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CHEMICAL BINDING OF SULFUR DIOXIDE IN A BUBBLING REACTOR WITH THE USE OF UREA

Introduction. *Integration of Ukraine into the European Union requires a significant reduction in pollutant emissions from industrial enterprises. Special attention is paid to the entry of suspended solid particles, nitrogen oxides, carbon dioxide and sulfur dioxide from thermal power plants into the atmosphere.*

Problem Statement. *Sulfur dioxide is one of the main pollutants of the environment. Its entry into the atmospheric air leads to the formation of acid rain, which negatively affects people, soil, plants, and ground structures.*

Purpose. *To study the influence of the initial mass content of urea in an aqueous solution and its temperature on the efficiency of the process of chemical binding of sulfur dioxide.*

Material and Methods. *Several scholarly research publications dealing with the removal of sulfur oxides from waste gases of thermal power plants by various methods and technologies with the use of urea have been considered. The research is based on a mathematical model of a bubbling type chemical reactor.*

Results. *A series of numerical experiments on a chemical reactor where urea is used as a source of ammonia to bind sulfur dioxide in solution has been conducted. The calculations have made it possible to determine the optimal temperature of the solution at a certain urea content. The temperature should be equal to approximately 57 °C, at an initial urea content of 1%, 40 °C, at a content of 5%, and 35 °C, at 10%. Under such conditions, the efficiency of the process of chemical binding of sulfur dioxide in the solution is close to 100%.*

Conclusions. *The analysis of the results of mathematical modeling of processes in a chemical reactor has shown that for the pair of parameters "temperature-urea content" there are values at which the efficiency of the binding process reaches almost 100%. To control the efficiency, it is advisable to use the potential of hydrogen of the solution at a level of 7 ± 0.5. The lower values of the potential of hydrogen indicate a drop in the process efficiency, while the higher values indicate an increase in the concentration of ammonia in the treated gases at the reactor outlet.*

Keywords: sulfur dioxide, bubbling chemical reactor, and urea solution.

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When coal is burned in thermal power plants of power plants and other industrial enterprises, many pollutants are formed and released into the environment. Suspended solid particles, carbon dioxide (CO_2), nitrogen oxides (NO_X), and sulfur dioxide (SO_2) enter the atmosphere the most. In recent decades, the spread of harmful emissions has caused serious environmental problems, such as urban smog, acid rain, and ozone depletion. The order of the Ministry of Ecology and Natural Resources of Ukraine [1] requires compliance with certain technological standards for permissible emissions of pollutants from thermal power plants. An electrostatic filter is widely used to reduce dust emissions. Several techniques have been developed and used to reduce NO_X emissions. Among them, there is selective catalytic reduction (SCR) [2] with an efficiency of 90—95% at an operating temperature of 200—500 °C and selective non-catalytic reduction (SNCR) [3] with an efficiency of 60—65% at an operating temperature of 800—1200 °C. In SCR and SNSR processes, a reducing agent is introduced into the flue gas to reduce NO_X to harmless molecular nitrogen (N_2). Currently, the most popular reducing agent is ammonia (NH_3) in aqueous or liquid form. The disadvantage of the methods is that SCR-technology has a high cost, and the surface of the catalyst is sensitive to poisoning by "dirty" gas flow, and SNCR-technology works only at high exhaust gas temperatures. In addition, during the reconstruction of the boiler unit of the thermal power plant, the SCR-method must be integrated into the high-temperature area of the process because it is not part of the original design. The method is used before the air heater. The SNCR-method is used behind the screens or further along the flow of flue gases in front of the convective shaft of the boiler unit. The use of SCR and SNCR requires a significant restructuring of the technological process and the design of the gas path of the boiler unit. The use also requires a significant reconstruction of the construction of the gas path of the boiler unit. The implementation of such solutions can disrupt the production process and have negative consequences for the operation of the boiler unit and lead to significant capital costs. This makes the methods less attractive for industrial use.

Currently, the problem of SO_2 pollution is effectively controlled. The most common method of desulfurization is the wet limestone-gypsum or ammonium process. Nitrogen monoxide makes up more than 90% of NO in flue gases and is very poorly soluble in water. A strong oxidizer must be used to convert NO into soluble nitrogen oxides. A urea solution can be used to reduce the cost of simultaneous SO_2 and NO_X removal and to improve the efficiency of NO_X removal from flue gases. Urea ($(NH_2)_2CO$) is a weakly alkaline reagent and a strong reducing agent. As compared with other absorption solutions, urea is a cheap and non-toxic substance. At the same time, the reaction products of simultaneous desulfurization and denitrification with the use of urea solution in the liquid phase are ammonium sulfate, carbon dioxide, and nitrogen. Ammonium sulfate can be recycled, and the gases can be directly emitted into the atmosphere.

THE USE OF UREA

To study the absorption of NO_X and SO_2 in urea solutions, the authors of [4] carried out continuous experiments in a packed column with counter flow of gas and liquid flows. The absorption column 1 m in height is filled with metal rings measuring 16 × 16 mm to increase the contact surface of the gas with the liquid. Against the background of the high efficiency of sulfur dioxide removal under different experimental conditions, the efficiency of nitrogen oxides removal is measured. The effect of urea concentration, operating temperature, initial value of the hydrogen index, degree of NO_X oxidation, SO_2 concentration, and oxidizing additive on the efficiency of NO_X removal is experimentally studied. The optimal conditions for the absorption column have been established. Analysis of the products of chemical reactions made it possible to find out the mecha-

nism of reactions and their general equations during simultaneous desulfurization and denitrification with a urea solution. The molar enthalpy of reactions, the molar Gibbs function and the equilibrium constants of chemical reactions have been calculated by thermodynamic methods. The results of the calculations have shown that the technology of simultaneous removal of pollutants is technically possible with an efficiency of almost 100%. For simultaneous desulfurization and denitrification of gas mixtures, urea is a promising absorption solution. It exhibits high SO_2 removal efficiency and more than 40% denitrification efficiency. The degree of oxidation of nitrogen oxides, additives and other factors have a great influence on the efficiency of denitrification. The oxidizer, as an additive in the solution, helps to increase the efficiency of denitrification by more than 50%. For the practical application of urea solution, optimal conditions for simultaneous desulfurization and denitrification of gases in a chemical reactor have been determined. At a reaction temperature of 60 °C, a solution pH of 5—9 and a mass content of urea of 5—10%, the amount of an additive of H_2O_2 or $NaClO_2$ should be about 1‰ by mass. Thus, the results of experiments prove the availability of technology for simultaneous desulfurization and denitrification of the outlet gases of thermal power plants with the use of urea solution.

Simultaneous desulphurization and denitrification allows the removal of SO_2 and NO_X from flue gases in one plant and the use of one absorbent. In [5], a process with the use of urea as an absorbent has been for the removal of SO_2 and NO_X in a semi-dry special pseudo-fluidized gushing bed. Such a semi-dry method has a huge potential for development and a wide cutting-edge value. The method overcomes two disadvantages of the wet process: the need for a large amount of urea and the treatment of wastewater. The researchers studied the chemical mechanism of SO_2 and NO_X absorption and the thermodynamics of their interaction with urea. It has been found that nitrogen oxides are reduced to molecular nitrogen. The working conditions of the spouted bed have been optimized based on the results of a series of experiments. The effect of the molar ratio of urea and gaseous pollutant, the temperature of the flue gases at the reactor inlet and its approach to the adiabatic water vapor saturation temperature has been studied based on the efficiency of SO_2 and NO_X removal. The results of the research create a basis for the commercial application of the technology of simultaneous desulfurization and denitrification of the outlet gases. It allows almost complete absorption of SO_2 and NO_X in flue gases. At the same time, it is a clean technology that ensures zero pollution. Experiments have shown that the approach of the gas temperature to the saturation temperature leads to a decrease in the efficiency of the process of removing both pollutants. The dependence of the efficiency of the process has a clearly expressed maximum at a molar ratio of urea to sulfur and nitrogen oxides of approximately 1.2. An increase in the temperature of the gases reduces the efficiency due to an increase in the droplet evaporation rate and a decrease in the gas residence time in the reaction zone. The semi-dry process of flue gas cleaning from the gushing layer eliminates the disadvantage of the wet process. In the semi-dry process of flue gas cleaning, the influence of the urea solution is crucial. Choosing a high-performance atomizer is an absolutely necessary step in an industrial application.

In recent years, ammonia-based wet desulfurization of flue gases has become increasingly popular. In the study [6], an aqueous solution of urea is used instead of anhydrous ammonia or its aqueous solution in the wet method of ammonia-based flue gas desulfurization. The necessary NH_3 is formed because of the hydrolysis of urea. The originality of the work is that a separate chemical reactor is used to generate ammonia during the hydrolysis of urea. In the reactor, the aqueous solution of urea is heated to a temperature of 120—160 °C to accelerate the hydrolysis process, and the pressure is maintained in the range of 0.4—0.7 MPa. The influence of temperature, pressure, ini-

tial mass content of urea in the solution on the intensity of urea conversion in the hydrolysis process has been studied. It has been established that with a mass content of urea of 30%, the optimal temperature is 140 °C and a pressure of 0.4 MPa. It should be noted that under these conditions, the conversion and output of urea can reach 86.75% and 49.11%, respectively. Finally, ammonia that is obtained under optimal conditions, is used to prepare an absorbent in the process of chemical binding of sulfur dioxide. Experiments on desulfurization have been carried out in a bubbling reactor. The influence of SO_2 concentration and liquid-gas ratio on desulfurization has been studied. The experimental results have shown that all indicators of desulfurization efficiency at different concentrations of SO_2 exceed 99%, and a higher liquid-gas ratio increases desulfurization efficiency. The corresponding range of the hydrogen indicator for an absorbent based on ammonia is 6.5—7.5. It has been also found that a higher concentration of SO_2 and a lower liquid-to-gas ratio can favor the formation of ammonium sulfate.

Pyrolysis can be used to obtain ammonia from urea. Pyrolysis of urea, from which ammonia for denitrification is produced, plays an important role in the process of removing nitrogen oxides. Research on urea pyrolysis has mainly focused on three components: urea pyrolysis to form isocyanic acid (HNCO), catalytic hydrolysis of HNCO, and catalytic pyrolysis of aqueous urea. In this work [7], a detailed review of the progress of urea pyrolysis research has been carried out. From the review of the literature, it can be concluded that although many studies have been carried out, attention has been focused mainly on the analysis of urea pyrolysis products and the study of catalysts used to increase the yield of ammonia. Little has been done to study the mechanism and develop a kinetic model with high accuracy, which is still very much needed today. Ideally, 1 mole of urea undergoes a two-step reaction to form 2 moles of NH_3: direct thermal decomposition of urea to NH_3 and HNCO and hydrolysis of HNCO to NH_3 and CO_2. Hydrolysis of HNCO over metal oxide catalysts can be basically defined as reaction process under mass-transfer control. It is also recognized that the HNCO hydrolysis reaction proceeds slowly without the aid of suitable catalysts. Whether in the presence or absence of water, TiO_2 has a relatively higher catalytic effect on urea pyrolysis and HNCO hydrolysis. Although much work has been done, the focus is on the analysis of urea pyrolysis products and the study of catalysts used to increase ammonia yields.

Ammonia poses a significant hazard and risk to the environment when used. It is a highly volatile noxious substance with an unpleasant odor that becomes unbearable even at very low concentrations. However, it has been known for a long time that ammonia is a good reagent for treatment of flue gases that are formed in the process of burning fossil fuels. Research [8] concerns methods and means of safe production of a relatively small amount (up to 50 kg/h) of ammonia. This work includes an experimental study of the hydrolysis of urea to produce ammonia in a reactor at a temperature from 110 °C to 180 °C and a pressure of 1 MPa with different initial mass content of urea (10%, 20% and 30%) and different stirring rates from 400 rpm up to 1400 rpm. A batch chemical reactor is used for the experiments. The effect on the rate of hydrolysis has been studied: temperature, initial concentration of urea and rate of mixing. The process takes place according to two reactions, with the formation of ammonium carbamate as an intermediate product. The analysis of the results of the experiments has shown that the kinetic equation of urea hydrolysis has the form $r_A = 2.89 \times 10^7 \cdot \exp(-8856.79/T) \cdot C_A$, where k_A is the reaction rate constant, s^{-1}; and C_A is the concentration of urea in the solution, kmol/m^3. It can be concluded that initially the reaction rate is slow. It becomes significant at about 130 °C. At this temperature, the formation of ammonia is higher than at lower temperatures. In addition, the stirring rate has a positive effect on the conversion, which from the beginning increases dramatically with increasing stirring rate. The results of the study indicate that urea hydrolysis

for ammonia production is a suitable technique for safe use in a coal-fired thermal power plant.

The publication [9] is in no way related to the use of urea in the process of chemical binding of sulfur and nitrogen oxides. The article is of great interest because it contains the results of the hydrolysis of $(NH_2)_2CO$. The authors of the publication set the following tasks: to determine the dependence of the urea hydrolysis rate on temperature; to obtain data on the rate of accumulation of ammonia and carbon dioxide in the solution under different temperature conditions. Urea and distilled water are used for kinetic studies. The experiments on a laboratory setup that has a glass reactor with a thermostat and an installed stirrer have been made. This design ensures uniform heating and chemical composition throughout the solution volume. The research has been conducted in the temperature range of 80—100 °C. The amount of urea remains constant and corresponds to a concentration of 120 kg/m^3. The content of urea in the solution is monitored at constant time intervals. At the same time, the content of free ammonia in the solution and carbon dioxide has been determined. As a result of research, kinetic curves of urea hydrolysis have been obtained in the form of changes in urea concentration over time. The experimental data have shown that the hydrolysis reaction is of the first order, the activation energy of urea is 88.36 kJ/mol, and the pre-exponential factor in the Arrhenius equation is 1.53×10^{10} s^{-1}.

With the growth of industrialization in the energy sector, the air is polluted by many substances emitted from coal-fired thermal power plants. Cleaning flue gas, especially at such power plants, requires the production of ammonia. The experiments on the kinetic study of urea hydrolysis with the use of a glass reactor have been carried out in [10]. First, the reactor is operated without stirring the solution, and then with its stirring. The study has shown that the conversion increases exponentially with increasing temperature and urea concentration. In addition, the influence of stirring rate, temperature, and concentration on the conversion has been studied. With the use of the theory of collisions, the temperature dependence of the rate constant of the direct reaction has been found. Based on the dependence, the activation energy of the reaction and the frequency coefficient, given the frequency of effective collisions between urea and water molecules, have been calculated. It has been observed that the rate constant of the forward reaction increases with increasing temperature. Upon stirring, the activation energy and frequency coefficient have been found to be equal to 59.85 kJ/mol and 3.9×10^6 min^{-1}, respectively, with the correlation coefficient and the standard deviation being equal to 0.98% and ±0.1%, respectively.

In [11], the process of thermal decomposition of urea in a chemical reactor with laminar flow has been studied. According to the results of the experiments, the mechanism of urea conversion and the rate of ammonia formation have been established. Processing of the measured concentration of urea during the process at different temperatures made it possible to determine the kinetic parameters of the decomposition reaction. The activation energy is 87.84 kJ/mol, and the pre-exponential factor is 9.925×10^6 s^{-1}.

This research is aimed at studying the process of chemical binding of sulfur dioxide in a bubbling-type reactor with the use of an aqueous solution of urea as part of the technology for simultaneous desulfurization and denitration of flue gases. To determine the influence of the variables on the efficiency of SO_2 removal, various operating parameters have been tested and optimal conditions for the process have been established.

MATHEMATICAL MODEL

The process parameters in chemical reactor have been calculatedby the modified mathematical model [12]. To determine the content of 18 types of molecules and ions, which are dissolved in water, the mathematical model considers 13 chemical protolytic reactions. The model is supplemented with the equation of hydrolysis of urea in so-

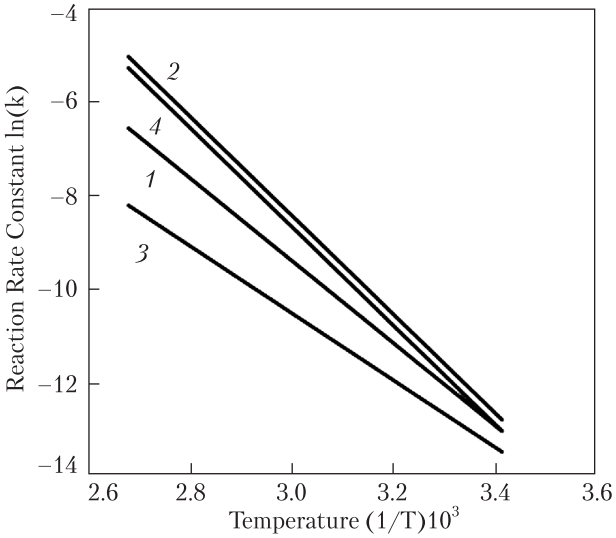

Fig. 1. Dependence of the reaction rate constant of urea hydrolysis according to the data: *1* — [8]; *2* — [9]; *3* — [10]; *4* — [11]

lution. The amount of decomposed urea during hydrolysis is determined by the reaction rate through the basic Arrhenius equation of chemical kinetics. The content of individual gases in the mixture is determined by inter phase mass transfer. The double film model is used to describe the process of mass transfer of gases through the surface at the gas-liquid boundary.

On the basis of literature data, it has been established that the process of removing sulfur dioxide from the outlet gases of thermal power plants with the use of an aqueous solution of urea is somewhat different from the process with ammonia. The difference is that urea is not a reactant as such but is a starting substance in a two-step process. At the first stage, urea is submitted to hydrolysis during which an intermediate product, ammonium carbamate ($NH_2CO_2NH_4$), is formed. In the second stage, $NH_2CO_2NH_4$ decomposes into ammonia and carbon dioxide. The urea hydrolysis reaction is exothermic, and the ammonium carbamate decomposition reaction is endothermic. As a result, the formation of NH_3 and CO_2 requires heating and quickly stops when the heat supply ends. The urea hydrolysis reaction is very fast, and the carbamate decomposition reaction, on the contrary, is slow. Thermodynamic analysis of the resulting reaction has shown that the process can proceed spontaneously (the change in Gibbs free energy in the reaction is less than zero because the energy of the starting substances exceeds the energy of the products) and the direct reaction prevails (the equilibrium constant is much larger than one). For the decomposition reaction, ammonium carbamate molecules must overcome an energy barrier, the activation energy (E_a). Therefore, the rate of the decomposition reaction has a finite value, in contrast to the protolytic reaction. The rate depends on the activation energy and temperature, according to the Arrhenius equation of chemical kinetics, and the concentration of urea in the solution.

To determine the rate of the hydrolysis reaction, special attention is paid to the activation energy. According to literature, the value of the activation energy ranges from 44 to 96 kJ/mol. As is known, E_a decreases in the presence of catalysts. For example, the metal body of the reactor can be a catalyst. Based on the Arrhenius equation, the activation energy does not depend on either temperature or pressure. The reaction rate constant (k) depends on the temperature. Increasing the pressure in the reactor allows increasing the temperature of the aqueous solution without evaporation. This increases the rate constant of the urea hydrolysis reaction.

In works on determining the kinetic parameters of hydrolysis without the use of catalysts, the results are somewhat different. The difference is influenced by the accuracy of the measurement of the process parameters, the conditions of the physical experiments, and possibly other factors. Figure 1 shows the dependence of the urea hydrolysis reaction rate constant according to data [8—11] in the temperature range of 20—100 °C. For clarity, the dependence is plotted in $\ln(k) - T^{-1}$ coordinates.

The mathematical model uses the kinetic parameters of the urea hydrolysis in an aqueous solution, which are given in [8]. As can be seen from

Fig. 1, they correspond approximately to the average reaction rate constant depending on the temperature, which is calculated according to the equation $k_A = A \cdot \exp(E_A/(R \cdot T))$, when the activation energy $E_A = 73.64$ kJ/mol and the preexponential factor $A = 2.89 \times 10^7$ s^{-1}.

NUMERICAL EXPERIMENTS

Calculations of the parameters of the process of chemical binding of sulfur dioxide in the aqueous solution of the bubbling reactor are performed at an initial SO_2 content of 758 ppm in the flue gases produced by burning anthracite coal. The experiments are carried out at an initial mass fraction of urea in an aqueous solution of 1%, 5%, and 10%. The temperature of the solution is kept constant during a certain time of reactor operation. The temperature values are taken from 20 °C to 90 °C with a discreteness of 10 °C, which makes it possible to carefully study the behavior of the process parameters in the reactor. The figures below show the change in the chemical binding efficiency of sulfur dioxide in the solution and the hydrogen value of the solution over the course of one hour of reactor operation.

Figure 2 shows the dependence of the binding process efficiency in a solution with an initial urea mass content of 1%. At a solution temperature of 20 °C, a sufficient amount of ammonia to bind 99.82% of sulfur dioxide accumulates in just 10 seconds. However, in 20 minutes of reactor operation, the efficiency of the process drops sharply to 6.21%, and after 60 minutes it reaches 2.41%. At 56 minutes there is an inflection point of the efficiency curve. The solution approaches the state of SO_2 saturation, as indicated by a decrease in the rate of absorption. The efficiency behavior is explained by the lack of ammonium (NH_4^+) in the solution, which reacts with sulfur dioxide. The fact is that due to the absorption and formation during hydrolysis of urea, carbon dioxide accumulates in the solution, which also reacts with ammonium. The worsening of the process conditions is also indicated by a sharp drop in the potential of hydrogen pH from 5.83 to 2.69, as can be seen from Fig. 3. A positive fact is the absence of ammonia in the waste gases, which is a very harmful air pollutant.

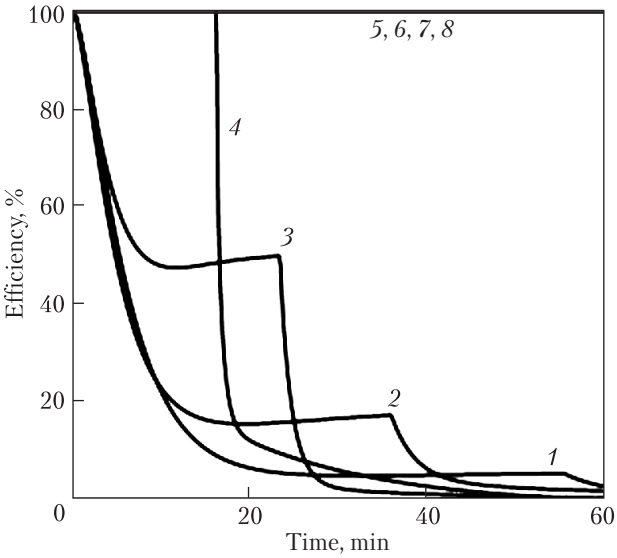

Fig. 2. Efficiency of the process at an initial mass fraction of urea of 1% in the solution with temperature: *1* — 20 °C; *2* — 30 °C; *3* — 40 °C; *4* — 50 °C; *5* — 60 °C; *6* — 70 °C; *7* — 80 °C; *8* — 90 °C

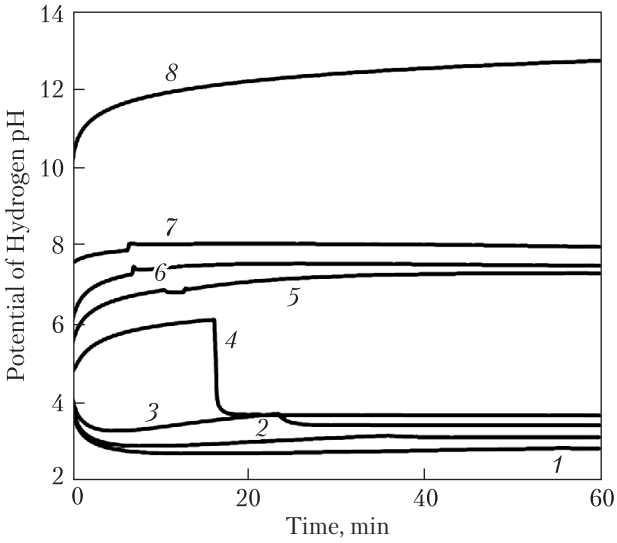

Fig. 3. The potential of hydrogen of the solution at an initial mass fraction of urea of 1% and temperature: *1* — 20 °C; *2* — 30 °C; *3* — 40 °C; *4* — 50 °C; *5* — 60 °C; *6* — 70 °C; *7* — 80 °C; *8* — 90 °C

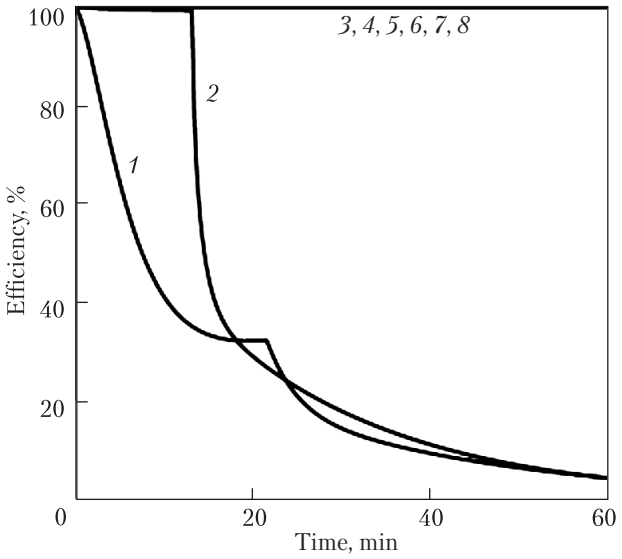

Fig. 4. Efficiency of the process at an initial mass fraction of urea of 5% in the solution with temperature: *1* — 20 °C; *2* — 30 °C; *3* — 40 °C; *4* — 50 °C; *5* — 60 °C; *6* — 70 °C; *7* — 80 °C; *8* — 90 °C

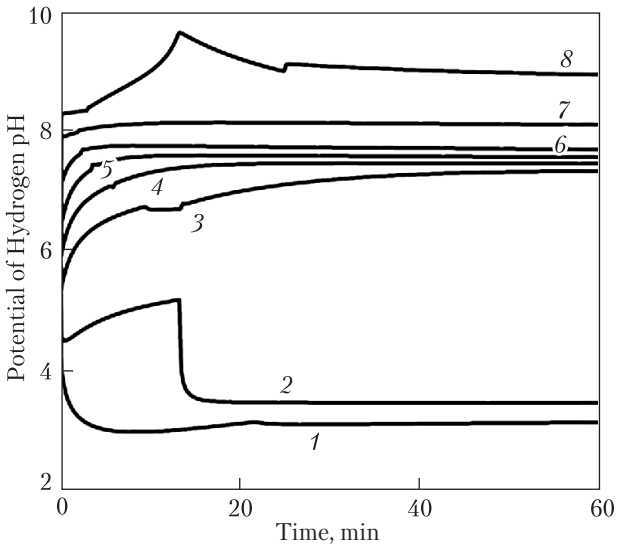

Fig. 5. The potential of hydrogen of the solution at an initial mass fraction of urea of 5% and temperature: *1* — 20 °C; *2* — 30 °C; *3* — 40 °C; *4* — 50 °C; *5* — 60 °C; *6* — 70 °C; *7* — 80 °C; *8* — 90 °C

The further temperature increase to 30 °C and 40 °C has a little effect on the nature of the process. The same inflection points are observed on the efficiency curves. They appear earlier in time due to a decrease in the solubility of gases in water, according to Henry's law, and with greater efficiency of the process. At a temperature of 50 °C, the efficiency behaves similarly, but for the first 16 minutes it remains at the level of 99.82—99.56%, and the value of pH remains close to 6. In addition, partial desorption of ammonia into the gaseous environment occurs with a maximum concentration of 2 mg/Nm^3 (Nm^3 is normal cubic meter). At a temperature of 60 °C and above, the efficiency of the process is about 100% for at least one hour. The flaw in the use of such operating modes of the reactor lies in the significant concentrations of ammonia in the gas mixture at the outlet, on average more than 90 mg/Nm^3.

As compared with the initial mass content of urea of 1% in the solution, increasing the content to 5% allows reducing the temperature at which the efficiency of the process remains at a high level for a long time. In Fig. 4, after 10 seconds from the start of reactor operation, at a solution temperature of 20 °C, the efficiency of the process reaches 99.87%. Then it drops sharply to 32.06%. The inflection point on the efficiency curve appears at 22nd minute due to a significant decrease in the absorption rate of sulfur dioxide, the efficiency drops to 30.72%. After 60 minutes of reactor operation, the efficiency becomes 4.39%. The potential of hydrogen in Fig. 5 from 5.83 is quickly falling to almost 3 and has been at the same level lately. There is no ammonia in the gases at the outlet of the reactor. In the mode of operation of the reactor at a temperature of 30 °C, the behavior of the process efficiency is like operation with a urea content of 1% and a temperature of 50 °C. The behavior differs in that the potential of hydrogen is lower, and there is no ammonia at the reactor outlet.

The reactor works with the efficiency of chemical binding of sulfur dioxide almost 100% at temperatures of 40 °C and above. The potential of hydrogen reaches values of 7—9. At a temperature of 40 °C, the average concentration of ammonia in the output gases reaches 22 mg/Nm^3, and at higher temperatures it exceeds 130 mg/Nm^3.

When the initial content of urea is doubled, the nature of the process is similar to the operating modes of the reactor with a content of 5% in the same temperature range (see Fig. 6 and 7). The hydrogen index is slightly higher at temperatures up to 40 °C, and ammonia in the output gases is no more than 2 mg/Nm^3. At a temperature of 40 °C and above, the pH value is in the range of 7...9. The concentration of ammonia at the outlet of the reactor exceeds 60 mg/Nm^3.

Additional calculations made it possible to determine the optimal temperature of the solution at a certain urea content. The temperature should be approximately 57 °C, at an initial urea content of 1%; 40 °C, at 5%; and 35 °C, at 10%. Under such conditions, the efficiency of the process of chemical binding of sulfur dioxide in the solution is close to 100%, and the concentration of ammonia in the outlet gases from the reactor does not exceed 30 mg/Nm^3.

Ammonia is a very dangerous chemical and therefore its production, storage, transportation, and use are associated with potential risks. The use of NH_3 requires compliance with strict safety and environmental regulations, which significantly limits the convenience of its use. In this regard, it is proposed to use urea as an alternative due to its non-toxicity, harmlessness, and impossibility of explosion. Urea is not an active substance in technologies for reducing emissions of sulfur dioxide and nitrogen oxides, but it is a source of obtaining ammonia in the processes of hydrolysis, thermolysis, or pyrolysis. The review of the literature has shown the possibility of effective use of urea to reduce emissions of SO_2 and NO_X with the waste gases of thermal power plants. For the purification of gases from harmful substances, researchers have proposed a variety of installations both in terms of technology and design.

In this research, there has been conducted a series of numerical experiments for a laboratory-scale bubbling-type chemical reactor that uses urea as a source of ammonia for the chemical binding of sulfur dioxide in solution. With this method, the rate of hydrolysis of urea and the rate of absorption of sulfur dioxide are the key factors affecting the efficiency of the reactor. According to Henry's law, the rate of absorption depends on

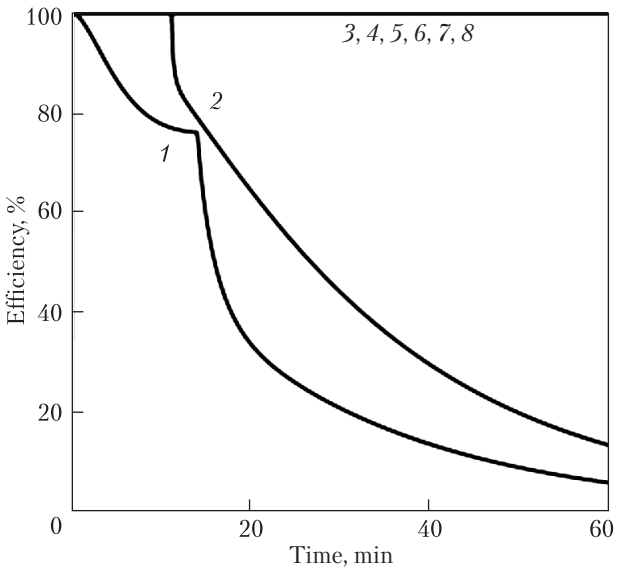

Fig. 6. Efficiency of the process at an initial mass fraction of urea of 10% in the solution with temperature: *1* — 20 °C; *2* — 30 °C; *3* — 40 °C; *4* — 50 °C; *5* — 60 °C; *6* — 70 °C; *7* — 80 °C; *8* — 90 °C

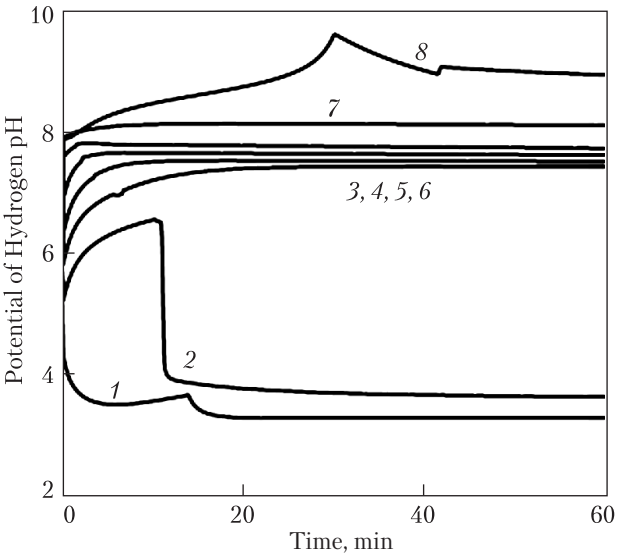

Fig. 7. The potential of hydrogen of the solution at an initial mass fraction of urea of 10% and temperature: *1* — 20 °C; *2* — 30 °C; *3* — 40 °C; *4* — 50 °C; *5* — 60 °C; *6* — 70 °C; *7* — 80 °C; *8* — 90 °C

the temperature of the medium, the partial pressure of the individual gas in the gas mixture, and its concentration in the liquid. In addition, the rate also depends on the specific surface area of the phase interface at the gas-liquid boundary of the bubble. According to chemical kinetics, the rate of hydrolysis depends on the temperature of the solution and the concentration of dissolved urea. The calculations have shown that increasing the temperature 5 times increases the rate of hydrolysis 650 times and increasing the initial urea content 5 times accelerates hydrolysis as little as 9 times. For effective removal of sulfur dioxide from the gas mixture, the rate of hydrolysis of urea must be matched with the rate of absorption of SO_2. During the hydrolysis of urea, ammonia and carbon dioxide that is chemically bound by the reagentappear in the solution. It has been found that, at a high concentration of dissolved ammonia, it is desorbed into a gaseous environment and worsens the environmental friendliness of the process. Thus, when determining the operating parameters of the reactor, it is necessary to consider the presence of CO_2 and NH_3 in the outlet gases.

The analysis of the results of modeling the process in the chemical reactor revealed that for the pair of parameters "temperature-urea content" there are values at which the binding efficiency reaches almost 100%, and the concentration of ammonia in the gas at the outlet of the reactor does not exceed 30 mg/Nm^3. Thus, the temperature should be approximately 57 °C, at a urea content of 1%, 40 °C, at 5%, and 35 °C, at 10%. It has been noticed that the duration of continuous operation of the reactor with a high efficiency depends primarily on the initial mass fraction of urea. When the "reserve" of urea decreases to a critical level, the efficiency of the process decreases, so it needs to be replenished. This can be done periodically or continuously, controlling the efficiency and concentration of ammonia. The potential of hydrogen pH can be used as a process indicator. Initially, the average pH of the solvent (water) is approximately 5.9. During reactor operation, it should be in the range from 6.5 to 7.5. A decrease in the indicator means a deterioration in the efficiency of the sulfur dioxide binding process in the solution. An increase in the indicator means that the efficiency remains high, but the concentration of ammonia in the gas at the outlet of the reactor is high. Thus, urea is spent inefficiently, which makes the process of cleaning flue gases from pollutants more expensive.

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ХІМІЧНЕ ЗВ'ЯЗУВАННЯ ДІОКСИДУ СІРКИ У БАРБОТАЖНОМУ РЕАКТОРІ З ВИКОРИСТАННЯМ СЕЧОВИНИ

Вступ. Інтеграція України у Європейський Союз вимагає суттєвого скорочення викидів забруднюючих речовин від промислових підприємств. Особливу увагу зосереджено на надходженні в атмосферу суспендованих твердих частинок, оксидів азоту, діоксиду вуглецю та діоксиду сірки від теплоенергетичних установок.

Проблематика. Діоксид сірки є одним з основних забруднювачів навколишнього середовища. Його потрапляння в атмосферне повітря призводить до утворення кислотних дощів, які негативно впливають на людей, ґрунт, рослини та наземні споруди.

Мета. Дослідити вплив початкового масового вмісту сечовини у водному розчині та його температури на ефективність процесу хімічного зв'язування діоксиду сірки.

Матеріали й методи. Розглянуто низку статей, присвячених видаленню оксидів сірки з відхідних газів теплоенергетичних установок різними методами та технологіями з використанням сечовини. Дослідження проведено на математичній моделі хімічного реактора барботажного типу.

Результати. Проведено серію числових експериментів на хімічному реакторі, де сечовина використовується як джерело амоніаку для зв'язування діоксиду сірки у розчині. Розрахунки дозволили визначити оптимальну температуру розчину при певному вмісті сечовини. При початковому вмісті сечовини 1% температура має сягати приблизно 57 °С, при 5% — 40 °С, а при 10% — 35 °С. За таких умов ефективність процесу хімічного зв'язування діоксиду сірки у розчині близька до 100%.

Висновки. Аналіз результатів математичного моделювання процесів у хімічному реакторі виявив, що для пари параметрів «температура—вміст сечовини» існують значення, за яких ефективність процесу зв'язування сягає майже 100%. Для контролю ефективності доцільно використовувати водневий показник розчину на рівні 7 ± 0.5. Нижчі значення показника вказують на падіння ефективності процесу, а вищі — на зростання концентрації амоніаку у оброблених газах на виході з реактора.

Ключові слова: діоксид сірки, барботажний хімічний реактор, розчин сечовини.