed by the presence of the last one in the water from water seal, which serves as waste gas absorber of synthesis process.

- The scheme of hydrazine sulfate synthesis must me isolated until the end of intermediate product stabilization.

- The maximum output of hydrazine sulfate at optimal molar ratio of components is 3 g in 1 dm^3 of urea production wastewater of sustainable composition.

The polarity of reaction mixture allows to use alternative power sources for reaction mixture heating. The design of hydrazine synthesis reactor allows to use less pressure in reaction zone, which is needed to intensify the synthesis of hydrazine from ammonia by Raschig's method, because electromagnetic waves accelerate the movement of molecules. It also increases the output of hydrazine from urea and biuret with low synthesis temperature. At hydrazine synthesis from urea by Hoffman's method at the beginning the reaction temperature should be at least 100 ^{0}C. This flow-sheet of hydrazine synthesis reduces energy cost by decreasing the temperature of hydrazine synthesis from urea. The symbiosis of the reactions of hydrazine synthesis from ammonia and urea increases the output of the final product and reduces the impact of adverse reactions (11), as evidenced by the absence of ammonium ions in hydrazine sulfate solution.

After the analysis of conducted research it is established that bound nitrogen utilization by processing it in hydrazine sulfate is technically possible.

References

1. Yakovlev, S. V., Prozorov, I. V., Ivanov, E. N. et al. (1991) Rational use of water resources. Moscow: Vyssh. shk., 400 p. [in Russian].
2. Gorlovskiy, D. M., Altshuler, L. N. and Kucheryavyy, V. I. (1981) Urea technology. L.: Khimiya, 320 p. [in Russian].
3. Temporary production regulations of urea production No. 59 (M–2 plant of JSC "Azot", Cherkasy) [in Russian].
4. The Agency of industrial news. Market research & business analytics. Nomenclature and classifications of products. Express analysis of the market "organic derivatives of hydrazine or hydroxylamine". Moscow, 2001–2016, available at: http://www.apn-ua.com/dkpp/21584. (Date of access: 18.02.2016) [in Russian].
5. Odritt, L. F. and Ogg, B. A. (1951) Hydrazine chemistry. New York, 237 p.
6. Ioffe, B. V., Kuznetsov, M. A. and Potekhin, A. A. (1978) Chemistry of hydrazine organic derivatives. L.: Khimiya, 224 p.[in Russian].
7. Grekov, A. P. (1966) Organic chemistry of hydrazine. L.: Tehnika, 235 p. [in Russian].
8. Overberger, Ch. J., Anselm, J.-P. and Lombardino, J. G. (1970) Organic compounds with related nitrogen-nitrogen. L.: Khimiya, 128 p. [in Russian].
9. Grekov, A. P. and Veselov, V. Ya. (1979) Physical chemistry of hydrazine. Kiev: Naukova dumka, 264 p. [in Russian].
10. Patent № 7118655 Direct synthesis of hydrazine through nitrogen fixation by means of two-photon absorptions. Takao Kondo, Kaoru Tsuyuki. Issue Date 10.10.2006.
11. Patent № 60077112 Direct synthesis of hydrazine and/or ammonia. Miyahara, Koshiro. 12.04.1985.
12. Malinin, K. M., Pesakov, I. L., Arkin, N. L. and Spinko, M. G. (1935) The technology of sulfuric acid and sulfur. Part One. Moscow: ONTI, 447 p. [in Russian].
13. Pavlov, C. F., Romankov, P. G. and Noskov, A. A. (1987) Examples and problems at the course of processes and apparatuses of chemical technology, 10th ed., revised and enlarged. L.: Khimiya, 576 p. [in Russian].
14. State standard 12.1.005-88. Maximum allowable concentrations of harmful emissions into the air of the working area, hazard class [in Russian].
15. State standard 12.1.007.76 Harmful substances. Classification and general safety requirements [in Russian].
16. Kolla, V. E., Berdynskyy, I. S. (1976) Chemistry and pharmacology of hydrazine derivatives. Yoshkar-Ola: Mar. kn. izd-vo, 264 p. [in Russian].

І. М. Демчук, *аспірант,*
e-mail: AnnaviAnnavi@yandex.ua
Г. С. Столяренко, *д.т.н., професор,*
завідувач кафедри хімічних технологій та водоочищення,
e-mail: htnr@rambler.ru
Н. І. Тупицька, *магістр кафедри хімічних технологій та водоочищення*
Черкаський державний технологічний університет
б-р Шевченка, 460, Черкаси, 18006, Україна

УТИЛІЗАЦІЯ ЗВ'ЯЗАНОГО АЗОТУ ШЛЯХОМ ПЕРЕРОБКИ В ГІДРАЗИН СУЛЬФАТ У ВИРОБНИЧИХ СТІЧНИХ ВОДАХ

Робота спрямована на зменшення стоків виробництва карбаміду за рахунок використання азотовмісних сполук конденсатів виробництва карбаміду як вторинної сировини. Метою роботи стала розробка способу утилізації аміаку та карбаміду як одних із основних складових азотовмісних стоків виробництв мінеральних добрив.

Як правило, азотовмісні стоки з концентраціями аміаку 3–10 % та карбаміду 1–5 % піддають десорбції та гідролізу. Основна частина стічної води після десорбції та гідролізу з масовою концентрацією карбаміду, не більшою ніж 300 мг/дм^3, і масовою концентрацією аміаку, не більшою ніж 100 мг/дм^3, надходить на доочищення на установки нітри-денітрифікації. Розробка альтернативної утилізаційної технології сприятиме зменшенню собівартості карбаміду на 5–7 % (залежно від конструкції установки та продуктивності агрегатів синтезу) за рахунок ліквідації стадії очищення конденсатів сокової пари.

Утилізація зв'язаного азоту у виробничих водах відбувається шляхом використання останніх як сировини для синтезу гідразин сульфату. За рахунок широкого спектра використання та високої вартості цього продукту розробка нових технологій синтезу матиме великий попит на внутрішньому та зовнішньому ринках, а використання маловартісної сировини робить цю схему економічно рентабельною.

Синтез гідразину як напівпродукту у виробництві гідразин сульфату з суміші аміаку та карбаміду до сьогодні не було розглянуто.

***Ключові слова**: азотовмісні стічні води, аміак, карбамід, гідразин, гідразин сульфат, утилізація, синтез, дослідження.*

Статтю представляє Г. С. Столяренко, д.т.н., професор, завідувач кафедри хімічних технологій та водоочищення.