HYDROGEN DISTRIBUTION IN ENCLOSURES: ON DISTINCTION CRITERION BETWEEN QUASI-HOMOGENEOUS MIXING AND STRATIFICATION MODES

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ABSTRACT

Understanding of the specific features of formation of the hydrogen-containing clouds inside of confined spaces is important for fire or explosion protection of the hydrogen facilities. Different sub-sonic modes of light gas (hydrogen and helium) release (with flowrates up to 0.1 g/sec) have been studied experimentally in sealed cylindrical vessel and in cubic enclosure with non-zero gas-tightness. During analysis of the experimental records, two different modes of hydrogen field evolution have been revealed. A criterion for differentiation between stratification and quasi-homogeneous mixing modes are proposed and justified on the base of obtained new experimental data and extension of the known analytical criteria.

1.0 INTRODUCTION

Due to the development of hydrogen energy, there are the questions connected with providing an advanced explosion and fire safety of new objects of civil technical infrastructure on which hydrogen is applied as the main power source. Hydrogen safety is also important for operation of nuclear power plants where during accidents a large amount of hydrogen can be allocated. A need of better understanding of hydrogen distribution as well as other light combustible gases for confined and semi-confined enclosures of various configurations dictates implementation of additional experimental and theoretical works in this area.

This work is devoted to studying the distribution of hydrogen in the confined rooms in which the cross sizes do not strongly differ from their heights. This type of enclosures can adequately model single garages for hydrogen cars, and also certain rooms at the nuclear power plants or at hydrogen-fueled industrial premises.

Leakages of hydrogen, which happen during equipment crashes, can be characterized by two main types of releases: in the form of a jet and in the form of a plume. Jet releases can occur at a point damage of pipelines which are located on external parts of the equipment, so that the gas can freely outflow to the room. Plume releases can be formed at a damage of the hydrogen equipment in the confined casings so that the gas before its outflow to the room is retarded on various mechanical obstacles. The jet releases are, mainly, characterized by a high speed and initial momentum and rather small diameter of a leak. The plume releases are, predominantly, characterized by a low initial speed and momentum and rather large effective diameter of a leak.

So-called plume formation distance L_j [5] is applied for the quantitative distinction of jet and plume release modes of a light gas, that is such distance from the release point in upward direction along the flow where momentum acquired owing to buoyancy becomes comparable with initial momentum of releasing gas stream. Thus, any releasing jet of a light gas at a vertical distance $z > L_j$ turns into a plume. Therefore they speak about the plume release mode of a light gas in the confined room when L_j is significantly less than vertical sizes of the room: $L_j << H$, and contrary they speak about the jet release mode when L_j is greater than vertical sizes of the room: $L_j > H$ (to be more precise, H is the distance from release point to ceiling). The value of L_j is calculated by the formula:

$$L_j = w_0 \cdot (\sqrt{D_0} / \sqrt{\Delta_0}) = 0{,}32 \cdot w_0 \sqrt{D_0}, \quad \Delta_0 = g \cdot (\rho_a - \rho_H / \rho_a) \tag{1}$$

where w_0 – initial release velocity, D_0 – release diameter , ρ_a – air density, ρ_H- hydrogen density, Δ_0 – initial buoyancy. The coefficient 0.32 is taken for hydrogen. For helium this coefficient will be 0.33.

The main objective of our study was experimental investigation of the hydrogen distribution characteristics in confined spaces in the jet and plume modes under controlled initial and boundary

conditions with high spatial and time resolution, and also the comparison of the obtained results with available theoretical models.

2. EXPERIMENTS

The main research tool was a specially developed system of data acquisition consisting of 24 digital gauges of hydrogen (helium) concentration and temperature, united in the common consecutive digital system of data collection connected to computer. The electronic platform of each gauge contained concentration sensors - heat conductivity meters TCG-3880 (Xensor Integration) and temperature sensors - chips DS18B20 (Dallas Semiconductors). All measurements and exchange of information on the network were carried out under control of the programmed microprocessor module on the basis of the single-crystal Atmel microcontroller, placed on the platform of each sensor. Data acquisition rate from the network matrix of gauges made up to 3 measurements per second simultaneously from all 24 sensors. Absolute long-time accuracy of measurement of volume concentration of these gases was 0.1 vol. %. Temperature control was fulfilled for elimination of heat convective flows. Accuracy of temperature measurements was 0,01 K. Also two digital overall pressure sensors linked to the common network of gauges was used. Details of data acquisition system are given in [6, 7].

Two experimental installations were used as confined volumes into which the hydrogen was released.

The first experimental chamber represented a hermetic vessel of "barrel" type of 4 m^3 in volume and of 1. 28 m in diameter into which hydrogen was released in a wide range of gas flows (from $0{,}005\times10^{-3}$ to $0{,}53\times10^{-3}$ m^3/sec.) regulated by a gas automatic batchers. The main part of gas mixture conditioning and transport system was the gas mixture preparation device. It allows to mix complex gas mixtures (up to 8 components) at the concentration range for every component from 0 to 100% with the step of 1/256 and relative accuracy 0.5%. Gas mixture preparation device permits to establish and to control a steady gas flow rate from $5\cdot10^{-6}$ to $7\cdot10^{-4}$ m^3/s. This "barrel" type experimental set-up was depicted in details in the works [6, 8]. It was specially designed and certificated for work with hydrogen and the other explosive gases.

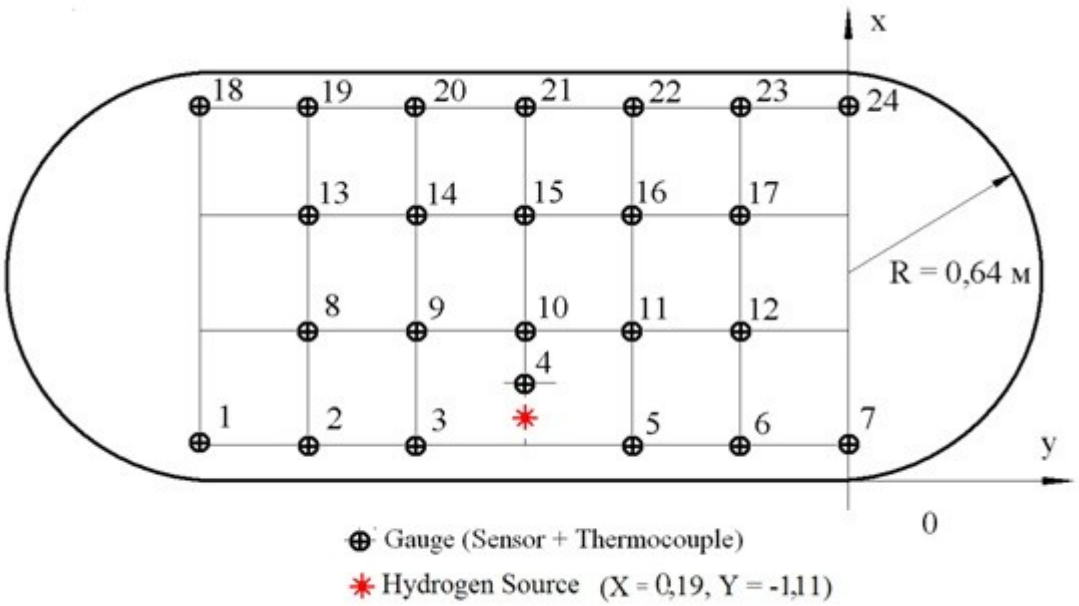

Figure 1. Scheme of spatial allocation of the hydrogen concentration and temperature gauges in the barrel-type experimental chamber.

"Barrel" was allocated inside the concrete dome. In our experiments, hydrogen was released into the chamber through a round opening of constant diameter D_0 = 14 mm located in the lower part of the cylindrical volume. At Fig. 1 the scheme of sensors' allocation is shown: the matrix of 24 gauges with sensors of hydrogen and temperature was mounted in the "barrel" on seven vertical rods allowing to fix position of each sensor in the plane of the vertical axial section of the cylinder.

The formation of a hydrogen-air mixture cloud was investigated during 15-30 min. of hydrogen release in vertical, horizontal and lateral directions. The releases were accompanied by the subsequent free dispersion (15-30 min.) of explosive mixture inside the volume. Because this chamber was hermetic the overall pressure increase occurred during the injection of hydrogen. Pressure increase was measured by two digital pressure sensors. Maximum value of this pressure increase was less than 10% of overall pressure inside of "barrel" [8].

Key parameters of the representative experiments in the sealed barrel in the case of vertical hydrogen releases are presented in Table 1. The experiment № 3 was fulfilled not only for upward release direction but also for lateral and downward release directions at the same injection point. For calculation of Reynolds number, the value of kinematic viscosity of hydrogen equals to $1 \cdot 10\text{-}4$ m^2/s was used. The diameter of the release pipe of D_0 = 14 mm was taken as the characteristic size . The given in Table 1 values of Reynolds numbers were estimated for the initial stage of the release.

One can see from the Table 1 that all hydrogen releases are of the plume type, because plume formation distance L_j in all cases is much less than the height of the barrel H equal to 1,28 m.

The main goal of experiments in this experimental chamber was clarification of the limits of applicability of the so-called «filling-box» model, offered by Baines and Turner [3] (1969) for the plume releases in the confined rooms.

Table 1. Hydrogen releases in sealed "barrel" (vertical releases case).

Exp.№	**Release flow rate Q_0 10^{-3} m^3/s**	**Release velocity w_0, m/s**	**Plume formation distance L_j, m**	**Ratio $\frac{L_j}{H}$**	**Reynolds number $\mathrm{Re} = \frac{w_0 D_0}{\nu_{H_2}}$**
3	0.52	3.38	0.13	0.102	470
4	0.43	2.79	0,11	0.086	390
5	0.29	1.88	0.07	0.055	260
12	0.020	0.13	0,005	0.004	18
13	0.005	0.032	0.001	0.0008	5

The second experimental chamber was a confined parallelepiped. it has approximately a cubic form of 9 m^3 volume and 2 m height. There were investigated both plume and jet modes of helium release – hydrogen substitute. In experiments under consideration, all venting windows and door were closed in order to minimize influence of the ventilation effects. However, despite precautions it wasn't completely hermetic, so it imitated usual rooms. In more details this experimental camera ("garage") is described in [9]. The scheme of arrangement of the gauges in "garage"-type experiments are shown in Fig. 2.

In Table 2 the parameters of the representative experiments in the "garage"-type experimental chamber are specified. Experiments were executed at the same helium release flow rate, but with different diameters of the release pipe. The point of the release was at 49 cm height from the room floor. Helium was released vertically during 25 minutes in each experiment. The values of Reynolds numbers in the table are counted for an initial region of the release flow where the initial diameter of the release pipe D_0 is taken as the characteristic size.

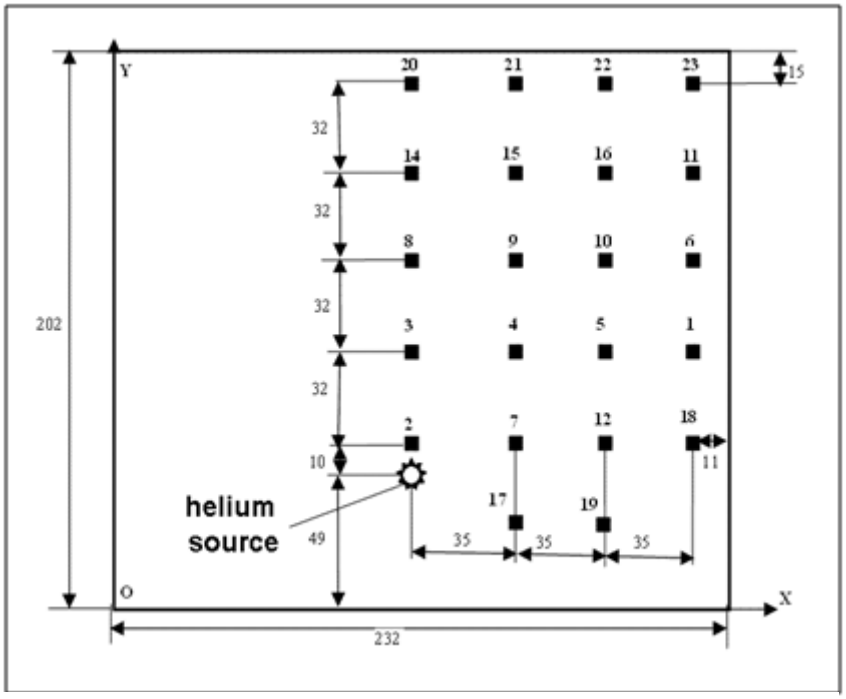

Figure 2. Gauges allocation scheme in the "garage"-type experimental chamber. The sizes are specified in centimeters.

Table 2. Hydrogen releases in "garage"-type chamber (closed ventilation windows and door).

Exp. №	**Release diameter D_0, mm**	**Helium release flow rate $Q_0\ 10^{-3}$ m^3/s**	**Plume formation distance L_j, m**	**Ratio $\frac{L_j}{H}$**	**Reynolds number** $\mathrm{Re} = \frac{w_0 D_0}{\nu_{H_2}}$	**Release type**
1	0,6	0,47	7,3	4,8	5400	Jet
2	1	0,47	4,8	3,1	4600	Jet
3	2	0,47	2,23	1,5	3000	Transitional
4	4	0,47	0,78	0,5	1500	Plume
5	8	0,47	0,28	0,18	750	Plume

The main objective of the experiments in the "garage"-type chamber was identification of the transition between two different types of light gas filling of the confined volume – stratification and mixing depending on conditions of helium release from the source point.

3. EXPERIMENTAL RESULTS

The primary theoretical model with which the experimental data obtained for the plume modes of hydrogen release are compared is the so-called "filling-box model", developed in the works of Morton, Turner and Baines [1,2,3]. In the confined room an upflowing turbulent plume forms vertically stratified ceiling layers of hydrogen-air mix descending with deceleration towards the floor. The following assumptions are taken into account in this model 1) fast spreading of hydrogen horizontally across the room in comparison with the speed of vertical descent of the ceiling layer; 2) absence of vertical mixing because of the stabilization of vertical streams by density gradient; 3) diffusion processes aren't considered. The quantitative comparison of experimental data with the theory in the plume mode releases was carried out according to the approximate analytical solution of the main equations of the filling-box model which proposed Worster and Huppert [4] in 1983. This solution gives stratification of hydrogen concentration from a maximum at the ceiling to some nonzero value on the first front, which propagates with deceleration down to the level of hydrogen release point. Stratification degree in this model doesn't depend on the hydrogen release flow rate. The analytical solution of the equations in this model is given in the form of dimensionless spatial and time profiles of concentration of hydrogen and described by quite bulky relations which, however, can be easily programmed on a computer for the purpose of comparison to experimental data.

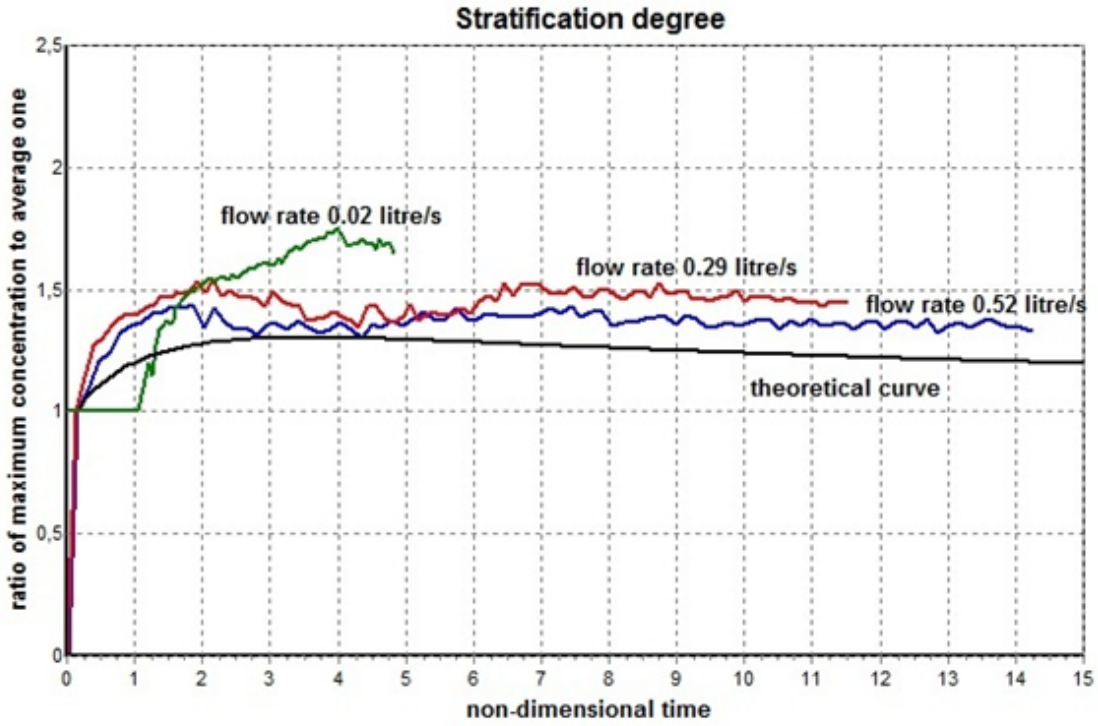

Figure 3. Ratio of maximum concentration to average one versus non-dimensional time for different flow rates at vertical hydrogen release.

In Fig. 3 the results of calculation of the vertical stratification degree are presented for experimental data with various hydrogen flow rates at the injection point from Table 1 for experiments №. 3, 5 and 12. Hydrogen concentrations on vertical were usually taken from the line of the sensors № 6, 12, 17, 23. These concentrations at any time were strongly the same as from other vertical lines of sensors except for the central line where hydrogen release occurred. The stratification degree is taken as the ratio of the maximum light gas concentration to the average one along a vertical line as it was

proposed by R.J. Harris in the work [10] in the capacity of the mixing degree. Still, as the lower point for averaging concentration procedure we took the level of the first front of hydrogen downward propagation in order to get an adequate stratification degree coefficient. At such a choice the stratification degree equal to 1 gives a homogeneous layer between ceiling and the first front. The value of this coefficient equal to 2 gives the linear decline of light gas concentration from ceiling to the first front. A value between 1 and 2 gives a slower than linear decrease of concentration and a value greater than 2 gives a faster than linear decrease of concentration from ceiling to the first front. In Fig.3 the experimental results for three different hydrogen release rates are compared depending on non-dimensional time, which is calculated in accordance with Worster and Huppert formalism [4] and is proportional to the volume release rate to the power of ⅓. All three experimental curves in Fig.3. correspond to the same physical time of hydrogen injection of 15 minutes. Also we can see in Fig.3 the theoretical curve for the proposed stratification degree calculated on the basis of Worster and Huppert time-dependent density profiles in a filling box [4]. It is independent upon the release flow rate.

The shown dependences correspond to the hydrogen release in upward direction. The similar dependences at the hydrogen lateral and downward releases differ weakly from these ones. It should be noted, however, that at the hydrogen release downward the stratification degree is slightly lower and mixing happens better. The highest stratification degree and, therefore, the lowest vertical mix occur at the hydrogen release in upward direction. It is shown in Fig.4.

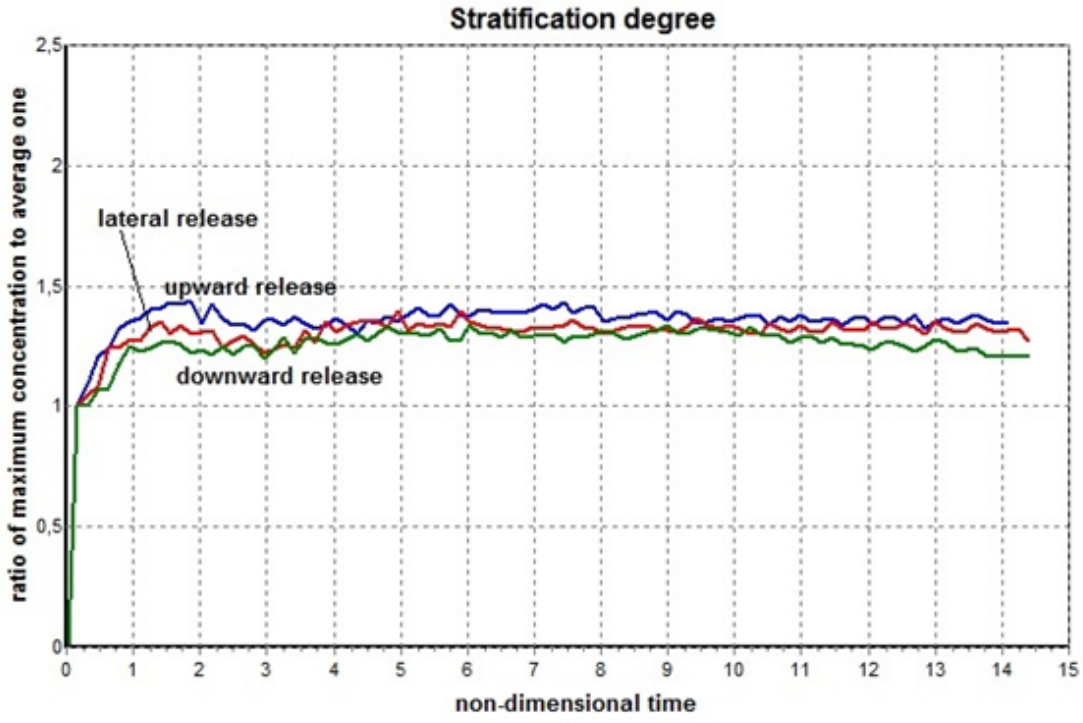

Figure 4. Ratio of maximum concentration to average one versus non-dimensional time for three different directions of hydrogen release at the same flow rate 0,52 litre/s.

From Fig. 3, it can be seen, that the stratification degrees (vertical inhomogeneities) in experiments No. 3, 4, 5 from Table 1, being characterized by rather high flow rates and initial Reynolds numbers Re > 250, weakly differ from each other and slightly differ from the theoretical curve. This slight difference with the theoretical curve we explain by a degradation of the first front by diffusion, which isn't taken into account by the theory. However in experiment No. 12, being

characterized by much smaller flow rate and initial Reynolds number Re ≈18, the stratification degree is visibly higher. As the quantitative model "filling box" of Worster and Huppert [4] doesn't give distinction in the stratification degree depending on the release flow rate (see the theoretical curve in Fig.3), it is possible to draw a conclusion that this model describes unsatisfactorily the hydrogen release in experiment No. 12 with a small flow rate.

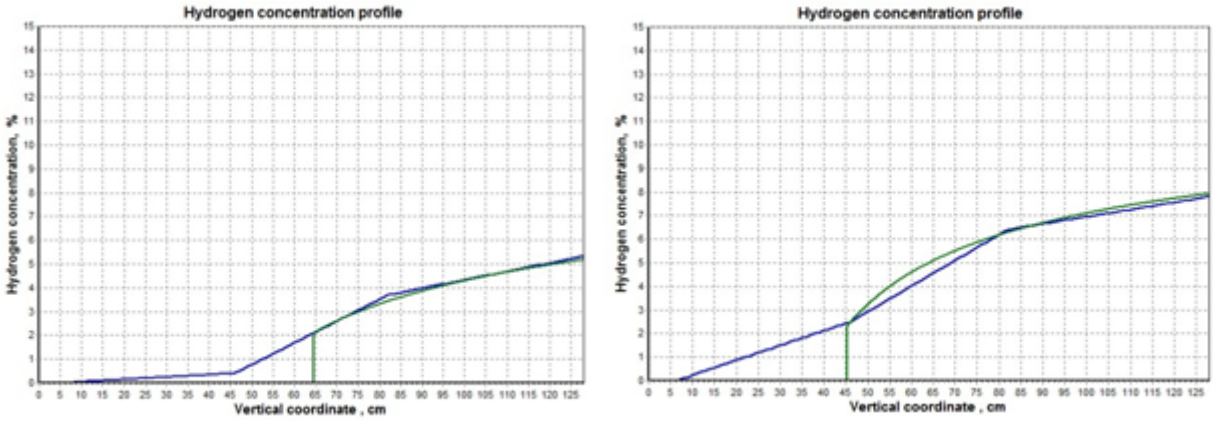

Figure 5. Experimental (blue) and calculated (green) profile of hydrogen concentration on vertical: flow rate - 0,29 litre/s, 5th and 10th minute, α = 0,08.

At Fig. 5, a comparison of experimentally measured spatial profile of hydrogen concentration and the profile counted on the basis of the quantitative model "filling box" in experiment No. 5 from Table 1 on 5th and 10th minutes is made. For turbulent entrainment coefficient α it was taken a typical value 0,08. It is apparently from the presented comparison that the theoretical model very precisely describes the profile of hydrogen concentration except for the degradation of the first front of concentration moving toward the floor. The theoretical model "filling box" gives concentration jump on the first front while in reality the first front is indistinct because of the processes of diffusion which aren't considered by the model. The experimental curves are constructed by a method of linear interpolation between indications of sensors without smoothing. Unsmooth form of these curves is explained by interpolation.

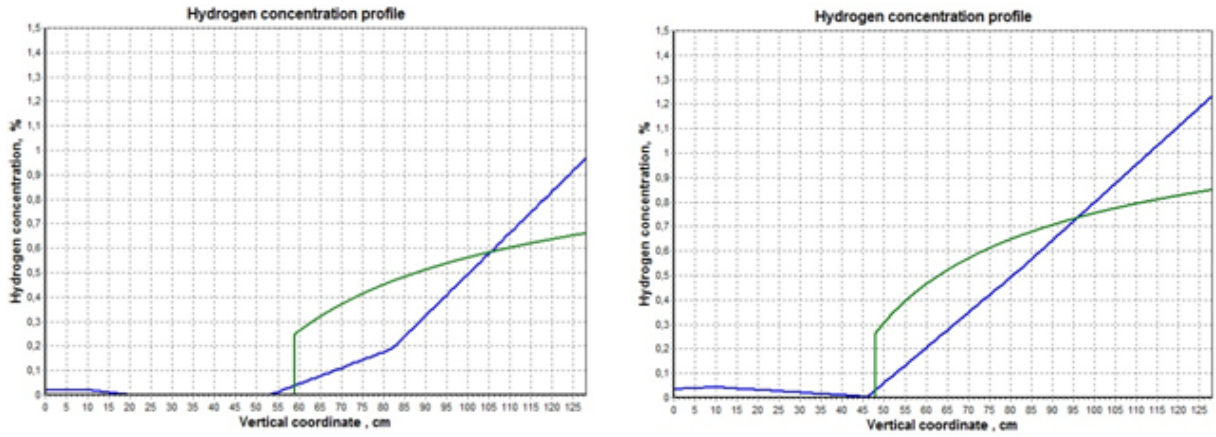

Figure 6. Experimental (blue) and calculated (green) profile of hydrogen concentration on vertical: flow rate - 0,02 litre/s, 10th and 15th minute, α = 0,08.

In Fig. 6 it is presented the comparison of experimentally measured spatial profile of hydrogen concentration and the profile counted on the basis of the quantitative model "filling box" in experiment No. 12 from Table 1 with α = 0,08 on 10th and 15th minutes.

It can be seen, that in this case the quantitative model "filling box" doesn't work: the experimental profile shows considerably big stratification in the ceiling layer, than it follows from the theoretical model. It corresponds also to the conclusion, drawn on the basis of Fig. 3 for the same experiment No. 12. We believe that experimental result is in good agreement with the results of the work [12] by B. Cariteau where at low flow rates the upper layer of nearly uniform concentration is formed directly under the ceiling, with higher concentration than theoretical model predicts, below which hydrogen concentration decreases quickly

For experiments, which have been carried out in the second, "garage"-type experimental chamber, the vertical concentration profiles in the region outside the upflowing stream in different time points were plotted. Such profiles for experiments No. 1 and No. 5 of Table 2 are shown in Fig. 7.

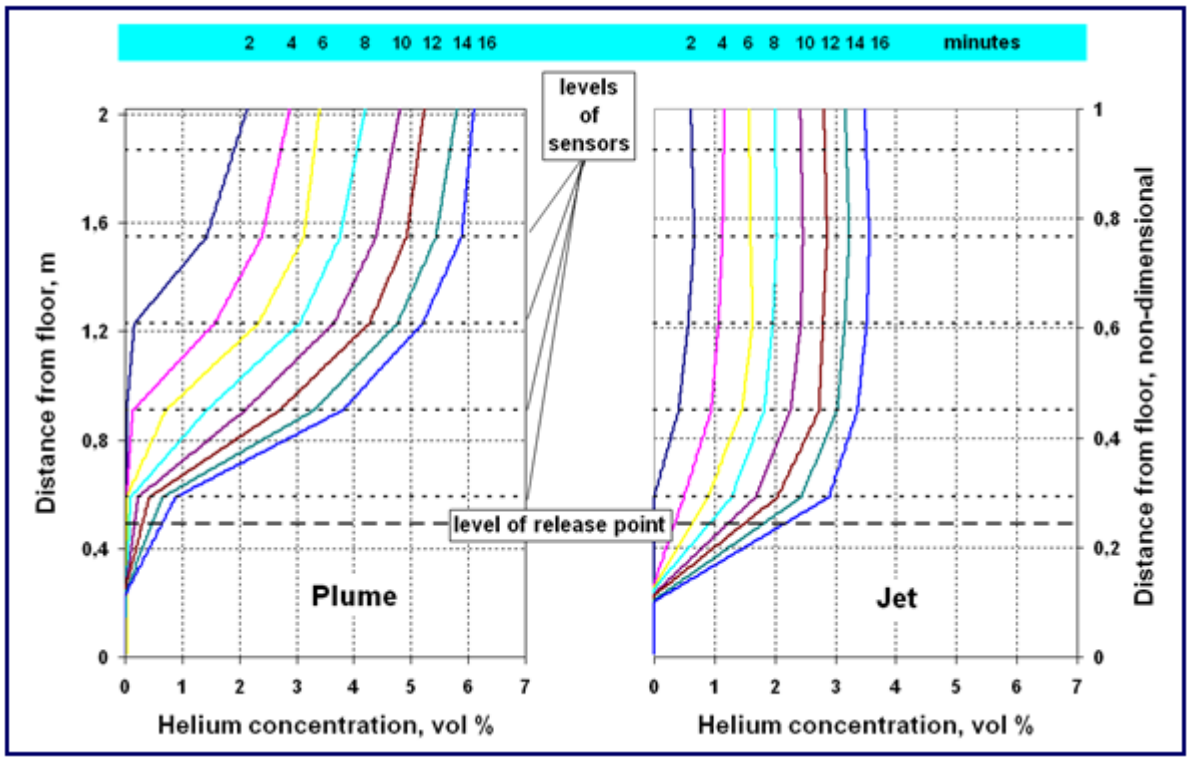

Figure 7. Difference of vertical profiles of hydrogen concentration in "garage"-type experimental chamber in the plume release mode (left picture) and in the jet release mode (right picture) at the same release rate 0.47 litre/s.

It can be seen from Fig.7, that profiles for the plume mode strongly differ from the profiles for the jet mode of helium release at the same initial flow rate. In case of the plume release modes the profiles of concentration are well described by the quantitative model "filling box" assuming stratification, how it was already shown for experiments on the first experimental barrel-type chamber (see Fig. 5). For the jet modes of helium release a sharp decrease of stratification degree is observed. Practically all space above the release point is uniformly filled with helium so concentrations at any level weakly differ from each other at any moment and are well described by the following time dependence:

$$C_{\text{H}} = \frac{Q}{V} t \qquad (2)$$

where Q – volume flow rate of a light gas, V –volume of chamber portion above the source. The exception is made by some small area directly over a helium source where concentration starts falling down and falls down to zero at level already below the source. Thus, there is a good mixing of helium with air practically in all volume above the source. Quantitatively the average gradient of concentration on two thirds of length from the ceiling to the source level for experiment No. 5 (Tab. 2) presented on the left in Fig. 6 surpasses order of magnitude the similar gradient for experiment No. 1 (Tab. 2) presented on the right side in Fig. 6.

In Fig.7, time evolution of explosive volume (4% < CH2 <74%) in case of plume (left slides) and jet (right slides) releases is presented for the same experiments No. 1 and 5 from Table 2. Two dimensional profiles were performed by an interpolation method according to concentration data given by 24 gauges. It can be seen from Fig.7 that time evolution of hydrogen-air mixture cloud (concentration within flammable range 4% < C_H <74%) in case of the plume release happens quite differently than in case of the jet release. In particular, in described experiments in case of the plume release with ratio $L_j/H = 0{,}18$ the flammable cloud appeared already on 7th minute, slowly increased and on 21th minute and occupied 60% of all room volume. But in case of the jet release with ratio $L_j/H = 4{,}8$ the flammable cloud appeared only on 19th minute, yet the volume of cloud began to grow very quickly and on 21th minute developed into 66% of all volume of the enclosure.

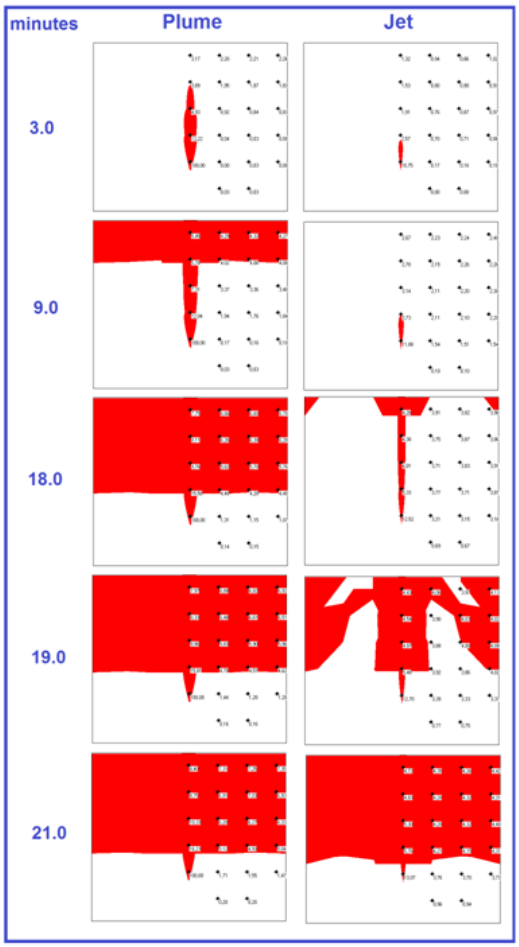

Figure 8. Time evolution of flammable cloud (4% < CH2 <74%) in case of plume release (left side) and jet release (right side) in "garage"-type experimental chamber.

4. DISCUSSION

Conducted experiments don't conclude all possibilities of the jet and plume releases in confined rooms with comparable vertical and horizontal sizes. For the plume modes according to recommendations and formulas of the work of Baines and Turner [3] (1969) we made analytical estimates of the ratio of competing forces: force of inertia I equal to buoyancy-induced plume momentum flux M_{plume}, to stabilizing buoyancy force B in the ceiling layer ($z \approx H$) with thickness about the radius of the plume near ceiling:

$$(I/B)_{plume} \approx \frac{9}{10}\pi\alpha\left(\frac{H}{L}\right)^2 \qquad (3)$$

where L – the cross sizes of the room, $\alpha \approx 0{,}08$. Baines and Turner hypothesized that vertically stratified ceiling layers develop when the stabilizing plume buoyancy force is greater than buoyancy driven plume momentum at the ceiling. This idea was numerically developed by Kaye and Hunt [11]. As long as the rooms for which the vertical and cross sizes differ not too much are considered, for any turbulent plume inside such a room where $L \geq H$ it turns out that $I/B \leq 0{,}3$ and overturning and mixing of the ceiling layers don't occur. It is also confirmed by conducted experiments, where for all cases of the plume release stratification is observed in accordance with the "filling box" model except for small flow rates where stratification degree even increases. Only for high and narrow rooms where $H/L \geq 2$ one should expect overturning of layers and mixing in the plume release mode. Thus, the criterion $L_j/H << 1$ at which the relation (3) is valid, automatically becomes also the criterion of stratification of layers in the mode of hydrogen plume release in the usual confined rooms where height does not exceed width too much.

For the jet and plume release modes the estimation of ratio of momentum fluxes was fulfilled for identical initial flow rates of hydrogen release:

$$M_{jet}/M_{plume} = 2{,}14 \cdot \left(L_j^{jet}/H\right)^{\frac{4}{3}} \qquad (4)$$

From where it follows that the condition of the jet release in a confined room $\frac{L_j}{H} >> 1$ automatically leads to that momentum of the jet under the ceiling M_{jet} will be much higher than momentum of the plume M_{plume} with the same release flow rate.

Then the criterion I/B for hydrogen jet gives:

$$(I/B)_{jet} \approx 0{,}86\left(L_j/L\right)^2 \qquad (5)$$

If L (cross size of the room) doesn't exceed height H too much, then:

$$(I/B)_{jet} \approx \left(L_j/H\right)^2 \qquad (6)$$

Thus, the criterion $L_j/H >> 1$ of the jet mode automatically leads to a prevalence of forces of inertia over stabilizing forces of buoyancy and, therefore, becomes also the criterion of mixing of layers over the source in the mode of jet release of hydrogen in confined rooms not too extended on their cross sizes L.

In case of the plume releases with a small initial flow rate our experiments revealed considerably larger degree of stratification than it is foretold by the quantitative model "filling box" developed by Worster and Huppert [4] (1983). That apparently is connected with inapplicability of the scheme of turbulent mixing accepted in the model, seemingly because at small flow rates a releasing gas stream is not turbulized considerably even at the contact with ceiling. In case of such releases, as experiments revealed, hydrogen creeps under ceiling as a thin layer which very slowly increases its thickness, extending in the direction downward to the release source. That creates essentially other mechanism, than in the filling-box model, of hydrogen filling of a confined room when under ceiling a peculiar "lens" with increased hydrogen concentration is formed, to all appearances,

owing to the lack of essential turbulent air entrainment by the upflowing plume.

5. CONCLUSIONS

Our main conclusion consists in that the plume releases of hydrogen in confined rooms with heights H not surpassing the cross sizes L too much always give vertical concentration stratification at filling a room with hydrogen while the jet releases always give a good mixing if the cross sizes L of a room do not surpass its height H too much. However, numerical values of distinctions of heights of confined rooms from their cross sizes, at which the specified regularities are still valid, need further specification.

Stratification degree of hydrogen concentration along vertical in the plume release modes is well described by the quantitative model "filling box" making allowance for degradation of the first front by diffusion. However experiments revealed that for the plume releases with very small value of the parameter $L_j / H \le 0{,}01$ being characterized by a small hydrogen flow rates and small initial Reynolds numbers $\mathrm{Re} \le 50$, vertical stratification degree of hydrogen concentration turns out to be significantly larger than the quantitative model "filling box" predicts.

ACKNOWLEDGMENTS

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REFERENCES

1. Morton, B.R., Taylor, G.I., Turner, J.S., Turbulent gravitational convection from maintained and instantaneous sources,. Proc. R. Soc. Lond., A 234, 1956, pp.1–23.
2. Morton, B. R., Forced plumes, J. Fluid Mech., 5, 1959, pp.151–163.
3. Baines, W.D., Turner, J.S., Turbulent buoyant convection from a source in a confined region, J. Fluid Mech., 37, 1969, pp.51–80.
4. Worster, M.G., Huppert, H.E., Time-dependent density profiles in a filling box, J. Fluid Mech., 132, 1983, pp.457–466.
5. Zalosh, R., Hydrogen mixing in large enclosures, HYSAFE Lecture, University of Ulster, August 24, 2006.
6. Denisenko V.P., Kirillov I.A., Korobtsev S.V., Nikolaev I.I., Kuznetsov A.V., Feldstein V.A., Ustinov V.V., Hydrogen subsonic upward release and dispersion experiments in confined cylindrical vessel, 2th International Conference on Hydrogen Safety, San Sebastian, 2007, p.106.
7. EU FP7, HYPER project. WP5 report. Scenario B Small foreseeable releases: KI Contribution, 2008.
8. Denisenko V.P., Kirillov I.A., Korobtsev S.V., Nikolaev I.I., Kuznetsov A.V., Feldstein V.A., Ustinov V.V, Experiments on the subsonic release and dispersion of hydrogen in cylindrical enclosure. Empirical analysis, Fire safety, 2011, №2, pp.38-46 (in Russian).
9. Denisenko V.P., Kirillov I.A., Korobtsev S.V., Nikolaev I.I., Hydrogen-air explosive envelope behavior in confined space at different leak velocities, 3rd International Conference on Hydrogen Safety, Ajaccio-Corsica, France, 2009, id 194.
10. Harris R.J., The investigation and control of gas explosions in buildings and heating plant, 1983, E & F N Spon Ltd.
11. Kaye N.B., Hunt J.R., Overturning in a filling box, Journal of Fluid Mechanics, v. 576, 2007, pp 297-323.
12. Cariteau, B., Brinster, J., Tkachenko, Experiments on the distribution of concentration due to buuoyant gas flow rate release in an enclosure, Int. J. of Hydrogen Energy, v.36, 3, 2011, pp.2505-2512.