

## Research of the Chlorine Sorption Processes when its Deposition by Water Aerosol

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**Abstract.** Modified stepwise model of gas sorption process with finely dispersed water flow. The sorption model allows forecasting the intensity of hazardous gases deposition with adequate for the emergency recovery conditions accuracy using minimum input parameters. This allows using the sorption model under the conditions of emergency and increasing the forecasting promptness. Use of chemical neutralizer is proposed to increase the effectiveness of chlorine hazardous gas deposition. Use of sodium hydroxide is proposed as the chlorine chemical neutralizer, which is easily dissolved in water, non-toxic and easy to store. An experimental laboratory facility was developed and created with the purpose of experimental verification of the sorption processes, which allows researching the sorption processes by liquid aerosols within a wide range of dispersity. Adequacy of the existing models as well as the modified one was verified experimentally. The verification results showed a 5% indicator of the theoretical and experimental results compliance.

### Introduction

Forecasting the emergency situation development is not a necessary stage for taking a certain managerial decision on accident elimination [1]. The forecasting process is especially essential in case of an emergency with gaseous hazardous substances emission. The most effective method for hazards reducing upon these kinds of emergencies is hazardous chemical substance gas-air cloud deposition with finely sprayed water stream [2]. Finely dispersed water streams are created by rescue teams on the way of hazardous gas cloud spreading. Due to a wide spread of wastewater treatment facilities where chlorine is used, emergencies with gaseous chlorine emission have gained widespread occurrence.

### Problem Formulation

To provide for sufficient accuracy in calculating the sizes of chemical contamination areas, one has to take into account a significant number of factors, which can conventionally be divided into two units – meteorological conditions, emission parameters and hazardous gas deposition parameters. The meteorological conditions include wind direction and velocity, air temperature and humidity, atmospheric pressure. The emission parameters include the type of chemical substance, its temperature, density and storage pressure, emission intensity. Under the conditions of rescue teams activities on a zone of emission localization, another unit is added to these factors, which includes the supply intensity of liquid for deposition, deposition area, the ability of the liquid supplied to absorb or chemically react with a hazardous chemical substance, etc. [3]. All of this significantly

complicates the work of the emergency recovery command centre work on forecasting the extent of damage, which can lead to taking belated and wrong managerial decisions.

### Analysis of Publications

The gas absorption kinetics with liquid aerosols is quite complex and multifactorial. At present, there are two drastically different approaches to solving this problem. These approaches differ in the solution accuracy level, amount of the required computing time spent, amount of input data and need for preliminary experimental studies.

To increase the accuracy of the sorption process mathematical description and universalism of calculation methods, simulation models have recently become widely spread.

Herewith, there are two different approaches to the models construction: kinetic multilayer model for gas-particle (KM-GAP) [4] and molecular dynamics (MD) simulations [5]. The MD model runs on GROMACS special computer calculation platform with additional TIP4P-Ew add-in for the liquid aerosol adsorption calculation. A comparative analysis of such models was conducted in the paper [6] and a high degree of the calculation results convergence was obtained. Although for the most mathematical models in KM-GAP and MD simulation complexes some admissions that simplify the calculation are adopted, these models are currently the most accurate methods for numeric calculation of the gas absorption rate by liquid. It should be considered that these calculations are quite laborious and need a significant amount of computing time, special software and a considerable amount of input data that cannot be always clearly determined and taken into account.

Modelling the gas sorption processes by liquid aerosols is a quite complex and multifactorial task. However, such calculations are quite laborious and require a significant amount of computing time, special software and considerable input data amount. These conditions are difficult to ensure under the conditions of emergency response;

Schwartz S. [7] proposed to consider the sorption process as individual physical and chemical stages. Nevertheless, mathematical derivations as per the proposed model are made with some simplification: e.g., the aerosol flow intensity effect on the sorption kinetics is not taken into account and no sufficient attention is paid to determining the accommodation coefficient, which, eventually, significantly narrows the possibilities of using this model.

### Aim of Paper

The aim of the work is development of models and methods for prediction the sorption rate of hazardous gases such as chlorine by finely dispersed water aerosol.

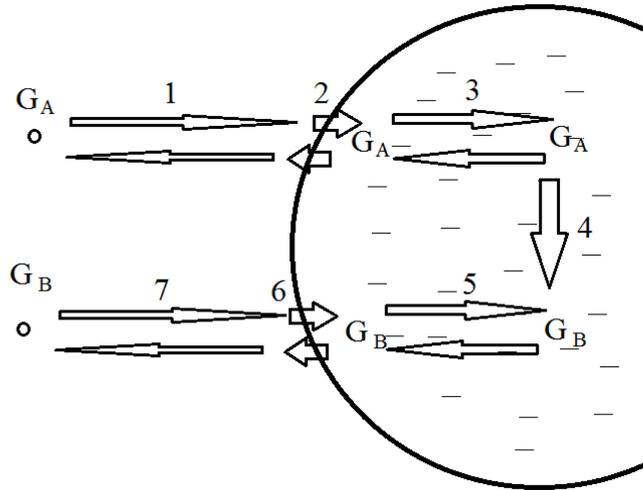
### Materials and Methods

According to the model proposed [7], the process of contaminant atmospheric gases washing out by water droplets can be divided into several individual stages. Schematic representation of these stages is shown in Fig. 1.

Content of stages:

1. Gas molecules ( $G_A$ ) transporting to the droplet surface due to diffusion in the gaseous phase;
2. Gas molecules ( $G_A$ ) absorption by droplet surface and balance achieving in the local area of the discontinuity surface due to gas desorption;
3. Absorbed gas molecules ( $G_A$ ) transporting to the droplet volume due to diffusion in liquid;
4. Chemical reactions of absorbed gas ( $G_A$ ) and water in the droplet volume with reaction products ( $G_B$ ) formation;
5. Reaction products ( $G_B$ ) transporting to the droplet volume;
6. Balance achieving in the droplet surface local volume B due to chemical reaction products adsorption-desorption;

7. Products molecules ( $G_B$ ) transporting from the droplet surface to the gas phase due to diffusion.



**Fig. 1.** Stages diagram of chemically hazardous gases absorption by atmospheric aerosols droplets

As is commonly known, gas physical and chemical properties affect the absorption process. With this regard, Henry constants, diffusion coefficient in the air and possible chemical reactions in water for the main hazardous gases penetrating the atmosphere in an emergency are considered in Table 1.

**Table 1.** Some of the contaminant gases physical and chemical properties affecting the absorption process ( $T=273K$ ,  $P=10^5$  Pa)

Gas	$H \cdot 10^4$ [8]*, ( $\text{mole} \cdot \text{m}^{-3} \cdot \text{Pa}^{-1}$ )	$D_g \cdot 10^4$ [8], ( $\text{m}^2 \cdot \text{c}^{-1}$ )	Gas-water reaction
$\text{NO}_2$	1.2	0.119	$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{NO}_3^- + \text{HNO}_2$
$\text{SO}_2$	150	0.122	$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ , $\text{H}_2\text{SO}_3 \rightleftharpoons \text{HSO}_3^- + \text{H}^+$
$\text{NH}_3$	2700	0.198	$\text{NH}_3 + n \cdot \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 \cdot n\text{H}_2\text{O}$
$\text{HCN}$	750	0.136	$\text{HCN} + 2\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{HCOO}^-$
$\text{COCl}_2$	1100	0.121	$\text{COCl}_2 + n \cdot \text{H}_2\text{O} \rightleftharpoons \text{COCl}_2 \cdot n\text{H}_2\text{O}$
$\text{HCl}$	1900	0.130	$\text{HCl} + n \cdot \text{H}_2\text{O} \rightleftharpoons \text{HCl} \cdot n\text{H}_2\text{O}$
$\text{H}_2\text{S}$	10	0.127	$\text{H}_2\text{S} \xrightarrow{\text{H}_2\text{O}} \text{HS}^- + \text{H}^+$
$\text{Cl}_2$	9.3	0.124	$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HClO}$

\* - data that slightly vary from source to source depending on the method for determination

As can be seen from Table 1, diffusion coefficients in the air for various gases slightly differ from each other, while the Henry constant of some gases differs by two or three orders, which, definitely, will affect the absorption kinetics. For those gases that dissociate in water into ions, the diffusion coefficient of the dissociation products in water shall be a bit higher, since it is mainly determined as per the products of reaction. For  $\text{NH}_3$ ,  $\text{COCl}_2$ ,  $\text{HCl}$  hydrated molecules, the coefficients of diffusion in water will be lower because of the increase in the molecular sizes and mass due to the hydration shell. Later on, these peculiarities will be taken into account when calculating the intensity of hazardous gases washing out.

Due to the gas desorption and the possibility of balance establishment, the complete washing out is not possible, so the limit purification degree 0.9 shall be set. Total limit values of chemically

hazardous gases significantly differ (Table 2), so for analysis, let us set the initial concentration of  $C_g^0 = 1 \text{ mole} \cdot \text{m}^{-3}$

**Table 2.** TLV<sub>ave d</sub> of some hazardous gases penetrating the atmospheric air in case of emergency [9]

Gas	NO <sub>2</sub>	SO <sub>2</sub>	HCl	HCN
$C_g^0, \text{mole} \cdot \text{m}^{-3}$	0.83	0.78	0.25	0.37
Gas	COCl <sub>2</sub>	H <sub>2</sub> S	Cl <sub>2</sub>	NH <sub>3</sub>
$C_g^0, \text{mole} \cdot \text{m}^{-3}$	0.033	0.24	0.65	2.35

## Research Results

The rate of chemically hazardous gas absorption by atmospheric aerosol is determined by the difference in rates of the process of desorption  $V_{\text{des}}$  and absorption  $V_{\text{abs}}$ :

$$\frac{dC_g}{d\tau} = V_{\text{des}} - V_{\text{abs}}, \quad (1)$$

where  $C_g$  – gas concentration in the atmosphere;  $\tau$  – time.

According to the stages 1–7, the mathematical expression for the adsorption rate is as follows:

$$V_{\text{abs}} = V_{\text{col}} \cdot \alpha \cdot K_{\text{dif}} \text{ or } V_{\text{abs}} = V_{\text{col}} \cdot \alpha \cdot K_r, \quad (2)$$

where  $V_{\text{col}}$  – rate of gas molecules interaction with water droplets;  $\alpha$  – coefficient determining the probability of gas molecules absorption by droplet surface;  $K_{\text{dif}}$  – coefficient determining the rate of gas diffusion inside droplet. When absorbed gas chemical reaction in the droplet volume, the coefficient  $K_{\text{dif}}$  is substituted with  $K_r$  – coefficient that takes into account gas molecules diffusion inside droplet as well as the gas-liquid chemical reaction rate.

To solve equations (1), let us consider the peculiarities of each stage below.

Quantitatively, the gas molecules collision with a droplet surface is determined by the diffusion coefficient in the air of certain gas and the probability of gas molecules collision with droplet surface. These parameters are easily determined based on the molecular-kinetic theory provisions, yet such a parameter as aerosol droplet size introduces here own peculiarities. In the normal atmosphere, water in the free molecular state is virtually absent. Free water molecules interact with either other atmospheric components, depending on their chemical nature, or combine into water clusters that can be considered as a high-dispersed aerosol with particles size up to 1000 Å. The Knudsen number  $Kn > 1$  corresponds with these particles in the atmosphere. These particles are characterized by Brownian motion and virtual absence of the sedimentation process. Therefore, the gases with water clusters interaction can formally be considered as gas molecules interaction with each other. The lower troposphere cloudless zones correspond with these conditions.

To determine the toxic gases rate of washing out of the atmosphere we need to compute the probability or frequency of gases molecules collision with water clusters. To do this one can use the Maxwell standard distribution:

$$dP(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2kT}} dv, \quad (3)$$

where  $P$  – gas molecules collision with water clusters probability;  $m$  – molecules mass;  $k$  – Boltzmann constant;  $T$  – gas temperature;  $v$  – gas molecules average velocity.

However, M. Smoluchowski and A. Einstein proposed a simpler model of two gases molecules frequency of collision, where the collision frequency coefficient ( $k_{\text{col}}$ ) is determined using diffusion coefficients:

$$k_{\text{col}}^k = 4\pi \cdot (R_g + R_k) \cdot (D_g + D_k), \quad (4)$$

where  $R_g$ ,  $D_g$  – molecular size and diffusion coefficient of chemically hazardous gas in the air;  $R_k$ ,  $D_k$  – size and diffusion coefficient of water cluster, respectively.  $R \approx \lambda$  is usually applied for molecules, where  $\lambda$  – free-path length of molecules.

Diffusion coefficients of gas molecules or water clusters ( $D_g$ ,  $D_k$ ) are determined from the general ratio:

$$D = D_0 \cdot \frac{P_0}{P} \cdot \left( \frac{T}{T_0} \right)^{1,75}, \quad (5)$$

where  $D_0$  – diffusion coefficient under the standard conditions ( $P_0 = 10^5$  Pa;  $T_0 = 273$  K);  $P$ ,  $T$  – respectively, gas or water (cluster) pressure and temperature at which the diffusion coefficient is determined.

In case if the diffusion coefficient is unknown for a particular gas under the standard conditions, Fuller, Shetler and Giddings semi-empirical equation can be used [10]:

$$D = \frac{0,986 \cdot 10^{-8} \cdot T^{1,75}}{P \cdot \left( v_{\text{gk}}^{1/3} + v_{\text{a}}^{1/3} \right)^2} \sqrt{\frac{1}{M_{\text{gk}}} + \frac{1}{M_{\text{a}}}}, \quad (6)$$

where  $v_{\text{gk}}$ ,  $M_{\text{gk}}$  – molar volume and molar mass of chemically hazardous gas or cluster of water;  $v_{\text{a}}$ ,  $M_{\text{a}}$  – air molar volume and molar mass.

At droplet sizes ( $R_{\text{drop}}$ ) greater than  $1 \mu\text{m}$   $\text{Kn} \rightarrow 0$ . With these sizes, collision with gas molecules does not significantly affect the droplets motion and they hover under the action of air flows. In this case, the gas-aerosol interaction can be considered as gas interaction with a stationary water droplet surface. These conditions are met by  $R_g \ll R_{\text{drop}}$  and  $D_g \gg D_{\text{drop}}$ , accordingly, the expression (4) takes the form:

$$k_{\text{col}}^{\text{drop}} = 4\pi \cdot R_{\text{drop}} \cdot D_g. \quad (7)$$

This ratio is valid for large drops of dispersed aerosol.

Within the droplet sizes range of  $0.1\text{--}1 \mu\text{m}$ , the transition process is implemented, herewith, the distribution function can be computed by solving the Boltzmann kinetic equation by adopting some simplification. The paper authors [11] proposed using for these modes the following expressions:

$$k_{\text{col}}^m = \frac{4\pi \cdot D_g \cdot (R_g + R_k)}{1 + \lambda \cdot \text{Kn}}, \quad \text{де} \quad \lambda = \frac{1,33 + 0,71 / \text{Kn}}{1 + \text{Kn}}. \quad (8)$$

Using the above coefficients  $k_{\text{col}}$  one can determine the collision frequency of the gas molecules with aerosol droplets under certain conditions:

$$V_{\text{col}} = k_{\text{col}} \cdot C_{\text{drop}} \cdot C_g, \quad (9)$$

where  $C_{\text{drop}}$  – water droplets concentration in the air.

The water droplets concentration in a unit volume of the atmosphere can be assumed as a constant ( $C_{\text{drop}} = \text{const}$ ) provided that the water droplets only absorb gas and do not coagulate with each other. The coagulation complete absence conditions in the real atmosphere are usually impossible, yet a quasi-constant volume-averaged concentration of water clusters is fully compliant with an atmosphere with constant meteorological conditions or, with a constant intensity water stream.

However, the aerosol in the atmosphere is polydispersed, so the droplet size distribution function  $f(R_{\text{drop}})$  shall be introduced to the equation (9).

Earlier, we considered the gas molecules with atmospheric aerosol droplets surface interaction frequency regularities. Yet gas molecules that collide with droplet penetrate the volume through the surface layer  $\Delta x \rightarrow 0$  thick with the  $\alpha$  probability (accommodation coefficient). Accordingly, gas molecules adsorption rate by the surface  $V_{\text{ads}}$  will be defined as:

$$V_{\text{ads}} = V_{\text{col}} \cdot \alpha . \quad (10)$$

Since Henry's law is valid for the dissolution process under the atmospheric conditions, the balance establishment rate in the droplet surface layer with (10) is defined as

$$V_{\text{ads}}^{\text{H}} = \frac{V_{\text{col}} \cdot \alpha}{4\pi \cdot H \cdot R_0 \cdot T} , \quad (11)$$

where  $H$  – Henry's constant;  $R_0$  – universal gas constant. The  $\alpha$  coefficient in the paper [11] is proposed to be selected out of the experimental data, herewith, the specified range  $\alpha \approx 10^{-2}-1$ , which narrows down the model scope of application and decreases its adequacy. Therefore, we attempted to calculate  $\alpha$ .

Earlier, it was noted that many authors when the desorption processes consideration paid no enough attention to determining the  $\alpha$  accommodation coefficient. Knudsen was the first who considered the gas molecules interaction process with the surface as well as determined the energy exchange effectiveness measure on the "gas-surface" distribution boundary by the  $\alpha$  accommodation coefficient. The accommodation coefficient shows a proportion of the gas molecules, absorbed by the droplet surface, of the total number of molecules that were in contact with the droplet surface.

The accommodation coefficient numerical calculation using the general molecular laws and Maxwell's equation is quite a difficult task due to the uncertainty of the gas molecules interaction with the droplet surface molecules. In addition, these calculations are carried out without account for the physical and chemical properties of the droplet surface the gas-liquid chemical interaction regularities. Therefore, currently, there are two main approaches to solving the accommodation coefficients determination problem exist.

The first one lies in the experimental determination of  $\alpha$  [12]. This method takes into account all kinds of possible physical and chemical interactions, yet it allows determining accommodation coefficient only for particular gas contact with particular surface under certain conditions, in addition, the determination results of  $\alpha$  slightly differ in various researchers due to variance in the experiment conduction methodologies.

Another approach for  $\alpha$  determining is based on the considered above adsorption process programming as well as in literature sources [13, 14]. Although this calculation method for  $\alpha$  is the most accurate, it has a number of aforementioned disadvantages for solving the problem of a prompt atmosphere purification from chemically hazardous gases.

On this basis, a simpler calculation method based on two boundary conditions of a free gas molecule and water surface interaction was proposed. When a droplet is collided by a gas molecule with kinetic energy greater than the water molecules bond energy on the droplet surface ( $E_g > E_{\text{d-d}}$ ), gas molecule breaks the  $\text{H}_2\text{O}-\text{H}_2\text{O}$  bond and penetrate the droplet surface layer. In case  $E_g < E_{\text{d-d}}$  the surface layer does not destruct and at the collision velocities that correspond with a free molecule of gas flying velocity, liquid behaves as incompressible and absolutely elastic. Since the mass of droplet is much greater than the gas molecule ( $m_g \ll m_d$ ), the gas molecule bounces after collision with the same energy that before the collision. However, at distances less than the Debye radius, the  $E_{\text{g-d}}$  chemical interaction forces that attract the gas molecule to the surface, act between the droplet surface molecules and the gas molecule. Under the condition of  $E_g \leq E_{\text{g-d}}$ , the gas molecule is absorbed on the droplet surface. Given that the hazardous gas molecule energies in the atmosphere

are distributed as per the Maxwell-Boltzmann law ( $f(E_g)$ ), based on the above-described considerations, we propose the following formula for determining the accommodation coefficient:

$$\alpha = 1 - \int_{E_{g-d}}^{E_{d-d}} f(E_g, T_g) dE_g. \quad (12)$$

The calculation results for some gases adsorption to the water droplet surface as per the model (12) shown in Table 3. Data from the literature obtained experimentally using KM- GAP and MD models are specified in the table for comparison.

**Table 3.** Accommodation coefficients of some gases with water surface ( $T=273K$ ,  $E_{d-d}=0.12e$ )

Contact gas	Value of $\alpha$ as per the model (12)	Value of $\alpha$ from literature sources	Nominal error, %
H <sub>2</sub> O	1	0.99 [4]	1.0
CH <sub>4</sub>	0.11	0.12 [4]	8.3
NH <sub>3</sub>	0.58	0.61 [14]	3.3
NO <sub>2</sub>	0.72	0.75 [14]	4.0
SO <sub>2</sub>	0.75	0.81 [15]	7.4
HCl	0.38	0.43 [4]	9.3

As can be seen from Table 3, calculations as per model (12) slightly differ from the literature data. In case of vapour of H<sub>2</sub>O, gases of NH<sub>3</sub>, NO<sub>2</sub> the relative error reaches up to 4%; for CH<sub>4</sub>, SO<sub>2</sub>, HCl – 7.4 % to 9.3 %. Therefore, for the atmospheric processes large-scale modelling as well as the meteorological situation long-term forecasting, the use of KM-GAP and MD calculation packages is more expedient. At the same time, when solving the tasks on prompt atmosphere decontaminating in case of emergency, where such an error value is not critical, and the calculation time and limitation in input data are of more significance, use of the proposed model is more expedient (12).

The proposed in the paper dependence for assessment of the gas diffusion rate effect in the droplet volume has repeatedly been verified by other researchers [15] and demonstrated high adequacy to the experimental data. According to [15], the coefficient that takes into account the diffusion rate of gas molecules inside the droplet volume is defined as

$$K_{d.a} = \frac{4H \cdot R_0 \cdot T}{\bar{v}_g} \sqrt{\frac{D_a}{\pi \cdot \tau}}, \quad (13)$$

where  $\bar{v}_g$  – average molecular velocity of gas in the air,  $\bar{v}_g = \sqrt{(8R_0T)/(\pi M_g)}$ ;  $D_a$  – coefficient of gas diffusion in liquid;  $\tau$  – process characteristic time;  $M_g$  – absorbed gas molar mass.

Yet one has to take into account the fact that expression (13) is only valid for gases that do not dissociate and do not chemically react with the droplet liquid.

By analogy with (13), an expression determining the reaction products diffusion can be written:

$$K_{d.a}^r = \frac{4H \cdot R_0 \cdot T}{\bar{v}_g^r} \sqrt{\frac{D_a^r}{\pi \cdot \tau}}, \quad (14)$$

where  $\bar{v}_g^r$  – average molecular velocity of reaction products in the air;  $D_a^r$  – diffusion coefficient of reaction products in liquid.

The effect of two processes parallel conduct in the droplet volume: gas diffusion and gas molecules with water molecules chemical reaction is taken into account by  $K_r$  coefficient (2), defined as [4, 12,15]

$$K_r = \frac{4H \cdot R_0 \cdot T}{\bar{V}_g} \sqrt{D_a \cdot \nu}, \quad (15)$$

where  $\nu$  – chemical reaction rate constant.

With account for the gas molecules adsorption and desorption processes parallel conduct from the droplet surface, we derived an equation for  $V_{des}$ , which is determined by gas content in the surface layer and gas partial pressure of the reaction products in the atmosphere ( $P_g$ ):

$$V_{des} = \frac{4\pi \cdot R_0 \cdot T \cdot C_g \cdot V_{col} \cdot \alpha}{P_g}. \quad (16)$$

In case of chemical reaction inside a droplet volume (except for dissociation, since the ions of dissociated molecules generate the original gas molecules when desorption), reaction products desorption from the droplet surface occurs. As shown above (16), the reaction products desorption rate is determined by their content in the surface layer, which varies depending on the rate of their generation and diffusion to the droplet surface:

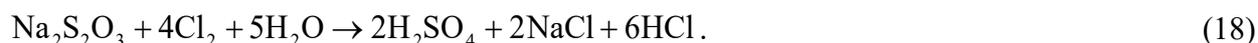
$$V_{des}^r = \frac{4\pi \cdot R_0 \cdot T \cdot C_g^r \cdot V_{abs} \cdot \alpha \cdot (K_r + K_{d.a}^r)}{P_g^r}, \quad (17)$$

where  $C_g^r$  – reaction products concentration in the air;  $P_g^r$  – reaction products partial pressure in the air.

Unlike ammonia, the water solubility of chlorine ( $Cl_2$ ) and phosgene ( $COCl_2$ ) is extremely low.

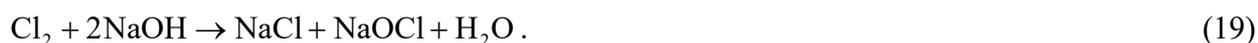
Low chlorine and phosgene solubility indicates a low intensity of these gases deposition by water aerosols. Therefore, to increase the atmosphere purification rate, neutralizers shall additionally be adopted.

Sodium thiosulfate is the most active chlorine neutralizer:



One can see from equation (18) that approximately 0.5 t of  $Na_2S_2O_3$  is required to neutralize 1t of chlorine. As can be seen from (18), the reaction occurs in aqueous solutions. However, sodium thiosulfate is a combustible and explosive substance.

Sodium hydroxide is an effective chlorine neutralizer:

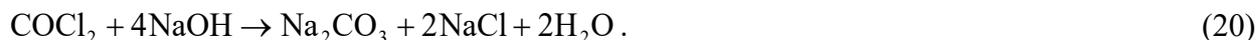


1.2 t of  $NaOH$  is required to neutralize 1 t of chlorine. Sodium hydroxide is well soluble in water, so aqueous solutions are usually used in the practice of degassing. As can be seen from (19), when chlorine neutralization with alkali, additional formation of salts that desublimates into hygroscopic crystals, and water occurs.

Phosgene ( $COCl_2$ ) is a no less hazardous substance that penetrates the atmosphere when man-caused emergencies (especially in the event of large-scale fires). Phosgene is referred to as "Carbonyl dichloride" in the professional literature. Phosgene does not exist in nature. It has become widely spread in the chemical industry, where it is used as an intermediate product in the production of, in particular, dyes, pesticides, pharmaceuticals, polymers, resins and hardeners. The annual production amounts to about 5 mln. tons. Phosgene is generated when chlorinated solvents

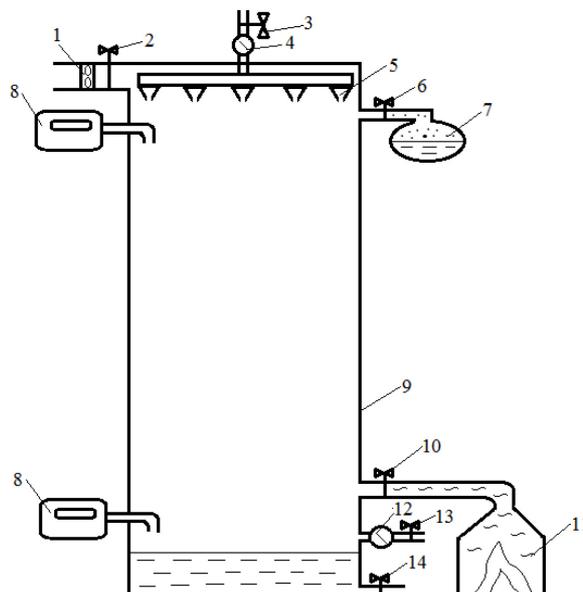
thermal decomposition or photooxidation as well as during the process of polyvinyl chloride (PVC) combustion.

Although phosgene solubility in water is low, it, like chlorine, is actively neutralized by sodium hydroxide:



From the equation of reaction (20), it can be determined that to neutralize 1 t of phosgene 1.6 t of sodium alkali or 16 t of its 10% aqueous solution is required.

A calculated and experimental comparative analysis of the aerosol flow intensity effect on the rate of chlorine washing out by water aerosol was conducted to verify the model (Fig. 2). Chlorine was selected as an example for the reason that for this gas, models using criterion equations and simulation mathematical models [4, 5] were considered quite comprehensively and repeatedly tested.



**Fig. 2.** Experimental facility for the mass exchange processes in the atmosphere researching diagram: 1 – fan; 2, 6, 10, 13 – gas shut-off valves; 3, 14 – liquid shut-off valves; 4 – liquid flow meter; 5 – spray nozzles; 7 – ultrasonic disperser; 8 – gas analyzers; 9 – body; 11 – combustion compartment; 12 – gas flow meter

An experimental laboratory facility, diagram of which is shown in Fig. 2, was developed and created for researching the processes of gaseous, liquid and solid dispersed substances (including fumes) deposition by various intensity and dispersity water aerosols.

To research the absorption process under various physical and chemical conditions, the chamber body is of sealed design.

To ensure the visual control of the sorption process the sealed cylindrical body chamber is made with a transparent wall. Detachable full cone spray nozzles are located in the upper part of the chamber. Liquid is supplied to the spray nozzles through a shut-off valve and a liquid flow meter. The possibility to adjust the liquid aerosol flow intensity and dispersity is achieved by changing the spray nozzles with various geometric parameters, replacement of some spray nozzles with plugs and liquid flow variation. A branch pipe with a shut-off valve and ultrasonic disperser is installed in the top part of the chamber for the introduction of a finely dispersed liquid aerosol of 0.01–0.5 dispersity into the volume of the chamber. In the upper part of the chamber, a branch pipe with a shut-off valve and exhaust gas are installed to remove residual gases and aerosols from the volume of the chamber. Gas analyzers suction branch pipes are installed at the top and bottom of the chamber that allow determining the volume-averaged concentration of the gas under absorption. A branch pipe with a shut-off valve is installed in the chamber bottom part to control the mass exchange intensity and the absorbent sampling. Gas (vapour) is introduced to the chamber volume

through a branch pipe with a shut-off valve and flow meter. Research is carried out both after establishing the stationary concentration in the chamber volume and the non-stationary mode.

To identify the gas content and continuous control over its concentration change, there are gas analyzers located in the chamber. Since gases may be spread unevenly over the chamber volume, gas analyzers are installed in the chamber upper and lower parts to determine the volume-averaged concentration.

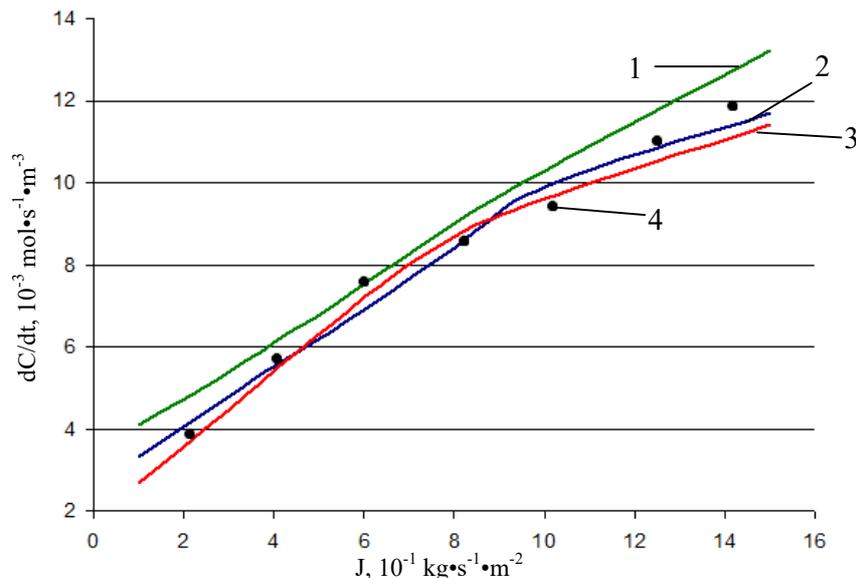
The chamber body sealed design allows experiments conducting both at a constant gas concentration and in a non-stationary mode.

During the experiment, one can perform the absorbent sampling to control its extent of saturation with the absorbed substance.

The droplets mass was determined by their dispersity calculation  $r \approx 0.8$  mm, the falling velocity was selected as average by volume based on the chamber height  $H = 2$  m. Measurements were conducted in a series of three experiments, from which the measured date average value was determined. It should also be noted that since the absorption rate is of the same power law dependence on the droplets concentration and size, but different flow intensity ( $J \sim C_{\text{drop}}$ ,  $J \sim R^3$ ), at the same flow intensity, a finely dispersed flow with a large concentration of droplets and absorption surface has privilege.

The research results on the hazardous gaseous substance deposition are shown in Fig. 3.

Based on the analysis of theoretical and experimental results one can conclude that MD simulation model is of the greatest experimental data description adequacy. The calculation errors range relative to curve 3 is 4–14 % for curve 1 and 0–6 % for curve 2. Between curves 2 and 3, there are intersection points, which indicates their adequacy in zones  $J = 4,2 \cdot 10^{-1}$  and  $8,7 \cdot 10^{-1} \text{ kg} \cdot \text{f}^{-1} \cdot \text{m}^{-2}$ . Another important moment of the stepwise absorption model is the fact that it allows taking into account most of the main physical and chemical absorption regularities. At the same time, the stepwise model we have supplemented (curve 2) is also of a high accuracy degree. Although the presented model has some discrepancy of the system physical properties under modelling (unevenness of heightwise droplet falling velocity, sizewise droplets distribution), the results obtained satisfactorily accord with the calculated (Fig. 3) and experimental data of other researchers [13, 15]. Herewith, the capabilities of the experimental facility represented in the paper allow modelling most of the physical and chemical properties both of the system and the substances taking part in it.



**Fig. 3.** The dependencies of the chlorine sorption rate by water aerosol on the flow intensity were obtained by calculation and experimentally: 1 – criterion equation calculation; 2 – calculation using the supplemented stepwise model; 3 – calculation using MD simulation mathematical model; 4 – experimental data

The model adequacy check was carried out according to Fisher's criterion:

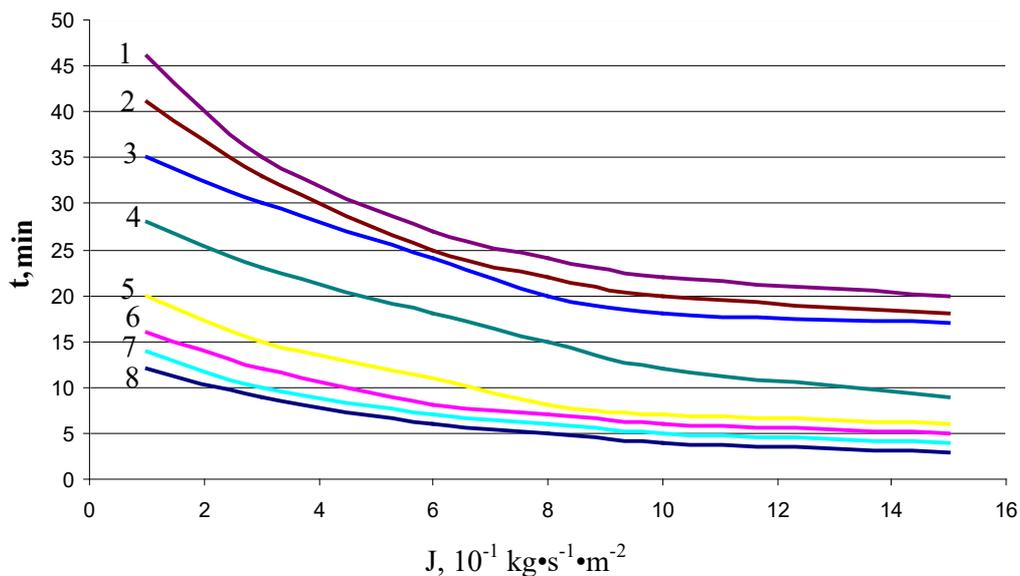
$$F = \frac{s_{ad}^2}{s_0^2} \leq F_{(0.05; f_{ad}; f_y)}, \quad (21)$$

where  $s_{ad}^2 = \frac{\sum_{u=1}^m (y_u^- - y_u)^2}{n - k - 1}$ ;  $s_0^2$  – zero hypothesis dispersion;  $y_u$  – calculated response value in  $u$ -th experiment;  $F_{(0.05; f_{ad}; f_y)}$  – Fischer's criterion at 5% significance level;  $f_{ad}$  – adequacy dispersion degrees of freedom number;  $f_y$  – reproduction dispersion degrees of freedom number.

$$F = 2,7862 < F_{(0.05; f_{ad}; f_y)} = 3,9381. \quad (22)$$

Accordingly, the modified model adequacy check yielded a positive result.

Since the washing out rate depends on time, considering the substance with a certain initial concentration washing out time instead of the instantaneous rate of washing out is expedient (Fig. 4). In this case, it is assumed that all gas is evenly distributed in the atmospheric boundary layer 5 m high.



**Fig. 4.** Dependence of the hazardous gases washing out time in the atmosphere on the flow intensity: 1 – NO<sub>2</sub>; 2 – Cl<sub>2</sub>; 3 – H<sub>2</sub>S; 4 – SO<sub>2</sub>; 5 – HCN; 6 - COCl<sub>2</sub>; 7 – HCl; 8 – NH<sub>3</sub>

According to Fig. 3 it can be seen that the gases washing out time from the atmosphere is in strict dependence on their solubility (see Table 1), i.e., the higher is the gas solubility the shorter is the washing out time. The greatest effectiveness of deposition is observed in the event of atmosphere pollution with ammonia, which is explained by the highest solubility of ammonia among the considered gases. The low washing out intensity of chlorine and hydrogen sulfide that belong to the II class of hazard substances shall be pointed out.

## Conclusion

The paper modifies the stepwise model of the gaseous hazardous substances sorption process by finely dispersed water aerosols that includes description of the hazardous gas diffusion in the atmosphere, its accommodation on the droplet surface, diffusion inside the droplet volume as well as the possibility of chemical neutralization by special additives.

Use of the modified stepwise absorption model considered in the paper for forecasting the chemically hazardous gases washing out processes by water aerosols is the most advisable. Since the absorption rate from the droplets concentration and their size is of the same power law dependence, but different flow intensity ( $J \sim C_{\text{drop}}$ ,  $J \sim R^3$ ), a finely dispersed flow with a high concentration of droplets and specific interphase surface absorbs more effectively at the same flow intensity.

The developed laboratory facility for the gaseous and dispersed substances deposition processes study represents a chamber for researching the mass exchange processes as well as the methodology of the experiments that allows checking the plausibility of the developed models for hazardous substances deposition by water aerosols when natural and man-caused emergencies response and recovery through gaseous hazardous substances deposition from the atmosphere.

The adequacy of the modified gas sorption model by finely dispersed aerosol with 5% adequacy as per Fisher's criterion has been confirmed experimentally. The modified model requires less amount of input parameters and, because of simplifying, increases the forecasting promptness.

Use of NaOH soluble additives is reasonable due to the low intensity of gaseous chlorine deposition by water aerosols. Aqueous solutions of NaOH are capable of chlorine and phosgene chemical neutralization, which, according to the considered sorption model, can significantly increase the intensity of such hazardous gases deposition.

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