Yu. N. Shebeko, I. M. Smolin, A. Ya. Korolchenko, A. P. Shevchuk, A. N. Borod-kin\*

(All Russia Scientific Research Institute for Fire Protection, 143900, Balashiha-3, Moscow region, Russia)

#### ABSTRACT

Results of experimental and theoretical investigations of fire — and explosion hazard of LPG storages are presented. Evaporation intensity from LPG pool and thermal radiation intensity distribution on the surface of cylindrical vessel with LPG from pool fire placed near the vessel were measured. Available mathematical models were verified and new models were proposed for such processes, as evaporation from pool, dispersion of vapour clouds, vapour cloud explosion, behaviour of vessel with LPG placed near pool fire, BLEVE, thermal radiation from pool fire. The results are used for ensuring of fire — and explosion safety of objects with LPG storages.

#### INTRODUCTION

LPG storages are widely used in modern petrochemical plants. and explosion hazard of these objects is extremly high. This fact is confirmed by a series of accidents with fires and explosions. wich took place elsewhere in the world (Mexico, 1984: Bashkiria. 1989; Alma-ata, Kazachstan, 1989; Belgorod, Russia, 1990 et al). Ensuring of fire - and explosing safety of LPG storages is impossible without detailed investigations of such problems as description of development of large - scale accidents with fires and explosions and creation of tools for their liquidation. The decision of these problems includes as a main part a creation of suitable mathematical models and their experimental verification. Some investigations of these problems are presented in literature (see, for example, [1-5]). This work is aimed on generalization and development of pointed above investigations.

Another athors of this report are: Malkin V.L., Simonov O.A., Gurinovich L.V., Popov S.A., Kolosov V.A., Smirnov E.V.

Copyright (c) 1995 by Yu.N.Shebeko, I.M.Smolin, A.Ya.Korolchenko, A.N.Borodkin et al. Published by Khabarovsk State University of Technology, with permission.

## **EXPERIMENTAL**

In order to verify the mathematical models some large-scale experiments were performed, concerning evaporation LPG from pools and thermal radiation intensity distribution on the surface of cylindrical vessel with LPG placed near pool fire. Evaporation of LPG took place from pool made by means of spilling of liquid LPG on the surface concrete, sand, clay or metal, restricted by low hight walls (hight is less than 0.2 m). Evaporation area was from 0.01 to 2.25  $m^2$ . The chanliquid level during the evaporation was monitored by means of elecric capasity transducer with record on PC/AT 286/287. Experiments investigation of thermal radiation intensity distribution were performed on arrangement, included fragment of side surface of cylindrical LPG storage vessel of volume 200 m<sup>3</sup>, water-cooled thermal radiation intensity tranceducers placed on the fragment and two low hight walls pools with areas of 100 (10\*10 m) and 225 (15\*15)m<sup>2</sup>. These pools were made by means of spilling of LPG or and pool fires were cretead by ignition of these spills. Signals from radiation intensity transducers were recorded on 286/287. LPG. which contains propane (98%(mass.)) and butane was investigated. In fig. 1-3 typical experimental (2%(mass.)),are presented which characterise the dependence of evaporation intensity  $\bar{W}$  and specific mass evaporated from  $1m^2$  m from time t, evaporation area S, wind velocity V, air temperature  $T_a$  and material of surface from which evaporation takes place. The value of W drops rapidly with time because of cooling of solid surface on which spill was made. With elevation of air temperature and decreasing of evaporation the value of W increases. This fact is due to increase of heat exchange intensity between liquid and environment.

In fig. 4, 5 typical experimental data are presented which characterise the dependence of thermal radiation intensity, q on angle between direction on tranceducer position and vertical direction distance between vessel fragment and pool fire (in fig.4 distance between vessel fragment and pool fire is 2m for pool area  $5\text{m}^2$  and 5m for pool area  $25\text{m}^2$  and more). Thermal radiation intensity q increases from very low value in the top of fragment to maximum value near the middle of fragment.

Influence of kind of fuel in pool fire was investigated. For the area of pool fire  $25m^2$  the maximum value q for oil is equal 8 kW\*m<sup>-2</sup>, and for LPG - 31 kW\*m<sup>-2</sup>. This effect is due to extinction of thermal radiation from fire by cool soot particles in peripherical part of flame in the case of oil, for which soot production is much greater than for LPG. With the increase of distance R from pool fire to vessel fragment thermal radiation intensity decreses rapidly.

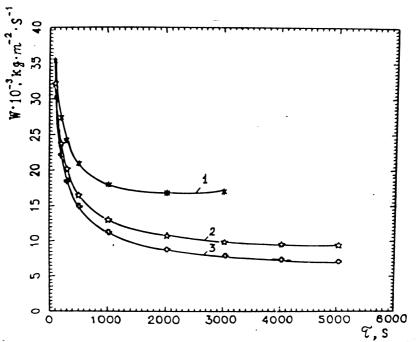
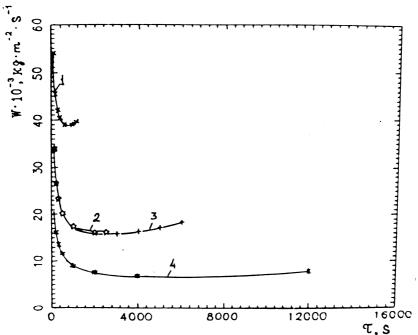


Fig. 1. Dependence of LPG evaporation intensity W from time t for various evaporation areas S. a - wind velocity  $V=0.4-2.0~{\rm m}*{\rm s}^{-1}$ . Surface material - sand.

Air temperature  $T_a = 19^{\circ} C$ . 1 - S=0.01 m<sup>2</sup>; 2 - S=0.04 m<sup>2</sup>; 3 - S=0.16 m<sup>2</sup>.



**τ,s** m<sup>2</sup>; V=1.0 b - Surface material - steel plate. 1 - S=0.01  $T_a = 31^{\circ} C$ ; 2 - S=0.01 m<sup>2</sup>; V=0.1-0.2 m\*s<sup>-1</sup>;  $T_a = 19^{\circ} C$ ; 3 - S=0.1 V=0.4-1.0 m\*s<sup>-1</sup>;  $T_a = 20^{\circ} C$ ; 4 - S=0.16 m<sup>2</sup>; V=0.4-1.0 m\*s<sup>-1</sup>;  $T_a = 20^{\circ} C$ .

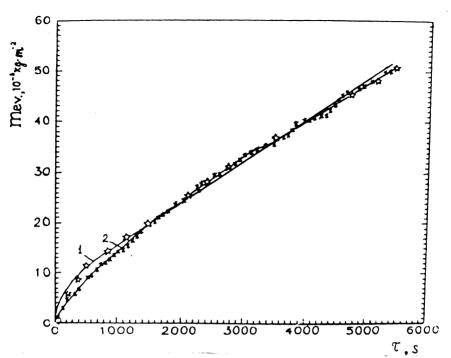


Fig. 2. Time dependence of specific evaporating mass of LPG m<sub>ev</sub>. S=0.04m<sup>2</sup>, V=0.7-1.4m\*s<sup>-1</sup>,  $T_a$ =14°C. Surface material - clay (1) and sand (2).

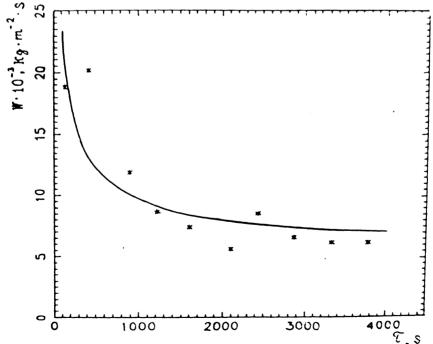


Fig. 3. Time dependence of evaporation intensity  $\tilde{W}$ . S=2.25m<sup>2</sup>, V=1-5m\*s<sup>-1</sup>, T = 6°C. Surface material - concrete. \* -experiment; -theory.

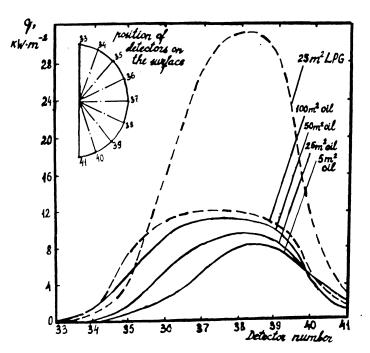


Fig. 4. Dependence of thermal radiation intensity q on the side vessel surface from angle for minimum distances from pool fires and various pool areas.

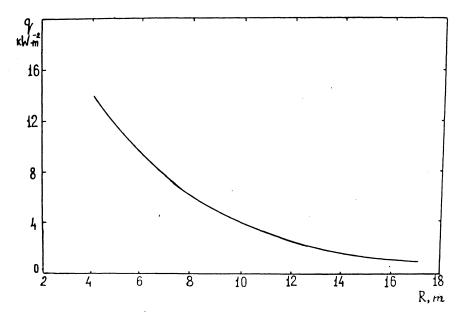


Fig. 5. Dependence of maximum value of thermal radiation intensity q from distance R between pool fire with area  $100\text{m}^2$  and vessel fragment. Combustible liquid - oil.

### Mathematical models

## a. Evaporation LPG from pools

Evaporation intensity of LPG from pools W (kg\*m-2\*s-1) can be descrtibed by the formula [6,7]:

$$W = (Q/L) M, \qquad (1)$$

weher Q - thermal flow to liquid phase of LPG,  $W*m^{-2}$ ; L - molar heat of evaporation LPG at considered temperature,  $J*mole^{-1}$ ; M - molar mass of LPG, kg\*mole<sup>-1</sup>.

Thermal flow Q has two main parts: thermal flow from solid surface Q (we propose that pool diameter is much greater than thickness of liquid layer), and thermal flow from ambient air  $Q_a$ . It was found earlier [6,7], that time of film boiling and mass of vapour appearing during film boiling, are very low in comparison with appropriate values for bubble boiling. Due to this fact, the value of Q can be described by an equation:

 $\begin{array}{c|c} Q_s = \lambda_s (\partial T_s/\partial x) \\ \hline \\ where \ \lambda_s - thermal \ conductivity \ coefficient \ of \ solid, \ \ W*m^{-1}*K^{-1}; \ T \end{array}$ 

temperature of solid, K; x - distance in the direction perpendicular to the solid surface, m (condition x=0 corresponds to boundary between solid and liquid). The value T can be described by a formula [8]:

where T - liquid phase temperature, K; T - initial temperature of solid, K, (we propose, that T is equal to temperature of air); a =  $\lambda_s/\rho_s$  c - temperature conductivity coefficient,  $m^2*s^{-1}$ ;  $\rho_s$  - density of solid,  $kg*m^{-3}$ ; c - thermal capacity coefficient of solid,  $J*kg^{-1}*K^{-1}$ ;  $\tau$  - time interval from the evaporation beginning, s;  $\Phi(y)$ - probability distribution function, described by the formula:

$$\Phi(y) = \frac{2}{\sqrt{\pi}} \int_{0}^{y} e^{-z^{2}} dz.$$

Using expression for convective part of thermal flow from [9], we can obtain for W the following formula:

$$W = \frac{M}{L} (T_o - T_e) \left( \frac{\lambda_s}{\sqrt{\pi a \tau}} + \frac{\lambda_a N u}{d} \right)$$

 $W = \frac{M}{L} \left(T_o - T_e\right) \left(\frac{\lambda_s}{\sqrt{\pi a \tau}} + \frac{\lambda_a \, \text{Nu}}{d}\right)$  were Nu=  $\alpha_a \, \text{d}/\lambda_a$  Nusselt number for thermal exchange between air and liquid;  $\alpha_a$  - thermal flow coefficient, W\*K<sup>-1</sup>\*m<sup>-2</sup>; d - effective pool diameter, m;  $\lambda_a$  - exchange thermal conductivity coefficient for air,

 $W*m^{-1}*K^{-1}$ .

Calculating results for evaporation intensity of LPG satisfactory agree with exerimental data (see fig. 3).

## b. Vapour cloud dispersion

Proposed by us vapour cloud dispersion model is based on results [16] and includes two phases of dispersion. Dispersion in the first phase is influenced by gravitational forces (falling phase). In the second phase (passive phase) cloud density is close to the air density, and dispersion is influenced by a turbulent diffusion.

For first phase we have used Van Ulden model. Temperature and concentration of LPG vapour inside cloud are proposed homogeneous. It was proposed that the vapour cloud has cylindrical form. Equations described cloud dispersion in the first phase have the following form:

$$\frac{dM_a}{dt} = \rho_a \pi r'^2 a_2 a_3 u_r Ri^{-1} + 2\rho_a a_1 \left(\frac{dr'}{dt}\right) \pi r' h, \qquad (5)$$

$$\frac{dT}{dt} = \left[ \left( \frac{dM_a}{dt} \right) C_{pa} (T_a - T_g) + \pi r^{2} (T_{gr} - T_g)^{4/3} \right] / (M_a C_{pa} + M_g C_{pg}), \quad (6)$$

$$\frac{d\mathbf{r}'}{dt} = a_4 \{ gh(\rho_{ga} - \rho_a) / \rho_{ga} \}^{1/2}, \tag{7}$$

where M<sub>a</sub> - air mass in cloud, kg;  $\rho_a$  - air density, kg\*m<sup>-3</sup>; r' - radius of cloud, m; h - hight of cloud, m; u<sub>r</sub> - wind velosity at the hight of 10 m, m\*s<sup>-1</sup>; Ri - Richardson number; a<sub>1</sub>, a<sub>2</sub>, a<sub>3</sub>, a<sub>4</sub>, - empirical coefficients; T - cloud temperature, K; T<sub>g</sub> - earth surface temperature, K; C<sub>g</sub>, C<sub>g</sub>, - thermal capacity coefficients for air and LPG vapour, J\* kg<sup>-1pg</sup> K<sup>-1</sup>. After ending of falling phase the second passive phase begins, which is described by the equation:

begins, which is described by the equation:
$$C(x,y,z) = \frac{2M_{g}}{(2\pi)^{3/2} 6^{2}_{y} 6_{z}} \cdot \exp\left[-\frac{(x-x_{c})^{2} + y^{2}}{6_{y}^{2}} - \frac{Z^{2}}{26_{z}^{2}}\right], \quad (8)$$

where 
$$-6^{2}(x) = 6^{2}(x) + 6^{2}(x-x)$$
, (9)  
 $6^{y^{2}}(x) = 6^{y^{2}}(x^{\circ}) + 6^{y^{2}}(x-x^{\circ})$ , (10)  
 $C(x,y,z) \stackrel{Z}{=} \text{concentration of LPG vapour in air, } kg*m^{-3}; x - \text{coordinate}$ 

 $C(x,y,z)^{\frac{z}{2}}$  concentration of LPG vapour in air, kg\*m<sup>-3</sup>; x - coordinate in wind direction from point of cloud appearance, m; x<sub>0</sub> - center cloud coordinate at the beginning of second phase, m;

$$6_{y}(x_{o}) = r'/2, 14,$$
 (11)  
 $6_{y}(x_{o}) = h/2, 14.$  (12)

Functions  $6_y$  (x-x<sub>o</sub>) and  $6_z$  (x-x<sub>o</sub>) are influenced by atmosphere stability class and are tabulated in [11]. For the dispersion of LPG vapour du-

ring contineous release near the ground surface we have used model analogous to described in [10].

Cloud of heavy gas in this model was described as a consequence of gaseous volumes moved in the wind direction. Concentration distribution in each of these volumes is described by a gaussian formula. The total gas concentration distribution is presented by the expression:

gas concentration distribution is presented by the expression.

$$C(x,y,z) = \sum_{j=0}^{1} \frac{2m_{j}}{6^{2}} \underbrace{6_{j}(2\pi)^{3/2}}_{j} \exp\left\{-\frac{(x-x_{j})^{2}+y^{2}}{26^{2}} - \frac{z^{2}}{26^{2}}\right\}, (13)$$

were  $m_{j}$  mass of heavy gas in j-s gaseous volume,  $kg^{z,j}$   $6_{y,j}$ ,  $6_{z,j}$  - dispensions of the expression.

persions of gas concentration distribution of j-s gaseous volume, m;  $x_{-}$  center coordinate of j-s gaseous volume, m.

It is accepted that wind direction is along x-axis. Description of heavy gas cloud dispersion during LPG evaporation from pool analogous formulated above is presented. The pool area is divided by small parts, each of these is considered as a point source of a contineous vapour release. Contributions of these parts are sumed up and made the total cocentration distribution.

Described above models are realized on PC/AT 286/287 computer. Calculated results coinside with satisfactory accuracy with experimental data [2,12,13].

## c. Vapour cloud explosion

Now there is not generally accepted reliable theoretical model for calculation of main parameters of vapour cloud explosion such as maximum pressure rise  $\Delta p$  and impulse of positive phase of shock wave i+. This fact is due to the significant dependence of above mentioned parameters in the case of deflagration from flame velocity The value of S is determined by flame front turbulization by various mechanisms, for example, autoturbulization, influence of obstacles and power ignition sources etc. Account of these factors is very compwhich dosn't have now satisfactory decision. licated task. semiempirical models are used. The more distributed method is of TNT - equivalent ( see, for example, [14]), in which shock wave parametres for vapour - cloud and TNT explosions are accepted as identi-Method, described in [15]. is based on classification of combustible mixtures according to burning velocity and obstacles characterized by blocking ratio. On this basis the possibility and probability of deflagration to detonation transition are qualitively evaluated. For our opinion the most reliable method for evaluation of parameters of vapour cloud explosions is the TNO - method [16]. The main features of this method are following. It is known that a combustion of vapour clouds in regime of deflagration in free space doesn't give rise shock waves with high amplitudes due to low flame velocity. For strong shock

wave initiation the special conditions are needed, such as restrictions the of vapour cloud by various obstacles. It is proposed that shock waves are initiated only by areas with obstacles, and parts of cloud without obstacles nevertheless they have large volumes of combustible mixture doesn't give contribution to shock wave initiation. By means of this method consequencies of well known Flixborough accident (UK, 1974) are satisfactory evaluated.

## d. Thermal radiation from pool fires

For calculation of thermal radiation intensity from LPG pool fires we have used known models (see, for example, [17]). Thermal radiation intensity on any elemantary area near the pool fire we have calculated by the formula:

$$q = \epsilon (1-\tau) \delta_0 T_f^4 \phi, \qquad (14)$$

where q - thermal radiation intensity, W\*m<sup>-2</sup>;  $\epsilon$ - absorption capability of flame ( for torch of thickness greater than 1 m  $\epsilon$ = 0.9-1.0);  $\tau$ - atmosphere absorption coefficient; 6 - Stephan-Bolzman constant, which is equal 5.67 \* 10<sup>-8</sup> W\*m<sup>-2</sup>\*K<sup>-1</sup>;  $T_f$ -flame temperature, K;  $\phi$ - angle coefficient.

We have assumed that torch has shape of vertical or inclined cylinder. For vertical cylinder the ratio of torch length 1 to its diameter D is described by the known formula [17]:

$$1/D = 42 \left(\frac{\dot{m}}{\rho_{h} \sqrt{gD}}\right)^{0.61},$$
 (15)

were m - fuel specific mass combustion rate, kg\*m^2\*^1s;  $\rho_{\rm b}$  - air density, kg\*m^3; g - earth gravitational constant, which is equal 9.81 m\* s^2.

The mean value of  $\dot{m}$  for LPG is equal 0.06 kg\*m<sup>-2</sup>\*s<sup>-1</sup>, therefore equation (15) becomes form:

$$1/D = 3.47D^{-0.31}. (16)$$

Described above method for thermal radiation calculation is sucsessfully used for determination of fire hazard of LPG storages .

# e.Behavior of vessel with LPG near pool fire

Description of behavior of vessel with LPG near pool fire has large practical importance for determination of possibility of BLEVE (Boiling Liquid Expansion Vapour Explosion) with shock wave and fireball

formation. Some models described heating of car and railway tanks of relative low capacity and atmospheric pressure tanks (see, for example, [15,18]) are presented in literature. But there are absent models for determination of safe distances between large stationary LPG and flammable liquids storages. We have proosed mathematical model for decision of this problem.

Proposed model includes four sub-models:

- 1. Thermal radiation source parameters calculation.
- 2. Calculation of internal pressure in vessel.
- 3. Determination of dry wall temperature distribution.
- 4. Determination of permissible radiation intensity and safe distance between storages.

The basis for thermal radiation source sub-model was described above. For calculation of internal pressure in vessel we have taken into account that this pressure depends on value of total thermal flow to liquid phase, type of product in the LPG storage and relief valve characteristics. In stationary regime total evaporation rate is equal to vapour relief rate through a valve. It was shown that internal pressure in the case of large vessels (greater than 50 m $^3$ ) doesn't exceed significantly pressure of relief valve operation even for thermal radiation intensity on the surface of vessel up to 40 kW\*m $^{-2}$ .

In order to calculate permissible dry wall temperature T the critical value of this temperature T is determined for each value of internal strains 6. If T is greater than T vessel destruction takes place. The dependence of 6 T for various types of steels is presented in [19]. Thus for each type of vessel and internal pressure P permissible dry wall temperature T can be determined. For determination of permissible thermal radiation intensity some propositions are made, which give the upper limit for dry wall temperature and thus some safety reserve. These propositions are:

- maximum wall temperature is observed for dry walls, but temperature of walls contacted with liquid phase doesn't exceed  $40 50^{\circ}$ C;
- after some time from fire begining wall temperature at each point reaches its stationary value, and then heat exchange process proceeds in stationary regime;
- thermal flow across wall has mainly crossectional direction;
- during the LPG vessel heating strong thermal stratification of vapour phase takes place, therefore in upper region of vapour space stagnation zone formed, and in this zone heat conduction from internal wall surface to vapour phase is negligible.

Typical calculated results of safety distance between LPG storages (horizontal cylindrical vessel with volume of  $200\text{m}^3$  or spherical vessel with volume of  $600\text{m}^3$ ) and flammable liquid (kerosene) storages are presented in the table.

Vessel parameters and safety distances	Values of parameters for following volumes (m³) of flammable liquid storages					
	1000	2000	5000	10000	20000	40000
Diameter of liquid	10.4	15.2	20.9	28.5	39.9	56.9
vessel, m Hight of liquid vessel, m Safety distances	11.9	11.9	14.9	17.9	17.9	17.9
for LPG vessels: cylindrical spherical	26 34	30 39	37 46	48 55	62 68	78 84

## CONCLUSIONS

Results of theoretical and experimental investigations directed to fire — and explosion safety of large LPG storages are presended. Thermal radiation intensity and their distribution across side surface of cylindrical vessel are measured. Evaporation intensity of LPG at various conditions was determined. Main features of theoretical models decribed physical processes at the accidents on LPG storages are stated. Proposed models and experimental results can be used for prediction of accident scenarios with fires and explosions on large LPG srorages.

#### REFERENCES

- 1. Marshall V., 'Main hazards of chemical industry', Mir, Moscow, 1989, pp. 1-571.
- 2. Komov V.F., Reutt V.C., Grishin V.V. et al., 'Fire engineering and extinguishing of fires', VNIIPO, Moscow, 1973, 3, pp. 18-24.
- 3. Fire's F.L.'Fire Engineering', 1989, 142, 1, 51.
- 4. Hadjisophocleous G.V., Sousa A.C.M., Venart J.E.S., 'Jouanal of Hazardous Materials', 1990, 25, 1-2, 19.
- 5. Leslie I.R.M., Birk A.M., 'Journal of Hazardous Materials', 1991, 28, 3, 329.
- 6. Komov V.F., Grishin V.V., Krivulin V.N., 'Problems of combustion and fire extiguishing', VNIIPO, Moscow, 1973, pp. 188-195.
- 7. Popov P.S., Reutt V.C., Grishin V.V., 'Express information VNIIPO. Series: Fire prevention in industry and building', VNIIPO, Moscow, 1974, 36, pp.1-14.
- 8. Vladimirov V.S., 'Mathematical physics equations', Nauka, Moscow, 1972.
- 9. Frank-Kamenezky D.A., 'Diffusion and heat conduction in chemical kinetics', Nauka, Moscow, 1987.

- 10. Ziomas I.C., Zerefos C.S., Bais A.F., 'Loss Prev. Process Ind.', 1989, 2, 194.
- 11. Burgess D.S., Zabetakis M.G., 'Rept. Invest. Bureau of Mines N7752', Bureau of Mines, Washington, 1973, pp. 1-26.
- 12. Van Ulden A.P., 'First Int. Symp, on Loss Prevention and Safety Promotion in the Process Ind.', 1974, pp. 221-226.
- 13. Brighton P.W.M., Prince A.J., Webber D.M., 'Journal of Hazardous Materials', 1985, 11, 1, 155.
- 14. 'Codes of practice for explosion safety ensuring of fire and explosion hazardous chemical and petrocchemical plants', Metallurgia, Moscow, 1989, pp.1-86.
- 15. Sherman M.P., Berman M., 'The possibility of local detonation during degraded core accidents in the Bellefonte nuclear power plant. NUREG/CR-4803. SAND 86-1180', Sandia National Laboratory, Albuquerque, 1987, pp.1-35.
- 16. Van den Berg A.C., 'Joutnal of Hazardous Materials', 1985, 12, 1, 1.
- 17. Babrauskas V., 'Fire Safety Journal', 1986, 11, 1-2, 33.
- 18. Safonov V.S., Tarabrin V.A., 'Tehnological aspekts of gas transport', VNIIGAS, Moscow, 1988, pp. 125-143.
- 19.'GOST 14249-80. Vessels and equipment. Codes for methods of stability calculations', GOSSTANDART, Moscow, 1980, pp.1-62