Influence of Water Salinity on Air Purification from Hydrogen Sulfide

Leybovych L.I., Patsurkovskiy P.A.
Admiral Makarov National University of Shipbuilding
Mykolaiv, Ukraine

Abstract. Mathematical modeling of «sliding» water drop motion in the air flow was performed in software package FlowVision. The result of mathematical modeling of water motion in a droplet with diameter 100 microns at the «sliding» velocity of 15 m/s is shown. It is established that hydrogen sulfide oxidation occurs at the surface of phases contact. The schematic diagram of the experimental setup for studying air purification from hydrogen sulfide is shown. The results of the experimental research of hydrogen sulfide oxidation by tap and distilled water are presented. The dependence determining the share of hydrogen sulfide oxidized at the surface of phases contact from the dimensionless initial concentration of hydrogen sulfide in the air has been obtained.
Keywords**:** hydrogen sulfide, oxidation, absorption, surface of phases contact.

Influență salinității apei asupra epurării aerului de la hidrogen sulfurat
Leibovici P.A., Pațiurcovschi L.I.
Universitatea Națională de proiectare de nave
Micolaiv, Ucraina
Rezumat. Cu utilizarea soft-ului FlowVision s-a realizat simularea procesului mişcării picăturilor de apă în curentul de aer în regim de «alunecare». Este prezentat rezultatul modelării matematice a mişcării apei în picătura cu diametru de 100 μm cu viteza de 15 m / s. S-a stabilit, că procesul de oxidare a hidrogenului sulfurat se produce pe suprafața de contact ale fazelor de stare. În lucrare este prezentată schema de principiu a ştandului experimental utilizat la cercetare procesului de purificare a aerului de hidrogenul sulfurat. Se prezintă rezultatele cercetărilor experimentale a procesului de oxidare a hidrogenului sulfurat din apa distilată şi din apa sistemului de alimentare centralizat. Este obținută relația, care permite calcularea cotei hidrogenului sulfurat oxidat pe suprafața de contact a stărilor de fază în funcție de valoarea concentrației hidrogenului sulfurat din aer prezentat în sistemul relativ de unități.
Cuvinte-cheie**:** hidrogen sulfurat, oxidarea, absorbarea, suprafaă de contact a fazelor.

Влияние солености воды на очистку воздуха от сероводорода
Лейбович Л.И., Пацурковский П.А.
Национальный университет кораблестроения имени адмирала Макарова
Николаев, Украина
Аннотация. В программном комплексе FlowVision выполнено математическое моделирование движения капли жидкости в потоке газа со «скольжением». Приведен результат математического моделирования движения воды в капле диаметром 100 мкм и скоростью 15 м/с. Установлено, что процесс окисления сероводорода происходит на поверхности контакта фаз. Представлена принципиальная схема экспериментального стенда для исследований очистки воздуха от сероводорода. Представлены результаты экспериментальных исследований окисления сероводорода водопроводной и дистиллированной водой. Получена зависимость, определяющая долю сероводорода, окисляемую на поверхности контакта фаз в зависимости от безразмерной начальной концентрации сероводорода в воздухе.
Ключевые слова**:** сероводород, окисление, абсорбция, поверхность контакта фаз.

Introduction

The release of harmful substances into the air near the location of sewage pumping stations (SPS) is one of sewage pumping problems.

Nitrogen dioxide, ammonia, methane, hydrogen sulfide, methyl mercaptan, ethyl mercaptan, carbon oxide and other harmful substances were identified in atmospheric air adjacent to SPS buildings [1, 2]. Hydrogen sulfide concentration in the air near SPS exceeds the concentration of a methyl mercaptan and other substances more than 200 times.

Special chemical reagents added to sewage allow reducing the emissions of hydrogen sulfide into the environment. However, it does not protect the air near SPS from hydrogen sulfide and other substances emissions [3, 4].
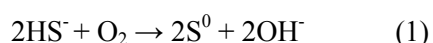
Therefore the actual problem of the environment protection is air purification from hydrogen sulfide at SPS [5]. Searching for effective and economical methods for the environmental protection from hydrogen sulfide near the SPS buildings is rather urgent. Therefore the parameters of the physical processes describing hydrogen sulfide oxidation by air oxygen require be identifying and studying.

A centrifugal-bubbling device is one of effective devices for hydrogen sulfide oxidation by air oxygen in a liquid phase [6]. The mass transfer surface is formed by air bubbling through the liquid layer. Hydrogen sulfide oxidation occurs at a high speed, because the mass transfer surfaces large and changes rapidly. However, bubbles with a size smaller than 0.002 m are not obtained during gas bubbling through the liquid layer [7].

Water droplets and bubbles participate in the process of the air purification from hydrogen sulfide. The necessity in decreasing of water droplets or bubbles size is indicated in the paper [8].

The small sizes of liquid drops allow performing the research of hydrogen sulfide oxidation by air oxygen rather accurately.

Hydrogen sulfide oxidation leads to the formation of elementary sulfur or sulfur oxides. Elemental sulfur (S^0), thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) are the major intermediates and products of hydrogen sulfide oxidation that were identified in the paper [9]:

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \qquad (1)$$

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (2)$$

$$2HS^- + 3O_2 \rightarrow 2SO_3^{2-} + 2H^+ \qquad (3)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (4)$$

The formation of elementary sulfur or sulfur oxides depends on concentrations of hydrogen sulfide and oxygen in the chemical reaction zone.

The concentration of hydrogen sulfide and oxygen in the reaction zone depends on diffusion coefficients of the substances in the liquid medium. These factors help to explain why the hydrogen sulfide oxidation, according to the pseudo first reaction order, range from 0.26 to 55.0 day^{-1} and correspond to half-life from 65.0 to 0.3 h [10]. Thus, the rate of chemical reaction between hydrogen sulfide and oxygen depends on hydrodynamic conditions in the reaction zone.

The investigation of hydrodynamic conditions in a «sliding» water drop moving in the air flow is one of the tasks of this paper. The term «sliding» indicates that velocities of water droplets and air flow are different.

Mathematical modeling of fluid motion in a «sliding» water droplet moving in air flow

The character of fluid motion in «sliding» water droplets moving was investigated in the paper [11]. The movement of water droplets with size less than 10^{-4} m was analyzed in this paper. The research was carried out by means of mathematical modeling. Water droplets with sizes from 10 to 100 microns can be received in modern devices providing the contact between gas and liquid with low energy consumption. Energy consumption for the increasing surface of liquid droplets area essentially depends on their size. The research results [11] cannot be used for the analysis of the changes in the surface of contact between gas and liquid in small water droplets. Therefore the mathematical model [8] of liquid drop motion in the air flow with «sliding» was created by the authors. The general view of the model geometry is shown in Fig.1. Mathematical modeling of water drop motion in the air flow with «sliding» ii implemented in the software package FlowVision. The result of mathematical modeling water circulation in a droplet with diameter 100 microns at the «sliding» velocity 15 m/s is presented in Fig.2.

The mathematical modeling of the hydrodynamic situation in the water droplet was carried out on the basis of Navier-Stokes equation:

$$\frac{\partial \overline{U}}{\partial t} + \left(\overline{U} \cdot \nabla \right) \cdot \overline{U} = -\frac{1}{\rho} grad\, p + v \cdot \Delta \overline{U}$$

The average integral velocities values of liquid transposition at the spherical droplets surface were obtained as a result of mathematical modelling of liquid droplets motion in air flow with «sliding» velocity up to 15 m/s. The values of these velocities are in the range $(1.4...5.5) \cdot 10^{-4}$ m/s.
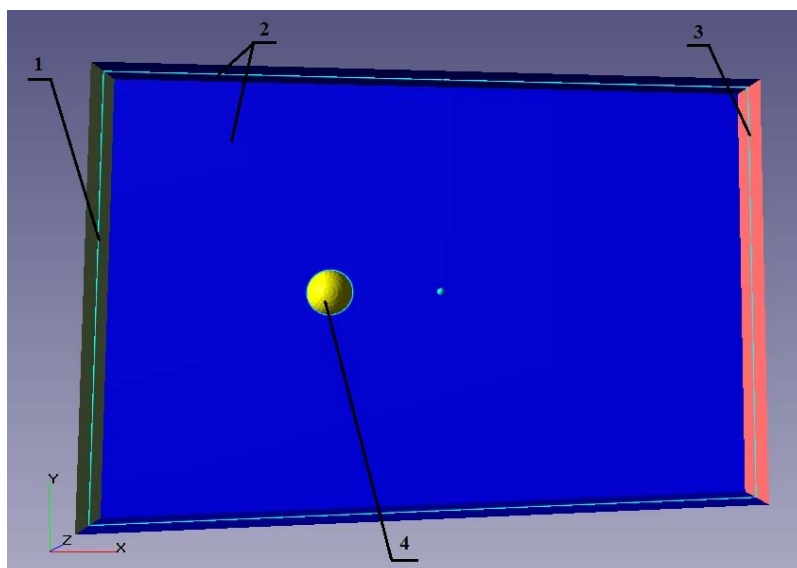
Fig.1. *General view of the model geometry:*
1 - air inlet; 2 - «sliding» wall; 3 - air outlet; 4 - droplet surface
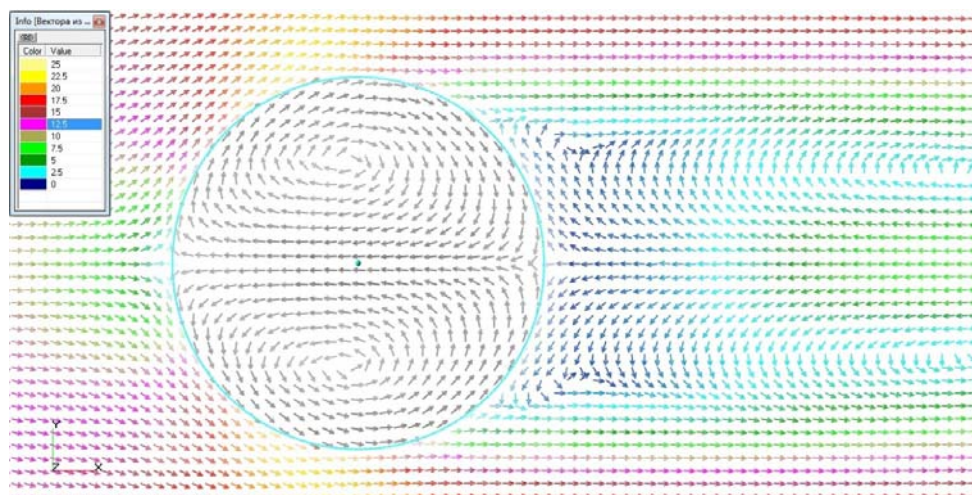
Fig.2. *Visualization of vectors velocity in a droplet with diameter 100 microns and «sliding» velocity of 15 m/s.*

The degree of droplets deformation estimates by means of the following parameter:

$$f = 1 + 0.081 \cdot We^{0.95}.$$

The maximum value of the Weber number does not exceed 0.37, which corresponds to $f = 1.03$. Thus, the droplets deformation is insignificant at «sliding» velocities up to 15 m/s. Therefore, it was assumed that a droplet has a spherical shape and does not undergo deformations during its existence time.

A good convergence in the dynamics of fluid flow in the droplets was obtained by the comparison of the received results of mathematical modelling with data [11]. This convergence confirms by the vortex shift in the front part of a spherical drop and flow separation at the back part of the droplet with the vortices formation.

It is important to note that hydrogen sulfide and oxygen diffusion coefficients in water at 20 ºC are very low: $D_{H2S} = 1.41 \cdot 10^{-9}$ m²/s and $D_{O2} = 1.8 \cdot 10^{-9}$ m²/s.

The following conclusions can be done from the analysis of mathematical modeling results of water droplets motion in the air stream with «sliding»:

- «sliding» of water droplets with the size less than 100 microns is stopped after 6...10 milliseconds;

- the moving distance of the chemical reaction front plane between hydrogen sulfide and oxygen inside the droplets does not exceed 2 microns.

The experimental setup description

The requirements for experimental setup were the following:

- to generate water drops with size less than 100 microns;
- to provide the time of drops existence less than 10 ms;
- to provide a good mix of gas-liquid stream at the minimum quantity of the water in the process of air purification from hydrogen sulfide.

These requirements were realized in the experimental setup shown in Fig. 3.

Hydrogen sulfide receiving was obtained in the special batcher by the following chemical reation:

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S \qquad (5)$$

The experimental setup has a closed contour. Generating hydrogen sulfide mixes up with the air circulating in the closed contour. H_2S dosage stops by disconnecting capacity 1 after reaching the necessary concentration in the closed contour. The mass-transfer device 3 is used to provide gas circulation in the closed contour. The gate 2 is used to provide the regulation of air consumption. The absorbent from electrochemical reactor 8 is fed into the inlet of the mass-transfer device branch pipe 3. The slot-hole separator 4 is used for the separation of fine liquid particles. The water circuit filling is carried out through the dispenser 6. The location of gas sampling for the further analysis of hydrogen sulfide content illustrated in Fig.3. The sampling system is represented by the compressor 9. H_2S concentration was measured by the gas analyzer 10. The definition of air consumption was performed by differential pressure at the diaphragm 11. Differential pressure was measured by the micromanometer 12. The setup was checked for leaks before starting the experiment.

The electrochemical reactor was switched-off in research experiments of water salinity influence on hydrogen sulfide oxidation efficiency.
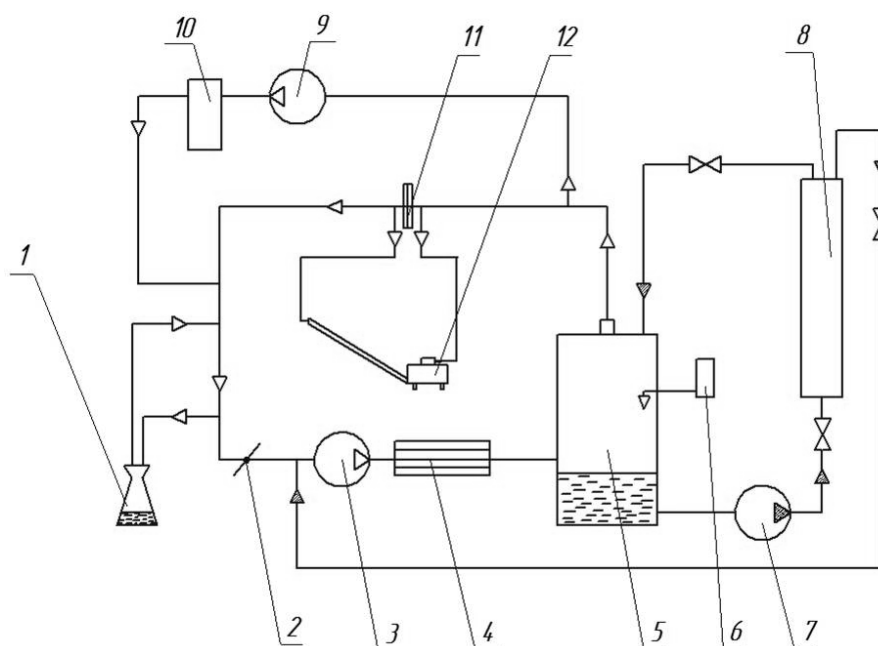
Fig.3. *The schematic diagram of the experimental setup for air purification from hydrogen sulfide: 1 – capacity for hydrogen sulfide receiving; 2 – gate; 3 – mass-transfer device; 4 – slot-hole separator; 5 – tank; 6 – water batcher; 7 – pump; 8 – electrochemical reactor; 9 – compressor; 10 – gas analyzer; 11 – diaphragm, 12 – micromanometer.*

The application of tap water and distillate as H_2S absorbent was investigated in 30-minute experiments.

Tap water had the following structure: nitrates oxidability - less than 50 mg/l; general rigidity - 9 mg/l; chlorides - 320 mg/l; sulfides -

400 mg/l; general alkalinity - 5,5 mg/l; calcium - 140 mg/l; pH = 7,2.

Distillate was obtained by vacuum distillation of tap water at the temperature about 45...50 °C.

Experimental data processing

To describe hydrogen sulfide oxidation kinetics, the following equation was used:

$$k = n_{H2S} \cdot \frac{R \cdot T}{p \cdot V} \cdot \ln \frac{1}{1 - \dfrac{C}{C_0}}, \qquad (6)$$

k - chemical reaction speed constant; n_{H2S} − number of H_2S moles in the air of the closed contour; R − universal gas constant; T - air temperature; p - air pressure; V - air volume; C, C_0 - current and initial H_2S concentration in the air. For the implementation of comparison and analysis possibility the experimental data were processed by the following dependence:

$$\bar{C} = f(\bar{T}). \qquad (7)$$

$\bar{C} = c_i/c_0$ – the ratio of current H_2S concentration to initial concentration; $\bar{T} = T_i/T$ - the dimensionless time of experiment defined as the ratio of the current time to total time of experiment.
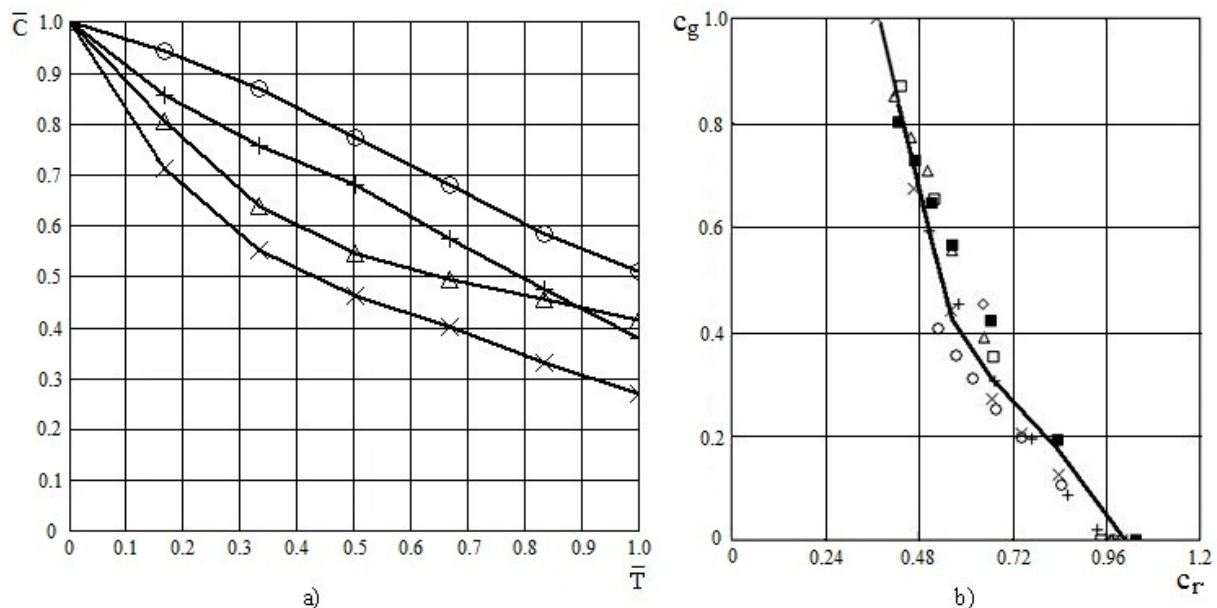
The research results of H_2S oxidation by tap water

The initial conditions of the experiments are shown in Table 1.

The research results of hydrogen sulfide oxidation on the surface of tap water drops are shown in Fig.4.

Table 1. The initial conditions of the experiments of H_2S oxidation by tap water

Symbols	G_{water}/G_{air}, kg/kg	Temperature, °C		Air humidity, %	The initial H_2S concentration, mg/m³
		air	water		
×	0,056	21,5	19,0	0,77	100
+	0,04	21,0	17,4	0,70	53
■	0,08	21,2	19,2	0,83	100
◊	0,056	16,9	13,8	0,70	94
Δ	0,053	20,5	17,9	0.76	87
○	0,066	21,1	18,2	0,80	46

Fig.4. *Dependence of hydrogen sulfide oxidation on the surface of tap water drops:*
a) results of measurements; b) generalized results of experimental research.

In Fig.4.b: C_g - the share hydrogen sulfide absorbed by water and oxidized by oxygen on the water droplets surface; C_r - the dimensionless initial concentration of H_2S in the air correlated with dimensionless temperature, irrigation coefficient and air humidity.

As a result of data processing (Fig.4.b) the following regression dependence was obtained:

$$C_g = \frac{0.9}{\left(C_r^2 + 0.8\right)} - 0.55 \cdot C_r^{1.5}; \qquad (8)$$

$C_r = C_{01}/c_{01} \cdot G_1$; C_{01} – the magnitude of H_2S concentration changes during the experiment, mg/m^3; c_{01} – the initial concentration of hydrogen sulfide in experiment, mg/m^3; G_1 – the correlation coefficient with temperature, air humidity and irrigation coefficient.
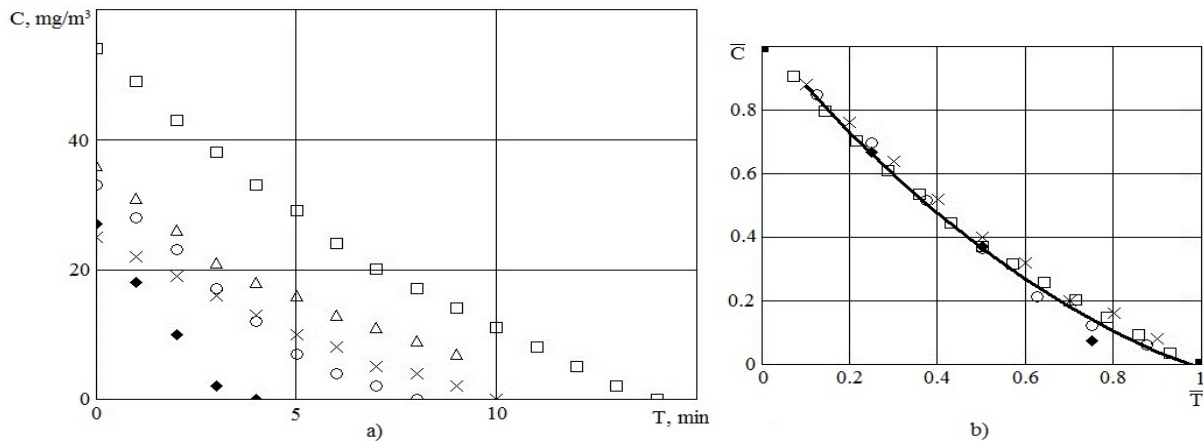
The research results of H_2S oxidation by distillate water

The initial conditions of the experiments are shown in Table 2.

The research results of hydrogen sulfide oxidation on the surface of distillate water drops are shown in Fig.5.

Table 2. The initial conditions of the experiments of H_2S oxidation by distillate water

Symbols	G_{water}/G_{air}, kg/kg	Temperature, ^{o}C		Air humidity, %	The initial H_2S concentration, mg/m^3
		air	water		
x	0.08	16.6	13.4	0,74	25
▲	0,093	18.0	15.4	0,79	27
○	0,093	16.7	14.2	0,86	33
♦	0,106	17.6	14,8	0,76	36
Δ	0,067	16.7	14.8	0.82	54

Fig.5. *Dependence of H_2S oxidation on the surface of distillate water drops:*
a) results of measurements; b) generalized results of experimental researches

In Fig.5.b: $\bar{C}$ - the value of dimensionless H_2S concentration; $\bar{T}$ - the dimensionless time of experiment.

Because of data processing (Fig.5.b), the following regression dependence was obtained:

$$\bar{C} = 1.028 - 1.609 \cdot \bar{T} + 0.567 \cdot \bar{T}^2 \qquad (9)$$

Discussion

The experimental setup (Fig.3) provides generation water drops with the size about 100

microns. These data are confirmed by measurements results presented in Fig.6.

The distribution of water drops according to sizes has a normal character in the range of sizes from 10 to 100 microns and the time of water drops existence in the air stream according to the calculations was about 6…8 milliseconds.

The total surface of all water drops generated exceeds the other surfaces of the experimental setup moistened with water more than 10 times.

The calculations of H_2S absorption by water were made based on Henry constants for the considered temperature range. The calculations showed that the amount of H_2S dissolved in water does not exceed 0,5% from the initial H_2S concentration value in the air. This means that H_2S oxidation process takes place on the interfacial surface.
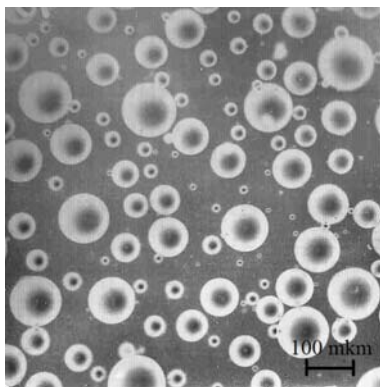
Fig.6. *Water drops distribution by sizes*

Sulfur oxides and hydrogen sulfide were detected in water after its contact with the air containing hydrogen sulfide. The experiments showed that H_2S (that did not contact with the air) was completely oxidized in water during 24 hours. The obtained results are in a good agreement with the data [10] about the chemical reaction speed of H_2S oxidation in water. The water pH value went down by 0.2 units after its contact with the air containing hydrogen sulfide.

The oxygen initial concentration in water ranges within 6-7 mg/l. The oxygen concentration in water reduces by about 0.3-0.4 mg/l after water spraying, contacting with H_2S and separating.

The conditions of water drops existence time in the air and H_2S concentration change in the closed contour allows to make some reasonable assumptions according physical processes taking place on the surface of small water drops.

The water spraying in humid air flow significantly increases the rate of H_2S oxidation in comparison with the oxidation process in humid air without water spraying [12].

However, tap water application (as a catalyst) for H_2S oxidation has shown the essential dependence of this process on the temperature level in the gas-liquid system and the amount of water, participating in this process. It can be assumed that salts of inorganic substances dissolved in water play the determining role in the catalytic properties of the interfacial surface.

The research of water distillate used as a catalyst (Fig.5) showed that H_2S oxidation intensity increases in several times. It gives the prerequisites for studying the intensification of H_2S oxidation process by using interfacial surface of distillate activated in the electrochemical reactor.

References
[1] Loseva Ya.P., Mishchenko Ya.V., Grivanova S.M. [Efficiency of evaporations dissipation from tanks sewage treatment plants in Vladivostok]. Effektivnost rasseivaniya ispareniy ot rezervuarov kanalizatsionnykh ochistnykh sooruzheniy goroda Vladivostoka. Fundamentalnye issledovaniya. 2013, no. 11, pp. 1383-1388. (In Russian).

[2] Sivret E.C., Nhat Le-Minh, Bei Wang, Xinguang Wang, Hung Le and Richard M.Stuetz. Impact of sewer emission dynamics on campaign design monitoring. Chemical Engineering Transactions, Vol. 40, 2014, pp. 43-48. doi: 10.3303/CET1440008.

[3] Nia Morteza and F. Othman. The Conference of energy and environment Taj Chandigarh, Chandigarh, INDIA, March 19-21, 2009, pp. 341-348.

[4] Zhang L., Keller J., Yuan Z.. Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing. Water Research, 43 (17), 2009, p. 4123-4132.

[5] Lebrero R., Rangel M.G., Muñoz R. Characterization and biofiltration of a real odorous emission from wastewater treatment plant sludge. *Journal of Environmental Management,* 2013, vol. 116, pp. 50–57. doi:10.1016/j.jenvman.2012.11.038.

[6] Ryazantsev A.A., Malikov A.S., Batoeva A.A., Faddeenkova G.A. [The liquid-phase hydrogen sulfide oxidation in the centrifugal-bubbling apparatuses]. Zhidkofaznoe okislenie serovodoroda v tsentrobezhno-barbotazhnykh apparatakh. *Zhurnal prikladnoy khimii*, 2007, T.80, Vyp.9. - Str. 1511-1515. (in Russian).

[7] Borisov I.I., Khalatov A.A., Shevtsov S.V. [About the size of the bubbles in the bubbling vortex layer]. O razmerakh puzyrkov v vikhrevom barbotazhnom sloe. *Promyshlennaya teplotekhnika*, 1996, T.18, no.1. - Str. 81–85. (in Russian).

[8] Leybovich L.I., Patsurkovskiy P.A. [Mathematical simulation of flow process of absorbent spherical particle by means of gas stream]. Matematicheskoe modelirovanie

protsessa obtekaniya sfericheskoy chastitsy absorbenta potokom gaza. *Sbornik nauchnykh trudov NUK,* 2014, no.5. - Str. 45-50. (in Russian).

[9] Cline J.D., Richards F.A. Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature and pH. *Environ. Sci. Technol.,* 1969, pp. 838–843. doi: 10.1021/es60032a004.

[10] Millero F.J. The thermodynamics and kinetics of the hydrogen sulfide system in natural waters. *Marine Chemistry,* 1986. vol. 18, pp. 121-147.

[11] Rivkind V.Ya. [About one stationary motion model of two environments with chemical reaction]. Ob odnoy modelnoy statsionarnoy zadache dvizheniya dvukh sred s khimicheskoy reaktsiey. Zapiski nauchnykh seminarov LOMI, 1973, no.35. - Str. 106-113.

[12] Patsurkovskiy P.A., Leybovich L.I. Materials of 2-nd International Conference on Sustainable Solid Waste Management. Athens. 12th–14th June 2014. Available at: http://athens2014.biowaste.gr/pdf/patsurkovskiy_leybovych.pdf (accessed 27.11.2015).

About authors:
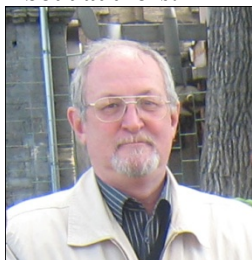
Leybovych L.I., Ph.D., Associate Professor of Technical Thermal Physics and Steam-Generating Units Department of Admiral Makarov National University of Shipbuilding. His research interests includes electrochemistry, mathematical modeling of heat and mass transfer processes.
E-mail:
recycle.lev@gmail.com

Patsurkovskiy P.A., assistant of Technical Thermal Physics and Steam-Generating Units Department of Admiral Makarov National University of Shipbuilding. His research interests includes mechanics of fluids motion, absorption, mathematical modeling of heat and mass transfer processes.
E-mail:
pavlo.patsurkovskyi@nuos.edu.ua