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The formation of acid rain in the atmosphere, adjacent to the TTP with the joint-condensing of sulfur dioxide and water vapor

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Abstract. Presents the results of mathematical simulation of the condensation process of sulphur dioxide and water vapor on the condensation nuclei surface under the action of natural factors. Numerical investigations were carried out for the summer at a moderate speed of the wind. The influence of the parameter of condensation on the speed of the process of sulfuric acid drops formation in the air space was analyzed. Time ranges, sufficient for the formation of the acid rain sedimentation in the atmosphere, adjacent to the areas of thermal power station work were established. It is shown that the speed of air masses movement effects on the process of acid anthropogenic admixtures dispersion in the atmosphere. Approbation of the obtained results was carried out by checking the difference scheme conservative and solution of test problems.

A significant contribution to the formation of sulfuric acid in the boundary layer of the atmosphere is contributed by thermal power plants [1]. When burning the natural fuel of power plants in the environment there are different pollutants [2]. Under the influence of natural factors the combustion products of coals may condense on the water droplets presenting in the atmosphere and reach the Earth's surface [3]. Most of them refers to the number of toxic, and even at relatively low concentrations cause the adverse effects on nature and human life [1, 2]. Table 1 shows the values of acceptable amounts of some contaminants contained in the flue gas in power station.

In this paper we study the processes of condensation of sulphur trioxide SO_3 and water vapor H_2O. Sulphur dioxide is formed in flues boilers of power plants by partial oxidation of SO_2 (up to 5% of the total SO_2) from the combustion of high-sulphur fuels, and belongs to a class of mild-hazard products [1, 2].

Earlier in [5–7] the process of acid rain formation in the airspace adjacent to the power plants, at different air temperatures and wind speeds was investigated. It was intended that the formation of sulfuric acid drops occurs only due to condensation of sulfuric anhydride on the condensation nuclei surface.

In real practice the atmosphere always contains water vapors of natural origin [7]. In addition, a significant increase of the water vapor concentration in the air is possible in areas adjacent to the power plants by emissions of H_2O due to the work of the heat engineering equipment of the station [1]. The analysis of processes of sulfuric acid drops formation in the air upon jointly proceeding processes of condensation of SO_3 and H_2O vapors on the condensation nuclei surface is of interest.

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Table 1. The permissible concentrations of contaminants [4].

Country	SO_2	NOx	hard particles
	mg/m^3		
Russia	2000 . . . 3400	320 . . . 700	100 . . . 500
Japan	550	205 . . . 980	50 . . . 300
USA	740 . . . 1480	605 . . . 980	40 . . . 125
France	400 . . . 2000	650 . . . 1300	50 . . . 100
Germany		200 . . . 1500	50 . . . 150

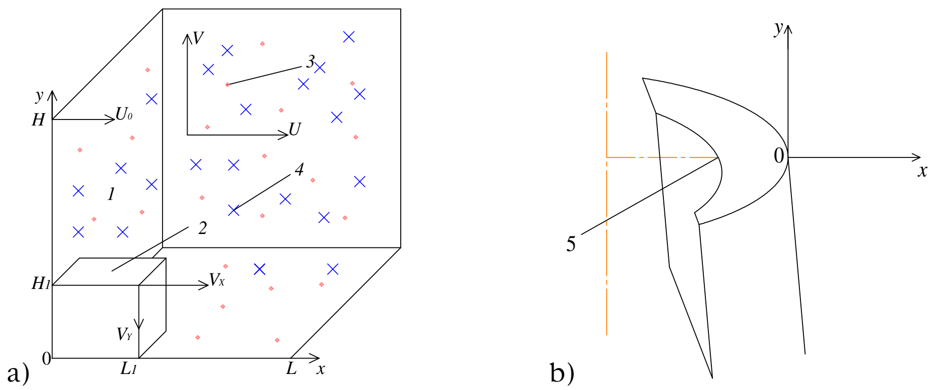

Figure 1. The scope of the problem solution in the initial moment: 1 – gas phase; 2 – core-condensing; 3 – sulphurous anhydride; 4 – water vapor; 5 – the mouth of the chimney power plants; U, V – velocity of motion of the gas environment in the direction of the X and Y axes, respectively; V_X, V_Y – particle velocity in the direction of the X and Y axes.

The purpose of this paper is the numerical analysis of the influence of humidity on the sulphuric acid drops formation in the atmosphere of the Land adjacent to the thermal power plants. The study of the joint condensation process of sulphur dioxide and water vapor in the summer period (air temperature 294 K) at wind speed of 5 m/s was conducted. Three categories of condensation nuclei were observed on the surface of which the drop that can reach the Earth's surface in the process of sedimentation is formed.

At statement of a problem the area for the airspace near the emission source of water vapor and sulfur anhydride (the anthropogenic component of products of combustion of coals) in atmosphere [1, 2] has been considered.

The rectangular shape of this region (Fig. 1a) was adopted. Figure 1 contains a single fragment of the solving problems domain, characteristic sizes of which are much larger than the characteristic sizes of condensation nuclei [5–7]. The main mechanisms of transport of anthropogenic gaseous components in practice are the convection and diffusion. When formulation of the problem those two factors were considered. The point corresponding to the interface of the mouth of the emission source (Fig. 1b) [5] was adopted as the central point of coordinates.

According to [1, 2] it was assumed that the formation of sulfuric acid drops is the result of condensation of SO_3 and water vapor at the surface of the "condensation nuclei" – microscopic drops of water. The speed of the thermodynamic process significantly depends on the temperature [8]. Accordingly the reliability of the simulation results of condensation process is determined by the accuracy of the condensation surface temperature determination.

It is known that the height of power plant's chimneys varies from 50 to 400 m [9]. When simulation of the process the fairly typical pipe height of 150 meters was considered.

Also it is known [10], that liquid droplets in flight, as a rule, are deformed. But taking this fact into account when solving the problem leads to a significant complication, as a mathematical model and calculation algorithm. Previously it was shown [11] that the shape of the drop is negligible effects on the results of mathematical simulation of the evaporation process while moving through the high-temperature gases.

The mechanism of the sulfuric acid formation [1, 2] is based on cooperation, where sulphurous anhydride SO_3 is absorbed by water vapor.

$$SO_3 + H_2O \to H_2SO_4 + Q. \tag{1}$$

The process of transfer of energy, momentum and mass in these circumstances is described by the system of non-stationary partial differential equations [12, 13], similar to [5–7]. It is considered that the temperature and concentration on the left border of the solution domain (chimney of TPP) do not depend on time. Unsteady two-dimensional equations of mixed convection in the approximation of the Boussinesq approximation [14] are used to model the changes in the main sought-for functions. Calculation of the condensation rate was conducted using the formula [8].

The boundary conditions were formed on borders of injection of sulphurous anhydride and water vapor:

$$X = L_1,\ 0 \le Y \le H_1: \begin{cases} \dfrac{\partial \Theta_1}{\partial X} = \dfrac{\lambda_2}{\lambda_1}\dfrac{\partial \Theta_2}{\partial X} + \dfrac{Q \cdot W_3^K \cdot L_1^2}{\Delta T \cdot \lambda_1} + \dfrac{Q \cdot W_4^K \cdot L_1^2}{\Delta T \cdot \lambda_1}, \\ \Theta_1 = \Theta_2,\ \dfrac{\partial C_3}{\partial X} = \dfrac{W_3^K \cdot L_1^2}{D \cdot \rho} + \dfrac{W_4^K \cdot L_1^2}{D \cdot \rho},\ \psi = \Omega = 0; \end{cases}$$

$$Y = H_1, 0 \le X \le L_1: \begin{cases} \dfrac{\partial \Theta_1}{\partial X} = \dfrac{\lambda_2}{\lambda_1}\dfrac{\partial \Theta_2}{\partial X} + \dfrac{Q \cdot W_3^K \cdot L_1^2}{\Delta T \cdot \lambda_1} + \dfrac{Q \cdot W_4^? \cdot L_1^2}{\Delta T \cdot \lambda_1}, \\ \Theta_1 = \Theta_2,\ \dfrac{\partial C_3}{\partial X} = \dfrac{W_3^K \cdot L_1^2}{D \cdot \rho} + \dfrac{W_4^K \cdot L_1^2}{D \cdot \rho}, \psi = \Omega = 0. \end{cases}$$

When X, Y – coordinates Cartesian coordinates $\Theta_{1,2}$ – temperature; ψ – a function of the current; Ω – whirlwind speed; C_3 – the concentration of sulfuric anhydride; Q – thermal effect of reaction, Dj/kg; $W^{K}_{3,4}$ – mass velocity of condensation, kg/(m^3 · s); L_1 – geometric size of particles (condensation nuclei), m; ρ – density, kg/m^3; D – coefficient of binary diffusion m^2/s; $\lambda_{1,2}$ – heat conductivity, Vt/(m· К); ΔT – temperature difference, К.

The boundary conditions on the other borders are identical [5–7]. The following assumptions were when setting objectives:

1. Evaporation of drops in the process of movement was not taken into account;
2. The influence of solar radiation was not taken into account;
3. The core of condensation has the shape of a cube.

The problem is solved by the finite difference method [15]. The solution of difference analogues of the differential equations and boundary conditions conducted by the method of variable directions and locally one-dimensional method [15].

To solve the formulated boundary problem it was used the algorithm [16, 17], developed for the decision of tasks of conjugate heat transfer in areas with a local energy source. Assessment of reliability of the obtained results was performed by verification of difference scheme conservative similar to [18].

Figure 2 shows the changes of the sulfuric acid drop sizes, depending on the time at various initial sizes of condensation nuclei.

The results (Fig. 2) of numerical investigations show that it is possible to form the sedimentary acid precipitation already through 1800 s since the beginning of the process on the condensation nuclei

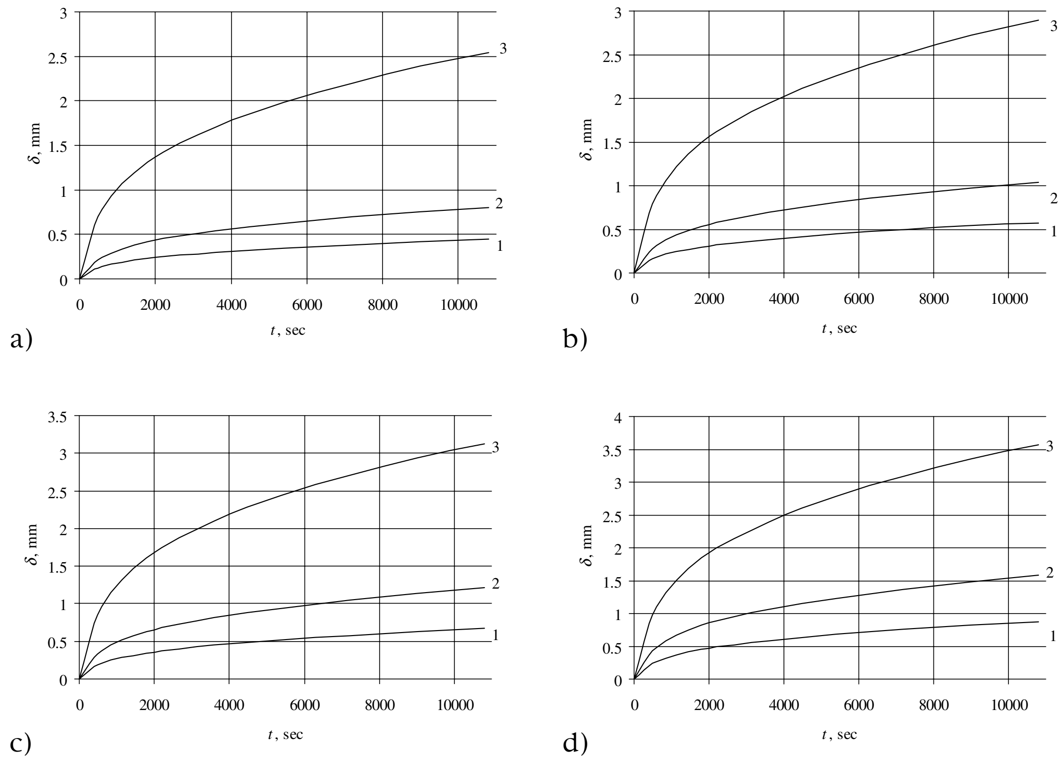

Figure 2. Changes of the sulfuric acid drops size: a) $\beta = 0,05$; b) $\beta = 0,1$; c) $\beta = 0,2$; d) $\beta = 0,4$ 1 – $\delta_0 = 0,8 \cdot 10^{-6}$ m; 2 – $\delta_0 = 1,0 \cdot 10^{-6}$ m; 3 – $\delta_0 = 5,0 \cdot 10^{-6}$ m; (β – the condensate coefficient, δ_0– the initial size of the condensation nuclei).

surface $\delta_0 = 5,0 \cdot 10^{-6}$ m. Further course of the simultaneous condensation process of sulphur dioxide and water vapor promotes the formation of sulfuric acid drops with sizes to $2,5 \cdot 10^{-3}$ m during the analyzed time interval.

It was established that formation of acid precipitation occurs on the condensation nuclei surface at $\delta_0 = 1,0 \cdot 10^{-6}$ m during 9000 and 7200 s, respectively, in the range of changes of the condensation coefficient from 0.1 to 0.2. For the considered period of time, the formation of sulfuric acid drops in the airspace adjacent to the power plants, with size from $1,0 \cdot 10^{-3}$ m to $1,2 \cdot 10^{-3}$ m is possible. Numerical evaluation of the particle border growth on the condensation nuclei surface at $\delta_0 = 5,0 \cdot 10^{-6}$ m illustrates the possibility of the sulphuric acid sedimentary drops formation during the 1800 s and 600 s since the beginning of the simultaneous introduction process of sulphur dioxide and water vapor at the surface of the "embryo".

The formation of sulfuric acid drops in the atmosphere of the Earth occurs more intensive on the condensation nuclei surface with initial size from $1,0 \cdot 10^{-6}$ m to $5,0 \cdot 10^{-6}$ m as the researches have shown.

Figure 3 shows the change of the sulfuric acid drops size in time for different values of the condensation coefficient. The presented dependences illustrate the intensive formation of sulfuric acid drops in the airspace adjacent to the power plants for a period of time up to 2000 s since the beginning of the process. The further process of particle border growth in the considered time interval, is slowing down. The reason is that the flue "torch" temperature is reduced almost to the ambient temperature during the period from 2000 s to 10 800 s.

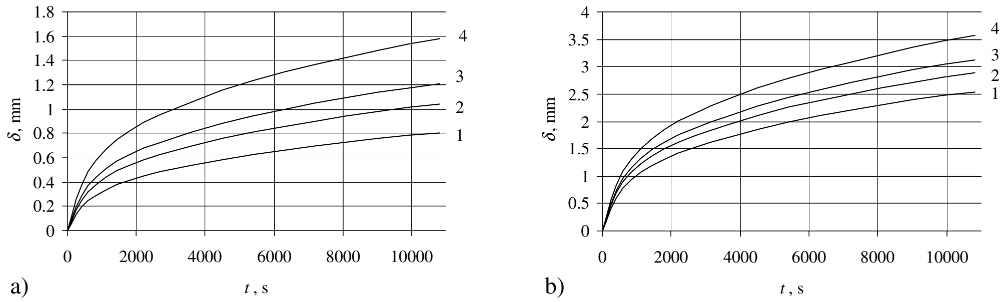

Figure 3. A formation of sulfuric acid drops on the condensation nuclei surface a) $\delta_0 = 1,0 \cdot 10^{-6}$ m; b) $\delta_0 = 5,0 \cdot 10^{-6}$ m; 1 – $\beta = 0,05$; 2 – $\beta = 0,1$; 3 – β =0,2; 4 – $\beta = 0,4$.

Table 2. Sizes of sulfuric acid drops with different mechanisms of acid precipitation formation.

t, s	Condensation of SO_3		Condensation of SO_3 and H_2O	
0	$\delta_0 = 0,001 \cdot 10^6, m$	$\delta_0 = 0,005 \cdot 10^6, m$	$\delta_0 = 0,001 \cdot 10^6, m$	$\delta_0 = 0,005 \cdot 10^6, m$
600	0,340	0,432	0,372	**0,960**
1800	0,533	0,633	0,626	**1,616**
3600	0,634	0,754	**0,812**	**2,096**
5400	0,720	0,855	**0,944**	**2,436**
7200	0,814	**0,967**	**1,048**	**2,706**
9000	**0,880**	**1,045**	**1,139**	**2,940**
10 800	**0,937**	**1,113**	**1,212**	**3,127**

The conducted numerical analysis of the process of sulfuric acid drops formation in the airspace adjacent to the power plants, on the condensation nuclei surface of different sizes and different values of the condensation coefficient, suggests that the simultaneous input of sulphur dioxide and water vapor at the particle surface contributes the most intensive formation of sedimentation sulfuric acid drops.

As the research showed [5–7], the formation of acid precipitation, capable to reach the Earth's surface at the expense of sedimentation process is possible at the condensation of sulfuric anhydride. Table 2 shows comparative results of the study of the acid rain formation process in the Earth's atmosphere on the condensation nuclei surface in the following cases:

1) the process of acid rain formation occurs when sulfuric anhydride condensation only;
2) formation of acid drops is performed by means of co-condensation of sulphur dioxide vapor and water vapor.

The results of simulation of the acid generation formation process on the condensation nuclei surface from $1,0 \cdot 10^{-6}$ m to $5,0 \cdot 10^{-6}$ m at a wind speed of 5 m/sec, and temperatures of the environment 294 K are presented To compare. At that the value of the condensation coefficient of sulphur dioxide and water vapor is 0.2.

The drops dimensions of acid precipitation presented in Table 2 allow drawing the conclusion that the joint condensation of sulphur dioxide vapors and water vapor significantly accelerates the process of the sedimentation precipitation formation. The particles ($\delta_0 = 1,0 \cdot 10^{-6}$ m) with sizes in 1,3 times more than at the sulfuric anhydride condensation only are formed during the considered time interval. Growth of sulfuric acid drop boundary on the surface of the embryo with size of $5,0 \cdot 10^{-6}$ m also significantly accelerates the formation of acid precipitation. The particles with a characteristic size up to 1 mm are formed already within 600 s, since the beginning of the process of condensation. The sulfuric acid drops with the diameter in 2,8 times more than at the sulfuric anhydride condensation only are formed during the concerned time interval.

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