Виробництво карбаміду супроводжується утворенням 1,5 м³ стічних вод на одну тону карбаміда у вигляді конденсату сокової пари. Для очищення від сполук Нітрогену, що містяться в конденсаті сокової пари, стоки піддають двоступеневої десорбції і гідролізу. Утилізація залишкових N-вмісних сполук в промислових умовах здійснюється на біологічних очисних спорудах. Незважаючи на те, що такий багатоступеневий спосіб очищення призводить до 72–77 %-го зниження сполук N, даний спосіб потребує високих витрат електричної та теплової енергії. Гідроліз та десорбція конденсату сокової пари оцінюється, як сучасний та найбільш перспективний спосіб утилізації стоків, який впроваджений на всіх установках синтезу карбаміду.

У роботі запропоновано новий метод утилізації N-вмісних сполук в конденсаті сокової пари виробництва карбаміду шляхом переробки аміаку, карбаміду та біурета в гідразин сульфат. Проведенними дослідженнями процесу синтезу гідразин сульфату з стоків виробництва карбаміду встановлені механізми, що протікають в процесі синтезу гідразин-сирцю в електромагнітному реакторі. Доведено, що запропонований спосіб утилізації є економічно рентабельним, екологічно безпечним та енергоефективним. Він зменшує навантаження на біологічні очисні споруди, знижує витрати електричної та теплової енергії. Завдяки цьому методу стає можливим переробка N-вмісних сполук конденсату сокової пари в дорогий продукт – гідразин сульфат. Експериментальними дослідженнями підтверджено, що електромагнітне випромінювання позитивно впливає на процес синтезу гідразину-сирцю. Це призводить до підвищення коефіцієнта корисної дії реактора синтезу гідразин-сирцю на 88 %. Проаналізовано три найбільш ймовірні хімізму проходження реакцій синтезу гідразин-сирцю з використанням неімпірічного методу квантової хімії. Показано, що при утилізації конденсату сокової пари в модельній установці шляхом переробки в гідразин сульфат, з урахуванням параметрів оптимізації, початковий вихід готового продукту становить 5,3 кг з 1 м³ N-вмісної сировини. При циркуляції (багаторазовому використанні) фільтрату як джерела сірчаної кислоти встановлено збільшення виходу кінцевого продукту до 6 кг з 1 м³ N-вмісної сировини. Проведена проекція результатів роботи модельної установки на промислові масштаби з урахуванням роботи агрегату синтезу карбаміду, продуктивністю 330000 т/рік. В результаті чого встановлено максимальну розрахункову виробничу потужність агрегату синтезу гідразин сульфату на рівні 132–150 кг/добу. З огляду на отримані дані розрахункової потужності роботи агрегату, розрахована рентабельність роботи агрегату синтезу гідразин сульфату. Встановлено: чистий прибуток при виробництві гідразин сульфату за запропонованою схемою становить не менше 12 %

Ключові слова: виробництво карбаміду, конденсат сокового пара, гідразин сульфат, гідразин-сирець, електромагнітний реактор, електромагнітне випромінювання

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CONVERSION OF N-CONTAINING COMPOUNDS OF FLASH STEAM CONDENSATE FROM CARBAMIDE PRODUCTION INTO HYDRAZINE SULFATE

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1. Introduction

Fast development of industry leads to an increase in technogenic load on the environment. The possibility of recycling of contaminated water will affect economic performance positively and save water resources.

The major part of wastewaters from carbamide production appears in the node of flash steam condensation during dehydration of the synthesis-solution of carbamide. Flash steam condensates (FSC) contain aqueous solutions of ammonium and N amide with a mass concentration of ammonia up to 5 % and carbamide up to 3 %, as well as dissolved carbon dioxide, in their composition. It is necessary to perform two-stage desorption and hydrolysis for purification of FSC from N compounds. The major part of wastewater with the mass concentration of carbamide of not more than 300 mg/dm^3

and the mass concentration of ammonia of not more than 100 mg/dm^3 is goes to purification after hydrolysis and desorption at biological treatment plants [1]. The efficiency of purification of wastewater, which contains bounded N, is about 77 % on average at plants for nitric-denitrification (NDF). The rest goes into the surface water and produces the "water bloom" phenomenon, which leads to an ecological catastrophe.

Water purification from compounds of Nitrogen (N), such as chlorination, ozonation, ultraviolet irradiation treatment, purification using ion exchange materials, electrolysis, ammonia airflow, requires a use of expensive reagents and special equipment, it is rather energy-intensive. These methods are ineffective in the case of purification of contaminated water from compounds, which contain amide and nitrate N.

The aim of many studies is the search for destructive methods of wastewater purification, therefore, this study highlights the progressive method of liquid waste purification, namely: the method of FSC recovery by synthesis of the intermediate product – hydrazine (N_2H_4) followed with processing into the final product – hydrazine sulfate (HS, $N_2H_4{\cdot}H_2SO_4$) [2].

We took FSC of the carbamide synthesis device according to the stripping process scheme with a production capacity of 330,000 tons/year as the basis for the study. That is, the object of the study was wastewater of carbamide production formed in the process of condensation of flash steam during dehydration of the synthesis-solution of carbamide before the stage of desorption and hydrolysis.

The amount of water to be removed from the process cannot be less than 0.3 m^3/t carbamide in theory in accordance with the stoichiometric equation of carbamide synthesis. This amount may reach 1.5 m^3/ton of carbamide in practice due to the use of steam ejectors [1]. For example, there not less than 222,000 m^3/year of FSC formed during production of carbamide with an output of 330,000 t/year.

The study is expedient, because there is no any method to dispose of FSC, which would give a possibility to reduce a load on biological purification plants and which would be economically cost-effective, environmentally safe and energy-efficient.

2. Literature review and problem statement

Paper [3] considers and analyzes destructive methods of utilization of N-containing compounds of FSC, namely:

1. It considers the most widespread method of purification of wastewater from carbamide production. FSC purification occurs by thermal decomposition due to a use of overpressure in a column device of a cascade type at a temperature of 423–535 K and pressure of 1.5–5.0 MPa, using 4–30 successive stages of the cascade. The method of wastewater purification is energy-intensive, since we use high pressure and temperature. The method does not provide a deep degree of FSC purification and it does give possibility to reuse it.

2. The paper analyzes the method of purification of wastewater from carbamide production by hydrolysis of N-containing compounds under heating and excess pressure. In this case, the hydrolysis goes in the presence of phosphoric acid, and alcohol or ketone dilute the solution obtained with subsequent separation of precipitate. The method turns out to be energy-intensive, cost-effective, economically unprofitable, technologically complicated and, in addition, FSC purification by this method does not give possibility to reuse it.

3. The study considers the method of wastewater purification from carbamide by sorption on strongly acidic cation exchangers with their subsequent regeneration by strong inorganic acids. The method is not widespread in practice, since it requires a use of expensive ion-exchange resins, a large amount of phosphoric acid for their regeneration, and it also leads to formation of new wastewater when washing ion-exchange resins from regeneration solutions.

4. Authors of the paper analyze the method of wastewater purification of carbamide production, which includes mixing of circulating flow and fresh flow of wastewater with air, evaporation, splash and emission of air with water vapor into atmosphere. There is a fresh flow of wastewater mixed in advance with a flow of air coming out of the evaporation zone. The considered method does not lead to obtaining of purified water, and it contaminates the atmosphere with N-containing products.

5. The paper performs a critical analysis of the following FSC purification method: wastewater purification occurs by treatment with active chlorine with air supply at a pH of 6.5–8 with subsequent anionization after hydrolysis and desorption. The considered method provides efficient purification of FSC and gives possibility to reuse it as feed water for boilers or in a system of circulating water supply. The method has several disadvantages: it is technologically complex and multi-stage, it occurs at excess pressure – from 0.28 to 1.8 MPa, it requires a large amount of steam at the stage of desorption and hydrolysis (occurs at high temperature and excess pressure). It requires additional reagents (compounds of active chlorine and regeneration solutions for ion-exchange materials) at the post-purification stage.

The main objective of paper [3] is an economic assessment of efficiency of introduction of recycling technologies of FSC by modernization of production through introduction of advanced technologies. The economic assessment of efficiency of introduction of recycling processing of FSC through creation of a utilization technology for the synthesis of HS confirmed the expediency of creation of recovery technologies for recycling of FSC. Thus, FSC recovery will reduce the cost price of carbamide by 2.2 %, provided that the production capacity of the carbamide synthesis unit is 360,000 t/year.

The most widespread thermal FSC purification methods (hydrolysis and desorption) are used in carbamide synthesis schemes by the project of "Urea Casale" company and carbamide synthesis schemes patented by "StamiSarbon" company [1]. These methods of FSC purification require post-purification of wastewater at nitro- denitrification plants (NDP).

NDP processes occur often in special multifunctional aerotanks-nitrifiers-denitrifiers with aerobic (oxidation of organic substances, nitrification of ammonium N) and anoxic (denitrification) zones arranged [4]; biological oxidation, nitrification of ammonium N and denitrification occur due to heterotrophic and autotrophic bacteria, which form the biocenose of a single active sludge (one-unit scheme); purified wastewater plays a role of an organic substrate at denitrification [5].

Work [6] considers practical implementation of NDP processes, which occur according to three schemes:

1) in facilities, which operate by the principle of biochemical reactors-displacers, where anoxic zones and aerobic

zones change each other by turns at one or several stages (Ludchak-Etinger schemes, Alpha, BARDENPHO);

2) in one building, by creation of aerobic and anoxic conditions (SBR-reactors) successive in time;

3) in facilities of the circulating oxidation channels successive type by successive repeated passage of the sludge mixture through aerobic zones and anoxic zones.

NDP facilities have a series of operational requirements, which are very difficult to meet fully. The high degree of wastewater purification and operation of these facilities depend on a number of factors, the main of them are:

1. Ensuring of the constancy of wastewater composition to maintain optimum conditions for the life of aerobic and anaerobic bacteria, namely: optimal concentrations of compounds, which contain compounds of bound N; at high concentrations of bound N in wastewater, the latter should be diluted with water before supply to NDP plants or, if possible, with household sewage, or they should be directed to the system of post-purification by ammonia blowing with air; presence of a sufficient amount of organic compounds that are not formed in production of mineral fertilizers, and therefore additional funds are expended for feeding in the form of organic substances such as methanol or ethanol; presence of a sufficient amount of biogenic elements, which include phosphorus; in the absence of phosphorus-containing substances in sewage, feed is also introduced; absence of toxic impurities in wastewater [7].

2. Provision of stable temperatures – not less than 4 °C and not more than 37 °C (preferably in the range of 20 (±2) °C). A sharp increase in temperature above the specified norm leads to "swelling" of silt, which is the result of an increase in the rate of biological oxidation. Lowering of temperature below the norm or its sharp drop lead to a decrease in number of microflora and microfauna in the biocenoses of active silt [7].

3. Provision of the necessary oxygen concentration in the system. The oxygen content should be in the range from 1 to 7 mg/dm^3 at constant temperature (20 (±2) °C) [8].

4. Provision of stable pH hydrogen system – within the range of 6.5÷7.5 [7].

5. Maintenance of silt in a hanged condition. It is necessary to predict the optimum rate of mixing of wastewater and active silt in aerotanks to provide this [9].

Achievement of these and many other factors of functioning of NDP plants affects reactivity and dosage of silt. The process of provision of optimal conditions for operation of NDP plants is energy intensive and costly. Failure to provide the optimal conditions for operation of plants leads to a decrease in the number of nitrifying and denitrifying bacteria, which affects the degree of wastewater purification negatively.

There was a critical analysis of the data of research on biological methods of purification of wastewater, which contains compounds of amide and ammonium N at higher concentrations than those which are supplied to NDP plants, carried out. Authors of work [10] investigated NDP processes of wastewater, which contains organic N-carbamide with the use of non-tissue biomass carriers. A 77 % efficiency of purification from compounds of Nitrogen was achieved. The main disadvantage of the method of purification of wastewater from carbamide is the concentration limit – the concentration of carbamide in wastewater should not exceed 0.045 % by mass (the concentration of carbamide in FSC~1.5 %). The method cannot replace the processes of hydrolysis. Paper [11] analyzes the developed method of removal of nitrogen compounds [11] from wastewater with the help of immobilized microalgae *Chlorellasp.* The disadvantage of this biological method of wastewater purification is the necessity to maintain stable pH at 6÷8 level; a low gradient of nitrogen concentrations and presence of phosphorus in wastewater. Taking into account pH FSC value, which is 10÷11, this method cannot be used to purify FSC without preliminary purification or dilution of wastewater.

We studied scientific works devoted to the purification of wastewater from production of melamine, where carbamide is present, for a full analysis of the methods of purification of wastewater from amide N. Paper [12] proposed to purify wastewater, which contains carbamide by thermal hydrolysis of wastewater in two stages. There were other methods of purification of melamine production wastewater analyzed, which made possible to reduce the amid nitrogen content in sewage. The main method was thermal destruction [13]. It did not differ fundamentally from the processes of hydrolysis, because it requires high temperatures and distillation of the gas phase.

Authors of paper [14] considered a possibility of application of membrane technologies for water purification from nitrogen compounds [14]. It is possible to use the reverse osmosis method only for purification of FSC [15]. Membrane methods provide a sufficient degree of purification of contaminated nitrogen wastewater, but the method is economically unprofitable.

Authors of work [16] considered a possibility of purification of wastewater, which contains carbamide by the method of electrochemical degradation. The work described the results of the study on decomposition of carbamide in the anode region using titanium and platinum electrodes [16]. They established that destruction of carbamide does not occur in an aqueous solution on Ti/Pt electrodes. The authors obtained a positive result only with the introduction of additional chemical compounds. Unfortunately, this method proved to be non-energy efficient; therefore, it did not find practical application.

Paper [17] studies the process of removal of ammonium ions (NH_4^+) from wastewater from production of 7-aminocaflosporanic acid by chemical precipitation of magnesium. The method requires the use of expensive reagents and does not provide for a possibility to reuse wastewater.

After an analysis of the above-mentioned destructive methods of purification of wastewater, which contains bound amide and ammonium N, it is appropriate to carry out investigations of recuperative methods of FSC purification.

Paper [2] presented the results of tests of a laboratory plant for the synthesis of HS with FSC made of borosilicate glass. It established the dependence of a value of a specific heat flow on temperature of a wall of the extraction pipe of the synthesis-solution from the synthesis reactor of raw hydrazine. The paper presented recalculation formulas for determination of temperature of the synthesis solution at the exit from the electron-manganese hydrazine synthesis reactor. The main disadvantage of the laboratory plant is the material of its implementation is borosilicate glass. It is not possible to use this structural material on the semi-industrial and industrial scale due to its physical properties. The positive point is the confirmation of possibility of synthesis of HS with FSC.

Paper [18] presents the results of operation of the plant for the synthesis of hydrazine with FSC in a wave reactor and the dependence of the degree of N_2H_4 oxidation in the process of full contact of a newly formed product with air under normal conditions. The authors found after the mathematical analysis of the results of study [18]: the newly formed N_2H_4 oxidizes

quickly in the synthesis solution if there is its direct contact with air. The degree of oxidation makes up 2.5 % per 1 minute in average in the first 2 minutes, then it goes down to 1 % per minute. The paper presented also the achieved maximum conversion rate of N total in N_2H_4. It was 4.3 %. The main disadvantage of the hydrazine synthesis process is the further stabilization of N_2H_4 and its removal from the process.

Paper [19] investigated a possibility of FSC recovery due to synthesis of hydrazine in an electromagnetic reactor (ER) and extraction of it in the form of a poorly soluble salt – $N_2H_{4\cdot H2}SO_4$. The removal of HS is possible due to the relatively low degree of solubility at low temperatures of the synthesis-solution. The authors established that the main stage in the process of synthesis of $N_2H_{4\cdot H2}SO_4$ is the phase of synthesis of the main semi-product – N_2H_4. The paper considered technology of recycling of wastewater from carbamide production to HS with the help of ER synthesis of hydrazine, as an alternative heat source and process catalyst by stages. It analyzed an influence of microwave radiation on the process of synthesis of raw hydrazine by the methods of Raschig and Hofmann. The authors proposed the chemism of the occurrence of homozylation processes in ER synthesis of raw hydrazine. Fig. 1 presents the design of the raw hydrazine reactor-mixer with sulfuric acid.

The process of synthesis of HS from a mixture of ammonia and carbamide with low concentration gradient using ER synthesis of raw-hydrazine is the latest development. There was only the technology of direct synthesis of hydrazine through fixation of nitrogen by means of two-photon absorption by activation of nitrogen and hydrogen molecules on a surface of a catalyst developed in recent years [20]. Other scientists did not consider synthesis of raw hydrazine with FSC, since the main task was the destruction of bounded N. The cause of necessity in development of low-waste technologies is the harmful man-made impact on the ecosystem. Improvement of technologies of production of mineral fertilizers is possible not only at the expense of an increase in the degree of transformation of raw materials into a final product, but also by reducing of the cost of energy resources spent on waste disposal. All of the previously considered destructive methods for the utilization of N-containing compounds in FSC (except purification on ion-exchange materials) require additional purification of wastewater at NDP plants, which provide a maximum degree of purification of wastewater from N compounds N at the level of 80 %. Thus, after analysis of works aimed at purification of wastewater from N compounds by biological methods, we did not find a method to destroy compounds of amide and ammonium N compounds with concentrations, which correspond to the quantitative composition of FSC.

Despite the possibility and expediency for the disposal of FSC by processing to HS, it is necessary to determine a situation in HS market, since the synthesis of an unclaimed compound eliminates any scientific value. Specifically, $N_2H_4\cdot H_2SO_4$ can be useful: for treatment of boiler water; as a renewing agent in the process of nickel plating; for production of pesticides and bactericides; as a vesicant for plastics and rubber production; as the main raw material for hydrazine [21]. Fig. 2 shows global statistics on the consumer demand for HS based on data from article [21].

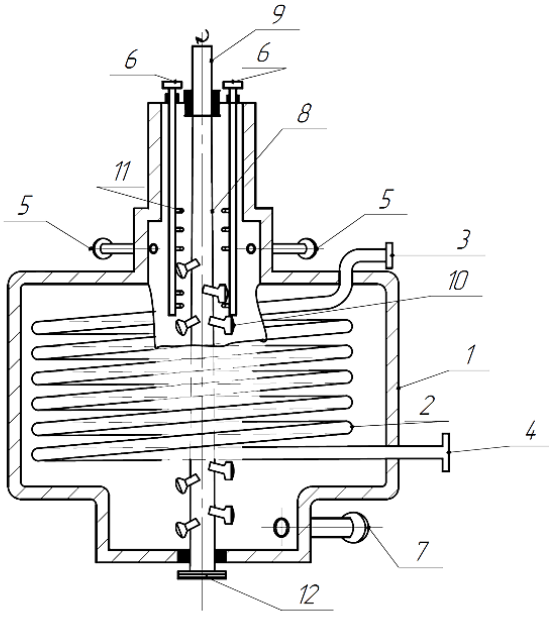


Fig. 1. Reactor-mixer of hydrazine sulfate synthesis: 1 — body; 2 – pipes; 3 —connecting pipe of coolant outlet; 4 — connecting pipe of coolant inlet; 5 — connecting pipe of the reaction mixture after the synthesis of raw hydrazine; 6 – connecting pipe of the inlet of filtrate and (or) concentrated sulfuric acid; 7 — connecting pipe of the outlet of the reaction mixture after neutralization; 8 — blade mixer; 9 — screw shaft; 10 — T-shaped blade; 11 – dispenser of filtrate and (or) concentrated sulfuric acid; 12 —brake

After an analysis of the above-mentioned destructive methods and recovery methods for FSC utilization, it is expedient to carry out research on the recuperation technology of disposal of FSC by processing to HS.

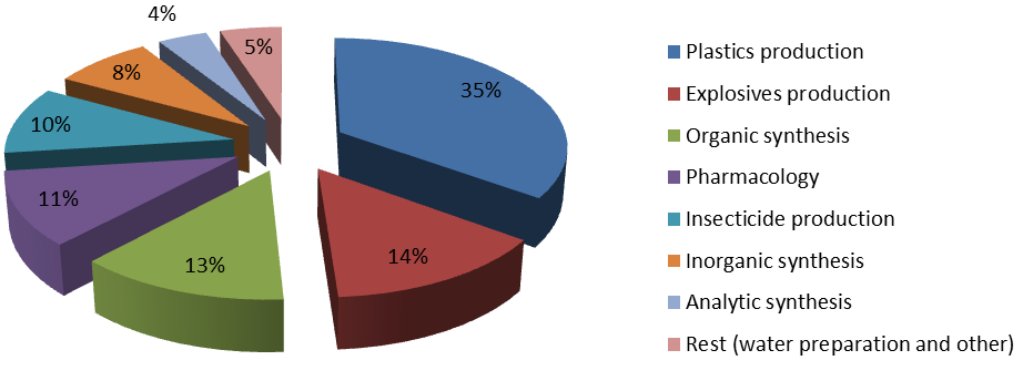


Fig. 2. Consumer demand for hydrazine sulfate (world statistics)

3. The aim and objectives of the study

The objective of the study was to develop theoretical, analytical and technological principles for the utilization of nitrogen containing FSC by processing into raw hydrazine and HS.

We solved the following tasks to achieve the objective:

– to perform a quantitative analysis of FSC;

– to propose, develop, and analyze a possible mechanism of synthesis of raw hydrazine from FSC in terms of quantum chemistry in the Born-Oppenheimer approximation by the method of analysis of molecular systems;

– to conduct a study into the influence of electromagnetic radiation with a frequency of 2.45 GHz on the efficiency of the reactor of synthesis of raw hydrazine;

– to run a regression analysis of the results of semi-industrial studies at a model plant for the disposal of FSC by HS synthesis and mathematical projection of the results of the study at the model plant on the industrial scale.

4. Materials and methods to study the synthesis process of disposal of FSC via the synthesis of $N_2H_4 \cdot H_2SO_4$

4. 1. Determining the quantitative composition of FSC

We used photometric, titrimetric, and atomic-absorption methods of analysis to analyze the object of the study. We selected FSC samples from the carbamide synthesis device with a productivity of 330,000 t/year according to the stripping process for analysis. We took samples of wastewater from FSC collector of FSC to a plastic container with a capacity of at least 2 dm^3. We delivered the sample to the laboratory, cooled it to a temperature of 20±2 °C and performed a quantitative analysis of wastewater.

We carried out measurement of the mass fraction of ammonia in FSC using the titrimetric method based on the neutralization of ammonia with a solution of hydrochloric acid in the presence of a red methyl indicator or blue bromophenol. The range of measurement of the mass fraction of ammonia was from 0.6 to 40 %.

We determined the biuret content in the sample by the photo-colorimetric method based on the interaction of biuret with an alkaline solution of copper sulfate and formation of a complex compound painted in blue. The presence of ammonia impedes definition of biuret, so we pre-distilled it with acetone or methanol. The range of measurements of the mass of biuret was from 0.005 to 2.5 %.

We carried out the measurement of the mass fraction of carbamide in wastewater by the titrimetric method based on previous mineralization of amidic N with sulfuric acid to ammonia N. Sulfuric acid releases during its further interaction with formaldehyde. A solution of sodium hydroxide titrates the released sulfuric acid in the presence of a mixed indicator. This technique provides determination of mass carbamide in a solution in the range of measurements from 0.5 to 20 %.

We determined the carbon dioxide (IV) content in FSC by potentiometric titration based on neutralization of sodium hydroxide added in excess with carbon monoxide (IV). The released ammonia is bound by formalin with formation of hexamethylenetetramine. A solution of hydrochloric acid titrates the excess of sodium hydroxide and sodium carbonate formed on the ion to a pH of 8.7. The measurement range of mass fraction of carbon monoxide (IV) was from 0.2 % to 40 %.

We used spectral analysis methods, namely atomic absorption analysis, to determine the quantitative content of metals in wastewater.

4. 2. Analysis of mechanisms of synthesis of raw hydrazine from FSC in terms of quantum chemistry in the Born-Oppenheimer approximation by the method of molecular systems analysis

We performed the analysis using quantum-chemical calculations in the Gaussian 09 program package. We analyzed energy parameters of the developed mechanism of processes occurring in ER synthesis of raw hydrazine. We calculated the molecular structure of the investigated compounds within the framework of the theory of functional density using the standard basis set 6-31+G(d) of B3LYP functional.

4. 3. Analytical control of the process of synthesis of HS with FSC

We developed an analytical base for the synthesis of hydrazine sulfate from FSC from carbamide production before the testing of the modeling plant.

We determined the mass fraction of hydrazine in aqueous solutions by titrimetric method. The basis of the method is oxidation of N_2H_4 with iodine (I_2) solution in a weakly alkaline medium. If the mass fraction of hydrazine was greater than 5 % in solutions, we used the direct titration method with I_2 solution until a obtaining of steady blue color. When measuring the mass fraction of N_2H_4 in solutions in the range from 0.005 to 5 %, we used the inverse titration method. In this case, added I_2 solution to the sample and titrated the excess iodine with a solution of sodium thiosulfate in the presence of starch after the oxidation of N_2H_4.

We used the photo-colorimetric method to identify the mass concentration of hydrazine in the range of 8 to 200 μg/dm^3. The basis of the method is the interaction of hydrazine with n-dimethylaminobenzaldehyde to form azine, which undergoes tautomeric rearrangement under the influence of hydrochloric acid. The compound formed colors the solution in an orange color.

We determined the mass fraction of active chlorine (Cl_2) in sodium hypochlorite, sodium hydroxide and sulfuric acid by titrimetric method in accordance with regulatory documentation for reagents.

We measured the mass concentration of residual Cl_2 using the titrimetric method. The basis of the method is the preliminary addition of potassium iodide to the sample and the titration of iodine released by a solution of sodium thiosulfate in the presence of starch.

We determined the quality of the final product - hydrazine sulfate and the by-product – decahydrate hydrogen sulfate in accordance with the regulatory documentation for reagents "GOST 5841-74 – Reagents. Sulfuric acid Hydrazine" and "GOST 4171-76 – Decahydrate sodium sulfate 10-aqueous. Specifications."

We determined the concentration of sulfate ions in the synthesis solution and filtrate by a titrimetric method based on the neutralization of sulfuric acid with a solution of sodium hydroxide in the presence of a blue bromophenol indicator.

4. 4. Description of the operation of the model plant for the conversion of N-containing compounds of FSC via the synthesis of HS

Basic stages of synthesis of hydrazine sulfate from secondary raw materials:

1. Preparation of raw materials. This stage includes determination of a quantitative composition of the main raw material – FSC and preparation of a solution of hypochlorite and sodium hydroxide for mixing with FSC.

2. Mixing of the main components of the reaction mixture.

3. Synthesis of raw hydrazine in the electromagnetic monomodal reactor – it is the main stage. The use of ER for the synthesis of raw hydrazine from a mixture of amide and ammonium N is the latest development.

4. Synthesis of hydrazine sulfate. Fig. 1 shows the design of the mixing reactor.

5. Concentration of synthesis solutions of hydrazine sulfate and removal of by-products.

6. Preservation and filtration.

7. Drying and packing.

Fig. 3, 4 show block diagrams of the process of synthesis of HS with FSC of periodic action.

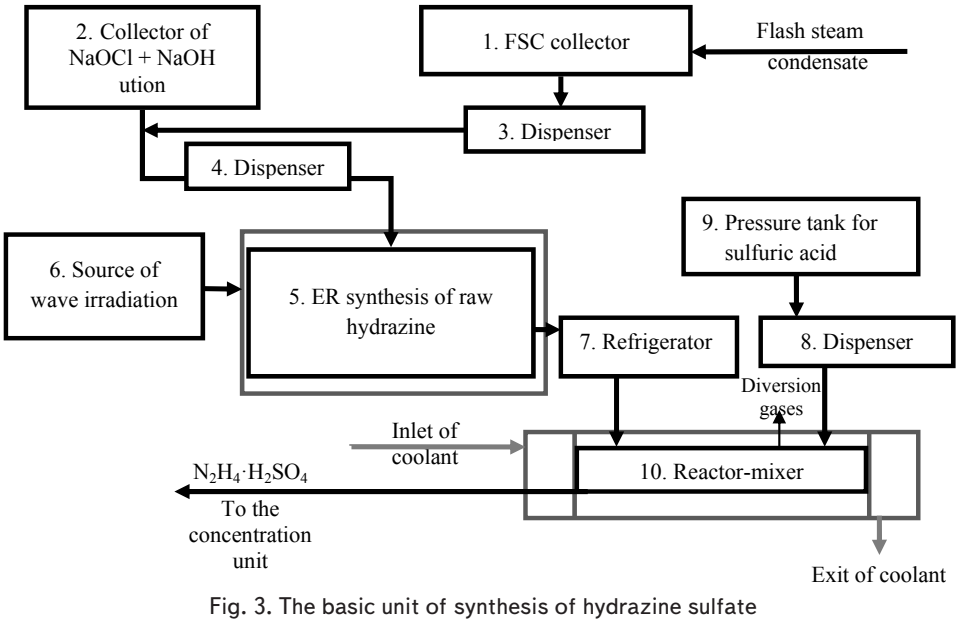


Fig. 3. The basic unit of synthesis of hydrazine sulfate

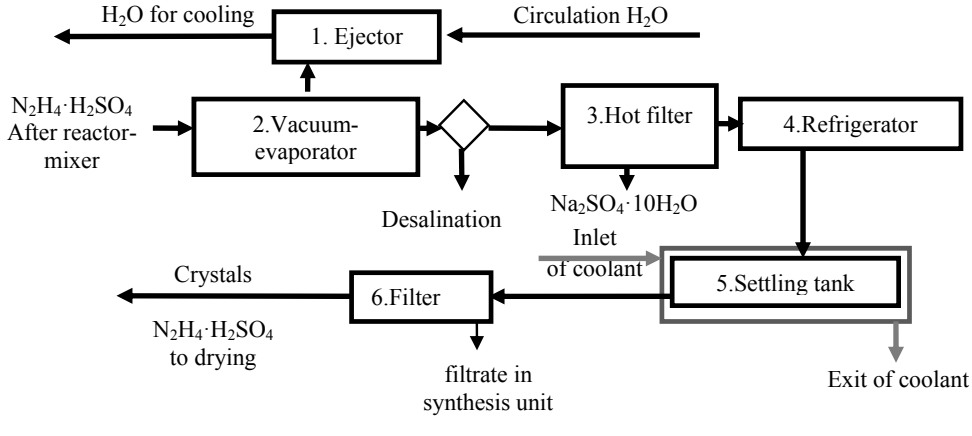


Fig. 4. Unit of concentration and separation from the process of the main and by-products

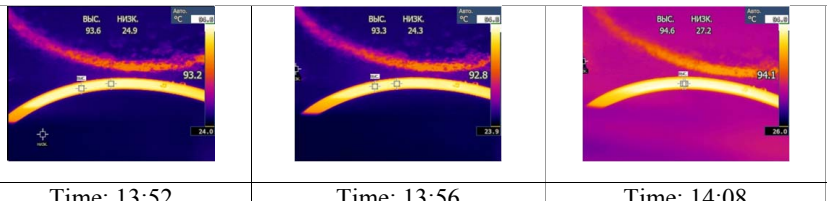
Description of the process on a model installation of periodic action. Nitrogen-containing wastewater goes through dispenser (3) from FSC collector (1), it mixes with the mixture (NaOCl+NaOH) coming from the collector of solution (NaOCl+NaOH) (2) and goes through dispenser (4) to ER synthesis of raw hydrazine (5). The reactor (5) is made of Fluoroplastic-4. Electromagnetic waves at length from 1 mm to 1 m with a frequency of 2.45 GHz from the source of wave radiation act on reactor (6). Technical characteristics of ER synthesis of raw hydrazine with a multimodal microwave distribution system in the reaction zone determine the frequency. The reactor (5) is in a protective housing, where microwaves, which reflect from walls, heat the reaction mixture to a temperature of 85÷96 °C. Control of the reaction temperature of the synthesis of raw hydrazine is impossible. We can measure the temperature of the reaction mixture at the outlet of reactor (5) as an alternative. We make a thermogram of the synthesis process by FLUKE-Ti-25 thermal imager, Fluke Corporation, USA, which allows measuring temperature of a wall of the outlet pipe (Fig. 5). We determine the reaction temperature of the synthesis of the semi-product is determined by the calculation method, taking into account the temperature of a wall of the outlet pipe.

The reaction mixture, together with the formed semi-product (hydrazine), enters the reactor mixer (10) through refrigerator (7). Fig. 1 shows the design features of reactor mixer (10) in more detail. Sulfuric acid enters the reactor of the synthesis of HS – reactor mixer (10) from pressure tank of sulfuric acid (9) with the help of dispenser (8). After completion of the synthesis process, $N_2H_4 \cdot H_2SO_4$ synthesis solution enters the concentrate and separates from the process of the main and by-products unit (Fig. 4), where HS solution evaporates under vacuum and goes out of the process.

The vacuum appears at the expense of the ejector (1), which, in this case, performs a combined role of the condenser of flash steam, because cold water is the operation flow. The vacuum evaporator (2) operates in the temperature range of 60÷75 °C of flash steam. The concentrated mixture passes hot filter (3) after the vacuum evaporator. It enters refrigerator (4), where it is cooled to a temperature not exceeding 18 °C. Next, the cooled mixture enters settling tank (5), where maturation and growth of $N_2H_4 \cdot H_2SO_4$ crystals occurs at a constant temperature of 12÷18 °C. The reaction solution with HS crystals enters filter (6). The filtrate with the concentration of sulfuric acid up to 60÷70 % comes back to the process of HS synthesis into mixing reactor (10) shown in Fig. 3. The reaction mixture

necessarily passes through hot filter (3), where crystals of decahydrate sodium sulfate are separated, if we use the filtrate as a source of sulfuric acid after the vacuum evaporation. If the critical value of the concentration of sodium chlorides reaches a level of 33.7 %, then the process of general crystallization will begin, that is, crystals of anhydrous Na_2SO_4 and NaCl will drop out in the precipitate at the temperature of 50÷60 °C. The solubility of sodium sulfate decreases with an increase in chloride concentration in the solution. Therefore, if the critical concentration of chlorides in the filtrate reaches the level of 20 % (in terms of NaCl), the filtrate should go to desalination, where all the dissolved salts are separated from the filtrate by evaporation with subsequent condensation of flash steams vapors, namely the mixture of anhydrous Na_2SO_4 and NaCl. Sour condensate, which is free from salts, returns to the process of synthesis of HS.

We wash the filtered HS with cooled to 2±1 °C distilled water from residual sulfuric acid and sent it to a drying temperature of 75 (±10) °C. We collect the finished product with a moisture content of up to 1.5 % in a storage tank for the finished product after drying. We store crystalline hydrazine sulfate in a sealed container without access to air and direct sunlight.



Time: 13:52	Time: 13:56	Time: 14:08
Maximum temperature, °C		
93.6	93.3	94.6
Average temperature of the synthesis process		93.8

Fig. 5 Examples of thermograms for the synthesis of raw hydrazine in a fluoroplastic synthesis reactor taken using FLUKE-Ti-25 thermal imager, Fluke Corporation, USA

4. 5. The course of the experimental study on the effectiveness of the modeling system

We treat FSC with an alkaline solution of active chlorine (NaClO) and direct it to a multimode ER synthesis to raw hydrazine. The synthesis of raw hydrazine occurs under the influence of wave irradiation at a frequency of 2.45 GHz at the temperature range of 263–373 K (atmospheric pressure). Next, the synthesis solution goes to neutralization of excess sodium hydroxide and to HS synthesis followed by the concentration of weak solutions of HS, separation of by-products (Na_2SO_4 and NaCl), and removal of the main product from the process.

We carried out the optimization of parameters of synthesis of raw hydrazine on a model plant of the synthesis of hydrazine sulfate from FSC using a passive experiment, since the difficulty of generating points of the input space determines the vector of a passive experiment.

4. 6. Analysis of the obtained experimental data on the operation of the model plant for the disposal of FSC via HS synthesis

We used Microsoft Office Excel 2010 and Advanced Grapher for regression analysis and construction of a graphical expression of the dependence of physical and chemical parameters of the process.

5. Results of studying the process of disposal of FSC via the synthesis of HS

5. 1. Quantitative analysis of FSC

Table 1 shows qualitative and quantitative compositions of FSC.

Table 1

Qualitative and quantitative composition of FSC of carbamide synthesis device

Indicator	Actual value of the gradient of mass concentration determined during operation	Water indicator pH	Density, g/cm^3
$CO(NH_2)_2$, %	0.80÷2.00	10.0÷10.4	1.006÷1.014
$C_2H_5N_3O_2$, %	0.01÷0.05		
NH_3, %	1.50÷5.00		
CO_2, %	1.20÷3.00		
H_2O, %	96.49÷94.95		

We determined values of the mass concentration of metals in wastewater collected from the collector of FSC device for the production of carbamide with the productivity of 330,000 t/year by the scheme of the stripping process. We defined the following metals: Fe, Cu, Ni and Cr. Table 2 shows the value of the gradient of mass concentration of metals in FSC after processing of all the values obtained.

There was a certain dependence of an increase in the amount of dissolved metal in the starting time compared with values of concentrations of metal ions in the process of stable operation of the device due to interruptions in the carbamide synthesis device.

Table 2

The value of the gradient of mass concentration of metals in FSC

Indicator	Fe, mg/dm^3	Cu, mg/dm^3	Ni, mg/dm^3	Cr, mg/dm^3
Value for the gradient of mass concentration	<0.006÷0.44	<0.006 (0.001÷0.005)	<0.006÷0.01	<0.006 (up to 0.0008)

5. 2. Mechanism of the synthesis of raw-hydrazine from FSC in terms of quantum chemistry in the Born-Oppenheimer approximation using the method of analysis of molecular systems

It is inappropriate to consider the process of the synthesis of hydrazine in terms of elementary chemistry. Electromagnetic vibrations increase vibration of molecules and provoke the rupture of donor-acceptor bonds in molecules with formation of radicals or ion-radicals. As known, reactivity of radical particles and ion radicals is much higher. Radicals and ion radicals serve as intensifiers of almost all processes, such as electromagnetic radiation, which increases frequency of vibration of molecules and formation of radicals or ion radicals.

Even though the nature of the Gibbs energy change (ΔG) makes it possible to determine the fundamental possibility of spontaneous process flow, the value (ΔG) is true for non-in-

sulated systems. The indicator of the difference in the sum of energies of the reaction products and output components is more informative. We calculated the total energy of particles, which act in these reactions. We can calculate the energy of a chemical particle by the methods of quantum chemistry in the Born-Oppenheimer approximation. It is one of the characteristics of the stability of a chemical particle. In this approximation, the energy of a chemical particle (total energy E_{tot}) consists of: kinetic energy of electrons (E_e^t); potential energy of the interaction of electrons and nuclei (E_{eN}^V); potential energy of the interaction of electrons (E_{ee}^V); potential energy of the interaction of atomic nuclei (E_{NN}^V). We determined the energy of a chemical particle from formula (1).

$$E_{tot} = E_e^t + E_{eN}^V + E_{ee}^V + E_{NN}^V. \quad (1)$$

It is rather difficult to follow up experimentally an influence of microwave irradiation on kinetics of a magnetic moment of the proposed method for the synthesis of raw hydrazine. It is complex due to the imperfection of the applied microwave equipment. Thus, electromagnetic reactors used in the study process had a multimodal microwave distribution system, so they were in a protective housing that made impossible to collect a sample during the synthesis process. Since the process proceeds arbitrarily and depends on distribution of waves in the reaction zone, that is, the removal of the synthesis solution from ER synthesis occurs unilaterally, it is impossible to control low rate of the synthesis solution at the output of ER. That is why the method of the synthesis of hydrazine sulfate from FSC is a rather complicated stochastic system. It is impossible to predict the progress of the process in stochastic systems, since it depends on random factors of influence. The random factors of the influence to the system are distribution of waves in the reaction zone; concentration gradient of the main components of the synthesis of hydrazine; presence of process inhibitors (corrosion products); initial temperature of secondary raw material. The main obstacle in the synthesis of raw hydrazine in a vapor-gas-liquid flow is occurrence of adverse reactions described in paper [2]. We carried out quantum-chemical calculations to establish the most energetically possible development of the process of oxidation of ammonia, carbamide and biuret to hydrazine in terms of quantum chemistry. We calculated the difference between energies of products and initial substances (ΔE) for the three most probable mechanisms of the reaction of synthesis of raw hydrazine from FSC taking into account low concentrations of substances gradients. According to the data of physical-and-chemical conditions for the hydrazine synthesis process, sodium hypochlorite is first decomposed into chlorinated acid (2), which in turn is decomposed into hydrochloric acid and an oxygen radical (3).

$$NaOCl+H_2O \rightarrow HOCl+NaOH, \quad \Delta E=149{,}76 \text{ kJ/mol}; \quad (2)$$

$$HOCl \rightarrow HCl+O^{\bullet}, \quad \Delta E=70{,}92 \text{ kJ/mol}. \quad (3)$$

If we do not take into consideration the low concentration gradients of the synthesis of the solution, then the synthesis of hydrazine from carbamide proceeds by reaction (4), and from ammonia – (5).

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

$$\Delta E=-199034{,}63 \text{ kJ/mol}; \quad (4)$$

$$2NH_3+NaOCl \rightarrow N_2H_4+NaCl+H_2O,$$

$$\Delta E=-181{,}06 \text{ kJ/mol}. \quad (5)$$

The first option of the mechanism of occurrence of reactions of synthesis of raw hydrazine:

First, reactions (2) and (3) proceed. Next:

$$CO(NH_2)_2+O^{\bullet} \rightarrow N_2H_4+CO_2,$$

$$\Delta E=-104{,}37 \text{ kJ/mol}; \quad (6)$$

$$(CO)_2(NH_2)_2NH+HOCl \rightarrow$$
$$\rightarrow CO(NH_2)_2+CO_2+NH_2Cl,$$

$$\Delta E=-71{,}11 \text{ kJ/mol}; \quad (7)$$

$$NH_3 \cdot H_2O+HOCl \rightarrow NH_2Cl+H_2O+HCl,$$

$$\Delta E=345807{,}77 \text{ kJ/mol}; \quad (8)$$

$$NH_3 \cdot H_2O+NH_2Cl \rightarrow N_2H_4+H_2O+HCl,$$

$$\Delta E=-0{,}76 \text{ kJ/mol}. \quad (9)$$

The second option of the mechanism of occurrence of the reactions:

First, reactions (2), (3) and (6) proceed. In addition:

$$(CO)_2(NH_2)_2NH+HOCl \rightarrow CONH_2Cl+CO_2+N_2H_4,$$

$$\Delta E=-49{,}49 \text{ kJ/mol}; \quad (10)$$

$$CONH_2Cl+O^{\bullet} \rightarrow NH_2Cl+CO_2,$$

$$\Delta E=-125{,}98 \text{ kJ/mol}. \quad (11)$$

Next, there is the course of reactions (8) and (9).

The third option of the mechanism of occurrence of the reactions:

There are the following reactions that proceed in line with this option (2), (3), (6), (9) to (11). In addition:

$$HOCl+HCl \rightarrow Cl_2+H_2O,$$

$$\Delta E=-65{,}86 \text{ kJ/mol}; \quad (12)$$

$$NH_3 \cdot H_2O+Cl_2 \rightarrow NH_2Cl+H_2O+HCl,$$

$$\Delta E=5{,}22 \text{ kJ/mol}. \quad (13)$$

We chose the magnitude of the difference in the sum of energy of products and the initial substances of the system, that is, all the reactions of the mechanism, as the determining factor for development of processes of the synthesis of hydrazine from FSC.

5. 3. Investigation of the influence of electromagnetic irradiation at a frequency of 2.45 GHz on the efficiency of the synthesis reactor of raw hydrazine

The rate of chemical reactions depends on reaction temperature and a rate of activation energy significantly. There is a change in dielectric properties of materials and the environment during heating in ER. Because of the dependence

of a change of dielectric permittivity on the coordinate of propagation of waves. Paper [21] reported data on an increase in the rate of reactions occurring under an action of electromagnetic radiation due to increased activation energy in a microwave system.

We performed our own investigation of the influence of electromagnetic radiation on the coefficient of the efficiency of the semi-product synthesis reactor in the laboratory. We conducted the synthesis of raw hydrazine out using heat transfer from a wall to a wall (by the thermal method of heating of reaction mixture). We conducted a series of laboratory syntheses of N_4H_4 with the use of ER synthesis of the semi-finished product with a multimodal wave distribution system from 1 mm to 1 m and a frequency of 2.45 GHz using a laboratory plant for the synthesis of N_4H_4, as shown in Fig. 6, with the identical parameters and the constancy of the composition of the reaction mixture. Table 3 shows results.

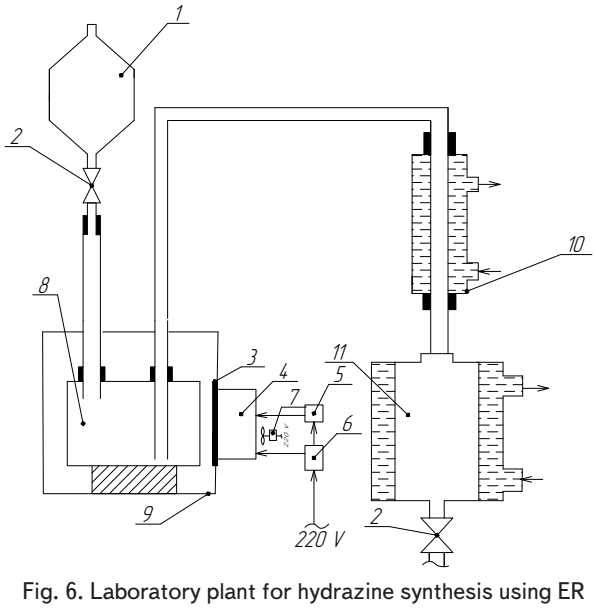


Fig. 6. Laboratory plant for hydrazine synthesis using ER synthesis with multimode wave distribution system of a length from 1mm to 1m and 2.45 GHz frequency: 1 — pressure tank with the reaction mixture; 2 — faucet; 3 — waveguide; 4 — magnetron; 5 — condenser; 6 — transformer; 7 — fan; 8 – electromagnetic reactor for the synthesis of hydrazine; 9 — body; 10 — heat exchanger; 11 — receptacle capacity

Table 3

Results of a series of experiments on the synthesis of hydrazine sulfate using a laboratory plant for the synthesis of raw hydrazine with the use of thermal methods of heating a synthesis solution and ER synthesis of semi-finished sulfate under atmospheric pressure

Series number of 10 experiments			1	2
Quantitative composition of FSC	$CO(NH_2)_2$	Mass concentration, %	1.72	1,52
	NH_3		2.90	3,70
	$C_2H_5N_3O_2$		0.25	0,09
	CO_2		3.0	2,1
	H_2O		92.13	92,59
Ratio of total Cl/N, mass fraction/of mass fraction			0.49/1	
t FSC before synthesis N_2H_4, °C			20	
t of NaOCl with NaOH solution before synthesis N_2H_4, °C			–10	
Average value of mass concentration of raw N_4H_4 in the synthesis solution, %	Synthesis of N_4H_4 using thermal methods of heating		0.008	0.006
	Synthesis of N_4H_4 in a multimodal ER		0.063	0.050

5. 4. Results of semi-industrial studies obtained at a model plant for the disposal of FSC via the synthesis of HS

There were some optimal parameters of synthesis of raw hydrazine and hydrazine sulfate set on the model plant of the synthesis of HS from FSC (Fig. 3, 4) by the method of passive experiment. Table 4 shows the results of the study aimed at determination of the optimal ratio of sodium hypochlorite in terms of Cl_2 in relation to the total N. The content of N in this case decreases to a total concentration of 4.248. We thermostated the temperature of the solution (NaClO+NaOH) and FSC for the experiment. The temperature of the mixture (NaClO+NaOH) was (–10) °C, FSC – 20 °C. Similarly, we carried out the rest of the studies to find extrema of variable parameters of the synthesis system. The temperature of raw hydrazine sample from the synthesis solution was 15 °C in all series of experiments. We carried out the analysis under normal conditions.

Fig. 7 shows the results of regression analysis of operation of the modeling plant for the synthesis of hydrazine sulfate using ER synthesis of raw hydrazine.

We established the maximum productivity of the model plant of hydrazine sulfate synthesis. It is 0.9 kg/day. The maximum load on the model plant provided the flow rate of the synthesis solution is 2 cm^3/s or 7.2 dm^3/h.

Table 4

Results of studying the synthesis of raw hydrazine at the model plant to determine the dependence of content of raw hydrazine on the ratio of NaOCl in terms of Cl_2 in relation to N total

Ratio of the number of weight parts of active chlorine in terms of Cl_2 per 1 weight part of ammonium and amidic total nitrogen converted to N atomic	0.29/1	0.49/1	0.50/1	0.55/1	0.57/1	0.67/1	0.78/1
Actual output of N_2H_4, determined experimentally, %	0.098	0.110	0.110	0.089	0.100	0.091	0.066
Flow rate of the reaction mixture, cm^3/sec	0.52	0.81	0.83	1.27	1.27	1.26	0.65
Coefficient of reduction of output of N_2H_4 taking into consideration flow rate of the reaction mixture	1.92	1.23	1.20	0.79	0.78	0.79	1.54
Content of N_2H_4 reduced to a common denominator taking into consideration flow rate of the reaction mixture, %	0.051	0.090	0.092	0.113	0.128	0.115	0.043
Content of N total in FSC, %	4.248	4.248	4.256	4.256	4.248	4.248	4.256
Content of N_2H_4 in the synthesis solution reduced to a common denominator taking into consideration flow rate of the reaction mixture and content of N total in FSC, %	0.051	0.090	0.092	0.113	0.128	0.115	0.043
Output of N_2H_4 from N total, %	2.10	3.71	3.79	4.66	5.27	4.74	1.77

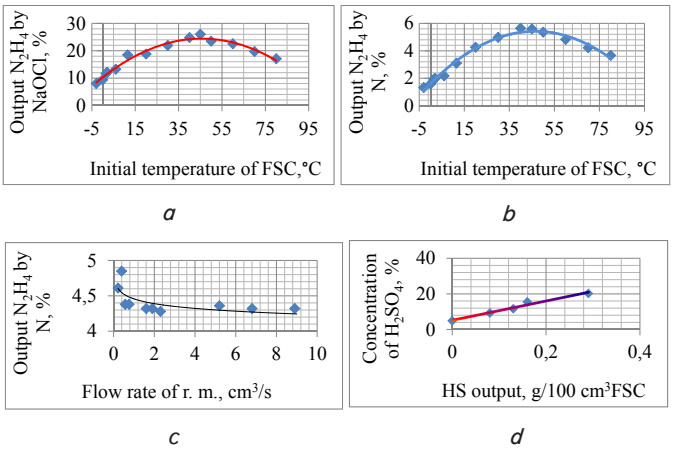


Fig. 7. Graphical expression of dependence: *a, b* – output of N_2H_4 in relation to sodium hypochlorite (*a*) and total nitrogen (*b*) on the initial temperature of the object; *c* – output of N_2H_4 on the flow rate of the reaction mixture; *d* – output of HS of 100 cm^3 of FSC on the content of sulfuric acid

6. Discussion of results of the synthesis of hydrazine sulfate from FSC

6. 1. Discussion of results of analyzing the quantitative composition of FSC

Absence of organic impurities determines the value of secondary raw materials – FSC. The present compounds of amid nitrogens transform into hydrazine by the Hofmat equations, and ammonium ions – by the Raschig equation.

6. 2. Discussion of results of analyzing the mechanisms of synthesis of raw hydrazine, which occur in ER

A change in energy in reaction (3) is less than in reaction (4), therefore reaction (3) is most probable, that is, the synthesis of hydrazine from carbamide will occur first, and then – the synthesis from ammonia.

Despite the sufficient condition of probability of occurrence of the synthesis of raw hydrazine from carbamide and the satisfactory condition – from ammonia, it is not possible to reach 100 % of the output due to the strong reactivity of newly formed hydrazine.

The value of the system energy amount is 345,852.214 kJ/mol for the first mechanism; it is 345,747.854 kJ/mol for the second option of the mechanism; and it is 0.204 kJ/mol for the third mechanism. Therefore, the reactions described in the third option of the mechanism will occur in a vapor-gas-liquid flow.

6. 3. Discussion of results of studying the influence of electromagnetic radiation at a frequency of 2.45 GHz on the efficiency of the raw hydrazine synthesis reactor

High-frequency irradiation provides contactless heating of the reaction mixture. We can observe an increase in the efficiency of ER due to heating of the reaction mixture "from the inside" and probable leakage of atomic radicals. In addition, microwaves intensify the process of contact of components of the reaction mixture (mixing), which is due to acceleration of motion of molecules. According to the results of the Table 3, we established an increase in the efficiency of ER synthesis of hydrazine by 88 %.

6. 4. Regression analysis of experimental data obtained at a model plant for the disposal of FSC via the synthesis of HS

We performed the regression analysis of the hydrazine output in relation to N total (Y_{14}) expressed as a percentage, depending on the ratio of NaOCl in terms of Cl_2 to N total in FSC (x_{14}) expressed in weight parts (w.p.) according to Table 4. The equation of approximation of experimentally obtained data (14) takes the form:

$$Y_{14} = -243{,}8 \cdot x_{14}^3 + 348{,}57 \cdot x_{14}^2 - 149{,}74 \cdot x_{14}. \qquad (14)$$

After studying Y_{14} (x_{14}) function in the given range of the ratio Cl_2 /1 w.p. N=0.1÷2, a number of approximation steps =200, equation (14) takes the form:

$$Y_{14}^1 = -243{,}8 \cdot 3 \cdot x_{14}^2 + 348{,}57 \cdot 2 \cdot x_{14}^2 - 149{,}74. \qquad (15)$$

Y_{14}^1 (x_{14}) function acquires a zero value at a ratio of 0.81 w.p. Cl_2 /1 w.p. N; the minimum value $Y_{14}^1 = 1{,}92$ %, at $x_{4.25}$=0.33 w.p. Cl_2/1 w.p. N; the maximum value $Y_{14}^1 = 5{,}19$ %, at x_{14}=0.63 w.p. Cl_2/1 w.p. N. Thus, the optimal ratio of w.p. Cl_2/1 w.p. N is 0.63 w.p.

The mathematical expression of the function of the polynomial approximation of the dependence of N_2H_4 output in relation to NaOCl (Y_{16}) and N total (Y_{17}) on the initial temperature of FSC (x_{16}) (Fig. 7, *a, b*)

$$Y_{16} = -0{,}0068 \cdot x_{16}^2 + 0{,}62 \cdot x_{16} + 10{,}28; \qquad (16)$$

$$Y_{17} = -0{,}0018 \cdot x_{16}^2 + 0{,}1637 \cdot x_{14} + 1{,}6181. \qquad (17)$$

We studied $Y_{16}(x_{16})$ and $Y_{17}(x_{16})$ functions to determine the optimal initial temperature of FSC (x_{16}). We set the following parameters: the minimum x_{16}=(–5); the maximum x_{16}=100; the number of steps of approximation =200. According to the parameters, of the equations (16) and (17) take the form:

$$Y_{16}^1 = -0{,}0068 \cdot 2 \cdot x_{16} + 0{,}6201; \qquad (18)$$

$$Y_{17}^1 = -0{,}0018 \cdot 2 \cdot x_{16} + 0{,}1637. \qquad (19)$$

Zeros of Y_{16}^1 (x_{16}) functions are absent, for $Y_{17}^1 = 0$ %, at x_{16}=99.94 °C; $Y_{16}^1 = 24{,}42$ %, at x_{16}=45.6 °C; $Y_{17}^1 = 5.34$ %, at x_{16}=45.47 °C. Thus, the optimum initial temperature of FSC is 45.5 °C.

Given a stable ratio of Cl_2/N=0.49/1 w.p. and the initial temperature of the mixture (NaOCl+NaOH)=(–10) °C and the reaction mixture flow rate of 1 cm^3/s – a yield of N_2H_4 is: in relation to NaOCl=24.4 %; in relation to N total=5.3 %. After a series of syntheses with observance of the given parameters under the condition of the constancy of mass concentration of N total Pin FSC – 4.257 %, the content of the semi-product makes up 0.11 % on average, which corresponds to the output of the finished product at a level of 4.5 g/dm^3 of FSC.

We performed regression analysis of data in Fig. 7, c. According to the data, we deduced the logarithmic dependence of the data of values of hydrazine outputs (Y_{20}) on the flow rate of the reaction mixture (x_{20}) entering the ER synthesis of raw hydrazine. The approximation equation has the form:

$$Y_{20} = -0{,}0969424 \cdot \ln(x_{20}) + 4{,}4566945. \quad (20)$$

After studying $Y_{20}(x_{20})$ function in the given range of flow rate (0.1÷10), the number of steps of approximation=200, equation (20) does not have zeros of function and extremums. We explain this phenomenon by the self-regulation of flow rate of the synthesis solution of ER synthesis of raw hydrazine. We established experimentally the maximum flow rate of synthesis solution of ER synthesis, it is 2 cm^3/s.

Mathematical expression of the linear approximation of the hydrazine sulfate output dependence ($x_{4.28}$) of 100 cm^3 of FSC on the content of free sulfuric acid ($Y_{4.28}$) (Fig. 7, d):

$$Y_{21} = 54{,}22 \cdot x_{21} + 5{,}183. \quad (21)$$

Thus, the optimal concentration of acid in the reaction mixture, which makes it possible to bound newly formed hydrazine fully to a more stable and low soluble salt – is HS is set at 25÷30 %.

We carried out utilization of FSC by the synthesis of HS taking into consideration extrema of optimization parameters obtained above. We defined that: the initial output of the finished product is 5.3 kg per 1 m^3 of FSC at utilization of FSC by processing into HS, provided that the synthesis of raw hydrazine goes in accordance with the above-mentioned optimal synthesis parameters. We observed an increase in the output of the final product up to 6 kg per 1 m^3 at repeated reuse of filtrate as a source of sulfuric acid, because of the partial solubility of HS in the reaction solution.

We established that the estimated performance of HS synthesis device with FSC is 132–150 kg/h or 48÷55 t/year in the course of the projection of the model plant's operation on productivity of a carbamide production plant with capacity of 330,000 t/year. We calculated the profitability of the device based on the obtained data on the calculated capacity of the device of the synthesis of HS from FSC. We established that net profit in production of hydrazine sulfate according to the scheme above is not less than 12 %.

The main disadvantages are formation of flash steam condensate in the concentration of the synthesis solution, which contains HS, hat the city of HS and necessity to desalt periodically the synthesis solution with formation of silt of the composition (Na_2SO_4+NaCl) and HS.

It is also necessary to elaborate an ER synthesis design of raw hydrazine-rust with a monomodular microwave distribution system in the zone of continuous microwave operation to intensify the synthesis process.

7. Conclusions

1. We performed a quantitative analysis of FSC. We established the gradient of mass concentration of ammonia (1.50÷5.00 %), carbamide (0.80÷2.00 %) and biuret (0.01÷0.05 %) according to the results of a series of studies.

2. We developed and analyzed the most probable mechanism for the synthesis of raw hydrazine-raw of nitrogen-containing FSC compounds from the point of view of quantum chemistry in the Born-Oppenheimer approximation by the method of molecular systems analysis.

3. We investigated an influence of electromagnetic radiation of frequency of 2.45 GHz on efficiency of raw hydrazine synthesis reactor. We defined an increase in the efficiency of ER synthesis of hydrazine by 88 % in comparison with the hydrazine synthesis reactor with a use of the thermal method of heating.

4. We tested a model plant for the conversion of nitrogen contained in FSC by the synthesis of HS. We performed a regression analysis of the results of semi-industrial studies on the model plant for disposal of FSC by the synthesis of HS and made a mathematical projection of the results of operation of the model plant on the industrial scale. We calculated the optimal ratio of w.p. Cl_2/1 w.p. N, which is 0.63 w.p. The optimum initial temperature of FSC is 45.5 °C. We established experimentally the maximum flow rate of the synthesis solution from ER synthesis, which is 2 cm^3/s. We determined the optimal concentration of acid in the reaction mixture, which makes it possible to bound newly formed hydrazine fully to a more stable and slightly soluble salt, HS, which is 25 to 30 %. We carried out the utilization of FSC by means of the synthesis of HS taking into consideration the extrema of optimization parameters obtained above. We established that the initial output of the finished product is 5.3 kg per 1 m^3 of FSC at utilization of FSC by processing into HS, provided that the synthesis of raw hydrazine goes in accordance with the above-mentioned optimal synthesis parameters. We observed an increase in the output of the final product up to 6 kg per 1 m^3 at repeated reuse of filtrate as a source of sulfuric acid, because of the partial solubility of HS in the reaction solution.

We established that the estimated performance of HS synthesis device with FSC is 132–150 kg/h or 48÷55 t/year in the course of the projection of the model plant's operation on productivity of a carbamide production plant with capacity of 330,000 t/year. We calculated the profitability of the device based on the obtained data on the calculated capacity of the device of the synthesis of HS from FSC. We established that net profit in production of hydrazine sulfate according to the scheme above is not less than 12 %.

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