

NONISOTHERMAL DESORPTION AND NUCLEATE BOILING IN A WATER-SALT DROPLET LiBr

by

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Experimental data on desorption and nucleate boiling in a droplet of LiBr water solution were obtained. An increase in salt concentration in a liquid layer leads to a considerable decrease in the rate of desorption. The significant decrease in desorption intensity with a rise of initial mass concentration of salt has been observed. Evaporation rate of distillate droplet is constant for a long time period. At nucleate boiling of a water-salt solution of droplet several characteristic regimes occur: heating; nucleate boiling; desorption without bubble formation; formation of the solid, thin crystalline-hydrate film on the upper droplet surface, and formation of the ordered crystalline-hydrate structures during the longer time periods. For the final stage of desorption there is a big difference in desorption rate for initial salt concentration (C_0) 11 % and 51 %. This great difference in the rate of desorption is associated with significantly more thin solution film for $C_0 = 11$ % and higher heat flux.

Key words: desorption, nucleate boiling droplet, water-salt solution

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1. Introduction

The absorber and desorber efficiency of thermotransformer is determined by the processes of absorption and desorption. The theory of absorption is presented in monograph [1]. The salt concentration during a nonisothermal absorption changes slightly. The concentration of salt and diffusion coefficient in a nonisothermal desorption vary in a wide range, and it greatly complicates the modeling. The nonstationary desorption processes of droplet aqueous salt solutions can be hardly described by the available theory of nonisothermal absorption, and they need experimental investigation in a wide range of temperatures and salt concentrations. Theoretical task can be formulated on the basis of experimental data. The phase equilibrium of aqueous salt solutions at the liquid-vapor interface is determined by concentration of dissolved substances together with the temperature and pressure [2-4]. In these solutions in contrast to the single-component liquids the third phase (solid state) can be formed during desorption. Evaporation of water droplets and films without nucleate boiling were studied in Refs. [5-11]. The evaporation rate is controlled by thermo-physical and geometric properties of the wall [12]. Experimental investigation of the effect of substrate thermal properties on droplet evaporation is presented in Ref. [13]. Thermal properties of the wall change the drop evaporation rate [14]. At high heat fluxes and nucleate boiling the droplet bottom area and the evaporation rate change in time. Droplet forces equilibrium is broken and we have to deal with a sliding contact line. Experimental studies in Ref. [15] using nanoparticles have shown that near the contact line there is the point of a change in rate direction caused by the Marangoni force. The direction depends on ratio of thermal conductivity coefficients of the wall material to liquid and the contact angle [16]. There is another important demonstration of the Marangoni force in the form of waves. At droplet evaporation, hydrothermal waves and instability can be generated. The nature of such waves is associated with thermo-capillary Marangoni stresses [17]. Critical heat flux depends on the Marangoni instability for microlayer bubble [18]. Droplets crisis behavior at high heat fluxes was considered in Refs. [19-20]. There is a multiphase gas-droplet flow during gas hydrate combustion. The reaction rate is controlled by this current [21]. Experimental investigation of mixtures and foreign inclusions in water droplets under high-temperature gas was considered in Ref. [22]. Evaporation, boiling and explosive breakup of heterogeneous droplet in a high-temperature gas was presented in Refs. [23-27]. Spreading behavior of a distilled water droplet on a superhydrophobic surface was considered in Ref. [28]. The contact line behavior of salt solution droplet differs substantially from the distillate [29]. Investigation of drop dynamic contact angle on copper surface was presented in Ref. [30]. Surface crystallization features at high temperature desorption of droplets discussed in Ref. [31].

In the existing literature practically there are small amounts of experimental data comparing the dynamics of high-temperature desorption of salt solution droplets without boiling and with the presence of the nucleate boiling. One of the main purposes of this paper is to make a comparison of the dynamics for different salt concentrations.

2. Experimental data and analysis

To register the current parameters of the droplet mass during nonisothermal desorption of aqueous salt solutions on the horizontal heating surface (Fig. 1), we used the weight experimental method: A – working heating surface of the wall; 1 – titanium cylinder; 2 – electric heater; 3 – screen thermal insulation; 4 – adjustable supports; 5 – analytical balance; 6 – thermocouples; 7 – flexible element of thermocouple; 8 – Dewar vessel; 9 – thermocouple switch; 10 – millivoltmeter; 11 – flexible element of electric wiring; 12 – laboratory transformer; 13 – temperature regulator; V and A – voltmeter and ammeter; 14 – puller ear; 15 – metering device; 16 – protecting screen; 17 – video and shooting cameras, thermal imager. The working section was located on a laboratory balance. The external pressure was 1 bar, the wall temperature was maintained constant $T_w = 80\text{ }^\circ\text{C}$. The initial temperature of the solution was $25\text{ }^\circ\text{C}$ and air humidity was 30 %. The initial volume droplet was constant $V_0 = 100\text{ }\mu\text{l}$.

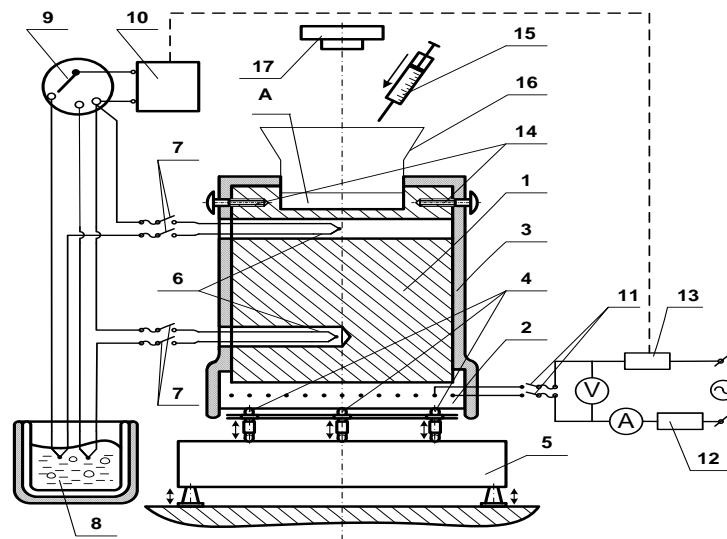


Fig. 1. Setup scheme for the work with a water-salt droplets

The use of the titanium working material allowed experiments with corrosive water solutions of LiBr at high surface temperatures. Solution LiBr mass concentrations values C_0 were determined by the standard densimeters. Metered volumes V_0 were put on the wall surface by microdispensers 15 (Fig. 1). The thermal fields of droplet surface were measured by the thermal imager 17. A reliability

of interface (liquid-air) temperature measurements was achieved due to the accurate choice of infrared camera radiation coefficient. Emissivity was changed with accuracy of 0.1. The difference between the temperature values measured by thermal imager 17 and the thermocouple did not exceed 1.8 °C. The measurement error of the infrared camera was within 2.5 %. The relative measurement error of drop weight did not exceed 18 %.

Comparative dependences without nucleate boiling for droplets evaporation of distilled water and for nonisothermal desorption of aqueous salt solutions droplets with variable C_0 LiBr and constant T_{w0} are presented in Fig. 2. The significant decrease in desorption rate was observed with a rise of time. The derivative of the mass curve decreases with increasing time. This regularity is determined by a decrease in pressure of saturated vapors of water above the droplet interfacial surface (liquid-gas) with a rise of salt concentration C over time t . Water evaporation curve has a quasi-linear character. The evaporation curve of the water-salt solution is essentially nonlinear and the evaporation rate decreases in time. When establishing the crystallization point after a long desorption time a crystalline thin film on the droplet surface is formed. There are several phases for this stage: the liquid salt solution, a solid crystalline hydrate film and water vapor.

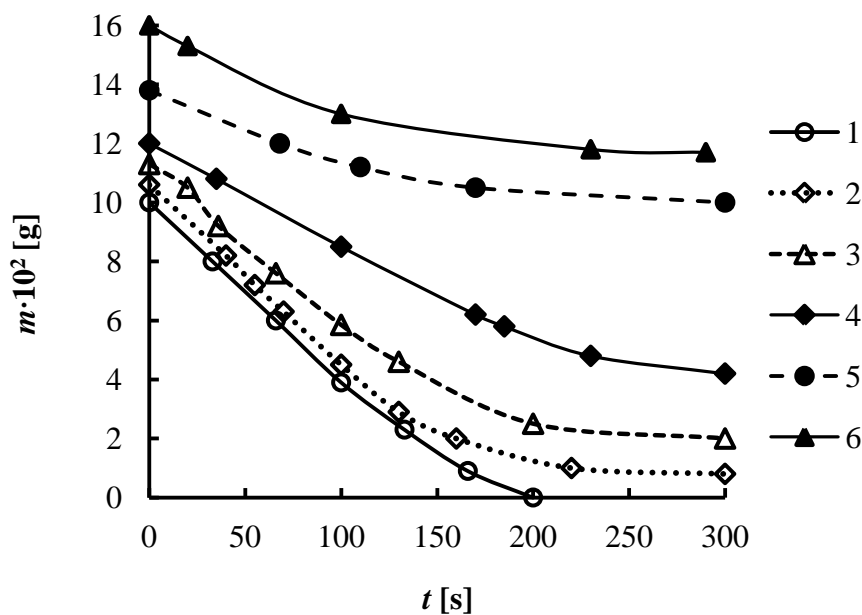


Fig. 2. Dependences for distillate droplet evaporation and desorption of aqueous salt solutions LiBr with different mass C_0 ($V_0 = 100 \mu\text{l}$; $T_w = 80 \text{ }^\circ\text{C}$): 1 - $C_0 = 0 \%$ (distillate), 2 - $C_0 = 6 \%$, 3 - $C_0 = 11 \%$, 4 - $C_0 = 23 \%$, 5 - $C_0 = 37 \%$, 6 - $C_0 = 51 \%$

Experimental data on the desorption of droplet aqueous salt solutions LiBr with the initial wall temperature $T_w = 130 \text{ }^\circ\text{C}$ and the initial salt concentration $C_0 = 11; 23; 37; 51 \%$ with nucleate boiling (curves 1-2) and without nucleate boiling (curves 3-4) are presented in Fig. 3. With increasing salt

concentration LiBr, the heat of desorption increases by tens of percents and equilibrium vapor pressure decreases many times and ΔT_w is insufficient to form R_{cr} in accordance with (1) [32],

$$\Delta T_w = \frac{2\sigma R T_s^2}{k p R_{cr}} \quad (1)$$

where R_{cr} is the minimal radius of micropore, which becomes active at given superheat ΔT_w ; R is universal gas constant; p is vapor pressure; k is specific heat of desorption; σ is surface tension; and T_s is temperature of vapor saturation. As a result, there is no nucleate boiling for curves 3-4. With increasing salt concentration the shift of equilibrium curve occurs.

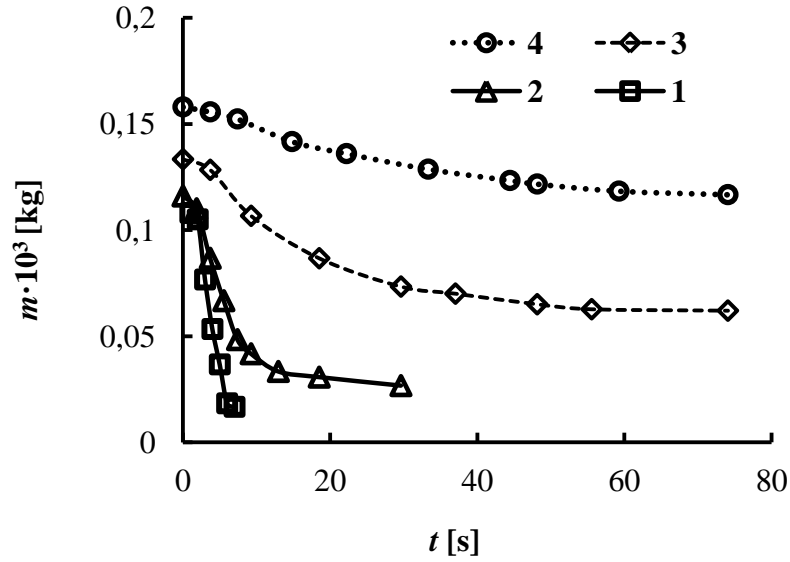


Fig. 3. Dependences for droplet desorption of aqueous salt solutions LiBr with different mass C_0 ($V_0 = 100 \mu\text{l}$; $T_w = 130 \text{ }^\circ\text{C}$): 1 - $C_0 = 11 \%$ (distillate), 2 - $C_0 = 23 \%$, 3 - $C_0 = 37 \%$, 4 - $C_0 = 51 \%$ (1-2 with nucleate boiling, 3-4 without nucleate boiling)

Successive stages of the transition of droplet nucleate boiling (a) to the desorption without boiling (b) and the formation of crystalline hydrates (c) are presented in the form of thermal images in Fig. 4.

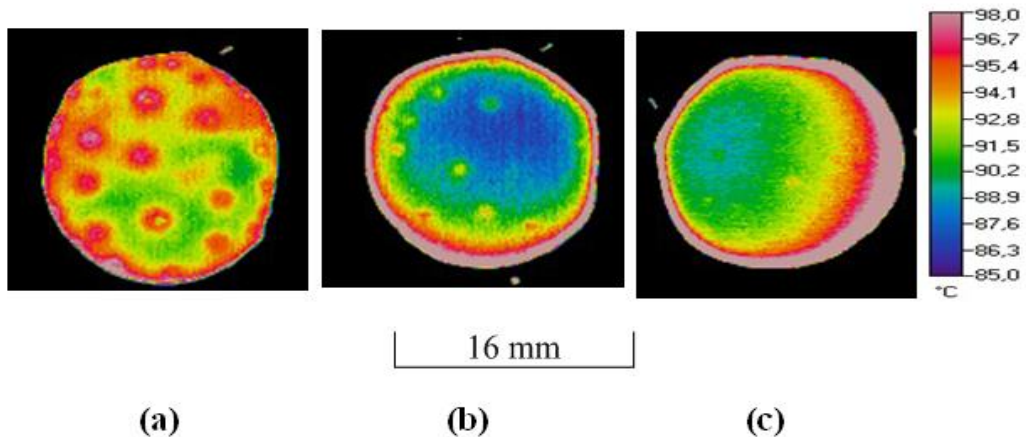


Fig. 4 Thermal images at nucleate boiling of a solution LiBr water droplet

A change in the desorption rate with time is shown in Fig. 5 (C_0 is initial salt mass

concentration, curve 1 for $C_0 = 11\%$; 2 - $C_0 = 23\%$; 3 - $C_0 = 37\%$; 4 - $C_0 = 51\%$). These curves have a maximum. A significant change in the desorption rate for solutions is one more important difference from the single-component volatile liquids when the specific evaporation heat remains constant throughout the evaporation time. The decrease in the water mass flux density can be seen from expression (2) [1], where C_s is equilibrium water concentration for the solution initial temperature T_0 ; C_0 is the initial water concentration, D is a solution diffusion coefficient, ρ is solution density, t is time, m_a is the water mass flux density through the interface ($C_0 \geq C_s$ for desorption). With a growth in time m_a decreases.

$$m_a = \frac{\rho\sqrt{D}}{\sqrt{\pi t}}(C_0 - C_s) \quad (2)$$

The salt concentration growth leads not only to the decrease in the water desorption rate, but also to a decrease in the desorption rate from the bubble microlayer surface, the rate of bubble radius increase in the solution LiBr is much lower than in pure water [33].

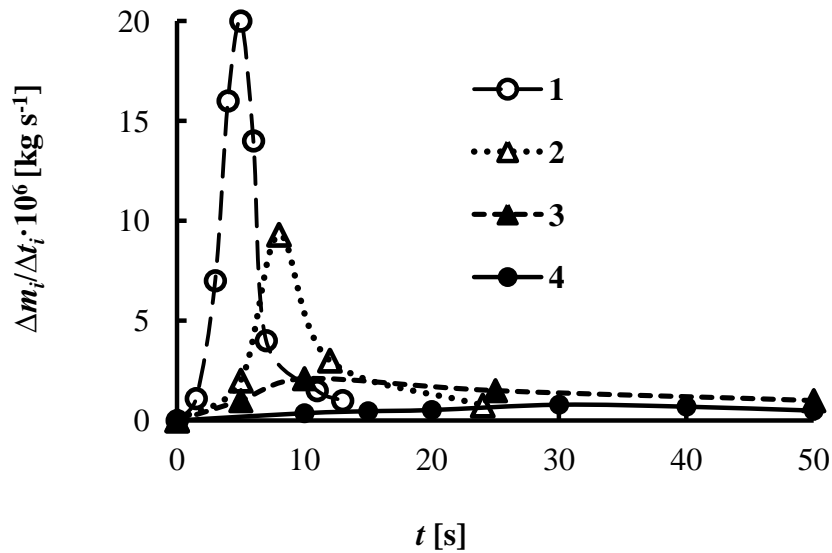


Fig. 5 A change in the desorption rate vs. time with nucleate boiling ($T_w = 136\text{ }^\circ\text{C}$; $V_0 = 100\text{ }\mu\text{l}$): 1 - $C_0 = 11\%$, 2 - $C_0 = 23\%$, 3 - $C_0 = 37\%$, 4 - $C_0 = 11\%$

The evaporation rate of solution LiBr droplet for $C_0 = 11\%$ and $t = 4-6\text{ s}$ is 30-40 times greater than that for $C_0 = 53\%$ (during nucleate boiling for curve 1). The rate of evaporation for curve 1 and $t = 13-15\text{ s}$ is 2 times greater than that for $C_0 = 53\%$ (without nucleate boiling for curve 1). This great difference in the rate of desorption for $t = 13-15\text{ s}$ is associated with significantly more thin solution film for $C_0 = 11\%$ and higher heat flux. There are several desorption regimes in Fig. 5 for curve 1: 1) droplet heating to the temperature of the boiling beginning (0-3 s); 2) the nucleate boiling regime (3-8 s); 3) the desorption regime without bubble formation (8-12 s); 4) the growth of the solid crystalline-hydrate film on the upper droplet surface (12-15 s). There are several desorption regimes

in Fig. 4: 1) droplet heating to the temperature of the boiling beginning (0-3 s); 2) the nucleate boiling regime (3-8 s); 3) the desorption regime without bubble formation (8-12 s); 4) the growth of the solid crystalline-hydrate film on the upper droplet surface (12-15 s).

3. Conclusion

The evaporation curve of the water-salt solution is essentially nonlinear and the evaporation rate decreases in time. When establishing the crystallization point after a long desorption time a crystalline thin film on the droplet surface is formed. There are several phases for this stage: the liquid salt solution, a solid crystalline hydrate film and water vapor. The evaporation rate of solution LiBr droplet for $C_0 = 11\%$, $T_w = 136\text{ °C}$ and $t = 4-6\text{ s}$ is 30-40 times greater than that for $C_0 = 53\%$ (during nucleate boiling). The rate of evaporation for indicated concentration and temperature and $t = 13-15\text{ s}$ is 2 times greater than that for $C_0 = 53\%$ (without nucleate boiling). At nucleate boiling of a droplet water-salt solution there are several characteristic regimes: heating; nucleate boiling; desorption without bubble formation; formation of the solid crystalline hydrate film. This great difference in the rate of desorption for $t = 13-15\text{ s}$ is associated with significantly more thin solution film for $C_0 = 11\%$ and higher heat flux.

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References

- [1] Nakoryakov, V.E., Grigorieva, N.I., Nonisothermal Absorption in Thermotransformers, Novosibirsk, Nauka, 2010
- [2] Lower, H., Thermodynamische und Physikalische Eigenschaften der wässrigen Lithium-Bromid-Lösung: PhD Dissertation.- Karlsruhe, 1960
- [3] Boryta, D.A., Solubility of lithium bromide in water between 50 and 100°C. (45 to 70% lithium bromide), *Journal on Chemical and Engineering Data*, 15 (1970), pp. 142-144
- [4] Nakoryakov, V. E., Experimental investigation of the nonstationary desorption of water-salt solutions in the spheroidal state, V .E. Nakoryakov and S. L. Elistratov, *Journal of Engineering Thermophysics*, 18 (2009), pp. 87-92
- [5] Grandas, L., Reynard, C., Santini, R., Tadrist, L., Experimental study of evaporation of sessile drop on a heated wall. Wetting influence, *Int. J. Therm. Sci.*, 44 (2005), pp. 137-146
- [6] Saada, M.A., Chikh, S., Tadrist, L., Numerical investigation of heat mass transfer of an evaporating sessile drop on a horizontal surface, *Phys. Fluids*, 22 (2010), pp. 112115
- [7] Brutin, D., Sobac, B., Rigollet, F., C.Le-Niliot, Infrared visualization of thermal motion inside a sessile drop deposited onto a heated surface, *Exp. Therm. Fluid Sci.*, 35 (2011), pp. 521-530

- [8] Orzechowski, T., Wciślik, S., Experimental analysis of the drop film boiling at ambient pressure, *Energy Conversion and Management*, 76 (2013), 918-924
- [9] Thokchom, A.K., Gupta, A., Jaijus, P.J., Singh, A., Analysis of fluid flow and particle transport in evaporating droplets exposed to infrared heating, *Int. J. Heat Mass Transfer*, 68 (2014), pp. 66-77
- [10] Volkov, R.S., Kuznetsov, G.V., Strizhak, P.A., The influence of initial sizes and velocities of water droplets on transfer characteristics at high-temperature gas flow, *Int. J. Heat Mass Transfer*, 68 (2014), pp. 66-77
- [11] Murisic, N., Kondic, L., On evaporation of sessile drops with moving contact lines, *J. Fluid. Mech.*, 679 (2011), pp. 219-246
- [12] Misyura, S.Y., Wall effect on heat transfer crisis, *Experimental Thermal and Fluid Science*, 70 (2016), pp. 389–396
- [13] David, S., Sefiane, K., Tadrist L., Experimental investigation of the effect of thermal properties of the substrate in the wetting and evaporation of sessile drops, *Colloid Surf.*, 298 (2007), pp. 108-114
- [14] Dunn, G.J., Wilson, S.K., Duffy, B.R., David, S., Sefiane, K., The strong influence of substrate conductivity on droplet evaporation, *J. Fluid Mech.*, 623 (2009), pp. 329
- [15] Xu, X., Luo, J., Marangoni flow in an evaporating water droplet, *Appl. Phys. Lett.*, 91 (2007), pp. 124102
- [16] Ristenpart, W.D., Kim, P.G., Domingues, C., Wan, J., Stone, H.A., Influence of substrate conductivity on circulation reversal in evaporating drops, *Phys. Rev. Lett.*, 99 (2007), pp. 234502
- [17] Karapetsas, G., Matar, O.K., Valluri, P., Sefiane, K., Convective rolls and hydrothermal waves in evaporating sessile drops, *Langmuir*, 28 (2012), pp. 11433-11439
- [18] Misyura, S.Y., Droplets boiling crisis of ethanol water solution on duralumin substrate with SiO₂ nanoparticles coating, *Experimental Thermal and Fluid Science*, 75 (2016), pp. 43–53
- [19] Nakoryakov, V.E., Misyura, S.Ya., Elistratov, S.L., Dekhtyar, R.A. Two-phase nonisothermal flows of LiBr water solution in minichannels, *Journal of Engineering Thermo-physics*, 23 (2014), pp. 257-267
- [20] Nakoryakov, V.E., Misyura, S.Y., Elistratov, S.L., Peculiarities of nonisothermal desorption of drops of lithium bromide water solution on a horizontal heated surface, *Journal of Engineering Thermophysics*, 20 (2011), pp. 338–343
- [21] Misyura, S.Y., Efficiency of methane hydrate combustion for different types of oxidizer flow, *Energy*, 103 (2016), pp. 430-439
- [22] Volkov, R.S., Kuznetsov, G.V., Strizhak P.A., Experimental investigation of mixtures and foreign inclusions in water droplets influence on integral characteristics of their evaporation during motion through high-temperature gas area, *International Journal of Thermal Science*, 88 (2015), pp. 193-200
- [23] Kuznetsov, G.V., Piskunov, M.V., Strizhak, P.A., Evaporation, boiling and explosive breakup of heterogeneous droplet in a high-temperature gas, *International Journal of Heat and Mass Transfer*, 92 (2016), pp. 360-369
- [24] Glushkov, D.O., Kuznetsov, G.V., Strizhak, P.A., Volkov, R.S., Experimental investigation of evaporation enhancement for water droplet containing solid particles in flaming combustion area, *Thermal Science*, 20 (2016), pp. 131-141

- [25] Volkov, R.S., Kuznetsov, G.V., Stizhak, P.A., The influence of initial sizes and velocities of water droplets on transfer characteristics at high-temperature gas flow, *International Journal of Heat and Mass Transfer*, 79 (2014), pp. 838 – 845
- [26] Glushkov, D.O., Kuznetsov, G.V., Strizhak, P.A., Influence of radiative heat and mass transfer mechanism in system “water droplet-high-temperature gases” on integral characteristics of liquid evaporation, *Thermal Science* 19 (2015) 1541-1552.
- [27] Piskunov M.V., Strizhak P.A., Volkov R.S., Zhdanova A.O., The features of heterogeneous water droplet evaporation in high-temperature combustion products of typical flammable liquids, *Thermal Science* (2016) (doi:10.2298/TSCI150814008P)
- [28] Feoktistov, D.V., Orlova, E.G., Islamova, A.G., Spreading behavior of a distilled water droplet on a Superhydrophobic surface, *MATEC Web of Conferenses* 23, 01054 (2015) <http://dx.doi.org/10.1051/mateconf/20152301054>
- [29] Feoktistov, D.V., Kuznetsov, G.V., Orlova, E.G., The evaporation of the water-sodium chlorides solution droplets on the heated substrate, *EPJ Web of Conferenses* 76, 012039 (2014) 1-8
- [30] Feoktistov, D.V., Orlova, E.G., Kuznetsov, G. V., Investigation of drop dynamic contact angle on copper surface, *EPJ Web of Conferenses* 82, 01053 (2015) 1-5
- [31] Nakoryakov, V.E., Misyura, S.Y., Elistratov, S.L., Nonisothermal desorption of droplets of complex composition, *Thermal Science*, 16 (2012), pp. 997-1004
- [32] Kutateladze, S.S., *Fundamental of Heat Transfer*, Academic Press, New York, NY, 1963
- [33] Misyura, S.Ya., High temperature nonisothermal desorption in a water salt droplet, *International Journal of Thermal Sciences*, 92 (2015), pp. 34-43